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Materials, Systems and Structures in Civil Engineering 2016
Segment on

Concrete with
Supplementary Cementitious Materials

Edited by
Ole M. Jensen, Konstantin Kovler and Nele De Belie
International RILEM Conference on
Materials, Systems and Structures in Civil Engineering 2016

segment on
Concrete with Supplementary Cementitious Materials
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Photo 1st cover page: Fly ash particles embedded in different reaction products. Width of photo approximately 650 μm. Credit: Keren Binyamin & Konstantin Kovler (Technion)

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• prepare technical recommendations for testing methods,
• prepare state-of-the-art reports to identify further research needs,
• collaborate with national or international associations in realising these objectives.
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PRO 113: Concrete with Supplementary Cementitious materials

PRO 114: Frost Action in Concrete

PRO 155: Fresh Concrete

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Preface

The conference “Materials, Systems and Structures in Civil Engineering – MSSCE 2016” is part of the RILEM week 2016, which consists of a series of parallel and consecutive conference and doctoral course segments on different topics as well as technical and administrative meetings in several scientific organizations. The event is hosted by the Department of Civil Engineering at the Technical University of Denmark and the Danish Technological Institute and it is held at the Lyngby campus of the Technical University of Denmark 15-29 August 2016.

This volume contains the proceedings of the MSSCE 2016 conference segment on “Concrete with Supplementary Cementitious Materials” (SCM). The conference segment is organized by the RILEM technical committee TC 238-SCM: Hydration and microstructure of concrete with supplementary cementitious materials. TC 238-SCM started activities in 2011 and has about 50 members from all over the world. The main objective of the committee is to support the increasing utilisation of hydraulic and pozzolanic industrial by-products, natural resources and societal waste to obtain more sustainable, less CO2-intensive binders for the construction industry. The TC serves as a knowledge platform where fundamental science and practical expertise are gathered to create a horizontal overview of the research area and to implement and promote the dissemination of more integrated generic approaches into the scientific community. One of the main challenges of the TC is to deal with SCM variability and binder diversification.

Some of the papers in these proceedings origin from the work in two COST actions: TU 1404 Service Life of Cement-based Materials and Structures and TU 1301 NORM for Building Materials. The papers from COST TU 1404 are spread across several MSSCE 2016 conference segments and it is planned that a separate set of electronic proceedings for this COST action will be published after the conference.

The present conference segment deals with theory, modeling, and results from experimental investigations with relation to the use of SCMs in concrete. The topics covered include characterization of SCMs, SCM reactivity in blended cements, cement-SCM interaction, SCM-admixture interaction, hydration products, pore solution composition, effect of SCM on fresh concrete, hardened concrete with SCM, SCM influence on microstructure and durability of concrete with SCM. All these topics have relation to the aforementioned RILEM technical committee 238-SCM. The conference segment is attended by more than 40 presenters from university, industry and practice representing 30 different countries. Hopefully, it will contribute to synthesis of research on concrete with SCMs and promote knowledge transfer from academia to practice. All contributions have been peer reviewed.

Ole Mejlhede Jensen    Konstantin Kovler    Nele De Belie

August 2016, Lyngby, Denmark
Welcome

Were you aware that a part of your daily language is likely to be in Danish? A thousand years ago the Danish word “Vindue” came along with the Vikings to England. Several hundred years later it reached North America, and from there – just two to three decades ago – almost every person in the world learned to understand and pronounce this word: “Windows”, which etymologically means “an eye to the wind”.

As a child your career as construction professional may have started with LEGO, and before you went to bed, your mother told you the unforgettable fairytales of H.C.Andersen. You may have grown up with the delicious taste of Lurpak butter on your bread, and though you might find it strange that “God plays dice with the Universe”, hopefully your school teacher told you that on this topic Einstein was flat out wrong and Niels Bohr was right. Right now you may prefer to be sitting in the sun with a chilled Carlsberg beer in your hand, enjoying the iconic view of the Sydney Opera House. All of it is Danish made, and many things around you at home, if not made in Denmark, were probably brought to you by Maersk, the world’s largest shipping company, the modern Danish Viking fleet.

Though Denmark is one of the world’s smallest countries, yet it stands – along with your country – among the greatest. On top of a thousand years of outreach from Denmark, your visit to the Danes is most welcome. On your approach to Copenhagen airport you had a view to wind turbines harvesting green energy, you saw record breaking bridges, and perhaps you got a glimpse of the island Ven where the nobleman Tycho Brahe literally speaking changed our view of the world through perfection of astronomical observations with his naked eye. In Copenhagen you may appreciate a walk in the fairytale amusement park TIVOLI, and in the Copenhagen harbour you may have a rendezvous with a Little Mermaid.

Of all things in Denmark you will surely enjoy the conference and doctoral courses Materials, Systems and Structures in Civil Engineering, MSSCE 2016 which are held in conjunction with the 70th annual RILEM week. On this occasion RILEM celebrates its 70 years birthday and thus maintains generations of experience. However, new activities and the in-built diversity keep RILEM fresh and dynamic like a teenager.

The event takes place in northern Copenhagen, Lyngby, at the campus of the Technical University of Denmark, 15-29 August 2016. MSSCE 2016 aims at extending the borders of the RILEM week by including doctoral courses, by involving a palette of RILEM topics in the conference and workshop activities, and by collaborating with other scientific organizations. The insight and outlook provided by this event make it RILEM’s technical and educational activity window.

It is a pleasure to share with you what is unique to RILEM and Denmark!

Ole Mejlhede Jensen, Technical University of Denmark
Honorary president of RILEM 2016, Chairman of MSSCE 2016
PERFORMANCE EVALUATION OF APLITE ROCK BASED GEO-POLYMER Binder

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(1) University of Stavanger, Stavanger, Norway

Abstract

Geo-polymer is considered as an alternative binder material to ordinary Portland cement (OPC) to enable greenhouse gas emissions to be minimized. Many researchers have evaluated the mechanical properties of fly ash based geo-polymer binders for structural engineering applications. This study focuses on the performance evaluation of aplite rock-based geo-polymer binders, which also consist of blast furnace slag and micro silica. It has identified the significant parameters that affect the performance of the aplite-based cement as Silicon dioxide (SiO₂): Aluminium oxide (Al₂O₃) ratio, Potassium silicate (k-silicate): Potassium hydroxide (KOH) ratio, KOH concentration and curing temperature. This manuscript illustrates the use of the Taguchi method for designing the optimal parameter combination that results in the optimal mixture of an aplite-based geo-polymer binder, which gives the highest compressive strength. The parameter design and the identification of the optimal mixture are performed via laboratory experiments and subsequent calculations.

1. Introduction

Ordinary Portland cement (OPC) is normally used as the main binder material in a concrete. It has been revealed that about 5%-7% of global greenhouse gas is emitted during the manufacturing process of OPC [1]. Furthermore, the manufacturing of OPC is an extremely energy-intensive process. Considering these facts, there has been a significant movement in recent decades to develop alternative binders to OPC. Hence, geo-polymer binders are becoming an attractive alternative to OPC, mainly due to their low environmental impact, reuse of waste material (i.e. fly ash and blast furnace slag (BFS)), good mechanical properties and durability [2]. Moreover, blast furnace slag and fly ash have become popular source materials for geo-polymers because they have high silica and alumina contents [3]. Hence, many researchers have explored the opportunity of using fly ash based geo-polymer binders as an alternative to OPC.
Aplite is an intrusive rock, abundant in Norway and consisting of SiO$_2$ and Al$_2$O$_3$, which seems to have the potential to be utilized in the development of aplite-based geo-polymer binders [2]. Furthermore, very few studies have been carried out on the development of aplite rock based geo-polymer. Therefore, this study focuses on the development of an aplite rock based geo-polymer binder combined with blast furnace slag and micro silica for structural engineering purposes. In general, a combination of sodium silicate (Na$_2$SiO$_3$) or potassium silicate (K$_2$SiO$_3$) and sodium hydroxide (NaOH) or KOH is most commonly used alkaline activator for geo-polymer binders [1, 2]. It has also been highlighted in the literature that various parameters affect the performance of geo-polymer binders, such as SiO$_2$:Al$_2$O$_3$ ratio, K-silicate: KOH or sodium silicate: NaOH, KOH concentration/NaOH concentration, curing temperature, curing time, solid/liquid ratio, etc. It is also vital to study the influence of such parameters to optimize the performance of geo-polymer binders.

The engineering ‘robust design’ approach or Taguchi method provides a systematic way to determine the influence of parameters on the mechanical properties of geo-polymer binders and to optimize the geo-polymer mixtures. This research focuses on the development of aplite rock based geo-polymer mixtures with the best mechanical properties; it uses the Taguchi method, considering the problem type as the “larger the better”.

2. Methodology for the experiment

Taguchi’s approach is widely used in parameter design; it provides engineers with a systematic and efficient method for determining near optimum design parameters [4, 5]. In this study, the Taguchi method has been used to determine the optimal parameter combination that results in the best compressive strength of geo-polymer. The method involves the following steps:

- **Define the problem**: In this case, the problem is the determination of the optimal levels of controlling parameters, which give the highest compressive strength of the geo-polymer binder.
- **Determination of the performance characteristic(s) and the measuring system**: The compressive strength of a mixture is measured in MPa.
- **Determination of the factors (parameters) affecting the performance characteristic(s)**: There are various parameters affecting the mechanical properties of the geo-polymer binder. SiO$_2$:Al$_2$O$_3$ ratio, K-Silicate: KOH ratio, curing temperature and KOH concentration are selected as significant parameters that affect the compressive strength of the geo-polymer binder.
- **Determination of the number of levels and values of the controllable variables (parameters)**: The approach employs standard tables known as orthogonal arrays (OA) that are used for the design of the experiments [5]. Only nine experiments are needed to study the entire group of experimental parameters using the L$_9$ orthogonal array, as shown in Figure 1. The figure gives a brief overview of how Taguchi’s approach can be used for planning an experiment.
Factors influencing the compressive strength

Levels of major influencing factors

Factors | Level 1 | Level 2 | Level 3
--- | --- | --- | ---
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

Number of experiments | Factor levels
--- | ---
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |

Run the experiment at laboratory scale

Calculate factor effects and find out the best settings of control factors

Use the additive formula to estimate the theoretical value of the compressive strength

Revise the factor levels

Yes

No

Figure 1: Framework of Taguchi method [4]

- **Determination of loss function and the performance statistics:** the “larger-the-better” (SMB) loss function is selected because the larger the compressive strength, the better the mechanical properties. The signal to noise ratios (S/N ratios) can be calculated as given in Eq. (1) [5].

\[
S/N \text{ ratio } (\eta_i) = -10 \log_{10} \left( \frac{1}{n} \sum_{i=1}^{n} \frac{1}{y_i^2} \right)
\]  

(1)

where,

\( n \) = number of replications

\( y_i \) = performance indicator value (\( i = 1,2,...,n \)), in this case, the compressive strength of the geo-polymer binder in MPa.

- **Conducting experiments and recording results**
- **Analyzing data and selecting the optimum value of the controllable variables.**
- **Testing the results.**
- **Evaluation, implementation and observation:** Under the optimal set points, the corresponding \( \eta_{\text{opt}} \) is calculated using the additive model for parameter effects using Eq. (2) [5].

\[
S/N \text{ ratio}(\eta_{\text{opt}}) = \alpha + \alpha_A^i + \alpha_B^j + \alpha_C^k + \alpha_D^l + \varepsilon_{ijkl}
\]  

(2)

where,

\( \alpha \) = overall mean S/N ratio for the compressive strength over all the possible combinations

\( i,j,k,l \) = particular levels of each of the parameters which were selected (so, in this model, \( i,j,k,l \) must all take on one of the values 1, 2 or 3)

\( \alpha_A^i \) = deviation from \( \alpha \) caused by setting parameter “A” at level \( i \) (similarly, other terms can be defined)
\[ \varepsilon_{ijkl} = \text{error term.} \]

The calculated \( \eta_{\text{opt}} \) represents the theoretical level of the compressive strength at optimal settings found by experimentation. It can be converted into predicted compressive strength at the optimal condition using Eq. (3), where “\( y \)” is the predicted compressive strength at optimal condition. However, a verification experiment shall be performed to investigate the accuracy of the optimal settings.

\[ Y = \sqrt{10^{\eta_{\text{opt}}/10}} \]  

(3)

3. Material and experiment

Ground aplite rock, BFS, micro silica, alkaline activator and distilled water were the materials used to prepare the geo-polymer binder. Initially, the aplite rock was crushed into small particle size and ground to 3.20 \( \mu \)m mean particle size. The ground aplite was used as a substitute material for cement and the usage of aplite can allow a reduction in use of cement. The specific surface area of the ground aplite is found as 1590.9m\(^2\) kg\(^{-1}\) [2] and the high specific surface area may help to make mechanically activated, resulting in high compressive strength. The chemical composition of the materials is given in Tab. 1, and Tab. 2 shows the densities of material used. Moreover, to enhance geo-polymerization, a calcium and aluminium-rich BFS was used as an additive, taking into consideration the fact that the aplite rock has lower aluminium content than other types of source materials such as fly ashes [2]. As there are few studies on aplite rock based geo-polymer, this study evaluates the performance of geo-polymer binders without aggregates to explore the opportunities for further studies. Further, combinations of potassium hydroxide and potassium silicate were used as alkaline activators in this study. Because, Khalifeh et al. [2] has found from their experiments that the combination of potassium hydroxide and potassium silicate gives better compressive strength than that of NaOH and Na\(_2\)SiO\(_3\). Moreover, Potassium hydroxide pellets were dissolved in distilled water to produce a potassium hydroxide solution of 3 M, 4 M and 6 M; potassium silicate solution (K\(_2\)SiO\(_3\)) consists of 38% K\(_2\)SiO\(_3\) and 62% H\(_2\)O. Tap water was used throughout the experiments.

3.1 Material

Table 1: Chemical composition of materials [2].

<table>
<thead>
<tr>
<th>(wt. %)</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
<th>TiO(_2)</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aplite rock</td>
<td>82.8</td>
<td>9.04</td>
<td>0.75</td>
<td>0.82</td>
<td>0.1</td>
<td>2.72</td>
<td>3.11</td>
<td>0.04</td>
<td>0.62</td>
</tr>
<tr>
<td>Micro silica</td>
<td>95.5</td>
<td>0.7</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.4</td>
<td>1</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>BFS</td>
<td>34</td>
<td>13</td>
<td>0</td>
<td>31</td>
<td>17</td>
<td>0.9</td>
<td>0</td>
<td>2.4</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 2: Density of materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aplite</td>
<td>1180</td>
</tr>
<tr>
<td>BFS</td>
<td>2910</td>
</tr>
<tr>
<td>Micro silica</td>
<td>1660</td>
</tr>
<tr>
<td>K₂SiO₃ solution</td>
<td>1321</td>
</tr>
</tbody>
</table>

3.2 Determination of the optimal mixture based on the compressive strength

The Taguchi method starts by identifying the parameters influencing the mechanical properties (i.e. compressive strength) of geo-polymer binders. Based on previous research [2, 6] and using expert knowledge, the potential four parameters were selected as ratio of SiO₂:Al₂O₃ (A), KOH concentration (B), curing temperature (C) and ratio of K₂SiO₃: KOH (D). Tab. 3 shows the selected levels of each parameter that defines the experimental region or region of interest. The matrix experiment selected for this study is given in Tab. 4. It consists of nine individual experiments corresponding to the nine rows that constitute the standard orthogonal array L₉ according to Taguchi’s approach. Four columns in Tab. 4 represent four parameters, as indicated by A, B, C and D in Tab. 3. Tab. 4 and Tab.5 provide the details of nine experiments and the composition of nine mixtures respectively. For example, in experiment 1, the geo-polymer mixture was prepared using ratio of SiO₂:Al₂O₃ (A) as 7.3, KOH concentration (B) as 3 M, curing temperature (C) as 25 °C and ratio of K₂SiO₃:KOH (D) as 0.5.

Table 3: Parameters and their levels used in this experiment.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ : Al₂O₃ (A)</td>
<td>7.3</td>
<td>6.4</td>
<td>8.4</td>
</tr>
<tr>
<td>KOH concentration (B)</td>
<td>3 M</td>
<td>4 M</td>
<td>6 M</td>
</tr>
<tr>
<td>Curing Temperature (C)</td>
<td>25 °C</td>
<td>40 °C</td>
<td>80 °C</td>
</tr>
<tr>
<td>K₂SiO₃:KOH (D)</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
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</table>
Table 5: Composition of the mixtures

<table>
<thead>
<tr>
<th>Material</th>
<th>Experiment number</th>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
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<tbody>
<tr>
<td>Aplite (g)</td>
<td></td>
<td>366</td>
<td>366</td>
<td>366</td>
<td>300</td>
<td>300</td>
<td>446</td>
<td>446</td>
<td>446</td>
<td></td>
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<tr>
<td>Micro silica (g)</td>
<td></td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
</tr>
<tr>
<td>Blast Furnace Slag (g)</td>
<td></td>
<td>182</td>
<td>182</td>
<td>182</td>
<td>248</td>
<td>248</td>
<td>102</td>
<td>102</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Water (g)</td>
<td></td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>KOH solution (g)</td>
<td>3M</td>
<td>149</td>
<td></td>
<td>64</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>4M</td>
<td></td>
<td>112</td>
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<td>149</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6M</td>
<td></td>
<td>112</td>
<td></td>
<td></td>
<td>64</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂SiO₃ solution (g)</td>
<td></td>
<td>75</td>
<td>112</td>
<td>160</td>
<td>160</td>
<td>112</td>
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<td>112</td>
<td>160</td>
<td>75</td>
</tr>
</tbody>
</table>

3.3 Sample preparation, casting and testing

Geo-polymer binder samples were prepared by mixing the dry material (aplite rock, micro silica, blast furnace slag) and alkaline activators (potassium silicate, potassium hydroxide and water) using a mixer. Initially, the dry materials were mixed, and then the alkaline activators and distilled water were poured into the pan and mixed continuously for approximately 2 min until the mixture was glossy and well combined. 50 mm*50 mm*50 mm geo-polymer cubes were cast and demoulded after 24 hours and water cured at the temperatures given in Tab. 3. The compressive strength of the geo-polymer cubes were tested at 1 day, 2 days, 7 days and 28 days. In addition to the compressive strength of the geo-polymer binder, density, initial setting time, flexure test and temperature development were also measured. Moreover, the density of each mixture was measured, and it varied between 1.88 and 1.9 g/cm³. However, this paper focuses only on the determination of the optimal compressive strength.

4. Results

To study the development of compressive strength of geo-polymer mixtures, 1-day, 2-day, 7-day and 28-day compressive strengths were measured and given in Tab. 6. ‘a’, ‘b’ and ‘c’ in Tab. 6 show the number of samples tested. For example, for the 1-day compressive strength
test, three samples were tested. However, the optimal compressive strength was determined based on the 28-day compressive strength. Using Section 2, Eq. (1), ‘Ș’ was calculated for each experiment and given in Tab. 7. The average ‘Ș’ value for each level of the four parameters (i.e. ratio of SiO₂:Al₂O₃ (A), KOH concentration (B), curing temperature (C) and ratio of K₂SiO₃: KOH (D)) is given graphically in Figure 2.

Table 6: Compressive strength of concrete.

<table>
<thead>
<tr>
<th>Exp.no</th>
<th>1 day</th>
<th>2 days</th>
<th>7 days</th>
<th>28 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.2</td>
</tr>
<tr>
<td>2</td>
<td>9.4</td>
<td>9.5</td>
<td>7.5</td>
<td>14.1</td>
</tr>
<tr>
<td>3</td>
<td>6.9</td>
<td>6.8</td>
<td>6.9</td>
<td>8.0</td>
</tr>
<tr>
<td>4</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>0.9</td>
<td>0.8</td>
<td>5.6</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>3.3</td>
<td>3.3</td>
<td>3.6</td>
<td>14.3</td>
</tr>
<tr>
<td>8</td>
<td>5.6</td>
<td>6.5</td>
<td>6.6</td>
<td>17.2</td>
</tr>
<tr>
<td>9</td>
<td>0.9</td>
<td>0.7</td>
<td>0.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Table 7: Matrix experiment with S/N ratio.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>S/N ratio (dB) (Ș) for 28 days compressive strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.3</td>
<td>3 M</td>
<td>25°C</td>
<td>0.5</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>7.3</td>
<td>4 M</td>
<td>40°C</td>
<td>0</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>7.3</td>
<td>6 M</td>
<td>80°C</td>
<td>2.0</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>6.4</td>
<td>3 M</td>
<td>40°C</td>
<td>0.5</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>6.4</td>
<td>4 M</td>
<td>80°C</td>
<td>0.5</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>6.4</td>
<td>6 M</td>
<td>25°C</td>
<td>0</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>8.4</td>
<td>3 M</td>
<td>80°C</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>8.4</td>
<td>4 M</td>
<td>25°C</td>
<td>0</td>
<td>26</td>
</tr>
<tr>
<td>9</td>
<td>8.4</td>
<td>6 M</td>
<td>40°C</td>
<td>0.5</td>
<td>17</td>
</tr>
</tbody>
</table>

The main objective in conducting this experiment is to determine the optimal level of each parameter that gives the highest compressive strength. According to the Taguchi approach, the optimal level for a parameter is the level that gives the highest value of average ‘Ș’ in the experimental region in Figure 2. Considering Figure 2, it can be found that the optimal level for the ratio of SiO₂:Al₂O₃ (A) is 8.4 (A3), the best KOH concentration (B) is 6 M (B3), the best curing temperature (C) is 25 °C (C1) and the best ratio of K₂SiO₃: KOH (D) is 1 (D2). However, when the curing temperature is 25 °C, the average ‘Ș’ is 21 dB and, when the curing temperature is 80 °C, the average ‘Ș’ is 19 dB. The difference between two average ‘Ș’ values is quite small. Hence, both 25 °C and 80 °C can be considered as the optimal levels for curing.
temperature. Therefore, the optimal combination is A3B3C1D2 or A3B3C3D2, where ‘A, B, C, D’ refer to the parameter and the digit refers to the relevant level from Tab. 3.

Using Eq. (2), the compressive strength under the optimal condition can be predicted. $\eta_{opt}$ can be estimated at the optimal condition as 36 dB and, using Eq. (3), the corresponding predicted compressive strength is estimated as 63 MPa, which is higher than the compressive strength found from nine experiments.

![Figure 2: Plot of parameter effect](image)

5. Conclusion

This manuscript illustrates the use of the Taguchi method for investigating optimal parameter levels that result in a mixture of aplite-based geo-polymer binder, which provides the best compressive strength. The analysis was performed for the 28-day compressive strength. Experiments reveal that the optimal levels for the ratio of SiO$_2$:Al$_2$O$_3$ (A) is 8.4 (A3), the best KOH concentration (B) is 6M (B3), the best curing temperature (C) is 25 $^\circ$C (C1) or 80 $^\circ$C (C3) and the best ratio of K$_2$SiO$_3$: KOH (D) is one (D2). The anticipated best strength under the optimal conditions has been calculated as 63 MPa. It has been observed that the anticipated strength value is better than the strength values measured in the nine experiments. It is also possible to verify the strength value under the optimal parameter combinations with the support of a verification experiment.

Future research shall be carried out to verify of the optimal level, taking into consideration all the mechanical properties, and to carry out sensitivity analysis among the parameter levels. Currently, the verification experiment is carrying out in the laboratory to verify the calculated highest compressive strength based on experimental findings. In addition, it is vital to carry
out further research by extending the experimentation with different sizes of coarse and fine aggregate to prepare aplite rock based geo-polymer concrete.

References


EVALUATION OF HARDENED STATE PROPERTIES OF GGBS-PC MORTARS MODIFIED BY SUPERABSORBENT POLYMERS (SAP)

Fernando do Couto Rosa Almeida (1), Agnieszka Joanna Klemm (1)
(1) Glasgow Caledonian University, Glasgow, UK

Abstract
This paper evaluates the effects of superabsorbent polymers (SAP) on autogenous shrinkage, mechanical properties and microstructural characteristics of mortars with different levels of cement replacement by ground granulated blast-furnace slag (GGBS). Two types of SAPs with different water absorption capacities in cement-paste solution have been considered. The effects of SAP on mortars have been assessed during the first 28 days. The results showed that both polymers used notably reduce autogenous shrinkage. Moreover, the type of SAP has an effect on the pore structure formation in hardened mortars and consequently influences their mechanical properties.

1. Introduction
Despite their worldwide popularity, cementitious materials are susceptible to cracking, triggered by self-desiccation processes and subsequent autogenous shrinkage. This effect can even be more critical in concrete with ground granulated blast-furnace slag (GGBS), as seen in previous studies [1]-[5].

In an attempt to limit autogenous shrinkage, superabsorbent polymers (SAP) can be used as internal curing agents. Basically, SAP is a cross-linked network of hydrophilic polymers with the ability to absorb and retain large volumes of water [6]-[7]. Figure 1 shows SEM micrographs of a SAP in dry and wet conditions. Due to its high capacity to provide water-filled cavities in hardened state, SAP may facilitate hydration processes and lead to densification of internal structure.

However, their full effect on the microstructure of hardened mortars is still unclear, especially in blended cements [8]-[12], in particular GGBS. Despite a slight retardation of strength development, long-term strength of mortars containing blended cements is not necessarily negatively affected by SAP [10]. In fact, SAP can promote creation of a dense network of...
CSH even in a collapsed state and subsequently lead to pores closures [11]. In this case, the effect of SAP is dual and counteracting due to its capacity to increase porosity and improve microstructure [10].

The effects of SAP on mechanical properties and porosity strongly depend on the polymer type and its water absorption/desorption kinetics [7][11][13]. Although [10] and [12] have considered the use of GGBS in their studies with SAPs, there is still no consensus on the combined effect of slag and polymers on hardened state mortars. Therefore, the paper aims to evaluate this effect by analysing mortars with different levels of cement replacement by GGBS. The investigation has endeavoured to relate the microstructural features with mechanical properties of mortars with GGBS-PC cements during the first 28 days.

2. Materials and methods

Mortars with different mix proportions were produced for the experimental study, considering different levels of Portland Cement (PC) replacement (CEM I 52.5N) by GGBS and different types of SAPs, including reference mortars without GGBS and/or SAP. Four levels of PC replacement by GGBS: 0%, 25%, 50% and 75% of the binder content (by mass) have been analysed. Table 1 shows the chemical and physical analyses of binder (CEM I and GGBS) used in the experimental study.

Table 1: Chemical and physical analyses of CEM I and GGBS.

<table>
<thead>
<tr>
<th>Compound (%)</th>
<th>Fineness (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
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</tr>
<tr>
<td>Al₂O₃</td>
<td>34.53</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td></td>
</tr>
<tr>
<td>LOI</td>
<td></td>
</tr>
</tbody>
</table>

Two different types of SAP have been used in the proportion of 0.25% by mass of binder: SAP X and SAP Y with water absorption capacities of 25-30 g/g and 35 g/g respectively, in cement paste solution. Both SAPs have particles sizes in the range of 63-125 μm. Fine sand contained 99.95% of particles below 0.6 mm [14]. Table 2 shows the mix proportions of all materials used for mortars preparation.
Table 2: Mix proportions of materials used for mortars production.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Type of SAP</th>
<th>CEM I (%) a</th>
<th>GGBS (%) a</th>
<th>SAP (%) b</th>
<th>Binder / Sand (b/s)</th>
<th>Water / Binder (w/b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R0</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>1:2</td>
<td>0.50</td>
</tr>
<tr>
<td>R25</td>
<td>-</td>
<td>75</td>
<td>25</td>
<td>-</td>
<td>1:2</td>
<td>0.50</td>
</tr>
<tr>
<td>R50</td>
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<td>50</td>
<td>-</td>
<td>1:2</td>
<td>0.50</td>
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<td>-</td>
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<tr>
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<td>SAP X</td>
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<td>-</td>
<td>0.25</td>
<td>1:2</td>
<td>0.50</td>
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<tr>
<td>X25</td>
<td>SAP X</td>
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<td>25</td>
<td>0.25</td>
<td>1:2</td>
<td>0.50</td>
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<tr>
<td>X50</td>
<td>SAP X</td>
<td>50</td>
<td>50</td>
<td>0.25</td>
<td>1:2</td>
<td>0.50</td>
</tr>
<tr>
<td>X75</td>
<td>SAP X</td>
<td>25</td>
<td>75</td>
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<td>Y0</td>
<td>SAP Y</td>
<td>100</td>
<td>-</td>
<td>0.25</td>
<td>1:2</td>
<td>0.50</td>
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<tr>
<td>Y25</td>
<td>SAP Y</td>
<td>75</td>
<td>25</td>
<td>0.25</td>
<td>1:2</td>
<td>0.50</td>
</tr>
<tr>
<td>Y50</td>
<td>SAP Y</td>
<td>50</td>
<td>50</td>
<td>0.25</td>
<td>1:2</td>
<td>0.50</td>
</tr>
<tr>
<td>Y75</td>
<td>SAP Y</td>
<td>25</td>
<td>75</td>
<td>0.25</td>
<td>1:2</td>
<td>0.50</td>
</tr>
</tbody>
</table>

a of the binder content  
b by mass of binder

Autogenous shrinkage (AS) was tested by the corrugated tubes method [15] (min 3 specimens for each mortar) from the final setting time until the age of 28 days, using a digital bench dilatometer. Mechanical properties were evaluated by standard flexural (3 samples for each mortar) and compressive (6 samples for each mortar) strengths determination methods [16] at ages of 7, 14 and 28 days. Specimens were cast into prismatic moulds (160 x 40 x 40 mm) and cured in the climate chamber (T = 21 ± 2 °C and RH = 40 ± 5%). Microstructural features were tested in terms of total porosity (%), median pore diameter (by volume), bulk density at 52 psia (g/ml) and pore size distribution (nm), using Mercury Intrusion Porosimetry (MIP) technique.

3. Results and discussion

Figure 2 shows the results of autogenous shrinkage (AS) over 28 days. Overall, SAP reduced AS of mortars with and without GGBS compared with the reference samples. Considering samples without SAP, autogenous shrinkage steadily increased considering different GGBS contents over the time. The higher level of cement replacement by GGBS, the greater was AS. At the end of 28 days, shrinkage values of about 350, 480, 560 and 640 μm/m for mortars with 0%, 25%, 50% and 75% of GGBS respectively were observed. Some authors attribute this increment in AS to a higher degree of hydration of GGBS, and therefore, greater degree of self-desiccation [2]-[4]. As a result of slag hydration, the amount of water in pores is reduced, leading to self-desiccation. In addition, CSH formed during the reaction produce a chemical shrinkage, since the volume of the hydrated products is less than
the sum of volume of water plus initial anhydrous products [5]. Thus, greater chemical shrinkage can lead to a faster and more intense self-desiccation, and results in larger AS. However in some cases, as in the current study, GGBS may slow down the hydration rate due to its larger particles when compared to PC (Table 1) and most importantly due to the lower amount of PC (lower alkali content required for activation of slag hydration). In this case, the use of GGBS may lead to finer pores, which in turn results in increased AS. The smaller capillaries the higher is tensile stress provoked by water menisci between the pores walls [5]. In any case, the increment of GGBS content can lead to formation of material which is more prone to deformation.

However, in the presence of SAP, this behaviour was sharply altered showing a significant reduction in AS for all levels of cement replacement by GGBS. Autogenous shrinkage was mitigated when using internal curing by SAP in mortars with slag. This reduction was also verified in cement paste with GGBS modified by SAP [12]. The principle of internal curing by means of SAP relates to the provision of water-filled cavities in hardened mortars, reducing AS [10]. Regarding the studied samples, SAP Y seemed to have better performance than SAP X, indicating different efficiencies for different polymers. However, all shrinkage values varied between 75 and 175 μm/m at 28 days. They represent reductions between 40 - 80% for SAP X and 65 - 90% for SAP Y, in comparison with reference mortars with the same GGBS content. As the slag content is increased, the reduction in autogenous shrinkage is more pronounced. It suggests that SAP has a positive effect on AS reduction, especially for high contents of slag when this diminution is maximized.
The results of compressive strength are shown in Figure 3. Overall, the increment of GGBS has reduced the compressive strength during the first 28 days.

![Figure 3: Results of compressive strength.](image)

The reduction of compressive strength for samples with higher contents of GGBS can be related to its slower process of hydration. This is because the higher the amount of GGBS, the lower is the content of calcium hydroxide responsible for the activation of hydration. It is expected that these reactions intensify and hydrated calcium silicates are formed in long term, resulting in mechanical strength similar to the reference mortar [5].

Besides, as it appears, the fineness of slag can also affect the rate of reaction. As seen in Table 1, GGBS particles considered in this study are bigger than those of cement Portland, thereby contributing to slower rates of reaction and hence, lower values for early strengths. As slag is not fine enough when compared with Portland cement, only a small part of it can react in the first weeks and the remainder may act as an inert aggregate, thereby reducing the overall strength.

Moreover, it is evident that the polymer type can have an influence on mechanical properties. SAP X seems to have similar performance to the reference sample for all ages tested. It indicates that SAP X can keep the same level of compressive strength when compared to all reference samples regardless of the GGBS contents. However, mortars with SAP Y seems to have lower compressive strength as the GGBS content is increased when compared with the respective sample without SAP. The reduction of strength at 28 days is in the order of 6%, 7%, 23% and 44% in comparison with the reference sample with 0%, 25%, 50% and 75% of slag content respectively. Thus, the type of SAP can affect compressive strength of mortars.

The results of flexural strength testing are shown in Figure 4. In general, increase of level of PC replacement by GGBS can lead to lower flexural strength during the first 28 days. Flexural strength had the same pattern of compressive strength when the addition of GGBS is considered. The greater the GGBS content, the lower was the strength during the first 28 days. The GGBS may have led to a lower rate of reaction resulting in lower values of mechanical properties in early ages.

Mortars with SAPs seem to have similar flexural strengths than the reference sample in the first days. However, with the exception of the mortar with high content of GGBS, samples with SAP X seem to have lower flexural strengths at 28 days. This reduction was less than 10% of the respective reference sample. While SAP X has slightly reduced flexural strength, SAP Y has increased those values in comparison with the reference samples.
This shows how the type of SAP, regarding its sorption capacity and kinetics, can influence mechanical properties of cementitious materials. Usually, premature release of water by SAP (before setting) into the cement-based matrix may lead to some decrease in mechanical strength. This effect can be attributed to some increase in the effective water/cement ratio and subsequently to higher porosity of mortar [13][17]. In contrast, for mixes with SAP that do not exhibit early water desorption, either no decrease or only a very moderate decrease in strength can take place. This may be explained by the release of stored water at later stages. In this case extra water may serve truly as internal curing water. The efficient mitigation of autogenous shrinkage and the enhanced degree of hydration seem to be sufficient to balance the negative effect of voids induced by SAP particles, since they have low desorption ratio [13].

In order to better understand the effect of SAP pores on the mechanical properties, microstructural characteristics of studied mortars were also analysed. The results of total porosity, median pore diameter (by volume) and bulk density obtained by means of MIP technique are shown in Table 3. Addition of SAP and higher contents of GGBS led to increased overall porosity during the analysed period. However, the type of SAP could define size of pores over time and influence mechanical features. Overall, bulk density varied between 1.88 – 2.04 g/mL for all samples in every age analysed. This range decreased at 28 days when the samples showed some variations between 1.93 – 2.01 g/mL. As bulk density is inversely proportional to porosity, the greater the porosity, the lower is the bulk density. In this way, bulk density seems to decrease with SAP addition as well as with the increment of GGBS content. The addition of GGBS seems to lead to increased porosity and increased median pore diameter. The higher the level of PC replacement by GGBS, the greater is the porosity and the pore size diameter during the first 28 days. It can be related to a low rate of slag reaction in comparison with higher contents of PC in the early ages. This increment in porosity may be directly associated with lower mechanical strengths as presented in Figures 3 and 4. Moreover, some authors [5] have related such increment of porosity by GGBS to the increase in autogenous shrinkage, as seen in Figure 2. The higher is the quantity of GGBS the higher the total pore volume, and hence the higher the likelihood of deformation. GGBS can also provide greater amount of finer pores (below 20 nm), as seen in the pore size distribution curves (Figure 5). The higher the GGBS content, the more significant is the presence of
smaller pores in the cementitious matrix. The finer structure of pores can lead to a greater shrinkage generated by the water menisci in the capillaries as discussed above.

Table 3: Microstructural features by MIP technique.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>7 days</th>
<th></th>
<th></th>
<th>14 days</th>
<th></th>
<th></th>
<th>28 days</th>
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<td>1.90</td>
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<td>1.88</td>
<td>21.7</td>
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</table>

SAP can also have a significant effect on the porosity of mortars. Depending on its sorption capacity and kinetics of the process, different sizes of pores can be left behind as SAP dries out in the cement matrix [11]. According to Table 3, SAPs facilitate increase in total porosity of mortars but also induce formation of different median pore diameters which in turn may influence compressive and/or flexural strength.

For instance, mortar with SAP X seemed to have smaller pores than the reference sample at 28 days. This trend may be observed in Figure 5 by comparing the reference and SAP X curves. As GGBS content is increased, the peaks formed by SAP X tend to shift to the right when compared with those formed by the reference samples, indicating a reduction in pores size diameter. In fact, this can also be observed when median pore diameters are compared for the same age of 28 days (Table 3). Despite higher porosity, SAP X seemed to produce smaller pores which may be more significant for flexural strength analysis. Samples with SAP X indeed presented lower values of this property than those obtained for reference mortars with the same slag content (Figure 4). Thus, SAP X can lead to decrease of pore size at 28 days, especially for higher quantity of GGBS, resulting in lower flexural strength. This reduction in pore size can be associated with the formation of hydration products that fill SAP voids facilitating formation of denser and more homogenous cementitious matrix [11]. Although
SAP X increases the total volume of pores, it can lead to formation of finer pores during the first 28 days.

![Figure 5: Pore size distribution curves at 28 days.](image)

Nevertheless, SAP Y seems to produce bigger pores when compared to samples without polymer. This increment in total porosity and pore size diameter can be verified by comparing both samples in Table 3 and Figure 5. In general, median pore diameter was larger for SAP Y samples when compared with the corresponding reference sample (same GGBS content) (Table 3). Also, the peaks of pore size distribution curve for SAP Y seemed to be shifted left, relative to the reference curve, representing increase in pore diameter (Figure 5). This difference is more pronounced for higher slag contents. This enlargement of pores can mainly affect compressive strength; these values were lower than those for reference samples with higher quantity of slag (Figure 3). While releasing internal curing water, SAP shrinks and leaves behind air voids, which act as weak spots in the material structure [7]. The formation of larger pores by SAP Y may be related to its higher water absorption capacity compared with SAP X. The higher the water absorption, the higher is the capacity to swell and form larger water reservoirs. When this water is released, bigger pores may be produced. Thus, although [18] have suggested that the differences in sizes and quantities of SAP pores do not
have an effect on strength development, the results showed that the pores formed by collapsed SAPs can affect mechanical strength in mortars with GGBS-PC cements up to 28 days. However, shape of mercury intrusion-extrusion hysteresis (Figure 6) indicates the pores are not well interconnected [11]. It is likely that these pores are of “ink-bottle” shape and/or are closed. Because of that, despite an increased porosity, the overall durability of SAP modified mortars is not compromised. In fact, durability can be improved by SAP modification [10].

Therefore, the sorption capacity and kinetics of SAPs can affect the pore structure formation and consequently influence mechanical properties of hardened mortars.

4. Conclusions

From the results obtained in the experimental study, the following can be concluded:

- Mortars with SAP can significantly decrease autogenous shrinkage (AS) for any studied GGBS content in comparison with the reference mortar. Reduction in AS is maximized for mortars with high quantity of GGBS, where the diminution is over 80%. The reduction of AS by SAP may decrease cracking susceptibility and hence increase sustainability level of cementitious material for more durable constructions;
- Mortar mixes with SAP X tend to have similar compressive strength but lower flexural strength, compared with the reference sample. This is because SAP X facilitates formation of smaller pores during the first 28 days, especially for high content of GGBS. However, SAP Y had a different performance; mortars with this polymer may develop larger pores than reference samples. This effect results in reduction in compressive strength at 28 days, in particular for high quantity of GGBS;
- SAP X seems to be more efficient in clogging their own pores (formed by itself) with products of hydration over the first month. In turn, SAP Y, which presents higher water absorption capacity, is responsible for creating larger pores in the matrix. Overall, although both SAPs increase the total porosity of mortars, these voids can be considered closed and/or “ink-bottle” shape.

Acknowledgements

The authors acknowledge CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico – Brazil) for the financial support and BASF for SAPs supply.
References

CAN SUPERABSORBENT POLYMERS MITIGATE SHRINKAGE IN CEMENTITIOUS MATERIALS BLENDED WITH SUPPLEMENTARY CEMENTITIOUS MATERIALS?

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Abstract

A promising way to mitigate autogenous shrinkage in cementitious materials with a low water-to-binder ratio is internal curing by the use of superabsorbent polymers. Superabsorbent polymers are able to absorb multiple times their weight in water and can be applied as an internal water reservoir to induce internal curing and mitigation of self-desiccation. Their purposefulness has been demonstrated in Portland cement pastes with and without silica fume. Nowadays, fly ash and blast-furnace slag containing binders are also frequently used in the construction industry. The results on autogenous shrinkage in materials blended with fly ash or blast-furnace slag remain scarce, especially after one week of age. This paper focuses on the autogenous shrinkage by performing manual and automated shrinkage measurements up to one month of age. Without superabsorbent polymers, autogenous shrinkage was reduced in cement pastes with the supplementary cementitious materials versus Portland cement pastes. At later ages, the rate of autogenous shrinkage is higher due to the pozzolanic activity of the supplementary cementitious materials. Internal curing by means of superabsorbent polymers is successful, independent of this long-term higher rate of shrinkage in mixtures with supplementary cementitious materials. Superabsorbent polymers proved to be successful in mitigating self-desiccation.

1. Introduction

Autogenous shrinkage predominantly occurs in systems with a low water-to-binder ratio. Upon mixing, when cement reacts with water, hydration products will be formed in the water-filled spaces between the solid particles. As a consequence of chemical shrinkage water menisci will progressively recede in the pore structure and thus create a reduction of the internal relative humidity, i.e. self-desiccation will occur, and due to increased hydrostatic tension forces, the distance between the solid particles will be reduced, i.e. autogenous shrinkage will occur. This may result in micro- and macro-cracking, impairing the overall
strength and durability. This cracking may accelerate ingress of water or gases and in the end thereby reduce the service life of the concrete.

Autogenous shrinkage can be mitigated by supplying an external or internal water source to the hydrating system which maintains the internal relative humidity. As internal water source, several materials can be used: lightweight aggregates, pumice, expanded clay, and superabsorbent polymers (SAPs) amongst others [1, 2]. In this paper, the focus lies on SAPs. Those materials may be able to absorb e.g. 500 times their own weight in fluids and to retain it in their polymeric structure. Upon mixing, they will absorb part of the mixing water. This water is then available to the cementitious matrix during hydration to mitigate autogenous shrinkage [3, 4]. By this method total autogenous shrinkage is reduced and even counteracted in time in cementitious materials made with ordinary Portland cement with or without silica fume [3-8]. Most concrete structures are made with binders containing supplementary cementitious materials (SCMs) like fly ash (FA) or blast-furnace slag (BFS). The influence of the SAPs on the autogenous shrinkage properties of those kinds of materials needs to be studied in detail.

In the literature, only few results of autogenous shrinkage in FA systems can be found. In one study [9] there was 200 μm/m shrinkage strain for a mixture with cement and a water-to-binder ratio of 0.30, 100 μm/m shrinkage strain for FA40 (with 60% of cement and 40% of FA in the binder), 50 μm/m shrinkage strain for FA60, 20 μm/m expansion strain for FA60IC (internal curing) and 60 μm/m expansion strain for FA40IC at an age of 14 days when using lightweight aggregates. In another study [10] for mixtures with a water-to-binder ratio of 0.30, a reference with OPC (at 192 days) showed 320 μm/m shrinkage strain, FA15 (with 85% of cement and 15% of FA in the binder) 250 μm/m shrinkage strain, FA30 220 μm/m shrinkage strain and FA45 150 μm/m shrinkage strain. The cement clinker and SCMs hydrate simultaneously and their reactions are influenced and stimulated by one another. The pozzolanic reaction (by FA) occurs at later time (after a couple of days) as pozzolans need to be activated by the alkaline environment and react with the calcium hydroxide generated by the cement hydration. As the degree of pozzolanic activity increases, the autogenous shrinkage may increase in time. At later ages, the rate of shrinkage is higher in FA mortars compared to pure cement systems. The influence of the internal curing in mixtures containing FA should also be investigated at later ages than 14 days and this data is lacking in the literature. Data from 14 days onwards would be very useful as the net overall shrinkage for FA systems may then exceed the one for the pure cement mixtures.

Next to FA, BFS was also point of interest in terms of autogenous shrinkage. According to the literature, the amount of autogenous shrinkage is higher compared to ordinary Portland systems [11, 12]. There was 310 μm/m shrinkage strain for a cement mixture with a water-to-binder ratio of 0.32, 380 μm/m shrinkage strain for BFS30 (70% of cement and 30% of BFS with a water-to-binder ratio of 0.32) and 420 μm/m shrinkage strain for BFS50 at an age of 200 days. The higher autogenous shrinkage could be due to the denser structure with smaller pores of the BFS cement paste. The smaller pores lead to higher capillary forces, thus increases autogenous shrinkage. A single study investigating internal curing showed that for blast-furnace-slag-blended cement mixtures, part of the autogenous shrinkage was eliminated due to internal curing, but the remaining shrinkage was very high [13]. The shrinkage was
approximately 1400 \( \mu \mathrm{m/m} \) shrinkage strain for BFSC-REF (BFS blended cement mixture), 600 \( \mu \mathrm{m/m} \) shrinkage strain for BFSC-SAP (mixture with BFS and internal curing), 200 \( \mu \mathrm{m/m} \) shrinkage strain for OPC-REF (ordinary Portland cement mixture) and 50 \( \mu \mathrm{m/m} \) shrinkage strain for OPC-SAP at an age of 7 days. Results from 7 days onwards are missing in the literature.

In this study, the effects of SAPs in FA and BFS blended mixtures were studied by monitoring the autogenous strain in time, up to one month.

2. Materials and Methods

2.1 Materials

A cement paste with a water-to-binder ratio (W/B) of 0.3 was used as a reference (R0.30). The cement was CEM I 52.5 N and FA and BFS were incorporated to additionally form manually blended cements. The chemical composition and the specific surface area of the used materials can be found in Table 1.

Table 1: Chemical composition of CEM I 52.5 N, Class F FA and BFS [mass-%] and specific surface (Blaine fineness).

<table>
<thead>
<tr>
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<th>CEM I 52.5 N mass-%</th>
<th>Class F FA mass-%</th>
<th>BFS mass-%</th>
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<tr>
<td>CaO</td>
<td>63.12</td>
<td>2.47</td>
<td>40.38</td>
</tr>
<tr>
<td>SiO₂</td>
<td>18.73</td>
<td>49.34</td>
<td>34.35</td>
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<td>Al₂O₃</td>
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<td>11.36</td>
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<td>0.48</td>
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<tr>
<td>SO₃</td>
<td>3.07</td>
<td>0.30</td>
<td>1.65</td>
</tr>
<tr>
<td>MgO</td>
<td>1.02</td>
<td>1.73</td>
<td>7.57</td>
</tr>
<tr>
<td>K₂O</td>
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<td>3.84</td>
<td>0.37</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.41</td>
<td>0.52</td>
<td>0.29</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>-</td>
<td>-</td>
<td>0.013</td>
</tr>
<tr>
<td>S²⁻</td>
<td>-</td>
<td>-</td>
<td>0.77</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>-</td>
<td>0.165</td>
</tr>
<tr>
<td>Specific surface</td>
<td>390 m² kg⁻¹</td>
<td>330 m² kg⁻¹</td>
<td>400 m² kg⁻¹</td>
</tr>
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</table>

The studied mixtures, all with a W/B=0.30, are the following (together with their percent replacement of the cement): FA15, FA30, FA50, BFS15, BFS30, BFS50 and BFS85. The mixtures were mixed according to the Standard EN 196-1 and were uniformly and homogenously mixed. The dosage of the superplasticizer was kept constant at an amount of 0.42 mass-% (by binder weight) polycarboxylate superplasticizer (Glenium 51, conc. 35%, BASF).

In systems with a water-to-cement ratio of 0.3 complete hydration is not possible. With an additional (entrained) water-to-cement ratio of 0.054 through pre-described water-filled SAP inclusions ((W/B)ₐ=0.054), internal curing takes over and the self-desiccation is mitigated.
The amount of mixing water absorbed by the SAP was determined in previous research [15, 16]. The amount of SAP to be added to receive an additional entrained water amount of \((W/B)_{e}=0.054\) was 0.22 mass-% (by binder weight) SAP. SAPs were added in addition (subscript in mixtures _SAP), as well as the additional water needed to induce internal curing, i.e. the SAP absorbed its water from the mix water. The SAP used in this research is a crosslinked copolymer of acrylamide and sodium acrylate (particle size 100.0 ± 21.5 μm), produced by bulk polymerization.

2.2 Methods

To determine time-zero to visualize the autogenous strain in time, the Vicat needle test according to the Standard ASTM C191-08 was used in triplicate.

To measure the autogenous strain, the Standard ASTM C1698-09 was followed. In this test, corrugated tubes with a length of 420 ± 5 mm and a diameter of 29 ± 0.5 mm were used. The length of the specimen was monitored either by means of a manually operated dilatometer or by means of an automated system where the dilatometers with samples were submerged in a polyalkylene-glycol thermobath, as can be seen in Figure 1. All automated measurements were done during temperature control at 20.0 ± 0.1°C. The temperature gradients in the specimens were acceptable [17].

Figure 1: Specimens (left) used for the automated autogenous shrinkage tests (right).

3. Results and discussion

Figure 2 shows the autogenous shrinkage of the specimens over time. The starting point of the curves is final setting time. This was determined by means of the Vicat needle test. The pozzolanic reaction occurs at late ages due to the consumption of or activation by calcium hydroxide and other alkaline components originating from the cement. This caused the setting of systems with higher amounts of FA to occur later in time. The position of the autogenous shrinkage curves is highly influenced by the accuracy of the measured time of final set as the rate of shrinkage is very high around this initial point. Furthermore, comparing the manual
discontinuous tests (dashed lines) with the automated continuous tests (solid lines), it is clear that the data corresponds well. In this way, the effects on the long term (between 7 and 28 days) could be studied and compared by both techniques [17].

Figure 2: Autogenous strain [μm/m] for cement paste mixtures with and without FA (a), with and without BFS (b), and with and without entrained water by superabsorbent polymers over 28 days. (--- = manual test curves; — = automated test curves)
The reference mixture with a water-to-binder ratio of 0.30 (R0.30) shows prominent shrinkage. This is due to the fine porosity formed in mixtures with a lower water-to-binder ratio, increasing the hydrostatic tension forces (capillary forces) and leading to the increase in self-desiccation and autogenous shrinkage. In time, the rate of autogenous shrinkage decreases as most of the hydration products have been formed. At 21 days, autogenous shrinkage has almost stopped completely.

The same mixture, but with SAPs added together with additional water (for SAP absorption during mixing), does not show this high-rate shrinkage. Just after setting, there is even a small expansion. This can be caused by several different mechanisms including crystallization pressure of calcium hydroxide [18]. The effect was not prominent and no bleeding occurred in this study. The mixture with (W/B)e=0.054 and SAP seems to mitigate autogenous shrinkage completely at this age, proving the compatibility of the used SAP with the mechanism of internal curing and the usefulness of the application of superabsorbent polymers to mitigate autogenous shrinkage in systems with ordinary Portland cement.

In Figure 2a, the FA systems and their shrinkage are shown. The amount of shrinkage is less in FA systems due to the lower amount of cement at early age, as the initial reaction rate and water consumption is lower. This leads to less autogenous shrinkage at early ages. Only after a couple of days, the pozzolanic reaction takes place, consuming the calcium hydroxide from the cement hydration reaction, increasing the autogenous shrinkage. This can be seen as the sudden increase in slope - or rate of the shrinkage curve - in time. The shift in slope occurs around 8 days and the increase in shrinkage is clearly seen as the curve is shifted downwards. This corresponds to the time where calcium hydroxide started to be depleted due to the pozzolanic reaction [19, 20]. In literature, the same trends at early age are found [10], but shrinkage is mostly monitored till seven days. If one would also do this with these obtained results, one would conclude that the shrinkage would come to a hold at the end of the test (FA50). That is why it is very important to study the effect for a longer time span, for example for one month. Long-term reactions, such as the pozzolanic reaction, influence the autogenous shrinkage properties at these later ages. If the amount of FA is high, i.e. 50% (FA50), the reaction degree of the FA decreases due to an insufficient amount of Ca(OH)2 formed during cement hydration [19]. At higher FA contents the FA would only function as a filler component.

In systems with FA and internal curing (_SAP), the autogenous shrinkage is mitigated (Figure 2a). Generally, superabsorbent polymers are able to mitigate autogenous shrinkage in FA systems with a low water-to-binder ratio.

In Figure 2b, the shrinkage results for the latent-hydraulic BFS mixtures can be found. It is a slow reacting material, leading to less strain at early ages. After 5 days, the rate of autogenous shrinkage is higher as the slag reaction takes place. On one hand, the microstructure in BFS systems should be denser and the pores smaller, which should lead to higher capillary forces, self-desiccation and autogenous shrinkage. On the other hand, the slag reaction occurs at later ages, thus the densification of the cementitious matrix would occur also at later ages. That is why the shrinkage is lower at early age. The level for maximum reaction degree of BFS in blended cement is approximately 60-70% [21], so in BFS85 not all BFS is used and it will act
as filler as well. There is almost no shrinkage in BFS85 mixtures at early age, due to the low calcium hydroxide amount from the hydraulic reaction of the cement. There is even a vast expansion at early age. In time there is a prominent shrinkage due to the slow latent hydraulic reaction of BFS. Re-absorption of bleeding water may also generate expansion, but bleeding was not clearly observed in any of the specimens. It could also be that the early-age expansion resulted from the later-occurring heat of hydration.

When using SAPs in BFS mixtures, autogenous shrinkage is again mitigated for all studied specimens. This shows the potential of SAPs for mitigating autogenous shrinkage in pure cement, FA and BFS blended cement systems. The ion concentration in the pore fluid is also different and the swelling capacity of the SAPs with mixing water may be expected to be different between the mixtures. This would lead to different internal curing amounts. Here, however, no differences were found in flow characteristics and macro porosity [15] between the different mixtures indicating that the absorption of pore fluids was the same in all mixtures.

The percentage of mitigated autogenous shrinkage for the different mixtures is shown in Table 2. The percentage was calculated as the autogenous shrinkage of a specimen without SAP at a specific age minus the shrinkage in a SAP specimen with the same matrix and age over the strain in the specimen without SAPs. A percentage of more than 100% indicates an expansion, and thus the shrinkage was completely compensated by the SAP.

Table 2: The percentage of mitigated autogenous shrinkage [%] over time.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td>0</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>SAP</td>
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<td>FA15_SAP</td>
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<tr>
<td>BFS50_SAP</td>
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</tbody>
</table>

* The values for BFS85_SAP are not given as they are off scale, but similar shrinkage mitigation for this mixture is evident from Figure 2.

Again, in all systems with SAPs, there is mitigation of autogenous shrinkage in time. The values over time are also comparable, demonstrating SAPs as good means of mitigation in time due to release of mixing water towards the cementitious matrix.

The results in this paper are for manually blended cement compositions (with FA or BFS). Commercially available cement types such as CEM II-III-IV-V are expected to follow the
same trend, but other initial constituents may be present. This may have an effect on the autogenous shrinkage properties.

4. Conclusions

- Irrespective to the mixture, both the manual and automated tests show the same trend and quantitative values. In this way, all obtained results are comparable.

- In both fly ash and blast-furnace slag systems, where part of the cement is replaced by SCMs, the initial total amount of autogenous shrinkage is lower compared to an ordinary Portland cement mixture with a water-to-binder ratio of 0.30.

- At later ages, the rate of autogenous shrinkage is higher compared to ordinary Portland cement mixtures. It is therefore important to study the effects of autogenous shrinkage on the long term, rather than stopping at an age of 7 days.

- Internal curing by means of superabsorbent polymers can be successfully applied independent of this long-term higher rate of shrinkage in mixtures with supplementary cementitious materials.

- Superabsorbent polymers are able to mitigate autogenous shrinkage in mixtures with a water-to-binder ratio of 0.30, with or without fly ash and/or blast-furnace slag as a supplementary cementitious material.

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INFLUENCE OF PARTICLE SIZE DISTRIBUTION OF SLAG, LIMESTONE AND FLY ASH ON EARLY HYDRATION OF CEMENT ASSESSED BY ISOTHERMAL CALORIMETRY

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Abstract
Supplementary cementitious materials (SCMs) enhance early hydration of cement through the provision of nucleation sites for the precipitation of hydration products. This effect contrasts with the dilution effect of the mineral addition to the cementitious system. In fact, the net effect on heat release during the first hours of hydration is the reduction of peak intensity. Then, only when the specific heat is evaluated in terms of cement weight the actual effect of the admixture on hydration may be assessed. In this sense, a clear difference may be expected in accordance with the replacement ratio and fineness of the SCM. Increased specific surface favors nucleation and it therefore enhances hydration. In this paper, cement pastes admixed with slag, limestone and fly ash in three different fineness levels and three replacing ratios were investigated through isothermal calorimetry. The filler effect of each SCM was in relation with the fineness and replacing ratio, with higher impact on the aluminate reaction than on the silicate reaction of cement.

1. Introduction
The hydration reaction of cement is an exothermic process. The total heat released during hydration is a function of the composition and relative amount of cementitious materials, and the water-cementitious ratio of the mixture. Isothermal (conduction) calorimetry allows continuous measurements of the progression of hydration at early ages, when the heat production rate is high. Most supplementary cementitious materials (SCMs) in hardening cementitious materials become active after a few days, when the alkalinity is high enough, caused by cement hydration. It is usually considered that the amount of reaction of SCMs in the first few days is very often negligible and their influence is usually associated with filler effect. Two main mechanisms are generally acknowledged for contributing to the filler effect: extra space and enhanced nucleation. First, at the same water to solids ratio, the water to clinker ratio is higher
when part of it is replaced by SCMs and there is more space for the hydration products of the clinker phases. Secondly and particularly for fine materials, the extra surface provided by the SCMs provides nucleation sites for the precipitation of hydration products of clinker. For example, the reaction of fly ash is slow at ambient temperatures, with marginal reaction degree up to 2 days [1]. Then, it contributes to increase the amount of portlandite compared to pure ordinary Portland cement (OPC) within the first days of hydration [2][3]. Subsequently, indications of fly ash reaction between 2 and 7 days are given by increased chemical shrinkage, bound water and reduced portlandite contents, with a consequential heat production by the SCM itself.

Even for slag, which is more reactive than fly ash, the amount of portlandite in slag blended systems remains similar or even higher (due to faster reaction of the clinkers caused by the filler effect) than in pure OPC systems during the first hours or days of hydration [2] [4], showing limited reactivity. However, Gruyaert [5] found that slag hydration already starts during the first days after mixing. Calorimetric measurements showed an extra hydration peak in the presence of slag and back-scattered electron (BSE) images indicated a slag hydration degree of 28% after 2 days for pastes with 50% of OPC replaced by slag. This early reaction might not be accompanied by portlandite consumption but it is indicated by heat production. In fact, reactivity of a SCM and its contribution to heat production are connected. Whereas some authors report decreased cumulative heat with increasing slag content [6], others suggest in contrast that the long-term heat of hydration is higher when the mixes contain slag [2]. In the first case, the low amount of heat evolved is related with limitations in the reactivity and hydraulic index of the slag. Different values for the contribution of slag reaction to heat production can be found in the literature. Schindler and Folliard [7] indicated values for the maximum heat released at the end of the reaction of 461 J/g, whereas values of 355 and 440 J/g were reported in [8] and [9], respectively. On her part, Gruyaert [3] estimated the potential heat production of slag in the range of 400 – 500 J/g. These variations also seem to be due to different reactivities and chemical compositions. With increasing slag content, it is generally assumed that also the rate of heat evolution decreases [6,10], what would in the opposite direction indicate a filler effect that cannot compensate the dilution effect.

Limestone is commonly considered to have a pure filler effect. However limestone powder cannot be considered totally inert due to the formation of carboaluminates; the impact of these products on heat release and microstructure formation may be considered secondary [11]. Increasing the specific surface of the reactant can increase the reaction rate. But for SCMs the effect of reducing particle size is more complex due to the filler effect. Grinding is a common manufacture procedure for slag and limestone. Pal et al. [12] found a strong correlation between the hydraulic index of slags and Blaine fineness, together with chemical composition and glass content, at both 7 and 28 days. Swamy [13] reported that an increase in fineness of two to three times that of OPC can favor several engineering properties such as bleeding, setting time, heat evolution, high strength and durability. Thus, for better performance, the fineness of slag must be greater than that of cement.

Grinding is also an alternative processing method for increasing fineness and reactivity of a fly ash (although typical morphology of particles is substantially modified). Experimental results have confirmed that grinding not only increases fineness, but also reactivity, acid neutralization capacity and pozzolanicity of fly ash [14].

Blended cements are usually produced by intergrinding cement clinker with SCMs. But differences in hardness of the constituents tend to accumulate the SCM in certain size
fractions. For the particular case of slag, which is the hardest component, it tends to accumulate in coarse-size fractions. This results in less reactivity of slag and a reduction in strength that must be compensated by grinding the mix to an even finer degree. The advantages of grinding clinker and slag separately and mix them in appropriate proportions, such as lower specific energy consumption, ease of manufacture, higher addition of slag, and higher flexibility in product quality arrangements [15], result in this frequent production practice in cement plants. Also interground limestone blended cements are usually considered bimodal in terms of particle size distribution due to different hardness of limestone and clinker. But in this case, limestone is the softer material, and it is finer than clinker particles in the cement. Then, limestone is more favoured than slag to produce filler effect to enhance hydration of interground cements.

This paper deals with the enhancement of cement hydration allowed by slag, limestone and fly ash in different fineness degrees and replacement levels. Through isothermal calorimetry, the quantification of the enhancement of cement hydration due to the heterogeneous nucleation effect at short hydration times up to 7 days was investigated.

2. Assessment of heat production and hydration degree

The heat of hydration of cement at complete hydration ($H_{cem}$) can be estimated from the weighted contribution of its constituents (Equation 1) [7]. Here, $H_{cem} = \text{total heat of hydration of the cement (J/g)},$ and $p_i = \text{weight ratio of i-th compound in terms of total cement content}.$

$$H_{cem} = 500p_{C5S} + 260p_{C3S} + 866p_{C3A} + 420p_{CLAF} + 624p_{C3S} + 1186p_{FreeCaO} + 850p_{MgO} \tag{1}$$

However, for blended systems, limited and varying data for the heat contribution of fly ash or slag can be found in literature. Some recommended values are 209 J/g [8] for fly ash and 461 J/g [8], 355-440 J/g [9], and 400-500 J/g [5] for slag. Limestone is usually considered as a non contributor to heat release itself [16].

Then, considering the relative cementitious materials content, the potential heat of hydration per unit weight of all the cementitious materials ($H_u$) at complete hydration is computed from Equation 2. Here, $p_{cem} = \text{cement weight ratio to total cementitious content},$ $p_{SCM} = \text{SCM weight ratio to the total cementitious content},$ and $h_{SCM} = \text{heat of hydration of SCM (J/g)}.$

The heat produced at a time $t$ divided by the total heat available provides a measure of the progress of hydration [17] (Equation 3), as a simplified indirect method of estimating the overall degree of hydration (it assumes a single value for the hydration degree for the mix of all clinker phases and slag) of the cementitious system. Where, $\alpha(t) = \text{degree of hydration at time t},$ and $H(t) = \text{cumulative heat of hydration released at time t (J/g)}.$

On the basis of the experimental determination of heat production during hydration, a best fit mathematical model has been suggested [18]. The s-shape of the hydration development can be accurately represented by the exponential formulation in Equation 4. Where, $Q(t) = \text{the cumulative heat production at time t},$ $\tau = \text{hydration time parameter (hours)},$ $a = \text{hydration shape parameter},$ and $Q_{ref} = \text{cumulative heat released after complete hydration}.$

From experimental data, values for $Q_{ref}$ lower than the potential long-term heat production, $H_u,$ have been obtained [5], mainly due to practical unfeasibility of achieving complete hydration at ambient temperature in accordance with the Mills equation (Equation 5) [19].
3. Materials and Methods

Two types of slag (SA and SB), one limestone (LA) and one fly ash (FB) were analysed in this study. Mineralogical and chemical compositions of raw materials are presented in Tables 1 and 2, respectively. Amorphous contents of slags and fly ash were determined by the Rietveld analysis of XRD with internal standard. Grinding in a laboratory ball mill was applied for obtaining three fineness levels. Particle size distributions measured by laser diffractometry are shown in Table 3. Each ground material is identified with increasing numbers (1 to 3) for increasing fineness.

With these materials pastes were prepared with a w/b ratio of 0.45 and replacement ratios of cement by SCM of 20, 40 and 60% for slag, 10, 20 and 30% for limestone and 20, 30 and 40% for fly ash. These pastes were manually mixed and immediately introduced in a conduction calorimeter for the determination of heat production under isothermal conditions at 20 °C. Measurements up to 150 h of hydration were obtained.

Table 1. Mineralogical composition of raw materials by XRD/Rietveld analysis (%).

<table>
<thead>
<tr>
<th>Material</th>
<th>C3S</th>
<th>C2S</th>
<th>C3A</th>
<th>C2AF</th>
<th>Anhydrite</th>
<th>Quartz</th>
<th>Magnetite</th>
<th>Calcite</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>60.2</td>
<td>22.0</td>
<td>10.8</td>
<td>2.7</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>LA</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>10.0</td>
<td>nd</td>
<td>75.2</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>FB</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>5.9</td>
<td>1.2</td>
<td>91.9</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>SA</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>0.4</td>
<td>nd</td>
<td>nd</td>
<td>99.6</td>
<td>nd</td>
</tr>
<tr>
<td>SB</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>1.2</td>
<td>nd</td>
<td>nd</td>
<td>98.8</td>
<td>nd</td>
</tr>
</tbody>
</table>

nd: below detection limit.

Table 2. XRF chemical compositions of raw materials (%).

<table>
<thead>
<tr>
<th>Material</th>
<th>LOI</th>
<th>Na2O</th>
<th>MgO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>SO3</th>
<th>K2O</th>
<th>CaO</th>
<th>Fe2O3</th>
<th>Free CaO(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>1.80</td>
<td>0.27</td>
<td>0.95</td>
<td>4.91</td>
<td>20.74</td>
<td>2.96</td>
<td>0.77</td>
<td>64.67</td>
<td>1.52</td>
<td>0.2</td>
</tr>
<tr>
<td>LA</td>
<td>37.29</td>
<td>1.25</td>
<td>1.41</td>
<td>1.28</td>
<td>8.15</td>
<td>0.05</td>
<td>0.28</td>
<td>48.45</td>
<td>0.88</td>
<td>0.5</td>
</tr>
<tr>
<td>FB</td>
<td>1.84</td>
<td>1.08</td>
<td>1.92</td>
<td>23.50</td>
<td>54.19</td>
<td>0.94</td>
<td>3.38</td>
<td>3.02</td>
<td>7.92</td>
<td>0.1</td>
</tr>
<tr>
<td>SA</td>
<td>nd</td>
<td>1.91</td>
<td>12.14</td>
<td>8.62</td>
<td>28.89</td>
<td>1.85</td>
<td>0.43</td>
<td>36.16</td>
<td>0.95</td>
<td>nd</td>
</tr>
<tr>
<td>SB</td>
<td>nd</td>
<td>0.35</td>
<td>8.18</td>
<td>11.36</td>
<td>33.70</td>
<td>0.03</td>
<td>0.34</td>
<td>38.34</td>
<td>0.43</td>
<td>nd</td>
</tr>
</tbody>
</table>

nd: not determined.
(1) determined by titration
Table 3. Particle size distribution of OPC and SCMs (μm).

<table>
<thead>
<tr>
<th>Mat.</th>
<th>OPC</th>
<th>LA1</th>
<th>LA2</th>
<th>LA3</th>
<th>FB1</th>
<th>FB2</th>
<th>FB3</th>
<th>SA1</th>
<th>SA2</th>
<th>SA3</th>
<th>SB1</th>
<th>SB2</th>
<th>SB3</th>
</tr>
</thead>
<tbody>
<tr>
<td>d10</td>
<td>3.1</td>
<td>2.5</td>
<td>2.2</td>
<td>1.6</td>
<td>2.1</td>
<td>1.7</td>
<td>1.4</td>
<td>1.0</td>
<td>0.8</td>
<td>0.9</td>
<td>2.2</td>
<td>1.8</td>
<td>1.3</td>
</tr>
<tr>
<td>d50</td>
<td>16.3</td>
<td>9.5</td>
<td>4.9</td>
<td>4.3</td>
<td>15</td>
<td>11</td>
<td>7.5</td>
<td>7.7</td>
<td>6.6</td>
<td>5.7</td>
<td>12.4</td>
<td>11</td>
<td>7.6</td>
</tr>
<tr>
<td>d90</td>
<td>57.9</td>
<td>76.4</td>
<td>51.1</td>
<td>26.7</td>
<td>89.3</td>
<td>44.7</td>
<td>25.2</td>
<td>56.7</td>
<td>58.4</td>
<td>25.8</td>
<td>32.1</td>
<td>32.9</td>
<td>32</td>
</tr>
</tbody>
</table>

Before mixing, the components were thermally conditioned at 20 °C to equilibrate them with the isothermal environment. As the components were manually mixed together and put outside the calorimeter, the first heat peak could not be registered completely and the integration of heat was done starting 30 min after contact between cement and water.

4. Results and Discussion

The evolutions of heat production for blended pastes are presented in Figures 1. Also results for paste made with OPC only (P) with the same water/binder ratio is presented for reference.

Figure 1. Heat production rate during hydration of pastes (for each SCM, A/B/C pastes indicate increasing replacement ratio, 20/40/60, 10/20/10 or 20/40/60%, respectively for slag, limestone and fly ash). Magnified frames show results for the first 24 h.
Both slags show the same trend with quantitative differences only. The increase in heat evolution during the acceleration period is steeper with higher replacing ratio and fineness. This acceleration period is associated with the accelerated formation rate of C-S-H. Also the maximum heat flow is higher, and the deceleration period steeper. This is consistent with an increase in the number of nucleation sites for enhanced cement hydration. Despite the heat maxima for slag blends increase in relation with the unblended reference, the rates of heat release decrease faster than for the reference and after approximately 24 h of hydration the difference among the curves (including the reference) is significantly reduced. Subsequently, heat release rate beyond 24h is increased with increasing fineness due to further enhancement of cement hydration and possibly also due to slag reaction on the basis of its higher specific surface and an earlier activation caused by higher amounts of portlandite release in the first hours. Then, for the case of the finest slags, their influence on the reaction rate seems not totally explained by the filler effect only, and also reaction may be considered. Moreover, there is a shift in the heat maximum for both slags when the replacement ratio is higher and the SCM is finer. For the reference sample the heat maximum corresponds to the enhancement of C_3S hydration, whereas a very smooth shoulder can be observed in correlation to C_3A reaction after the depletion of the calcium sulphate phases [10,20–22]. For the blended mixes, this shoulder is related to the filler effect and connected with the fineness of the blends [16]. The effect becomes more noticeable with increasing content, and for 40% of slag it already becomes a third peak that exceeds the one corresponding to the silicate reaction and becomes the heat maximum itself. For 60% replacement this shift is extreme and it is difficult to notice the contribution of the silicate reaction. This change is not only quantitative, as also earlier times for the heat maximum were obtained with increasing replacing ratios and fineness levels. This is obvious when the heat maximum corresponds to a different reaction, but it is also noticed when comparing blended pastes with 40 and 60% of slag, where earlier times for the heat maximum are also noticed. Higher replacing ratios mean lower C_3A to react. If aluminate is the only responsible, then the total heat released by this phase should be lower as the dilution effect results in less C_3A content. The enhancement of C_3A reactions seems not to completely explain the higher heat maximum caused by slag. Lothenbach et al [23], on the basis of the work of Kocaba [4], suggested that this is due to fillers and SCMs promoting the nucleation of the hydrates forming during this aluminate reaction instead of reacting themselves, but results from the present study suggest that this effect is dependent on the reaction of slag in connection with its fineness and replacing ratio. Previously, similar effects on the aluminate peak have been reported for slag blends and attributed to an early reaction of the slag itself [24,25]. This seems to be supported by the values for cumulative heat (Figure 2), which show much higher values for slag blends than those corresponding to the cement in the mix. Especially for fly ash blends, but also for limestone blends in a lower degree, it seems that nucleation effects may be even more marked in the case of the hydration products of the aluminate phase. The additions of these fine materials have a limited impact on the silicate reaction, but the relative impact on the aluminate reaction is much more significant. The aluminate peak is sharpened, becoming narrower and higher with increasing fineness and replacement ratio. This illustrates that the seeding effect of SCMs is affecting the aluminate reaction more than the silicate reaction. This is also supported by a study on blends with completely inert fillers [22].
Also limestone accelerates the OPC hydration as it is seen that there is an impact on the slope of the heat evolution curve during the acceleration period. The second peak appears slightly earlier with increasing limestone content and fineness level (Figure 1). This is not the case for fly ash, where the heat release is maintained or slightly delayed (Figure 1). This retarding effect of fly ash on the cement hydration is repeatedly reported in the literature [24][26]. The results indicate that the dilution effect from SCMs has an acceleration effect, but for the case of fly ash other factors are more important in the presence of this SCM.

The accelerating influence from SCMs depends on their specific surface for allowing heterogeneous nucleation. As the fineness of the SCMs becomes finer than that of cement, the contribution of heterogeneous nucleation towards the acceleration of the cement hydration is more noticeable. However the acceleration period is not significantly modified, with the maximum heat evolution occurring a little earlier or more or less at the same time. An exception should be made for slags but this is due to a shift of the main reaction contributing to the maximum peak. This maximum corresponds to impingement of hydration products and growth controls the reaction kinetics beyond this heat peak [27]. The deceleration period starts when C–S–H grows out from the cement grains in a diffuse manner [28]. Then, the diffuse layer does not seem to affect the silicate reaction and C-S-H growing during the deceleration period, and enhancement of hydration by SCMs does not result in an extended thermal power. This might be attributed to the extra space that the SCMs allow, which compensates the higher amount of early hydration products. Moreover, for the particular case of limestone, it is seen that with increasing replacing ratio (up to at least 30%), hydration enhancement (i.e., provision of more nucleation sites) overrides the dilution effect provided by additional space, and deceleration is then a little earlier due to greater diffusion control.

Figures 2 show decreasing cumulative heat production for pastes with increasing SCM content. However, this does not necessarily mean that the total heat production at time ‘infinity’ for pastes with slag is considerably lower than for the plain paste. The estimated values of $Q_e$ obtained by fitting Equation 4 are shown in Figure 3. Only for replacement levels of 30% or more for limestone and fly ash the total heat production decreases considerably compared to that of OPC paste.

The effect of slag on $Q_e$ is much less than that of limestone and fly ash, even more considering that higher replacement ratios have been applied for slags. This is caused by the reactivity of slags, which is much faster than that of fly ash, whereas limestone releases no heat at all. Moreover, for increasing fineness also $Q_e$ increases. For the particular case of fly ash and limestone, little difference can be seen with a replacement ratio of 20%, but when this is increased to 30%, a significant decrease with the coarser fly ash is noted in comparison with the coarser limestone. For the case of slags, it is very remarkable that the release of heat due to reaction of slag plus the enhancement of cement hydration compensate the dilution effect of the SCM. In general terms, the heat release was reduced with replacing ratio only for the case of fly ash and in less extent for limestone.

Due to incomplete hydration, $Q_e$ extrapolated from Equation 4 results in a lower value than that for the potential heat release, $H_{cem}$, according to Equation 1 and composition in Tables 1 and 2 ($Q_e=388$ and $H_{cem}=492$ J/g for P). The ultimate hydration degree defined as $Q_e/H_{cem}$ for P is 0.79, which is in between and agrees with values obtained by Gruyaert [5] for OPC (0.72-0.73 for w/c=0.40 and 0.82-0.85 for w/c=0.50). When $H_u$ is computed for the blended...
pastes, different ultimate hydration degrees for the different blends are obtained (Figure 4). Here, potential heat release values of 210 and 450 J/g were considered for fly ash and slag, respectively. For limestone, no heat release was considered. All the ultimate hydration degrees obtained are higher than the ultimate hydration ratio of Mills (1.03 \cdot \frac{w/b}{(0.194+w/b)}), 0.72 for w/b = 0.45, but some lower hydration degrees are obtained for the coarser SCMs in relation with the reference paste.

Figure 2. Effect of the SCM content on the cumulative heat production at early ages.

Figure 3. Effect of the SCM content on the long-term cumulative heat production.
5. Conclusions

From the results of isothermal calorimetry of OPC blends with slag, limestone and fly ash, in three different fineness levels, the following is concluded:

- The filler effect of the three types of SCM showed higher impact on the aluminate reaction than on the silicate reaction of cement, and this effect was increased with the replacing ratio and fineness of the SCM.

- An acceleration of hydration was obtained with slag and limestone blending. This acceleration increased with replacing ratio and fineness. No acceleration was obtained with fly ash, and the effect was solely noticed on aluminate reaction.

- For the finest slags, the main peak shifted from the silicate reaction to the aluminate reaction, in connection with remarkable filler effect. However, increases in heat release cannot be completely explained with the filler effect, and considering the contribution of slag reaction itself seems necessary even as early as before 24 h of hydration.

- Increasing fineness of slag, fly ash and limestone showed a significant impact on hydration of cement, and the convenience of separate grinding that allows improved design of blended cements in which the SCM has a smaller particle size than clinker particles, with increased filler effect and reactivity, is shown.

References


REACTIVITY OF FLY ASH IN THE PRESENCE OF CHEMICAL ACTIVATORS

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(3) Saint-Gobain Weber, Datteln, Germany

Abstract
The hydration of a fly ash - Portland cement blend (70/30 by mass) without and with the addition of activators (potassium sodium silicate, sodium carbonate, sodium oxalate and potassium citrate) was examined. Measurements of setting time and strength were performed as well as analyses of the hydrate assemblages and of the composition of the pore solution. The influence of the activators on fly ash reactivity was determined using a pozzolanity test in combination with thermodynamic modelling, which allowed the calculation of the reaction degree of the fly ash. The activators enhanced compressive strength at early age, but decreased strength at late age. All activators increased pH and decreased thus the calcium concentrations in the pore solution. Higher undersaturation with respect to alite led to a faster reaction of alite and thus to early setting and a high early strength. On the long term, the high alkali concentrations lowered compressive strength. Thermodynamic modelling indicated that the high pH values due to the high alkali concentrations destabilized ettringite. The pozzolanic reaction of the fly ash could be enhanced by some of the activators, which seems to be mainly an influence of the increased pH values.

1. Introduction

The use of fly ash (FA) as total or partial replacement of Portland cement (PC) in blended cements, dry mix mortars or concrete is a frequent solution for decreasing the use of Portland cement clinker and therefore the consumption of energy and the production of CO₂.

A possibility for the use of high quantities of fly ash in building materials is their application in alkali activated binders [1-3]. However, generally high additions of strong alkaline activators are needed in such systems, which might cause health issues, especially when such binders are used in dry mix mortar formulations (e.g. tile adhesives), where the workers get into contact with the highly alkaline material. A mixture of fly ash as major binder component with Portland cement avoids the use of alkaline solutions. As fly ash reacts only slowly in
such systems, activation of the fly ash is needed, preferably avoiding highly alkaline conditions. The use of different such “mild” activators including alkali carbonates and sulfates [4-7] and organic activators with carboxylate groups such as lactates or citrates as summarized in [8] has been reported previously. However there is a lack of detailed studies of activators with limited alkalinity regarding their efficiency in accelerating very high volume fly ash hybrid binders based on low calcium fly ash and Portland cement. In this contribution, a study of the interaction of a siliceous fly ash-PC blend with different “mild” activators is summarized [8]. A possible application of such binders would be their use in dry mix mortars (e.g. tile adhesives) where a high compressive strength is not necessary.

2. Experimental

2.1 Materials
Portland cement (CEM I 52.5 N acc. to EN 197-1) and a siliceous fly ash (type V according to EN 197-1) were used as raw materials. Their chemical compositions and their particle size distributions are given in [8]. As inert reference material, quartz powder with a similar particle size distribution than the fly ash was used. Potassium sodium silicate ((K,Na)2SiO3, 2 mass-% referred to binder), sodium carbonate (Na2CO3, 3 mass-%), sodium oxalate (Na2Oxalate, 8 mass-%) and potassium citrate (K3Citrate, 3 mass-%) were used as activators. The selection of the activators and their dosages was based on a previous screening test regarding setting times.

2.2 Methods
All experiments were carried out at 20°C. Cement pastes containing 70 mass-% of FA (or 70 mass-% of quartz powder) were blended with a IKA Ultra-Turrax T50 mixer at 360 rpm for 30 s and then at 600 rpm for another 30 s using a water to binder ratio (w/b) of 0.40. The activators were added as dry powders. Setting times were measured according to EN 196-3 at a relative humidity of 70%. X-ray diffraction analyses of the hydrated pastes were carried out after a hydration time of 28 days. The hydration was stopped by solvent exchange using first isopropanol and then diethyl ether. X-ray patterns were recorded using a Panalytical X’Pert Pro MPD diffractometer in a 0-0 configuration with CoKα radiation and X’Celerator detector. After 6 h, 1, 7 and 28 days of hydration, pore solutions were extracted using the steel die method [9]. The concentrations of Na, K, Ca, Al, Si and sulfate were measured by ion chromatography (Dionex DP ICS-3000). The hydroxide concentrations of the pore solutions were determined in undiluted samples with a combined pH electrode calibrated against KOH solutions of known concentrations. In order to determine the reactivity of the fly ash in the presence of the activators, the consumption of portlandite due to the reaction of the fly ash in a simulated PC environment (a slurry of Ca(OH)2 + CaCO3 + KOH) was determined according to [10] and compared to the changes observed in a quartz reference. The decrease of portlandite content with hydration time can be used as characteristic value for the pozzolanic reaction and for the reaction degree of the fly ash, taking the partial consumption of the Ca(OH)2 by some of the activators into consideration. The reaction degree of the fly ash was calculated by thermodynamic modelling referring to the amount of the Ca(OH)2 consumed by the fly ash.
Thermodynamic modelling was performed using the Gibbs free energy minimisation software GEMS [11,12] using the Nagra/PSI Thermodynamic database [13] expanded with additional data for solids relevant for cementitious systems [14-16] and for oxalate and citrate (a summary of the data used for the organics is given in [8]). GEMS was used to calculate (i) the effective saturation indices (SI) of the solid phases [17] based on the pore solution composition, (ii) the hydration degree of the fly ash based on its consumption of Ca(OH)\(_2\) in the pozzolanity test and (iii) the influence of the added activators on the hydrate assemblage of the fly ash-PC blend after 28 days assuming complete hydration of the PC and a fly ash reaction degree of 7% in agreement with [18].

Compressive strength was measured on mortars according to EN 196-1 with a w/b ratio of 0.50. The prisms were demoulded after 1 day curing at 20°C/>95% relative humidity and cured subsequently at 20°C in sealed bags. Compressive strength was tested after 1, 3, 7, 28 and 91 days.

3. Results and discussion

3.1 Setting time
The fly ash-PC blend shows an initial set after 9 h and a final set after 19 h (Figure 1), which is in agreement with the low content of Portland cement. All activators decrease setting times compared to the plain binder.

![Figure 1: Setting time of the PC/FA-blend without and with activators](image)

3.2 Compressive strength
Compressive strengths of the fly ash-PC and the quartz-PC blends are comparable during the first 7 days of curing, as mainly the PC has reacted (Figure 2). The compressive strength of the quartz blend shows only a slight strength gain between 7 and 91 days while the compressive strength of the fly ash blend continues to increase with time and reaches 35 MPa after 91 days, indicating that the fly ash contributes positively to the long-term development of compressive strength.

All activators increase compressive strength after 1 day indicating activation of PC and/or fly ash. However, at later hydration times they decrease compressive strength compared to the plain binder which could be related to the presence of high alkali concentrations. It has been
observed [19] that the addition of alkali hydroxide solutions to Portland cement pastes decreased the compressive strength and increased porosity at comparable degree of clinker reaction.

Figure 2: Mortar compressive strength of the PC/FA-blend without and with activators

3.3 Hydration degree of fly ash

Figure 3 shows the fly ash reaction degree as obtained by comparison of the observed consumption of portlandite with the expected consumption of portlandite based on mass balance calculations using GEMS. In the plain binder, the reaction degree of the fly ash increases with time and reaches approximately 20% after 91 days. With the exception of K₃Citrate, all activators enhance the reaction degrees of the fly ash significantly after 28 days and slightly after 91 days. K₃Citrate retards the fly ash reaction in agreement with [20], who observed a decrease of the glass dissolution rate under alkaline conditions in the presence of citrate. Although the mechanisms responsible for the observed decrease of glass dissolution are not clear, it can be speculated that the formation of citrate complexes at the glass surface could be an explanation for the observed decrease of reaction.
3.4 Hydrate assemblage and composition of pore solution

Monocarbonate, hemicarbonate, ettringite and portlandite are identified as crystalline hydration products of the plain fly ash-PC blend after 28 days in agreement with [4] (Figure 4). C-S-H cannot be detected by XRD due to its ill-crystalline/amorphous nature, but its presence was derived from the TGA data (see [8]). The pH values increase up to 7 days of hydration due to dissolution of alkalis from the anhydrous compounds and due to a reduction of the amount of pore solution with ongoing hydration (Figure 5a).

After 28 days the pH decreases in agreement with [10], indicating the pozzolanic reaction of the fly ash. The pore solutions are initially saturated with respect to Ca(OH)$_2$ (Figure 5b), C-S-H (not shown) and oversaturated with respect to ettringite (Figure 5c). After 1 day, when the calcium sulfate has been consumed, the solutions are saturated with respect to ettringite and become, due to the reaction of the fly ash, slowly undersaturated with respect to portlandite, indicating the consumption of portlandite in the pozzolanic reaction.

The same crystalline hydration products were detected in the fly ash blended PC without and with (K,Na)$_2$SiO$_3$ (Figure 4). However, the amount of portlandite is significantly lower in the presence of the activator. Thermodynamic calculations indicate that the addition of (K,Na)$_2$SiO$_3$ increases the total amount of C-S-H and decreases the amount of portlandite due to the reaction of portlandite with (K,Na)$_2$SiO$_3$ (Figure 6). Furthermore the amount of ettringite is expected to decrease due to the very high pH and higher ionic strength, which destabilizes the water-rich ettringite in comparison to AFm phases [4,21].

The pH is approximately 0.3 units higher than in the sample without activator (Figure 5a). The solution is initially saturated with respect to portlandite (Figure 5b) and C-S-H (not shown) and becomes undersaturated with respect to portlandite with time. The ettringite oversaturation decreases along time (Figure 5c).
Figure 4: XRD patterns of the PC/FA-blend without and with activators hydrated for 28 days. A = alite, B = belite, C = calcite, CSH = C-S-H, CO = calcium oxalate monohydrate, E = ettringite, Hc = hemicarbonate, M = mullite, Mc = monocarbonate, OA = oxalate-AFM, P = portlandite, Q = quartz

Less portlandite is present when Na₂CO₃ has been added (Figure 4). In addition, only low amounts of ettringite are present after 28 days, while the formation of monocarbonate is favoured in the presence of the activator. In agreement with the experimental observations, thermodynamic modelling (Figure 6) indicates that less portlandite is present and that monocarbonate is stabilized on the expenses of ettringite due to the increase of pH and carbonate concentration.

A relatively high pH is observed in the case of Na₂CO₃ activator (Figure 5a), which results from the reaction according to Eq. (1). The calculated effective saturation indices (Figure 5c) indicate that the solutions are only initially oversaturated with respect to ettringite, but become undersaturated with time, consistent with the presence of little ettringite. The solutions remain oversaturated with respect to calcite during the first week and are always undersaturated with respect to portlandite (Figure 5b).

\[
\text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + 2\text{Na}^+ + 2\text{OH}^- \quad (1)
\]

**Na₂Oxalate** significantly increases the reactivity of the fly ash (Figure 3) due to the very distinct pH increase caused by the high amount of activator used. The addition of sodium oxalate results in the presence of very little portlandite after 28 days (Figure 4). The formation of Ca-oxalate is observed according to Eq. (2) leading to a pH increase.

\[
\text{Na}_2\text{C}_2\text{O}_4 + \text{Ca(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O} + 2\text{Na}^+ + 2\text{OH}^- \quad (2)
\]
No ettringite is observed by XRD (Figure 4). A second AFm phase, probably a “hemi-oxalate” $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.5\text{Ca(OH)}_2 \cdot 0.5\text{CaC}_2\text{O}_4 \cdot 9\text{H}_2\text{O}$ [22] might be present, however it could not clearly be identified in the XRD data, as its main reflections overlap with those of monocarbonate. The absence of ettringite may again be related to the high pH (Figure 5a) and ionic strength in the pore solution. Thermodynamic modelling (Figure 6) confirms that the addition of Na$_2$Oxalate lowers the amount of portlandite strongly while Ca-oxalate is formed and ettringite is destabilized. As there are no thermodynamic data available yet for “hemi-oxalate”, it could not be included in the modelling.

![Figure 5:](image)

a) measured pH of the pore solution
b) effective saturation index (eff. SI) of portlandite calculated by GEMS
c) effective saturation index (eff. SI) of ettringite calculated by GEMS

A negative effective saturation index corresponds to undersaturation, a positive value corresponds to oversaturation.

The pH (Figure 5a) of the pore solution is particularly high due to the high quantity used. The solutions are always undersaturated with respect to portlandite (Figure 5b) and slightly undersaturated with respect to ettringite (Figure 5c), consistent with the XRD data. The solutions are near saturation with respect to C-S-H (not shown).

After 28 days, a similar amount of portlandite is observed in the presence of K$_3$Citrate (Figure 4) compared to the reference paste without activator. Thermodynamic modelling (Figure 6) shows that adding potassium citrate is expected to lead to the formation of a small quantity of calcium citrate ($\text{Ca}_3\text{(C}_6\text{O}_7\text{H}_5)_2\cdot 4\text{H}_2\text{O}$), which could not be identified by XRD probably due to a too low content, but else does not change significantly the kind or amount of the hydration products. A slight decrease of the amount of ettringite and portlandite and an

47
increase of the amount of AFm are calculated due to the increase in ionic strength. The presence of K$_3$citrate leads to relatively pH values (Figure 5a) in the pore solution. The solutions are saturated with respect to portlandite (Figure 5b), C-S-H (not shown) and ettringite (Figure 5c).

Figure 6: Stable hydrate assemblages after 28 days calculated by GEMS of the PC/FA-blend without and with activators assuming hydration degrees of 100% for PC and 7% for FA

4. Conclusions

The hydration of a fly ash-PC blend (70/30 by mass) without and with the addition of activators was examined. The activators (potassium sodium silicate, sodium carbonate, sodium oxalate and potassium citrate) where chosen as they increase pH to stimulate fly ash dissolution but avoid too highly alkaline conditions due to health issues as the binders should be suitable for dry mix mortars. Without activators the fly ash reacts and the reaction contributes significantly to the development of compressive strength after 7 days and longer. The addition of the activators enhances the compressive strength at early age. All activators increase the pH values and decrease thus the calcium concentrations in the pore solution. Lower calcium concentrations lead to a higher undersaturation of alite and thus a faster reaction of alite [23,24], providing early setting and high early strength. On the long term, the high alkali concentrations lower the compressive strength after 91 days and lead to a (partial) destabilization of ettringite.

The pozzolanic reaction of the fly ash (in a simulated PC medium) is not or only slightly enhanced by Na$_2$CO$_3$. Na$_2$Oxalate and (K,Na)$_2$SiO$_3$ accelerate the fly ash reaction due to the increased pH. K$_3$Citrate is found to hinder both the fly ash and the PC reaction.
The late compressive strength decreases with increasing pH values observed in the pore solution, confirming earlier observation in Portland cement pastes [19] that high pH values are negative for long-term compressive strength. However, it is unclear whether this strength decrease is related to the very fast initial reaction and thus to the formation of more dense and less well interlocked hydrate assemblage, whether the properties of C-S-H are negatively influenced or whether the (partial) destabilization of ettringite is the reason for this strength decrease at later age. Sodium oxalate and (K,Na)$_2$SiO$_3$ accelerate both the setting and the early compressive strength of the fly ash-PC blend. Furthermore, they show better compressive strengths at later ages compared to the other activators.

References

COMPARISON OF REACTION DEGREES OF SLAG AND FLY ASH OBTAINED BY THERMOGRAVIMETRY AND SELECTIVE DISSOLUTION

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Abstract
The evolution of the reaction degree of supplementary cementitious materials (SCM) with time is an important aspect regarding the design and use of blended cements. However, this quantification is complex due to the multiple actions of SCM in the cementitious system, such as the filler effect, the consumption of CH and the formation of secondary calcium silicate hydrates. In this sense, different methods for the estimation of the reaction degree may be recommended for each type of SCM. Some of them are indirect methods that quantify hydration products and compute a reaction degree on that basis, e.g. thermogravimetric analysis, and others are direct methods that measure the amount of unreacted SCM, e.g. selective dissolution. In this paper, thermogravimetric analysis and selective dissolution are applied to estimate the reaction degree of cement pastes admixed with 40% slag or 30% fly ash. Curing periods ranged from 1 till 90 days. Results from both methods are compared and some comments on practicalities for their application are made. Although not enough evidence could be collected for any of the applied methods to be considered as a reference method, the simultaneous application of these two techniques offers increased reliability than when only one method is applied.

1. Introduction
The extent of the reaction of supplementary cementitious materials (SCM) in cementitious mixtures is a key question for the use of blended cement. Finding an answer for this question is not an easy task due to several reasons such as the reaction of clinker being affected by the "filler effect" from SCM, unreacted SCM being difficult to quantify due to its amorphous nature, and the reaction of SCM in cementitious materials being more complex and with a very probable different rate than in synthetic alkaline or lime saturated solutions [1].
Different methods have been attempted for the quantification of the reaction of SCM in cementitious systems, and the convenience of one or another depends on the type of SCM in question. All methods have some drawbacks and at present there is no full agreement on a specific method for reference. Some methods are direct, in the sense that they attempt to quantify the amount of unreacted SCM in the sample (and thereby the amount of reacted SCM by difference with the original content); whereas other methods are indirect, as they quantify other phases in the microstructure that are produced or consumed during the reaction of the SCM (and by simplified computations a reaction degree of the SCM is obtained).

Selective dissolution (SD) of hardened samples is a direct quantification method that aims to dissolve all phases in the hardened sample but the unreacted SCM. Two of the most accepted methods use the EDTA+DEA+TEA solution for slag blends and the HCl+salicylic acid for fly ash blends [1]. Selective dissolution has received some criticism in relation with the actual selectivity of the dissolution [1]. In fact, the technique should be named “preferential dissolution”, instead, as part of unreacted SCM is dissolved whereas parts of clinker and hydrates are undissolved at the same time. Moreover, possible precipitation of some compounds during drying should be added to the computation.

Several corrections have been proposed for more accurate results from SD. Lumley et al [2] suggested to correct undissolved fractions of slag blended mixes after EDTA dissolution for the formation of hydrotalcite-like phases, considering that the mass formed from the MgO in the reacted slag is $2.35 \times M$ ($2.35 = \text{mass hydrotalcite/mass MgO}$, and $M = \text{MgO content of the slag}$). This correction is still missing the amount of hydrotalcite-like phases that can be formed from dissolved cement, which will not be very significant if the MgO content of cement is low. It should be mentioned that this correction is based on the assumption that all MgO from dissolved slag contributes to precipitation of hydrotalcite-like phases, and this should still be experimentally quantified. Moreover, there is a fraction of undissolved alumina silicate hydrates [2], which should be also accounted for by a corresponding correction of the remaining fraction. Also for slag, in the CEN Standard [3] for anhydrous cements the values of residues are multiplied by 1.05 to account for dissolved unreacted slag. However, the actual amount of slag that dissolves varies significantly, and it is convenient to analyse the solubility of pure slag to make a more accurate correction. On the other hand, it might be alleged that this soluble fraction of slag is also the most reactive, and this correction would then not be necessary for advanced reaction degrees [1]. Finally, the acid solution used for fly ash blends is unable to dissolve some components of the Portland cement (mainly sulfate), and the residue should be analysed for its sulphate content ($\text{SO}_3$) and corrected accordingly. Vollpracht et al [4] demonstrated that sulphate bearing phases like ettringite or monosulfate in hydrated cement paste are in fact dissolved but, during drying, they precipitate later in different phases from the original, and this sulphate correction is then necessary.

Even with the corrections mentioned above, some studies claim that large, non-quantifiable systematic errors remain from different assumptions leading to large differences in the obtained reaction degrees for fly ash or slag reacted [5-6]. These inaccuracies are generally considered to result in an underestimation of the reaction degree in the order of 10% [1].
Among indirect methods, evaluation of the bound water content from the weight loss of samples between 105°C and 1000°C is the most widespread technique to assess the hydration degree of unblended Portland cements.

First, the overall reaction degree can be represented by the ratio of the bound water content at a certain time t (or maturity M if temperature is not constant) \( \left( w_b(t) \right) \), to the ultimate bound water content \( w_b(\infty) \) [7]. Here, the value at infinity can be determined from a three parameter equation (Equation 1) that fits experimental data of \( w_b \) as a function of time [7], which is based on the one from Hansen and Pedersen [8] for describing strength development. This Equation has been also applied by [9] to calculate overall reaction degrees of OPC pastes and OPC pastes admixed with slag.

\[
w_b = w_{b,\infty} \cdot \exp \left[ -\left( \frac{t}{\tau} \right)^\alpha \right]
\]

But the application of this technique for blended mixes is more complicated than for pure OPC pastes, as is it not possible to distinguish between the bound water involved in the reaction of the SCM and that involved in the reaction of the clinker phases. In fact, there is a change with time in the amount and chemical composition of hydrates in correspondence with products derived from hydration and from pozzolanic reaction [10]. Then, the only option seems to make a comparative analysis between blended mixes and unblended mixes that could help in the quantification or the reaction of the SCM on the basis of the differences.

In order to assess the reaction degree of SCMs, the consumption of portlandite (CH) can be considered. The reaction of SCM is separated from hydration of clinker by considering the consumption of CH in the blended mix that is compared to a reference unblended mix. This information is obtained from thermogravimetric analysis, with a quantification of CH from the weight loss in the range of 410-480°C. The weight loss during CH dehydroxylation can be used to compute the amount of CH, considering the ratio between the molecular weights of CH and water. Based on the amount of CH in the mix, Pane and Hansen [7] developed a method to quantify the reaction of SCMs. The consumption of CH during its reaction is derived from different plots of the CH-content (per g OPC) versus \( w_b \) (per g OPC) for unblended and blended pastes. From this difference, Equation 2 allows the computation of the reaction of the SCM. Here, the reaction of the clinker might be accelerated and enhanced due to the filler effect of SCMs, and the comparison with a mix blended with an inert filler as reference instead of a plain unblended mix has been suggested [1].

\[
r_S(w_b) = \frac{CH_{OPC}(w_b(t)) - CH_{blend}(w_b(t))}{CH_{OPC}(w_b(\infty)) - CH_{blend}(w_b(\infty))}
\]

A different approach considers simplified mass balance calculations to estimate the degree of reaction of SCM based on the CH consumption [11]. However, there are some variations in the composition of C-S-H that might result in unreal estimations if an erroneous Ca/Si ratio is considered. Appropriate values for the Ca/Si ratio are difficult to be obtained given the variability of this phase in hardened pastes [12]. The presence of an SCM leads to a decrease
of the Ca/Si ratio of the C-S-H even in the presence of CH [11-13]. This indicates that some calcium for the pozzolanic reaction is coming from the C-S-H, and that the value of the Ca/Si ratio is dependent on the reaction degree of the SCM itself. A serious underestimation of the degree of reaction of the SCM results if only the CH consumption is considered.

Given the mentioned drawbacks of quantification methods for the reaction degrees of SCMs, it seems convenient that multiple methods are applied for increased reliability. Then, the impact of unresolved variables is reduced.

In this paper, two methods for the determination of the reaction degree of slag and fly ash in cement pastes are compared: selective dissolution (SD) and thermogravimetry (TG). Samples with two slags and two fly ashes were prepared and hydrated for up to 90 days. Then, hydration was stopped and the reaction degree was estimated by the aforementioned methods.

This paper presents the results obtained at Ghent University during a Round Robin Test on methods for quantification of reaction degrees of SCMs, carried out within RILEM TC 238-SCM, Working Group 2.

2. Experimental

2.1 Materials

Two ground granulated blast furnace slags (S1 and S2) and two fly ashes (F1, calcareous, and F2, siliceous) were analysed. Cement pastes with ordinary Portland cement (PC) and replacement ratios of 40% for slag or 30% for fly ash were prepared and seal cured for 1, 7, 28 and 90 days. Reference pastes blended with 30 and 40% quartz (Q) were also prepared. The w/b was 0.40. Properties of raw materials are presented in Table 1.

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th>Particle size distribution (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al₂O₃ SiO₂ CaO Na₂O K₂O MgO Fe₂O₃ SO₃ d10 d50 d90</td>
</tr>
<tr>
<td>S1</td>
<td>11.6 36.5 40.8 0.5 7.5 1.4 2.1 3.1 18.3 42.5</td>
</tr>
<tr>
<td>S2</td>
<td>11.6 36.7 38.9 0.2 0.7 7.8 0.5 2.8 1.1 8.0 30.8</td>
</tr>
<tr>
<td>F1</td>
<td>19.8 42.3 20.7 0.3 1.5 2.2 8.2 1.4 1.7 10.0 30.8</td>
</tr>
<tr>
<td>F2</td>
<td>24.4 70.8 0.1 0.1 0.6 0.2 2.2 - 1.1 8.2 31.0</td>
</tr>
<tr>
<td>PC</td>
<td>5.7 19.3 63.7 0.2 1.2 1.6 3.6 3.2 1.2 13.0 49.9</td>
</tr>
<tr>
<td>Q</td>
<td>1.0 97.9 0.0 - 0.8 - 0.0 - 2.9 10.2 30.7</td>
</tr>
</tbody>
</table>

After curing, samples were cut into discs approximately 2-3mm thick and hydration was stopped by solvent exchange with isopropanol. Then, vacuum dried samples were stored under vacuum until tested. Soda lime was located in the vacuum chamber to prevent
carbonation, and the outer layer of discs was pre-emptively disregarded for analyses due to the same reason. Analyses were performed on samples manually ground with mortar and pestle to particle sizes < 63 μm. Grinding was done immediately before testing.

2.2 Methodology

2.2.1 Selective dissolution (SD)

The methods followed were those described in CEN/TR 196-4 [3]. After dissolution, residues were collected by vacuum filtration in pre-dried glass fibre filters, washed and dried at 100 °C. Results are the average of triplicate determinations. For the computation of reaction degrees, the residues per 100 g of cement paste ignited at 1000 °C were considered.

For fly ash cement pastes, samples were treated with a solution of HCl + salicylic acid in methanol for 30 min. The procedure applied to the raw fly ashes resulted in residues of (79.48 ± 0.54)% and (99.68 ± 0.25)% for F1 and F2, respectively. The high solubility of F1 in association with its calcareous nature causes a high uncertainty for the computation of reaction degrees from residues of hydrated blended pastes. Therefore, only reaction degrees for F2 are presented. Moreover, the method applied for fly ash pastes results in sulfate bearing phases like ettringite or monosulphate, which are initially dissolved but precipitate later as gypsum, and during the drying of the residue bassanite is formed [4]. Therefore, corrections for sulphate contents were made. Sulfate contents of residues were determined by the combustion infrared detection technique. Reaction degrees for F2 were computed from Equation 3 derived from [4] and [14]. Where $w_2$ is the weight of residue [g], $w_j$ is the ignited weight of sample [g], $w_{2o}$ is the weight of residue for pure OPC sample [g], $w_{1o}$ is the ignited weight of pure OPC sample, $a/(a+b)$ is the content of SCM (a) to the total amount of cementitious material (a+b), $b/(a+b)$ is the content of OPC (b) to the total amount of cementitious material (a+b), $w_a/a$ is the relative residue of the SCM, and $S_{ro}$ is the SO$_3$ content of $w_{2o}$ by weight. Reaction degrees for slag were computed from the Equation 4 [14], where no correction for hydrotalcite-like phases is considered. Where $w_2$ is the weight of residue [g], $w_j$ is the ignited weight of sample [g], $a/(a+b)$ is the content of SCM (a) to the total amount of cementitious material (a+b), $b/(a+b)$ is the content of OPC (b) to the total amount of cementitious material (a+b), $w_a/a$ is the relative residue of the SCM, and $w_b/b$ is the relative residue of the OPC.

$$
\alpha = 1 - \frac{1 - 1.813 \cdot Sr}{a+b} \cdot \frac{w_2}{w_1} - \left(1 - \frac{w_{2o}}{w_{1o}}\right) \cdot \frac{\frac{b}{a+b} \cdot (1 - 1.813 \cdot Sro) \cdot w_{2o}}{a+b} \cdot \frac{w_{1o}}{a+b}
$$

(3)

For slag cement pastes, samples were treated with EDTA+TEA+DEA solution for 120 ± 5 min. The procedure applied to the raw slags resulted in residues of (95.03 ± 0.14)% and (95.20 ± 0.73)% for S1 and S2, respectively. Reaction degrees for slag were computed from the Equation 4 [14], where no correction for hydrotalcite-like phases is considered. Where $w_2$ is the weight of residue [g], $w_j$ is the ignited weight of sample [g], $a/(a+b)$ is the content of SCM (a) to the total amount of cementitious material (a+b), $b/(a+b)$ is the content of OPC (b) to the total amount of cementitious material (a+b), $w_a/a$ is the relative residue of the SCM, and $w_b/b$ is the relative residue of the OPC.

$$
\alpha = 1 - \frac{w_2 + \frac{a}{a+b} \cdot \left(1 - \frac{w_a}{a}\right) \cdot w_1 - \frac{b}{a+b} \cdot \frac{w_b}{b} \cdot w_1}{a+b \cdot \frac{a}{w_1}}
$$

(4)
2.2.2 Thermogravimetry (TG)
Samples of approximately 50 mg were exposed under an inert atmosphere of nitrogen to increasing temperatures, ranging from 20 °C to 1100 °C at a rate of 10 °C/min. Reaction degrees were computed following the procedure according to Pane and Hansen [7], by which CH consumption by the pozzolanic reaction is computed from the difference in the CH-bound water relationship between the blended cement paste and the non-blended cement paste. The tangential method was used for determination of the water loss due to CH dehydroxylation. For TG computations, the correction for the calcite content in the samples was disregarded, as the loss at this temperature range might be due to some interlayer isopropanol. Bound water was computed from the weight loss between 105-1000 °C.

3. Results and Discussion

Figure 1 shows the relationship between bound water and CH contents obtained by TG for the different pastes. The effect of the filler effect on this relationship seems slight, pastes with 30 and 40% of quartz (Q30 and Q40) show little higher values of CH content than those for the unblended paste (PC) around 20% of bound water content, but fitting the three series together results in little differences from separate fittings. Instead, Q30 and Q40 show simultaneous higher values than PC for both bound water and CH contents. This is to be expected, as the filler effect causes an enhancement of hydration, but there is no mechanism of CH consumption involved, and in consequence the relationship between the chemically bound water and this hydration product should remain the same. This consideration is not valid if the comparison is made for the same curing period, as the progress of hydration is sensible to filler effect. Therefore, if the same value for \( w_b(t) \) is considered for the unblended and blended pastes, i.e. the comparison is made on the basis of equivalent hydration degree and not equivalent curing time, any influence of filler effect is avoided (as shown in Figure 1).

Moreover, there is no clear distinction between both types of slags, and what is more, neither between both types of fly ash (even when one was calcareous and the other siliceous). This could suggest that a general correlation may be proposed for each type of SCM, and further research in this regard seems interesting.
The fittings in accordance with Equation 1 for the evolution of bound water content are shown in Figure 2, where fair correlations can be seen however additional data for longer curing periods would be necessary for full validation of the three fitted parameters. Still, the obtained results are consistent with the model from Equation 1 and bias seems independent of the curing period. A particular issue for fly ashes is that bound water seems to increase linearly with the logarithm of time, and very high values for the ultimate bound water content were obtained (64.3 and 46.8 % for F1 and F2, respectively) in comparison with the values for slags which seem more realistic (37.5 and 35.3 % for S1 and S2, respectively). These rather unreal values for the fly ashes are a result of their very slow reaction rate, and more extended curing periods must be investigated for improved results. Then, the method by Pane and Hansen [7] as it is, seems more appropriate to be used for computation of the reaction degree of slag than fly ash blended pastes.

Figure 2. Bound water in blended cement pastes, measured values versus estimated values from (1) [7-8].

The reaction degrees of slag and fly ash, determined by means of SD and TG, are presented in Figures 3 and 4, respectively. From the comparison of the reaction degrees obtained by the applied methods, it can be seen that the differences are within the estimated precision ranges reported in [1] for these methods. Results from the SD method consistently resulted in lower values than results from TG.

For the case of slags, the lower values for the reaction degrees obtained by the SD method are only partially due to no correction for the undissolved hydrotalcite-like phases being made. Additionally, the computation in Equation 2 considers that the dissolved fraction of raw SCM is completely unreactive, and it is then discounted for the reaction degree. However, it is very likely that being this fraction the most soluble under chemical attack, it is also the most
reactive in the cement paste. Then, this correction would lead to inaccurate values for later curing periods due to the consideration of the soluble fraction as non-reactive. This consideration is also valid for the siliceous fly ash but as the soluble fraction of this raw material is much lower (0.32% for F2 vs. 4.97 and 4.80% for S1 and S2, respectively), the impact on the result is much lower. Finally, it should be mentioned that in the method based on TG the reaction degree is defined as the reaction at a certain moment relative to the maximum reaction that is possible (at infinity). This does not necessarily correspond with complete reaction of SCM, but with the maximum bound water content that the blend may reach. Differently, for the computation from SD, the reacted SCM (obtained by difference on the basis of the residual SCM) is compared with the initial amount of SCM. Then, whereas the SD method computes the reaction degree relative to the total amount of SCM, the TG method computes the reaction degree relative to the maximum reacting SCM.

In this sense, when reaction degrees are corrected by the hydrotalcite-like phases formed from the reacted slag, increases of 21.4 and 22.4% are obtained for reaction degrees of S1 and S2, respectively (in accordance with the correspondent MgO content of slag that reacted and assuming a value for the stoichiometric coefficient of 2.35). Then, values are more similar but still lower than those obtained by TG. However, the correction by hydrotalcite-like phases is
not accurate if the proportion of this phase in the residue is not further investigated, as the assumption of all dissolved MgO favouring the formation of precipitated products should be experimentally demonstrated. Then, even when this correction favours the consistency of results, its basis should be further investigated for appropriate correction coefficients.

More similar values were obtained for F2, where corrections for precipitated bassanite computed from SO₃ contents of the residues have been applied.

When the relative differences between the two quantification methods (i.e., $|\alpha_{TG} - \alpha_{sd,diss}| / (0.5(\alpha_{TG} + \alpha_{sd,diss}))$) for the different curing periods are analysed (Figure 5), high values for 1 day for the three blends (S1, S2 and F2), and no significant variation between 7, 28 and 90 days, are observed. It should be noted that corrections due to the hydrotalcite-like phases contents of residues from slag blends are not considered in this comparison. The origin of these differences seems to be a systematic error that is rather independent from the value for the reaction degree. Then, the relative difference seems higher for 1 day only due to the small value of the reaction degree.

![Figure 5. Evolution with time of relative difference between TG/SD and the average of both.](image)

4. Conclusions

Reaction degrees of slag and fly ash were measured by SD and TG on blended cement pastes for curing periods between 1 and 90 days, the following conclusions are derived from the results:

- The method based on the ultimate bound water content and portlandite consumption applied for the analysis of TG data seems appropriate for slag, but some conceptual inconsistencies were obtained when applied for fly ash. This is in connection with the different reaction rate of each SCM. More research on reaction of fly ash is necessary, involving extended curing periods to obtain more realistic ultimate bound water contents.
- For the SD method, correction of reaction degrees of slag due to formation of hydrotalcite-like phases is convenient to avoid systematic underestimation. However, composition of the residues must be investigated for hydrotalcite-like phases contents in order to apply correct coefficients.
Results illustrate the accuracy of both methods. Given that there is no reference method for comparison at present, the simultaneous application of both methods offers an increased reliability of the values obtained for the reaction degree, with special consideration of the practical nature of these two methods when applied for this purpose.

Acknowledgments

The authors greatly appreciate comments and discussion from all members of RILEM TC 238-SCM. Special thanks go to Paweł Durdziński and Karen Scrivener (EPFL) for the preparation and delivery of samples analysed in this study, and which are part of a more extended Round Robin Test; and to Anja Vollpracht (RWTH-Aachen) for SO₃ analyses of residues from fly ash blends.

References

PARTICLE SIZE DISTRIBUTION AND SPECIFIC SURFACE AREA OF SCM’S COMPARED THROUGH EXPERIMENTAL TECHNIQUES

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Abstract
Supplementary cementitious materials (SCMs) are mainly used to produce a green concrete. To reach that goal effectively, it is highly important to adequately characterize the SCMs. It is well known that particle size distribution (PSD) and fineness of SCMs have a great influence on concrete properties. Traditionally, cement fineness has been assessed by the specific surface area (SSA) through the Blaine method (BM). However, the BM has the simplification of considering ideal spherical shape particles. The BET theory has also been used to calculate SSA, however, also some assumptions may lead to inaccuracy in the calculations. Both PSD and SSA can be evaluated through Laser Diffractometry (LD), but this technique also considers ideal spherical particles as a simplification. Regardless of the mentioned drawbacks, these techniques provide useful information to characterize SCMs provided that the limitations are considered. In this paper, Ground Granulated Blast Furnace Slag (GGBFS), Natural Pozzolan (NP) and Limestone Powder (LP) are tested using the BM, LD, and nitrogen adsorption. Particle texture and shape are assessed through petrography and scanning electron microscope (SEM). Results from BM, BET and LD are compared, analysing the possible effects of particle shape and texture.

1. Introduction

Fineness from supplementary cementitious materials (SCMs) is generally evaluated as an influencing parameter on the properties of concrete. However, the assessment of fineness through different experimental techniques is not usually considered adequately, and some limitations are disregarded leading to an incorrect interpretation of results. Generally, standard methods used to assess physical properties of cement have been straightforwardly applied for SCMs without any modification. However, the same techniques may not always be applicable due to differences in shape and size of SCMs.
For the determination of the specific surface area (SSA), the Blaine method (BM) has been commonly used for cement [1-3]. BM is a rather empirical method particularly designed for cements, and therefore its application for SCMs requires some adaptations. For example, a different plunger has been proposed by [4] to avoid removing it. This modified plunger was used by [5] to test silica fume with unsatisfactory results as a well compacted bed could not be achieved.

Alternatively to the BM, laser difractometry (LD) is a quick technique that uses the optical properties of the powder to evaluate both its SSA and its particle size distribution (PSD). LD has been fairly well described in [6-8], where the importance of the dispersion conditioning and the correct selection of the optical parameters are highlighted. Another technique for SSA determination is the use of the Brunauer, Emmett, and Teller (BET) theory [9] which is based on the amount of gas adsorbed on a monomolecular layer on the surface. This has the evident advantage of not assuming a specific particle shape; however, some simplified assumptions, as the existence of a homogenous covering layer [10] may not lead to the actual SSA value.

In this study, fineness of Ground Granulated Blast Furnace Slag (GGBFS), Natural Pozzolan (NP) and Limestone Powder (LP) is measured and compared with the three techniques. Guidelines in ASTM C204-07 [11] for the application of the Blaine method to materials other than cement are followed. Some recommendations in addition to those in the literature are proposed to obtain reliable results from LD. Finally, the results are compared with characterization through petrography and scanning electron microscopy (SEM), with assessment of particle shape and texture and their influence on the values obtained and the theoretical considerations of each method.

2. Materials and methods

2.1. Materials
This study includes analysis of ground granulated blast furnace slag (GGBFS), natural pozzolan from volcanic origin (NP) and limestone powder (LP). Both GGBFS and NP were first dried in oven for 24 h, and then ground in a laboratory ball mill for cement, with the aid of cyleps. The grinding process was carried out for 1.5 h for the GGBFS and 2.0 h for the NP. LP was also processed in an industrial ball mill. The chemical composition of the materials is shown in Table 1. The chemical analysis was performed by X-ray fluorescence and the density was determined according to ASTM C188-15 [12].
Table 1: Chemical compositions of GGBFS, NP and LP.

<table>
<thead>
<tr>
<th></th>
<th>GGBFS</th>
<th>NP</th>
<th>LP</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>36.16</td>
<td>1.34</td>
<td>48.85</td>
</tr>
<tr>
<td>SiO₂</td>
<td>28.89</td>
<td>62.53</td>
<td>8.15</td>
</tr>
<tr>
<td>MgO</td>
<td>12.14</td>
<td>1.13</td>
<td>1.41</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.62</td>
<td>10.76</td>
<td>1.28</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.91</td>
<td>5.66</td>
<td>1.25</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.85</td>
<td>0.34</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.95</td>
<td>1.81</td>
<td>0.88</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.46</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.43</td>
<td>3.67</td>
<td>0.28</td>
</tr>
<tr>
<td>MnO</td>
<td>0.43</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>LOI</td>
<td>nd-</td>
<td>nd-</td>
<td>37.29</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.92</td>
<td>2.41</td>
<td>2.71</td>
</tr>
</tbody>
</table>

nd = not determined

2.2. Methods
2.2.1. Blaine method
The BM test was performed according to ASTM C204-07 [11], where the special consideration for materials other than cement intends to consider the possible differences in density, porosity or shape in relation to a standard reference material.

2.2.2. Laser diffraction
The particle size distribution by means of LD was determined using a particle analyser Malvern Mastersizer 2000 E, wet unit Hydro 2000SM (A). Isopropanol (IPA) was used as a dispersant for the three SCMs. For the refractive index \( m = n + ik \), different values of refraction index \( n \) and absorption coefficient \( k \) were used for each SCM, according to the data found in literature [6-8]. Those combinations of values which had the best fit and less weight residual were selected. Selected values of \( n \) and \( k \) are presented in Table 2.

As described in [6] duration of dispersion, ultrasonication frequency, stirrer rate, measurement time and obscuration levels were first optimized in order to obtain reliable results for each of the SCMs. Particular attention was paid to the dispersion procedure since failure in this step leads directly to erroneous results. The selected procedure consisted of 5 minutes of ultrasonic bath (35 kHz, 320 W), 1700 rpm for the stirrer rate, 20 s of measuring time and 11.5 ± 0.5% of obscuration level. After the de-agglomeration of the particles was finished, a syringe was used to collect the sample and place it inside the diffractometer. The same procedure (stirring speed, sonification time and frequency, sample and background measurement time, obscuration level) was applied for all the SCMs changing only the values of \( n \) and \( k \) for each particular case.
Table 2: Selected optical parameters of the SCMs.

<table>
<thead>
<tr>
<th></th>
<th>GGBFS</th>
<th>NP</th>
<th>LP</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>1.62</td>
<td>1.49</td>
<td>1.57</td>
</tr>
<tr>
<td>k</td>
<td>0.1</td>
<td>0.1</td>
<td>0.05</td>
</tr>
</tbody>
</table>

2.2.3. BET method

For quantitative analysis, adsorption and desorption curves using nitrogen at 77 K were determined with a Micromeritics Asap 2020. Before measurement, samples were dried at 105°C and kept in a desiccator until testing. The BET adsorption theory was used for the determination of surface area, using the corresponding values of the relative pressure between 5-35% of the adsorption curve.

2.2.4. Petrographic characterization

2.2.4.1 Petrographic microscope

Petrographic characterization of the SCMs was done in accordance to ASTM C295 [13]. The equipment used is an Olympus BH2-UMA petrographic microscope. This instrument includes an Infinity 1-3C digital camera of 13.1 megapixels. Image processing was done with Infinity Analyze 5.0 software.

2.2.4.2 Scanning electron microscope (SEM)

The SEM allows analysing materials morphology with micrometric detail. All the information registered can be translated into external morphology and materials orientation [14]. A SEM 505 Philips was used to perform the characterization.

3. Results

3.1. Blaine method

Some difficulties for achieving an adequate bed height with a given porosity (\(\varepsilon\)) have been found when testing SCMs [5]. The ASTM C204-07 addresses this problem by calculating a constant (b) appropriate for each sample, which is obtained by plotting the values of \(\sqrt{\varepsilon^3 \cdot T}\) versus \(\varepsilon\) and determining the y-intercept by linear regression. For the calculation of the value of b, a minimum of 12 determinations have to be made.

Four samples of each SCM were tested at four different \(\varepsilon\) values, and the b characteristic value of each SCM was calculated. The results of the SSA and the bed porosity range used for each material are shown in Table 3.
Table 3: Blaine SSA and bed porosity range of the SCMs

<table>
<thead>
<tr>
<th></th>
<th>GGBFS</th>
<th>NP</th>
<th>LP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity values</td>
<td>0.53,0.55,0.57,0.59</td>
<td>0.53,0.55,0.57,0.59</td>
<td>0.47,0.49,0.51,0.53</td>
</tr>
<tr>
<td>Surface area (m²/kg)</td>
<td>341±4</td>
<td>858±12</td>
<td>646±5</td>
</tr>
</tbody>
</table>

3.2. Laser diffraction

It has been pointed out by several authors [5, 7, 8] that the chosen refractive index has a great influence on the results of PSD measured by LD. This is directly related to the basic principle of laser diffractometry given that scattering arises when there are differences in the refractive index of the particle and the surrounding medium [15]. If there is no information available about the optical properties of the sample, generally different combinations of n and k are tested, and then the most appropriate combination is chosen from the results obtained. The weight residual indicates how well the optical model of Mie fits the registered scattering pattern, and it is defined as the % error between the data measured and data corrected with parameters [16]. In order to keep a standard criterion, the weight residual of each measurement was compared in this study. The lowest value obtained for the different values of m used was considered the most reliable combination. LP measurements had the lowest mean weight residual and NP had the highest weight residual value. Figure 1 shows the PSD of triplicate measurements for each SCMs. Table 4 shows the values of surface area, dv10, dv50 and dv90 for each SCMs, using the described procedure and the optical parameters indicated in Table 2. The calculations of the surface area were made under the assumption of spherical particles.

Figure 1: Particle size distribution of LP, NP and GGBFS
Table 4: PSD of the SCMs

<table>
<thead>
<tr>
<th></th>
<th>GGBFS</th>
<th>NP</th>
<th>LP</th>
</tr>
</thead>
<tbody>
<tr>
<td>dv10 (μm)</td>
<td>1.14± 0.03</td>
<td>1.36±0.001</td>
<td>1.27 ± 0.12</td>
</tr>
<tr>
<td>dv50 (μm)</td>
<td>12.73 ± 0.67</td>
<td>7.05± 0.02</td>
<td>7.67 ± 0.63</td>
</tr>
<tr>
<td>dv90 (μm)</td>
<td>66.27 ± 7.18</td>
<td>28.14± 0.16</td>
<td>72.88 ± 10.4</td>
</tr>
<tr>
<td>Surface area (m²/kg)</td>
<td>566 ± 13</td>
<td>701±2</td>
<td>606 ± 13</td>
</tr>
</tbody>
</table>

3.3. BET method

Values obtained from the adsorption and desorption nitrogen curve are shown in Figure 2. With the BET theory, the SSA accessible to nitrogen molecules were calculated within the low RH range of the adsorption isotherms. The results obtained were 987.3m²/kg, 2255.7m²/kg and 3900.4m²/kg for GGBFS, NP and LP respectively.

![Figure 2: Sorption and desorption curves from Nitrogen gas of LP, NP and GGBFS](image)

3.4. Petrographic characterization

3.4.1. Petrographic microscope

Figure 3 shows two petrographic images with 100x and 200x magnification for GBFFS (A.1 and A.2), LP (B.1and B.2), and NP (C.1and C.2). Their description is as follows.

3.4.1.1. GGBFS

The material is mainly composed of irregular and/or plank-shaped particles, which have a sharp or hook-shaped end (A.1, A.2). All particles are transparent with high relief. With crossed polars they are mostly isotropic, showing their amorphous character. Though, there are some anisotropic grains with high birefringence, which belong to crystalline particles of tabular development, possibly melilite. Particle size is estimated to be in the range 10-75 μm.
3.4.1.2. LP
Under polarized light transparent or grey/yellow particles can be seen (B.1, B.2). Their shape is mainly sub-rounded, some smaller than 5 μm, and some particles have a maximum size of 10 μm. Due to their small size; these particles have a tendency to agglomerate, forming aggregates up to 100 μm, although these agglomerations are rare. Under crossed polars LP particles show a high interference color, similar to yellow, and typical of calcite.

3.4.1.3. NP
NP sample is mainly composed of vitreous transparent particles, of low relief, irregular morphology and conchoids and sharp edges typical of this kind of materials (C.1, C.2). Their size range is mainly between 2-20 μm. Some minor large (60-100 μm) brown sheet-like particles, corresponding to biotite are also present. All these petrographic characteristic are typical of a glassy material from volcanic origin.

Figure 3: Petrographic microphotographs with parallel light with 100x and 200x of magnification of GGBFS (A1,A2), LP (B.1, B.2) and NP (C.1,C.2), respectively

3.4.2. SEM characterization
Figure 4 shows two SEM images for GBFS (A.1 and A.2), LP (B.1, B.2), and NP (C.1 and C.2). Their description is as follows.

3.4.2.1. GGBFS
A wide variation in the grain size can be seen for the GGBFS samples in A.1 and A.2. Individual particles are angular or sub-angular and have a smooth surface, in some particles micrometric pores can be seen with spherical morphology. This could be attributed to the fast
cooling of the particles when they formed. A detailed picture of this is shown in A.2., where a 50μm particle can be seen filled with smaller GGBFS particles.

3.4.2.2. LP
From B.1 and B.2 images, high content of fine particles of the material can be seen, especially in the range of 0.1-5 μm, but with some minor content of large particles (50-100 μm) sometimes as a product of agglomeration of smaller particles. Most of the particles are sub-rounded and smaller particles can be seen adhered in their surface.

3.4.2.3. NP
Particle size range of NP is generally around 50 μm or lower, as seen in C.1 and C.2. NP particle shape is mostly angular or sub-angular, of conchoidal fracture, with sharp edges - typical for vitreous materials—and smooth surface. Some smaller particles can be seen adhered as well.

Figure 4: SEM micrographs of GGBFS (A.1, A.2), LP (B.1, B.2), and NP (C.1, C.2).

4. Discussion
Figure 5 presents a comparison between the SSA obtained with BM, LD and BET, where a clear discrepancy among the different techniques can be seen. In the case of the BM, low standard deviations were found for the SSA calculation considering the characteristic b value for each sample. According to the results, NP is the finest SCM, followed by LP and GGBFS.
This seems to be in disagreement with the petrographic and SEM observations, where LP seems to have the smallest particle size. There is a wider particle size range for LP, resulting in a lower specific surface in spite of the high number of fine particles. This is due to the prevalence of large and heavy particles over the high surface area of small particles. Although it is very difficult to make this objective evaluation by simple observation. Calculations of the span of the distribution were made as the difference between $d_{90}$ and $d_{10}$, divided $d_{50}$. The results for GGBFS, LP, NP and were 5.12, 9.34, 3.80, and respectively. This parameter is a measurement of the width of the distribution, where LP has the broadest PSD.

The value of the median size, $\bar{x}$, and the uniformity factor, $n$, were calculated from the Rosin, Rammler, Sperling and Bennett (RRSB) distribution, graphical linearization was based on the 0.5-80% part of the PSD. The results from triplicate measurements of $\bar{x}$ are 20.49, 12.30 and 10.18 $\mu$m for GGBFS, LP and NP respectively. The results of $n$ are 0.75, 0.97, and 1.06 for GGBFS, LP and NP respectively. There is a clear distinction in the highest value of the median particle size, for GGBFS in relation to the other, which indicates its coarser PSD.

Also, part of this difference could be attributed to the particles shape and packing of the sample bed, since the air flow around a rounded particle (which is the case of LP) would be faster than through semi-angular particles, as is the case for NP particles. Furthermore, the compaction of the sample bed may not be the same for different particle shapes and hence results would not be totally comparable. In fact, it has been suggested [6] that there is no possible comparison if the reference material does not have similar shape, particle size distribution, and surface properties to the material of interest. Then, in spite that the method proposed by the standard [11] intends to account for these differences, the practical approach still does not provide completely reliable results. Even some authors [17], completely disregard the method for considering it an indirect and too simplified method.

With regards to the LD technique, NP seems to be the finest SCM, followed by LP and GGBFS. The high value obtained for NP could be explained by the particle shape of the sample, which is mostly angular or sub-angular, of conchoidal fracture and sharp edges. These characteristics significantly differ from the assumption of spherical particles for the computation of SSA from LD results. This simplification also causes the largest weight residual values for NP among the three materials. The fact that GGBFS and LP have similar SSA values for LD but not for BM also shows the influence of the particle shape. It seems that particle shape does not allow the same compaction factor for BM, but the influence is not so significant for LD, as the particle size distribution is not so different. Furthermore, rounded LP particles have a better fit to the hypothesis for the calculations (also represented in the lower weight residual value obtained for LP) while GGBFS SSA is influenced by the angle in which its semi-angular or planked-shaped particles would pass through the incident laser beam.

From BET results, LP has the larger SSA, followed by NP and GGBFS. From XRD with Rietveld analysis, a composition of 75% calcite and 10% quartz was determined for LP. Clay impurities could not be detected, but it would still be possible that this is the cause for such a high SSA from BET calculations. These calculations assume a monolayer covering the area of each particle and then particle shape is automatically taken in consideration and has been
considered a good representative technique of the SSA [18]. Yet, it is not possible to verify that always a continuous and perfectly uniform monolayer is achieved. Besides, the size of the adsorbate can modify the BET results [10]. It can also be seen that BET SSA values are always larger than those from BM and LD, for all SCMs. This has also been mentioned before by [5], and it is attributed to the fact that gas molecules access cracks and pores of the particles. In this sense, nitrogen adsorption is not much affected by aggregation of particles, which was mostly observed for LP, and whereas this aggregation results in lower SSA computed from BM or LD (as they assume an aggregate as an individual spherical particle), nitrogen is able to penetrate spaces between particles in these aggregates and the SSA computed on this basis is higher. From the comparison, it is derived that SSA values computed from BM and LD are reduced because in this case the inner porosity is not considered and in the case of LP also by aggregation of particles.

Figure 5: Comparison among BM, LD and BET surface area results for each SCMs.

5. Conclusions
Results from different commonly used techniques have been presented for the evaluation of the particle size and SSA of GGBFS, NP and LP.

Particle shape showed significant influence on the results obtained. This is specially seen for SSA calculations with BM and LD since the assumptions of spherical particles can greatly influence the results. Particularly the BM does not show reliable results, given that it cannot effectively evaluate the SSA for comparative purposes if the particle shape interferes in the bed compaction. On the other hand, LD for particle size distribution seems to be a consistent method in order to obtain reliable results regarding PSD, but SSA computed on this basis may be inaccurate. Furthermore, it is highly recommendable to achieve good particle dispersion and to evaluate different refraction index and absorption coefficient combinations and select the one with the lowest weight residual value. In the case of the BET SSA calculations, results were found to be in agreement with the characterization by microscopy. Moreover, increased
values for the SSA were obtained from nitrogen adsorption in correspondence with the consideration of inner porosity and the limited influence of particle aggregation on the results. Each technique has its own limitations, and each SCMs its own characteristics, therefore absolute values should be carefully considered, and keeping in mind the limitations.

References


EFFECT OF SCMS ON HYDRATION KINETICS OF PORTLAND CEMENTS

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\textsuperscript{(2)} HeidelbergCement Technology Center GmbH, Leimen, Germany

Abstract

Blending of Portland cement with limestone or quartz leads generally to an acceleration of the PC reaction, while fly ash can delay the onset of the acceleration period. Investigations using a cement replacement of 50 wt\% showed a significant acceleration in the presence of limestone, related to enhanced C-S-H nucleation on calcite. Measurements of the concentrations in the pore solution indicated that this increased nucleation, which facilitates C-S-H formation, results in stronger undersaturation with respect to alite and thus in faster alite dissolution. In general a faster dissolution was observed for those blends where a higher degree of undersaturation with respect to alite was present. Blends with high sulfate and/or high aluminium concentrations in the pore solution reacted slower, indicating that high aluminium and sulfate concentrations can retard alite hydration, thus confirming the results reported from studies on pure clinker phases. The investigations indicate that the mechanisms controlling the early hydration of composite cements are a complex combination of their surface characteristics and their influence on the pore solution composition.

1. Introduction

Supplementary cementitious materials (SCMs) are more and more important as mineral additions, especially in Portland cement-based composite cements. They affect the reaction of Portland cement (PC) depending on the type of SCM and hydration time. SCMs influence the early hydration of the PC mainly by the so-called filler effect which consists of two different aspects: i) The presence of additional surface sites can accelerate the hydration during the first hours as more surface for nucleation and growth of hydrates is available. This effect is more distinct for calcite than for other surfaces, but is also observed if PC is blended with quartz or blast-furnace slag. ii) The amount of Portland cement reacted after 1 day and longer is higher as more water and more space for the growth of hydrates is available.
The number of C-S-H nuclei on calcite particles is significantly higher than on quartz and blast-furnace slag [1]; while the underlying processes that cause this effect remain unclear, the effect itself explains the accelerating effect of limestone in blended cement [2]. In the case of fly ash a different behavior can be observed. Blending Portland cement with fly ash can lead to retardation of the hydration, especially if a very fine fly ash is used [3]. It has been argued that this effect is caused by interactions of alumina from the fly ash and calcium from the pore solution or by chemisorption of calcium ions on the surface of the fly ash [4, 5]. In contrast to the early promotion of PC reaction due to the presence of additional nucleation sites, the use of a higher water-to-cement ratio generally retards the early hydration of PC and of alite, in particular. A possible explanation could be the higher calcium concentrations due to lower pH values in a diluted system. In addition to the effect of calcium concentration, also aluminium concentrations and the degree of undersaturation of the pore solution with respect to alite can be expected to play an important role. Alite dissolution is faster at higher undersaturation and slower at near equilibrium conditions [6]. The effect of the degree of undersaturation on dissolution kinetics is strong if the solutions are moderately undersaturated, while at high degree of undersaturation the reactions are rather limited by the number of surface sites and changes in the degree of undersaturation have little effect as discussed in detail in [6-8]. The interplay of undersaturation with respect to C₃S and oversaturation with respect to C–S–H determines the overall hydration kinetics of alite [9]. Nucleation processes play an important role for the reaction kinetics as any factor that eases the formation of nuclei leads to faster C-S-H growth and a higher undersaturation with respect to C₃S resulting in faster alite dissolution. However, not only nucleation and the degree of undersaturation with respect to alite influence reaction kinetics but also the availability of space and the presence of different ions. Aluminium and sulfate have been observed to retard the reaction of alite [7, 10], which has been related to a hindered growth of C-S-H due to a poisoning by aluminium [10] and/or to hindered dissolution of alite due to binding of aluminium and sulfate on the alite surface sites [7]. The retardation of the alite reaction in blended cements containing fly ash could thus be related to the presence of more aluminium and/or sulfate in the pore solution. Knowledge on the influence of aluminium and calcium results mainly from investigations of dissolution of laboratory synthesized clinker phases in diluted suspensions. The complexity of the systems increases dramatically from pure phases and lab clinkers towards industrial available “real” materials and blends thereof at realistic water-to-binder ratios where the combination of both dissolution and precipitation reaction determines the observed hydration kinetics. In the present study the early hydration of binary cement-based systems with fly ash, limestone and quartz is investigated by isothermal calorimetry and the composition of the pore solution chemistry is analyzed. Saturation indices were calculated in order to gain information on the oversaturation/undersaturation with respect to C₃S, portlandite and Ca-rich C-S-H.

2. Materials and methods

Blends of different SCMs (Si-rich fly ash (FA), limestone (L) and inert quartz powder (Qz) as reference) with Portland cement (PC; CEM I 52.5 R) with a cement replacement level of 50 wt.% were used. A summary of the investigated systems is given in Table 1. While the total SO₃ content of the neat cement is 2.8 wt.%, the blended systems contain only 1.4 wt.%. The
anhydrous blends were homogenized for 2 hours in a Turbula Mixer. A water-to-solid ratio (w/s) of 0.75 was used for all pastes investigated, unless otherwise indicated. The relatively high water-to-solid ratio was selected to ease the collection of the pore solutions.

Table 1 – Mix design and surface area of the investigated blended cements.

<table>
<thead>
<tr>
<th>Notationa</th>
<th>C</th>
<th>FA</th>
<th>L</th>
<th>Qz</th>
<th>Total</th>
<th>w/s</th>
<th>SAb [cm²/g PC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>100</td>
<td>100</td>
<td>0.75</td>
<td>d</td>
<td>3700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-Qz</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>0.75</td>
<td>5700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-FA</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>0.75</td>
<td>7100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-L</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>0.75</td>
<td>6300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a C - Portland cement, FA - Si-rich fly ash, L - limestone, Qz – quartz. b Calculated from surface areas of raw materials; normalized to the mass of PC in the blend.

The heat flow of the investigated systems was determined at 20 °C with an eight channel TAM Air Isothermal Calorimeter from TA Instruments, USA. The samples were mixed ex-situ which results in the loss of the initial minutes but allows a better reproducible mixing. 6 g of anhydrous powder was mixed with 4.5 g of deionized water with an electric stirrer for 1 minute at 500 rpm. The heat flow of two separate runs for each system was recorded and no significant difference was observed between the two runs.

For pore solution analysis, 700 g of anhydrous powder were mixed with deionized water, filled in 500 ml PE bottles, capped, sealed and stored at 20°C. The samples were regularly shaken to avoid sedimentation. After 5 min, 0.5, 1, 2, 4 and 6 hours the pore solutions were extracted from the not yet hardened pastes using pressure filtration and the solutions were filtered through a 0.45 μm nylon filter. The total concentrations of elements were determined by ICP-OES Varian Vista-Pro, the pH values with a pH electrode calibrated against KOH solutions of known concentrations.

Based on the measured concentrations in the pore solutions saturation indices were calculated in order to display the degree of oversaturation/undersaturation of the pore solution with respect to C₃S, C-S-H and portlandite. The calculations were carried out using the geochemical code GEMS 3.3 [11]. The default thermodynamic database [12] was expanded with the cement specific cemdata07 database [13, 14], with data for C-S-H [15] and for the solubility referring to the protonated surface sites of C₃S as defined by Nicoleau et al. [6].

3. Results and discussion

3.1 Effect of availability of water on the heat flow

The influence of the water-to-cement ratio on the specific heat flow of Portland cement is presented in Figure 1. No significant influence is observed the first 2 hours but a slower increase of the heat flow rate during the acceleration period at higher water-to-cement ratio and a lower maximum heat flow between 12 and 13 hours. This behavior reveals a strong influence of the water-to-cement ratio on the alite reaction, the dominant reaction during early
cement hydration [16]. After 1 day and longer, however, a higher total heat is observed. While the water-to-cement ratios of the neat Portland cement systems are identical with the water to-solid ratios, the water-to-solid ratio of the quartz blend (0.75) reflects an effective water-to-cement ratio of 1.5 if 50 wt.% of the cement is replaced by quartz. Despite this, the Portland cement in the quartz blend reacts considerably faster than PC0.75 and PC1.5 and its reaction is comparable to PC0.5 during the acceleration period. As the reaction of quartz is negligible, the acceleration of the alite reaction could be related to the presence of additional surfaces for the nucleation of C-S-H which increases from 3700 cm²/g PC for neat Portland cement to 5700 m²/g PC for the quartz blend and or to changes in the pore solution as discussed in further detail below.

Figure 1: Specific heat flow of PC at various water-to-cement ratios. The water-to-solid ratio of the Qz blend (50 wt.%) corresponds to an effective water-to-cement ratio of 1.5. All curves are normalized to the mass of PC in the system.

### 3.2 Effect of SCMs on the heat flow

Similar to quartz, also fly ash and limestone react hardly during the first hours of hydration but add some additional surface to the system where nucleation could occur. Although the fly ash and limestone blend have a comparable surface area as quartz, they exert a strongly different influence on the early hydration as shown in Figure 2. The fly ash blend and the neat cement proceed similarly indicating that the fly ash investigated has little influence on the overall behavior of the system during the early hydration compared to neat cement. Thus, the apparent retarding effect of the fly ash (prolonged induction period) is partially related to the
higher effective water-to-cement ratio in the fly ash blend compared to neat Portland cement with the same total water-to-binder ratio. The comparison of plain cement with the quartz system shows an acceleration of the Portland cement hydration by the quartz, which is related to the additional surface site of quartz and/or to differences in the pore solution. The fastest reaction is observed in the presence of limestone. The surface of calcite provides excellent conditions for nucleation of C-S-H [1] such that the overall hydration reaction is accelerated.

Figure 2: Measured heat flow in the first 24 hours of hydration. Note that all curves are normalized to the mass of PC.

Figure 3 plots the appearance of the onset of the acceleration period as a function of the specific surface area per g PC. As already discussed above a higher effective water-to-cement ratio in the blends leads to retardation in the case of neat cement (cf. slightly later onset of C\textsubscript{1.5} compared to C in Figure 1). In the case of FA the additional surface does not lead to any significant acceleration while in the case of quartz some acceleration is observed and a much more distinct acceleration in the case of limestone. The differences in the surface area of the blended systems are relatively small and thus a similar effect on the reaction kinetics could be expected if the surface area would be the only influence. The slight acceleration in the case of quartz seems to be related to the presence of additional surface, as increasing the available surface area of SCMs has been reported to accelerate hydration [4, 17, 18]. The more pronounced effect of limestone might be rationalized by the surface properties of calcite which provide excellent conditions for nucleation of C-S-H [1, 18]. However, the variability of the results indicates that additional effects such as the degree of undersaturation with respect to alite and the composition of the pore solution could play a decisive role.
3.3 Effect of aluminium and sulfate concentration

The presence of SCMs affects the composition of the pore solution, in particular pH values, calcium, alkali and sulfate concentrations as discussed in more detail in Schöler et al. [19]. The lower alkali concentrations in the blended systems result in approximately 0.2 units lower pH and a small increase of calcium concentrations. Blending with limestone decreases strongly the aluminium concentration is solution, while for the blend with fly ash an increase of aluminium concentrations relative to the plain cement and quartz blend was observed. Alkali and sulfate concentrations are lower in the blends than in the neat cement (Figure 4) as both alkali and sulfate in the pore solution mainly originate from the PC while the presence of SMCs dilutes the alkali sulfates. The notable exception is the PC blended with FA, where a clear increase of alkali and sulfate concentrations relative to the quartz reference is observed (Figure 4) as alkali sulfate are also present in the fly ash [19]. An increase of aluminium and sulfate concentrations are known to slow down alite dissolution [7]. In fact the highest aluminium and sulfate concentrations have been measured for the cement with fly ash while they decrease for neat cement and quartz and are lowest for the blend with limestone; the same order as observed for the heat flow discussed in Figure 2. The close negative relation of aluminium and sulfate concentrations with the heat sustain that both high aluminium and sulfate concentrations slow down alite hydration [7]. Plotting the heat flow as a function of the aluminium and sulfate concentration after 2 hours of hydration
(Figure 4) clearly reveals a decrease of the heat flow with increasing aluminium and sulfate concentrations and confirms that the aluminium and sulfate concentrations exert a negative effect on the dissolution of alite. In contrast to the aluminium and sulfate concentrations no such systematic effect is observed for increasing calcium concentrations.

![Figure 4: Specific heat flow at 2 hours of hydration as a function of (a) Al-concentrations and (b) SO₄-concentrations after 2 hours of hydration. Heat flow values are normalized to the amount of PC in the system.](image)

While the sulfate concentrations in the pore solution are determined by the amount of alkali sulfate in the PC and the FA, the concentrations of aluminium depend on pH, the sulfate concentrations and the degree of oversaturation with respect to ettringite. During the early hydration, aluminate and ferrite phases react and the aluminium released is precipitating as ettringite. The PC and the blend with fly ash, which have the highest sulfate concentrations show a higher oversaturation with respect to ettringite (see [19]) indicating that the precipitation of ettringite is more slow in these two systems than in the blends with quartz or limestone, hence higher aluminium concentrations are present. The kinetic hindrance of the ettringite precipitation could be related to the higher sulfate concentration in these systems as Damidot [20] has shown that higher sulfate (and aluminium) concentrations can lead to higher oversaturation with respect to ettringite. While in the case of neat Portland cement the low calcium concentrations (due to higher pH) are responsible for the relatively high sulfate concentrations, the readily soluble sulfate from the fly ash causes the higher sulfate concentrations in the fly ash blend. The limestone blends have the lowest aluminium concentrations, which could indicate the calcite also favors ettringite nucleation.

### 3.4 Effect of SCMs on saturation with respect to CaS, portlandite and C-S-H

In addition to the effect of aluminium and sulfate concentration, the degree of undersaturation with respect to alite is one of the main factor affecting the rate of alite dissolution as has been
discussed in detail by Nicoleau et al. [7]. The lower alkali concentrations in the blended cements result in lower pH and higher calcium concentrations than in the plain cements as shown in Figure 5. The solution of the plain PC and of the limestone blend show the highest degree of oversaturation with respect to portlandite while the oversaturation with respect to high Ca/Si C-S-H is highest for plain cement and the fly ash blend, which showed the highest aluminium and sulfate concentrations. Less oversaturation is observed for the quartz blend and none for the blend with limestone. Undersaturation with respect to alite followed the same order; it is lowest in the case of Portland cement and for the blend with fly ash, which is consistent with the slower reaction of these systems observed by calorimetry. The blend with limestone, which showed the fastest reaction during the calorimetric measurements, exhibits also the strongest undersaturation with respect to alite followed by the quartz blend, thus confirming that the controlling factor for alite dissolution is the degree of undersaturation.

![Figure 5: Concentrations of sulfate in the pore solutions and calculated saturation index of C₃S. The relative error is ~5% of the concentration measured.](image)

Figure 6 illustrates that initially the pore solutions systems are close to the solubility of the protonated surface sites of C₃S [6] and that the concentrations approach the C-S-H solubility with progressing reaction. Thereby a significant difference between the limestone containing blend and the other two blends can be observed. The limestone blend reaches equilibrium with respect to C-S-H very fast, while the other systems remain oversaturated up to 6 hours.
The general trends of dissolution (and precipitation reactions) are consistent with the observed degree of undersaturation at least along the lines of plain Portland cement, quartz and limestone blend. However, the relatively slow reaction of C-FA cannot be explained by the degree of undersaturation only but seems to be related to the higher aluminium concentrations.

Figure 6: Calcium and silicon concentrations of the pore solution compared to the solubility of portlandite, C-S-H and C3S.

4. Conclusions

The results presented in this study compare the early hydration of Portland cements blended with different types of SCMs. The investigations of the changes in the pore solution during the early hydration show that the same factors as in diluted systems dominate the kinetics. Higher degree of undersaturation with respect to C3S and lower aluminium and sulfate concentration accelerate the reaction. Similarly additional C-S-H nuclei (due to more surface or the presence of limestone) lead to faster C-S-H precipitation, higher undersaturation with respect to alite and thus to faster hydration. The exact interplay between these factors in real systems depends on many factors. The aluminium concentrations are strongly affected by the kinetics of ettringite precipitation, which can be hindered at high sulfate concentrations and accelerated in the presence of limestone. The various factors controlling the hydration make investigations in cement pastes challenging and further research is needed both in synthetic systems dissolution of alite and in cements to better understand the factors controlling the early hydration of Portland cement in the presence of SCMs.

References


EFFECT OF FLY ASH ON PORE STRUCTURE OF HARDENED CEMENT PASTE MEASURED BY THERMOPOROMETRY

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Abstract
Mercury intrusion porosimetry (MIP) has been widely used for evaluating the pore structure of hardened cement paste. However, testing procedures involving mercury are dangerous and cause environmental damage. Therefore, in this study, we investigated the pore structure of hardened cement paste mixed with fly ash using thermoporometry by means of low-temperature differential scanning calorimetry measurements, as an alternative to MIP. The suitability of this approach to evaluating the pore structure of hardened cement paste was demonstrated in this study.

1. Introduction
When evaluating the durability of a concrete structure, it is necessary to know its precise mechanical and transport properties, such as compressive strength, elastic modulus, diffusion, and permeability. These properties are strongly influenced by the pore structure of concrete, and therefore, it is very important to study the pore structure of concrete as accurately as possible. Mercury intrusion porosimetry (MIP) has been widely used for evaluating the pore structure of concrete and hardened cement paste [1]. However, it has been demonstrated that MIP cannot measure the real pore structure because of the ink-bottle effect [2]. In addition, it is necessary to dry the samples before conducting MIP measurements. Moreover, testing procedures involving mercury are dangerous and cause environmental damage. To overcome such problems, thermoporometry (TPM) using low-temperature differential scanning calorimetry (LT-DSC) has been suggested as a possible option to measure the pore structure of cementitious materials [1]. Some studies on LT-DSC have reported the relationship between the freezing temperature of pore water and the pore radius [3,4,5,6]. TPM has been used to investigate the behavior of freeze-thawing action and the transport properties of cementitious materials [7,8,9]. Some discussions about the measurement technique and analysis of TPM can be found in the literature [6,10], but further research is necessary. Conversely, numerous studies comparing the pore volume measured with MIP and the
properties of hardened cement paste have been conducted [11,12,13,14,15]. However, no studies comparing the pore structure, measured with TPM, and the properties of hardened cement paste mixed with fly ash have been conducted. Fly ash is a pozzolanic material that can modify the pore structure of hardened cement paste. Therefore, in this study, TPM using LT-DSC was applied to the hardened cement paste mixed with fly ash, in order to investigate the effect of the pore structure on the properties of this material.

2. Experimental Procedure

2.1 Materials
In this study, ordinary Portland cement (OPC, with density: 3.17 g/cm$^3$, specific surface area: 3340 cm$^2$/g) and fly ash (density: 2.33 g/cm$^3$, specific surface area: 3960 cm$^2$/g) were used. The water-to-binder ratio (W/B) of the blended cement paste samples were 0.3, 0.5, and 0.7. The replacement ratio of the fly ash was 0.15 and 0.3, as shown in Table 1. The paste was mixed repeatedly to avoid bleeding, after which it was placed in a mold. After 24 h, the specimens were demolded, and cured in saturated lime water at 40 °C for 28 and 91 days, aiming to accelerate the reaction of the fly ash.

<table>
<thead>
<tr>
<th>W/B</th>
<th>Replacement ratio of fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3-0</td>
<td>0.3</td>
</tr>
<tr>
<td>0.3-0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>0.5-0</td>
<td>0.5</td>
</tr>
<tr>
<td>0.5-0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>0.5-0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>0.7-0</td>
<td>0.7</td>
</tr>
<tr>
<td>0.7-0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

2.2 Measurement

2.2.1 Thermoporometry (TPM)
Several pieces of the hardened cement paste (HCP) samples, weighing 28 mg each, were cut from the cured test piece under saturated conditions and measured with LT-DSC, to obtain the quantity of heat of the exothermic peak during the freezing process. Each HCP sample was placed in a sealed aluminum pan to prevent water evaporation during the measurement. The testing conditions were as follows: the initial temperature was 10 °C, the temperature during cooling process ranged from –60 to 10 °C, and the cooling rate was 2.0 °C/min. As a reference value, alumina powder was measured simultaneously. The pore radius was determined as in [3, 5,16]:

$$R_{\text{freeze}} = - \frac{73.031}{\Delta T} + 0.095 \quad (1)$$

$$R_{\text{melt}} = - \frac{38.172}{\Delta T} + 0.36 \quad (2)$$

where $R_{\text{freeze}}$ denotes the pore radius during the freezing process (nm), $R_{\text{melt}}$ is pore radius during melting process (nm), and $\Delta T$ represents the temperature difference between 273 (K).
and measured temperature (K). It has been reported that the composition of the pore solution has little influence on the pore radius [6], and therefore, the equations for distilled water have been employed in this study. The pore volume at an arbitrary pore radius was calculated from the measured heat release, density of ice, and enthalpy change as follows [3]:

\[
\Delta H = 333.9 + 1.797\Delta T
\]

(3)

\[
P_w = \frac{Q_{\Delta T}}{\Delta H}
\]

(4)

where \(\Delta H\) is the enthalpy change of \(H_2O\) at the liquid–solid phase transition (J/g), \(P_w\) represents pore volume, and \(Q_{\Delta T}\) denotes heat release.

2.2.2 Compressive strength
The uniaxial compressive strength of each sample was determined using cylindrical specimens (average of 3 samples), 50 mm in diameter and 100 mm high each.

2.2.3 Ultrasonic pulse velocity
The ultrasonic pulse velocity of each sample was also measured using cylindrical specimens (average of 3 samples), 50 mm in diameter and 100 mm high. The longitudinal elastic wave velocity (P wave) was recorded for each specimen, as well as the ultrasonic pulse velocity, using its transmission time and its length.

2.2.4 AC impedance measurement
The dimensions of the specimens employed to measure the electrical conductivity were 40 mm \(\times\) 40 mm \(\times\) 40 mm, and stainless electrodes (40 mm \(\times\) 30 mm \(\times\) 0.3 mm) were embedded 30 mm inside the sample, as shown in Fig.1. The effective area of the electrodes was 30 mm \(\times\) 30 mm, and their AC impedance was in the range of 4 Hz to 5 MHz, as recorded with an impedance analyzer (HIOKI IM3570). After the measurements, a Nyquist plot was drawn from the acquired data, and the bulk resistivity \(\sigma\) was determined at the location where the plotted electrode resistivity (straight line) crossed a circle. The conductivity of the pore solution, \(\sigma_0\) was then calculated based on previous studies on the degree of hydration and the chemical composition of the cement [17,18,19]. The normalized conductivity \(\sigma/\sigma_0\) was obtained by means of the bulk resistivity, \(\sigma\), and \(\sigma_0\).

2.2.5 Mercury intrusion porosimetry (MIP)
MIP has been used to measure the pore size distribution for pores with diameters ranging from 3 nm to 400 \(\mu m\) (curing ages: 28, 91 days). The specimens for this test were dried using the freeze-dry method.
2.2.6 Loss of ignition
The loss of ignition, \( W_L \), was measured from 105 to 950 °C to determine the degree of hydration in the specimens. The non-evaporable water content of the fully hydrated cement paste was 0.23.

2.2.7 Porosity
The porosity was determined from the density of the specimen and the difference between the weight of the saturated and that of the dry sample (dried to 105 °C).

3. Results and discussion

3.1 Properties of hardened cement paste
The properties of the hardened cement pastes are shown in Figs.2, 3, and 4. The compressive strength and ultrasonic pulse velocity of the specimen increased with curing age, as shown in Figs.2 and 3, respectively. The increase in this magnitude for the specimen mixed with fly ash was higher than of the one for the OPC specimen. The normalized electrical conductivity decreased with curing age, as shown in Fig.4. The normalized conductivity for the specimen mixed with fly ash was lower than of the one for OPC, and it was expected that the ion migration changed significantly.

3.2 Pore size distribution
The pore size distribution of blended cement pastes at 28 days, measured with TPM during the melting process, is shown in Fig.5. TPM cannot detect pores with radii exceeding 200 nm, as demonstrated in previous studies [1,20]. As the replacement ratio of fly ash increased, the pore volume followed the same trend. The pore size distribution measured with MIP is represented in Fig.6, yielding the same trend as for the TPM results. There was only one peak in the TPM measurement, while several peaks were observed with MIP; this could have been due to an ink-bottle effect.
Fig. 2 Compressive strength of blended cement pastes

Fig. 3 Ultrasonic pulse velocity of blended cement pastes

Fig. 4 Normalized conductivity of blended cement pastes
3.3 Relationship between pore volume and other properties

Fig. 7 shows plots for the pore volume measured with MIP and TPM, vs. the compressive strength. It can be seen how the compressive strength decreased when pore volume increased for both measurement methods. In the present study, this relationship was expressed as an exponential function, as in a previous publication [21]. The correlation coefficient between the pore volume measured with MIP and the strength was better than that obtained with TPM. This is because MIP can detect larger pores, which affect the compressive strength.

Fig. 8 shows the pore volume vs. ultrasonic pulse velocity (UPV). The relationship between these magnitudes has also been shown to follow an exponential trend [21]. The correlation between the total pore volume and UPV was very high because the UPV is greatly influenced by the solid connectivity in the hardened cement paste. The correlation coefficient between the UPV and the pore volume measured with MIP is higher than with TPM.
Fig. 7 shows pore volume vs. electrical conductivity, showing that the later increased with the former. The relationship between the pore volume and the electrical conductivity was expressed as an exponential function in this study. This relation is similar to Archie’s law [22]. The correlation of the total pore volume and electrical conductivity as shown in Fig. 9a was not that good, while it was much better when it was considered separately in fly ash paste and OPC (Figs. 9b and c). This difference is caused by the composition of pore solution and the surface charge at the pore wall [23].

As mentioned above, the compressive strength and the ultrasonic pulse velocity of the hardened cement paste, mixed with fly ash, were strongly related to the total pore volume measured with TPM and MIP. That is, it is demonstrated that it is possible to estimate the mechanical properties of hardened cement paste with TPM using LT-DSC. However, to obtain the electrical conductivity it is necessary to consider it for OPC and fly ash paste separately.
Fig. 9 Pore volume measured with MIP and TPM, vs. the normalized conductivity (a: complete specimen, b: OPC, c: fly ash).

(a)

(b)

(c)
4. Conclusion

The application of TPM using LT-DSC measurements as an alternative to MIP has been investigated in this study. The compressive strength, ultrasonic pulse velocity, and electrical conductivity were measured, as well as the properties of hardened cement paste with fly ash. Good correlations between the pore volume, measured with TPM, and all these properties have been demonstrated. In particular, the compressive strength and the ultrasonic pulse velocity of hardened cement paste mixed with fly ash were shown as strongly related to the total pore volume, when measured with TPM. It is concluded that it is possible to estimate the mechanical properties of hardened cement paste mixed with fly ash with TPM using LT-DSC. Although the correlation between these properties and the pore volume obtained with TPM is lower than with MIP, the possibility of using TPM as a substitute for MIP in the estimation of the mechanical properties of hardened cement paste mixed with fly ash is thus proposed as a feasible alternative. However, for obtaining an accurate estimation of the electrical conductivity, it is necessary to measure it for OPC and fly ash paste separately.

Acknowledgment

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RADIOLOGICAL STUDY OF CEMENTS AND GEOPOLYMERS

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Abstract

The aim of this study has been to determine the activity concentration of $^{40}$K and radionuclides from the $^{238}$U and $^{232}$Th decay series in commercial cements, some industrial wastes and geopolymers and to calculate their activity concentration levels after the cement hydration/activation at 28 days to ascertain the effect of these processes on their final activity concentrations. The highest activity concentration levels of radionuclides from uranium and thorium series have been obtained in the fly ashes, slags and calcium aluminate cement. When a blend among industrial wastes and cement is realised, the radionuclides activity concentration are calculated on the grounds of their percentages in the blend material and tested by its experimental measurement. Once the hydrated/activated cements and geopolymers have been obtained, a proportional decrease to the percentage of added water is observed in the radionuclides activity concentration for the hydrated cements and no-correlation in the case of $^{40}$K in geopolymers pointing to an increase of this isotope in the sodium compounds used for its activation.

1. Introduction

Construction and more specifically the Portland cement industries are excellent targets for the reuse and valorisation of waste and by-products from a wide variety of industries. A broad range of types of waste can be valorised in the preparation of cements and eco-efficient cements.

A number of procedures are in place to obtain more eco-efficient cement. Perhaps one of the most widespread practices entails the use of secondary cementitious materials (SCMs) to replace part or nearly all of the clinker in Portland cement. Of the 27 types of ordinary cement listed in European standard EN 197-1:2011 [1], 26 contain some manner of mineral addition:
limestone, blast furnace slag, siliceous or calcareous fly ash, sintered schist or silica fume. Most of these additions are industrial by-products or naturally occurring radioactive materials (NORMs).

Another avenue for manufacturing eco-efficient cements is the development of new materials wholly different from ordinary Portland cement. Thanks to their excellent properties, alkali-activated cements (also known as geopolymers), are among the most prominent of these new materials [2-6]. Alkaline activation calls for two basic components: preferably amorphous or vitreous aluminosilicates and an alkaline activator. The aluminosilicates may be natural products such as metakaolin or industrial by-products such as blast furnace slag or aluminosiliceous fly ash. The alkaline solutions able to interact with aluminosilicates to generate such new binders include, mainly, alkaline metal or alkaline-earth hydroxides (ROH, X(OH)₂ and R₂O(n)SiO₂-type siliceous salts known as waterglass (where R is an alkaline ion such as N, K or Li). Patents have been awarded for the use of industrial waste or by-products such as ash from rice husks, silica fume and urban and industrial vitreous waste glass as potential alkaline activators to replace the family of substances known as waterglass [7-9]. Here also, the main components of these cements are NORMs.

The most recent legislation in Europe about safety standards for protection against the dangers arising from exposure to ionizing radiation is the European Directive 2013/59 Euratom [10]. This specifies that building materials are in the scope of this regulation but also with the existing standards about construction products. The indoor gamma radiation emitted from these has to be established introducing requirements on the recycling of residues from industries processing naturally-occurring radioactive materials. The quantity adopted in this Article 75, as a reference level for indoor external exposure due to gamma radiation emitted by building materials, is 1 mSv per year.

Several authors have studied the natural radioactivity of cements and their constituents [11-17]. Missaq et al. [13] showed that the radon emission coefficient and production rate in building materials depend on their porosity. Trevisi et al [15] showed the different radionuclides concentrations in cements with pozzolans and other mineral additions. K. Kovler et al. [16] have demonstrated that despite higher 226Ra content in fly ashes (more than 3 times to OPC. Piedecausa et al. [18] revealed the need to establish criteria for monitoring such waste and analysed risk rates by country. Nonetheless, no thorough data have been published comparing the radioactive content in hydrated paste to the radioactivity of its component materials. Nor has the literature addressed the radioactive rates and content in alkali-activated cements or geopolymers, materials of great promise in the twenty-first century.

The original radioactive content in several types of cement (ordinary Portland, Calcium aluminate cements and alkali-activated cements) and their constituents were determined in the present study. The activity concentration after cement hydration/activation was also analysed to ascertain the effect of these processes on final radioactivity.
2. Experimental work

Table 1 gives the XRF-determined chemical composition of the materials used in this study. In addition to the commercial cements listed, other binders were prepared by blending CEM I 52.5R cement and mineral additions (limestone, slag, fly ash and silica fume) as follows:

- 50 % CEM I+50 % slag (OPC+50 % S)
- 50 % CEM I+50 % fly ash (OPC+50 % FA)
- 50 % CEM I+50 % limestone (OPC+50 % L)
- 90 % CEM I+10 % silica fume (OPC+10 % SF)

Table 1: Chemical composition of commercial cements, mineral additions and glass waste (% wt)

<table>
<thead>
<tr>
<th></th>
<th>OPC</th>
<th>White-OPC (W-OPC)</th>
<th>CAC LIMESTONE (L)</th>
<th>SLAG (S)</th>
<th>FLY ASH (FA)</th>
<th>SILICA FUME (SF)</th>
<th>GLASS WASTE (WGLASS) (&lt;45 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20.5</td>
<td>20.0</td>
<td>3.3</td>
<td>0.3</td>
<td>35.3</td>
<td>46.3</td>
<td>49.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.4</td>
<td>3.3</td>
<td>44.9</td>
<td>0.04</td>
<td>13.6</td>
<td>31.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.1</td>
<td>0.3</td>
<td>15.0</td>
<td>0.1</td>
<td>0.4</td>
<td>4.5</td>
<td>0.1</td>
</tr>
<tr>
<td>MnO</td>
<td>0.02</td>
<td>1.7</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
<td>0.1</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>3.7</td>
<td>1.80</td>
<td>0.8</td>
<td>0.9</td>
<td>4.1</td>
<td>1.3</td>
<td>0.2</td>
</tr>
<tr>
<td>CaO</td>
<td>57.0</td>
<td>68.0</td>
<td>33.5</td>
<td>54.6</td>
<td>41.0</td>
<td>4.9</td>
<td>0.5</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.6</td>
<td>1.3</td>
<td>0.3</td>
<td>0.4</td>
<td>0.01</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.4</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>1.3</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.2</td>
<td>0.0</td>
<td>1.5</td>
<td>0.01</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>1.0</td>
<td>0.05</td>
</tr>
<tr>
<td>SO₃</td>
<td>6.4</td>
<td>3.6</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>SiO₂ reactive</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>36.4</td>
<td>92.7</td>
<td>-</td>
</tr>
<tr>
<td>Blaine (m²/kg)</td>
<td>501.7</td>
<td>-</td>
<td>342</td>
<td>-</td>
<td>325</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BET (m²/g)</td>
<td>1.2</td>
<td>-</td>
<td>4.4</td>
<td>-</td>
<td>2.7</td>
<td>20.3</td>
<td>-</td>
</tr>
<tr>
<td>Dv(μm) 10</td>
<td>1.2</td>
<td>2.1</td>
<td>2.0</td>
<td>0.8</td>
<td>0.9</td>
<td>1.8</td>
<td>0.3</td>
</tr>
<tr>
<td>50</td>
<td>7.1</td>
<td>15.5</td>
<td>13.7</td>
<td>3.6</td>
<td>13.1</td>
<td>13.8</td>
<td>10.5</td>
</tr>
<tr>
<td>90</td>
<td>22.5</td>
<td>37.4</td>
<td>49.1</td>
<td>35.1</td>
<td>38.4</td>
<td>59.3</td>
<td>-</td>
</tr>
</tbody>
</table>

*LOI: Loss on Ignition; CAC: Calcium Aluminate Cement

Table 2 shows the hydration/activation conditions used in this investigation [19].

Radiological characterization of the samples was carried out by gamma spectrometry. Radionuclides occurring in natural decay series headed by 238U and 232Th as well as 40K were determined in the samples using a system constituted by three High-purity Germanium
detectors. One of the detectors is coaxial Type p, and the other two, BEGe Type (Broad Energy Germanium detectors). The detectors have an active surface from 26 to 38 cm\(^2\) and 2 keV resolution for \(^{60}\)Co and intrinsic efficiencies from 30 to 100 %.

\(^{226}\)Ra and \(^{232}\)Th determination was based on the detection of emissions of their daughter nuclides, \(^{214}\)Pb and \(^{228}\)Ac respectively, since their own gamma emitting lines are not of sufficient intensity (\(^{222}\)Th at 63.8 keV) or present significant interferences with other naturally occurring radionuclides (186.1 keV from \(^{226}\)Ra and 185.7 keV from \(^{226}\)U). In order to ensure secular equilibrium between \(^{226}\)Ra and \(^{232}\)Th and their progenies, measurement containers (plastic cylinders 75.4 mm of diameter, 31 mm height), were hermetically sealed to avoid \(^{222}\)Rn losses and stored for at least 25 days before their measurement. \(^{40}\)K was directly measured by its emission at 1460.8 keV. Counting times of 60000 seconds were selected for all the samples. Tab. 3 summarizes the energy and emission probabilities of the gamma lines used for the radiological characterization of the samples.

The activity concentration index normally used to characterise building materials poses certain practical problems. One is that \(^{226}\)Ra and \(^{232}\)Th are determined indirectly by measuring their daughters in the natural radioactive series, assuming that they are in equilibrium. This is the procedure of choice because these radionuclides are more readily identified in the spectrum or their emission probability is higher at the peak studied. \(^{226}\)Ra reaches equilibrium after 20-30 days, forming \(^{214}\)Bi and \(^{214}\)Pb, providing the container holding the sample can be sufficiently sealed and no \(^{222}\)Rn is lost through its walls. In addition to \(^{40}\)K, \(^{214}\)Pb (\(^{226}\)Ra) and \(^{228}\)Ac (\(^{232}\)Th) were selected here for calculating the index in the cements and potentially recyclable materials, blended cements containing both and the end product, i.e., hydrated cement containing some of the recyclables.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution</th>
<th>L/S ratio</th>
<th>SiO(_2)/Na(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>Water</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>W-OPC</td>
<td>Water</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>CAC</td>
<td>Water</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>OPC + 10% SF</td>
<td>Water</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>OPC + 50% S</td>
<td>Water</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>OPC + 50% FA</td>
<td>Water</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>OPC + 50% L</td>
<td>Water</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Wg-AAS</td>
<td>Sodium silicate</td>
<td>0.4</td>
<td>0.86</td>
</tr>
<tr>
<td>Glass-AAS</td>
<td>NaOH/Na(_2)CO(_3) + glass waste</td>
<td>0.4</td>
<td>0.86</td>
</tr>
<tr>
<td>N/15Wg-AAFA</td>
<td>NaOH 10M + sodium silicate</td>
<td>0.3</td>
<td>0.19</td>
</tr>
<tr>
<td>Glass-AAFA</td>
<td>NaOH 10M + glass waste</td>
<td>0.3</td>
<td>0.11</td>
</tr>
</tbody>
</table>

The activity concentration index \(I\) was calculated from the following equation:

\[
I = \left( \frac{C_{\text{214Pb}}}{300} + \frac{C_{\text{228Ac}}}{200} + \frac{C_{\text{40K}}}{3000} \right)
\]  

(1)
Its uncertainty was computed as:

\[ u(I) = \sqrt{\left(\frac{1}{300}\right)^2 u^2(C_{214Pb}) + \left(\frac{1}{200}\right)^2 u^2(C_{228Ac}) + \left(\frac{1}{300}\right)^2 u^2(C_{40K})} \]  

\[ I = \text{Activity concentration index; } C_{214Pb} = \text{214Pb activity concentration; } C_{228Ac} = \text{228Ac activity concentration; } C_{40K} = \text{40K activity concentration; } u(C_{214Pb}) = \text{uncertainty of 214Pb activity concentration; } u(C_{228Ac}) = \text{uncertainty of 228Ac activity concentration; } u(C_{40K}) = \text{uncertainty of 40K activity concentration.} \]

The mean index uncertainty was calculated as:

\[ u(I)_{\text{mean}} = \frac{1}{2} \sqrt{u^2(I)_1 + u^2(I)_2} \]  

\[ u(I)_{\text{mean}} = \text{Uncertainty of index mean; } u^2(I)_1 = \text{Uncertainty of the index of the first measurement; } u^2(I)_2 = \text{Uncertainty of the index of the second measurement.} \]

3. Results and discussion

Activity concentration of natural radionuclides in anhydrous cements and different wastes and mineral additions used in cement preparation is shown in Table 3.

The highest radionuclide content in the uranium series was found in coal combustion (fly ash) and metallurgical industry (blast furnace slag) by-products. The \( 226\text{Ra} \) content (i.e., the \( 214\text{Pb} \) or daughter level) ranged from 126 Bq·kg\(^{-1}\) in fly ash to 151 Bq·kg\(^{-1}\) in slag. The lowest values for \( 238\text{U} \) decay chain natural radionuclide content were found in glass waste, anhydrous OPC, limestone and silica fume. The activity concentration for the two considered radionuclides ranged from <2.9 Bq·kg\(^{-1}\) (\( 234\text{Th} \)) to 1.4 Bq·kg\(^{-1}\) (\( 214\text{Pb} \)). The intermediate values, 64.9 Bq·Kg\(^{-1}\)(\( 234\text{Th} \)) to 57.1 Bq·Kg\(^{-1}\)(\( 214\text{Pb} \)), were observed in anhydrous white OPC and CAC.

The findings for the \( 232\text{Th} \) series followed a similar pattern, except for CAC, which exhibited the highest values, similar to the concentrations observed for fly ash: 130 Bq·kg\(^{-1}\)(\( 228\text{Ac} \)) to 134 Bq·kg\(^{-1}\)(\( 211\text{Pb} \)). The lowest activity concentration values, ranging from <0.6 Bq·kg\(^{-1}\)(\( 212\text{Pb} \)) to 19.0 (\( 212\text{Pb} \)) Bq·kg\(^{-1}\), were found for glass waste, limestone and silica fume, as in the \( 238\text{U} \) decay chain. In slag, radioactivity was lower in the thorium than in the uranium series, while intermediate concentrations were observed for slag and anhydrous OPC (see Table 3).

\( 40\text{K} \) is a natural potassium radioisotope present in every other components of the terrestrial crust. Here the highest values were found in glass waste, ranging from 513 to 873 Bq·kg\(^{-1}\) (\( 40\text{K} \)). The lowest were recorded for white OPC, CAC, silica fume, slag and limestone, at <2.5
to 100 Bq·kg⁻¹ (⁴⁰K) in silica fume. The intermediate values were observed for OPC and fly ash, at up to 321 Bq·kg⁻¹ (⁴⁰K) in the latter.

Table 3: Activity concentration of natural radionuclides in cements and mineral additions (some of them are industrial wastes) (in Bq·kg⁻¹) (uncertainty, k=2) and activity concentration index (uncertainty, k=2)

<table>
<thead>
<tr>
<th>Series</th>
<th>OPC</th>
<th>W-OPC</th>
<th>FA</th>
<th>CAC</th>
<th>SF</th>
<th>S</th>
<th>Wglass</th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{239}$U</td>
<td>19.30±1.50</td>
<td>58.50±3.20</td>
<td>130.00±7.10</td>
<td>73.80±6.20</td>
<td>-</td>
<td>156.40±6.80</td>
<td>11.40±1.10</td>
<td>17.50±2.40</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>19.23±0.54</td>
<td>57.10±0.80</td>
<td>127.40±1.30</td>
<td>64.90±0.96</td>
<td>1.4±0.21</td>
<td>147.20±1.40</td>
<td>8.73±0.19</td>
<td>16.98±0.50</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>18.9±0.54</td>
<td>4.81±0.52</td>
<td>130.30±1.50</td>
<td>131.20±1.60</td>
<td>-</td>
<td>45.70±0.86</td>
<td>5.83±0.22</td>
<td>-</td>
</tr>
<tr>
<td>$^{214}$Pb</td>
<td>19.13±0.74</td>
<td>4.36±0.31</td>
<td>133.80±1.30</td>
<td>137.40±1.20</td>
<td>0.82±0.18</td>
<td>42.90±1.20</td>
<td>6.28±0.12</td>
<td>-</td>
</tr>
<tr>
<td>$^{228}$Ac</td>
<td>5.76±0.26</td>
<td>1.36±0.13</td>
<td>41.33±0.57</td>
<td>42.42±0.59</td>
<td>-</td>
<td>14.71±0.30</td>
<td>1.86±0.07</td>
<td>-</td>
</tr>
<tr>
<td>$^{212}$Pb</td>
<td>237.90±0.30</td>
<td>84.60±3.40</td>
<td>316.40±5.90</td>
<td>41.40±5.30</td>
<td>95.80±1.50</td>
<td>76.30±2.70</td>
<td>226.80±4.40</td>
<td>-</td>
</tr>
<tr>
<td>$^{208}$Tl</td>
<td>5.76±0.26</td>
<td>1.36±0.13</td>
<td>41.33±0.57</td>
<td>42.42±0.59</td>
<td>-</td>
<td>14.71±0.30</td>
<td>1.86±0.07</td>
<td>-</td>
</tr>
<tr>
<td>$^{40}$K</td>
<td>0.238±0.0045</td>
<td>0.242±0.004</td>
<td>1.18±0.01</td>
<td>0.88±0.008</td>
<td>&lt;0.044</td>
<td>0.74±0.006</td>
<td>0.133±0.002</td>
<td>&lt;0.064</td>
</tr>
</tbody>
</table>

The radioactivity data in blended cements containing supplementary cementitious materials (SCM) are given in Table 4. These data show that suitable mineral additions can reduce radioactivity in the by-product where the activity concentration in the starting material is known. Although here radioactivity was measured in the blends (cement + silica fume, cement + slag, cement + fly ash and cement + limestone) by gamma spectrometry, it could have been deduced from the percentage of each constituent and the respective percentage of the radionuclide found with the original data and the empirical values in Table 4.

Table 4: Activity concentration of natural radionuclides in blended cement in (Bq·kg⁻¹) (uncertainty, k=2) and activity concentration index (uncertainty, k=2)

<table>
<thead>
<tr>
<th>Material (Blend)</th>
<th>$^{239}$U</th>
<th>$^{235}$U</th>
<th>$^{232}$Th</th>
<th>$^{214}$Pb</th>
<th>$^{228}$Ac</th>
<th>$^{212}$Pb</th>
<th>$^{208}$Tl</th>
<th>$^{40}$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC + 10% SF</td>
<td>17.7±1.5</td>
<td>17.49±0.69</td>
<td>16.69±0.56</td>
<td>18.41±0.46</td>
<td>5.77±0.28</td>
<td>230.6±5.4</td>
<td>0.2186±0.0041</td>
<td></td>
</tr>
<tr>
<td>OPC + 50% S</td>
<td>107.5±6.5</td>
<td>83.85±0.90</td>
<td>31.4±0.74</td>
<td>32.40±0.50</td>
<td>10.72±0.27</td>
<td>158.3±3.7</td>
<td>0.4892±0.0049</td>
<td></td>
</tr>
<tr>
<td>OPC + 10% FA</td>
<td>78.4±3.5</td>
<td>72.90±0.80</td>
<td>71.90±0.99</td>
<td>74.70±0.70</td>
<td>24.40±0.38</td>
<td>277.6±3.0</td>
<td>0.6951±0.0060</td>
<td></td>
</tr>
<tr>
<td>OPC + 10% L</td>
<td>22.2±2.4</td>
<td>17.91±0.35</td>
<td>9.38±0.20</td>
<td>9.65±0.31</td>
<td>2.997±0.062</td>
<td>119.8±2.9</td>
<td>0.1465±0.0018</td>
<td></td>
</tr>
</tbody>
</table>

The radioactivity data in 28-day solid hydrated/activated cements and cements with mineral additions are given in Table 5. The activity concentration was lower per unit of mass in the hydrated than in the anhydrous unblended and blended cements because the concentration of the materials themselves was lower due to the presence of hydration water (30-40%).
The radionuclide activity concentration in alkaline cement pastes (Wg-AAS, Glass-AAS, N/15Wg-AAFA and Glass-AAFA) (see Tab. 5) was calculated on the grounds of the percentage of slag or fly ash in the anhydrous geopolymers and in the hydrated end product. $^{40}K$ concentration rises in such activated materials because the potassium impurities often present in the NaOH activator raise the $^{40}K$ potassium content in the end product.

Table 5: Activity concentration in blended and non-blended cements after hydration or alkaline activation (in Bq kg$^{-1}$) (uncertainty, $k=2$)

<table>
<thead>
<tr>
<th>Series</th>
<th>$^{238}U$</th>
<th>$^{232}$Th</th>
<th>$^{234}$Th</th>
<th>$^{214}$Pb</th>
<th>$^{214}$Ac</th>
<th>$^{212}$Pb</th>
<th>$^{208}$Tl</th>
<th>$^{40}$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAW MATERIAL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OPC</td>
<td>16.3 ± 5.3</td>
<td>7.86 ± 0.60</td>
<td>12.2 ± 0.57</td>
<td>13.83 ± 0.60</td>
<td>4.3 ± 7.8</td>
<td>166.7 ± 6.7</td>
<td>0.1428 ± 0.0041</td>
<td></td>
</tr>
<tr>
<td>W-OPC</td>
<td>47.6 ± 3.4</td>
<td>26.96 ± 0.73</td>
<td>3.52 ± 0.55</td>
<td>3.42 ± 0.16</td>
<td>1.080 ± 0.091</td>
<td>59.0 ± 3.2</td>
<td>0.1271 ± 0.0038</td>
<td></td>
</tr>
<tr>
<td>CAC</td>
<td>60.0 ± 3.8</td>
<td>28.6 ± 1.7</td>
<td>86.7 ± 2.1</td>
<td>98.9 ± 1.8</td>
<td>29.19 ± 0.79</td>
<td>17.2 ± 3.4</td>
<td>0.535 ± 0.011</td>
<td></td>
</tr>
<tr>
<td>BLEND</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OPC + 10% SF</td>
<td>15.4 ± 4.4</td>
<td>6.97 ± 0.59</td>
<td>12.02 ± 0.98</td>
<td>13.31 ± 0.58</td>
<td>3.87 ± 0.31</td>
<td>165.1 ± 6.8</td>
<td>0.1384 ± 0.0057</td>
<td></td>
</tr>
<tr>
<td>OPC + 50% S</td>
<td>71.2 ± 5.9</td>
<td>41.5 ± 1.1</td>
<td>23.0 ± 1.1</td>
<td>22.76 ± 0.69</td>
<td>7.49 ± 0.38</td>
<td>114.1 ± 5.4</td>
<td>0.2914 ± 0.0069</td>
<td></td>
</tr>
<tr>
<td>OPC + 50% FA</td>
<td>66.7 ± 6.7</td>
<td>49.1 ± 1.3</td>
<td>55.1 ± 1.7</td>
<td>62.2 ± 1.1</td>
<td>18.48 ± 0.64</td>
<td>211.6 ± 8.0</td>
<td>0.5097 ± 0.0099</td>
<td></td>
</tr>
<tr>
<td>OPC + 50% L</td>
<td>15.7 ± 3.1</td>
<td>9.35 ± 0.33</td>
<td>6.55 ± 0.78</td>
<td>7.09 ± 0.48</td>
<td>2.30 ± 0.30</td>
<td>86.8 ± 4.8</td>
<td>0.0928 ± 0.0044</td>
<td></td>
</tr>
<tr>
<td>GEOPOLYMERS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wg-AAS</td>
<td>91.3 ± 3.6</td>
<td>48.7 ± 1.1</td>
<td>22.84 ± 0.71</td>
<td>23.3 ± 0.69</td>
<td>7.7 ± 0.39</td>
<td>77.0 ± 5.0</td>
<td>0.3022 ± 0.0054</td>
<td></td>
</tr>
<tr>
<td>Glass-AAS</td>
<td>94.4 ± 6.7</td>
<td>54.5 ± 1.4</td>
<td>23.78 ± 0.81</td>
<td>24.99 ± 0.83</td>
<td>8.04 ± 0.41</td>
<td>89.2 ± 4.8</td>
<td>0.3303 ± 0.0064</td>
<td></td>
</tr>
<tr>
<td>N/15Wg-AAFA</td>
<td>56.4 ± 5.7</td>
<td>36.44 ± 0.97</td>
<td>67.8 ± 1.4</td>
<td>75.1 ± 1.3</td>
<td>21.57 ± 0.59</td>
<td>57.8 ± 15</td>
<td>0.6531 ± 0.0092</td>
<td></td>
</tr>
<tr>
<td>Glass-AAFA</td>
<td>57.4 ± 3.2</td>
<td>37.9 ± 1.1</td>
<td>62.2 ± 1.2</td>
<td>75.1 ± 1.2</td>
<td>22.62 ± 0.63</td>
<td>550 ± 14</td>
<td>0.6207 ± 0.0084</td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusions

Further to the present findings, the uranium series radionuclide concentration in the materials studied is, in descending order:

Fly ash > anhydrous CAC > slag > anhydrous OPC ≈ anhydrous W-OPC > L-SF = glass waste

Radioactivity in cements containing mineral additions (SCM) mirrors the activity concentration in the component materials.
Activity concentration is lower per unit of mass in hydrated cements than in their anhydrous components because the concentration of the materials themselves is lower in the former. The extent of the decline closely parallels the proportion of hydration water (30-40 %).

The radionuclide activity concentration in alkaline cement pastes (Wg-AAS, Glass-AAS, N/15Wg-AAFA and Glass-AAFA) is calculated on the grounds of the percentage of slag or fly ash in the geopolymers and in the hydrated end product. $^{40}$K concentration rises in such activated materials due to the use of NaOH, which often contains potassium impurities that raise the $^{40}$K potassium content in the end product.

Acknowledgements

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References

SUPPLEMENTARY CEMENTITIOUS MATERIALS IN THE ERA OF SUSTAINABLE CONCRETE

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Abstract
Concrete looks often as non-friendly from an environmental point of view. Further developments and new techniques should continue to be introduced into the cement and concrete industry. This will provide distinct alternatives to an OPC dominated cement market. One of such strategies is based on advanced concrete technology concepts, which enables the reduction of the quantity of cement used in concrete, by combining supplementary cementitious materials, fillers, and various admixture technologies. The production of the so-called “low water demand binder” (LWDB) is considered to be an example of such approach. The LWDB technology makes it possible to produce binders with a wide range of material composition and properties varying from multicomponent low-clinker binders with 15…25% of clinker consume to pure clinker binders, the mineral part of which is presented only by clinker component and gypsum. Clinker consumption per 1 m³ of concrete and per 1 MPa of concrete strength, as well as specific energy inputs seems to be brought down to an extraordinary low level that allows considering LWDB as next-generation cement. Development of the codes, standards, guidelines, and training and certification programs will play a significant role in the elaboration and acceptance of the alternate concrete design.

1. Introduction
Concrete is considered to be a universal material for construction starting from the rise of civilization. Versatility of concrete is intimately connected with the simplicity and convenience of its production, relatively low cost, integrity and uniformity of structures, durability and high service life in various aggressive environments.

At the same time, the image of concrete is often perceived as “gray”. Word “concrete” is associated with high labor intensity, solidity, heavy environmental impact due to the quarrying operations, etc. To a large extent, this perception is promoted by the fact that,
according to Gigaton Throwdown Initiative [1], the “the cement industry is responsible for estimated 5% of global CO₂ emissions or 2.1 gigatons CO₂/year”. Indeed, when producing cement clinker, in the course of decomposition of raw components 0.53 kg of CO₂ per one ton of clinker are formed as well as 0.37 kg are emitted in the process of fuel combustion, and thus, the general environmental impact reaches 0.9 t of CO₂/t of clinker. Taking into account the annual increase in production and use of cement up to 4 billion tons (which is expected to double by 2050 due to the global population growth on the planet), this fact poses a considerable threat to the mankind, in whole. According to Intergovernmental Panel on Climate Change (IPCC), if necessary actions are not be taken to cut back the carbon emissions, in about 30 years from now the CO₂ concentration will reach 450 ppm – the danger point above which the irreversible climate will occur.

Because until quite recently cement industry was the main "polluter", the best efforts were focused on the improvement of technological processes in cement industry and decrease in clinker consumption due to the production of mixed cement, when natural or artificial mineral additives are using (including even inert chemically, as is the case with limestone or quartz fillers), and by the simultaneous improvement of grain size composition of cement.

The production of the so-called “low water demand binder” (LWDB) is considered to be an example of such approach.

2. Background

The main principle of low water demand binder preparation is mechanic and chemical activation of rationally selected raw mix including clinker component, mineral additives, gypsum and organic modifying agent (M) which contains high range water-reducing admixture.

LWDBs were invented in 1984 [2]. The production of low water demand binder is carried out under prespecified conditions in the grinding mills which are traditionally used in the cement industry, i.e. tube mills with special ball charges. In such a case, the preference is given to the closed cycle grinding with the use of separator mills, which are rather widespread. LWDBs and methods of making the same were patented in Russia and worldwide [3, 4].

Using range of physical and chemical research methods, Auger-spectrometry and gel-chromatography including, main interaction stages of solid-phase chemical reaction were established: 1) molecular-dense aggregation; 2) chemisorption; 3) implosion (term used in tribology) of organic matter of M into the PCC surface layers to the depth ca. (1-2)×10⁻⁶ m during mutual contacting between comminuting Portland cement clinker particles with M adsorbed on them as a solid lubricant in friction pairs; 4) throttling (organic M separation in process by chain length and molecular mass); 5) cladding of the active zones on clinker surfaces by M [5]. The effect of the M nanolayers formation on the surface of clinker grains was recently demonstrated (so-called “nanoencapsulation”) [6].
Importantly, in the production of LWDBs the amount of expensive and energy consuming clinker can be drastically reduced. The LWDB technology makes it possible to produce binders with a wide range of material composition and properties varying from multicomponent low-clinker binders with 15…25% of clinker consume (LWDB-15…LWDB-25, where number means a clinker content) to pure clinker binders, the mineral part of which is presented only by clinker component and gypsum (LWDB-100) [7].

The use a high volume of mineral additives (sand, limestone or various industrial by-products, e.g. granulated blast furnace slag; fly ash; glass or ceramic breakage, etc) gives an important economic and ecological impact.

Production parameters and type (kind) of binders determine both properties and the field of their application. The field of application of low clinker binders is limited to unreinforced and low-reinforced structures which are used under stable temperature and dry environment and for which the increased durability requirements aren't imposed.

On the contrary, LWDB-100 differs in high physical and mechanical properties and durability. That's why, the use of high performance concrete based on LWDB-100 is considered to be technically reasonable and economically viable when constructing important and unique engineering structures.

It should be noted that LWDB-50 corresponds to ordinary Portland cement on strength and hardening rates under the same curing. As usual, mineral additives considerably promote the optimization of heat release and structure formation processes of concretes, based on LWDB-50, and also increase of their sulfate resistance and resistance to leaching. These advantages are supported by the results of numerous experiments conducted at many institutes in the Russian Federation, as well as abroad. In case of equal frost resistance, in comparison with Portland cement concrete, one may consider LWDB-50 to be a complete and reasonable replacement for good quality standard Portland cement. In case of the increased requirements to cement and concrete, the application of LWDB-70 with the properties in between LWDB-50 and LWDB-100 is reasonable.

Both low-clinker binders and pure clinker LWDB-100, which represent extreme cases of low water demand binders, can't be considered as materials capable to replace general-purpose cement on industrial scale. However, the first ones differ in considerable decrease in clinker component and are more ecologically desirable in spite of limited application field, including mortars and some dry mixes.

Thus wise, in the production of LWDBs the amount of expensive and energy consuming clinker can be drastically reduced. To use a high volume of mineral additives (sand, limestone or various industrial by-products: granulated blast furnace slag; fly ash; glass or ceramic breakage) has an important economic and ecological impact.

In the light of the combination of high construction and technical properties and a limited amount of clinker, binders, containing 50…70% of the clinker component, are of great interest. For example, through industrial tests in Turkey it has been shown that the strength of...
Concrete based on LWDB with 70% of the granulated slag and LWDB with 55% of sea sand, and also LWDB produced with 35% of limestone, is only slightly lower than the strength of concrete test specimen made of ordinary Portland cement.

Concrete based on LWDB with 55% of the trass has a bit lower strength, and this can be balanced by the increase of LWDB-45 in concrete for 10...15% [8].

After thorough laboratory experiments and pilot approbation, the development of low water demand binder technology was confirmed in industrial scale at cement plants of the Russian Federation (Belgorod), Ukraine (Zdolbunov), Azerbaijan (Karadag) and at the regional grinding installations located in some regions of the Russian Federation (Ivanovo, Samara, etc.), as well as abroad (the USA, Spain, Germany, Ireland, Israel, Turkey, Argentina and in some other countries) [9]. The results of the industrial approbation have demonstrated considerable advantages of a new binder as compared to the traditional cement. The realization of these advantages gives the chance not only to use new technical solutions, but also to solve a number of the related ecological problems.

3. Outline of experiment – “intergrinding” vs “interblending”

The composite binder preparation conditions envisaged mechanochemical activation of components ensuring reduction of their water demand; in this connection and in compliance with the established practice the binders produced by the “intergrinding” technique (IG) are designated as LWDB with indication of the clinker component per cent content, while the binders produced by the “interblending” technique (IB) are designated as BCB (blended composite binders) with indication of the clinker component per cent content also.

Preparation of BCB includes thorough mechanical blending (without grinding) of pre-milled (mechanically activated) clinker cement with a finely dispersed additives. For LWDB – “interground” composite binders – the joint mechanochemical activation of clinker cement and additives was provided, as described hereinbefore.

3.1 Materials

Raw materials available on market were used: Portland cement of CEM I 52.5 grade (M600 under GOST 10178), natural quartz sand, and blast furnace slag. Based on PNS superplastisizer, modifier (M) for LWDB preparation had been used. For offsetting of the water demand growth by mixes with “interblended” binders when adding water, PNS superplasticizer was additionally introduced.

3.2 Binders composition

Different types of binders were prepared and tested (Table 1). Additive content in binders was varied from 50% to 70%. Best technological parameters for their preparation were determined from grinding kinetics of binder components. SO₃ content was 3.5% (by mass of clinker only).
Table 1: Tested binders with different clinker content.

<table>
<thead>
<tr>
<th>№№</th>
<th>Binder</th>
<th>Type of binder</th>
<th>Composition of binder, % mass.</th>
<th>BET surface area, m²/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Portland cement</td>
<td>NPC</td>
<td>100 – – –</td>
<td>370</td>
</tr>
<tr>
<td>2</td>
<td>BCB-50</td>
<td>IB</td>
<td>50 25 25</td>
<td>470</td>
</tr>
<tr>
<td>3</td>
<td>LWDB-100</td>
<td>IG</td>
<td>100 – – –</td>
<td>470</td>
</tr>
<tr>
<td>4</td>
<td>LWDB -50</td>
<td>IG</td>
<td>50 25 25</td>
<td>470</td>
</tr>
<tr>
<td>5</td>
<td>LWDB -30</td>
<td>IG</td>
<td>30 35 35</td>
<td>470</td>
</tr>
</tbody>
</table>

Alongside with concrete mixes based on composite binders the concrete based on the initial Portland cement as well as on purely cement mechanically activated binder (LWDB-100) were tested. The tests were conducted both with mortars and ordinary concretes using quartz sand (Msa=2.63), coarse two-fraction sand and crushed granite of 5-20 mm size as aggregates.

3.3 Experimental methods

Efficiency of modifier was evaluated by its influence on normal consistency, setting time of cement paste, and water demand of standard mortar as well as on strength of specimens made from this mortar. Normal sand corresponding to requirements of EN 196 was used to prepare standard mortar.

Grinding kinetics was determined in lab ball mill using mineral additives that were preliminary dried and crushed down to grains of 5 mm diameter as maximum.

Determination of characteristics of binders and cements was made according to current Russian standards GOST 310.1…GOST 310.3, GOST 310.4-81. Strength tests were made according to GOST 10180 with mortar (1:3) specimens using normal sand and keeping in mind lower water demand of LWDB-based mortars. W/C ratio was specified for made LWDB mortars under requirement of target consistency (determined by flow-table) that was equal to consistency of mortars made of Portland cement with W/C=0.5 to ensure equal workability of mortars.

Such procedure of strength testing for LWDB is specified in actual Russian Specifications for these types of binders — TU 5744-002-00369171-97. The practice of W/C varying when consistency is fixed is specified also in USA (ASTM C 109) and Russian (GOST 310.4) standards.

Slump and bleeding of concrete mix were tested according to Russian standard GOST 10181. Some properties of concrete mix were determined in accordance with EN 12350. Concrete strength at the age of 1, 2, 3, 7 and 28 days was tested according to GOST 10180 and EN 12390 with cube specimens 10x10x10 cm.

3.4 Proportioning of concrete

The mixture proportions of concrete used in experiments were chosen to provide concrete mix slump of 3 – 4 cm at binder consumption 350 (or 575) kg/m³.
4. Results and Discussion.

4.1 Properties of LWDB

Efficiency of mechanical-chemical interaction in process of LWDB formation was evaluated by comparison of physical-mechanical properties of LWDB having various content of additives with analogous properties of Portland cement (both materials had similar granulometry by Blaine).

Results of physical-mechanical tests of derived binders are presented in Table 2. They demonstrate that sufficient reduction of water demand for all types of LWDB was obtained, and high strength is ensured at any time of hardening.

LWDBs with mineral additions were produced under the same parameters. Time of grinding was reduced only, taking into consideration abrasion action of hard impurities in grains of sand and slag upon clinker under a process of intergrinding.

Table 2: Test results of different binders.

<table>
<thead>
<tr>
<th>Binder</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dosage of PNS, % cement mass</td>
<td>0</td>
<td>0</td>
<td>1.2</td>
<td>1.8</td>
<td>0.9</td>
</tr>
<tr>
<td>PNS application method</td>
<td>-</td>
<td>-</td>
<td>water of mixing</td>
<td>when grinding</td>
<td>when grinding</td>
</tr>
<tr>
<td>W/B</td>
<td>0.50</td>
<td>0.50</td>
<td>0.38</td>
<td>0.30</td>
<td>0.31</td>
</tr>
<tr>
<td>Consistency by flow, mm</td>
<td>135</td>
<td>130</td>
<td>130</td>
<td>135</td>
<td>134</td>
</tr>
<tr>
<td>Compressive strength, MPa, at the age of, days</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 days</td>
<td>22</td>
<td>14</td>
<td>24</td>
<td>38</td>
<td>26</td>
</tr>
<tr>
<td>28 days</td>
<td>62</td>
<td>55</td>
<td>65</td>
<td>93</td>
<td>77</td>
</tr>
<tr>
<td>Compressive strength after steam treatment, MPa</td>
<td>35</td>
<td>28</td>
<td>37</td>
<td>68</td>
<td>59</td>
</tr>
</tbody>
</table>

*Number of binder - according to Table 1

Results in Table 2 show that that interaction between clinker minerals and modifier took place under specified regime in IG process as contrasted to IB.

Strength characteristics of LWDB-50 are very high (they meet the requirements for cements of class 52.5R according to EN 197-1), and they are higher than strength for control Portland cement. Strength of LWDB-30 corresponds to 42.5R class and higher.

Particle analysis showed that unlike control Portland cement pure clinker LWDB-100 is characterized with more narrow grain distribution by size and relatively increased content of particles having diameter of 10-20 mkm, concurrent with relatively lower content of particles having diameter of 100...200 mkm.
LWDB-50 is approaching to LWDB-100 by granulometry, and this binder is characterized with domination of particles having diameter of 20 mkm and lowered content of fractions 50...100 mkm and more than 100 mkm.

4.2 Properties of concrete

Concrete mixes made of LWDB-100 and LWDB with mineral additions demonstrate reduction of water requirement, that is characteristic for all of them, and this reduction corresponds to reduction of water demand for binders, generally (Table 3).

Table 3: Fresh and hardened concrete properties.

<table>
<thead>
<tr>
<th>Binders by Table 1</th>
<th>Binder cement content of the mix, kg/m³</th>
<th>W/B</th>
<th>Slump, cm</th>
<th>Compressive strength, MPa, at the age of days</th>
<th>Performance indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 28 after steam treatment</td>
<td>Clinker consumption, kg/MPa*</td>
</tr>
<tr>
<td>1</td>
<td>375</td>
<td>0.48</td>
<td>3 - 4</td>
<td>23.1 40.3 35.1</td>
<td>375 9.31</td>
</tr>
<tr>
<td>1</td>
<td>575</td>
<td>0.32</td>
<td>3 - 4</td>
<td>32.2 58.2 46.3</td>
<td>575 9.88</td>
</tr>
<tr>
<td>2</td>
<td>375</td>
<td>0.50</td>
<td>3 - 4</td>
<td>12.4 37.3 27.2</td>
<td>187.5 5.03</td>
</tr>
<tr>
<td>2</td>
<td>375</td>
<td>0.40</td>
<td>3 - 4</td>
<td>22.2 40.3 36.3</td>
<td>187.5 4.65</td>
</tr>
<tr>
<td>3</td>
<td>375</td>
<td>0.28</td>
<td>3 - 4</td>
<td>47.4 88.4 64.3</td>
<td>375 4.24</td>
</tr>
<tr>
<td>4</td>
<td>375</td>
<td>0.30</td>
<td>3 - 4</td>
<td>32.2 76.1 51.5</td>
<td>187.5 2.46</td>
</tr>
<tr>
<td>5</td>
<td>375</td>
<td>0.32</td>
<td>3 - 4</td>
<td>24.3 43.9 36.6</td>
<td>112.5 2.56</td>
</tr>
</tbody>
</table>

* At the age of 28 days

It should be noted that concrete mixes made of any LWDBs had lowered slump loss in time, in comparison with concrete mixes made of control Portland cement.

Strength of concrete made of LWDB-100, including early strength, is substantially higher than one for concrete made of control Portland cement. Concrete made of LWDB-50 with blast furnace slag and sand has higher strength properties also in comparison with control concrete and blended binder. Signally that concrete made of LWDB-30 had the same strength as control concrete based on OPC at any ages. Further increase in additive content above these limits may lead to a proportional reduction of strength.

For concretes with composite “interblended” binder, considering restrictions for the same material consumption and mix characteristics, at 2 and 28 days the strength was 12 - 22 and 37 - 40 MPa, respectively.

5. Conclusion.

The mankind goes through the change of civilization technical paradigm. In conditions of the planet population growth, which, undoubtedly, will fatally affect the energy consumption and increase in global emissions of CO₂ in the atmosphere, in construction we will witness quite rapid displacement of traditional materials and technologies by energy-saving and material-efficient solutions.
Further developments and new techniques will play a significant role in facilitating a holistic industrial ecological approach to cement from a fundamental level. This will provide distinct alternatives to an OPC dominated cement market.

Ultimately, alternative cements should provide a relatively simple and straightforward solution for replacing OPC and must be cost-competitive for large-volume use. But the full potential of novel cements can be realized only through additional investigation and characterization of novel binders, with the help of advanced techniques and methods.

One of them may be LWDB. The specific consumption of aggregates (SCA), according to [10] - the weight ratio of aggregate + fillers to cement - proper to LWDBs in concrete seems to be so great for an inorganic cements (max. 13 for OPC vs. max. 27 for LWDB) that it enables to regard LWDBs as a new generation of cements. The cause of mentioned is M-grafting on cement surface. LWDB changes radically strength properties of cementitious materials because LWDB/aggregate energy is closed to polymer binder/aggregate energy, and SCA of named binders becomes approximately equal. Thus, in LWDB technology the intergrinding takes stand of water-soluble polymer-mediator from known technologies [11].

Technological process of LWDB production becomes very simple that makes it practically universal. Whereas almost any binders can be produced in the form of LWDBs, these binders can be considered as new generation not only of Portland cement, but also of lime, gypsum, slag cements, alumina cements and others. If M cost will be lowered, in the next years many binders will be prevailing as LWDB.

The physical and mechanical properties of concretes based on LWDB conform to the level of guideline values for the relevant strength classes, thereby allowing structural design using conventional calculation tools used for ordinary concretes. The exposed high frost resistance and water impermeability of these concretes allow recommending them for manufacture of building components and construction of facilities to be subject in operation not only to intensive mechanical loading but also to corrosive chemical and climatic effects [12].

The results of the accomplished research have demonstrated also that the application of LWDBs technology provides control of the properties of the HVMA /ECO- cement; use a high volume of indigenous materials in the cement without strength loss; the production of super-high strength cement using selected IBPW. The technology of LWDBs provides an opportunity for using a wide range of by-products and waste.

Current approaches ensuring sustainable development of construction engineering with the use of structural concrete are already obviously inefficient. Instead of the outdated “cement strategy” new approaches emerge which take into account the latest advances in the field of concrete technology and structural calculations according to their full service life [13]. Growth in the codes, standards, guidelines, and training and certification programs will play a significant role in the development and acceptance of alternative cements. They can become a basis for the solution of a global problem to hold off an increasing environmental impact by providing 50% decrease in CO2 emission and energy consumption in construction production.

In this connection, a popular quotation by P.K. Mehta’s becomes especially urgent: “....the
future of the cement and concrete industries would very much depend on the ability to interlink the growth of these industries with the goal of sustainable development…” [14].

References

REALIZING THE STRENGTHS OF SCM CONCRETES BY RECOGNIZING THEIR WEAKNESSES

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Abstract

Concretes made with supplementary cementitious materials can improve the physical properties and durability of concretes in many ways, but if differences in SCM concretes are not recognized by designers, concrete suppliers and contractors, then the potential improvements may not be realized and construction problems may occur. The concerns with potential for problems may grow as owners and designers specify “green concrete” to meet sustainability ratings. Preventing problems and obtaining better concrete with SCMs is not difficult but there needs to be recognition of the potential for impacts on required curing periods and construction schedules, especially in extreme climates. For example, cold temperatures typically have bigger impacts on reducing rates of reaction and development of early-age properties of SCM concretes than with portland cement concrete. However, due to the sensitivity of SCM hydration to temperature, the opposite is often true in hot climates, where expected reductions in temperature rise of mass concrete may not occur unless very high levels of SCMs are used. There is also a need for longer-term retention of capillary pore water with SCMs to allow for the different rates of reaction. After reviewing both the positive and potential negative impacts of various SCM concretes on durability and engineering properties, methods of design to maximize the positives are discussed.

1. Introduction

Concretes including supplementary cementitious materials (SCMs) and blended cements have been in use for almost as long as portland cement concretes. Well-made concretes with SCMs can exhibit better resistance to fluid penetration and enhanced durability in many aggressive environments relative to those made with portland cement alone. However, in many cases specifying agencies or designers place limitations on the use of SCMs in concrete due to perceived concerns with durability (e.g. deicer scaling resistance), based on results from inadequate standard test methods that do not relate to field performance. As well, even when
specified to meet sustainability targets, contractors often do not favor use of high-volume SCM concretes as they are concerned with the potential for lower early-strength development and delays in construction schedules.

Such concerns have been increased by unfavorable research results where performance of SCM concretes have been compared to Portland cement concrete after short curing periods and using test methods performed at 28-day that were developed for Portland cement concrete. Many SCM concretes, especially those containing low-CaO fly ash, do not develop their potential engineering properties until 56 or even 91 days of age, so test comparisons made at only 28 days or earlier are not indicative of the long-term performance over the lifecycle of the structure; this is especially true for durability-related tests initiated at 28 days. Because of its earlier strength development, Portland cement has a better tolerance to poor site curing practices than concretes with high SCM replacement levels, or when using curing practices that were developed for Portland cement concretes. This is especially true in cold weather applications, since temperature affects the hydration rate of most SCM concretes more than with Portland cement: a disadvantage at low temperatures but an advantage at higher temperatures. These differences in rate of development of engineering properties of SCM concretes can be mitigated by re-proportioning mix designs or by inclusion of highly reactive SCMs such as silica fume or metakaolin in ternary cementitious blends.

2. “Strengths” of using SCMs

Fly ash or slag used as SCMs in concrete can provide enhanced durability and long-term strength. In addition, fly ash especially can improve workability or reduce water demand. Fly ash or slag at sufficient cement replacement levels can reduce heat of hydration and be less prone to thermal cracking in mass concrete applications. Secondary hydration reactions reduce capillary pore conductivity and interfacial transition zone (ITZ) porosity, thus reducing the ingress of aggressive fluids containing chlorides [1]. As well, alumina-bearing SCMs can provide increased levels of chloride binding, further slowing chloride ingress [2, 3]. Sufficient levels of appropriate SCMs can mitigate deleterious alkali-silica reaction (ASR) by incorporation of alkalis into C-S-H or C-A-S-H of lower Ca/Si ratio [2], and by reducing the levels of calcium hydroxide in the paste fraction. Calcium exchange for alkalis in the alkali silica gel increases its viscosity and swelling potential, in addition to recycling the alkalis [4]. Well low-CaO fly ashes are effective at mitigating ASR, many high-CaO fly ashes (>18%) are not, but these can be used in ternary blends with 5-10% silica fume to provide sufficient mitigation [5].

Sulfate resistance of concrete can be provided by SCMs instead of using low-C3A Portland cements. The appropriate level of slag will depend in part on its alumina content as well was whether it contains interground calcium sulfate and/or calcium carbonate. Typically 50% slag is sufficient to provide equivalent performance to sulfate-resistant Portland cements as long as the slag alumina content is below 11% [6]; with high-alumina slags as much as 70% slag as well as interground additions of calcium sulfate maybe required [7]. Silica fume also improves sulfate resistance [8] as do low-CaO Class F fly ashes, but many fly ashes with CaO
contents in excess of about 17% do not [9]. Use of silica fume together with high-CaO fly ash can result in good sulfate resistance [10].

Delayed ettringite formation (DEF) has the potential to cause deleterious cracking of certain concrete mixtures when early-age temperatures are in excess of 70°C, with increased risk of DEF if the temperature exceeds 85°C. These high temperatures can occur due to high heat of hydration, or excessive applied curing temperatures. Alumina-bearing SCMs can be effective in preventing DEF when concrete is exposed to such high temperatures [11].

A comprehensive reference describing the many advantages of SCM concretes in chloride, marine, sulfate and freezing and thawing exposures was written by Thomas [12].

3. Weaknesses

As previously stated in the introduction, the main concern and potential weakness are that at high cement replacement levels, and especially in cold weather, fly ash or slag concretes can result in longer setting times and slower early-strength development of concrete. Hydration rates of slag, and even more so with low-CaO Class F fly ash, are much slower at low temperatures than is portland cement. As a result, in Canada and other northern climates, ready mixed concrete producers often cut back on SCM levels in cold weather for normal applications. However, if this weakness is recognized, then producers can re-proportion mixtures to compensate, including use of lower water to cementitious materials ratios and accelerating admixtures. As well, in cold weather, or in cases where high-volume SCM concrete mixtures are specified for special properties or for sustainability reasons, contractors need to be prepared to take appropriate actions to obtain the desired concrete properties and to maintain construction schedules, such as by insulating forms and/or providing heated enclosures. Placement of thermocouples in structural elements can be used to obtain the in-situ maturity and therefore more accurate strength predictions than is obtained from site cast strength specimens.

In cases of hot weather conditions, the hydration of some SCM concretes can be accelerated, relative to portland cement. This can be advantageous in terms of attaining engineering properties at earlier ages, but if it is intended to have low heat mixtures to minimize thermal cracking in mass concrete applications, then higher levels of SCMs may need to be used in hot weather.

While problems are rare, the ones associated with use of concretes containing higher levels of SCM replacement typically occur due to lack of awareness of all parties as to the potential differences in fresh and early-age performance from that of portland cement concrete or to lack of site preparedness in accommodating those differences in the construction process.

There are a wide range of pozzolanic and hydraulic materials that are used as SCMs in concrete. They have different compositions, different rates of reaction and different impacts on development of concrete properties. While in some cases, they can be interchanged, each one needs to be understood to accommodate the differences noted above. There are fewer sources of slag and silica fume, and their quality is controlled by the producers of iron or
silicon alloys, so they tend to be fairly uniform. At power plants, different coal sources, boilers and plant operations result in a wider range of fly ash compositions and resultant impacts on concrete properties. With the exception of high-purity metakaolin, the composition and properties of natural pozzolans, as well as the potential need for thermal processing, can cause their impacts on concrete to vary widely. As well, their availability is often limited geographically, thus limiting them to local use.

4. Potential Issues with SCM Concrete

4.1 Sulfate Optimization and Chemical Admixture Issues

One of the advantages of using blended hydraulic cements in lieu of SCMs added at the concrete plant is that the sulfate content of the blended cement can be optimized; this is especially important when SCMs contain reactive aluminates as is the case with some Class C fly ashes, high-alumina slag or metakaolin. But this still does not prevent problems in concrete because certain chemical admixtures, or combinations of chemical admixtures, can interact with the binder, for example by competing for sulfates or limiting the effectiveness of sulfates by preferential adsorption, and can result in an under-sulfated concrete system.

Chemical admixtures may also perform differently in the presence of SCMs, especially as stated above with SCMs that contain reactive alumina such as high-alumina slag or some high-CaO Class C fly ashes that also contain high levels of alkali-sulfates. In some cases, problems only occur when the concrete is placed at high temperatures. Hot-weather problems have resulted in severely retarded strength development, but were prevented when sulfate content of the cement was increased [13]. Use of calorimetric methods has been useful in detection of setting time and early strength issues as well as in determining solutions to such problems [14,15].

As one example of admixture-specific effects, Hooton and Vassilev [16] found that a vinsol resin air entraining admixture (AEA) did not provide adequate air void spacing factors in concrete containing 35 and 50% slag, but did with concrete made with the portland cement alone; this resulted in poor deicer scaling performance of the slag mixtures. When the AEA was changed to a synthetic detergent, adequate air void spacing and good scaling performance were attained with an otherwise identical 50% slag mixture. As well, some SCMs, such as fly ash may require additional dosages of AEA to achieve required air contents due to adsorption of admixtures by residual carbon in the fly ash, or more recently by addition of powder-activated carbon to reduce mercury emissions at the power plant.

All cementitious materials need to be properly dispersed to maximize their efficiency and to produce concrete with more uniform microstructure. To achieve this, almost all ready mixed and precast concrete operations uses water-reducing admixtures that also disperse the fine powders. In the case of high surface area materials such as silica fume and metakaolin, high-range water reducing admixtures are also typically required. With the increased sensitivity of many SCM concretes to slower property development in cold weather and accelerated development in hot weather, increased attention has to be paid to use of accelerating and retarding admixtures respectively. This has not been much of a problem in urban areas,
because with technical support from the admixture suppliers, concrete producers are able to develop the experience to judge admixture needs and dosages for different environmental conditions and applications.

4.2 Need for Adequate Curing

Portland cement concretes develop most of their engineering properties at or before 28 days. In fact, with currently produced cements having high C₃S contents and high-efficiency grinding circuits, as well as current mix design to accommodate accelerated construction practices, many portland cement concretes are developing their design strengths in as little as 7 days. This rapid development of strength means that poor construction practices where little attention is paid to curing, can still result in concretes that may perform adequately (except when in a severe durability exposure). However, with the possible exception of high surface area, rapidly reacting SCMs such as silica fume and metakaolin, such short or non-existent curing periods are often not adequate to develop the properties of more slowly reactive SCMs such as slag, fly ash and natural pozzolans. However, strength development is not a good indicator of the potential for durability problems arising from poor curing practices, since strength test specimens are sufficiently large to maintain their internal moisture up to 28 days. In practice, poor durability can result because the capillary porosity in the near-surface zones of concrete structures dries out too soon, preventing further hydration, and the “cover concrete” does not develop adequate levels of impermeability, abrasion or scaling resistance. Hooton et al [17] showed that inadequate or limited curing periods had a strong effect on increasing the near-surface rate of chloride diffusion to depths of 20-40 mm, thus reducing the time to corrosion of SCM and high w/cm mixtures.

As one example of the negative impact of using test methods designed for Portland cement concretes, Boyd and Hooton [18] found that the results of ASTM C672 [19], 14-day moist cured, deicer salt scaling tests, with freezing cycles initiated at 28 days of age was not indicative of pavement field performance of 35 and 50% slag concretes, but was sufficient for the portland cement control concrete. When companion test slabs were left in field conditions for about 4 months before scaling tests were initiated, scaling of the slag concretes was much reduced and these longer-term test results better predicted the field performance after 10-years. More recent scaling tests have also shown that field performance of SCM concrete sidewalks was much better than predicted by Ontario Ministry of Transport and ASTM C672 tests where freezing cycles are initiated at 28 days. This has resulted in development of a new CSA test procedure that better relates to field performance [20,21].

4.3 Design to Realize the Benefits of SCMs

The slower setting time and lower early strength concerns can be compensated for by appropriate adjustments to mix design. Mix design needs to involve more sophistication than simple mass (or volume) replacement of cement by an SCM. To obtain equal 1-day strengths (if needed for construction scheduling), water to cementitious materials ratios may need to be reduced, unit water contents reduced through increased dosage of water-reducing admixtures, by use of accelerating admixtures, or by use of appropriate ternary cementitious mixtures. As stated previously, in cold weather, the mix proportions may need to be re-adjusted since the rates of reaction of SCMs are typically more sensitive to cold temperatures than portland cement.
5. Synergies with Ternary Blends

High-performance concretes usually contain SCMs as well as low w/cm to improve long-term strength and reduce ingress of aggressive fluids for provision of long service life. To obtain high 1-day strengths, silica fume is typically added in addition to either slag or fly ash. This creates an optimized ternary blend concrete that combines both early and later age advantages.

As an example, in 1985 at the Scotia Plaza tower in Toronto, the columns and central core concrete provided strengths in excess of 20MPa at 11 hours to allow jump forms to be raised, and exceeding the 70-MPa 91 day design strengths with strengths of 90 MPa [22,23]. The required 11-hour strengths were verified by measurement of pull off strengths prior to loosening of column forms. This approach has been used since then on many more towers in Toronto, with specified strengths of 85 MPa, and similar approaches have been used in other North American cities using fly ash and silica fume For example, the Society Tower in Cleveland was completed in 1990, using 90 MPa concrete with 27% slag and 7% silica fume [24].

Ternary blends were used for 40 high-performance concrete bridge decks completed during Toronto’s airport expansion in 2004. It was found that the slag helped reduce the required dosage of HRWRA, thus making the concrete less “sticky” during finishing operations, as well as acting reduce the heat of hydration. No problems with workability or entrained air content were reported during continuous placements of up to 1200 m³, even in cold weather conditions. The 28-day strengths averaged 50.5 MPa with a coefficient of variation of 3.5 MPa. The resultant chloride diffusion rates were low (2.5 x 10⁻¹² m²/s as measured by ASTM C1556; 600 coulombs as measured by ASTM C1202).

As one example of use of ternary blends in Chicago, in 2005, the mass mat foundation for the Trump Tower was placed using self-consolidating concrete with high levels of cement replacement with both slag and Class-C fly ash, a w/cm = 0.26-0.28 with a design strength of 70 MPa. 28-day strengths in excess of 80MPa were obtained but a maximum temperature of 68°C was maintained, and differential temperatures were minimized using insulation on top of the slab [25]. For the columns of the 110 storey, 415 m tower, 90-day strengths of 85 MPa were specified while the outrigger wall beams had 90-day design strengths of 110 MPa; both were SCC with minimum slump flow of 600 mm using quaternary binders of fly ash, slag and silica fume [26]. The tower was completed in 2009.

The high level of calcium in Class-C ash can improve the early hydration rate of slag. Similarly, for a wide range of concrete applications, a blended SCM consisting of slag and a high-calcium, high-alkali fly ash has been found to provide both good early and late age properties [27].

The high-strength, self-consolidating concrete in the 540 m tall Freedom Tower in New York City used pumpable quaternary cement mixtures, with 7.5% silica fume, 7.5% fly ash and 52.5% slag at w/cm = 0.24 to attain design strengths of up to 100 MPa and an elastic modulus of 48 GPa while also controlling thermal cracking in the massive foundation and core elements [28].
Ternary cements have also been used for high-performance precast concrete tunnel liners on several 100-year service life projects in Ontario, Canada [29,30]. In one project, fly ash and silica fume were used and in more recent projects, slag and silica fume have been used at w/cm of 0.31 to attaining strengths of 75 MPa, in excess of 60 MPa design strengths and with chloride diffusion rates of less than 6 x 10^{-13} m²/s and a coulomb ratings of 400-600.

The success of ternary mixtures has also resulted in the production of ternary blended cements made using slag and silica fume [31] and also using fly ash and silica fume in Quebec, Canada.

In both laboratory ASTM C1567 mortar bar and ASTM C1293 concrete prism tests and in large field exposure specimens, silica fume plus slag ternary mixtures have shown excellent performance [1]. Concrete beams 0.6 x 0.6 x 2.0 m as well as pavement sections made with 3.8% silica fume and 25% slag have not shown any damage after 20 years outdoor exposure [32]. Without the silica fume, 50% slag was required to mitigate ASR damage, but 50% slag was higher than what the Ontario Ministry of Transportation wanted to use due to concerns regarding de-icer salt scaling.

In laboratory tests, El-Dieb and Hooton [33] showed that silica fume-slag ternary concretes had extremely low permeability to water. McGrath and Hooton [34] showed that these systems have high resistance to chloride diffusion. Nokken and Hooton [35] found that electric conductivity of ternary blends were lower than with slag or silica fume (SF) alone. In addition, Titherington and Hooton [36] showed that when exposed to accelerated curing (held at 9h at 65°C), 18h strengths of over 40 MPa could be obtained and the ternary systems maintained low chloride diffusion coefficients better than portland cement concretes as shown in Table 1.

Using this technology, ternary blends have been used to produce high-performance precast bridge girders in Ontario (Slag plus silica fume) and Nova Scotia (fly ash plus silica fume). These high-temperature cured girders attain 12-14h strengths in excess of 40 MPa that allows post-tensioning, as well as providing high chloride penetration resistance.

6. Summary and Conclusions

SCM concretes, if properly designed, placed and cured will produce concrete with superior long-term engineering properties and durability to portland cement concrete.

Obtaining good quality, durable concrete with SCMs is not difficult but the differences between SCMs and portland cement need to be recognized along with an adequate understanding of the impacts of the various types and replacement levels of SCMs on both development of concrete properties and concrete construction at the ambient environmental conditions.

As well, if contractors are not sufficiently aware of the influence of high levels of SCMs on concrete setting, early-age strength for construction scheduling, and curing, then problems
may develop on site especially in cold weather conditions, or the durability of the structure may not live up to owner expectations.

This paper is not intended to provide a comprehensive coverage of all potential issues but it serves to highlight some of the issues that impact on the successful use of SCM concretes.

Table 1: 18 h Strength and 28 day chloride resistances of concrete exposed to either accelerated curing at 65°C, or ambient at 23°C, then cured in air until 28 days except as noted [36, 37]. Notes: Migration tests were described in McGrath and Hooton [38].

GUbSF8 is the Canadian CSA designation for blended cement with 8% silica fume.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Curing</th>
<th>18hr Strength (MPa)</th>
<th>ASTM C1202 (Coulombs)</th>
<th>Non-steady state chloride migration ((10^{-12} \text{ m}^2/\text{s}))</th>
<th>Steady-state chloride migration ((10^{-12} \text{ m}^2/\text{s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% PC</td>
<td>ambient</td>
<td>24.2</td>
<td>2280</td>
<td>4.4</td>
<td>4.0</td>
</tr>
<tr>
<td>100% PC</td>
<td>accelerated</td>
<td>31.3</td>
<td>3120</td>
<td>20.1</td>
<td>18</td>
</tr>
<tr>
<td>4% SF</td>
<td>ambient</td>
<td>25.6</td>
<td>520</td>
<td>1.1</td>
<td>0.92</td>
</tr>
<tr>
<td>4% SF</td>
<td>accelerated</td>
<td>40.7</td>
<td>980</td>
<td>2.9</td>
<td>2.7</td>
</tr>
<tr>
<td>4% SF</td>
<td>+ 6d moist cure</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4% SF</td>
<td>accelerated</td>
<td>40.9</td>
<td>1050</td>
<td>7.2</td>
<td>4.5</td>
</tr>
<tr>
<td>8% SF</td>
<td>ambient</td>
<td>24</td>
<td>270</td>
<td>0.48</td>
<td>0.28</td>
</tr>
<tr>
<td>8% SF</td>
<td>accelerated</td>
<td>45.4</td>
<td>230</td>
<td>1.0</td>
<td>0.95</td>
</tr>
<tr>
<td>4% SF + 25% Slag</td>
<td>ambient</td>
<td>17.5</td>
<td>310</td>
<td>0.86</td>
<td>0.55</td>
</tr>
<tr>
<td>GUbSF8 + 25% Slag</td>
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<td>25.6</td>
<td>260</td>
<td>0.91</td>
<td>0.52</td>
</tr>
<tr>
<td>8% SF + 25% Slag</td>
<td>ambient</td>
<td>12.7</td>
<td>175</td>
<td>0.41</td>
<td>0.18</td>
</tr>
<tr>
<td>8% SF + 25% Slag</td>
<td>accelerated</td>
<td>40.5</td>
<td>125</td>
<td>0.57</td>
<td>0.54</td>
</tr>
</tbody>
</table>

References


DURABILITY OF HIGH VOLUME FLY ASH CONCRETE

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Abstract
Concrete is the most used construction material in the world. Also, it is the least energy consuming material in terms of its production compared to other building materials. The use of Fly ash as supplementary cementitious material (SCM) in concrete is well-known because of the durability and cost effectiveness it attributes to the concrete industry. Internationally, cement production is reached to 4.3 billion tonnes in the year 2014. The carbon print of the cement production is raising the importance of increasing the percentage of replacement with fly ash in a dramatic level such as more than 50% which is known as high volume fly ash concrete (HVFAC). This paper presents the durability properties of HVFAC with 50% replacement. The main drawback of fly ash replacements above 20% is the low strength developments compared to OPC concrete. To address this problem, ultra-fine fly ash (UFFA) and lime water as mixing water are used in this project along with raw fly ash and tap water. Also, concrete with OPC is taken as control mix. All concrete mixes are tested for compressive strength, water absorption, carbonation, chloride penetration, and sulphate resistance. All properties are found to be having superior durability compared to OPC concrete.

1. Introduction
Concrete is the least energy consuming material in terms of its production compared to other building materials [1]. But the degree of durability of each type of concrete depends on its exposure to the environment and the properties it is defined for. Exposure to repeated cycles of wetting and drying conditions, freezing and thawing, seawater, groundwater containing sulphates, and industrial effluents are the severe environmental conditions with which many concrete structures need resistance against.
Permeability is the main factor which affects the durability of concrete. Supplementary Cementitious Materials (SCMs) can reduce the permeability of concrete and make concrete denser. Use of SCMs not only improves the durability of concrete but also provides physical and environmental benefits to concrete.

Spherical shape of fly ash is one of the main reasons for the better durability of fly ash concrete. Fly ash has been shown to decrease concrete permeability by reducing mixing water requirements and by converting easily leachable Ca(OH)₂ to C-S-H. Water tightness plays an important role in reducing all durability problems such as chloride ion penetration, sulphate attack, ASR and corrosion of reinforcement etc, [2,3].

The benefits of fly ash concrete in fresh and hardened states along with sustainability issue due to the cement production enabled the concrete researchers to investigate more about replacing more than 50% of fly ash by mass, so called High Volume Fly Ash Concrete (HVFAC) [4].

It is estimated that globally, only 20% of available fly ash is being utilized in cement and concrete industry [2]. Australia is a country where there is a huge dependency on thermal power plants for electricity generation, where fly ash is produced as a by-product in coal combustion. As per Ash Development of Australia, about 12.5 Mt of fly ash produced in the year 2002, of which only 4.1 Mt is utilized effectively of which 1.37 Mt in concrete rest being in other applications [5]. Whereas 1 ton of cement is producing around 0.7 ton of CO₂ in Australia. Hence, reducing cement by replacing with fly ash not only helps to reduce the CO₂ emissions due to cement but also reduces the waste produced by coal combustion (fly ash). Since 1975, some 16 million tonnes of greenhouse gas emissions have been abated by the use of FA in the manufacture of cement and concrete [5]. Hence, HVFAC can address the two environmental problems caused by cement production and environmental waste caused by disposing of fly ash in the landfills.

2. Background

In practice, the quantity of fly ash to replace cement is limited to 15–20% by mass of the total cementitious material. Well cured super plasticized HVFAC containing 50-60% of fly ash shows relatively better early strengths and durability properties [2].

The combination of particle packing effect due to spherical shape, low water content and pozzolanic reaction results in denser microstructure which is highly crack resistant and durable [2]. Because of the denser microstructure, HVFA shows lower permeability, there by producing concrete having better resistance to chloride and sulphate ion ingress. The excess lime consumed by pozzolanic reaction not only controls ASR in later years but also decreases carbonation [6]. Well cured HVFAC shows superior durability properties than OPC concrete [7]. Research of Rivera et.al [8], showed that using higher volumes of fly ash ranging from 40-80% s has howed lower permeability (2300 Coulombs at 56day and electrical resistivity (60 ohm-m at 56day). However, there was a research gap to improve the properties HVFAC where the slow strength development is major drawback when used for structural purpose.
The pozzolanic activity of a fly ash is proportional to the amount of particles under 10 μm, whereas particles larger than 45 μm show a little or no pozzolanic activity [2, 9]. Though some researchers reported increased compressive strength with use of UFFA compared with raw fly ash [10, 11], there is very little research is conducted on durability properties of HVFAC using UFFA. Researcher Xu, 1997 showed that the durability properties get better with ultra-fine fly ash (UFFA) [12].

To improve the performance of a mortar containing HVFA, an investigation was carried out by Dr Patnaikuni’s team in RMIT, where they experimented using saturated lime water as mixing water in concrete mortar which gave same strength as normal cement mortar at early ages and higher strength at the age of 56 days[13].

This study shows a development of HVFAC with UFFA and limewater as mixing water to develop a concrete which can compete with OPC in strength development and has superior mechanical and durability properties with 50% replacement [14, 15]. The methodology and the experimental results of compressive strength and durability test results are presented in this paper.

3. Experimental Program

The experimental program consisted of conducting compressive strength test at 28 and 56 days and durability tests such as chloride sulphate penetration tests, carbonation and water absorption tests which are planned at 56 day curing age of concrete.

The experimental plan consists of 4 mixes having 50% replacement with fly ash with 0.3 w/b ratio. This mix proportions needed high range water reducer (HRWR) to maintain low w/b ratio and to get workable concrete. Type of fly ash and mixing water are kept as variables. Table 1 shows the mixes planned for this program.

Table 1: Experimental Plan

<table>
<thead>
<tr>
<th>Mix</th>
<th>Fly ash (%)</th>
<th>Cement (%)</th>
<th>Type of Fly ash</th>
<th>Mixing water</th>
</tr>
</thead>
<tbody>
<tr>
<td>No 1</td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>Tap water</td>
</tr>
<tr>
<td>No 2</td>
<td>50</td>
<td>50</td>
<td>UFFA</td>
<td>Tap water</td>
</tr>
<tr>
<td>No 3</td>
<td>50</td>
<td>50</td>
<td>Raw fly ash</td>
<td>Lime water</td>
</tr>
<tr>
<td>No 4</td>
<td>50</td>
<td>50</td>
<td>UFFA</td>
<td>Lime water</td>
</tr>
</tbody>
</table>

3.1 Mix proportion of the concrete

The mix design for the concrete was prepared based on proposed method of high performance concrete mix design [17]. The mix proportion for 1 m³ of concrete using w/binder ratio of 0.3 is given in Table 2.
The use of high volume UFFA reduced the use of HRWR by 1.6 times in comparison to HRWR used in normal cement concrete. Moreover, it needed only half of HRWR compared to high volume raw fly ash.

Table 2: Mix proportion of high volume ultra-fine fly ash concrete

<table>
<thead>
<tr>
<th>Mix</th>
<th>Cement (kg/m³)</th>
<th>Fly ash (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>Aggregate fine (kg/m³)</th>
<th>Aggregate coarse (kg/m³)</th>
<th>HRWR (litre/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No 1</td>
<td>450.0</td>
<td>-</td>
<td>137.0</td>
<td>912.0</td>
<td>994.0</td>
<td>13.9</td>
</tr>
<tr>
<td>No 2</td>
<td>225.0</td>
<td>225.0</td>
<td>141.0</td>
<td>835.0</td>
<td>994.0</td>
<td>7.0</td>
</tr>
<tr>
<td>No 3</td>
<td>225.0</td>
<td>225.0</td>
<td>139.0</td>
<td>811.0</td>
<td>994.0</td>
<td>10.2</td>
</tr>
<tr>
<td>No 4</td>
<td>225.0</td>
<td>225.0</td>
<td>141.0</td>
<td>835.0</td>
<td>994.0</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The smaller amount of plasticizer in fly ash concrete is because of the spherical shape of fly ash which reduces the friction between cement and aggregates and results in an increase of workability of fresh concrete [18]. This reduction in amount of plasticizer will lead to lower cost of concrete production.

3.2 Materials & Method

For this research, type 1, OPC cement and low calcium fly ash from Tarong power plant which is classified as ASTM C 618 class F [16] fly ash having specific gravity 2.05 were used as binders. The coarse aggregate used was gravel, having specific gravity 2.85 and the maximum size of coarse aggregate was 10 mm. Uncrushed river sand was used as fine aggregate. The specific gravity of fine aggregate was 2.6. The HRWR used was sodium naphthalene formaldehyde sulphonate with density of 1.2 kg/litre. The specific gravity of hydrated lime used for making the lime water was 1.9. The following explanation given in 3.2.1 and 3.2.2 regarding preparation of UFFA and lime water was extracted from [13, 14]

3.2.1 UFFA

UFFA is prepared by grinding the raw fly ash with the help of a micronizer of diameter 2 inches. The micronizer is a jet mill which can reduce the size of fly ash using particle-on-particle impact which leads to increase in the surface area of fly ash. The surface area of fly ash increased from 364m²/kg for raw fly ash to 525 m²/kg for ultra-fine fly ash giving a 40% increase in the fineness of fly ash after the grinding process in micronizer [13, 16].

3.2.2 Lime water as mixing water

The saturated lime water was made by dissolving 3 grams of hydrated lime powder in 1 litre tap water. After allowing to sediment for 24 hours, the top layer of the water was taken and used as mixing water while the solid hydrated lime was left on the bed. The saturated lime water has different properties compared to tap water as shown in Table 3.
The density of saturated lime water was slightly higher than that of tap water since some hydrated lime particles are dissolved in it (0.08%). Furthermore, the alkalinity of saturated lime water is much higher than that of the tap water. The increase of alkalinity in lime water which resulted from Ca(OH)₂ (hydrated lime) will be useful when reacting with pozzolanic material like fly ash.

Table 3 : Properties of mixing water

<table>
<thead>
<tr>
<th>Water</th>
<th>Density</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>0.9909</td>
<td>8.5</td>
</tr>
<tr>
<td>Saturated lime water</td>
<td>0.9917</td>
<td>11.4</td>
</tr>
</tbody>
</table>

4. Results & Analysis

All of the specimens were made of cylinders of 100 Ø x 200 mm and then cut to a height corresponding to the kind of test. All of the specimens were cured by immersing in a water tank with a temperature of 24°C until the day of test.

4.1 Compressive strength

The compressive strength test was conducted as per Australian Standard (AS) 1012.9-1999 [19]. The results of compression strength of concrete at the age of 14 days, 28 days and 56 days are shown in Table 4.

Table 4: Compressive strength of the concrete

<table>
<thead>
<tr>
<th></th>
<th>14 d (MPa)</th>
<th>28 d (MPa)</th>
<th>56 d (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC, tap water (No 1)</td>
<td>50.0</td>
<td>79.0</td>
<td>84.5</td>
</tr>
<tr>
<td>UFFA, tap water (No 2)</td>
<td>-</td>
<td>71.0</td>
<td>74.5</td>
</tr>
<tr>
<td>Raw fly ash, lime water (No 3)</td>
<td>-</td>
<td>66.5</td>
<td>72.0</td>
</tr>
<tr>
<td>UFFA, lime water (No 4)</td>
<td>45.0</td>
<td>78.5</td>
<td>85.0</td>
</tr>
</tbody>
</table>

The compressive strength result shows that the high volume fly ash concrete could achieve strength which nearly met the strength of normal cement concrete even though the amount of ultra-fine fly ash used is 50% as cement replacement. The use of lime water as mixing water increased the compressive strength of high volume fly ash concrete in comparison to earlier studies by other researcher who have used normal water. More over the compressive strength of fly ash concrete is increased with the increase of curing age.

4.2 Water Absorption

Water absorption of concrete test was conducted after curing it for 56 days on cylinders of Ø100 x 60mm height which was cut from cylinders of Ø100 x 200mm. The test was conducted based on Australian Standard (AS 1012.21., 1999) [20]. As per the standard,
immersed water absorption and apparent volume of permeable voids (AVPV) was determined and the results are shown in Table 5.

Table 5: Water absorption test results of concrete

<table>
<thead>
<tr>
<th>%</th>
<th>No 1</th>
<th>No 2</th>
<th>No 3</th>
<th>No 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immersed Absorption</td>
<td>2.53</td>
<td>1.57</td>
<td>1.87</td>
<td>1.11</td>
</tr>
<tr>
<td>AVPV</td>
<td>6.98</td>
<td>4.34</td>
<td>5.10</td>
<td>3.36</td>
</tr>
</tbody>
</table>

Table 5 shows that the use of high volume UFFA reduces water absorption and AVPV significantly in comparison to normal cement concrete. It indicates that the concrete produced using UFFA either using tap water or saturated lime water is denser than normal concrete. Similarly, Iyer and Stanmore (1999) also reported the decrease of water absorption with the increase of fly ash fineness [21].

In addition high volume raw fly ash also has lower water absorption and apparent volume of permeable voids in concrete in comparison to normal cement [22]. The lower water absorption of high volume fly ash concrete was possibly caused by reduction of Ca(OH)₂ as a result of fly ash reaction in concrete. In addition the un-hydrated fly ash particles act as filler in concrete pores [23, 9].

The lower voids in fly ash concrete as shown by apparent volume of permeable voids (AVPV) test of fly ash concrete leads to lower rate of absorption. The lower voids in fly ash concrete results in excellent criteria for durability based on the criteria of durability from Vicroads Classification [24].

4.3 Rapid chloride penetration test

Rapid chloride penetration of concrete is conducted at the age of 56 days as described in ASTM C 1202-97 [25] on small cylinders of size 100 Ø x 50 mm which are cut form 100 Ø x 200 mm cylinders. Chloride Permeability is measured as the current passed in coulombs through the concrete sample whose one side is immersed in 3% NaCl and other end is in 0.3 M NaOH solutions and with a potential difference of 60 V. The results are tabulated and presented in Table 6.

Table 6: Rapid chloride penetration test results

<table>
<thead>
<tr>
<th></th>
<th>No 1</th>
<th>No 2</th>
<th>No 3</th>
<th>No 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Permeability (coulombs)</td>
<td>1165</td>
<td>211</td>
<td>293</td>
<td>210</td>
</tr>
</tbody>
</table>

The result shows that the use of high volume fly ash significantly improves the durability of concrete by reducing chloride ion penetrability from low in normal cement concrete to very low [25] as also reported by other researchers [26, 27]. It indicates a very small pore and void in high volume fly ash concrete. Furthermore the use of high volume UFFA gives further increase in concrete durability compared to high volume raw fly ash concrete due to lower
chloride ion penetrability. In addition there is no influence of using lime water as mixing water in high volume UFFA concrete for chloride ion penetrability improvement.

4.4 Sulphate Resistance Test
The sulphate absorption test in this research is focused on the investigation of sulphate attack using absorption mechanism for preconditioning specimens. Hence, the test is conducted using the standard ASTM C 1585-04 [28] on small cylinders of size 100 Øx 50 mm. The results are shown in Table 7.

Table 7: Initial and secondary rate of sulphate absorption

<table>
<thead>
<tr>
<th>x 10^4 mm/sqrt(time in sec)</th>
<th>No 1</th>
<th>No 2</th>
<th>No 3</th>
<th>No 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial rate absorption</td>
<td>10.4</td>
<td>7.03</td>
<td>7.918</td>
<td>6.5</td>
</tr>
<tr>
<td>Secondary rate absorption</td>
<td>2.65</td>
<td>2.025</td>
<td>1.595</td>
<td>1.702</td>
</tr>
</tbody>
</table>

The results of initial and secondary rate of absorption shows that the secondary rate of absorption is significantly lower than the initial rate of absorption because after longer period of test, the moisture content in concrete increases and only a small amount of liquid can be absorbed. When comparing the sulphate initial rate of absorption it can be observed that higher compressive strength produces lower rate of absorption. This result is confirmed with the rate of absorption of concrete No 2 which has lower rate of absorption in comparison to concrete No 3. (Table 4 and Table 7).

Moreover, high volume fly ash concrete has lower rate of absorption, both for initial and secondary rate of absorption in comparison to OPC concrete. This lower rate of absorption is related to apparent volume of permeable voids (AVPV) test of fly ash concrete, which shows excellent durability criteria according to CCAA Report, 2009 [24].

4.5 Accelerated Carbonation Test
Carbonation test was conducted based on RILEM recommendation on measurement of concrete carbonation depth. The carbonation test for this research was accelerated carbonation test which employed a carbonation chamber to keep the specimen for testing at 7 days and 28 days. The carbonation chamber was maintained with a carbon concentration of 3.5% and relative humidity of 65% and a temperature of 25°C. The specimens for this experiment have dimensions of 100 mm diameter and 60 mm height and were cut from cylinder of diameter 100 mm x 200 mm height. Moreover, the top and bottom surfaces of specimens were sealed using epoxy resins to allow the carbonation only to occur through curved surface.

At the end of testing days, the specimens were taken out from the testing chamber and cut into two pieces. The depth of carbonation is measured using phenolphthalein liquid which is sprayed to the concrete after exposure to carbon gas environment [29, 30]. The un-carbonated area changes to purple colour, whereas the carbonated area stays colourless. The depth of the colourless portion is measured with callipers or scale which is measured in mm as average of different depths taken along the length of the specimen.
The depth of carbonation measurement for all of mixes (Table 8) shows that the high volume fly ash concrete experiences higher carbonation attack from carbon dioxide in the atmosphere, and the carbonated region is deeper than OPC concrete.

<table>
<thead>
<tr>
<th>Carbonation exposure time</th>
<th>No 1</th>
<th>No 2</th>
<th>No 3</th>
<th>No 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>7days</td>
<td>-</td>
<td>0.7</td>
<td>4.4</td>
<td>0.5</td>
</tr>
<tr>
<td>28days</td>
<td>0.2</td>
<td>2.4</td>
<td>6.8</td>
<td>1.7</td>
</tr>
</tbody>
</table>

But the use of lime water increases carbonation resistance of fly ash concrete as more Ca(OH)₂ is available in concrete, and it needs more CO₂ to neutralize the concrete. The use of high volume UFFA increases the concrete carbonation resistance in comparison to the use of high volume raw fly ash. The increase might have resulted from the decrease of permeable voids volume (AVPV) in concrete that makes concrete denser and offer better resistance to the ingress of CO₂. Similarly, Das and Pandey (2011) have examined the increase of carbonation resistance which is caused by the increase of fly ash fineness [31]. Hence, from Table 8, it can be observed that the effect of using just UFFA is more than the effect of just lime water on the resistance of carbonation. The combine effect of UFFA & lime water is showing better result.

In addition, the longer the concrete is exposed to carbon dioxide, the deeper the carbonation in concrete, especially for high volume raw fly ash concrete.

5. Conclusion

The use of UFFA gives further improvement in durability of concrete from the result of water absorption test, rapid chloride penetration test and sulphate resistance test. In addition high volume UFFA needs only half dosage of superplasticizer in comparison to normal cement. Using lime water as mixing water acts like activator by promoting more pozzolanic reaction because of the Ca(OH)₂ in lime water.

To sum up, this experimental work demonstrated that the high volume fly ash concrete can be produced with almost the same strength as that of OPC, but with superior durability by using UFFA and lime water as mixing water.

The following conclusions can be made from the study

- High volume fly ash concrete is showing superior durability than OPC.
- Using UFFA is increasing compressive strength there by durability due to its fineness.
- Adding limewater as mixing water improves the compressive strength by providing extra Ca(OH)₂ required for the pozzolanic reaction.
- The combination of UFFA and lime water is giving excellent results in durability as well as strength enhancement of high volume fly ash concrete.
References


NATURAL ZEOLITES AS SCMS: CHALLENGES AND SOLUTIONS

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Abstract

Natural zeolites are abundant in many regions. While high purity zeolites are used in other industries, low purity zeolites are underutilized and can find beneficial use as supplementary cementitious materials (SCMs) in concrete. However, these low purity, natural zeolites present challenges as SCMs because of their high water demand and variable reactivity. In this paper, the effects of two natural clinoptilolite zeolites on the properties of cement-based materials are discussed. Further, the role of chemical and physical treatments to the zeolites is addressed. The results show that both zeolites are pozzolanically reactive, increasing the compressive strength of mortars and consuming calcium hydroxide, with the coarser zeolite showing less promising performance. A calcination pre-treatment at 800°C had little effect on the pozzolanic reactivity of the zeolites tested; however, a considerable reduction in flow resistance of the pastes containing the calcined zeolites occurred compared to the pastes containing uncalcined zeolites. Pre-treating the coarser zeolite in acid solutions improved reactivity through increased surface area and increased SiO$_2$/Al$_2$O$_3$ ratio. Milling the coarser zeolite improved pozzolanic reactivity by reducing particle size.

1. Introduction

Zeolites are aluminosiliceous materials that have unique microporous molecular structures. They naturally occur in deposits where volcanic ashes and rocks have reacted over time with alkaline groundwater [1]. Most low purity, naturally-occurring zeolites are underutilized industrially because they contain mixed forms of zeolites and are contaminated with other minerals such as clays, quartz, micas, glass, feldspar, cristobalite and biotite. These natural zeolites cost less than their pure analogs and may be beneficial as SCMs in concrete, but their behavior in cementitious mixtures is not well understood, limiting their use.
The goal of the research presented here was to examine the pozzolanicity of natural zeolites and to determine if physical and chemical pre-treatments to the zeolites could improve underperforming zeolites, thereby addressing some of the challenges in using these materials as SCMs. There is precedent to the use of pre-treatments on zeolites. For example, Habert et al. [2] used heat treatments on natural zeolites to dehydroxylize clay impurities present in the natural minerals and to destabilize the zeolite structures. Mertens et al. [3] examined the effects of composition, surface area, and cation content on the reactivity of natural zeolites in lime solutions. They noted that the SiO₂/Al₂O₃ ratio influences reactivity and that the surface area correlates with the initial reactivity (< 1 day). The results of these two studies indicate that the reactivity of naturally-occurring zeolites can be controlled through targeted pre-treatments.

The results presented here represent a subset of data gathered in our laboratory on several sources of zeolites as part of multiple research projects focused on zeolites and natural pozzolans [4-6], including impacts on fresh and hardened properties and pre-treatments to modify performance. Only two zeolites were chosen as case studies for this paper, in the interest of brevity.

2. Materials and Methods

Results from research on two natural, clinoptilolite zeolites from the USA are presented here. The zeolites are referred to as Zeolite-Z and Zeolite-T and come from different geographic regions of the United States. The impurities present in these zeolites are somewhat different; both zeolites contain some quartz and cristobalite, while only Zeolite-T contains montmorillonite clay and anorthite impurities [7]. However, the most notable difference between the materials is their particle size distribution as measured by laser diffraction, shown in Table 1 [7]. Interestingly, though the median particle size is quite different, the specific surface areas are similar. This is because much of the surface area in zeolites arises from internal porosity [6]. An ASTM C618 [8] Class F fly ash was used as a reference SCM to compare against the zeolites. All SCMs were used as a 20 wt.% replacement of an ASTM C150 [9] Type I portland cement (OPC).

Compressive strength testing of cement mortars was performed as a way to indirectly evaluate pozzolanic reactivity since pozzolans increase later age strength. ASTM C109 [10] was followed, but a fixed water-to-cementitious materials ratio (w/cm) was used rather than the variable w/cm specified in the standard. Pozzolanic reactivity of the zeolites was directly...
measured using the Chapelle test [11] and by measuring the calcium hydroxide contents of hydrated pastes (w/cm = 0.4) using thermogravimetric analysis [12]. Effect of zeolites on cement paste workability (w/cm = 0.45) was examined using an MCR 301 Anton Paar rotational rheometer [7].

Zeolites were first tested in their as-received state, without grinding or drying. Three different pre-treatments were used on Zeolite-T to manipulate its effects on the properties of cement pastes and mortars: milling using a rotational steel ball-mill at 85 rpm followed by drying at 105°C [10], calcination to 800°C [6,7,14], and acid treatment by soaking in solutions of varying concentrations of hydrochloric, nitric, and acetic acid, then thoroughly rinsing and drying [12]. Zeolite-Z was also treated using calcination to 800°C to manipulate its rheological performance [7]. Further details on testing and the pretreatment methods can be found in the cited works.

3. Results

The results presented in this paper represent those from parallel studies of the same materials. This gives rise to some difficulty in presenting the data because the samples used in the studies were made at different times with different mixture and testing parameters. Therefore, an effort is made here to present some of the data, but to focus on trends in observed results rather than direct numerical comparisons.

Results of compressive strength testing of cement mortars containing 20 wt.% replacement of cements with fly ash or zeolites are shown in Figure 1 [4,5]. The w/cm used was 0.55. Zeolite-Z performed very similarly to the Class F fly ash, whereas the Zeolite-T was detrimental to strength development. This discrepancy is likely due to the significant differences in particle size between the two zeolites, with the median particle size of Zeolite-Z and the fly ash being more similar to each other than to Zeolite-T.

Interestingly, the pozzolanic reactivity, as measured by the Chapelle test, was higher for both zeolites than for the fly ash (Table 2) [15]. This test measures reactivity in a super-saturated calcium hydroxide solution at a high temperature (80°C), and is considered to be a predictor of pozzolanic “potential” in a cementitious system; however, it does not evaluate pozzolanic rate [15]. The results suggest that Zeolite-T has more pozzolanic potential than revealed by compressive strength data. In order to improve the performance of Zeolite-T, several strategies were used: milling, calcination, and acid treatment.

3.1 Milling

Milling was conducted to determine if a reduction in particle size would be accompanied by a direct increase in mortar compressive strength. Milling for 8 hours reduced the median particle size of Zeolite-T to 7 μm, which is similar to the median size of Zeolite-Z. A negligible increase in surface area (from 59 to 66 m²/g) occurred from milling since the internal porosity was not altered significantly [13]. The compressive strength of mortar cubes made with a 20 wt.% replacement of milled Zeolite-T increased significantly, as shown in Table 3. (The mortars made with milled zeolite in Table 3 were from a different study than
the mortars shown in Figure 1 and had a w/cm of 0.51. Thus, the data in Table 3 are presented as a percentage of the OPC control mortars. The data in Table 3 for untreated zeolites were taken from Figure 1.) The relative difference between the zeolite mortars and OPC controls was similar for the milled Zeolite-T and Zeolite-Z. This demonstrates that particle size directly controls zeolite reactivity. Further, it is clear that all materials are pozzolanic since the strength relative to the control increased with time.

![Figure 1. Effect of zeolites on compressive strength of mortars (w/cm = 0.55)](image)

Table 2: Chapelle test results

<table>
<thead>
<tr>
<th>Material</th>
<th>Ca(OH)$_2$ fixed (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite-Z</td>
<td>925 ± 27</td>
</tr>
<tr>
<td>Zeolite-T</td>
<td>690 ± 28</td>
</tr>
<tr>
<td>Class F fly ash</td>
<td>476 ± 9</td>
</tr>
</tbody>
</table>

Table 3: Compressive strength of mortars containing untreated zeolites and treated Zeolite-T (% of OPC control)

<table>
<thead>
<tr>
<th>Material</th>
<th>3 day</th>
<th>7 day</th>
<th>28 day</th>
<th>90 day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated – Zeolite-Z</td>
<td>70%</td>
<td>93%</td>
<td>113%</td>
<td>115%</td>
</tr>
<tr>
<td>Untreated – Zeolite-T</td>
<td>68%</td>
<td>71%</td>
<td>73%</td>
<td>79%</td>
</tr>
<tr>
<td>Milled for 8h – Zeolite-T</td>
<td>88%</td>
<td>100%</td>
<td>125%</td>
<td>120%</td>
</tr>
<tr>
<td>Calcined at 800°C – Zeolite-T</td>
<td>63%</td>
<td>67%</td>
<td>73%</td>
<td>85%</td>
</tr>
</tbody>
</table>
3.2 Calcination
The effect of calcination on zeolite performance was also explored in order to see if a breakdown in clinoptilolite crystal structure rendered a zeolite more reactive. The data included here are for calcination at 800°C, though other temperatures were also studied [6,14]. After calcination, the median particle size increased slightly, by 9%, and the surface area decreased by 22%. Though calcination was shown to effectively amorphize the clinoptilolite mineral and clay impurities [6,7,14], the still high particle size limited improvements in compressive strength from this type of processing (Table 3). Nonetheless, it should be noted that strength was not decreased significantly by the calcined material compared to the untreated material.

Where calcination really impacts performance is with respect to workability [7]. Viscosity is a material’s resistance to flow, and higher viscosities are associated with increased flow resistance. The Bingham model is commonly used to estimate the plastic viscosity of cement-based materials [16,17], where the plastic viscosity is determined from the slope of the line in a shear-stress-shear rate plot (i.e., the flow curve). Additionally, the apparent viscosity at a particular shear rate can be used as a measure of viscosity under the following conditions: when non-linear behavior is not observed in the flow curve (since this is a requirement of the Bingham model) or when one is interested in examining a material’s flow behavior at a particular shear rate [18]. As shown in Figure 2, both Zeolite-Z and Zeolite-T pastes had high viscosities. After calcination, the viscosity of the Zeolite-T paste became almost identical to the control, and even the calcined Zeolite-Z paste viscosity was reduced. The reduction in viscosity with calcination is likely due to increased particle size and reduced surface area, reducing water demand.

Figure 2: Effect of zeolite calcination pretreatment on the rheological response of the cement pastes (w/c=0.4).
3.3 Acid Treatment
Soaking zeolites in acid solutions has the potential to increase the SiO₂/Al₂O₃ ratio, reduce crystallinity, remove impurities, and increase in specific surface area [12]. In this study, the crystal structure and impurities in Zeolite-T did not change appreciably with acid treatment. However, approximately a 40% decrease in aluminum content in acid treated samples occurred, while the aluminum content in water-soaked samples decreased by only 8% (data not shown) [12]. BET specific surface area values were increased up to 50%.

In the acid treatment study, pozzolanic reactivity was evaluated through the measurement of calcium hydroxide content in hydrated pastes containing 20 wt.% replacement of cement with zeolite (w/cm=0.4). An example of the effect of acid treatment on calcium hydroxide content of hydrated pastes is shown in Figure 3. While the untreated zeolite was clearly pozzolanic, since the calcium hydroxide content is lower than in the control paste, the acid-treated zeolites were even more pozzolanic. Interestingly, the low concentration acid solutions are just as effective as the high concentration one. These results suggest that the dealumination and increase in specific surface area from acid treatment can improve the reactivity of these materials [12].

![Figure 3: Calcium hydroxide content of hydrated pastes containing acid-treated Zeolite-T](image)

4. Conclusions
Natural zeolites are pozzolanic materials that increase compressive strength of mortars and consume calcium hydroxide in solutions and in cement pastes. However, the properties of these materials are variable, depending on the source and properties of the material such as particle size, specific surface area, and SiO₂/Al₂O₃ ratio. It is promising that these properties
can be easily manipulated through chemical and physical treatments such as milling, calcination, and soaking in acid solutions to address issues with flow resistance, pozzolanicity, and strength development. Pretreatments give us a toolbox that will facilitate the use of natural zeolites as SCMs.

Acknowledgements

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References

EFFECTS OF W/P RATIO AND LIMESTONE FILLER ON PERMEABILITY OF CEMENT PASTES

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Abstract
Because of environmental and economic benefits, a fraction of cement is increasingly replaced by limestone fillers raising a question on to what extent limestone fillers affect the durability of cementitious materials. This work aims at understanding the effects of water/powder (w/p) ratio and limestone filler replacement on water permeability of cement pastes. A newly proposed technique using a controlled constant flow concept was applied to measure permeability of hardened cement paste samples following a factorial experimental design. It was observed that both limestone filler and w/p ratio significantly influence the water permeability. At a given w/p ratio, adding limestone filler made the microstructure coarser, especially for high w/p ratio. Nevertheless, if the comparison is based on a given water/cement (w/c) ratio instead of w/p ratio, the limestone filler replacement refined the microstructure in terms of capillary porosity and pore size distribution, resulting in permeability decreases of cement pastes. Furthermore, a modified Carmen-Kozeny relation was established which enables prediction of the permeability from capillary porosity and the critical pore diameter.

1. Introduction

Durability and performance of concrete are affected by a number of chemical degradation phenomena such as carbonation [1], calcium leaching [2], sulphate attack, chloride attack, and corrosion of the reinforcement bars [3]. Diffusivity and permeability of concrete determine how fast aggressive substances penetrate into concrete, thereby influencing almost all mentioned degradation mechanisms. Therefore, these are fundamental parameters for characterizing long-term performance of concrete rather than the standard compressive/tensile strengths.

There are many factors influencing the permeability of cement-based materials. Several factors are classified as extrinsic related to experimental conditions such as applied pressure,
size of sample [4] and confining pressure [5]. Variation of these factors can cause a change of several orders of magnitude in permeability. Beside extrinsic factors influencing the permeability include porosity, pore size distribution, tortuosity, specific surface and micro cracks. These parameters are basically controlled by the water to cement ratio, particle size distribution (cement + aggregate), age of sample and type of constituent materials. Concrete with larger pore size has higher permeability than concrete with smaller pore size despite the same total porosity. This effect is normally reflected through the critical pore size. It is obvious that pore connectivity is one of the most critical factors influencing the permeability. Pores which are blocked cannot transport any fluid. The type of constituent materials mainly affects permeability through hydration degree, especially at early ages. As shown in many studies [6-10], the permeability increases with increasing w/c ratio because of a higher porosity at higher w/c ratio. However, to the knowledge of the authors, no direct connection between water to cement ratio and permeability has been proposed. A direct relation between porosity and permeability has been introduced by some researchers [11-15]. Nevertheless, porosity alone should not be a unique factor influencing the permeability, i.e. samples with the same porosity may have different permeability. Few researchers have studied the effects of limestone filler replacement on permeability, but many questions still remain, though replacing part of cement by limestone fillers is getting more attention in recent years because of its environmental and economic benefits. Most studies [16-18] agree that there is no significant change in transport properties as long as limestone filler replacement is less than 10%. On the contrary, other studies [19, 20] found that oxygen permeability decreases with increasing limestone filler replacement. Some authors also state that concrete with limestone filler replacement increases the carbonation rate compared to concrete with the same water/powder (w/p) ratio [19, 21, 22].

In the present study, the newly developed method to measure permeability of saturated materials [23, 24] was applied to investigate the effects of limestone filler replacement and w/p ratio on permeability of cement pastes. The effects of microstructural properties on permeability were deeply studied. Furthermore, a modified Carmen-Kozeny relation was established which enables predicting the permeability from capillary porosity and the critical pore diameter.

2. Experiments

2.1 Materials

Experiments were performed on cement pastes made from cement, tap water and limestone filler. Type I ordinary Portland cement (CEM I 52.5 N) was used. The cement has quite high Blaine specific surface of 4350 cm$^2$/g. Limestone filler (Calcitec 2001S) used has a Blaine specific surface of 3500 cm$^2$/g and a CaCO$_3$ content of 98.30%. Superplasticizer Glenium 27 was added to the mix with content of 0.5% with respect to mass of cement.

2.2. Factorial experimental program

In order to investigate the effects of w/p ratio and the cement replacement by limestone filler (ls/p) on water permeability, diffusion of dissolved gas, carbonation and Ca-leaching, a factorial experimental design (Table 1) has been proposed. In cement industry, Portland
limestone cements have been produced by inter-grinding clinker and limestone (and gypsum) in which different limestone/(limestone + clinker) ratios are initially chosen. Therefore, the “water/cementitious material” ratio for Portland limestone cement is actually the “water/powder” ratio. To keep consistence, w/p ratio and limestone filler replacement were chosen in this study instead of w/c ratio and limestone filler replacement. However, the dilution effect due to limestone filler addition can be easily investigated by converting w/p ratio to w/c ratio.

Table 1: Detail of factorial experiment design: LS = limestone filler; SP = superplasticizer

<table>
<thead>
<tr>
<th>Run</th>
<th>Cement</th>
<th>LS</th>
<th>Powder</th>
<th>Water</th>
<th>w/c</th>
<th>w/p</th>
<th>ls/p</th>
<th>SP</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>450</td>
<td>0</td>
<td>450</td>
<td>146</td>
<td>0.325</td>
<td>0.325</td>
<td>0.325</td>
<td>0</td>
<td>2.3</td>
</tr>
<tr>
<td>2</td>
<td>360</td>
<td>90</td>
<td>450</td>
<td>191</td>
<td>0.531</td>
<td>0.425</td>
<td>0.425</td>
<td>20</td>
<td>1.8</td>
</tr>
<tr>
<td>3</td>
<td>450</td>
<td>0</td>
<td>450</td>
<td>191</td>
<td>0.425</td>
<td>0.425</td>
<td>0.425</td>
<td>0</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>405</td>
<td>45</td>
<td>450</td>
<td>169</td>
<td>0.417</td>
<td>0.375</td>
<td>0.375</td>
<td>10</td>
<td>2.0</td>
</tr>
<tr>
<td>5</td>
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<td>90</td>
<td>450</td>
<td>146</td>
<td>0.406</td>
<td>0.325</td>
<td>0.325</td>
<td>20</td>
<td>1.8</td>
</tr>
</tbody>
</table>

2.3. Determination of water permeability using a controlled constant flow method

Cement paste was poured in a cylindrical PVC tube with inner diameter of 97.5 mm. The sample was cured in a sealed condition in a temperature controlled room (22 ± 2°C) for 27 days. The 28-day-cured cement paste was sawn into 25 mm thin slices embedded into the polycarbonate part of the permeability cells. The samples were afterwards saturated in lime water. The saturated samples were then connected to permeability setup (Fig. 1) to determine the saturated permeability using a controlled constant flow method as described in [24].

![Fig. 1: Schematic test setup for permeability determination](image-url)
3. Results and discussion

3.1. Factorial experimental results

The determined permeability coefficients of cement pastes with w/p ratios ranging from 0.325 to 0.425 and limestone filler replacement ranging from 0 to 20% (see Table 1 for the detail of mix design) are represented by cube and interpolated surface (using Akima’s polynomial method [25]) plots in Fig. 2. It can be seen in the surface plot that, to improve the impermeability, one should choose a mix design with a low w/p ratio and low limestone filler replacement. In order to clearly visualize the effects of w/p ratio and limestone filler replacement on permeability, the main effects and interaction plots were built using statistical software Minitab [26]. The main effects plot (Fig. 3a) shows that the permeability strongly decreases with decreasing w/p ratio and limestone filler replacement. There does not seem to be a large difference in the magnitude of the effects of w/p ratio and limestone filler replacement as its quite similar slopes (referred to the changes of the response when factorial values vary from low to high levels). The regression equation (first-order) of logarithm of permeability coefficient is obtained as follows:

\[
\log_{10}(k) = -17.65 + 12.47 \text{ls/p} + 11.74 \text{w/p} - 21.15 \text{ls/p} \times \text{w/p}
\]  

where \( k \) is the permeability coefficient [m/s]; \( \text{ls/p} \) is the ratio of limestone filler over powder (cement + limestone filler); \( \text{w/p} \) is the ratio of water over powder. The correlation coefficient \( (r^2) \) is 0.9965 indicating that the predicted model fits the experimental data well.

The interaction plot (Fig. 3a) enables us to visualize the interaction effect (i.e. the combined effects of factors on the dependent measure. When an interaction effect is present, the impact of one factor depends on the level of the other factor) of w/p ratio and limestone filler replacement on the permeability. As the connected lines of factor levels are not parallel to each other, there might be interaction. However, the interaction is not significant because the extent of departure is small. The interaction is getting stronger with the increase of w/p ratio and limestone filler replacement.
3.2. Pore structure and its effect on water permeability

The porosity and pore size distribution are shown in Fig. 4. At a given w/p ratio, adding limestone filler made the microstructure coarser, especially for high w/p ratio (i.e. sample S2 vs. sample S3). However, at a given w/c ratio, the limestone filler replacement refined the microstructure of the cement pastes. As evidenced in Table 2, sample S3 had higher porosity and bigger average pore diameter compared to sample S4 (10% limestone filler replacement) despite its quite similar w/c ratio (0.425 and 0.416). In most cases, the samples with larger porosity and coarser pore size distribution resulted in higher water permeability. However, sample S5 did not follow the general trend as it showed higher water permeability despite smaller porosity and finer pore size distribution compared to sample S4 (see Fig. 4). This phenomenon might be a consequence of different air void content or macro pores in two samples. Unfortunately MIP experiment does not generally enable to detect air voids because air voids are only intruded after threshold pressure is reached, and thus counted for smaller pores. Furthermore, big pores may be intruded by mercury before increasing pressure, and are thereby not counted in total porosity.

Table 2: Summary of MIP results of reference samples

<table>
<thead>
<tr>
<th>Parameters</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/p</td>
<td>0.325</td>
<td>0.425</td>
<td>0.425</td>
<td>0.375</td>
<td>0.325</td>
</tr>
<tr>
<td>l/s/p</td>
<td>0</td>
<td>0.2</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Permeability coefficient, m/s</td>
<td>10^{-13.8}</td>
<td>10^{-11.9}</td>
<td>10^{-12.6}</td>
<td>10^{-12.9}</td>
<td>10^{-12.7}</td>
</tr>
<tr>
<td>Accessible porosity, %</td>
<td>10.40</td>
<td>23.65</td>
<td>16.48</td>
<td>13.73</td>
<td>12.92</td>
</tr>
<tr>
<td>Average pore diameter (4V/A), nm</td>
<td>22.67</td>
<td>29.87</td>
<td>26.09</td>
<td>24.24</td>
<td>25.40</td>
</tr>
<tr>
<td>Critical pore diameter, nm</td>
<td>25.74</td>
<td>49.87</td>
<td>32.00</td>
<td>36.41</td>
<td>29.03</td>
</tr>
<tr>
<td>Specific surface, m^2/g</td>
<td>7.77</td>
<td>14.90</td>
<td>10.58</td>
<td>9.44</td>
<td>7.56</td>
</tr>
</tbody>
</table>

Fig. 5 compares the measured permeability with literature values. Note that only results of the mixtures without limestone filler (S1 and S3) in the factorial experimental program and results in a separate study [24] using the proposed method are shown in Fig. 5. In general, the results obtained with the tested experimental setup are consistent with published data, especially with the data of [27] based on a traditional method in which a constant hydrostatic
pressure of about 3 bar is applied to truncated conical samples until a steady state flow is
obtained (approximately 4 weeks). The favourable agreement gives confidence in the validity
of the developed method. Permeability coefficients obtained from this study are lower than
the results of Ye [28] and Goto et al. [7] by one order of magnitude, and higher than the
results obtained from beam bending [9] and dynamic pressurization [29] methods although
the values from beam bending and dynamic pressurization methods were obtained at earlier
curing ages (21 and 14 days, respectively). The differences are attributed to variations in
blending of the samples, curing conditions and the fineness of the cement used and especially
to differences in the calculation of permeability values between direct and indirect methods.
The way to pour and blend cement paste significantly influences the permeability, especially
at high w/c ratios in which the cement pastes tend to develop vertical channels [27] if there is
no sufficient solution to prevent bleeding. In this study, the bleeding potential was reduced
thanks to short height and wide diameter of the mould besides good vibration during casting.

![Figure 4: Porosity versus pore diameter determined by MIP (a) and differential pore size
distribution determined by MIP (b)](image)

![Figure 5: Permeability of cement pastes at different w/c ratios and comparison of the current
test results versus literature data: (*) measured at 21 days of curing, (**) measured at 14 days
of curing, for the rest at 28 days of curing)](image)
The studied samples were cured in saturated lime water before testing while Ye only cured samples in sealed condition [28]. The degree of hydration of the lime water saturated curing samples is much higher than sealed curing samples; as such, there are more empty pores in the sample under sealed curing conditions [28, 30]. Additionally, the specific surface area (4350 cm$^2$/g) of the Portland cement type I used in this study is higher than the ones used in the studies of Ye and Goto et al [7] while lower than the Portland cement type III (ASTM) used in the studies of Vichit-Vadakan et al. [9] and Grasley et al. [29]. It is believed that the degree of hydration is accelerated if the sample is cured in saturated lime solution and/or when the fineness of the cement is higher. Therefore, the porosity significantly reduces [31] and as a consequence the permeability decreases. The work of Banthia et al. [32] also showed a lower permeability of cement type III paste compared to cement type I paste. The interactions between water and cement matrix could be reduced in this proposed method because the continuous hydration of mature cement paste was limited because of the relatively short measurement time in the proposed method. Furthermore, the measurement was conducted on lime water saturated samples in a closed system which could decrease the dissolution of Ca(OH)$_2$ and the carbonation of dissolved Ca(OH)$_2$ – one of the main mechanisms of self-healing property of cement-based materials [33].

3.3. Discussion on the effect of limestone filler and w/p ratio on permeability

In general, the total capillary porosity of cement paste is expected to decrease when its w/p (or w/c) ratio is lower [7, 34-36]. In this study, this trend is confirmed again by increasing 58% and 83% the MIP porosity when w/p ratio increases from 0.325 to 0.425 for sample with and without 20% limestone filler replacement, respectively. The decrease in capillary porosity (which is composed mainly of large and connected pores) leads to a limitation or a decrease of pathways in hardened cement paste resulting in a reduced permeability.

Literature on the effects of limestone filler addition on transport properties of cement-based materials is quite scattered. Most studies [16-18] agree that there is no significant change in transport properties as long as limestone filler replacement is less than 10%. Tsivilis et al. [18] measured the gas and water permeability of concretes with different limestone filler replacements (up to 35%). The gas permeability increases with the increase of limestone filler replacement while the water permeability exhibits an opposite behaviour. However, the change in permeability is not that significant (less than 30%) which might not be different enough to overwhelm the error on permeability measurement. The high w/c ratios (0.62 and 0.7) may result in a minor effect on the permeability characteristics as stated by the authors. On the contrary, Matthews [19] found that oxygen permeability decreases with increasing limestone filler replacement (up to 25%). In this case, the w/c ratio is 0.6 which is a bit lower than one of Tsivilis’ study. Moir et al. [20] also found that the presence of limestone slightly reduces the oxygen permeability concretes made with 5 or 25 % limestone filler replacement. Ramezanianpour et al. [16] measured the water penetration depths of concrete mixtures made with 0, 5%, 10%, 15% and 20% limestone filler replacements. The authors found that the minimum water penetration depth is obtained for the mixture with 10% limestone filler replacement. Adding 20% limestone filler replacement results in the worst water permeability regardless curing ages.

Generally, the reduction of transport properties is attributed to the nucleation effect of fine particles of CaCO$_3$ which refines the pore structure of pastes. The connectivity of the pore structure is reduced. On the other hand, the increase in transport properties normally relies on
the hypothesis that fluid transports faster in the interfacial transition zone between bulk cement paste and limestone particles. Furthermore, water demand (for the same hydration degree) is lower for limestone-cement paste if limestone filler is considered as inert filler. Thus, with the same w/p ratio, more water in limestone-cement paste results in more pores after hydration and setting. In order to know which effects are dominant, knowledge of the quality of limestone filler and cement, which is characterized by particle size distribution, and compositions of both cement and limestone filler is needed. The method to incorporate cement/clinker with limestone (blending or inter-grinding) may affect the properties of limestone-cement-based materials as it might produce somehow different particle size distributions. In this study, limestone filler was added to plain cement by blending. The particle size distribution of the limestone filler was coarser than the one of the cement. For these reasons, it might support the finding that with the same w/c ratio, limestone filler replacement increases the porosity resulted in water permeability increase in this study.

3.4 Correlation between pore structure parameters and water permeability

This section aims at finding how water permeability is correlated to key pore structure parameters as determined by MIP. The main parameter influencing permeability is accessible porosity. However, porosity itself is not well correlated with the water permeability as shown in Fig. 6a. Another factor significantly affecting the water permeability is the pore size distribution which is characterized by several parameters including critical, threshold (the largest pore size at which pore volume is significantly increased) and average pore diameters. Furthermore, water permeability also depends on tortuosity which accounts for the tortuous and reduced transport pathway. However, it is impossible to measure tortuosity directly. The authors of this work tried to relate the water permeability with 2 measureable parameters: accessible porosity and critical pore diameter (from MIP experiments) by modifying the Carman-Kozeny relation [37] as follows:

\[ k_w = \frac{\phi}{(1 - \phi)^2} \]

Fig. 6: Correlation of intrinsic water permeability and accessible porosity (a) and \(d^2 \phi^{2.5} / (1 - \phi)\) (b)
By plotting the intrinsic water permeability (converted from hydraulic conductivity) versus $d_n^2 \frac{\theta^{2.5}}{(1-\theta)}$, we found a good correlation with correlation coefficient of 0.99 as shown in Fig. 6. The slope yields value of $\zeta = 0.0017$ [\text{\textsuperscript{-}}]. The relationship gives an estimation of permeability if the key parameters (determined by MIP) are known.

4. Conclusions

In this study, the effects of limestone filler replacement and w/p (w/c) ratio on microstructure, and water permeability were investigated. The permeability results obtained from the newly developed method were comparable with results from studies reported in literature even though there were some variations due to differences in sample preparation and cement type. It was observed that both limestone filler and w/p ratio had significant influences on water permeability. Permeability was increased with the increase of w/p ratio and limestone filler replacement. However, there was no interaction effect between w/p ratio and limestone filler replacement in the testing range (w/p = 0.325; 0.375; 0.425 and ls/p = 0; 0.1; 0.2). At a given w/p ratio, adding limestone filler made the capillary pore coarser, especially for high w/p ratio. Nevertheless, if the comparison is based on a given w/c ratio instead of w/p ratio, the limestone filler replacement refined the microstructure resulting in permeability decreases of cement pastes.

The water permeability was highly correlated to key pore structure parameters obtained from MIP experiments: accessible porosity and critical pore diameter. A good correlation between intrinsic water permeability and $d_n^2 \frac{\theta^{2.5}}{(1-\theta)}$ was found. However, more experimental data are needed to validate this relation.

Acknowledgements

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References

PREDICTIONS OF THE MECHANICAL PERFORMANCE OF CONCRETE MADE WITH TERNARY CEMENTS

Kim-Séang Lauch (1), Vinciane Dieryck (1), Benoit Parmentier (1)

(1) Belgian Building Research Institute, Limelette, Belgium

Abstract

To assess the suitability for use of composite cements for concrete, the mechanical performance of concrete made with ternary cements containing Portland cement (OPC), blast furnace slag (S) or fly ash (FA) and limestone filler (L) has been compared to predictive models from Eurocode 2. Eight blended cements of different proportions of OPC (from 45% to 65%), S and FA (from 10% to 30%) and L (from 5% to 35%) were selected alongside five reference cements (CEM I 52.5 R HES, CEM II/B-M (L-S) 32.5 R, CEM II/B-M (LL-S-V) 32.5 N, CEM II/B-V 32.5 R and CEM III/A 42.5 N LA). Two types of mixes were produced using constant water to cement (w/c) ratios of 0.45 and 0.55 and cement contents of 340 kg/m³ and 300 kg/m³ respectively. The results indicate that setting time and mechanical properties (compressive and indirect tensile strengths, modulus of elasticity as well as total shrinkage and creep) are mainly proportional to the clinker content and inversely proportional to the limestone filler content. Ternary cements containing slag seem overall to give a better concrete mechanical performance than those containing fly ash. The results show that the predictive models may not be suitable for most tested cements.

1. Introduction

As the production of Portland cement is responsible for significant amount of CO₂ emissions, replacing the clinker with by-products such as blast furnace slag (S) and fly ash (FA) is a compelling solution to reduce the environmental impact of concrete. The production of these supplementary cementitious materials (SCMs) tends to decrease in Belgium, while limestone filler (L) is abundantly available. Several studies investigated the synergetic action of these SCMs [1–5]. It has been found that a small dosage of limestone filler could have a beneficial effect on the early age properties of concrete, while fly ash and blast furnace slag contribute to the long-term mechanical properties as pozzolanic reaction rate is slower than hydration of Portland cement. These antagonist properties of limestone filler and fly ash or slag make these
ternary mixes particularly interesting. The European standard EN 197-1 [6] includes requirements for cements for use in concrete. The aim of this study is to evaluate the performance of concrete made with newly developed ternary cements OPC-S-L and OPC-FA-L to assess their suitability for use for concrete. This approach is inspired by the methodology from Belgian standard NBN B 15-100 [18]. This paper focuses on the comparison of the mechanical performance of concrete made with ternary cements with the predictive models from Eurocode 2 (EC2) [19]. Fresh properties and setting time, compressive and indirect tensile strengths, modulus of elasticity, shrinkage and creep tests were carried out. Durability study is the subject of a companion paper by the same authors [7].

2. Experimental program

2.1 Materials

Composite cements were prepared by mixing CEM I 52.5 R HES (OPC), ground granulated blast-furnace slag (S), fly ash (FA) and limestone filler (L). As a set regulator, gypsum had been added with a concentration to obtain a total sulfate content of 3%. Chemical and mineralogical characterization showed that the studied SCMs meet all the requirements from standard EN 197-1, regarding the properties of the cement constituents [7]. Then the physical, chemical and mechanical properties of the ternary cements, with different proportions of Portland cement, blast-furnace slag or fly ash and limestone were determined. Two series, presented in Tab. 1, had been conducted. In series 1, ternary blended cements with slag (OPC-S-L) were studied, with reference cements CEM I 52.5 R HES, CEM II/B-M (L-S) 32.5 R and CEM III/A 42.5 N LA. In series 2, ternary cements with fly ash (OPC-FA-L) were investigated with reference cements CEM I 52.5 R HES, CEM II/B-M (L-L-S-V) 32.5 N and CEM II/B-V 32.5 R. All the ternary cements, except CEM 3 [40OPC 30FA 25L], meet the requirements from the standard EN 197-1, regarding the compressive strength, initial setting time and soundness. The results show that ternary OPC-S-L cements reach higher compressive strength classes than OPC-FA-L cements.

2.2 Concrete mixes

Two types of concrete have been chosen, named T(0.45) and T(0.55) with w/c ratios of 0.45 and 0.55 respectively. The desired slump and the aimed compressive strength class are 120 ± 30 mm, C35/45 and 180 ± 30 mm, C25/30 respectively for the two types. The concrete mixes have been formulated so that the grading curve follows the limits specified in the standard EN 480-1 [8] (see Fig. 1), as specified by standard NBN B 15-100. There exists a slight difference between the two series: series 2 contains more fines below 0.5 mm. A polycarboxylic-ether superplasticiser has been used. The concrete mixes are more thoroughly described in the companion paper [7]. The concrete samples are conserved during 24h at a temperature of 20 ± 2°C. After removal, the specimens are placed in water at the same temperature for curing during a variable period depending on the test.

2.3 Testing methods

Fresh properties tests consisted in measuring the slump, density and air content according to standards EN 12350-2 [9], EN 12350-6 [10] and EN 12350-7 [11] respectively. Setting time was carried out on concrete according to the Kelly-Bryant method described in a Belgian standard NBN B 15-204 [12]. This pull-out test was carried out on two moulds of 15 cm x 15 cm x 60 cm size, equipped with 10 steel rods of 10 mm diameter and 220 mm length. About 4 hours after casting, the rods were pulled out one after another at regular intervals and the pull-out forces or bonding strengths are recorded.
<table>
<thead>
<tr>
<th>Series 1 (OPC-S-L)</th>
<th>OPC (%)</th>
<th>S (%)</th>
<th>FA (%)</th>
<th>L (%)</th>
<th>Blaine surface (cm²/kg)</th>
<th>Strength class (mortar)</th>
<th>Superplasticiser PCE (%)</th>
<th>Slump (mm)</th>
<th>Density (kg/m³)</th>
<th>Air content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 52.5 R HES (batch 1)</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4780</td>
<td>52.5 R</td>
<td>0.80</td>
<td>0.25</td>
<td>140</td>
<td>175</td>
</tr>
<tr>
<td>CEM II/B-M (L-S) 32.5 R</td>
<td>74</td>
<td>12</td>
<td>0</td>
<td>14</td>
<td>3737</td>
<td>32.5 R</td>
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<td>0.20</td>
<td>125</td>
<td>180</td>
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<td>59</td>
<td>41</td>
<td>0</td>
<td>0</td>
<td>4591</td>
<td>42.5 N</td>
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<td>0.20</td>
<td>120</td>
<td>190</td>
</tr>
<tr>
<td>CEM 1 [65OPC 30S 5L]</td>
<td>65</td>
<td>30</td>
<td>5</td>
<td>5</td>
<td>4770</td>
<td>52.5 N</td>
<td>0.40</td>
<td>0.25</td>
<td>118</td>
<td>185</td>
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<tr>
<td>CEM 3 [45OPC 30S 25L]</td>
<td>45</td>
<td>30</td>
<td>25</td>
<td>4630</td>
<td>42.5 N</td>
<td>0.25</td>
<td>0.20</td>
<td>108</td>
<td>180</td>
<td>2394</td>
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<td>CEM 6 [500PC 20S 30L]</td>
<td>50</td>
<td>20</td>
<td>30</td>
<td>4430</td>
<td>42.5 N</td>
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<td>0.20</td>
<td>130</td>
<td>180</td>
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<tr>
<td>CEM 10 [55OPC 10S 35L]</td>
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<td>10</td>
<td>35</td>
<td>4260</td>
<td>42.5 R</td>
<td>0.30</td>
<td>0.20</td>
<td>113</td>
<td>185</td>
<td>2384</td>
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<table>
<thead>
<tr>
<th>Series 2 (OPC-FA-L)</th>
<th>OPC (%)</th>
<th>S (%)</th>
<th>FA (%)</th>
<th>L (%)</th>
<th>Blaine surface (cm²/kg)</th>
<th>Strength class (mortar)</th>
<th>Superplasticiser PCE (%)</th>
<th>Slump (mm)</th>
<th>Density (kg/m³)</th>
<th>Air content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 52.5 R HES (batch 2)</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4930</td>
<td>52.5 R</td>
<td>2.00</td>
<td>1.30</td>
<td>160</td>
<td>170</td>
</tr>
<tr>
<td>CEM II/B-M (LL-S-V) 32.5 N</td>
<td>71</td>
<td>7</td>
<td>9</td>
<td>13</td>
<td>3360</td>
<td>32.5 N</td>
<td>1.00</td>
<td>0.60</td>
<td>90</td>
<td>160</td>
</tr>
<tr>
<td>CEM II/B-V 32.5 R</td>
<td>78</td>
<td>0</td>
<td>22</td>
<td>0</td>
<td>2960</td>
<td>32.5 R</td>
<td>0.85</td>
<td>0.60</td>
<td>95</td>
<td>165</td>
</tr>
<tr>
<td>CEM 1 [65OPC 30FA 5L]</td>
<td>65</td>
<td>-</td>
<td>30</td>
<td>5</td>
<td>4110</td>
<td>52.5 N</td>
<td>1.20</td>
<td>0.80</td>
<td>133</td>
<td>190</td>
</tr>
<tr>
<td>CEM 3 [45OPC 30FA 25L]</td>
<td>45</td>
<td>-</td>
<td>30</td>
<td>25</td>
<td>4120</td>
<td>-</td>
<td>0.70</td>
<td>0.60</td>
<td>135</td>
<td>160</td>
</tr>
<tr>
<td>CEM 6 [500PC 20FA 30L]</td>
<td>50</td>
<td>-</td>
<td>20</td>
<td>30</td>
<td>4230</td>
<td>32.5 R</td>
<td>0.70</td>
<td>0.60</td>
<td>100</td>
<td>190</td>
</tr>
<tr>
<td>CEM 10 [55OPC 10FA 35L]</td>
<td>55</td>
<td>-</td>
<td>10</td>
<td>35</td>
<td>4440</td>
<td>32.5 R</td>
<td>1.00</td>
<td>0.70</td>
<td>110</td>
<td>190</td>
</tr>
</tbody>
</table>

(*) Not measured.
Compressive strength was measured at 2, 7, 28 and 91 days, according to EN 12390-3 [13], on three cubes of 15 cm side. Indirect tensile strength was measured at 28 days according to EN 12390-6 [14], by splitting six core samples of 113 mm diameter and 113 mm length. The (static compression) modulus of elasticity, total shrinkage and creep were measured according to Belgian standards NBN B 15-203 [15], NBN B 15-216 [16] and NBN B 15-228 [17] respectively. Each test used three prisms of 10 cm x 10 cm x 40 cm side. The samples were cured for 7 days under water at 20°C and then conditioned in a climatic chamber at 20°C and 60% relative humidity for 21 days. The shrinkage deformations $\varepsilon_{\text{shrinkage}}$ are measured from day 7 to day 91, and to the age of 7 months for the compositions where creep is also measured. The modulus of elasticity was measured at 28 days ($E_{cm,28}$) with a load applied at a third of the concrete compressive strength. The same load is applied to creep samples since day 28 for 6 months. The creep deformations $\varepsilon_{\text{creep}}$ and the creep coefficient $\varphi$ were then calculated by the following equations:

$$
\varepsilon_{\text{creep}} = \varepsilon_{\text{total}} - \varepsilon_{\text{shrinkage}} - \varepsilon_{\text{initial}} \quad (1)
$$

$$
\varphi(t) = \frac{\varepsilon_{\text{creep}}}{\varepsilon_{\text{initial}}} \quad (2)
$$

$$
\varepsilon_{\text{initial}} = \frac{F_I}{E_{cm,28}} \quad (3)
$$

Where $F_I$ is the initial applied force and $S$ the surface where the force is applied (100 mm x 100 mm in this case).

2.4 Evaluation approach

The evaluation approach of the performance of concrete is inspired by the methodology from Belgian standard NBN B 15-100 [18]. For the mechanical properties, upper and lower boundaries from predictive models from Eurocode 2 (EC2) [19] are specified in which the results should lie. The values in bold in the tables 2 and 3 are outside the limits. The influence of the composition on the concrete properties was analysed by correlation coefficients ($R$).
3. Results and discussion

3.1 Fresh properties
The dosages of superplasticiser (PCE) and the results of slumps, density and air content are presented in Tab. 1. In series 1, the dosage for the ternary cements OPC-S-L ranges from 0.2 – 0.4%, while in series 2, it ranges from 0.6 – 1.2% (by mass of cement). This difference could be explained by the difference in the grading curves of the concretes (see Fig. 1). Concretes from series 2 contain more fines, which could require a higher dosage of admixture. The air content is higher for a lower density and a higher dosage of PCE. In their compatibility study between polycarboxylate-based admixtures and blended-cement pastes, Alonso et al. [20] found that slag adsorbs less admixture and requires less PCE than fly ash to establish inter-particle repulsion. This could explain the better efficiency of PCE with slag (less dosage needed). The dosages of admixture are not excessive for concretes made with ternary cements. They stay in the recommended range from the manufacturer.

3.2 Setting time
The bonding strengths (single values) over time of series 1 and series 2 concretes are presented in Fig. 2 and Fig. 3. This method is also explained and compared to non-destructive (ultrasonic and electric) methods in the following papers [23, 24]. All ternary cements concretes, except CEM 3 [45OPC 30S 25L] show an evolution of the setting between the evolutions obtained by the reference concretes. In series 1, the evolution of setting of concretes made with OPC-S-L cements seems to be proportional to the limestone filler content, as CEM 1 [65OPC 30S 5L] concrete, with 5% of limestone filler, hardens quicker than CEM 10 [55OPC 10S 35L] concrete, with 35% of limestone filler. In series 2, it seems that the clinker content has more influence.

3.3 Compressive strength
The 28 days compressive strengths for series 1 and 2 concretes are presented in Tab. 2. The average compression strength \( f_{cm,cube} \) was measured on three cubes of 15 cm side. The characteristic strength \( f_{ck,cyl} \) is calculated from the following equation Eq. (4), according to the evaluation approach. This value is then compared to the aimed compressive strength (35 MPa for T(0.45) and 25 MPa for T(0.55) concretes).

\[
f_{ck,cyl} = \frac{f_{cm,cube}}{1.2} - 8 \tag{4}
\]

In series 1, CEM 1 and CEM 3 concretes reach the aimed values. In series 2, only CEM 1 concretes reach the aimed compressive strength classes. The difference between the two series for concretes with the same reference cement CEM I 52.5 R HES could be due to the difference in the grading curve. The results show that the compressive strength decreases with decreasing clinker content (correlation coefficient \( R = 0.9 \) in average) and increasing limestone filler content (\( R = -0.8 \)). This could be explained by the dilution effect [2–5]. In series 1, CEM 10 [50OPC 10S 35L] concrete has the highest limestone filler content and presents the lowest strength. Concretes made with OPC-S-L cements present similar compressive strengths as the ones with reference concretes. In series 2, CEM 3 [45OPC 30FA 25L] concrete has the lowest clinker content and presents the lowest strength. Except for CEM 1 concrete, OPC-FA-L concretes present lower compressive strength than the reference concretes.
Table 2: 28 day compressive and indirect tensile strengths, modulus of elasticity and total shrinkage at 91 days for concretes of series 1 (OPC-S-L) and series 2 (OPC-FA-L). In bold: values that do not satisfy the criteria of the evaluation approach.

<table>
<thead>
<tr>
<th></th>
<th>Compressive strength (MPa)</th>
<th>Indirect tensile strength (MPa)</th>
<th>Modulus of elasticity (MPa)</th>
<th>Total shrinkage 91 days (µm/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_{cm,\text{cube}}$</td>
<td>$f_{ck,\text{cyl}}$</td>
<td>$f_{ck,\text{cyl}}$</td>
<td>$f_{ck,\text{cyl}}$</td>
</tr>
<tr>
<td>Series 1 (OPC-S-L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEM I 52.5 R HES (batch 1)</td>
<td>72.6</td>
<td>57.0</td>
<td>52.5</td>
<td>39.5</td>
</tr>
<tr>
<td>CEM II/B-M (L-S) 32.5 R</td>
<td>45.7</td>
<td>37.2</td>
<td>30.0</td>
<td>23.0</td>
</tr>
<tr>
<td>CEM III/A 42.5 N LA</td>
<td>69.4</td>
<td>54.1</td>
<td>49.8</td>
<td>37.1</td>
</tr>
<tr>
<td>CEM 1 [65OPC 30S 5L]</td>
<td>68.0</td>
<td>50.7</td>
<td>48.7</td>
<td>34.3</td>
</tr>
<tr>
<td>CEM 3 [45OPC 30S 25L]</td>
<td>53.8</td>
<td>40.4</td>
<td>36.8</td>
<td>25.7</td>
</tr>
<tr>
<td>CEM 6 [50OPC 20S 30L]</td>
<td>49.9</td>
<td>36.5</td>
<td>33.6</td>
<td>22.4</td>
</tr>
<tr>
<td>CEM 10 [55OPC 10S 35L]</td>
<td>45.0</td>
<td>31.0</td>
<td>29.5</td>
<td>17.8</td>
</tr>
<tr>
<td>Series 2 (OPC-FA-L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEM I 52.5 R HES (batch 2)</td>
<td>80.2</td>
<td>65.0</td>
<td>58.8</td>
<td>46.1</td>
</tr>
<tr>
<td>CEM II/B-M (L-S-V) 32.5 N</td>
<td>47.9</td>
<td>34.8</td>
<td>31.9</td>
<td>21.0</td>
</tr>
<tr>
<td>CEM II/B-V 32.5 R</td>
<td>53.4</td>
<td>40.2</td>
<td>36.5</td>
<td>25.5</td>
</tr>
<tr>
<td>CEM 1 [65OPC 30FA 5L]</td>
<td>57.9</td>
<td>36.5</td>
<td>40.2</td>
<td>22.4</td>
</tr>
<tr>
<td>CEM 3 [45OPC 30FA 25L]</td>
<td>35.1</td>
<td>20.4</td>
<td>21.2</td>
<td>9.0</td>
</tr>
<tr>
<td>CEM 6 [50OPC 20FA 30L]</td>
<td>36.8</td>
<td>24.0</td>
<td>22.7</td>
<td>12.0</td>
</tr>
<tr>
<td>CEM 10 [55OPC 10FA 35L]</td>
<td>42.9</td>
<td>24.0</td>
<td>27.8</td>
<td>12.0</td>
</tr>
</tbody>
</table>

(*) Not measured.
De Weerdt [1] studied the synergetic effect between fly ash and limestone filler in ternary cements and found that the composition with 30% of fly ash and 5% of limestone filler was the optimum in terms of compressive strength. The evolutions of the strengths from 2 days old to 91 days old for T(0.45) concretes are shown in Fig. 4. At 2 days, OPC-S-L and OPC-FA-L cements have similar strengths. At 7 days and later ages, OPC-S-L cements present larger compressive strengths than OPC-FA-L cements (up to 35% higher for CEM 3 made with slag). This has already been observed previously because slag is not only pozzolanic but also hydraulic [3, 21]. This additional reactivity gives thus a less porous concrete than with fly ash.

3.4 Indirect tensile strength
The indirect tensile strengths at 28 days (mean of six individual values) are shown in Tab. 2. The results of ternary cements OPC-S-L and OPC-FA-L are in general lower than the ones of the reference concretes. As for the previous mechanical properties, the indirect tensile strength seems to be mainly influenced by the clinker \( R = 0.9 \) and limestone filler \( R = -0.8 \) contents. The evaluation approach defines two borders, based on \( f_{cm,cube} \), which 5 of the 6 individual values have to be within:

\[
\begin{align*}
  f_{ct,exp,5\%} &= 0.23 \left( \frac{f_{cm,cube}}{1.2} - 8 \right)^{2/3} \\
  f_{ct,exp,95\%} &= 0.43 \left( \frac{f_{cm,cube}}{1.2} - 8 \right)^{2/3}
\end{align*}
\]

Tab. 3 shows the six individual values as well as the corresponding borders for T(0.45) series 2 concretes. Regarding ternary OPC-FA-L cements, only CEM 1 satisfies the criteria. The values outside the borders (in bold) are all above the superior limit \( f_{ct,exp,95\%} \). The few results for OPC-S-L cements shown in Tab. 2 satisfy the criteria. One can observe that indirect tensile strength at 28 days is higher than the predicted value for most cements. If this underestimation is confirmed in the long term, it might have an impact on the quantity of reinforcing bars, which is proportional to the tensile strength, to avoid brittle failure or even limit crack openings.

3.5 Modulus of elasticity
The results of modulus of elasticity are presented in Tab. 2. In series 1, the results of ternary OPC-S-L cements are similar to the reference cement CEM III/A 42.5 N LA. In series 2, the results of ternary OPC-FA-L cements are in general inferior to the reference cements. Again, the main factors influencing this property seem to be the clinker \( R = 0.8 \) and limestone filler \( R = -0.7 \) contents. Ternary cements OPC-S-L show higher values than OPC-FA-L cements (up to 14% for CEM 3 made with slag). The relation of modulus of elasticity with the compressive strength is presented in Fig. 5. The evaluation approach defines two borders:

\[
\begin{align*}
  E_{cm1} &= 21 \left( \frac{f_{cm,cube}}{1.2} - 8 \right)^{0.3} \\
  E_{cm2} &= 23 \left( \frac{f_{cm,cube}}{1.2} + 8 \right)^{0.3}
\end{align*}
\]

The figure also shows the theoretical E-modulus from Eurocode 2 (see Eq. (9)), and borders of \( E_{cm} \pm 30\% \) from the Model Code 2010 [22].

Table 3: 28 days indirect tensile strengths reached for type T(0.45) series 2 concretes (OPC-FA-L) and borders of the evaluation approach. In bold: values outside the borders.
Indirect tensile strength at 28 days

<table>
<thead>
<tr>
<th>Criteria (borders)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f_{ct}</td>
<td>s_p</td>
<td>5% f_{ct}</td>
<td>s_p</td>
<td>95%</td>
<td></td>
</tr>
<tr>
<td>CEM I 52.5 R HES (batch 2)</td>
<td>5.09</td>
<td>6.25</td>
<td>5.75</td>
<td>5.4</td>
<td>5.78</td>
<td>6.14</td>
</tr>
<tr>
<td>CEM II/B-M (LL-S-V) 32.5 N</td>
<td>4.76</td>
<td>4.36</td>
<td>4.21</td>
<td>4.3</td>
<td>3.97</td>
<td>4.24</td>
</tr>
<tr>
<td>CEM II/B-V 32.5 R</td>
<td>4.25</td>
<td>4.37</td>
<td>4.19</td>
<td>4.34</td>
<td>4.21</td>
<td>4.68</td>
</tr>
<tr>
<td>CEM 1 [65OPC 30FA 5L]</td>
<td>4.84</td>
<td>4.73</td>
<td>4.08</td>
<td>4.34</td>
<td>5.12</td>
<td>4.3</td>
</tr>
<tr>
<td>CEM 3 [45OPC 30FA 25L]</td>
<td>3.08</td>
<td>3.43</td>
<td>3.3</td>
<td>3.48</td>
<td>3.6</td>
<td>3.53</td>
</tr>
<tr>
<td>CEM 6 [50OPC 20FA 30L]</td>
<td>3.99</td>
<td>3.32</td>
<td>3.32</td>
<td>3.41</td>
<td>3.45</td>
<td>3.26</td>
</tr>
<tr>
<td>CEM 10 [55OPC 10FA 35L]</td>
<td>3.77</td>
<td>3.81</td>
<td>3.66</td>
<td>3.75</td>
<td>4.03</td>
<td>4.02</td>
</tr>
</tbody>
</table>

A reduction factor of 10% of $E_{cm}$ for limestone aggregates, cited in EC2, has not been applied.

$$E_{cm} (GPa) = 22 \left( \frac{0.8 f_{cm,cube}}{10} \right)^{0.3}$$  \hspace{1cm} (9)

Fig. 5 shows that all ternary OPC-S-L and OPC-FA-L cements are above the predicted $E_{cm}$ and that several are above the $E_{cm}$ border. These large moduli of elasticity could be explained by the high hardness of the limestone aggregates, as demonstrated by a fragmentation test (Los Angeles coefficient of 20). One can observe that the modulus of elasticity at 28 days is higher than the predicted value for most cements. For some applications like industrial floors where shrinkage is restrained, the developed stress could be more important because of a higher modulus of elasticity.

### 3.6 Total shrinkage

The shrinkage deformations of T(0.45) series 1 concretes are shown in Fig. 6. The deformations are less important for ternary OPC-S-L cements than for reference cement CEM I 52.5 R HES. It is the same for type T(0.55). For series 2, CEM 1 concrete shows a higher or similar deformation than reference CEM I 52.5 R HES, respectively for types T(0.45) or T(0.55). This reduced shrinkage with ternary OPC-S-L cements compared to Portland cement was also found by Courard and Michel [6]. According to them, due to less reactive materials, the mixtures containing slag probably do not attract water at the same rate, which may induce less chemical shrinkage. The influence of clinker and limestone filler contents is less significant for series 2 but it is for series 1 (R of 0.8 and -0.7 respectively). Concretes made with OPC-S-L cements present smaller deformations than OPC-FA-L cements (up to 29% for CEM 1), as shown by the total shrinkage at 91 days in Tab. 2. The evaluation approach defines two limits ± 49% of the shrinkage curve from Eurocode 2. This EC2 curve has been computed with a tool which takes into account the compressive strength class of cement and concrete, the average cross section radius, the relative humidity and number of curing days. Fig. 7 shows for example the results for CEM 1 [65OPC 30FA 5L] concrete. The experimental shrinkage is slightly lower than the predicted one but stays within the boundaries from the criterion.
Figure 2: Bonding strength of series 1 concretes (OPC-S-L).

Figure 3: Bonding strength of series 2 concretes (OPC-FA-L).

Figure 4: Comparison of compressive strength at 2, 7, 28 and 91 days for T(0.45) concretes of the series 1 (OPC-S-L) and series 2 (OPC-FA-L).
Figure 5: Modulus of elasticity – compressive strength relation for series 1 and 2 as well as theoretical values $E_{cm} \pm 30\%$ and borders $E_{cm1}$ and $E_{cm2}$.

Figure 6: Total shrinkage for T(0.45) series 1 concretes.

Figure 7: Experimental and EC2 total shrinkage for T(0.45) series 2 concrete CEM 1.

Figure 8: Experimental and EC2 creep for some T(0.45) concretes of series 1 and 2.
3.7 Creep
Creep tests were carried out on some concretes only. The results are shown in Fig. 8. For series 1, CEM 1 concrete shows the lowest creep while CEM 10 concrete shows a creep 65% higher. For series 2, CEM 6 concrete has a creep similar to the reference CEM II/B-V 32.5 R. The evaluation approach requires that experimental creep should lie within two limits ± 34% of the creep from Eurocode 2. This EC2 curve has been computed taking into account the compressive strength of concrete, the type of cement, the average cross section radius, the relative humidity and the age of concrete at the beginning of the test. Fig. 8 presents for example the EC2 curves for CEM 6 [50OPC 20FA 30L] concrete. For all ternary cements, experimental creep is lower than the predicted one but they stay in the ± 34% boundaries. It is difficult to draw trends but it seems that the presence of slag or fly ash is beneficial to reduce creep. One can observe that creep is lower than the predicted value for all cements. It might be positive for many applications as long term deflections under permanent load could be limited. But for applications where shrinkage is restrained, a low creep in compression might induce generally less relaxation in tension and hence generate higher tensile strains and more important cracking.

4. Conclusions
The effects of ternary cements made with blast furnace slag or fly ash (with a content up to 30%) and limestone filler (with a content up to 35%), on the fresh properties and mechanical performance of concretes were investigated. The following conclusions, for the tests conditions and materials of this study, can be drawn:

- Setting time and mechanical properties (compressive and indirect tensile strengths, modulus of elasticity, total shrinkage) are essentially influenced by clinker ($R > 0.8$) and limestone filler ($R < -0.7$) contents, as shown by correlation coefficients;
- Ternary OPC-S-L cements seem in general to contribute to a higher mechanical performance than ternary OPC-FA-L cements;
- Except for shrinkage and creep, most of the tested ternary cements did not satisfy the requirements of the evaluation approach.

This study shows that despite the fact that ternary cements with high amount of limestone and slag or fly ash meet the requirements of European standard EN 197-1 in terms of initial setting time, soundness and compressive strength, these cements could not be used in concrete in all applications. Predictive models of the mechanical performance may not be suitable for most of the tested composite cements. There are some cases for which these poor predictions could have an impact in terms of underutilization of the performance of the material depending on the applications. A more thorough statistical research should be made but this first study shows that the predictive models from Eurocode 2 are not valid for most of the tested ternary cements. Finally, it could be interesting to perform ring tests in order to study the cracking susceptibility due to restrained shrinkage.

Acknowledgements
The authors would like to acknowledge the Wallonia Government (Belgium) for the financial support as well as the National Centre for Scientific and Technical Research for the Cement Industry for the production and characterization of the ternary cements.
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DURABILITY OF CONCRETE MADE WITH TERNARY CEMENTS CONTAINING SLAG OR FLY ASH AND LIMESTONE FILLER

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Abstract

The durability of concrete made with ternary cements containing Portland cement (OPC), blast-furnace slag (S) or fly ash (FA) and limestone filler (L) has been investigated according to a comparative approach to assess the suitability for use of these composite cements for concrete. Eight blended cements of different proportions of OPC (from 45% to 65%), S and FA (from 10% to 30%) and L (from 5% to 35%) were selected and compared with five reference cements (CEM I 52.5 R HES, CEM II/B-M (L-S) 32.5 R, CEM II/B-M (LL-S-V) 32.5 N, CEM II/B-V 32.5 R and CEM III/A 42.5 N LA). Two types of mixes were produced using constant water to cement (\(w/c\)) ratios of 0.45 and 0.55 and cement contents of 340 kg/m³ and 300 kg/m³ respectively. Carbonation, freeze-thaw with de-icing salts, chloride diffusion and sulfate attack tests were carried out on concretes and mortars. The results indicate that a high content of slag and fly ash reduces chloride diffusion and sulfate attack. Resistance to carbonation and freeze-thaw decreases with limestone filler content. Ternary cements containing slag seem overall to give a better concrete durability than those containing fly ash.

1. Introduction

The development of alternative binders such as binary and especially ternary cements has rapidly increased these past decades. Blast-furnace slag (S) and fly ash (FA) are by-products commonly used as supplementary cementitious materials (SCMs). In Belgium, the production of these by-products tends to decrease while limestone filler (L) is abundantly available. Several studies investigated the synergetic action of these SCMs [1–5]. It has been found that a small dosage of limestone filler could have a beneficial effect on the early age properties of concrete, while fly ash and blast-furnace slag contribute to the long-term mechanical properties as pozzolanic reaction rate is slower than hydration of Portland cement (OPC). These antagonist properties make these ternary mixes particularly interesting. These SCMs are also favourable to sulfate resistance [6] but have a negative effect on carbonation [7].
Some effects of ternary cements on concrete durability are not thoroughly investigated yet, namely frost with de-icing salts resistance [8]. The European standard EN 197-1 [9] includes requirements for cements for use in concrete. Questions arise as to whether these requirements are sufficient to use these cements in all applications. The aim of this study is to evaluate the performance of concrete made with newly developed ternary cements OPC-S-L and OPC-FA-L, according to a comparative approach to assess their suitability for use for concrete. This approach is based on the determination of the performance equivalence of concretes made with these ternary cements compared to reference concretes made with industrial cements, which satisfy the requirements of standard EN 197-1. This paper focuses on the durability properties of these concretes. Carbonation, freeze-thaw with de-icing salts, chloride diffusion and sulfate attack tests were carried out on concretes and mortars. Two methods (EN 12390-11 and NT Build 443) were used and compared for the chloride diffusion test. Fresh and mechanical properties of these concretes are the subject of a companion paper by the same authors [10].

2. Experimental program

2.1 Materials
Composite cements were prepared by mixing CEM I 52.5 R HES (OPC), ground granulated blast-furnace slag (S), fly ash (FA) and limestone filler (L). As a set regulator, gypsum had been added with a concentration to obtain a total sulfate content of 3%. Chemical and mineralogical characterization showed that the studied SCMs meet all the requirements from standard EN 197-1, regarding the properties of the cement constituents. Slag contains more than 60% by mass of CaO, MgO and SiO\textsubscript{2} and the ratio (CaO + MgO)/SiO\textsubscript{2} is above 1. Fly ash is characterized by a low loss on ignition (category A), a CaO content below 10% and a SiO\textsubscript{2} content above 25%. Limestone filler contains 100% of calcite. The clay content is inferior to 1.2 g/100 g filler and the total organic content (TOC) is inferior to 0.5%.

Then the physical, chemical and mechanical properties of the ternary cements, with different proportions of Portland cement (OPC between 45 and 65%), blast-furnace slag or fly ash (S or FA between 10 and 30%) and limestone filler (L between 5 and 35%), were determined. Two series had been conducted. In series 1, ternary blended cements with slag (OPC-S-L) were studied, with reference cements CEM I 52.5 R HES, CEM II/B-M (L-S) 32.5 R and CEM III/A 42.5 N LA. In series 2, ternary cements with fly ash (OPC-FA-L) were investigated with reference cements CEM I 52.5 R HES, CEM II/B-M (LL-S-V) 32.5 N and CEM II/B-V 32.5 R. For the sulfate attack test, a high sulfate resistant cement has also been tested: CEM I 52.5 R LA – SR 3. Nearly all the ternary cements meet the requirements from the standard EN 197-1, regarding the compressive strength, initial setting time and soundness. Eight cements compositions have been chosen and are presented in Tab. 1. The results show that ternary OPC-S-L cements reach higher compressive strength classes than OPC-FA-L cements.

2.2 Concrete mixes
Two types of concrete have been chosen, named T(0.45) and T(0.55). The cement content, w/c ratio and the desired slump are 340 kg/m\textsuperscript{3}, 0.45, 120 ± 30 mm and 300 kg/m\textsuperscript{3}, 0.55, 180 ± 30 mm respectively for the two types. The fine aggregates consist of sea sand and rolled sand. The coarse aggregates consist of crushed limestone with a maximum nominal size of 20 mm.
Table 1: Composition (% by mass), Blaine surface and compressive strength class for cements of series 1 (OPC-S-L) and series 2 (OPC-FA-L).

<table>
<thead>
<tr>
<th>Series 1 (OPC-S-L)</th>
<th>OPC (%)</th>
<th>S (%)</th>
<th>FA (%)</th>
<th>L (%)</th>
<th>Blaine surface (cm²/kg)</th>
<th>Strength class (mortar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 52.5 R HES (batch 1)</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4780</td>
<td>52.5 R</td>
</tr>
<tr>
<td>CEM II/B-M (L-S) 32.5 R</td>
<td>74</td>
<td>12</td>
<td>0</td>
<td>14</td>
<td>3737</td>
<td>32.5 R</td>
</tr>
<tr>
<td>CEM III/A 42.5 N LA</td>
<td>59</td>
<td>41</td>
<td>0</td>
<td>0</td>
<td>4591</td>
<td>42.5 N</td>
</tr>
<tr>
<td>CEM 1 [65OPC 30S 5L]</td>
<td>65</td>
<td>30</td>
<td>-</td>
<td>5</td>
<td>4770</td>
<td>52.5 N</td>
</tr>
<tr>
<td>CEM 3 [45OPC 30S 25L]</td>
<td>45</td>
<td>30</td>
<td>-</td>
<td>25</td>
<td>4630</td>
<td>42.5 N</td>
</tr>
<tr>
<td>CEM 6 [50OPC 20S 30L]</td>
<td>50</td>
<td>20</td>
<td>-</td>
<td>30</td>
<td>4430</td>
<td>42.5 N</td>
</tr>
<tr>
<td>CEM 10 [55OPC 10S 35L]</td>
<td>55</td>
<td>10</td>
<td>-</td>
<td>35</td>
<td>4260</td>
<td>42.5 R</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series 2 (OPC-FA-L)</th>
<th>OPC (%)</th>
<th>S (%)</th>
<th>FA (%)</th>
<th>L (%)</th>
<th>Blaine surface (cm²/kg)</th>
<th>Strength class (mortar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 52.5 R HES (batch 2)</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4930</td>
<td>52.5 R</td>
</tr>
<tr>
<td>CEM II/B-M (LL-S-V) 32.5 N</td>
<td>71</td>
<td>7</td>
<td>9</td>
<td>13</td>
<td>3360</td>
<td>32.5 N</td>
</tr>
<tr>
<td>CEM II/B-V 32.5 R</td>
<td>78</td>
<td>0</td>
<td>22</td>
<td>0</td>
<td>2960</td>
<td>32.5 R</td>
</tr>
<tr>
<td>CEM 1 [65OPC 30FA 5L]</td>
<td>65</td>
<td>-</td>
<td>30</td>
<td>5</td>
<td>4110</td>
<td>52.5 N</td>
</tr>
<tr>
<td>CEM 3 [45OPC 30FA 25L]</td>
<td>45</td>
<td>-</td>
<td>30</td>
<td>25</td>
<td>4120</td>
<td>-</td>
</tr>
<tr>
<td>CEM 6 [50OPC 20FA 30L]</td>
<td>50</td>
<td>-</td>
<td>20</td>
<td>30</td>
<td>4230</td>
<td>32.5 R</td>
</tr>
<tr>
<td>CEM 10 [55OPC 10FA 35L]</td>
<td>55</td>
<td>-</td>
<td>10</td>
<td>35</td>
<td>4440</td>
<td>32.5 R</td>
</tr>
</tbody>
</table>

The concrete mixes have been formulated so that the grading curve follows the limits specified in the standard EN 480-1 [11], as shown in Fig. 1. There exists a slight difference between the two series: series 2 contains more fines below 0.5 μm. A polycarboxylic-ether superplasticiser has been used. The dosage has been adjusted to reach the desired slump. The water absorbed by the aggregates and supplied by the superplasticiser have been taken into account in the mixing water. The mix proportions are detailed in Tab. 2.

The concrete samples are conserved during 24h at a temperature of 20 ± 2°C. After removal, the specimens are placed in water at the same temperature for curing. For the durability tests, a water curing period of 91 days has been chosen to provide ideal hydration conditions for these cements. Indeed, a good curing is important for these composite cements as highlighted by several authors [8, 12–14]. For sulfate attack test, standard mortars (EN 196-1 [15]) were cured in water during 28 days.

2.3 Testing methods
Accelerated carbonation tests were carried out following standard EN 13295 [16] on three prismatic samples of 10 cm x 10 cm 40 cm in size, for the two types of concretes. After
curing, the samples were conserved in a climatic chamber during 14 days until constant mass. Then they were transferred in the carbonation chamber with a CO₂ content of 1% at a temperature of 20 ± 2°C and relative humidity of 60 ± 10%. The carbonation depth was measured with a phenolphthalein solution at 7, 14, 28, 56 and 91 days of carbonation.

The resistance of freeze-thaw cycles with de-icing salts was measured according to EN 12390-9 (slab test) [17] on T(0.45) concretes. Four cylindrical samples of 113 mm x 50 mm were cored after curing. They were conserved in a climatic chamber during 14 days and then prepared with resin. They were subjected to 56 cycles of freeze-thaw with a solution of NaCl (1 cycle lasts 24h). The loss of material at the surface was collected and weighted after oven-drying at 105°C, at 7, 14, 28, 42 and 56 days.

Chloride diffusion test was carried out according to EN 12390-11 [18] and NT BUILD 443 [19] on T(0.45) concretes. Three cylindrical samples of 100 mm x 70 mm were cored after curing, then saturated in water under vacuum and then immersed in a solution of Ca(OH)₂ (EN method) or directly saturated and immersed in a Ca(OH)₂ solution (NT method). The samples were then immerged in a NaCl solution with a concentration of 30 g/l during 91 days (EN method) or with a concentration of 165 g/l during 35 days (NT method). Samples are taken at different depths (x) to measure the chloride concentration (C(x,t) and initial content Cᵢ). The diffusion coefficient (Dₜₙₑₓ) is then calculated from the chloride concentration profile, according to the following Eq. (1), by least-squares method:

\[
C(x,t) = C_i + (C_e - C_i) \left(1 - \text{erf} \left( \frac{x}{\sqrt{4D_{\text{net}} t}} \right) \right)
\]  

(1)

Sulfate attacks were carried out on mortar samples of 2 cm x 2 cm x 16 cm in size at a temperature of 20°C, according to CUR 48 [20]. Three prisms were immerged in a sulfate solution (16 g/l SO₄) and three others were placed in water, as control specimens. The length variation is measured and compared with the control specimens, during 365 days.
Table 2: Concrete mix proportions (kg/m³) for series 1 (OPC-S-L) and series 2 (OPC-FA-L).

<table>
<thead>
<tr>
<th></th>
<th>Series 1 (OPC-S-L)</th>
<th>Series 2 (OPC-FA-L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T(0.45)</td>
<td>T(0.55)</td>
</tr>
<tr>
<td>Cement</td>
<td>340</td>
<td>300</td>
</tr>
<tr>
<td>Fine aggregates (sea sand and rolled sand) 0/5</td>
<td>703</td>
<td>705</td>
</tr>
<tr>
<td>Fine aggregates (rolled sand) 0/4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coarse aggregates (crushed limestone) 4/20</td>
<td>1198</td>
<td>1201</td>
</tr>
<tr>
<td>Superplasticiser* (%)</td>
<td>0.15 – 0.8</td>
<td>0.2 – 0.25</td>
</tr>
<tr>
<td>Mixing water</td>
<td>161</td>
<td>173</td>
</tr>
</tbody>
</table>

*The superplasticiser dosage (% by mass cement) was adjusted to reach the desired slump.

2.4 Comparative approach
The evaluation of performance of concrete made with these new ternary cements OPC-S-L and OPC-FA-L consists in a comparative approach inspired by the methodology from Belgian standard NBN B 15-100 [21]. All the results are compared with the ones obtained on reference concretes, with a weighting factor of 20% or 40%. For series 1, the reference could be either concrete made with CEM I 52.5 R HES or with CEM III/A 42.5 N LA. For series 2, the reference is CEM I 52.5 R HES. The criteria are indicated by a red line in the graphs.

3. Results and discussion
The fresh and mechanical properties are presented in the companion paper [10]. The compressive strengths of OPC-S-L cements are higher than OPC-FA-L cements, which has already been observed on mortars (strength class in Tab. 1).

3.1 Carbonation
The results of the carbonation depths of T(0.55) concretes are presented in Fig. 2 for series 1 and Fig. 3 for series 2. The results of T(0.45) concretes are lower, as w/c ratio is lower and cement content is higher, but the trends are similar.

The comparative approach requires that at 56 days, the carbonation depth (d) should be inferior or equals to 1.2 times the depth of the reference concrete: \( d_{56} \leq 1.2 \times d_{56,\text{ref}} \). For series 1, at 56 days, the reference concrete made with CEM III/A 42.5 N LA has a carbonation depth of 6.5 mm. Only the CEM I [65OPC 30S 5L] concrete, with the highest clinker content and the lowest limestone filler content, meets the criterion of \( 6.5 \times 1.2 = 7.8 \) mm. For series 2, no OPC-FA-L cement satisfies the criterion as CEM I 52.5 R HES concrete shows a high resistance to CO₂ penetration. The difference for concretes with the same reference cement CEM I 52.5 R HES could be due to the difference in the grading curve (see Fig. 1).

Carbonation resistance decreases with decreasing clinker content and increasing limestone filler content. Indeed, carbon dioxide present in the atmosphere reacts with cement hydration products such as portlandite Ca(OH)₂, which buffers the pH. The quantity of portlandite in blast-furnace slag or fly ash concrete is significantly reduced due to pozzolanic reaction and
lower clinker content [5, 12, 14]. Limestone filler worsens the carbonation resistance, which has also been observed by Courard and Michel. They found that the “open” porosity increases with limestone filler content [5]. When comparing the two series, ternary OPC-S-L cements present a higher resistance to carbonation than OPC-FA-L cements. The presence of slag seems to give a denser material than fly ash, as it has pozzolanic as well as hydraulic properties [3].

3.2 Freeze-thaw with de-icing salts
The results of cumulated loss of materials of T(0.45) concretes are presented in Fig. 4 for series 1 and in Fig. 5 for series 2. For series 1, results of concretes with cements CEM 1, CEM 3 and CEM 6 have been withdrawn due to incoherent results.

The comparative approach requires that at 28 cycles, the cumulated loss of material (S) should be inferior or equals to 1.2 times the one of the reference concrete: $S_{28} \leq 1.2S_{28,\text{ref}}$. At 28 days, concrete reference CEM I 52.5 R HES has a cumulated loss materials of 1.1 kg/m² for both series. In series 1, CEM 10 [55OPC 10S 35L] concrete is just above the criteria (1.1 x 1.2 = 1.32 kg/m²) but it performs better than the reference concrete CEM II/B-M (L-S) 32.5 R. In series 2, no OPC-FA-L concrete satisfies the criteria but CEM 1 [65OPC 30FA 5L] concrete performs slightly better than reference concrete CEM II/B-M (LL-S-V) 32.5 N.

The criteria at 28 days appears to discriminate against concrete containing slag, as pointed out by Chidiac and Panesar [8]. Indeed, after 56 freeze-thaw cycles, CEM 10 [55OPC 10S 35L] concrete resists better than CEM I 52.5 R HES concrete. In series 1, it is difficult to report trends as only four different cements have been tested. In series 2, the scaling resistance seems to be reduced with increasing limestone filler content. CEM 1 [65OPC 30FA 5L] concrete presents a better resistance than CEM II/B-M (L-S) 32.5 R, which contains 13% of limestone filler. CEM 10 [55OPC 10FA 35L] concrete shows the worst performance, with a cumulated material loss of over 15 kg/m² after 56 cycles. When comparing series 1 and 2, concretes made with OPC-FA-L cements seem to have more scaling damage than OPC-S-L cements. For binary slag cements, several authors indicated that an adequate entrained air void system could prevent such freezing and thawing attack [12, 14, 22].

3.3 Chloride diffusion
The diffusion coefficients obtained for T(0.45) concretes are presented in Fig. 6 and Fig. 7 for series 1 and series 2 respectively. Two different test methods have been compared for OPC-S-L cements: EN 12390-11 and NT BUILD 443.

The comparative approach requires that the diffusion coefficient ($D_{\text{ref}}$) should be inferior or equals to 1.4 times the one of the reference concrete: $D_{\text{ref}} \leq 1.4 D_{\text{oss}}$. In series 1, concrete reference CEM I 52.5 R HES has a diffusion coefficient of $9.85 \times 10^{-12}$ m²/s with the European method, which gives a criteria of $13.8 \times 10^{-12}$ m²/s. All concretes made with OPC-S-L cements, except the CEM 10 [55OPC 10S 35L], satisfy the requirement. This is also observed for the NT BUILD method, with a criteria of $9.5 \times 10^{-12}$ m²/s. For series 2 (OPC-FA-L), CEM 10 [55OPC 10FA 35L] concrete does not satisfy the criterion either. The difference observed between CEM I 52.5 R HES concretes of the two series could be due to the difference in the concrete grading curve, as seen in Fig. 1. Series 2 concretes contain more fines, which could lead to a denser material and thus the diffusion could be more hindered.

In series 1, the resistance to chloride penetration seems to be improved by the presence of slag, while the presence of limestone filler seems to not have an influence on it. CEM III/A
42.5 N LA [59OPC 41S], CEM 1 [65OPC 30S 5L] and CEM 3 [45OPC 30S 25L] concretes show low diffusion coefficients compared to CEM I 52.5 R HES concrete. This positive effect of slag compared to clinker is explained by a higher chloride binding capacity with formation of Friedel’s salts [23]. Besides, the C-S-H produced by reaction of slag and characterized by a lower Ca/Si ratio have a higher chloride adsorption [12, 22]. Kayali et al. [23] have also highlighted the role of hydrotalcite, a significant hydration product of slag blends, in chloride binding. In series 2, the presence of fly ash also seems to have a beneficial effect against chloride penetration. CEM II/B-V 32.5 R [78OPC 22FA], CEM 1 [65OPC 30FA 5L], CEM 3 [45OPC 30FA 25L] and CEM 6 [50OPC 20FA 30L] concretes show a better resistance to chloride penetration than CEM I 52.5 R HES concrete. This is also due to a higher chloride binding capacity of fly ash compared to Portland cement [24]. When comparing OPC-S-L and OPC-FA-L cements according to the European standard, it seems that fly ash performs better than slag regarding resistance to chloride diffusion, which is in contradictory of what Ytterdal [24] found. But Ytterdal compared mortars with 30% replacement of fly ash and mortars with 50% replacement of blast-furnace slag. When comparing the two test methods, EN 12390-11 gives significantly higher values, which could be due to the different procedure test (saturation under vacuum and immersion during 91 days). The standard deviations are particularly higher too for this method. It is thus always important to consider the test method while discussing about diffusion coefficients.

3.4 Sulfate attack

The results of the linear expansion of mortars immersed in a sulfate solution for one year are presented in Fig. 8 and Fig. 9 for series 1 and series 2 respectively. In the latter, a sulfate resistant cement CEM I 52.5 R LA – SR 3 has also been tested. The comparative approach requires that the linear variation (L) at 365 days should be inferior or equals to 1.2 times the one of the reference mortar: \( L_{365} \leq 1.2 L_{365,\text{ref}} \) or that \( L_{365} \leq 0.05\% \).

In series 1, mortars made with CEM III/A 42.5 N LA [59OPC 41S], CEM 1 [65OPC 30S 5L], CEM 3 [45OPC 30S 25L] and CEM 6 [50OPC 20S 30L] present a linear deformation inferior to 0.02%. This beneficial effect of slag on sulfate resistance is due to lower content of tricalcium aluminate C₃A, which is the main expansive reactive material [5, 12], and due to the low aluminum content of slag [12, 14]. Besides, Courard and Michel [5] noticed that the sulfate resistance of mixtures containing slag was not influenced by limestone fillers, contrary to Portland cement mixtures, for which the relative deformation increases with limestone filler content, up to 15%. Hossack and Thomas [6] observed that limestone content in combination with fly ash or slag had little to no effect on sulfate resistance. In series 2, it appears that the mortar made with CEM I 52.5 R LA – SR 3 performs better than the CEM I 52.5 R HES but shows an expansion of about 1% after one year. Again, mortars made with CEM II/B-V 32.5 R [78OPC 22FA], CEM 1 [65OPC 30FA 5L], CEM 3 [45OPC 30FA 25L] and CEM 6 [50OPC 20FA 30L] present a linear deformation inferior or equals to 0.1%. When comparing the two series, it seems that fly ash is even more favourable to resistance to sulfate attack than blast-furnace slag. This has also been observed by Hossack and Thomas [6]. They found that the intensity of ettringite peaks was greater in fly ash mortar bars than slag mortar bars, which may indicate a lower permeability and thus a less resistance to sulfate. The risk of thaumasite formation for sulfate attacks at 5°C on OPC-S-L cements has been previously discussed by Rondeux et al. [25]. The beneficial effect of slag to prevent damage due to sulfate attacks at low temperature has not been observed for OPC-FA-L cements.
4. Conclusions

The effects of ternary cements made with blast-furnace slag or fly ash (with a content up to 30%) and limestone filler (with a content up to 35%), on the durability of concretes were investigated. The following conclusions, for the tests conditions and materials of this research, can be drawn:

- Blast-furnace slag and fly ash have a beneficial effect on chloride diffusion and sulfate attack thanks to a higher chloride binding capacity and a lower C₃A content;
- Limestone filler, coupled with blast-furnace slag or fly ash, has no significant influence on chloride diffusion and sulfate attack resistance (at 20°C), but well a negative effect on freeze-thaw with de-icing salts resistance;
- Carbonation resistance decreases with decreasing clinker content and increasing limestone filler content;
- Ternary OPC-S-L cements seem in general to contribute to a better durability performance than OPC-FA-L cements;
- Except for chloride diffusion and sulfate attack, most of the tested ternary cements did not satisfy the requirements of the comparative approach.

This study shows that despite the fact that ternary cements with high amount of limestone and slag or fly ash meet the requirements of European standard EN 197-1 in terms of initial setting time, soundness and compressive strength, these cements could not be used in concrete in every environment. It is necessary to always assess the suitability for use of new composite cements for concrete. An adjustment of the concrete mix (cement content, w/c, grading curve…) or special precautions (thicker covering…) shall be necessary to use these ternary cements in specific environments or applications. Finally, it should be noted that a long curing period is highly recommended for these composite cements.

Acknowledgements

The authors would like to acknowledge the Wallonia Government (Belgium) for the financial support as well as the National Centre for Scientific and Technical Research for the Cement Industry for the production and characterization of the ternary cements.

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COMPARISON OF THE EXPANSION OF MORTAR CONTAINING SHELL POWDER OF SURF CLAM AND SCALLOP

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Abstract
Differences in the expansion characteristics of mortars manufactured with various fractions of cement replaced by surf clam shell powder (aragonite CaCO₃) or scallop shell powder (calcite CaCO₃) were investigated. The expansion characteristics were evaluated by conducting restrained expansion tests on the mortars in accordance with the testing methods for expansive additives for concrete given in JIS A 6202. The expansion characteristics of the mortars at an early age were also evaluated by conducting length change tests using a corrugated mold based on ASTM C1698. For a given amount of added shell powder, there are differences in the amount of expansion between scallop shell and surf clam shell, with the latter causing expansion at lower added amounts. Additionally, when SEM was used to observe the fracture surfaces of the mortars containing shell powder, large numbers of needle crystals were observed, and are thought to be related to the cause of expansion.

1. Introduction

The cracking of concrete structures is problematic because it leads to various issues relating to function, aesthetics, and durability. Concrete shrinkage is one cause of cracking, and a widely used method of preventing shrinkage is the addition of expansive admixtures. Expansive admixtures have a wide range of uses including increasing the bending/tensile resistance of reinforced concrete by chemical prestressing.

Currently, we are conducting research aimed at effectively utilizing the shell of the Sakhalin surf clam, which is a specialty of the city of Tomakomai in Hokkaido, Japan. However, the abundance of surf clam shells is relatively low and the number of areas producing the shells are limited, which makes it impossible to ensure a stable supply and difficult to reduce costs through mass production. This has delayed the establishment of a system for effectively utilizing the surf clam shells. In contrast, a similar fishery-related waste product—the scallop
shell—is being used effectively because it is abundant and can be reliably supplied in industrial quantities. Even if the same method of use was applied to the limited quantities of surf clam shells, the level of demand would not be the same. Therefore, it is necessary to come up with a product with higher added value than that of scallop shells in order to use surf clam shells effectively.

Previous research found expansion in mortar after replacing 10% of the cement with burned surf clam shell powder [1]. The expansion was determined to be due to Ca(OH)$_2$ formed by CaO in the burned surf clam shell powder reacting with water, and a potential use of the surf clam shell powder as the basic ingredient in a lime-based expansive admixture was suggested. However, when burned, the main component of the abundant scallop shell is also CaO, so scallop shells are highly likely to cause similar expansion.

Surf clam shells are CaCO$_3$, like scallop shells, but the crystalline structure is different. Scallops consist of the predominant calcite-type CaCO$_3$, whereas surf clam shells are composed of aragonite CaCO$_3$. Aragonite CaCO$_3$ is a metastable phase found only in some corals and shells. This structure is harder than the calcite, and its characteristics include a phase transition into calcite when burned at around 500 °C. However, it has been confirmed that the main component in both surf clam and scallop shell powder becomes CaO when burned at 1,000 °C.

This study aims to find an inherent advantage in burned surf clam shells by examining the differences in expansion performance between mortars manufactured with a portion of cement replaced by burned surf clam or scallop shell powder.

2. Experimental outline

The compressive strength and amount of expansion of the mortars was measured in order to examine differences in the expansion characteristics between the mortars containing burned HP and those containing burned SP. Component analysis was also performed to investigate the cause of the mortar expansion. Each experimental method is shown below.

2.1 Method of producing burned shell powder

Before starting the experiment, the surf clam and scallop shells were washed and dried before being crushed and passed through a 75-μm sieve, and then burned for 1 hour at 1,000 °C. The burned shells were again crushed and processed into powder, and this powder was used to replace some of the cement used in the production of mortars.

2.2 Materials and mixtures

Using ordinary Portland cement (density: 3.14 g/cm$^3$) and river sand (surface-dry density: 2.77 g/cm$^3$), mortar specimens were prepared with 5%, 10%, or 15% of the cement mass replaced by burned surf clam shell powder or burned scallop shell powder (hereafter, HP5, HP10, HP15, and SP5, SP10, SP15, respectively). Similarly, mortar specimens for which 5% or 10% of the cement was replaced with a lime-based expansive admixture (hereafter, B5,
Table 1: Chemical composition.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burned surf clam shell (HP)</td>
<td>0.05</td>
<td>0.03</td>
<td>0.19</td>
<td>98.0</td>
<td>0.08</td>
<td>0.24</td>
</tr>
<tr>
<td>Burned scallop shell (SP)</td>
<td>0.10</td>
<td>0.04</td>
<td>0.00</td>
<td>98.0</td>
<td>0.53</td>
<td>0.43</td>
</tr>
<tr>
<td>Expansive admixture (B)</td>
<td>4.20</td>
<td>1.10</td>
<td>1.00</td>
<td>74.0</td>
<td>0.51</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 2: Mixtures.

<table>
<thead>
<tr>
<th></th>
<th>W/C (%)</th>
<th>Water (g)</th>
<th>Cement (g)</th>
<th>HP,SP,B (g)</th>
<th>Sand (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>50</td>
<td>218</td>
<td>436</td>
<td>0</td>
<td>1113</td>
</tr>
<tr>
<td>HP5,SP5,N5</td>
<td></td>
<td></td>
<td>414</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>HP10,SP10,B10</td>
<td></td>
<td></td>
<td>392</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>HP15,SP15</td>
<td></td>
<td></td>
<td>370</td>
<td>66</td>
<td></td>
</tr>
</tbody>
</table>

B10) were prepared, as well as a plain mortar (hereafter, N). Table 1 shows the chemical composition of the materials used, and Table 2 shows the specimen mixtures.

2.3 Compressive strength test
Square pillar specimens of size 40 × 40 × 160 mm were produced in accordance with Japanese Industrial Standards (JIS) R 5201 [2]. The specimens were removed from their molds 24 hours after pouring, and cured in water at 20°C. A compressive strength test was carried out at material ages of 7 days and 28 days.

2.4 Restrained expansion test
A restrained expansion test was conducted on the mortars in accordance with the standard for expansive additives for concrete, JIS A 6202 [3], in order to quantitatively evaluate the amount of expansion. A restraint with an approximate total length of 158 mm (mortar section, approx. 135 mm) was installed in a mold, and mortar was poured inside. When installing the restraint, gaps between the mold and the restraint were packed to prevent the restraint from lifting up due to movement of the shaking table and to prevent mortar from adhering to the tip of the gauge. The mold was removed after 1 day, and the length of the specimen was measured before curing in a 20 °C water bath. The length of the specimen was measured and the expansion rate was calculated until the mortar reached an age of 7 days. Three specimens were analyzed for each of the mixtures.

2.5 Mortar specimen length change test
A length change test according to the American Society for Testing and Materials (ASTM) C1698 [4] was employed as a method of measuring the expansion of the mortar, and it was
decided to study the expansion characteristics of the mortar at an early age. This test was originally intended to evaluate autogenous shrinkage at low water-cement ratios, and is a method of examining length change in cement paste or mortar poured in a corrugated mold using a dial gauge based on the length when set [5], [6]. This research enhanced the test apparatus by replacing the dial gauge with a laser displacement meter so that the length change could be measured directly straight after pouring.

A polyethylene corrugated mold approximately 30 mm in diameter and 425 mm in length was installed vertically on top of a shaking table, and the mortar was poured in from the top while the table was vibrated. Then, a Teflon stopper was put on to make a specimen for measuring length change. This was installed on a platform fixed at a 30° angle in a temperature-controlled room at 20°C, and length change was measured using the length change measuring device shown in Photo.1. The measurable range using this test apparatus was -10 to +10 mm.

2.6 Other tests
Samples were collected from the specimens after the compressive strength test, and these samples were immersed in acetone and, after the hydration reaction was halted, dried in a vacuum. Chemical analysis was carried out using thermogravimetry-differential thermal analysis (hereafter, TG-DTA) and powder X-ray diffraction. Pieces of samples were also collected from the specimens after the length change test and were examined using a scanning electron microscope (SEM).

3. Expansion characteristics of the mortars

3.1 Compressive strength test
Figure.1 shows the results of the compressive strength test on the mortar specimens at an age of 7 days. Taking the ordinary mortar as a reference, the compressive strengths of HP5, SP5, and SP10 were slightly reduced. However, HP10 had a compressive strength of around 5
N/mm², which is very low. The reason for this is that the square pillar specimen HP10 expanded considerably, such that a change in length of approximately 10 mm in the long-axis direction occurred (Photo.2), which generated many tiny cracks. In SP10, visible expansion was not identified, and there was little reduction in the strength. When the amount of added shell powder was increased to 15%, the HP15 and SP15 specimens expanded so much that they broke apart, and it was not possible to measure their compressive strengths. These results show that burned SP and burned HP display similar expansion characteristics, but a larger amount of burned SP is needed to generate expansion.

The mortar for which 5% of the cement was replaced with an expansive admixture had a compressive strength of 40 N/mm² or more at an age of 7 days, while the mortar for which 10% of the cement was replaced with an expansive admixture had a strength slightly lower than that of N and roughly the same as the mortar made with HP5.

3.2 Restrained expansion test
Figure 2 shows the results of the restrained expansion test on the mortars manufactured with a replacement ratio of 10%. The amount of change was based on the length of the restraint
directly before pouring, which was measured using a dial gauge. The rate of change in length 1 day after pouring was large for HP10 at around 0.12% and small for B10 at around 0.02%. Afterwards, HP10 demonstrated expansion until the mortar was 2 days old, reaching a rate of change of 0.17%, and then showed almost no further change in length. Meanwhile, SP10 and B10 demonstrated expansion of 0.1%–0.12% until the mortar was 2–3 days old, and then continued to expand slightly. Specimen N demonstrated slight shrinkage until mold removal, and subsequently showed almost no change in length.

Figure 3 shows the rate of change in length based on the length at a material age of 1 day. Specimens HP10, SP10, and B10 all showed considerable expansion of 0.06%–0.09% for about 1 day due to being submerged in water. There appeared to be little difference between any of the specimens with respect to the amount of rapid expansion due to underwater curing after mold removal.

3.3 Length change test using corrugated mold

Figure 4 shows the results of the length change test on the mortar specimens manufactured with a replacement ratio of 10%. Displacement indicates a change in length from the initial
length of the corrugated mold of 425 mm. All specimens demonstrated shrinkage for 4–5 h directly after mixing, which was considered to be due to cement hydration. After shrinking rapidly, N showed almost no change in length. HP10 underwent considerable expansion after shrinking until an age of 1 day, and then showed almost no change in length. This is thought to be because the cause of the expansion is the reaction between CaO and water, and the quantity of water for the reaction is limited inside the airtight space of the corrugated mold.

Meanwhile, SP10 and B10 did not show rapid expansion like HP10, but instead expanded gradually after the end of the initial shrinkage. These results confirmed that, compared to burned SP and B, burned HP causes extremely large expansion within a short period of time.

### 3.4 Expansion characteristics of mortar containing burned surf clam shell powder

The results of the restrained expansion test and the corrugated mold test show that the surf clam shell, scallop shell, and lime-based expansive admixture tend to exhibit different expansion characteristics. More specifically, mortar containing scallop shell or expansive admixture expanded continuously. In contrast, mortar containing surf clam shell expanded rapidly in an environment with abundant water, such as that directly after mixing, but then did not expand further unless water was newly supplied. Burned shell is CaO, which is the same as the main component in the lime-based expansive admixture. However, before firing, HP is aragonite-type CaCO$_3$ and SP is calcite-type CaCO$_3$. SP is therefore considered to exhibit expansion characteristics similar to those of the lime-based expansive admixture, which is presumed to have been manufactured from a similar calcite-type CaCO$_3$. These differences in expansion characteristics could potentially be used to precisely control the concrete volume such that it would be possible to inhibit volumetric change in a particular stage of the hydration process.

### 4. Evaluation of Ca(OH)$_2$ in mortars

#### 4.1 Thermogravimetric-differential thermal analysis

Figure 3 shows the results of a thermogravimetric-differential thermal analysis (TG-DTA) of Ca(OH)$_2$ carried out on mortars aged 7 days with a 10% replacement ratio. The TG-DTA was
conducted with an airflow of 25 ml/min and a temperature ramping rate of 10 °C/min, and
alumina was used as the reference material.

Whereas the ordinary mortar contained about 1% Ca(OH)$_2$, the mortars with a 10% replacement ratio all contained approximately 2.0% Ca(OH)$_2$. In brief, mixing burned shell powder or expansive admixture into the mortar increases the amount of Ca(OH)$_2$, which is the cause of expansion, but no correlation is found between the expansion amounts. This indicates that expansion appears not to occur simply due to the formation of a large quantity of Ca(OH)$_2$.

4.2 Powder X-ray diffraction (XRD)

Figure 6 shows the XRD results of N, HP10, SP10, and B10 aged 7 days. All of the mortars show clear Ca(OH)$_2$ peaks, but the Ca(OH)$_2$ peak at approximately 18° is very large for HP10, which showed extraordinary expansion. The 18° peak is also large for B10, although not as large as for HP10. The 18° peak value is usually the second peak of Ca(OH)$_2$, but it becomes the strongest peak depending on the crystal orientation. These results suggest not only an increase in the amount of Ca(OH)$_2$ produced but also the crystalline structure is important in generating the expansion. However, further consideration will be needed to yield any findings about this reasoning.
4.3 Scanning electron microscopy (SEM)

Photo 3, 4, and 5 are SEM images of fracture surfaces of HP10, SP10, and B10. Large numbers of needle crystals ranging in size from several $\mu$m to 10 $\mu$m were identified in all of these fracture surfaces. Needle crystals are generally considered to be ettringite, but in
ettringite, most needle crystals are several \( \mu \text{m} \) in size. The crystals found in these powders are thought to differ from typical ettringite because of their large size. Additionally, comparing the SEM images for HP10, SP10, and B10, the crystals in HP10 and SP10 are relatively larger, but the length and shape of the crystals are similar.

The XRD results identified large peaks near the \( \text{Ca(OH)}_2 \) peak values of 18°, 34°, and 50° in all of the specimens. Peaks were also identified near the ettringite peak values of 9°, 15°, and 18° in B10. This is considered to be because the low dosage-type lime-based expansive admixture contains approximately 16% SO₃, as shown in Table 1, so the environment is such that ettringite forms easily. HP10 and SP10 contain very little SO₃, so no ettringite peaks were identified for those powders. Because large amounts of needle crystals were found in the SEM images, if the needle crystals in HP10 and SP10 were assumed to be ettringite, there would be large peaks near the ettringite peak values of 9°, 15°, and 18°. Therefore, it is considered likely that the needle crystals identified in the HP10 and SP10 specimens are not ettringite.

It is appropriate to consider the cause of expansion in mortar containing burned shell powder to be the formation of \( \text{Ca(OH)}_2 \). \( \text{Ca(OH)}_2 \) is generally considered to be a hexagonal plate-like crystal, but taking into account the TG-DTA and XRD results, it is reasonable to conclude that the needle crystals are related to \( \text{Ca(OH)}_2 \). This suggests the possibility that when an admixture with a reaction mode that is not dependent on the usual cement hydration reaction is used, the crystal morphology is different from usual, and care must be taken when determining materials solely by shape.

5. Conclusion

In this study, mortars containing burned surf clam shell and burned scallop shell powders were manufactured, and experiments regarding the expansion characteristics of these mortars were carried out. The results can be summarized as follows:

- For a given amount of shell powder added, there are differences in the amount of mortar expansion between surf clam shell and scallop shell, with the former causing expansion at lower added amounts.
- The results of the restrained expansion test showed that the mortar containing burned surf clam shell has the greatest expansion rate from pouring to mold removal. Additionally, with regard to expansion due to underwater curing after mold removal, all of the mortars expanded significantly for 1 day from the start of underwater curing, and there did not appear to be any large difference in the expansion rates. However, the mortars containing burned surf clam shell did not subsequently expand at all, whereas the mortars containing burned scallop shell and expansive admixture continued to gradually expand.
- The results of the length change test using a corrugated mold showed that the mortar containing burned surf clam shell displayed the greatest amount of expansion until an age of 1 day, but hardly changed in length after that. The mortars containing burned scallop shell and expansive admixture expanded less than the mortar containing burned surf clam shell, but gradual yet continuous expansion was identified after 1 day.
The quantitative TG-DTA showed that when the mortars have a replacement ratio of 10% or more, roughly the same amount of Ca(OH)₂ is formed. However, in HP10, which showed extraordinary expansion, the powder X-ray diffraction peak at 18° was large, suggesting that not only an increase in the amount of Ca(OH)₂ formed, but also the crystalline structure is important in generating expansion.

SEM observations identified needle crystals ranging in size from several μm to 10 μm in the mortars containing burned shell powders. Because no ettringite peaks were identified in the powder X-ray diffraction, it is inferred that the needle crystals are not ettringite. It is likely that they are related to Ca(OH)₂, which is the cause of the expansion.

References

ECO-CONCRETE FOR PRECAST ELEMENTS WITH EFFECTIVE MINERAL MICRO- AND ECO-FILLERS

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Abstract
One essential requirement of precast concrete is a high early age strength, usually reached by a high content of fine Portland cement (OPC). In times of climate change, however, a reduction of the global warming potential GWP and demand of primary energy PE of concrete is a desirable goal that can be reached by a low content of OPC. In this study it is shown, how mineral micro-fillers (MFs) in combination with so-called eco-fillers (EFs) can help to reduce the content of OPC of precast concrete leading to a reduction of GWP (up to -24 %) and PE (-14 %) while keeping an early age strength as high as that of a standard precast concrete. It is analysed how different fillers, depending on their fineness and type, influence the early- age- (i.e. 8 h with heat treatment), 28 d- strength, workability and demand of superplasticizer. Powder-materials of limestones, dolomites and ground granulated blast-furnace slag were used as very fine MFs (d_{50} < 3 \mu m) and EFs (3 \mu m \leq d_{50} \leq 30 \mu m).

1. Introduction
The purpose of this study is to develop eco-friendly precast concrete with high early-age strength, suitable workability and with low environmental impact compared to normal concrete acc. to Austrian standards the ÖNORM B 4710-1, which is the national application of EN 206-1. To achieve this goal so-called micro- and eco-fillers which are declared as inert and ground granulated blast-furnace slag (GGBFS) as hydraulically active powder were used. The mix design method in acc. to [1] was used to improve the packing density and workability of pastes, implicitly of concrete. The average particle diameter of MFs should be sufficiently small to fill the voids of the cement particles (or mixture of cement and other particles that represents the paste) and to enhance packing density [1].
Several authors [2], [3] and [4] have shown the influences of fine limestone on the hydration of cement pastes. This is comprising an increase of the compressive strength at early ages. This effect can be explained as an interaction between the calcium silicate phases (alite) and calcium carbonate (CaCO$_3$), which accelerates the hydration of C$_3$S and modifies the Ca/Si ratio of C-S-H [3]. [5], [6] and [7] showed principles of designing ecological concrete by particle packing optimization and ordinary Portland cement (OPC) reduction. With an optimized mix, the water and cement content of a concrete mix can be reduced while maintaining the same or even a higher w/c-ratio. This leads to a reduction of the w/p-ratio (water/powder-ratio).

In this study we investigated how fine mineral powders may affect the packing density, influence the early-age-compressive strength and the 28 d compressive-strength development of pastes and concretes. Furthermore it was analysed if the same consistency class of concrete can be achieved with optimized pastes while maintaining the same sand-, gravel- and recycling materials-content, superplasticizer amounts.

2. Materials characterisation

Possible materials, which can partly substitute OPC in concrete according to the principles mentioned above, were investigated concerning their GWP (global warming potential, CO$_2$-equivalent) and PE (primary energy input) by a software designed for life cycle analysis (LCA) [8] and according to ISO 14044 : 2006. For details see [9], results in Table 1.

For particle packing optimization, grain fineness (see Fig. 1), packing densities of source materials and the interaction of very fine particles are decisive [5]. The particle size distributions of materials was made by laser diffraction with a HELOS H2395, which recognized the particles bigger than 0.45 $\mu$m. Blaine values were measured in accordance to EN 196-6. The used cements were a CEM I 52,5 R and a CEM II/A-S 52,5 N containing about 95 % and 80 % of clinker, respectively.

Table 1 shows properties of source materials covered in this paper. The values for water demand $V_{ws}/V_p$, which is the volume of water at saturation point and $V_{w,f,i}/V_p$, which is the volume of water for a certain flowability and $V_p$, $V_b$, $V_c$ and $V_{clinker}$ which are the volumes of powder, binder, cement and clinker in water-powder mixes, were determined in accordance to [1]. This method combines the so-called “mixing energy method” (MEM) of Marquardt [10] which can be used to determine the void content of a powder by its water demand at the saturation point, with the “spread flow test” (ST) according to the procedure of Okamura [11] for determining the flowability and the strength of the paste.
Figure 1: Particle size distribution of used materials

Table 1: Properties of investigated materials

<table>
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<th>type</th>
<th>material</th>
<th>density $\rho_0$ [g/cm$^3$]</th>
<th>mean diameter $d_{50}$ [μm]</th>
<th>Blaine-value $V_{w,v}/V_p$</th>
<th>water demand (void content) $V_{w,v}/V_p$</th>
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<th>PEI [MJ/t]</th>
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</table>
3. Methods

For the pastes, the spread flow (fi) is determined on a dry glass plate with a Hägermann cone (according to EN 1015-3 but without any shocks). Additionally the corresponding water demand (Vwf,i/Vp) is recorded. Water-powder mixes with different spread flows were manufactured and prisms 40/40/160 mm were cast, to test the compressive strength (n=3 specimen) after 24 hours acc. to EN 196-1. It was ensured, that no desegregation of the fresh pastes and no bleeding occurred.

The specified fresh and hardened concrete properties were determined according to ONR 23303 [12]. The flow value after 30 min (A30) was checked by the flow-table test (EN 12350-5 : 2009) in order to ensure the workability for a sufficiently long period in the production process, in addition to the flow value after 10 minutes (A10). The ratio value of A30 min to A10 min has given a characteristic of "maintaining consistency". The compressive strength of concretes was tested on concrete cubes (150 mm, average of n = 3 cubes), manufactured and stored acc. to ONR 23303 [12] ( 3 samples of each mix /series were heat-treated after production to 8,0 hours at about 35 ° C). As an indicator for the durability performance, the open porosity was determined in accordance to EN 1936 (Natural stone test methods).

4. Results of eco-paste and eco-concrete

A way to demonstrate the equivalence of eco-concrete or eco-paste with standard-concrete or standard-paste is to compare criteria for performance in terms of workability and strength. For this study, the reference is a concrete with a maximum grain size of 16 mm designed with w/b of 0,53; see details in Table 2 and Table 3. This type of concrete is defined in ÖNORM B 4710-1 to be exposed to moderate water pressure, rain, frost and a weak chemically corrosive environment (XC3/XD2/XF1/XA1L). This standard-concrete belongs to the type of typical standard concretes for precast elements in a consistency class “F 45”- soft consistency with a mean spread diameter of 45 cm on the flow table - reached with a typical dosage of superplasticizer (0,5 M% of cement) in the mix.

Table 2 contains the results of the mix proportions, the recipe parameters and the properties of pastes in terms of workability, strength and fineness of three main categories: ref I- (with OPC 2), eco I-A- (OPC2 : LE : MF) and eco I-B (OPC1 : GGBFS : LE : MF)-category. The I- A and the I-B category include three different pastes, which distinguish themselves through the fineness of micro filler (MF), but have the same values of recipe parameters (Vw/Vclinker, Vw/Vl and Vw/Vp).

Table 3 shows the mix proportions of the reference concrete and of eco-concretes with ecologically optimized paste compositions and different type of eco- and micro-fillers. Each optimized granular powder-mix has a higher packing density (lower Vwf,i/Vp) and a lower w/p-ratio (or lower Vwf,i/Vp) than the paste of the reference concretes. The OPC-pastes and eco-pastes from Table 2 were used to produce concretes of constant workability with constant volume of paste, air content and sieve line of the aggregates. The consistency of concrete was adjusted to a desired (F45) value by adding superplasticizer (see Table 3).
**Table 2: Mix proportions and pastes performance results**

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<td>4760</td>
<td>4276</td>
<td>5073</td>
<td>4800</td>
<td>4437</td>
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</table>

* - (M %) = OPC + 0,8*GGBFS  
** - Blaine-value (powder mix) = \( \Sigma \) (volumetric fraction of each powder * Blaine powder of each powder)

**Table 3: Mix proportions and concrete performance results**

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<th>Ref.</th>
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<th>II-A1</th>
<th>II-A2</th>
<th>II-A3</th>
<th>II-B1</th>
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<td>70/0/</td>
<td>234</td>
<td>235</td>
<td></td>
</tr>
<tr>
<td>CEM II/A-S 52,5 N</td>
<td>-</td>
<td>330</td>
<td>255</td>
<td>255</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GGBFS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>37</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>limestone eco</td>
<td>-</td>
<td>72,8</td>
<td>109</td>
<td>75</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>limestone micro</td>
<td>-</td>
<td>36</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>dolomite micro</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
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<tr>
<td>fine aggregate &lt; 0,1mm</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>36</td>
<td></td>
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<tr>
<td>sand (0-4)</td>
<td>708</td>
<td>778</td>
<td>778</td>
<td>768</td>
<td>694</td>
<td></td>
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<tr>
<td>gravel (4-8)</td>
<td>727</td>
<td>793</td>
<td>793</td>
<td>783</td>
<td>732</td>
<td></td>
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<tr>
<td>gravel (8-16)</td>
<td>94</td>
<td>89</td>
<td>89</td>
<td>88</td>
<td>88</td>
<td></td>
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<tr>
<td>recycling material (0-16)</td>
<td>176</td>
<td>154</td>
<td>154</td>
<td>159</td>
<td>161</td>
<td></td>
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<tr>
<td>water (total)</td>
<td>1,62</td>
<td>2,16</td>
<td>2,25</td>
<td>1,71</td>
<td>1,75</td>
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<tr>
<td>w/b by mass</td>
<td>0,532</td>
<td>0,605</td>
<td>0,605</td>
<td>0,604</td>
<td>0,607</td>
<td></td>
</tr>
<tr>
<td>Vw/vc by volume</td>
<td>1,703</td>
<td>1,935</td>
<td>1,936</td>
<td>2,110</td>
<td>2,122</td>
<td></td>
</tr>
<tr>
<td>Vw/vc by volume</td>
<td>-</td>
<td>1,703</td>
<td>1,935</td>
<td>1,936</td>
<td>1,856</td>
<td>1,866</td>
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<tr>
<td>Vw/vp by volume</td>
<td>-</td>
<td>1,49</td>
<td>1,16</td>
<td>1,15</td>
<td>1,13</td>
<td>1,15</td>
</tr>
<tr>
<td>flow spread (flow table) with SP [mm]</td>
<td>431</td>
<td>520</td>
<td>450</td>
<td>470</td>
<td>540</td>
<td></td>
</tr>
<tr>
<td>compressive strength 5h (with heat treatment) [MPa]</td>
<td>9,2</td>
<td>12,5</td>
<td>9,7</td>
<td>14,5</td>
<td>12,1</td>
<td></td>
</tr>
<tr>
<td>compressive strength 28d (fcp,28d) [MPa]</td>
<td>45,1</td>
<td>55,3</td>
<td>52,4</td>
<td>62,6</td>
<td>61,8</td>
<td></td>
</tr>
<tr>
<td>open porosity %</td>
<td>17,4</td>
<td>13,6</td>
<td>13,7</td>
<td>13,7</td>
<td>13,5</td>
<td></td>
</tr>
<tr>
<td>GWP [kg CO₂/m³]</td>
<td>260</td>
<td>206</td>
<td>205</td>
<td>204</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td>PE [MJ/m³]</td>
<td>1399</td>
<td>1227</td>
<td>1219</td>
<td>1198</td>
<td>1205</td>
<td></td>
</tr>
</tbody>
</table>
5. Performance of eco-paste and -concrete based on workability, strength and ecological impact

The results of testing the paste- and concrete-properties are presented in Table 2 and Table 3. The performance counters early-age- and (28 d)- strength, spread flow by paste without and by concrete with compacting energy, consistency, GWP and PEI for all mixtures, are plotted, as normalized, graphically (see Figure 4 and Figure 5) related to the value of the reference-paste and -concrete.

The evaluation of the series I (pastes) showed equal or better performance regarding early-strength (24 h) compared to reference paste ref. I. The early-strengths (24 h) of eco I-A1 and eco I- A2, due those two different micro-fillers, were increased up to 36 %. Although the early –strengths (24 h) of eco I-A3 remain at the same value of the reference pastes, the OPC content is 30 % less, which implies a better environmental performance.

In case of eco I-B series (developed with OPC 1) significant increases of 24 h- compressive strength (32 - 61 %) were reached, while the workability was nearly equal to the reference paste ref. I (made with OPC 2).

The evaluation of the series II (concretes) showed equal or better performance regarding early-strength (8,0 h with HT), 28 d- strength, open porosity and ecological impact compared to the reference concrete ref. I. The early-strength increased between 30 to 40 % and the GWP could be reduced by approximately 20 % (eco I-A1, eco I- B1, eco I–B2). A similar reduction was achieved even for the eco I-A2-concrete, made CEM II/A-S 52,5 N (OPC2). For the development of eco-concretes with CEM I 52,5 R (OPC 1), eco I-B1 and eco I-B2 from series I the substitution of cement by GGBFS, LE and LM or DM was 37,5 %, while the amount of superplasticizer was equal to the reference concrete ref. I (made with CEM II/A-S 52,5 N). Consequently the environmental impact of eco I- B1 und eco I- B2 regarding the GWP and PE values was reduced about 24 and 14 %, respectively.

Figure 4: performance series I (paste) Figure 5: performance series II (concrete)
6. Discussion

Compared to the findings in [3] relating to limestone, the mixes in this paper with very fine micro-fillers of limestone powder (eco II-A1) and of dolomite powders (eco II-B1), reached high fcp (8 h)/fcp (28 d)-ratios (see also Figure 5). This implies that not only limestone but also dolomite as very fine micro-fillers have a significant influence on the early-age-strength (8 h with HT) while this effect is not as prominent for the 28 d-strength. Lothenbach [2] explained this effect with the “enhanced nucleation”. This means that particularly for fine materials, the extra-surface provided may act as nucleation sites for hydration products at early ages. In addition to that, we assume that enhanced packing density plays a major role. The thickness of the water film surrounding particles in packing-optimized pastes is thin and the cement spacing is low which seems to influence the speed of early strength development.

Teichmann [13] found a maximum effect of the fine micro-filler (in his case a quartz powder d₀ = 2,4 μm) on the 28 d-strengths in comparison to ref. paste with OPC CEM I 32,5 R and OPC CEM I 32,5 R + inert filler (with the same fineness as the cement). Teichman [13] achieved the maximum effect of the fine micro-filler especially with low w/c-value = 0,35 of the pastes. In our paper, contrary to [13], the eco pastes (w/b = 0,61) had not the same value compared to ref. paste (w/c=0,53). However, w/p-values were decreased in both studies.

Within a linear function fcor, see eq. (1), three terms are considered. For all terms, results of the eco-pastes are related to the reference-paste. The function is plotted versus the compressive strength fcp (24h), see Fig. 6(b).

\[
f_{\text{cor}} = \frac{\omega_{(\text{eco})}}{\omega_{(\text{ref})}} + \frac{\psi_{(\text{eco})}}{\psi_{(\text{ref})}} + \frac{\text{Blaine}_{(\text{ref})}}{\text{Blaine}_{(\text{eco})}}
\] (1)

The first term is the volumetric water/clinker-ratio (\(\omega = \frac{V_{w,fi}}{V_{\text{clinker}}})\). Values of \(\omega_{(\text{eco})}/\omega_{(\text{ref})}\), higher than 1,0 show, that a higher \(V_{w,fi}/V_{\text{clinker}}\)-ratio of a powder mix has a decreasing effect on the (24 h) compressive strength. Because of the two different clinker contents of the used cements (CEM I 52,5 R and CEM II/A-S 52,5 N) the \(V_{w,fi}/V_{\text{clinker}}\)-ratio is a better indicator on the early strengths than the \(V_{w,fi}/V_{\text{cement}}\)-ratio. The second term is the volumetric water/powder-ratio (\(\psi = \frac{V_{w,fi}}{V_{p}}\)). Values lower than 1,0 indicate a positive effect of \(V_{w,fi}/V_{p}\) of eco pastes related to reference on the (24h) compressive strength of pastes. The third term \(\frac{\text{Blaine}_{(\text{ref})}}{\text{Blaine}_{(\text{eco})}}\) shows, by values lower than 1,0, the positive effect of increasing fineness of eco-paste related to reference on the (24 h)-compressive strength. It is assumed that each of the three terms influences the 24 h compressive strengths of pastes having the same weighting.

The correlation between function fcor and strength fcp (24 h) is remarkably higher (R²=0.97) than the correlation of \(V_{w,fi}/V_{\text{clinker}}\)-ratio (see Table 2) and strength (R²=0.54), see Fig. 6(b). Higher \(V_{w,fi}/V_{\text{clinker}}\)-ratios reached higher compressive strengths, which is not in accordance to well-known experience and literature [14]. A functional relation is derived acc. to eq. (2).
Since pastes initially had different workabilities, a certain amount of superplasticizer had to be added to the concrete mixes in order to achieve a spread flow of 45cm. It is remarkable that for the reference- and eco-pastes (eco I-B1 and eco I-B2) with a constant spread-flow the same amount of superplasticizer (1.6 kg/m³) was needed to achieve the same consistency class of concrete.

The open porosity as a durability indicator was reduced by approximately 20 % for all eco-concretes compared to the corresponding reference concrete. The pH-values of all investigated concretes (reference and ecos) were nearly constant for all mixes (pH=12.6±0.1), which indicates a sufficient corrosion protection for steel reinforcements [1]. Future research will determine whether the usage of fine limestone and dolomite as micro-filler will have a decisive impact on durability tests such carbonation depth.

7. Conclusion and Outlook

Very fine limestone as well as dolomite powders, micro-filler with d₉₀ < 3 μm, are capable of accelerating the strength development of clinker- reduced pastes and concretes effectively. A linear function fcp (24 h) (see equation (2) and Figure 6(b)) can be used to precisely estimate the early-age-compressive strengths of pastes based on the compressive strength of the mix design parameters \( \frac{V_w}{V_{clinker}} \), \( \frac{V_w}{V_p} \) and Blaine-values of the pastes. Our results have shown that the effect of high early-strength mainly depended on the fineness of the mineral powders and not on the mineral type of limestone or dolomite.

In this study it was shown, that an ecological optimization by using eco- and micro-fillers increased the 24 h - compressive strength up to 60 %, while maintaining a similar workability compared to the reference paste. Superplasticizer was not used in higher dosages.

Another finding of this study is that sand, gravel and recycling materials (0/16 mm) did not “disturb” the optimized pastes in terms of achievable workability and strengths. OPC-pastes
and eco-pastes of constant workability may be used to produce concrete of constant workability if the volume of paste, air content and sieve line of aggregates is constant. The consistency of the concrete could be adjusted to a desired value by adding superplasticizer while the demand of superplasticizer was equal for OPC- and eco-pastes with equal workability.

The open porosity of all eco-concretes was 20% lower than the reference concrete. This is indicative for sufficient durability.

**Summed up essential findings:**

- reduction of $V_w/V_p$ (i.e. enhanced packing density and reduced water demand) enhanced the early age strength despite of an increase of $V_w/V_{clinker}$
- increased early-age-strength was reached with a very fine limestone powder as well as a dolomite powder. The grade of fineness seems to influence the early-age strength improvement while the mineral type seems not to be significant.
- the following parameters have to be considered to predict early-age-compressive-strength (24h) of paste; so that a functional relationship was derived:
  1) $V_w/V_{clinker}$
  2) $V_w/V_p$
  3) fineness

The aim of improving ecological performance (GWP ↓ and PE ↓), while keeping even early-age-strength at the level of the reference concrete was reached or exceeded.

**Acknowledgements**

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THE EFFECT OF SCM REPLACEMENT ON AUTOGENOUS DEFORMATION OF HIGH PERFORMANCE CONCRETE

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Abstract

High-performance concrete (HPC) typically has a low water to cementing materials ratio (w/cm), high binder content and may contain high levels of supplementary cementitious materials. Therefore, it can be more vulnerable to early-age cracking due to higher early-age deformations resulting from autogenous and drying shrinkage as well as thermal gradients. In this study, HPC was made with two types of blended cements containing 8% SF mixed with two types and replacement levels of GGBFS (25%, 50%) by mass of cement at 0.33 w/cm. Linear autogenous deformation was measured at constant temperature using a copper mould (75x75x500mm) with circulating cooling water (in order to decouple autogenous from thermal deformation). It was found that early-age volume change increased as the fineness of blended cement and the GGBFS increased.

1. Introduction

High cement content HPC with low w/cm less than 0.36 can undergo significant reduction in internal relative humidity (self-desiccation), and therefore an increase in early-age volume change. The risk of autogenous deformation in the HPC can adversely influence the crack resistance and durability of reinforced concrete structures; autogenous deformation is a significant component of volume changes [1, 2, 3, 4]. HPC normally include different supplementary cementitious materials (silica fume, slag, etc). Several studies show that silica fume (SF) replacement increases the early age deformation [5, 6, 7]. However for ground granulated blast-furnace slag (GGBFS), contradictory findings have been observed in the literature. Some studies showed a reduction in autogenous deformation when cement is partially replaced by GGBFS while others showed improved early-age shrinkage. Wu et al. [8] observed a reduction in chemical shrinkage for low-alumina content slag cement (9.5%) versus OPC. On the other hand, opposite behaviour was observed by Lee et al. [9] with high alumina content of GGBSF (14.6%), with autogenous shrinkage increases up to 37% at 50% replacement of cement. A study was conducted at University of Toronto by Perez [10] with
two types of slag with two alumina contents (high level 13.6%, and low level 10.2%). The low-alumina slag mixture exhibited less drying shrinkage in comparison to the one with high-alumina slag.

Several test methods [11, 12, 9, 13, 14] to measure autogenous shrinkage at isothermal conditions were developed previously. Table 1 presents the specimen dimensions, presence of insulation/or not, and the test temperature for these previous experiments used to decouple the thermal deformation from autogenous deformation. The test set up used in this paper intend to reduce the prism cross section and increase the number of copper loops in order to reduce the temperature difference between the copper wall and the centre of the specimen to be 0.5±0.25 °C to ensure sufficient decoupling of autogenous and thermal deformation. Section 2 explain the detailed test set up and the experimental program.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample Size (W x H x L) mm</th>
<th>Insulation thickness (mm)</th>
<th>Temperature °C</th>
<th>Decoupling technique To maintain Constant Temperature</th>
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<tbody>
<tr>
<td>[11]</td>
<td>100x100x620</td>
<td>100</td>
<td>20</td>
<td>controlled water circulation</td>
</tr>
<tr>
<td>[12]</td>
<td>100x100x500</td>
<td>35</td>
<td>20</td>
<td>controlled water circulation</td>
</tr>
<tr>
<td>[13]</td>
<td>150x150x1000</td>
<td>40</td>
<td>10, 20, 30, 40</td>
<td>controlled water circulation</td>
</tr>
<tr>
<td>[9]</td>
<td>100x100x400</td>
<td>N.A.</td>
<td>20±1</td>
<td>controlled room temp.</td>
</tr>
<tr>
<td>[14]</td>
<td>100x100x400/and 100x100x1200</td>
<td>N. A.</td>
<td>20</td>
<td>controlled room temp.</td>
</tr>
</tbody>
</table>

This study focuses on the effect of using different levels of slag replacement, and it is part of an ongoing experimental research study on the early volume change of HPC in bridge decks.

2. Test set-up and experimental program

2.1 Autogenous Deformation Apparatus
A schematic drawing of the test set up and mould cross section for measuring autogenous strain are presented in Figures 1a and 1b. Shrinkage was measured using concrete prisms of 75x75x500 mm. An insulated isothermal chamber was controlled with a constant temperature 20 °C water bath. The water was circulated through the copper tubes welded to outer walls of the copper mould. The copper walls were insulated with 50mm thick Styrofoam. The length change was measured at both ends (using external Linear Variable Deferial Transducers (LVDTs)) in addition to an embedded strain gauge in the middle of the prism (see Figure 1b). The LVDTs were connected to stainless steel pins embedded in the concrete at each end of the prism.
The mould was oiled (to minimize friction between the copper wall and the specimen), and was lined with one layer of plastic sheet. Test results on identical mixes showed that this apparatus has good reproducibility with an error of 1-3%.

2.2 Experimental Program

The experimental program was designed to assess the autogenous deformation of HPC mixtures for up to 168 hours. The cement binder included CSA A3000 blended portland cement interground with 8% silica fume (Type GUb-SF8) and ground granulated blast furnace slag (GGBFS). HPC mixtures were made using two sources of GUb-SF8 blended cements used together with 25 and 50% by mass replacement levels of GGBFS. The blended cement and slag were mixed at a water/binder ratio of 0.33. Table 1 shows the chemical and physical properties for the blended cements and slag. Table 2 shows mixture proportions of the HPC concretes. Superplasticizer and water reducing admixtures were used to maintain slump at 150±15 mm and to provide efficient dispersion. The concrete mix proportions are shown in Table 2. Coarse aggregates of 19mm nominal maximum size were selected as the standard size for this research project, as it is typically used by Ministry of Transportation Ontario (MTO) bridge decks. The coarse aggregate was pre-washed to achieve saturated state dry surface. The fine aggregate was natural sand with 4.75mm maximum nominal size, its absorption and its finesses modulus were 1.12%, and of 2.8, respectively.

3. Test results and discussion

Figure 1 presents the autogenous strains of the embedded strain gauge vs time of the different HPC mixtures (at controlled isothermal temperature of 20 °C). The ΔT (between the copper wall and middle of the concrete cross section) is less than 0.75 °C. In the Figure, the solid lines represent the HPC mixtures with 25% GGBFS replacement with the two different cements (A&C) and dotted lines represent mixtures with 50% slag replacement. The rate of autogenous strain increases rapidly in all the specimens between 4 and 12 hours of age. The higher the GGBFS replacement percentage, the lower the autogenous strain. As expected, the
concrete with the higher fineness blended cement exhibited greater autogenous strain. The results are in agreement with previous studies [5, 6, 7], the higher silica fume contents (when 25% GGBFS was used), the greatest autogenous deformation. The C-25GGBFS exhibits a higher rate of strain within the first 24 hours in comparison to the low fineness cement A-25GGBFS. The higher GGBFS replacement slows down the reaction at early age and therefore reduces the ultimate autogenous strain.

### Table 2. Blended Cement and GGBFS Properties

<table>
<thead>
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<th>Cement ID</th>
<th>Cement Type GU8SF</th>
<th>GGBFS</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>GU8SF A</td>
<td>GU8SF C</td>
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<tr>
<td>Blaine Fineness (m²/kg)</td>
<td>585</td>
<td>787</td>
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<td>LOI</td>
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<tr>
<td>SiO₂</td>
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<tr>
<td>Al₂O₃</td>
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<td>4.72</td>
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<tr>
<td>Fe₂O₃</td>
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<td>2.23</td>
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<td>CaO</td>
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<td>56.71</td>
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<tr>
<td>MgO</td>
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<td>2.23</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.7</td>
<td>4.07</td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total Alkali (Na₂Oeq)</td>
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### Table 3. Concrete Mixtures

<table>
<thead>
<tr>
<th>Cement binder proportion</th>
<th>Cement GU8SF (kg/m³)</th>
<th>Slag (kg/m³)</th>
<th>Fine Aggregate (kg/m³)</th>
<th>Coarse Aggregate (kg/m³)</th>
<th>Water (kg/m³)</th>
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</thead>
<tbody>
<tr>
<td>GU8SF (A)+25%GGBFS</td>
<td>349 (6% SF)*</td>
<td>116</td>
<td>624</td>
<td>1065</td>
<td>153</td>
</tr>
<tr>
<td>GU8SF (A)+50%GGBFS</td>
<td>232.5 (4%SF)</td>
<td>232.5</td>
<td>621</td>
<td>1067</td>
<td>153</td>
</tr>
<tr>
<td>GU8SF (C)+25%GGBFS</td>
<td>349 (6%)</td>
<td>116</td>
<td>622</td>
<td>1068</td>
<td>153</td>
</tr>
<tr>
<td>GU8SF (C)+50%GGBFS</td>
<td>232.5 (4%SF)</td>
<td>232.5</td>
<td>623</td>
<td>1066</td>
<td>153</td>
</tr>
</tbody>
</table>

*Note: %SF means the actual silica fume content of overall cement binder
Figure 3 shows the correlation between the strain measured by the embedded strain gauge and the combined strain measured by the two lvdt. An excellent linear correlation was found however, the lvdt strains give higher values that those from the embedded strain gauge. Using embedded strain gauges have potential for more accurate measurement of autogenous shrinkage as they are not affected by external sources of error as the external lvdt including variations in room temperature ($23 \pm 2^\circ C$) that may affect the lvdt cores and connecting rods.

4 Conclusions

Autogenous strains of four HPC mixtures were measured at constant temperature. Concrete containing 25% GGBFS replacement showed higher development of strain at early-age and that is attributed to the higher (6%) silica fume content. Higher slag replacement (50%) and
lower silica fume content (4%) reduced the overall ultimate autogenous strain by 40-50%.
Embedded strain gauges exhibited a good correlation with the external LVDT readings.

Acknowledgements
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CALCINED DREDGED SEDIMENTS AS SUPPLEMENTARY CEMENTITIOUS MATERIALS: PROPERTIES AND POZZOLANIC REACTIVITY

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Abstract
Dredging of ports, harbours and waterways generates large amounts of sediments that find few applications and need to be disposed of. The dredging sediments in this study originated from the port of Antwerp, contained mainly SiO2, CaO, Al2O3 and Fe2O3 and comprised as major mineral phases clays (2:1 clays and kaolinite), quartz, calcite and an amorphous phase. Sulfur and chloride contents were relatively low. Flash calcination at 820, 865 and 905°C reduced the total organic carbon fraction but did not alter the content of chloride and sulfate. The calcination treatment resulted in the dehydroxylation of the clay minerals and partial decarbonation of the calcite. Part of the CaO released in the decomposition of the calcium carbonates reacted with the dehydroxylated clays to form an amorphous, partially vitrified calcium-aluminosilicate reactive phase. Melt formation and sintering were more extensive at higher calcination temperatures (865 and 905°C); however this did not change the particle size distribution significantly, but did lead to a remarkable reduction in the BET specific surface area and related particle surface roughness. The calcined dredging sediments showed a pozzolanic reactivity superior to that of Class F fly ash as demonstrated in a lime reactivity test by isothermal conduction calorimetry. The reactivity test clearly demonstrates the elevated potential of calcined dredged sediments as a new pozzolanic SCM for the production of low–CO2 blended cements.

1. Introduction
Dredging, treatment and disposal of harbour sediments is a continuous and costly operation which is unavoidable to access to ports. At present dredging sediments are mostly landfilled or disposed of in marine repositories because of a combination of properties that make their use as raw material difficult. Challenges are high water contents, potential presence of
pollutants (organics, heavy metals), and variations of the properties of the dredged sediments (composition, granulometry).

Dredged sediments are generated at large volumes. For the whole of Europe the yearly amount of dredging sediments is estimated at 300 Mt. In the port of Antwerp (Belgium) maintenance of waterways by dredging of sediments generates about 450.000 t (dry matter) each year. The dredging operations in the port of Antwerp are preceded by an extensive sampling campaign to determine the degree of contamination of the sediments in place. Contaminated sediments can thus be separately dredged and strictly separated from non-contaminated sediments. Next, the dredged sediments are treated to 1) separate the sand fraction (>63 μm) and 2) mechanically dewater the fine fraction (<63 μm) by membrane filter presses in the AMORAS facility, located in the port of Antwerp. The AMORAS dredging sediment treatment scheme is shown in Figure 1. Several process steps (temporary deposition and mixing in underwater cells and settling ponds) results in extensive homogenisation of the treated sediments. A long term sampling campaign has shown that the final filter cake residue is homogeneous and constant in composition and granulometry over time. At present the filter cakes are landfilled in a disposal site and new applications are sought to avoid capacity problems at the longer term.

Figure 1. Treatment scheme for dredging sediments at the AMORAS site (Port of Antwerp).

New applications should be able to cover the generated volumes of filter cakes. In this respect the filter cakes could be used as raw material for construction materials, and in particular for producing cement and concrete. Cements blended with supplementary cementitious materials (SCMs) derived from industrial residues such as coal fly ash and iron blast furnace slag are commonly used. New SCMs are being tested to cut costs and the environmental impact of Portland clinker production. One SCM type that has received much attention recently is calcined clays. Among the many clay types, kaolins have proven to be the most reactive in
combination with cement when properly calcined (650-850 °C) [1]. Other clay minerals, such as illite were found to be less reactive when calcined [2].

This paper reports on the potential use of flash calcined filter cakes from the port of Antwerp as SCMs. First, the physical and chemical properties of the untreated and the calcined filter cakes are determined; next, the results of a new calorimetry based lime reactivity test are described.

2. Materials and methods

A representative sample of the filter cakes was selected for activation by flash calcination. Three calcination temperatures were assessed: 820, 865, and 905 °C. Henceforth, the resulting samples are designated as "FC 820", "FC 865" and "FC 905", respectively. Before calcination the filter cake was dried at 110 °C until constant mass and subsequently ground.

The dry matter content of the filter cake was determined by drying at 105°C until constant mass. The chemical composition was determined by ICP-OES and anion chromatography. The specific surface area was measured using multi-point BET N$_2$ adsorption. Both the chemical composition and the specific surface area are reported in Table 1.

XRD data were collected using a X’Pert PRO diffractometer (CuKα). Rietveld analysis was performed using HighScore Plus software following [3]. The external standard approach was used to determine the amorphous phase content. The phase quantification results are given in Table 2.

Electron microscopy was carried out on carbon coated, resin impregnated polished sections. A FEI Quanta 200 scanning electron was used in back scattered electron (BSE) mode.

The pozzolanic reactivity of the calcined filter cakes was evaluated by measuring the heat release of the exothermic pozzolanic reaction in a model mix of calcined filter cake and Ca(OH)$_2$ with additional alkalis and sulfate. Alkalis and sulfates are added to simulate the environment of Portland cement reaction. A hydration temperature of 40 °C was applied to accelerate the pozzolanic reaction and reduce experimentation times. The heat release was measured up to 5 days of reaction using a TAM air isothermal calorimeter. The mix design and operational procedures are further detailed in [4]. For comparison an unreactive sample of ground quartz and a regular siliceous Fly ash (class F) are included.

3. Results and discussion

3.1. Properties of flash calcined dredged sediments

The mechanical dewatering of the dredged sediments produces filter cakes in which the measured dry matter (dm) content was 66 ± 3 mass%. The filter cake contained mainly SiO$_2$. The other major chemical components were CaO, Al$_2$O$_3$ and Fe$_2$O$_3$. The elevated Loss On
Ignition (LOI) value is due to significant levels of bound water, organic carbon compounds and inorganic carbonates. Some amorphous phase is present, this is partly related to minor amorphous silica (micro-organism) and nano-crystalline clay minerals and iron (hydr)oxides typical products of weathering processes. Upon calcination the organic carbon compounds are decomposed and volatilized, reducing the total organic carbon level to 0.25 ± 0.06 mass%. Sulfur and chloride contents were relatively low. The sediments were dredged from brackish water; however, most of the chloride was removed with the water during the mechanical dewatering. Flash calcination at 820-905°C did not significantly reduce chloride and sulfur contents of the material. However, due to low chloride content of the initial filter cakes the calcined material complied with the regulations for non-reinforced and regular reinforced concrete. When used in combination with a low Cl-clinker the resulting cement can also comply for pre-stressed reinforced concrete (Cl <0.1 wt.%) [5].

The BET specific surface area results for the calcined filter cakes are shown in Table 1. Here, significant changes were noted among calcination temperatures. The higher the calcination temperature, the lower the specific surface area. This is beneficial for low water demand of fresh concrete mix, hereby for the workability of fresh concrete.

### Table 1: Chemical composition and BET specific surface area of raw filter cake, the filter cake flash-calcined at 820, 865 and 905 °C and the reference fly ash class F.

<table>
<thead>
<tr>
<th>Material</th>
<th>FC 820 (wt.% dm)</th>
<th>FC 865 (wt.% dm)</th>
<th>FC 905 (wt.% dm)</th>
<th>Fly ash F (wt.% dm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>37</td>
<td>53.69</td>
<td>54.34</td>
<td>54.12</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10</td>
<td>10.43</td>
<td>10.15</td>
<td>10.71</td>
</tr>
<tr>
<td>CaO</td>
<td>12</td>
<td>12.48</td>
<td>12.24</td>
<td>13.32</td>
</tr>
<tr>
<td>MgO</td>
<td>1.6</td>
<td>1.71</td>
<td>1.71</td>
<td>1.82</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.8</td>
<td>8.69</td>
<td>8.28</td>
<td>8.66</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.5</td>
<td>0.81</td>
<td>0.78</td>
<td>0.82</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.9</td>
<td>2.11</td>
<td>1.94</td>
<td>2.13</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.8</td>
<td>0.89</td>
<td>0.97</td>
<td>0.99</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.2</td>
<td>1.50</td>
<td>1.52</td>
<td>1.57</td>
</tr>
<tr>
<td>Cl</td>
<td>0.1</td>
<td>0.14</td>
<td>0.16</td>
<td>0.19</td>
</tr>
<tr>
<td>TOC</td>
<td>3.6</td>
<td>0.31</td>
<td>0.25</td>
<td>0.18</td>
</tr>
<tr>
<td>LOI</td>
<td>22</td>
<td>2.90</td>
<td>2.10</td>
<td>2.39</td>
</tr>
<tr>
<td>BET (m²/g)</td>
<td>-</td>
<td>8.95</td>
<td>4.98</td>
<td>3.35</td>
</tr>
<tr>
<td>D₅₀ (μm)</td>
<td>7.2</td>
<td>17.6</td>
<td>16.8</td>
<td>19</td>
</tr>
</tbody>
</table>

The phase quantification results of the Rietveld analysis are given in Table 2. The XRD patterns clearly demonstrated a structural decomposition of the main clay minerals. At the
lowest calcination temperature of 820 °C all kaolinite and more than a half of the 2:1 clays (illite) were decomposed. At higher temperatures this decomposition was more complete as reflected by the decreasing content of 2:1 clays and the increasing amorphous fraction in Table 2. This amorphous fraction constituted about half of the calcined material and slightly increased with calcination temperature up to 905 °C.

Calcium carbonates (calcite, aragonite) were largely decomposed in the calcination process. A few percent of calcite remained after calcination. Part of the CaO released in the decomposition of the calcium carbonates reacted with sulfate to form anhydrite. A small amount of free lime was found in the calcined samples.

Table 2. Phase composition of untreated and flash calcined filter cakes and the fly ash.

<table>
<thead>
<tr>
<th>Phase composition (wt.%)</th>
<th>Filter cake</th>
<th>FC 820</th>
<th>FC 865</th>
<th>FC 905</th>
<th>Fly ash F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz (SiO₂)</td>
<td>20</td>
<td>26</td>
<td>27</td>
<td>25</td>
<td>13</td>
</tr>
<tr>
<td>Alkali feldspars ((Na,K)AlSi₃O₈)</td>
<td>4</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Calcite (CaCO₃)</td>
<td>13</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Other carbonates</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite (FeS₂)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anhydrite (CaSO₄)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Free lime (CaO)</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-oxides (hem/mag) (Fe₂O₃/Fe₃O₄)</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:1 clay (illite)</td>
<td>34</td>
<td>14</td>
<td>6</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Kaolinite (Al₂Si₂O₅(OH)₄)</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mullite (Al₄₋₂Si₂₋₂O₁₀₋₄₋₃)</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous</td>
<td>17</td>
<td>45</td>
<td>49</td>
<td>51</td>
<td>71</td>
</tr>
</tbody>
</table>

A representative BSE image of FC 865 is shown in Figure 2. The polished section shows cross-sections of microspheres, particle aggregates and homogeneous quartz grains. The spheres were mostly hollow with many irregular smaller cavities. Gas formation within (partially) molten droplets resulted in inflation and formation of hollow particles. This process is well-known from fly ashes produced in coal combustion or municipal solid waste incineration. In contrast, the agglomerate particles were composed of many smaller particles and did not show signs of melting. Next to spheres and aggregates also larger, angular and compositionally homogeneous particles were observed. These correspond to quartz and feldspar grains.
3.2. Pozzolanic reactivity of flash calcined dredged sediments

Since the pozzolanic reaction is exothermic, measuring the heat release of a model system consisting of the SCM, excess portlandite and water and added alkalis and sulfates enables to directly monitor the reactivity of the SCM.

The calorimetry test results in Figure 3 give the heat release from the pozzolanic reaction of the calcined dredged sediments at fixed times of 1 and 3 days. These are compared to the heat release for a well-known SCMs such as fly ash from coal combustion and inert quartz powder. It can be observed that the calcination temperature had little effect on the pozzolanic reactivity. Compared to the other SCMs, the calcined dredging sediments were found to be significantly more reactive than the regular siliceous fly ash commonly used as SCM.
Flash calcination of the dredged sediment filter cakes from the port of Antwerp is considered as a potentially viable means to produce an alternative SCM for the production of low-CO$_2$ blended cements. The main conclusions of this study are that:

- Flash calcination reduced the total organic carbon content by 85% or more. Sulfate and chloride levels are essentially the same before and after calcination. Chloride levels were below limit values for use in regular non-reinforced and reinforced concrete.
- An X-ray amorphous phase formed during calcination makes up the main part of the calcined material. Other major phases were quartz and feldspars. Minor phases present were calcite (CaCO$_3$), free lime (CaO) and anhydrite (CaSO$_4$).
- Increasing the calcination temperature from 820 to 905 °C had little impact on the chemical or mineralogical composition, nor on the pozzolanic reactivity.
- Increasing the calcination temperature leads to a significant decrease of the BET specific surface area.
- Unexpectedly, solidified glass spheres indicated that melting of some particles occurs during flash calcination. Next to melting also sintering occurred. Both melting and sintering explained the decrease in specific surface area at higher temperatures.
The pozzolanic reactivity of the calcined dredged sediments was surprisingly found to be superior to siliceous fly ash in a calorimetry based pozzolanic reactivity test. This is a first promising step in finding a viable application of the dredged sediment filter cake as SCM.

References


HIGH VOLUME FLY ASH HYBRID ALKALI ACTIVATED CEMENTS AND CONCRETES FOR INDOOR APPLICATION

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(2) National Aviation University of Ukraine.

Abstract
Fly ash is one of the most shared wastes in the world. Traditional technologies makes it possible to replace about 30% of the cement by fly ash, but alkali activated cements could content up to 70% of fly ash by volume. It had been developed such high volume fly ash alkali activated cements and concretes on their basis, but there were no studies on radiation impact of such material, especially for indoor application. Present paper discloses applicability of fly ash alkali activated cements for indoor application.

1. Introduction
Coal ash is one of the larger residues in the world. Total volume of ash in the storages only in Ukraine – about 400 million ton and rising [1]. But this waste has very low level of utilization and so it is just storing in the fields.

Fly ashes are divided in two groups by chemical composition – high-calcium with CaO content over 10% by mass (class C according to ASTM classification) and low-calcium ashes (less then 10% of CaO, class F). High-calcium ashes have low binding properties and could be used as binder materials for manufacture construction with low strength demands. Low-calcium ashes have no binding properties in normal conditions and thus they should be activated in some way. Low-calcium ashes are dominating in the whole volume of ashes being produced.

At present time fly ash is a typical constituent of the cement. It is well-know that maximal content of fly ash in OPC type could be up to 35%, and 55% – for OPC type IV. Fly ash – sulfate – silica cements allows to use up to 65% of ash. However, such cements have a lot of problems in service properties (setting times and others). So, they are not so effective and
could not be used widely. Prof. Glukhovskii offers to produce fly ash alkaline-alkali earth activated cements, which could content to 70% of fly ash (in our days, such cements mostly called hybrid alkali activated cements). And a higher content have alkali activated cements (named soil silicates, geocements or geopolimers). They are able to content 90% of ash. But these materials have difficult technology of manufacture, require temperature curing, and so they could be used only for special application. For indoor application there are recommended hybrid alkali activated cements.

That is why as an object of given studies were taken hybrid alkali activated (alkaline-alkali earth) fly ash cements and concretes on their basis.

2. Experimental

A typical class F fly ash from a Ukrainian power plant was used (chemical composition is shown in Table 1), with Blaine specific surface of 800 m$^2$/kg. Characterizations of the raw materials are given in Fig.3.

There were two different Ca-containing additives used:

• type I OPC, with a compressive strength of 50 MPa measured by a standard method;
• ground (450 m$^2$/kg) blast furnace slag (GGBS).

Hybrid alkali activated cement was manufactured by joint grinding of all the components in the ball mill.

Mathematical plan of experiment and analysis of results were done using program “Statistica 5.0”.

Table 1: Chemical compositions of fly ash.

<table>
<thead>
<tr>
<th>Name</th>
<th>Content of oxides, % by mass</th>
<th>LOI, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(No 1) Fly ash of hydroremoval</td>
<td>SiO$_2$: 47.01, TiO$_2$: 0.97, Al$_2$O$_3$: 17.04, Fe$_2$O$_3$: 8.15, FeO: 0.23, MnO: 1.41, MgO: 3.05, CaO: 0.48, Na$_2$O: 1.60, K$_2$O: 0.32, P$_2$O$_5$: 0.06, SO$_3$: 2.47</td>
<td></td>
</tr>
<tr>
<td>(No 2) Fly ash of dry removal</td>
<td>SiO$_2$: 48.20, TiO$_2$: 0.89, Al$_2$O$_3$: 19.65, Fe$_2$O$_3$: 4.50, FeO: 3.15, MnO: 0.11, MgO: 1.36, CaO: 2.18, Na$_2$O: 1.04, K$_2$O: 2.78, P$_2$O$_5$: 0.02, SO$_3$: 0.11, FeO: 16.02</td>
<td></td>
</tr>
<tr>
<td>(No 3) Fly ash of dry removal</td>
<td>SiO$_2$: 50.94, TiO$_2$: 0.94, Al$_2$O$_3$: 24.56, Fe$_2$O$_3$: 13.25, FeO: - 0.03, MnO: 1.98, MgO: 2.86, CaO: 0.69, Na$_2$O: 2.69, K$_2$O: 0.02, P$_2$O$_5$: - 1.36</td>
<td></td>
</tr>
<tr>
<td>(No 4) Fly ash of hydroremoval</td>
<td>SiO$_2$: 39.99, TiO$_2$: 1.04, Al$_2$O$_3$: 13.85, Fe$_2$O$_3$: 12.86, FeO: 0.02, MnO: 1.96, MgO: 3.54, CaO: 1.40, Na$_2$O: 2.30, K$_2$O: 0.19, P$_2$O$_5$: 0.38, SO$_3$: 0.18, SO$_3$: 21.86</td>
<td></td>
</tr>
<tr>
<td>(No 5) Portland cement PC I-500</td>
<td>SiO$_2$: 23.40, TiO$_2$: - 5.17, Al$_2$O$_3$: 4.12, Fe$_2$O$_3$: - - 0.88, FeO: 64.13, MnO: 0.41, MgO: 0.33, CaO: - 0.55, Na$_2$O: 0.20, K$_2$O: - 1.62, SO$_3$: -</td>
<td></td>
</tr>
<tr>
<td>Granulated blast furnace slag</td>
<td>SiO$_2$: 39.40, TiO$_2$: 0.26, Al$_2$O$_3$: 6.80, Fe$_2$O$_3$: 0.32, FeO: 0.32, MnO: 5.19, MgO: 47.38, CaO: 0.60, Na$_2$O: 0.52, K$_2$O: - 1.62, SO$_3$: -</td>
<td></td>
</tr>
</tbody>
</table>
3. Results and discussion

The very important question of alkali activated cement application is that they should meet standard requirements for ordinary cements, because most customer in present time are not ready to change their traditional recipes and technologies. So there was done an experiment on influence of composition of hybrid alkali activated cement on fly ash basis (type and quantity of Ca-containing component) on service properties of cements. The results of tests are given in Table 2 and Figure 2.

Table 2: Characteristics of hybrid alkali activated cements.

<table>
<thead>
<tr>
<th>Nos</th>
<th>Portland cement clinker</th>
<th>Ash - No 3</th>
<th>GBS</th>
<th>Na₂CO₃</th>
<th>Plastici- cizer</th>
<th>Paste of normal consistency, %</th>
<th>Initial setting time, min</th>
<th>Flow (cone), mm W/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>60</td>
<td>40</td>
<td>5</td>
<td>1</td>
<td>25.7</td>
<td>75</td>
<td>115/0.34</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>60</td>
<td>30</td>
<td>5</td>
<td>1</td>
<td>25.5</td>
<td>70</td>
<td>112/0.34</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>80</td>
<td>-</td>
<td>5</td>
<td>1</td>
<td>26.7</td>
<td>80</td>
<td>108/0.31</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>70</td>
<td>-</td>
<td>5</td>
<td>1</td>
<td>26.0</td>
<td>75</td>
<td>110/0.32</td>
</tr>
<tr>
<td>5</td>
<td>OPC CEM II/A-400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>27.8</td>
<td>85</td>
<td>112/0.38</td>
</tr>
</tbody>
</table>
As it seems from the given results, cements under study are similar on their characteristics to the OPC. They have similar paste on normal consistency, initial setting times, compressive strength. However, composition with fly ash and GGBS has very low strength and could not be recommended for application (in case of using of sodium carbonate as an alkaline component). Such service properties could be explained by phase composition of hybrid cements. Results of X-RAY and DTA tests are given in Figure 3. All tests were done after 28 days of normal hardening.

Analysis of the results of physical-chemical studies shows, that phase composition of hybrid cements is mostly represented by CSH (B) \( (d = 0.304; 0.299; 0.281; 0.203; 0.18 \text{ nm}) \), \( \text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O} \) \( (d = 0.188; 0.273; 0.274; 0.418 \text{ nm}) \), \( \text{NaCa}_2[\text{Si}_3\text{O}_8(\text{OH})] \) \( (d = 0.290; 0.274; \) ...
0.192 nm) and the rests of $\beta$-SiO$_2$ from the initial fly ash composition ($d = 0.424; 0.334; 0.245; 0.212$ nm).

Also it was studied influence of type of alkaline activator on structure of hybrid cements on fly ash basis. The results of SEM analysis (Figure 4) have shown that composition with the sodium metasilicate have more fine crystalline structure comparing with those with sodium carbonate and mix of alkaline components. Their structure is denser; crystals have different dimensions and provide higher service properties of hardened stone, first of all, compressive strength (Figure 5).

![Figure 4: SEM images of hybrid cement specimens aged 28 day: a) soda ash (5% by mass); b) sodium metasilicate (5% by mass); c) sodium metasilicate (6% by mass) + soda ash (4% by mass).](image)

It is objective that different type and quantity of an alkaline component make a great influence on compressive strength of the cement, so as also type of curing. It is observed that steam curing of hybrid cements leads to the lost of compressive strength at 30...40%.

The best variants of alkaline components are sodium carbonate and mix of sodium carbonate and metasilicate. They provide formation of denser structure, as it shown before, and higher service properties. Sodium metasilicate itself is not effective in such systems.

However, cement systems on sodium carbonate and sodium metasilicate shows mostly equal strength, so there is now reason to use more expensive mix of alkalis. For the next tests could be recommended cement composition with the soda ash as an alkaline component.

Test results of optimization of alkaline component content in the hybrid cement are given in Figure 5 (b).

Analysis of given results suggested to show that 1% of alkali at this system is not enough for normal hardening. Optimal quantity of sodium carbonate it is between 4 and 5% by mass of the cement. Introducing of 7% of alkaline component to the cement here seems to be not effective because of very small increasing of service properties and higher price. Also that could lead to obtaining some problems with service properties in the future.
As a result of provided studies and chemical composition of raw ashes the conclusion could be done, that for equal condition of tests the higher strength it is obtained for cements with the higher volume of silica and alumina oxides in the ash (Table 3). The compressive strength of cements of their basis can vary from 25 to 40 MPa depending on ash (No 4 and No 3). However, analysis of properties of cements on the basis of ashes No 3 and No 1 shows that compressive strength is not only function of chemical composition of fly ash. Also there are others very important characteristics: glass content in the ash, content of mullite and other crystalline phases, content of unburned particles. That is why ash from dry removal technology is better for hybrid cement production than ash from hydro removal scheme.

Table 3: Cement compressive strength (28 days) vs. content of (SiO\textsubscript{2} + Al\textsubscript{2}O\textsubscript{3}) of fly ash.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>No 4</th>
<th>No 2</th>
<th>No 1</th>
<th>No 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2} + Al\textsubscript{2}O\textsubscript{3}, %</td>
<td>53.84</td>
<td>60.66</td>
<td>75.24</td>
<td>75.91</td>
</tr>
<tr>
<td>Soda ash (5 % by mass)</td>
<td>24.60</td>
<td>28.70</td>
<td>35.00</td>
<td>40.90</td>
</tr>
</tbody>
</table>

Taking into account all listed below fly ash No 3 was taken as a main component of cement for the next studies. It were chosen two cement compositions with different quantity of fly ash and type of Ca-containing component and provided studies of possibility of replacement Portland cement clinker by OPC type I. The composition and results of study are given in Table 4.

As it seems from the given results, it absolutely possible to replace clinker by OPC Type I cement due to the almost similar results of service properties tests. Moreover, using of OPC as a constituent of hybrid alkali activated cements on fly ash basis make it possible to have a little bit wider setting times and also higher initial compressive strength.
Replacing of Portland cement clinker by OPC Type I is very important because this make it possible to simplify technology of hybrid cement manufacture. There will be no reason to find the ways to buy clinker and ground it somewhere. It is much easily to take and industrial product with the known properties.

Table 4 Properties of hybrid fly ash alkali activated cements.

<table>
<thead>
<tr>
<th>CaO-containing additive</th>
<th>FA No3</th>
<th>Soda ash</th>
<th>plasticizer</th>
<th>Paste of normal consistency, %</th>
<th>Initial setting time, min</th>
<th>Flow value (cone), mm W/C</th>
<th>Strength, Rcomp/Rflex, MPa, after hardening for ≤ 2 days 3 years</th>
<th>Steam curing (80°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (portland cement clinker)</td>
<td>70 5 0.75</td>
<td>26.0</td>
<td>I-02</td>
<td>110</td>
<td>0.32</td>
<td>2.00</td>
<td>1.09</td>
<td>19.4</td>
</tr>
<tr>
<td>30 (PC-500)</td>
<td>70 5 0.75</td>
<td>26.0</td>
<td>I-30</td>
<td>106</td>
<td>0.34</td>
<td>4.12</td>
<td>1.44</td>
<td>20.6</td>
</tr>
<tr>
<td>10 (portland cement clinker)</td>
<td>60 5 0.75</td>
<td>26.3</td>
<td>I-10</td>
<td>107</td>
<td>0.33</td>
<td>4.08</td>
<td>1.08</td>
<td>24.4</td>
</tr>
<tr>
<td>10 (PC-500)</td>
<td>60 5 0.75</td>
<td>25.0</td>
<td>I-20</td>
<td>112</td>
<td>0.34</td>
<td>5.40</td>
<td>1.20</td>
<td>25.5</td>
</tr>
</tbody>
</table>

On the basis of taken cement (with OPC as a calcium component) it was made mix design of concrete composition. Compositions of concrete and test results are given in Table 5.

Table 5: Properties of concretes on the basis of hybrid fly ash alkali activated cements.

<table>
<thead>
<tr>
<th>CaO-containing additive in concrete</th>
<th>Concrete composition,% by mass</th>
<th>Slump</th>
<th>Strength, Rcomp., MPa, after hardening for ≤ 2 days 3 years</th>
<th>Steam curing (80°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement Sand Aggregate 5...10 mm Aggregate 10...20 mm</td>
<td>mm</td>
<td>2 days 7 days 28 days 3 years</td>
<td></td>
</tr>
<tr>
<td>30 (PC-500)</td>
<td>350 780 330</td>
<td>830</td>
<td>12</td>
<td>12.8</td>
</tr>
<tr>
<td>10 (PC-500)</td>
<td>350 780 330</td>
<td>830</td>
<td>12</td>
<td>14.4</td>
</tr>
</tbody>
</table>

As it seems from the taken results, fly ash AAC concretes are showing high strength grows even after 28 days of hardening.

However, good strength is not only factor for judgment about application ability of material. Ecological aspects of using materials are also very important.
There were done no studies on radiological characteristics of AAFA concretes for common application. However, we could make some calculation using room model [12] and so as we know radiological characteristics of raw materials.

Table 6: Radiological characteristics of raw materials [13].

<table>
<thead>
<tr>
<th>Material</th>
<th>Activity, Bq/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ra</td>
</tr>
<tr>
<td>Fly ash</td>
<td>149.0</td>
</tr>
<tr>
<td>Slag</td>
<td>225.7</td>
</tr>
<tr>
<td>OPC</td>
<td>45.5</td>
</tr>
<tr>
<td>Sand</td>
<td>15.1</td>
</tr>
<tr>
<td>Granite aggregate</td>
<td>50.6</td>
</tr>
</tbody>
</table>

According to the results of provided study, activity concentration index ACI of the cement with higher content of fly ash (66.2% by mass of cement) is a little bit higher then 1...1.27, so there should be done some extra calculation to make conclusion about this material possibility to be used for indoor application. For the other cement with 56.7% of fly ash ACI=0.987, so it could be used for indoor application without any limits.

However, we never use cement as itself, we use some materials on cement basis. So it was done calculation on AAFA concrete radiological characteristics (using room model).

Calculation results suggested to show that both concrete under study (using two types of cement) have ACI lower than 1...0.885 and 0.839 for concrete on the basis of cement with fly ash content 66.2 and 56.7% by mass respectively.

Thus a way both types of concretes could be used for indoor application without any limits.

4. Conclusions

Possibility of use different types of fly ash Class F was shown. It is set that the most effective way of hybrid alkali activated cement on fly ash basis manufacture is using of ashes from dry removal technology with high glass content and small content of unburned particles.

Physical-chemical analysis of cement structure shows that new formation of hybrid cement are represented by CSH (B), \( \text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_8\cdot4\text{H}_2\text{O} \), NaCa[Si3O8(\text{OH})] and the rests of \( \beta\text{-SiO}_2 \) from the initial fly ash composition. Also it is found that sodium carbonate provides achievement of denser structure than in case of using of sodium metasilicate.
It is set that optimal content of sodium carbonate in the cement composition lays within the ranges 4…5% by mass, allowing to obtain initial setting times over 1 hour and compressive strength at 28 das about 40 MPa.

It was shown possibility to replace Portland cement clinker in the hybrid cement composition by OPC Type I without losing of service properties, making it possible to simplify technology of such cement manufacture.

There were shown possibility of concretes on fly ash alkali activated basis to be used for indoor application without any limits.

Acknowledgments
The authors would like to acknowledge the contribution of the COST Action TU1301.

References


PHYSICAL AND MECHANICAL PROPERTIES OF CEMENT MORTARS WITH BIOMASS ASHES AS SCM

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Abstract
Utilization of biomass ashes as building material or as raw material in the manufacture of building products can be regarded as a sustainable form of utilization as the use of ashes saves the use of non-renewable resources, reduces the amount of agricultural waste and CO₂ emission. Significant agricultural residues of field production in Serbia are: wheat straw, corn cobs, soy straw, sunflower husk and oil rape straw. The study contains data on physical properties, chemical characteristics and pozzolanic properties of sunflower straw and husk, soya and wheat straw and mixture of soya and wheat straw. Comparative analyses of the results of their pozzolanic activity tests have influenced further use of wheat straw and mixture of wheat and soya straw as supplementary cementitious materials in preparation of mortars. This paper also presents experimental research of influence of chosen biomass ashes on physical and mechanical properties of cement mortars. A comparative analysis of compressive strength, drying shrinkage and capillary water absorption of cement mortars was conducted. Content of ashes was varied from 10 to 30% in relation to cement mass. The results suggest that the biomass ashes can be used in mortars as substitutes of cement without compromising their mechanical performances.

1. Introduction
In recent years, extensive research has been conducted on industrial byproducts and other waste materials which are suitable for use as binder substitutes in cement formulations. The use of these materials brings a number of benefits including reduced cost and a reduction in the environmental impacts caused by waste disposal and cement production. The cement industry is responsible for a significant proportion of carbon dioxide (CO₂) released into the atmosphere. Utilization of industrial by-products substitutes natural resources and provides an alternative for natural minerals [1]. Currently, supplementary cementitious materials (SCMs), particularly industrial by-products, are used to partially replace Portland cement in concrete. Fly ash, silica fume, and slag are
examples of SCMs that are waste products from industrial processes. However, these materials are not available in large quantities at a low cost uniformly around the world. Natural SCMs such as volcanic ash, calcined clays, and agricultural residue ash are gaining more attention for use as SCMs because of their low cost, availability, and excellent reactivity in concrete. Every year, millions of tonnes of agricultural residues such as corn stover, wheat straw, and rice straw are produced worldwide. Agricultural residue ash such as corn stover ash, rice straw ash and wheat straw ash are potential resources for SCM production [2]. Based on the physical, chemical and morphological properties, it is reported that biomass ash, an industrial by-product of thermal power industries, has a substantial potential for use as a pozzolanic mineral admixture and/or as an activator/binder in cement-based materials [3]. The average production of biomass waste from agriculture, per year in Vojvodina is around 9 million tons, while the same potential, in Serbia, is estimated at almost 13 million tons. This study contains data on physical properties, chemical characteristics and pozzolanic properties of sunflower straw and husk, soya straw, wheat straw and mixture of soya and wheat straw. Comparative analyses of the results of the pozzolanic activity tests have influenced further investigation of wheat straw and mixture of wheat and soya straw ashes as supplementary cementitious materials in preparation of mortars. Most of this paper presents experimental research of physical and mechanical properties of cement mortars with biomass ashes as supplementary cementitious materials.

2. Experimental investigation

Biomass ashes used in this experimental study were obtained from the three largest manufacturers of biomass ash in Serbia. In the first phase of the experiment, the following properties for selection of appropriate ashes were tested:
- Basic physical properties (density, specific surface area),
- Chemical composition and
- Pozzolanic activity.
After determining physical, chemical and pozzolanic properties of all biomass ashes, two of them (wheat straw ash and mixed soya and wheat straw ash) were selected as supplementary cementitious materials for preparation of mortars. The following properties were investigated on hardened mortars:
- Pore size distribution at the age of 28 days,
- Compressive strength at different ages (7, 28, 60, 90 and 180 days),
- Capillary water absorption at the age of 28 days,
- Shrinkage of up to 60 days.

2.1 Methods
Specific surface area of biomass ashes was determined according to Blaine air permeability method given in standard SRPS EN 196-6 [4]. The chemical composition of ashes was determined using EN 196-2 [5] and ISO 29581-2 [6]. The pozzolanic activity of biomass ashes was determined using standard SRPS B.C1.018-2001[7]. According to this standard first step was testing of pozzolanic activity of mixture of cement (mc) and potential pozzolana (m_pozz) in proportion mc:m_pozz=1:1. Testing procedure is given in standard EN 196-5. After the positive pozzolanic activity was obtained, the class of
pozzolanic material was determined based on 7 day compressive ($f_{cm}$) and flexural ($f_{fm}$) strength of standard mortar prisms (SRPS B.C1. 018-2001). Mortars were prepared with following mass proportions: $m_{sl}:m_{bash}:m_{ss} \approx 1:2:9$ and water/binder ratio 0.6 (where: $m_{sl}$ – mass of slaked lime; $m_{bash}$ – mass of biomass ash; $m_{ss}$ – mass of CEN standard sand). Specimens were hermetically packed and cured 24h on 20°C, then 5 days on 55°C. After cooling of specimens in next 24h up to 20°C, compressive and flexural strength were tested. The pore size distribution was determined by mercury intrusion porosimetry (Hg Porosimeter Carlo Erba 2000 WS, Italy), diameter range of 0.02–200 μm. Mortar samples were oven-dried at 50°C for three days. At this temperature the C-S-H structure, ettringite and other hydration products should remain, while the pore structure could be coarsened and micro-cracks could be made due to generation of thermo-hydric stresses.

Compressive strength of all types of mortars was tested according to EN 196-1 [8]. Samples for testing of compressive strength were cured in water to the anticipated age. Drying shrinkage of all investigated mortars is tested in accordance with procedure described in SRPS B.C8.029 [9]. Measurements of length changes were conducted on standard mortar prisms after 3, 4, 7, 14, 21, 28, 35, 42, 49 and 56 days. During the experiment the specimens were kept in climate chamber at the temperature of 20°C and 70% relative humidity.

The rate of water absorption of mortars was determined using a test method described in ASTM C1585 [10]. Water absorption was determined on 100mm diameter disc, with a length of 50 mm, at the age of 28 days, in time intervals for a total of 8 days. Initial measurements were made at intervals of 1, 5, 10, 30 and 60 minutes, and every hour up to 6h from the first contact of the specimens with water, followed by daily measurements for 8 days.

### 2.2 Component materials

For experimental investigation of biomass ashes as supplementary cementitious materials, the following materials were used:
- Portland cement CEM I 42,5R (Lafarge-BFC Serbia),
- Wheat straw ash (P), “Mitrosrem” Sremska Mitrovica, Serbia, Fig.1,
- Soya straw ash (S), “Mitrosrem” Sremska Mitrovica, Serbia,
- Mixed soya and wheat straw ash (PS), “Sojaprotein” Bečej, Serbia, Fig.2,
- Sunflower husk ash from the chimney (PSuLJD), “Mitrosrem” Sremska Mitrovica,
- Sunflower husk ash from the furnace (PSuLJL), Oil mills plant “Srpska Crnja” Serbia,
- Standard sand in accordance with EN 196-1 [8],
- Superplasticizer HRWRA (SikaViscoCrete 3070, Sika Switzerland),
- Distilled water.

Figure 1: Wheat straw ash, divided in fractions.  
Figure 2: Mixed soya and wheat straw ash.
All raw biomass ashes were prepared by drying and sieving. Within experiment the fraction 0-0.125mm was used.

2.3 Mix proportions for mortars

The experimental study was carried out on seven mortar mixtures. Reference mortar (E) was prepared with Portland cement as binder, standard sand and water. In three mortar mixtures (P10, P20 and P30) the part of cement was replaced with 10%, 20% and 30% of wheat ash (P). In the remaining three mortars (PS10, PS20 and PS30) the part of cement was replaced with mixed wheat and soy straw ash (PS), likewise. The mix proportions of these seven mortars are given in Table 1.

Table 1: Labels and compositions of mortar mixtures.

<table>
<thead>
<tr>
<th>Mortar type</th>
<th>E</th>
<th>P10</th>
<th>P20</th>
<th>P30</th>
<th>PS10</th>
<th>PS20</th>
<th>PS30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement, g</td>
<td>450</td>
<td>405</td>
<td>360</td>
<td>315</td>
<td>405</td>
<td>360</td>
<td>315</td>
</tr>
<tr>
<td>Wheat ash, g</td>
<td>-</td>
<td>45</td>
<td>90</td>
<td>135</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wheat and soy ash, g</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>45</td>
<td>90</td>
<td>135</td>
</tr>
<tr>
<td>Water, g</td>
<td>225</td>
<td>225</td>
<td>225</td>
<td>225</td>
<td>225</td>
<td>225</td>
<td>225</td>
</tr>
<tr>
<td>Standard sand, g</td>
<td>1350</td>
<td>1350</td>
<td>1350</td>
<td>1350</td>
<td>1350</td>
<td>1350</td>
<td>1350</td>
</tr>
<tr>
<td>Superplasticizer, g</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>2.025</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1 Physical properties, chemical composition and pozzolanic properties

Table 2 shows physical properties of tested biomass ashes. Ashes P, S and PS showed significantly higher values of specific surface area than PSuLJD and PSuLJL ashes, but lower bulk density values. Ash PSuLJD has a slightly higher specific mass than PSuLJL ash. P and PSuLJ ashes showed slightly higher specific mass than others with specific mass around 2400 kg/m³. Bulk density values are inversely proportional to the specific surface area.

Table 2: Physical properties of tested biomass ashes.

<table>
<thead>
<tr>
<th>Ash</th>
<th>Specific mass (kg/m³)</th>
<th>Bulk density (kg/m³)</th>
<th>Specific surface area (Blaine) (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>2340</td>
<td>452.3</td>
<td>4369</td>
</tr>
<tr>
<td>P</td>
<td>2400</td>
<td>255.3</td>
<td>7580</td>
</tr>
<tr>
<td>S</td>
<td>2600</td>
<td>303.1</td>
<td>7661</td>
</tr>
<tr>
<td>PSuLJD</td>
<td>2420</td>
<td>641.0</td>
<td>2819</td>
</tr>
<tr>
<td>PSuLJL</td>
<td>2610</td>
<td>540.6</td>
<td>2493</td>
</tr>
</tbody>
</table>

Content of SiO₂, Al₂O₃, Fe₂O₃ oxides has the greatest importance for potential pozzolanic materials. The chemical composition of tested biomass ashes is given in Table 3. PS and P ashes have the highest values of the total amount of those oxides, while PSuLJ ashes contain...
lowest amount of mentioned oxides among the tested biomass ashes. PSuLJ ashes have higher Na$_2$O and K$_2$O content than PS.

The content of alkaline oxides (Na$_2$O and K$_2$O) and alkaline earth oxides (CaO and MgO), loss of ignition and the sulfates content are particularly pronounced within PSuLJ ashes. Presence of high amount of K$_2$O (18.43%), low content of Al$_2$O$_3$ (0.19%) and significant content of SiO$_2$ (51.93%) in P ash most likely lead to the glass formation at relatively low temperatures. Baxter and Jenkins [11] point out that the formation of the glassy phase occurs when the ratio of oxide is SiO$_2$/K$_2$O $>4:1$. Among tested biomass ashes, closest ratios are obtained for P and S ashes, Table 3. The formation of glassy phase and not so high temperature in the boiler during combustion (760°C) lead to a greater amount of amorphous phase and greater pozzolanic activity.

Table 3: Chemical composition of tested biomass ashes (wt% of ash).

<table>
<thead>
<tr>
<th>Ash (%)</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Other</th>
<th>LOI</th>
<th>SiO$_2$/K$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>53.21%</td>
<td>4.00%</td>
<td>2.69%</td>
<td>13.45%</td>
<td>1.90%</td>
<td>0.23%</td>
<td>0.41%</td>
<td>12.05%</td>
<td>1.75%</td>
<td>10.19%</td>
<td>4.40</td>
</tr>
<tr>
<td>P</td>
<td>51.93%</td>
<td>0.19%</td>
<td>1.39%</td>
<td>14.28%</td>
<td>2.07%</td>
<td>1.15%</td>
<td>0.43%</td>
<td>18.43%</td>
<td>1.67%</td>
<td>9.27%</td>
<td>2.82</td>
</tr>
<tr>
<td>S</td>
<td>13.80%</td>
<td>1.76%</td>
<td>1.45%</td>
<td>47.53%</td>
<td>7.76%</td>
<td>0.44%</td>
<td>0.07%</td>
<td>5.23%</td>
<td>2.99%</td>
<td>18.60%</td>
<td>2.63</td>
</tr>
<tr>
<td>PSuLJD</td>
<td>1.04%</td>
<td>0.29%</td>
<td>0.79%</td>
<td>33.77%</td>
<td>8.15%</td>
<td>2.69%</td>
<td>0.48%</td>
<td>28.15%</td>
<td>3.36%</td>
<td>21.73%</td>
<td>0.04</td>
</tr>
<tr>
<td>PSuLJL</td>
<td>1.77%</td>
<td>0.43%</td>
<td>1.25%</td>
<td>30.63%</td>
<td>11.18%</td>
<td>3.70%</td>
<td>0.32%</td>
<td>27.76%</td>
<td>3.50%</td>
<td>19.68%</td>
<td>0.06</td>
</tr>
</tbody>
</table>

After confirming positive pozzolanic activity of tested biomass ashes, mechanical properties (compressive and flexural strength) were tested to define pozzolanic material Class (Table 4). Only P and PS ashes have Class 5 (criteria: $f_{cm} \geq 2MPa$ and $f_{cm} \geq 5MPa$). Other ashes had low mechanical properties that were not sufficient to express through Class.

Table 4: Mechanical properties of tested biomass ashes.

<table>
<thead>
<tr>
<th>Ash (%)</th>
<th>PS</th>
<th>P</th>
<th>S</th>
<th>PSuLJD</th>
<th>PSuLJL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{cm,avg}$ [MPa]</td>
<td>2.58</td>
<td>2.96</td>
<td>1.038</td>
<td>0.828</td>
<td>0.852</td>
</tr>
<tr>
<td>$f_{cm,avg}$ [MPa]</td>
<td>6.25</td>
<td>7.2</td>
<td>2.5</td>
<td>2.35</td>
<td>2.35</td>
</tr>
</tbody>
</table>

3.2 Pore size distribution

Total porosity of tested mortar types, as well as percentage share of macropores ($D>50nm$) and mesopores and micropores ($D<50nm$), according to [12], is presented in Table 5. Results indicate that the total porosity increases as content of wheat straw ash and soy straw ash increases, which should cause an impact on the mechanical properties and permeability of these mortars. The pore-size distribution, in Figure 3, indicates that the dominant pores interval for all samples is from 0 to 0.06μm. Biomass ashes contribute to the larger pores quantity increase. However, due to the pozzolanic properties of the ashes, as content of C-S-H products increases, content of pores smaller than 30nm is also increased. This pore size is too small to have an adverse effect on the strength and permeability of the hydrated cement paste.
However, these small voids are a real source of water, and its removal under certain conditions may contribute to drying shrinkage and creep.

Table 5: Total porosity of mortars and share of macropores, mesopores and micropores, in %.

<table>
<thead>
<tr>
<th>Mortar type</th>
<th>E</th>
<th>P10</th>
<th>P20</th>
<th>P30</th>
<th>PS10</th>
<th>PS20</th>
<th>PS30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro- and mesopores</td>
<td>3.38</td>
<td>5.0</td>
<td>3.99</td>
<td>7.02</td>
<td>2.63</td>
<td>4.48</td>
<td>6.66</td>
</tr>
<tr>
<td>Macropores</td>
<td>3.6</td>
<td>4.5</td>
<td>6.9</td>
<td>6.3</td>
<td>5.8</td>
<td>5.2</td>
<td>6.7</td>
</tr>
<tr>
<td>Total porosity</td>
<td>6.98</td>
<td>9.5</td>
<td>10.89</td>
<td>13.32</td>
<td>8.43</td>
<td>9.68</td>
<td>13.36</td>
</tr>
</tbody>
</table>

Figure 3: Pore-size distribution determined by Mercury intrusion porosimetry.

3.3 Compressive strength

Compressive strength of tested mortars for different ages is shown in Table 6. Comparing the values of compressive strength at the age of 28 days, it is obvious that by increasing ash content, the compressive strength of mortars is decreased. However, mortars P10 and PS10 showed negligibly smaller compressive strength than reference mortar.

Table 6: Compressive strengths of tested mortar types at the age up to 180 days.

<table>
<thead>
<tr>
<th>Mortar type</th>
<th>E</th>
<th>P10</th>
<th>P20</th>
<th>P30</th>
<th>PS10</th>
<th>PS20</th>
<th>PS30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{cm,28}$ (MPa)</td>
<td>46.00</td>
<td>45.31</td>
<td>43.62</td>
<td>36.98</td>
<td>45.52</td>
<td>42.19</td>
<td>36.88</td>
</tr>
<tr>
<td>$f_{cm,60}$ (MPa)</td>
<td>52.29</td>
<td>49.58</td>
<td>46.04</td>
<td>43.54</td>
<td>48.96</td>
<td>46.35</td>
<td>41.25</td>
</tr>
<tr>
<td>$f_{cm,90}$ (MPa)</td>
<td>52.50</td>
<td>53.33</td>
<td>52.71</td>
<td>45.73</td>
<td>52.92</td>
<td>50.94</td>
<td>44.10</td>
</tr>
<tr>
<td>$f_{cm,180}$ (MPa)</td>
<td>55.60</td>
<td>56.54</td>
<td>55.73</td>
<td>51.25</td>
<td>55.82</td>
<td>54</td>
<td>49.38</td>
</tr>
</tbody>
</table>

Based on the results of other ages, it can be concluded that reference cement mortar gained most of its compressive strength by the age of 60 days. On the other hand, due to pozzolanic activity, all types of mortars containing wheat straw and soy straw ash showed increase of compressive strength over time. At the ages of 90 and 180 days, mortars P10, P20 and PS10 attained even higher compressive strengths than reference mortar. Therefore, the beneficial
effect of adding biomass ash in cement mortars is more noticeable at later ages. Changes of compressive strength of testing mortars (P10, P20, P30, PS10, PS20 and PS30) in relation to corresponding strength of reference mortar (E) are shown in Figure 4.

Figure 4: Changes of compressive strength of testing mortars.

3.4 Drying shrinkage

Obtained values of drying shrinkage are given in Table 7.

Table 7: Drying shrinkage deformations of mortars in mm/m.

<table>
<thead>
<tr>
<th>Mortar type</th>
<th>Age, days</th>
<th>E</th>
<th>P10</th>
<th>P20</th>
<th>P30</th>
<th>PS10</th>
<th>PS20</th>
<th>PS30</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
<td>0.167</td>
<td>0.188</td>
<td>0.188</td>
<td>0.146</td>
<td>0.167</td>
<td>0.167</td>
<td>0.135</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.281</td>
<td>0.354</td>
<td>0.365</td>
<td>0.365</td>
<td>0.323</td>
<td>0.333</td>
<td>0.302</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.354</td>
<td>0.458</td>
<td>0.500</td>
<td>0.510</td>
<td>0.458</td>
<td>0.479</td>
<td>0.469</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>0.458</td>
<td>0.573</td>
<td>0.625</td>
<td>0.688</td>
<td>0.552</td>
<td>0.573</td>
<td>0.563</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0.500</td>
<td>0.625</td>
<td>0.688</td>
<td>0.771</td>
<td>0.646</td>
<td>0.656</td>
<td>0.646</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.500</td>
<td>0.635</td>
<td>0.688</td>
<td>0.792</td>
<td>0.646</td>
<td>0.656</td>
<td>0.646</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>0.573</td>
<td>0.708</td>
<td>0.760</td>
<td>0.854</td>
<td>0.688</td>
<td>0.687</td>
<td>0.667</td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>0.698</td>
<td>0.792</td>
<td>0.854</td>
<td>0.948</td>
<td>0.781</td>
<td>0.760</td>
<td>0.750</td>
</tr>
<tr>
<td></td>
<td>56</td>
<td>0.698</td>
<td>0.792</td>
<td>0.854</td>
<td>0.948</td>
<td>0.781</td>
<td>0.760</td>
<td>0.750</td>
</tr>
</tbody>
</table>

By the analyses of shrinkage curves the following conclusions could be derived:

- All types of mortars have intensive shrinkage up to the age of 49 days.
- Reference cement mortar has the lowest measured shrinkage value.
- With the increase of wheat straw ash content, the value of shrinkage of mortars P10, P20 and P30 increase. Therefore, mortar with wheat straw ash content of 30% has the highest shrinkage value.
Shrinkage of mortars PS10, PS20 and PS30 is smaller in comparison to mortars P10, P20 and P30. The influence of different content of biomass ash on shrinkage value of mortars PS10, PS20 and PS30 is no significant, especially up to 42 days. All mortar types have the shrinkage values in range from 0.5-1.0 mm/m, so they belong to moderate shrinkage mortar group [13]. Therefore, differences between shrinkage of reference mortar and mortars containing biomass ashes are negligible. Change of drying shrinkage deformations with time is shown in Figure 5.

Figure 5: Change of drying shrinkage of tested mortar mixtures in the relation to time.

3.5 The water sorptivity test
Recorded change in mass over time was used to calculate the absorption, I, as the change in mass divided by the product of the cross-sectional area of the test specimen and the density of water. The results are shown in Figure 6. The initial rate of water absorption (Si, mm/s^{1/2}) is calculated as the slope of the line that is the best fit to I data between 1 min and 6 h. The secondary rate of water absorption (Ss, mm/s^{1/2}) is calculated as the slope of the line that is the best fit to I data between 1 and 7 days. Both rates are given in Table 8.

Comparing values of initial rate of water absorption (Si) with percentage share of macropores (Pmp), given in Table 5, it can be noted that increasing content of macropores in mortars leads to the increase of initial rate of absorption. This relation is clearly observed in case of mortars E and PS10. Satisfactory correlation between Si and Pmp can be established for remaining mortar types. A low deviation of results is present due to different distributions of macropores in mortars (Fig. 3).

Secondary rate of water absorption (Ss) cannot be determined for P series of mortars as the data do not follow linear relation and show systematic curvature. E mortar has the lowest Ss, while increasing of biomass ash content leads to a slight increase of Ss, so that mortar PS30 shows highest value of absorption. Coefficient of variation is 7.7% for PS mortars, indicating small differences between Ss and kinetics of water absorption.
Table 8: Initial and secondary rates of absorption

<table>
<thead>
<tr>
<th>Mortar type</th>
<th>Initial absorption</th>
<th>Initial rate of absorption $\text{SI} (\text{mm/s}^{1/2})$</th>
<th>Secondary absorption</th>
<th>Secondary rate of absorption $\text{SS} (\text{mm/s}^{1/2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>0.0037$\sqrt{t} + 0.062$</td>
<td>0.0037</td>
<td>0.0010$\sqrt{t} + 0.557$</td>
<td>0.0010</td>
</tr>
<tr>
<td>PS10</td>
<td>0.0039$\sqrt{t} + 0.020$</td>
<td>0.0039</td>
<td>0.0013$\sqrt{t} + 0.554$</td>
<td>0.0013</td>
</tr>
<tr>
<td>PS20</td>
<td>0.0046$\sqrt{t} + 0.062$</td>
<td>0.0046</td>
<td>0.0013$\sqrt{t} + 0.732$</td>
<td>0.0013</td>
</tr>
<tr>
<td>PS30</td>
<td>0.0060$\sqrt{t} + 0.134$</td>
<td>0.0060</td>
<td>0.0014$\sqrt{t} + 0.986$</td>
<td>0.0014</td>
</tr>
<tr>
<td>P10</td>
<td>0.0058$\sqrt{t} + 0.078$</td>
<td>0.0058</td>
<td>0.0008$\sqrt{t} + 1.142$</td>
<td>*</td>
</tr>
<tr>
<td>P20</td>
<td>0.0050$\sqrt{t} + 0.074$</td>
<td>0.0050</td>
<td>0.0004$\sqrt{t} + 0.956$</td>
<td>*</td>
</tr>
<tr>
<td>P30</td>
<td>0.0054$\sqrt{t} + 0.099$</td>
<td>*</td>
<td>0.0004$\sqrt{t} + 0.932$</td>
<td>*</td>
</tr>
</tbody>
</table>

* a linear regression cannot be established, a correlation coefficient less than 0.98

4. Conclusion

Based on the performed experimental research and the analysis of obtained results, the following conclusions are derived:

- The incorporation of biomass ash in cement mortar provided compressive strength comparable to reference concrete, especially at later ages. Mortars with biomass ash showed a noticeable strength development up to the age of 180 days. Mortars P10, P20 and PS10 gained even higher compressive strength than reference cement mortar. This strength development is a consequence of the pozzolanic characteristics of these ashes.
- Mortars in which up to the 20% of cement was replaced with wheat ash or with combination of wheat and soy ash have negligible decrease in 28-day compressive strengths (up to 7%) in relation to the reference mortar. Therefore, cement mortar can be produced by using biomass ashes as substitutes of cement in amounts up to 20% without compromising their mechanical properties.
All types of mortars containing biomass ash showed higher shrinkage compared to the reference mortar. With the increase of wheat straw ash content, the value of shrinkage increased, while the value of shrinkage slightly decreased as the total content of combined wheat straw ash and soy straw ash increased.

Results of the water sorptivity test indicate that E mortar showed the lowest initial cinetics of water absorption, while mortars containing biomass ashes, showed higher cinetics. Thus, E mortar has the lowest both initial and secondary rate of water absorption. However, in secondary water absorption period, there are no noticeable differences in water absorption cinetics between reference cement mortar and mortars with biomass ashes.

Increased content of $K_2O$ in tested biomass ashes could be potentially deleterious for durability of concrete, especially for alkally-aggregate reaction and this phenomena will be studied in further research.

Acknowledgements
The research work reported in this paper is a part of the investigation within the research project TR 36017 "Utilization of by-products and recycled waste materials in concrete composites in the scope of sustainable construction development in Serbia: investigation and environmental assessment of possible applications", supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

References
[4] SRPS EN 196-6: Methods of testing cement - Determination of fineness
[5] EN 196-2: Methods of testing cement - Chemical analysis of cement
[8] SRPS EN 196-1: Methods of testing cement - Determination of strength
DIFFERENTIATING THE PHYSICAL AND CHEMICAL EFFECTS OF SUPPLEMENTARY CEMENTITIOUS MATERIALS IN CEMENT MORTARS

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(1) Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India

Abstract
Supplementary Cementitious Materials (SCMs) influence the properties of fresh and hardened concrete. The incorporation of SCMs, either as a replacement of the cement or as an addition to the cementitious matrix, leads to an improvement in the strength and durability of concrete. While the pozzolanic reaction of the reactive siliceous components in the SCM has a large role to play in the enhancement of the properties, the secondary filler role of the SCMs can also be significant. Conventional reactivity determination for SCMs does not address the issue of understanding both physical and chemical synergies in the cementitious system, as a result of which the potential of the SCM is not fully utilized. This paper describes an experimental study on the differentiation of the physical and chemical effects of the SCM. The different SCMs used were Type ‘F’ and Type ‘C’ fly ash, Ground granulated blast furnace slag, and Quartz powder. The compressive strength and water sorptivity were assessed after 28 days. The results indicate that the physical effect can be specifically outlined by the understanding of the particle packing characteristics of the cement matrix, which helps in providing the contribution in the overall effect of the SCM.

1. Introduction

Supplementary Cementitious Materials (SCMs), in addition to imparting increased strength and durability to concrete, help in reducing the quantity of cement consumed thereby protecting the environment from global warming and issues related to safe disposal of these SCMs, a majority of these being industrial wastes.

SCMs have particle sizes that are almost similar to or even lesser than that of cement particles. The mechanical strength and durability of a cementitious system increases with the addition of these mineral admixtures due to interface refinement and the pozzolanic effect. This improvement in properties of concrete is accomplished in the following two simultaneous and
synergistic approaches [1-4]: 1. Physical Filler effect and 2. Chemical Pozzolanic effect. Decoupling of these two components is important in optimization of their manufacturing process [2].

When these SCMs are added, they create a large number of nucleation sites over which the hydration products may get deposited. This makes the microstructure more dense. In addition, when excessive quantity of SCMs is added, the superfluous small grains of pozzolans may fill the voids and further increase the density leading to enhancement in strength and durability of concrete. Goldman and Bentur [5] emphasized the importance of microfiller effect in increasing the strength by comparing silica fume and carbon black in concrete. Souri et al. [6] reported that at early ages, the performance of both SCM and filler based cementitious systems were similar and better than the control mix (100% cement). After 2 days, the SCM based system started showing improved functioning, which was attributed to the pozzolanic reaction.

Some researchers have used chemically inert fillers such as carbon black, quartz powder, limestone powder, etc. for estimating the physical filler component from the total pozzolanic effect. Isaia et al. [1] tried to segregate the physical filler effect and the chemical pozzolanicity effect by carrying out tests using limestone powder as filler. The unitary strength gain i.e. the strength per unit mass of Portland cement in the mixture was calculated in MPa per kg of cement. The filler effect of the respective quantity of limestone filler mixture was deducted from the total effect of the same quantity of pozzolanic mixture to obtain the chemical pozzolanic effect of the added SCM. It was also reported that the SCM and filler materials used for the study were of different fineness values.

However, the same particle size needs to be maintained for obtaining more accurate results and this was followed in a study carried out recently by Zunino and Lopez [2] for decoupling the physical and chemical effects of SCM. Here, all the materials including the filler had particle size distribution in a similar range as that of cement, which allowed comparison of materials with similar total reactive surface. The plotting of results using the normalized values with respect to OPC gives a better understanding of the material behavior in terms of pozzolanicity and paves an excellent way to segregate the physical and chemical effects.

Lawrence et al. [3] and Cyr et al. [4] added an extra dimension by segregating the physical filler effect into dilution effect and heterogeneous nucleation effect. An empirical model was developed based on semi-adiabatic calorimetric measurements which was mainly related to the specific surface area of the SCM. This quantifies the variation of the degree of hydration stimulated by the use of inert fillers in cementitious systems.

The current study is yet another attempt to segregate the physical and chemical effects of SCMs, with a view of improved utilization of the SCMs in concrete.
2. Methodology

2.1 Materials
Ordinary Portland Cement 53 grade conforming to IS 12269, Type ‘F’ fly ash, Type ‘C’ fly ash, slags from two different sources – Slag A and Slag J, and quartz powder were used in this study. The physical and chemical properties of the study materials are given in Table 1 (the particle size distribution data, unavailable at present, will be presented at the conference).

Table 1: Properties of materials used as binder.

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Gravity</th>
<th>Blaine’s Fineness (m²/kg)</th>
<th>Loss on ignition (%)</th>
<th>Approximate chemical composition (C : S : A : F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC 53 grade</td>
<td>3.18</td>
<td>310</td>
<td>0.9</td>
<td>65 : 20 : 5 : 4</td>
</tr>
<tr>
<td>Type ‘F’ fly ash</td>
<td>2.17</td>
<td>330</td>
<td>0.6</td>
<td>2 : 59 : 30 : 4</td>
</tr>
<tr>
<td>Type ‘C’ fly ash</td>
<td>2.59</td>
<td>390</td>
<td>2.5</td>
<td>14 : 40 : 32 : 6</td>
</tr>
<tr>
<td>Slag ‘A’</td>
<td>2.86</td>
<td>430</td>
<td>1.5</td>
<td>32 : 32 : 21 : 2</td>
</tr>
<tr>
<td>Slag ‘J’</td>
<td>2.87</td>
<td>360</td>
<td>1.2</td>
<td>36 : 34 : 17 : 1</td>
</tr>
<tr>
<td>Quartz powder</td>
<td>2.65</td>
<td>290</td>
<td>0.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Approximate chemical composition by X-ray fluorescence

2.2 Methods
Compressive strength tests were performed on 50 mm mortar cubes prepared with the following combinations of binders:

- OPC 53 Grade – 100% (Control mortar - CM)
- Type ‘F’ fly ash – 20% and 30% (FFA20 and FFA30 respectively) replacement
- Type ‘C’ fly ash – 20% and 30% (CFA20 and CFA30 respectively) replacement
- Slag ‘A’ – 30% and 50% (AS30 and AS50 respectively) replacement
- Slag ‘J’ – 30% and 50% (JS30 and JS50 respectively) replacement
- Quartz powder – 10%, 20%, 30%, and 50% (QP10, QP20, QP30, and QP50 respectively) replacement

Constant binder to sand ratio of 1 : 2.75 and water/binder value of 0.5 by mass was adopted. The specimens after demoulding were cured in saturated limewater and tested at 1, 3, 7, 28 and 90 days. In addition, sorptivity tests were also conducted, on 50 x 50 x 25 mm specimens sliced out of the 50 mm cubes, at 28 days. The test procedure was based on the South African Durability Index Testing Procedure Manual (2009) [7] and the measurements from the test were used to calculate porosity of the SCM-based mortar.
3. Results

Table 2 provides the mortar compressive strength values obtained for various curing ages and the porosity values of various mixes calculated from sorptivity measurements on the mortar samples cured at 28 days.

Table 2: Compressive Strength and Porosity of SCM-based mortar samples.

<table>
<thead>
<tr>
<th>Mix Details</th>
<th>Compressive Strength (MPa)</th>
<th>Porosity (%) at 28 days curing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 day</td>
<td>3 days</td>
</tr>
<tr>
<td>Control Mortar</td>
<td>14.55</td>
<td>25.49</td>
</tr>
<tr>
<td>FFA20</td>
<td>11.37</td>
<td>17.26</td>
</tr>
<tr>
<td>CFA20</td>
<td>12.23</td>
<td>20.52</td>
</tr>
<tr>
<td>FFA30</td>
<td>8.35</td>
<td>15.03</td>
</tr>
<tr>
<td>CFA30</td>
<td>10.32</td>
<td>16.71</td>
</tr>
<tr>
<td>AS30</td>
<td>18.61</td>
<td>27.16</td>
</tr>
<tr>
<td>JS30</td>
<td>11.45</td>
<td>16.60</td>
</tr>
<tr>
<td>AS50</td>
<td>14.60</td>
<td>31.05</td>
</tr>
<tr>
<td>JS50</td>
<td>8.27</td>
<td>15.96</td>
</tr>
<tr>
<td>QP10</td>
<td>12.87</td>
<td>28.02</td>
</tr>
<tr>
<td>QP20</td>
<td>13.54</td>
<td>20.72</td>
</tr>
<tr>
<td>QP30</td>
<td>9.87</td>
<td>15.89</td>
</tr>
<tr>
<td>QP50</td>
<td>5.43</td>
<td>8.00</td>
</tr>
</tbody>
</table>

4. Discussion

4.1 Compressive Strength

The compressive strength values of control mortar cubes at various ages are reduced by 10%, 20%, 30%, and 50% and these are compared with the strength of mortar mixes with cement replaced by quartz powder at 10%, 20%, 30%, and 50% and the difference in the corresponding strength values gives an idea of the contribution by physical filler effect for various replacements. These are illustrated in Figure 1 (a) to (d).

From the graphs, it is evident that the strength values of quartz powder – based mortar cubes are lesser than that of the respective reduced cement mortar cubes, the exception being 10% replacement (see Figure 1(a)). Therefore, the physical filler effect is exhibited only up to an optimum percentage of about 10%, whereas for the higher replacement levels, there is a decrease in cement hydration. This reduction in strength may be attributed to non-availability
of sufficient space for the formation of hydrated products. On the other hand, for 10% replacement of quartz powder, as suggested by several researchers [3 and 4], the following two opposing principal mechanisms contribute to this filler effect and enhance the strength:

1) Dilution effect: Due to reduction in the quantity of cement by replacement of filler, the water-cement ratio increases and hence there is dilution. Due to lesser quantity of available cement, the hydrated products formed is also less which leaves more space for further hydrated products. Additionally, as the effective w/c is greater, there is more chance of hydration.

2) Surface or fineness effect: Extra surface provided by fine filler materials acts as more nucleation sites for the cement hydration products and this is referred to as the heterogeneous nucleation effect.

The overall contribution from the SCM is calculated from the difference between the strength values of SCM-based mortar and the corresponding strength values of control mortar for different replacement levels and curing ages. The physical filler effect, on the other hand, is

![Figure 1. Quantification of physical filler effect due to the addition of quartz powder](image)
calculated from the results for quartz powder. Based on the performance of quartz powder, the expected contribution of the filler effect is presented in Table 3.

Table 3: Filler contribution (excess strength in MPa) expected based on quartz powder result.

<table>
<thead>
<tr>
<th>Age in Days</th>
<th>1 day</th>
<th>3 days</th>
<th>7 days</th>
<th>28 days</th>
<th>90 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% replacement</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.90</td>
<td>0.33</td>
<td>3.75</td>
<td>-0.70</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>30% replacement</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.32</td>
<td>-1.95</td>
<td>0.69</td>
<td>-3.05</td>
<td>-1.51</td>
<td></td>
</tr>
<tr>
<td>50% replacement</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1.85</td>
<td>-4.75</td>
<td>-2.86</td>
<td>-3.47</td>
<td>-4.16</td>
<td></td>
</tr>
</tbody>
</table>

Thus, the chemical contribution of the SCM into the system can be obtained by deducting the physical filler effect from the overall SCM contribution. Table 4 shows the calculated total contribution to the strength values by the addition of SCMs, their physical filler effect, and chemical pozzolanic effect for various combinations of mortar mixes. The physical and chemical effects can be more accurately evaluated if the SCM and the filler have the same particle size distribution.

Table 4: Separation of Physical and Chemical contribution of SCM in the cementitious system.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Mix Details</th>
<th>Age of Curing (Days)</th>
<th>Compressive Strength (MPa)</th>
<th>Total contribution of SCM</th>
<th>Physical filler effect</th>
<th>Chemical Pozzolanic effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FFA20</td>
<td>1</td>
<td>-3.18</td>
<td>1.90</td>
<td>-5.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>-8.23</td>
<td>0.33</td>
<td>-8.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>-4.32</td>
<td>3.75</td>
<td>-8.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>28</td>
<td>-5.75</td>
<td>-0.70</td>
<td>-5.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>0.79</td>
<td>0.02</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CFA20</td>
<td>1</td>
<td>-2.32</td>
<td>1.90</td>
<td>-4.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>-4.97</td>
<td>0.33</td>
<td>-5.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>-5.02</td>
<td>3.75</td>
<td>-8.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>28</td>
<td>-5.31</td>
<td>-0.70</td>
<td>-4.61</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>-3.72</td>
<td>0.02</td>
<td>-3.74</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>FFA30</td>
<td>1</td>
<td>-6.20</td>
<td>-0.32</td>
<td>-5.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>-10.46</td>
<td>-1.95</td>
<td>-8.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>-9.84</td>
<td>0.69</td>
<td>-10.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>28</td>
<td>-9.08</td>
<td>-3.05</td>
<td>-6.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>-0.61</td>
<td>-1.51</td>
<td>0.90</td>
<td></td>
</tr>
</tbody>
</table>
The chemical contributions of the fly ashes and the slags are presented in Figures 2 and 3 respectively. The trends clearly indicate that the fly ashes are able to significantly contribute only after 7 days, probably because of the overall retardation in strength development. Further, while the Type F fly ash leads to a significant increase in the strength at later ages because of the pozzolanic contribution, there is only a limited increase in the case of Type C fly ash. Among the two slags, Slag A provides very early contribution because of its higher fineness (as reported by Blaine’s method), which results in a better reactivity. On the other hand, there is limited contribution by Slag J until 7 days, probably because of lower reactivity levels.
4.2 Porosity
Porosity of 28 days cured mortar samples prepared for different combinations was calculated from the results of the sorptivity test. From Figure 4, it can be seen that a good inverse correlation exists between the compressive strength and porosity values at 28 days for all the mixes including SCM-based mortars. The trendline is plotted in the figure for 5 points, including CM, QP10, QP20, QP30, and QP50. In other words, this trendline would simply reflect the compressive strength – porosity relationship when cement is the only reacting component. While both fly ashes at 20% replacement appear close to the trendline, the 30% replacement mixes are to the right of the trendline, implying the porosities are higher than expected for the compressive strength level. For all the slag combinations, the points are to the left of the trendline, implying the porosities are lower for the expected strength level. The results suggest that there is considerable difference in the distribution of pore sizes. At low replacement levels of fly ashes, the pore structure does not seem to be altered, while for
higher replacement levels, there is a possible shift towards coarser pore sizes. On the other hand, for all the slag combinations, there may have been a larger fraction of pores in the smaller sizes, which cannot be determined in the sorptivity test. Further investigations by Mercury Intrusion Porosimetry are necessary in order to ascertain this fact.

Figure 4. Variation of compressive strength with porosity at 28 days

5. Summary

Most of the previous studies on understanding the pozzolanic activity of SCM in cementitious systems have concentrated only on reporting their overall performance rather than distinguishing their physical and chemical contributions. Decoupling of these two components is important for better understanding of the behaviour of SCM-based systems and therefore this study is taken up in order to segregate the physical and chemical effects of SCMs through strength and sorptivity measurements.

The physical and chemical contributions of two fly ashes (one of Type ‘F’ and the other of Type ‘C’) as well as two different slags were assessed in cement mortars by comparison with the performance of similarly sized quartz powder at equivalent replacement levels. The methodology used in the study could pave the way for understanding the contribution of SCMs in concrete. However, for better effectiveness, the methodology should also consider the influence of SCM reaction on the cement hydration, as a result of the change in the space available for hydration.

References


Abstract
Portland cement is a major responsible in global warming and climate change contributing currently about 7% to greenhouse gas emission. New cements with a lower clinker-cement factor are currently under development to help in this environmental and social topic. Coal bottom ash is a by-product, formed together with the coal fly ash produced during the coal combustion, in thermo-electrical power stations. A main difference between both ashes is the quite different grain size among other properties. The aim of this paper is to evaluate the feasibility of ground coal bottom ash as a potential cement constituent. This paper compares both coal ashes from a chemical and durable point of view and estimates the service life of reinforced concrete and other cement-based materials made of coal bottom ash considering the carbonation resistance by means of on-site measurements. Results show that the use of the carbonation models presented in Annex 9 of the Spanish Structural Concrete regulation, EHE-08, gives longer corrosion initiation periods, and then, longer service lives than using the experimental carbonation coefficients. Ground coal bottom ash and coal fly ash mortars perform similarly.

1. Introduction
Nowadays, composite cement production according to EN 197-1:2011 increases in Europe due to environmental and social concerns [1]. Limestone (L or LL), siliceous fly ash (V), natural pozzolans (P) and ground granulated blast-furnace slag (S) are the most frequently used cement constituents in Europe. Their effects on concrete are well known [2]. In some cases, mentioned effects are a direct consequence of the pozzolanic reaction of some cement constituents (coal fly ash, natural pozzolans and silica fume among others). This reaction consist of the reaction between the silicon dioxide, SiO₂, with the portlandite, Ca(OH)₂, produced from the hydration of the clinker calcium silicates (C₃S and C₂S). Given that,
ground bottom ash has demonstrated a good pozzolanic performance [3]. Nevertheless, coal bottom ash is usually used without grinding as an aggregate [4], and in many cases, dumped in a landfill site.

Coal bottom ash and coal fly ash are produced together in the same boiler in coal fired electrical power plants. Then, a similar chemical composition in both ashes is expected [3]. It is well-known that mortars and concretes made of coal fly ash perform quite well in aggressive environments as a consequence of its low permeability [5]. They have low chloride diffusion coefficients, a good frost-thaw resistance and so on [6]. Also, coal bottom ash could perform in a similar way than coal fly ashes refilling partially the mortar and concrete pores and the aggregate-paste and reinforcement-paste interfaces. This filling effect enhances the concrete compressive strength and durability when the cement-based material is well-cured.

The Spanish Structural Concrete regulation, EHE-08 [7], for the first time, included the durability limit state in 2008. Article 8 of mentioned regulation provides a set of tables where the thickness and quality of the concrete cover (minimum cement content and maximum water-cement ratio) and the maximum crack width are specified for a standard service life of fifty years, depending on the aggressiveness of the environment. This procedure is easy and provides a good result. In addition, the Spanish Structural Concrete regulation in Annex 9, offers some models for estimating reinforced concrete service life with regard to reinforcement corrosion due to concrete carbonation or chloride ion ingress. The results obtained with these models are expected to be more accurate than those obtained with the procedure explained previously. In this paper, the carbonation model was employed with the carbonation coefficients obtained experimentally. These data are compared with the theoretical model proposed in the Spanish Structural Concrete regulation, EHE-08 [7].

The aim of the present paper is to estimate the service life of reinforced concrete made of coal bottom ash considering its carbonation resistance based on on-site measurements.

2. Experimental

2.1 Materials
A CEM I 42.5 N cement according to the European standard EN 197-1:2011 [1] was used. This was selected as reference material. Blended cements were produced in the laboratory made of coal fly ash, coal bottom ash and the reference cement. Coal fly ash and coal bottom ash were provided by ENDESA-Carboneras. Coal bottom ash was ground to fineness similar to that of the Portland cement (5-8% residue on 45 μm sieve) using a ball mill (48 litters of capacity), whereas coal fly ash was employed without any particular treatment. Mortars were composed of blended cement, standard sand (NORMSAND acc. to EN 196-1) and distilled water.

2.2 Chemical and physical characteristics
The chemical composition of the reference cement and coal fly ash and bottom ash is shown in table 1. Analyses of SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, SO₃, K₂O, Ti₂O₅, P₂O₅ were performed by XRF with a Bruker S8 Tigger 4kW model. Loss on ignition (LOI), insoluble
residue (IR) and chloride content were determined according to the European standard EN 196-2:2005.

The Blaine fineness of the cement and ashes, i.e. the specific surface area, was obtained by the Blaine air permeability test, which is described by the American standard ASTM C204 - 16 “Standard Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus”. Specific surface Blaine of the bottom ash (BA), fly ash (FA) and cement used in the present study were 3463 m²/kg, 3976 m²/kg and 4050 m²/kg, respectively.

Table 1: Chemical composition of fly ash (FA) bottom ash (BA) and cement /%.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>Ti₂O₅</th>
<th>P₂O₅</th>
<th>LOI</th>
<th>IR*</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>20.9</td>
<td>4.3</td>
<td>3.5</td>
<td>62.7</td>
<td>1.9</td>
<td>3.4</td>
<td>0.9</td>
<td>0.25</td>
<td>0.10</td>
<td>3.7</td>
<td>1.04</td>
<td>0.023</td>
</tr>
<tr>
<td>Fly ash, FA</td>
<td>50.5</td>
<td>28.9</td>
<td>4.7</td>
<td>5.0</td>
<td>1.8</td>
<td>0.21</td>
<td>0.8</td>
<td>1.56</td>
<td>0.76</td>
<td>3.6</td>
<td>71.3</td>
<td>0.000</td>
</tr>
<tr>
<td>Bottom ash, BA</td>
<td>52.2</td>
<td>27.5</td>
<td>6.0</td>
<td>5.9</td>
<td>1.7</td>
<td>0.13</td>
<td>0.6</td>
<td>1.53</td>
<td>0.74</td>
<td>1.8</td>
<td>75.7</td>
<td>0.001</td>
</tr>
</tbody>
</table>

2.3 Natural carbonation testing

The European technical specification, CEN/TS 12390-10 “Testing hardened concrete. Part 10: Determination of the relative carbonation resistance of concrete”, gives two alternative methods to determine concrete carbonation resistance. Firstly, the concrete or mortar can be exposed to a natural outdoor environment but sheltered from rain. Secondly, they could be held in a climatic chamber at 0.035±0.005% of CO₂ concentration, a temperature of 20±2°C and a relative humidity of 65±5%. The first procedure was selected in this research work because is believed to be more realistic (Figure 1). Mentioned European technical specification establishes a testing time of 18 months, nevertheless, the testing time continued over an extended period of time of 180 and 360 days in this study.

Figure 1: Test site for natural exposure at IETcc.
Chemical composition and the fineness are the two main characteristics in coal bottom ash materials. In particular, the sum of some acidic oxides, \( \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \), is a key parameter which is used in some standards to classify coal fly ashes. According to the American standard ASTM C 618-12a, when \( \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \) is higher than 70.0%, the coal fly ash is classified as Type F. In this research, such value is 85.6% and 84.4% for coal bottom ash and coal fly ash, respectively, and they are higher than ≥70.0%. It is also observed that both data are quite similar with each other.

Also, Type F coal fly ash presents a low amount of calcium content. In this research, total CaO is 5.9% and 5.0% for coal bottom ash and coal fly ash, respectively. Finally, it can be highlighted the extremely low loss on ignition (LOI), of 1.80% and 3.6% for coal bottom ash and coal fly ash, respectively. This parameter is related to the unburned carbon content in both ashes. Evaluating the mentioned above parameters, it is realised that both ashes fulfil the requirements of the European standard EN 450-1:2012.

The coal bottom ash was ground to fineness in order to get a residue about 5-7% on 45 μm sieve, similar to that of commercial common Portland cements. The grinding process increases the specific area promoting the bottom ash pozzolanic activity and pore filling effect. A better parameter for describing the fineness of the cement and other cementitious materials is the specific surface area, called the Blaine fineness. Finally, the specific surfaces Blaine of the coal bottom ash (BA), coal fly ash (FA) and cement of 3463 m²/kg, 3976 m²/kg and 4050 m²/kg, respectively, give a clue about the potential reactivity of these materials.

3.1 Coal bottom ash mortar carbonation

A good durability performance of coal fly ash in some aggressive environments has been reported in many publications [6]. However, carbonation resistance of coal fly ash concretes and mortars is not good. The present research selected the carbonation testing to check the durability performance of mortars made of coal bottom ash or coal fly ash. Service life estimation also was given considering the most usual models regarding carbonation of reinforced concrete. The natural carbonation testing is the best scenario to be able to get realistic estimations. Then, measurements of carbonation depth were measured at 180 and 360 days of exposition at 20-25°C and 50-60% RH sheltered from rain. These conditions are in accordance with the procedure called “environment B” referred to in the European technical specification CEN/TS 12390-10:2007.

Concrete carbonation is a well-known process of calcium carbonate (CaCO₃) formation when carbon dioxide, CO₂, reacts with calcium phases, Ca(OH)₂, and water (H₂O), which are present in the pore solution of the concrete. Initially, carbon dioxide (CO₂) and water (H₂O) react to form carbonic acid (H₂CO₃) according to in Eq. (1).

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3
\] (1)

The carbonic acid formed according to Eq. (1) reacts with the calcium phases according to Eq. (2).
Figure 2: Depth of carbonation at 180 and 360 days of coal bottom ash (Ω) and coal fly ash (β) mortars.

Carbonation depth results were fitted to Eq. (3) in order to get the carbonation coefficient, A, and the parameter b. Both of them depend on the mortar quality and environmental conditions. In this study, b was considered to be equal to 0.5.

\[ x = A t^\beta \]  

Figure 3 shows the carbonation coefficient, A (mm/yr\(^{0.5}\)) calculated from Eq. (3). It is possible to realise that the carbonation coefficient at 180-days could be grouped into two main areas. The first one is formed by mortars made of CEM I and CEM II/A-V, whereas the second one is formed by CEM II/B-V and CEM IV/A (V) mortars. No differences were detected between coal bottom and coal fly ash mortars performance. Moreover, their carbonation coefficient of CEM II/A-V cement is similar to that of the reference mortar made of CEM I. The 360-days carbonation coefficient increases with the amount of ash in the mortar, i.e. from CEM I to CEM IV/A (V). As expected, the reference mortar offers the best performance with regard to the carbonation resistance. In general, it can be said that at low coal ash levels, coal bottom ash carbonation coefficient is higher than that of the coal fly ash (CEM II/A-V). On the contrary, at high coal ash levels the opposite trend is observed (CEM IV/A (V)). Only in the case of CEM II/B-V mortars no differences were found between coal bottom ash (Ω) and coal fly ash (β).
Experimental carbonation coefficient increases over time. Therefore, reinforced concrete service life estimation should be done carefully. From carbonation coefficients obtained at 180 days, considering a concrete cover of 30 mm, corrosion initiation periods due to carbonation could last from 8 to 18 years; whereas, for 360 days carbonation initiation periods, they last from 4 to 18 years.

3.2 Service life estimation

In the case of reinforcement corrosion, there are two types of models. Firstly, the empirical models (based on the experimental data fitting) and secondly, the theoretical ones based on the physicochemical process of aggressive penetration and reaction with the cement. The theoretical models often use empirical coefficients to fit the model to the experimental values obtained [9]. Most of the carbonation models consider the cement type and amount as a key parameter to be considered because of its great influence on the CO₂ reaction with the Ca(OH)₂ formed during cement hydration [10, 11].

The initiation period model most widely used model is a solution of Fick's second law applied to the diffusion of gases (CO₂) and aggressive ions (chlorides, sulphates, etc.) through the concrete cover, which was shown in Eq. (3). It was added to EHE-08 (Annex 9) to calculate the initiation period [7].

The propagation period model assumes a constant corrosion rate, \( V_{corr} \), during the propagation time, \( t_p \), and the loss of material \( X \) is given by Eq. (4). Also, the cross-area loss in the steel bar, \( X_a \), can be determined by Eq. (5).

\[
X = V_{corr} \cdot t_p \quad \text{[mm]} \\
X_a = \frac{X}{\pi b_d^2} 
\]
\[ X_a = 80 \times 37 \text{ [\mu m]} \]  

where:
\( t_p \) = propagation time, in years.
\( C \) = concrete cover thickness, in mm.
\( \Theta \) = reinforcement diameter, in mm.
\( V_{corr} \) = corrosion rate, in \( \mu m/\text{year} \).

Table 3: Corrosion rate \( V_{corr} \) according to the general exposure class.

<table>
<thead>
<tr>
<th>General class of exposure</th>
<th>( V_{corr} ) (( \mu m/\text{year} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal High humidity</td>
<td>Ha</td>
</tr>
<tr>
<td>Low/medium humidity</td>
<td>IIb</td>
</tr>
<tr>
<td>Marine Aerial</td>
<td>IIIa</td>
</tr>
<tr>
<td>Submerged</td>
<td>IIIb</td>
</tr>
<tr>
<td>In tidal zone</td>
<td>IIIc</td>
</tr>
<tr>
<td>With chlorides other than from the marine environment</td>
<td>IV</td>
</tr>
</tbody>
</table>

Propagation period ends when an unacceptable reinforcement loss of section occurs or when some cracks appear in the concrete cover. Eq. (6) is obtained from Eqs. (4) and (5). In the absence of specific experimental data, the corrosion rate, \( V_{corr} \), may be taken from Table 3.

\[ t_p = \frac{80}{37} \times C / V_{corr} \text{ [years]} \]  

The carbonation coefficient \( K_c \) can be calculated by using Eq (7), while the environmental parameter, \( c_{env} \), and the air-entraining factor, \( c_{air} \), may be taken from Table 4. The parameters \( a \) and \( b \), which depend on the type of cement, could be taken from Table 5. Finally, the average concrete compressive strength, \( f_{cm} \), expressed in N/mm\(^2\), can be calculated from the specified characteristic strength \( (f_{ck}) \) from Eq. (8).

\[ K_c = c_{env} \times c_{air} \times a \times f_{cm}^b \]  

where

\[ f_{cm} = f_{ck} + t \]  

Parameters \( a \) and \( b \) depend on the type of cement and in Table 5 can be found some contradictory data for these two parameters. For instance, \( a \) and \( b \) have the same values for a CEM I, common Portland cement without addition, and for a CEM V, common Portland cement with ground granulated blast-furnace slag and pozzolans. In consequence, it is highly recommended to get experimental data for \( a \) and \( b \).

Table 4: Environmental coefficient, \( c_{env} \), and air-entraining factor, \( c_{air} \) of Eq. (7) according to Annex 9 of EHE-08 [7].
Considering several concretes made of CEM I, CEM II/A-V, CEM II/B-V and CEM IV/A (V) with a characteristic strength of 25 N/mm², which are used to produce a sheltered from rain reinforced concrete structures (C_{env} = 1) and without entrained air agent (C_{air} = 1), the carbonation rates calculated by using Eq. (7) are shown in Table 6.

Table 5: Coefficients a and b of Eq. (7) according to Annex 9 of EHE-08 [7].

<table>
<thead>
<tr>
<th>Binder</th>
<th>EN 197-1:2011 Common Portland cement</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common Portland cement</td>
<td>CEM I, CEM II/B-S, CEM II/B-L, CEM II/B-LL, CEM II/B-M, CEM V</td>
<td>1800</td>
<td>-1.7</td>
</tr>
<tr>
<td>Portland cement + 28% fly ash</td>
<td>CEM II/B-P, CEM II/B-V, CEM IV/A, CEM IV/B</td>
<td>360</td>
<td>-1.2</td>
</tr>
<tr>
<td>Portland cement + 9% silica fume</td>
<td>CEM II/A-D</td>
<td>400</td>
<td>-1.2</td>
</tr>
<tr>
<td>Portland cement + 65% slag</td>
<td>CEM III/A, CEM III/B</td>
<td>360</td>
<td>-1.2</td>
</tr>
</tbody>
</table>

The carbonation coefficient, K_c, ranges from 4.72 to 5.42 mm/year^{0.5}. Therefore, considering a concrete cover of 30 mm, corrosion initiation periods due to carbonation could last from 30 to 40 years. These values are lower than the obtained experimentally. Then, this approach cannot be considered valid for the purposes of carbonation initiation periods estimation.

Table 6: Carbonation coefficient, K_c (mm/year^{0.5}), of a concrete with a characteristic strength of 25 N/mm² using equation (10) (Annex 9 of the EHE-08).

<table>
<thead>
<tr>
<th>CEM</th>
<th>K_c (mm/year^{0.5})</th>
<th>C_{env}</th>
<th>C_{air}</th>
<th>a</th>
<th>b</th>
<th>f_{ck}</th>
<th>f_{cm}</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4.72</td>
<td>1</td>
<td>1</td>
<td>1800</td>
<td>-1.7</td>
<td>25</td>
<td>33</td>
</tr>
<tr>
<td>II/A-V</td>
<td>4.72</td>
<td>1</td>
<td>1</td>
<td>1800</td>
<td>-1.7</td>
<td>25</td>
<td>33</td>
</tr>
<tr>
<td>II/B-V</td>
<td>5.42</td>
<td>1</td>
<td>1</td>
<td>360</td>
<td>-1.2</td>
<td>25</td>
<td>33</td>
</tr>
<tr>
<td>IV/A (V)</td>
<td>5.42</td>
<td>1</td>
<td>1</td>
<td>360</td>
<td>-1.2</td>
<td>25</td>
<td>33</td>
</tr>
</tbody>
</table>

4. Conclusion

Coal bottom ash mortars showed a moderate carbonation resistance similar to that of coal fly ash mortars. Therefore, ground coal bottom ash alone or mixed with fly ash is suitable to be used in cement production. Then, it could be assumed that there are not significant differences between coal fly ash and coal bottom ash with regard to the carbonation resistance. In the present study, special attention was given to the coal bottom ash used as cement constituent...
and degree of carbonation when such blended cements are added to concrete structures. This approach can be applied to other new cement constituents such as paper sludge, among others.

Natural carbonation testing is suggested to be the best way to get real carbonation coefficients. The theoretical model checked is this study is not valid for carbonation initiation period estimation.

Acknowledgements
The financial support of the IECA (Research Contract ‘Durable physico-chemical characterization of cement-based materials with industrial by-products’ - AU 23-10 Contract) is gratefully acknowledged.

References

PHYSICAL PROPERTIES AND PORE SOLUTION ANALYSIS OF ALKALI ACTIVATED FLY ASH-SLAG PASTES

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(1) Materials and Environment (Microlab), Faculty of Civil Engineering and Geosciences, Delft University of Technology, The Netherlands

Abstract

The technology of alkaline activated materials (AAMs) has become a sustainable alternative to cement production with respect to CO₂ emission and energy consumption. This technology is based on by-products usage from industrial energy and manufacturing processes, such as fly ash or blast furnace slag. The long-term performance of AAMs is decisive for their structural application. Generally, physical properties, such as porosity, pore size distribution, internal pore surface and connectivity determine material long-term behavior. Characterization of these properties in activated fly ash, slag and their blends was performed by Mercury intrusion porosimetry (MIP), Nitrogen adsorption and ESEM. Since the microstructure is greatly influenced by dissolution rate of fly ash and slag in selected activator, the pore solution was characterized by inductively coupled optical emission spectrometry (ICP-OES). Mixtures with the following fly ash and slag content (100:0, 70:30, 50:50, 30:70, 0:100 wt.%) have been prepared using sodium hydroxide/sodium silicate solutions. The increase of slag amount produces highly dense and refined microstructure, where only gel pores were identified and measured by Nitrogen adsorption. ICP-OES analysis has shown high concentrations of sodium and sulfur in solutions of slag rich mixtures, while Al, Si, Ca were almost completely absent from solution suggesting their total incorporation into reaction products of pastes.

1. Introduction

Fly ash (FA) and blast furnace slag (BFS) are used for decades as a partial replacement of cement in concrete in order to make a balance between cost and environmental considerations. When FA, BFS or other aluminosilicate precursors are alkali activated the final product is cement free material with similar or enhanced properties compared to the Ordinary Portland cement based materials [1, 2]. Regarding that, alkaline activation is a feasible and effective technology able to valorize numerous industrial by-products and to provide environmental friendly building materials. In alkali-activated systems based on fly ash, slag or their blend,
the knowledge on the physical properties (permeability, porosity, tortuosity, pore size distribution) is of paramount significance for an accurate prediction of the water, CO₂, Cl⁻, sulfates transport into the concrete.

The pore size distribution (PSD), porosity (pore volume fraction) and internal pore surface area are parameters that are scarcely investigated in alkali activated binders. The main challenge in the characterization of the pore structure in AAMs is in the formation of highly dense microstructure. One approach is use of X-ray based techniques such as those used in the literature [6, 7, 9, 13, 14, 15, 19]. Regarding these techniques, the examination of the porous AAMs is very hard. This can be attributed to several reasons. The size of the sample (nano-, micro-) is often not compatible with the resolution of the used technique. On the other hand, such a small samples request longer curing ages in order to be enough mature and do not crack under preparation process. Furthermore, the results from these studies are difficult to be compared. MIP technique is usually most used for pore structure characterization in Ordinary Portland cement based materials. Ma has showed that MIP can be used for identification of the pore size range from 6 nm to 350 μm in alkali activated fly ash [11]. However, the pore structure characterization of alkali activated fly ash and/or slag binders is very difficult to be obtained through MIP, since slag presence greatly densifies microstructure as reported elsewhere [9, 12, 16]. The use of nitrogen adsorption can be an alternative to identify finer pore sizes in the range of 2 to 100 nm, such as gel pores found in slag rich AAMs.

The aim of this paper is to evaluate the influence of fly ash/slag ratio on the pore structure of alkali activated pastes. In order to achieve this aim MIP technique was used. In addition, nitrogen adsorption was applied to identify pore geometry that was not accessible by mercury intrusion. According to Lloyd et al. [5], formulation of inorganic polymer cement is essential in limiting alkali diffusion in the paste; in particular, the presence of calcium has reduced alkali mobility, through denser and refined pore structure. Therefore, characterization of the pore solutions and pore solution alkalinity has been performed for investigated mixtures at the curing age of 28 days in order to underline Ca²⁺ presence from slag. ESEM observations of the microstructures were done to highlight the role of slag in favoring geopolymerization reactions revealing morphology of the studied pastes. The most striking differences between pore structures of the most used alkaline activated fly ash, blast furnace slag binders and their blends will be discussed.

2. Materials and methods

2.1. Materials and sample preparations
The paste mixture designs have been developed with the following FA/BFS ratios 100:0, 70:30, 50:50, 30:70, 0:100 wt. % named S0, S30, S50, S70, S100, respectively. The chemical and mineral compositions of FA and BFS are shown in Table 2.1 and Fig. 1, respectively. FA was sourced from VLIEGASUNIE BV and BFS was supplied by ORCEM, the Netherlands. FA has a specific gravity of 2440 kg/m³ and 82% of particles with size less than 45μm, compared to 2890 kg/m³ and 95% of particles with an average size of 45μm for BFS. The alkaline activator consisted of sodium hydroxide (NaOH) and sodium silicate (Na₂SiO₃) with modulus ratio Mₛ=3.37 (SiO₂/Na₂O, mol-based ratio). FA was mainly glassy with some
crystalline inclusions of mullite, hematite and quartz, while BFS was fully amorphous. The activator to binder ratio was fixed at 0.4. The alkaline activator has been prepared one day before casting. A commercial Hobart mixer was used for mixing with two minutes low-speed and half minute high-speed mixing. Paste samples were cast in steel prisms (40x40x160 mm) to provide adequate compaction since the plastic or other materials moulds can not transfer vibrations as efficiently as steel mould. Samples were demoulded 24h after casting and cured for additional 27 days in the fog room at 99% RH and room temperature.

Table 2.1: Chemical composition of FA and BFS deduced from X-ray fluorescence

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>K₂O</th>
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<th>P₂O₅</th>
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<tr>
<td>BFS</td>
<td>34.40</td>
<td>11.53</td>
<td>39.1</td>
<td>7.81</td>
<td>1.42</td>
<td>1.6</td>
<td>0.23</td>
<td>0.58</td>
<td>-</td>
<td>-</td>
<td>1.15</td>
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<tr>
<td>FA</td>
<td>54.28</td>
<td>23.32</td>
<td>4.23</td>
<td>1.62</td>
<td>8.01</td>
<td>0.64</td>
<td>0.85</td>
<td>1.97</td>
<td>1.23</td>
<td>0.54</td>
<td>3.37</td>
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</tbody>
</table>

Figure 1. XRD patterns of unreacted fly ash and blast furnace slag

2.2. Test methods
The total porosity and pore size distribution were measured by mercury porosimetry (MIP) and nitrogen adsorption. The sample preparation for MIP and nitrogen adsorption measurements has followed the procedure described elsewhere [10, 11]. Pore solutions were extracted following the procedures described by Barneyback et al. [20]. The samples were prepared in polyethylene jars with an inner diameter of 34 mm and a height of 68 mm and cured for 28 days. Pressures of up to 750 MPa were used to extract pore fluid from the samples (Fig.2). After extraction, the pore solution was filtered and half of each solution was diluted using nitric acid (0.2 vol.%). The diluted solutions were analyzed using VARIAN Vista 720 ICP-OES machine. The non-diluted solutions were left for the measurement of OH⁻ concentration in the pore solution by titration against HCl acid.
3. Results

3.1. Pore structure
The porosity of alkali activated fly ash, slag and blended pastes measured as total mercury intrusion volume ranged from 0.02 ml/g to 0.25 ml/g (Table 3.1). The mean pore diameter (0.11 μm) was possible to be determined only for alkali activated fly ash based paste. For the systems with slag mean size of the pores was not accessible.

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Total intrusion volume [ml/g]</th>
<th>Mean pore diameter [μm]</th>
<th>Total porosity [%]</th>
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<tr>
<td>S0</td>
<td>0.251</td>
<td>0.11</td>
<td>37.06</td>
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<tr>
<td>S30</td>
<td>0.096</td>
<td>-</td>
<td>14.87</td>
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<td>S50</td>
<td>0.045</td>
<td>-</td>
<td>7.48</td>
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<td>S70</td>
<td>0.039</td>
<td>-</td>
<td>6.65</td>
</tr>
<tr>
<td>S100</td>
<td>0.02</td>
<td>-</td>
<td>3.68</td>
</tr>
</tbody>
</table>

The typical capillary pores generally observed in cement paste were not found in the studied pastes, which is in line with previous work [11]. In a clear contrast to [11], a small number of large cavities were observed in fly ash paste, partially bounded by the aluminosilicate gel in the captured BSE images (Fig. 5) and partially resulted from the unreacted fly ash particles. The tested alkali activated fly ash paste has high porosity and large pore size distribution. This is mainly caused by relatively lower chosen alkaline concentration in this study than in [11], ambient curing conditions and relatively larger particle size of fly ash. When slag is used, pore size distribution changes to small pore size which is consistent with work of Provis et al. [9]. The dense microstructure is assigned to slag larger surface area and its amorphous content which increase slag reactivity and dissolution. BSE images (Fig. 5) showed that capillary pores cannot be detected for mixtures S50, S70, S100. This is in line with the study of Lloyd.
et al. [13]. The authors reported that capillary pores have been absent in well-reacted alkali-silicate activated inorganic polymer paste due to the uniform growth of the gel through the sample.

In blended pastes, the potential in space-filling properties of C-A-S-H gel and the N-A-S-H-type gel is more dominant. When two gels are coexisting it is thought that voids and pores within the geopolymer binder become filled with the C-S-H gel, bridging the gaps between the different hydrated phases and unreacted particles [12]. In particular, the 3D N-A-S-H network is intersected with 2D C-A-S-H gel giving denser and more homogeneous matrix in studied blended systems (S30, S50, S70).

The differences in total porosity of mixtures S50, S70 and S100 is slightly changed from 7.48% to 3.68% (Table 3.1) suggesting that beyond 50% fly ash replacement does not have significant influence on total porosity change. In addition, the identification of the characteristic peaks in differential curves for S50, S70, S100 was not feasible by MIP technique. Therefore, pore structure was further studied by Nitrogen adsorption (Fig. 4).

Nitrogen adsorption determines nano or gel pores that are beyond the detection range of mercury intrusion method. Coupled with MIP it fully covers the pores range. Curves for S50 and S70 mixtures have showed gel peaks around 4 nm (Fig. 4). In addition, sample S100 was expected to have peak shifted less than 4 nm. Instead, it was shifted to higher value. Fast setting of slag leads to shorten time for the final completion and consequently might be that sample is not well compacted during mixing procedure. However, total mercury intrusion volume has been the lowest for S100 (Fig. 3). Such low porosity may be due to the highest content of slag and higher space filling capacity for C-A-S-H than N-A-S-H, since C-A-S-H bounds more water. The gel pore peaks for S0 and S30 samples has not been detected in Fig. 4. This is consistent with the findings of Ma et al. [14] where for a given alkaline activator composition (SiO2:Na2O=0.5:1.5) the similar positions of peak were observed. In pastes with increasing slag content pore became refined and capillary peaks could not be observed any longer. For instance, such low porosity can be found in UHPC, ultra-high performance concrete.
cement-based composites with advanced properties containing nanoscale pozzolans [18]. The samples S50, S70, S100 in Fig. 3 are remarkably free of intrusion, indicating that the pores are smaller than the estimated 7 nm lower limit of MIP in this study. In addition, it should be noted that the total porosity for S50, S70, S100 may be higher than calculated (Table 3.1) because the mercury could not be intruded into very fine pores (<7 nm) which are present in high Ca alkali activated binders [13] or well cured low Ca geopolymer binders [7].

Figure 4. Pore size distributions (Nitrogen adsorption) of alkali activated pastes at 28 days

In addition to porosity measurements, the imaging of the microstructure morphology was taken by the backscattered electron (BSE) detector in order to identify and distinguish the pores on slice surfaces. The BSE image for fly ash based mixture S0 showed highly heterogeneous matrix with different sizes of spherical glassy unreacted fly ash particles suggesting partially reacted fly ash. Some particles are intact or interconnected with other spheres. The pores in the image are in the gel around unreacted particles or they are originated from porous spherical shells where activator was diffusing during the activation (Fig.5). As increasing slag content, the matrix becomes denser. The irregular particles shapes are assigned to slag grains which are embedded into gel matrix or they surrounded fly ash particles. Dissolution process is different for fly ash and slag due to their different chemical composition, particle size and surface area. Distribution of this gel in the matrix depends on the activation and curing conditions. Microstructures of S50, S70 and S100 are more compacted and consisted mainly of amorphous material particles where superficial porosity is reduced compared to S0 and S30 mixtures.

3.2. Pore solution analysis

The pore solutions from the hardened pastes containing different proportions of fly ash and blast furnace slag have been extracted at curing age of 28 days and analyzed to determine concentrations of dissolved ions (Fig. 6). The ICP-OES measurements of the pore solution composition have indicated that the pore solution of alkali activated fly ash and slag pastes were dominated by Na and Si that are dissolved from the activator and S that is released from the raw material. The Na content has increased in the pore solution with increase of slag in the binder. The Na concentration in the pore solution implies less Na in the gel formed after
alkaline activation of slag. In clear contrast to Na, Ca content is reduced significantly when the slag was added, suggesting that Ca is incorporated into the gel. The sulfur concentration in S70 and S100, on average, is triple as much in the mixtures with slag content below 50wt.%. Further studies are needed in order to evaluate the effect of sulfur content on the material properties. The concentration of Si varies, it increases for S50 and S70 compared to S30, and decreases compared to S100. The concentration of Al keeps at a very low level and does not change tendency throughout the studied mixtures. After dissolution, it is likely that most Al is incorporated into the reaction products. The concentration of Mg was under the measurement limit of ICP-OES test. It is assumed that Mg was involved in formation of OH-hydrotalcite during the slag activation.

Figure 5. BSE images of alkali activated pastes at 28 days

The pH appears to be slightly increased with slag addition (Fig. 7), as the same w/b ratio and composition of the activator were used in all mixtures. Therefore, the basicity of the slag has contributed to some level.
The most important observation is that irrespective of the mixture tested, the pH of the pore solutions at 28 days for all five mixtures is beyond 13 which will preserve the reinforcement from corrosion long enough before the corrosion initiates in an alkali activated fly ash/slag system. The pH beyond 13 was also reported after shorter period of time, i.e. 3h, 24h, 48h to 7d for alkali activated slag [4], either activated with sodium silicate or sodium hydroxide. According to these findings, the pH of pore solutions undergoes slight variations with the reaction time compared to original alkaline solution. The concentrations of Si, Ca, Al, and Mg from slag have been reported to be strong functions of the pH [3]. High pH increases the concentration of Si and Al, but reduces that of Ca and Mg in the pore fluids. It was found that the pH of the mixing solution must be higher than 11.5 to effectively activate slag. At a pH lower than 11.5, the equilibrium solubility of silica is low, and slag simply does not dissolve. Thermodynamic functions such as standard free energy and equilibrium constants of each species have been used to describe pH-dependent solubilities [3]. The rate of the slag dissolution influences the pore solution composition, which in turn determines calcium amount available to be embodied into reaction products. Less calcium in the pore solution will mean more of it in the solid phases. This will reduce pore space, considering its filling by the gel where calcium is bonded to other elements, as it is assumed in this study regarding negligible amount of Ca in the pore solution (Fig. 6), compared to the total Ca content.

4. Discussion

Due to different fly ash slag ratios in the studied pastes, the significant differences in the pore structure properties are observed. The presence of slag exerts a significant improvement in the pore structure features. As the calcium content of the system increases if more slag is in the system (S30→S100), the amount of Na⁺ in the pore solution increases (Fig. 6), suggesting a strong preference for incorporation of calcium over monovalent cations such as Na into the reaction products. The calcium concentration in the pore solution stays below 2 mmol/L in all solutions (Fig. 6). In addition, it could be observed from BSE images that with more than 50wt.% of slag very voluminous gel microstructure was formed. This is in line with findings of Puertas et al. [17]. Higher slag content in the system increases dissolution rate and
consequently hardening is faster, favoring high amount of the products forming along dense distribution different to that obtained in fly ash rich mixtures. Increase of the slag content decreases the total porosity by a factor of 10 (37.06% to 3.68%, Table 3.1). When slag was present beyond 50wt.% no capillary pores were formed, instead only gel pores were present. The higher reactivity of the calciumsilicate glass slag relative to the aluminosilicate glass in fly ash results in a higher reaction degree. The use of a blended system with higher slag content leads to a very dense microstructure, which restricts mercury intrusion significantly when porosity was tested. The size of the gel pores corresponding to 2-4 nm was measured by nitrogen adsorption technique, as they were not accessible by MIP. Study of pore solution composition through ICP-OES measurements provided valuable information on different elements concentration, suggesting their influence on pore network building and features, in particular of calcium. To conclude, using slag which is rich in calcium increases the pore solution alkalinity and refines pore network. This is important durability asset which indicates low permeable system of AAMs based on slag usage.

5. Conclusions

From the physical properties and pore solution analysis of alkali activated fly ash-slag pastes, the following conclusions can be drawn:
- In slag rich systems there is a substantial decrease in total porosity where pore size distribution was difficult to be accessed by mercury intrusion porosimetry technique. Therefore, nitrogen adsorption was employed to characterize very fine pores whose range was less than 7nm.
- The pore solution composition and alkalinity measurements provided important data on influence of calcium presence. With more calcium from the slag, microstructure was refined. This could be observed from BSE images that have been taken for studied pastes.
- The pH of the pore solutions for all investigated mixtures is beyond 13 which would protect the reinforcement from corrosion for long period.
- Although, the pore size distribution analysis in AAMs was possible by coupled MIP and nitrogen adsorption techniques, the total porosity is difficult to be quantified with only those methods, rather the use of multiple techniques is needed.

References

CARBONATION MECHANISM OF DIFFERENT KINDS OF C-S-H: RATE AND PRODUCTS

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Abstract
During the carbonation of cement paste blended with supplementary cementitious materials, the C-S-H with different Ca/Si ratios, formed from the hydration and pozzolanic reactions, are the major calcium-bearing phases which react with CO₂. Therefore, it’s important to study the carbonation mechanism of different C-S-H phases. In this paper, the pure C-S-H phases (Ca/Si ratio: 0.66 to 2.0) were synthesized and used for the accelerated carbonation test. Synthesized C-S-H phases with different Ca/Si ratio were identified by X-ray diffraction and 29Si nuclear magnetic resonance. The carbonation rate and products of different C-S-H phases are also determined. The results show that pure C-S-H phases with different Ca/Si ratio (lower than 1.40) can be synthesized in the lab. The structure of synthesized C-S-H is similar to the C-S-H(I) reported by Taylor. The mean chain length of the C-S-H decreases dramatically when the Ca/Si ratio increases from 0.66 to 1.40, then it keeps no change. The portlandite appears in the products when the designed Ca/Si ratio is over 1.40. The C-S-H with lower Ca/Si ratio is decomposed faster than that with a higher Ca/Si ratio. All the C-S-H phases are fully decomposed to CaCO₃ and silica gel after 3 days’ accelerated carbonation.

1. Introduction
Carbonation of C-S-H has been studied by many authors [1, 2]. It is a complex decalcification-polymerization process of the C-S-H and the formation of amorphous silica gel, see Eq. (1).

\[ C_{x}SH_{y} + x\bar{C} \rightarrow xC\bar{C} + SH_{y} + (x-t)H \]  

(1)

It is reclaimed that, in cement notations, \( C = CaO \), \( H = H₂O \), \( S = SiO₂ \), \( A = Al₂O₃ \), and \( \bar{C} = CO₂ \). \( x, y \), and \( t \) are the molecular numbers. According to the Eq. (1), the carbonation mechanism, like reaction rate and products, depends on the properties of C-S-H like Ca/Si.
(C/S) and H₂O/Si (H/S). It is better to study the carbonation mechanism of C-S-H on the basis of the C-S-H structure.

The C-S-H phase has a layer structure can be inferred from the refined structure of 11Å tobermorite (Ca₄.5Si₆O₁₆(OH)·5H₂O) [3]. The layer structure of 11Å tobermorites consists of three parts: CaO₂ sheet, ‘dreierkette’ form SiO chain and interlayer, illustrated in Fig. 1a. In the CaO₂ sheet layer, the 7-fold coordinated Ca²⁺ share all the oxygen atoms with Si⁴⁺ in SiO chains of SiO₄ tetrahedra on both side of the CaO₂ layer. In the SiO chain layer, SiO₄ tetrahedra coordinate themselves to Ca ions by linking in a dreierketten arrangement, to repeat a kinked pattern after three tetrahedra[4]. Two of the tetrahedra are linked to CaO polyhedral by sharing O-O edges with the central Ca-O part of the layer, called paired tetrahedra (PT); the third tetrahedra shares an oxygen atom at the pyramidal apex of a Ca polyhedron, called bridging tetrahedra (BT). There are Ca²⁺ cations and water molecules in the interlayer.

Comparing with the tobermorites, the major difference of the structure of C-S-H in Portland cement concrete, is that the chains of SiO₄ tetrahedra are broken. The C-S-H contains dimeric, pentameric and even higher polymeric species of SiO₄ tetrahedra, resulting in chains of 2, 5, …, (3n-1) SiO₄ tetrahedra. It is proved by experimental studies[5-7] and molecular modeling research[8]. Fig. 1a illustrates the pentameric unit, in which a bridging SiO₂ (Q₂⁻) connects two dimers, resulting in two SiO₄ end-groups (Q⁺) and two ‘paired’ SiO₄ sites (Q₂⁻). Normally, the Q₁ or Q₂ SiO₄ tetrahedra is absent in the C-S-H produced by the Portland cement hydration.

![Figure 1 Schematic of the layer crystal structure for the 11 Å tobermorite. The upper part shows different types of SiO4 tetrahedra in a pure pentameric silicate chain, which is a characteristic feature of the ‘dreierketten’-based models for the C-S-H phase. The lower part illustrates the possible incorporation of Al in the bridging site and the formation of Q2(1Al) tetrahedra in C-(A-)S-H. b. Comparing between the interlayer structures of 11 Å tobermorite and 14 Å tobermorite.](image-url)
The C/S of C-S-H in the concrete is normally higher than 0.83. The increase of the C/S in C-S-H based on the tobermorite structure can be caused by: omission of the bridge tetrahedra and incorporation of additional calcium in the interlayer. If all the bridge tetrahedra are removed, the C/S can increase to 1.25[9, 10]. Further incorporation of extra Ca\(^{2+}\) in the interlayer can form the C-S-H with a much higher C/S. The theoretical value is 1.50 when all the bridge sites are removed and taken up by extra Ca\(^{2+}\)[9]. The extra Ca\(^{2+}\) is normally balanced by the omission of H\(^+\) or the incorporation of OH\(^-\) or both. If the amount of extra Ca continues increasing and achieves a C/S even higher than 1.5, the structure of C-S-H is more close to the C-S-H/CH ‘solid solution’ (T/CH model)[9].

From the above discussion, three types of Ca exist in the C-S-H structure (classification by the position of Ca): Ca in the CaO\(_2\) sheet layer, Ca in the interlayer, Ca from the CH in the ‘solid solution’. The proportion of them varies from C-S-H to C-S-H. Apparently, to remove the Ca from the above three chemical site needs different energy, which means the decalcification rate are different among C-S-H phases. Moreover, the removal of Ca in the latter two site causes less changes of the structure than that in the CaO\(_2\) sheet layer. This is why the decalcification of C-S-H may cause the shrinkage of cement paste, especially for the C-S-H with Ca/Si lower than 1.2 [11].

The aim of this work is to synthesize the single C-S-H phase with different C/S and study their carbonation rate and products. Base on this, to explain the phase transformation and microstructure development of blended cement paste during the carbonation, discovered in the former research [12].

2. Experiments and test methods

2.1. Raw Materials

The raw materials used in the synthesis are CaO and fumed silica. CaO is freshly prepared by the calcination of CaCO\(_3\) under 1000 °C for at least 4 hours before synthesis. Fumed silica is from Sigma-Aldrich, with the surface area of 175-225 m\(^2\)/g.

2.2. Synthesis of C-S-H with different C/S

C-S-H gels were prepared by using stoichiometric amounts of CaO and fumed silica, to give approximate C/S ranging between 0.66 and 2.0. The solid phases were mixed together with CO\(_2\)-free water. The water/solid ratio was 50:1. The solution was stirred by magnetic stirrer at around 20 °C. The whole synthesis procedure was under N\(_2\) protection in case of carbonation. After 2 or 4 weeks’ reaction, samples of solid and liquid were extracted as a slurry. Solids were obtained by filtering the slurries through a Balston No. 45 paper. Then they were quickly moved into the vacuum drying chamber and dried under 35 °C for 24 h. Then the sample was stored in the desiccator with the relative humidity of 30%, controlling by the standard saturated CaCl\(_2\)·6H\(_2\)O solution. The set-up of the synthesis device is illustrated in Fig.2. The mix design of different C-S-H is described in Tab. 1.

2.3. Accelerated carbonation of C-S-H

Well-dried C-S-H samples were grinded into powders and moved into a carbonation chamber. The CO\(_2\) concentration is maintained at 3% ± 0.2 automatically by the solenoid valve.
connected with a CO₂ sensor. The temperature is regulated at 20 °C and the relative humidity is controlled at around 75% by using the saturated NaCl solution). The carbonation time varies from 0.5 h to 7 days.

2.4. Test methods

Test methods used for the identification of different types of C-S-H and the carbonation products were X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). Major crystalline phases in the products were tested by XRD. The X-ray source used is Cu K radiation (λ = 0.154056 nm, 60 mA, 40 KV). The scan step size was 0.02°, from 5° to 70° (2θ). The scan time per step is 8 s. The FTIR spectra were collected over the wavelength range of 4000 to 400 cm⁻¹ by the TM 100 Optical ATR-FTIR spectrometer. The resolution was 4 cm⁻¹. The samples were grinded into powders with same fineness as that required for the XRD test.

Solid state ²⁹Si single pulse magic angle spinning (MAS) NMR spectra were acquired using a BrukerMSL-400 spectrometer (magnetic field of 9.8 T; operating frequencies of 79.5 MHz). C-S-H powders were packed into the zirconia rotor sealed at either end with Teflon end plugs, and spun at 6 kHz in a Varian 7 mm wide-body probe. The spectra were acquired using a pulse recycle delay of 5 s, a pulse width of 4.97 μs, and an acquisition time of 20 ms; 2002 scans were collected for each sample. ²⁹Si chemical shifts are given relative to tetrakis (trimethylsilyl) silane (TTMS) at -9.8 ppm, with kaolinite as an external standard at -91.2 ppm.

Table 1 Mass fraction of raw materials for preparing different C-S-H

<table>
<thead>
<tr>
<th>Sample NO.</th>
<th>Ca/Si ratio</th>
<th>CaO (g)</th>
<th>SiO₂(g)</th>
<th>H₂O (g)</th>
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</table>
3. Results and discussion

3.1. Synthetic products identification

3.1.1. XRD

XRD test results of synthetic products are described in Fig. 3. The identical peaks with the d-spacing of 3.04, 2.79, 1.82, 1.66 Å indicate that the C-S-H phase synthesized in this study is similar to C-S-H (I), which is one of the C-S-H phases found in the Portland cement concrete[13]. Due to the high reactivity of fumed silica, the C-S-H phases can be formed after 2 weeks' reaction, see Fig. 3 (a). When the designed C/S is less than 1.40, only C-S-H phase exists in the product with no trace of unreacted raw materials or carbonation product; otherwise, the portlandite appears, see Fig. 2 (b). This is consistent with other researchers’ results[14, 15].

3.1.2. NMR

The NMR test results of synthetic products are described in Fig. 4a and 4b. The peaks around -78 ppm and -85 ppm indicates the Q^1 and Q^2 type of tetrahedra respectively. Apparently, the peak intensity of Q^1 increases with the increase of the C/S while that of Q^2 decreases.

The increase of C/S in C-S-H can be caused by the omission of the bridge tetrahedra in the silicate chain, based on the structure of tobermorite. The consequence is the decrease of the proportion of Q^2 tetrahedra and the formation of more Q^1 tetrahedra. Moreover, the mean silicate chain length (MCL) will decrease. The MCL was calculated from the NMR data using Eq. (2).

\[
MCL = \frac{2(Q^1 + Q^2)}{Q^1}
\]

In which, the \(Q^1\) and \(Q^2\) indicate the fractions of Si present in \(Q^1\) and \(Q^2\) tetrahedra respectively. Quantitative information on the fractions of \(Q^1\), \(Q^2\) tetrahedra was obtained by the deconvolution of the single pulse spectra. The spectra were fitted to Gaussian/Lorentzian...
mixed function using the dmfit2015 software. The fitting result of an example is illustrated in Fig. 5.

The deconvolution process is performed on all the $^{29}$Si NMR test results of C-S-H with C/S ranging from 0.66 to 2.0. The MCL is calculated and plotted with the C/S, comparing with the results from other researches of synthesized C-S-H in the solution [13, 16-20], see Fig. 6.

![Figure 5 $^{29}$Si NMR test results of C-S-H with different C/S (0.66-2.0), a- synthesis for 2 weeks; b-synthesis for 4 weeks.](image1)

![Figure 4 Fitting results of $^{29}$Si NMR spectrum (Ca/Si = 1.4, synthesis for 4 weeks).](image2)

![Figure 6 Calculated mean silicate chain length (MCL) of C-S-H with different C/S.](image3)

The MCL of the C-S-H decreases with the increasing C/S when the C/S is lower than 1.4. Then the MCL stays at around 2–3 tetrahedron units long. This can just verify the evolution model of C-S-H with higher C/S based on the tobermorite (Ca/Si = 0.83). By omission the bridge tetrahedra, the C/S will increase; meanwhile, the long silicate chain will be broken into shorter polymeric species of SiO$_4$ tetrahedra. Therefore, the MCL of C-S-H decreases
with the increase of the C/S. The C/S increases to 1.25 by the omission of all the bridge tetrahedra in the silicate chain. The further incorporation of Ca in the interlayer can achieve the C/S of 1.4, which will not affect the MCL. This is why the MCL of C-S-H keeps unchanged when the C/S increases above 1.4. The structure of C-S-H with the C/S higher than 1.4 can be explained by the ‘T/CH’ model, a ‘solid solution’ of C-S-H and CH.

Results in Fig. 6 also prove that the C/S of the synthetic C-S-H is quite close to the designed value. Considering together with the XRD test results, the conclusion can be made that the single C-S-H (I) phase with different C/S (lower than 1.4) is successfully synthesized in this research, and the experiment set-up can prevent the carbonation effectively.

3.2. Carbonation of C-S-H with different C/S

To avoid the effects from the carbonation of portlandite, only the C-S-H with the C/S of 0.66 to 1.40 were used in the carbonation study. The carbonation product was analyzed by NMR and FTIR. The results are shown and discussed as follows.

The $^{29}$Si NMR test results of carbonated C-S-H with different C/S are shown in Fig. 7. The characteristic peaks at around -101 and -111 ppm indicate the $Q^3$ and $Q^4$ tetrahedra, respectively. After carbonation, the fraction of $Q^3$ and $Q^4$ tetrahedra increases while the
fraction of $Q^1$ and $Q^2$ tetrahedra decreases at the same time. This indicates the polymerization process of the silicate chain and the removal of Ca in the CaO$_2$ sheet layer. The consequence is the linkage of the adjacent silicate chains and to form the silicate network in two and three dimensions. Whatever the C/S is, the silicate in the final carbonation products of C-S-H is silica gel, not the mixture or ‘solid solution’ of CaCO$_3$ and C-S-H with lower C/S$^{[21]}$.

Although the alkalinity of C-S-H is much lower than portlandite, the carbonation of C-S-H is quite faster under the accelerated condition. Nearly all the C-S-H are decomposed into silica gel after 3 days’ carbonation.

In the FTIR spectra of C-S-H, there is a characteristic peak at around 970 cm$^{-1}$. This peak indicates the Si-O stretching vibrations of $Q^2$ tetrahedra, which shifts to the lower frequency with increasing of C/S$^{[22]}$. In the contrary, the position of this peak shifts to the higher frequency. The FTIR tests were performed on the C-S-H with the C/S of 0.66 to 1.40. The carbonation time varied from 0.5 h to 24 h. The test results are compared in Fig. 8.

![FTIR test results of different types of C-S-H, carbonated for different time](image)

The shoulder peak at around 1066 cm$^{-1}$, which is also indicating to the Si-O stretching vibrations of $Q^2$ tetrahedra, has an obvious growth after carbonation. This peak only appears...
in the FTIR spectrum of C-S-H with low C/S or in the tobermorite. Meanwhile, the intensity of the peak at around 970 cm\(^{-1}\) decreases dramatically. The changes of these two peaks during the carbonation reveal the progressive polymerization of silicate chains.

The peak at around 875 and 1400~1500 cm\(^{-1}\) represents the bending (v2) of CO\(_3^{2-}\) and the stretching (v3) of CO\(_3^{2-}\), respectively. Both of them have a dramatic increase in the intensity when the shoulder peak (1066 cm\(^{-1}\)) grows into an obvious and independent peak. For example, it can be observed in the spectrum when the C-S-H with the C/S of 0.66 is carbonated for 3 h. This ‘critical’ time is 6h for the C-S-H with the C/S of 0.86 and 12 h for the rest two types of C-S-H. This change in the FTIR spectra indicates that the silicate chain in the C-S-H starts to be destructed by the carbonation. Comparing this “start time” among different types of C-S-H, it can be concluded that the carbonation rate of the C-S-H with a higher C/S is lower than that of the C-S-H with the lower C/S. High Ca C-S-H has a better resistance to the carbonation.

4. Conclusions

In the paper, the C-S-H with different C/S, identified by XRD and \(^{29}\)Si NMR, is successfully synthesized from CaO and fumed silica in the solution protected by the N\(_2\) flow. The carbonation mechanism of C-S-H including final products and rate are studied by NMR and FTIR. The carbonation resistance among different types of C-S-H are discussed. The main conclusions are as follow:
- The single phase of C-S-H(I) can be synthesized when the Ca/Si ratio is no more than 1.40; otherwise the portlandite appears.
- The structure of C-S-H with the C/S lower than 1.25 can be derived by missing the bridge tedrahedra based on tobermorite; the incorporation of extra Ca\(^{2+}\) can achieve a much higher C/S of 1.40; The structure of C-S-H with the C/S higher than 1.4 can be explained by the ‘T/CH’ model, a ‘solid solution’ of C-S-H and CH.
- The final silicate in the products is silicate gel. The C-S-H with high C/S has the better resistance to the carbonation.

Acknowledgements

The authors are grateful for the help from technicians and experimental supports from Microlab, Delft University of Technology.

References


INVESTIGATION OF THE MOISTURE INFLUENCE ON PERMEATION PROPERTIES OF ALKALI-ACTIVATED SLAG CONCRETE

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(4) School of the Built Environment, Ulster University, Newtownabbey, UK

Abstract
This study reports an experimental investigation designed to assess the influence of near-surface moisture contents on permeation properties of alkali-activated slag concrete (AASC). Three AASC and normal concretes with compressive strength grades ranging from C30 to C60 were tested under five different drying periods. Assessment of moisture distribution was achieved using 100 mm diameter cores with drilled cavities. Results indicate that air permeability of AASC is very sensitive to the moisture content and its spatial distribution, especially at relative humidity above 65%. To control the influence of moisture on permeation testing, the recommendation of this paper is that AASC specimens should be dried in controlled conditions at 40 °C for 10 days prior to testing. It was also concluded from this study that AASC tends to perform less well, in terms of air permeability and sorptivity, than normal concrete for a given strength grade. This conclusion reinforces the need to further examine AASC properties prior to its widespread practical use.

1. Introduction
Impacts of climate change on society are evident from the recent events and concentration of CO₂ in the atmosphere presents a major factor closely linked with global temperature fluctuations [1]. With the cement industry representing around 5% of global CO₂ emissions [2], development of innovative, low CO₂-impact binding materials is an area attracting intense research interest at present.

One possible alternative is alkali-activated slag, a clinker-free binder significantly differing from traditional Portland cement (PC) [3-5]. The production of 1 ton of alkali-activated slag cement emits around 0.18 tonnes of CO₂ to the environment, approximately 80% less than ordinary PC [2,4,5]. Despite this fact, however, the widespread commercial adoption of
AASC has been limited to date owing, in part, to its relatively limited record of durability in service.

To become established as a successful alternative to PC-based concrete, AASC must offer similar durability and long-term resistance levels to aggressive agents. To address this issue within a realistic experimental timeframe, developing an understanding of cover concrete permeation properties (including water absorption, permeability and diffusivity) directly impacting ingress rates of aggressive substances from the environment, is essential.

Prior to all permeation testing, initial conditions of samples must satisfy certain requirements as specified in classical theories. Drying is an unavoidable preconditioning procedure for gas permeability, gas adsorption, gas diffusion and water absorption. However, despite the existence of numerous drying methods for PC samples [6-8], no drying methods have specifically been developed for AASC to date. While the effect of different drying techniques on the microstructure of conventional PC samples is well studied, proposed techniques are likely not be suitable for drying AASC samples due to inherent microstructural and gel chemistry differences. As Collins and Sanjayan [9] have pointed out, AASC samples are more sensitive to moisture loss than PC-based materials and may undergo a continuous sequence of irreversible decomposition reactions during drying. Meanwhile, the correct interpretation of permeation test results requires determination of internal moisture content and its distribution [6,8]. This is a further area where in-depth research is lacking for AASC.

Against this background, the main aim of this work is to propose a preconditioning regime suitable for obtaining reliable data when measuring AASC permeation properties. To achieve this, a research programme was undertaken to establish effects of various preconditioning regimes and moisture contents on key properties including relative humidity, air permeability, sorptivity and porosity.

2. Materials and test methods

2.1 Concrete mix proportion and raw materials
Granulated blast furnace slag (GGBS) supplied by Chongqing Iron and Steel Group and Portland cement (PC) conforming to GB-175 [10] were used, the chemical composition of which is summarised in Table 1.

The activator for AASC was a mixture of NaOH solution and liquid sodium silicate. The NaOH solution was prepared by dissolving NaOH pellets (99% purity) in water and the liquid sodium silicate (Na$_2$O: 29.03%, SiO$_2$: 12.07% by mass) was mixed with the NaOH solution in a pre-specified ratio to give a combined modulus of Ms=1.2 (defined as the mass ratio of SiO$_2$ to Na$_2$O). The NaO$_2$ dosage was kept constant for preparing AASC, 5% of the GGBS content.
Table 1: Chemical composition of GGBS and PC (percent by mass, %).

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Loss</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGBS</td>
<td>31.63</td>
<td>13.42</td>
<td>1.32</td>
<td>9.12</td>
<td>36.35</td>
<td>0.34</td>
<td>0.46</td>
<td>0.61</td>
<td>6.75</td>
</tr>
<tr>
<td>PC</td>
<td>21.33</td>
<td>5.80</td>
<td>2.57</td>
<td>6.01</td>
<td>60.21</td>
<td>0.70</td>
<td>0.21</td>
<td>-</td>
<td>6.67</td>
</tr>
</tbody>
</table>

The fine aggregate used was medium graded natural sand (fineness modulus: 2.60) and the coarse aggregate was 10 and 20 mm crushed basalt in equal proportions, conforming to GB/T-14684 [11] and GB/T-14685 [12], respectively. Aggregate moisture content was controlled by drying in an oven at 105±5°C for 24 hours followed by cooling to 20±1°C for one day before casting concrete. The mix proportions of the concrete tested in this investigation are given in Table 2, along with the general properties, e.g. air content, slump and compressive strength.

Table 2: Mix proportions and general properties of concrete tested in this study.

<table>
<thead>
<tr>
<th>Concrete type</th>
<th>AASC</th>
<th>NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength grade</td>
<td>C30</td>
<td>C60</td>
</tr>
<tr>
<td>Binder (GGBS for AASC and Portland cement for NC) (kg/m³)</td>
<td>400</td>
<td>480</td>
</tr>
<tr>
<td>Water (kg/m³)</td>
<td>157.6</td>
<td>117.6</td>
</tr>
<tr>
<td>Superplasticiser (%)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Water glass, Ms: 1.2 (kg/m³)</td>
<td>82.5</td>
<td>82.5</td>
</tr>
<tr>
<td>NaOH (kg/m³)</td>
<td>12.9</td>
<td>-</td>
</tr>
<tr>
<td>Fine aggregate (kg/m³)</td>
<td>740</td>
<td>790</td>
</tr>
<tr>
<td>Coarse aggregate (kg/m³)</td>
<td>1110</td>
<td>1035</td>
</tr>
<tr>
<td>Slump (mm)</td>
<td>200</td>
<td>145</td>
</tr>
<tr>
<td>Air content (%)</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>Compressive strength at 28 day (MPa)</td>
<td>34.6</td>
<td>53.6</td>
</tr>
</tbody>
</table>

Note:
1. Superplasticiser refers to percentage of cement content.
2. Ms is defined as the mass ratio of SiO₂ to Na₂O.

2.2 Specimen preparation
Two 300×250×150 mm slabs and six 100 mm cubes were manufactured for each mix to facilitate permeation studies and compressive strength testing. All specimens were covered with a polythene sheet, de-moulded the following day and placed in a curing room.
(temperature: 20±2°C, relative humidity: 95±5%). Cube specimens were removed at the age of 28 days and tested for compressive strength.

After 56 days, six 100 mm diameter cores were extracted from the slab specimens for each concrete and saturated by incremental immersion for 10 days, details of which are given in previous studies [13, 14]. At the completion of the saturation process, the saturated mass ($M_s$) and the dimensions (radius, $r$ and length, $l$) were measured. The six cores for each mix were then placed in a drying cabinet (temperature: 40 °C; relative humidity: 35 %) and were divided into two groups as follows:

1) Three cores were used to study the relationship between air permeability and moisture condition. After five different drying periods (5, 10, 15, 20 and 25 days), the three cores for each mix were removed from the oven, wrapped in a polythene sheet and cooled to room temperature (around 20°C, 55% RH) for 1 day. Air permeability and relative humidity measurements were then carried out and, the specimens placed in the drying cabinet. After undertaking the last set of air permeability and relative humidity tests, water absorption testing was carried out in accordance with BS-EN: 13057 to determine sorptivity values [6].

2) The other three cores for each concrete mix were used to assess capillary and gel porosity. To estimate capillary porosity, the cores were placed in the drying cabinet at 40 °C until constant mass ($M_{40C}$) was achieved. To assess gel porosity, the cores were then placed in an oven at 105 °C to reach the mass equilibrium state ($M_{105C}$).

2.3 Test methods

2.3.1 Relative humidity on the surface and in the 20mm drilled hole

In this study, RH measurements were carried out on sample surfaces and within drilled 20 mm deep holes using an RH probe, which is shown in Figure 1. After measurements were taken, the drilled holes were sealed with rubber plugs fitted with silicone to ensure that the reading in the cavity was not affected by ambient conditions. Both RH and temperature was recorded for each measurement after stabilisation was reached that generally taking around 40 mins to achieve. Two replicates were performed for each test set (one measurement in each of the test cores), the mean value of which was reported.

2.3.2 Air permeability test

Figure 2 shows the surface mounted air permeability test instrument used in this study to assess both AASC and NC, further details of which are reported in the literature [13]. The test area considered was the inner 50 mm circle of the 100 mm cylindrical specimen, isolated using a base ring. The instrument was manually pressurised by a syringe and when the pressure in the test chamber reached 0.5 bar, the test commenced automatically. The pressure inside the test chamber then decreased due to air escaping through the pores in each specimen. The rate of pressure decay was monitored every minute for 20 minutes and used to compute the air permeability index, API (unit: ln(bar)/min) using the following equation:

$$API = \frac{\ln \frac{P_0}{P_t}}{t_i - t_f}$$

(1)
where \( t \) is the time (s); \( P_0 \) and \( P_t \) (N/m\(^2\)) are the pressures in the chamber at the start and at any time, \( t \), respectively. Three samples were tested for each concrete mix and the detail procedures are reported in previous studies [13, 14].

**2.3.3 Capillary porosity and gel porosity**

Porosity was determined by the mass difference of water-saturated and dried samples at different temperatures. Capillary and gel porosity was determined based on sample mass loss after drying at 40 °C and 105 °C respectively and using the following equations:

\[
\text{Capillary porosity: } f_c = \frac{M_o - M_{40^\circ C}}{\rho_w \pi r^2 l} \times 100\% \tag{2-1}
\]

\[
\text{Gel porosity: } f_g = \frac{M_o - M_{105^\circ C}}{\rho_w \pi r^2 l} \times 100\% \tag{2-2}
\]

where \( M_o \) is the mass of a saturated sample (kg); \( M_{40^\circ C} \) and \( M_{105^\circ C} \) are the mass of a sample after drying at 40 °C and 105 °C (kg); \( \rho_w \) is the density of water (kg/m\(^3\)); \( r \) is the radius of the sample (m); \( l \) is the length of the sample (m).

**3. Results and discussion**

**3.1 Moisture condition after drying**

Figure 3 summarises relative humidity (RH) results for both NC and AASC specimens after different drying periods. As expected, moisture loss from all concrete is reflected by a general trend of decreasing RH values with increasing drying periods. For RH values at the surface of both AASC and NC at different strength grades considered, it is also clear from Figures 3-a and -c that no typical patterns exist, suggesting that the concrete type and compressive
strength level have minimal impact on the surface humidity during drying. With respect to RH within the drilled 20 mm cavities (Figures 3-b and -d), RH values were consistently higher than surface measured values. This indicates that, for both NC and AASC specimens, moisture gradients were formed during the drying process and a moisture equilibrium state was not established.

Furthermore, the results of AASCs show that drying for 10 days at 40 °C caused a substantial RH drop at the 20mm cavity (from 80% to 60%) and further drying did not result in significant RH reductions. On the contrary, a more constant rate of reduction in RH readings for NC was observed. Secondly, no noticeable difference in RH within the 20 mm cavities was identified for the three AASCs considered, suggesting a minimal impact of compressive strength grade (or w/b) on the 20 mm RH. For NC, a more noticeable difference in RH values with time existed between different mixes. This was most pronounced for the C30 mix, which consistently exhibited higher (on average 5%) RH levels than C45 and C60 mixes across the drying time intervals considered. Differences of C45 and C60 were less significant.
The above observations emphasise the influence of concrete type on the features of RH variations in the drying process. Indeed, investigations of concretes comprising 50 % GGBS concluded that they tend to dry more rapidly than similar concrete made with plain Portland cement [6,13]; a trend consistent with the results obtained from this study.

Considering the variation of RH results, evaporable moisture in the AASC specimens dried out more quickly than for NC. After drying for 10 days, the RH values for AASCs were typically around 60 %, regardless of compressive strength grade. This is considerably less than NC, which requires at least 20-day drying to achieve a similar moisture condition.

3.2 Porosity after drying
Regarding the relationships of RH versus drying duration plotted in Figure 3, the controlling influence on the trends noted was capillary moisture loss, which occurred at the controlled drying environment of 40 °C considered. Not affecting the results in Figure 3 was physically bonded or adsorbed moisture on gel surfaces, which is typically lost at temperature around 100 °C [4,6,8]. In this element of the study, on the basis of the mass loss of a saturated specimen dried at 40°C and 105°C, respectively, till constant mass.

Influences of concrete type and compressive strength grade on capillary and gel porosity are shown in Figure 4, which for both AASC and NC shows increasing total porosity with decreasing compressive strength; an expected trend due to established relationships between w/b ratio and compressive strength [7,8]. At all three strength grades considered, also clear from Figure 4 is consistently higher total porosity for AASC (ranging from 10.13 to 13.12%) compared to NC (ranging from 8.77 to 12.79%). This is justifiable given the inherently high strength hydration products associated with AASC [5]. As such, in this study higher water/solid ratios were consistently used for AASC, relative to NC (see Table 2), to achieve comparable compressive strength, thereby resulting in higher levels of ultimate porosity.

3.3 Air permeability after drying
The relationship between API and drying period are plotted in Figure 5, which clearly indicates generic effects of compressive strength (increasing strength resulting in decreasing API), concrete type (API higher for AASC than NC for each strength grade considered) and drying duration (generally increasing API values with increasing drying period). In terms of the latter effect for AASC, an increase in drying period from 5 to 10 days resulted in a significant rise of API (more than 200%), with increases beyond this time diminishing significantly in value (less than 5%). This trend suggests that for AASC, undertaking air permeability measurements after a minimum of 10 days initial drying at 40 °C is likely to minimise the risk of result being compromised by moisture effects. For NC, on the other hand, results obtained from this study compare favourably with previously published data [6], indicating minimal effects of moisture on API beyond 20 days of drying at 40 °C [13, 14].
To further investigate the influence of moisture on air permeability of AASC and establish a moisture requirement for a reliable air permeability measurement, Figure 6 provides the normalised air permeability for AASC and NC plotted against corresponding RH values measured in the 20 mm deep specimen cavities. It is clear that AASC and NC follow a similar trend. More specifically, at RH below 65%, the normalised air permeability of both AASC and NC are generally constant, suggesting that moisture effect has been removed, while the effect of moisture is highly significant for wet concrete specimens with RH > 70%. Consequently, for AASC it is reasonable and practical not to consider a correction factor to the air permeability, when the relative humidity at the surface region is below 65%. This recommendation for the AASC air permeability measurement is consistent with the NC.

In addition, the air permeability of both AASC and NC falls as the compressive strength grades rise. It clearly indicates that even with similar capillary porosity (as illustrated in Figure 4) and compressive strength (as given in Table 2), concrete specimens do not necessarily exhibit similar permeation properties (shown in Figure 5 and 6) and the concrete type could also significantly affect relevant performance. This is because the w/b of NC needed to be lowered by a greater proportion to achieve the designed compressive strength. Thus, the pore structure of NC was improved that probably exceeded the benefits from hydration products from AASC. As such, the performance difference between NC and AASC cannot be judged by compressive strength alone.
4. Conclusions
From the experimental results represented in this study, AASC has a rapid moisture loss rate up to 10 days of drying, afterwards the moisture at 20 mm in AASC becomes stabilised. Unlike NC, the strength grade (or w/b) of AASCs has no influence on changes in RH values at 20 mm irrespective of the drying duration. For a given compressive grade, AASC has a higher capillary porosity than NC and is more permeable in terms of air permeability. Furthermore, the air permeability of AASC increased with an increase in the drying duration and became stable after 10 days of drying. Therefore, to eliminate the influence of moisture on air permeability, the AASC samples can be dried for 10 days at 40 °C or an RH value of <65% on the surface and at 20 mm is achieved.

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References


THE RATE OF STRENGTH DEVELOPMENT OF MORTAR MIXES WITH SCMs AT ELEVATED CURING TEMPERATURES

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Abstract
The early age strength development of mortars containing ground granulated blast furnace slag (ggbs) at levels of up to 70% of the total binder have been investigated to give (1) guidance as to their early age strength development and (2) how this is affected by curing temperature. 28-day target mean strength for all concrete specimens was 55 MPa. Supplementary cementitious materials (SCMs) such as ggbs were used to give similar 28-day compressive strengths to those with neat Portland cement (PC). However, their early age strengths are shown to be significantly lower than PC when cured at 20°C. High curing temperatures benefit ggbs mixes much more than Portland cement mixes. Measurements of temperature rise under adiabatic conditions have shown that high levels of cement replacement by ggbs, e.g. 70% are required to obtain a significant reduction in the peak temperature rise. Even though the temperature rise using ground granulated blast furnace slag (ggbs) is lower than from using Portland cement, it is shown that it still influences significantly the early age strength contribution of ggbs. Maturity measurements are needed to take advantage of such enhanced early age strengths. Precast concrete factories, for example, should confirm that the actual compressive strength of the concrete in the structural element at the time of lifting operations exceeds the required strength. Maturity functions like the Nurse-Saul and Arrhenius based one proposed by Freiesleben Hansen and Pedersen (FHP) have been examined for their applicability to ggbs mortars. Activation energies, required as input for the FHP equation, have been determined according to ASTM C1074-98. The inaccuracies in the strength predictions of both maturity functions have been quantified and the reasons identified to enable future improvements.

1. Introduction
There has been a major change in recent years in that cements other than CEMI (what would have been called neat Portland cement) are gaining popularity because of their lower carbon
footprint. This is the result of partial cement replacement with supplementary cementitious materials (SCMs) one of them being ground granulated blast furnace slag (ggbs). Characteristic compressive strength is normally specified for 28-days and these cements with SCMs may be used to design concrete and mortar mixes of equivalent 28-day strength as neat Portland cement (PC) or CEMI. However, their early age strength development is not only significantly different but it is also affected to a greater extent by curing temperature.

High early age strengths, e.g. 15 MPa at 16 hours, are needed by precast concrete factories for lifting operations in order to maintain their daily production of structural and non-structural elements. The factors affecting strength at early ages must therefore be considered. These factors include the composition of the concrete mixture, such as cement type and SCM addition, and the use of retarding or accelerating admixtures. The strength development of a concrete is also influenced by temperature. Strength gain is more rapid at higher temperatures and slower at lower temperatures and if the temperature is too low then strength gain will cease altogether. The internal concrete temperature in a precast factory will depend on the temperature of the heating/casting bed, on the heat of hydration produced by the cement reaction, the size and shape of the structural element, the ambient temperature, and the use of insulation.

SCMs, such as fly ash and ggbs, have not gained popularity for precast work because they gain strength more slowly at standard curing temperatures. This is despite that previous studies [1,2,3] concluded that SCMs are heavily penalised by standard curing regimes. At elevated temperatures there can be a significant improvement in the early age strength of blended cement concretes containing fly ash and ggbs [2,3]. The rate of reaction is clearly increased by temperature and once initiated it continues even when the external source of heat is removed, indicating an activation effect [2].

The work described here aimed at:

- Quantifying the effect of high early age curing temperature on the strength enhancement of neat Portland cement as well as mortars with up to 70% ggbs of the total binder content.
- Determining the suitability of maturity functions, like the Arrhenius based one proposed by Freiesleben Hansen and Pedersen (FHP) [4], for ggbs mortars.

Relationships between strength and maturity were determined using data from cubes cured at 20°C. These relationships were then used together with the adiabatic temperature history to predict the strength development under adiabatic curing conditions. Activation energies determined from 50mm mortar cubes cured at 10, 20, 30, 40 and 50°C, were used in the FHP equation to determine the equivalent age of 50 mm cubes cured under adiabatic curing conditions.

2. Materials and experimental procedures

A concrete mixture of Grade C45 (target 28-day strength of 55 MPa) was used as the basis for determining the mix proportions of “equivalent” mortar mixtures shown in Table 1. The...
control mixture used neat Portland cement as the binder (PC45) and percentage of ggbs as part of the total binder investigated were 20, 35, 50 and 70%.

Table 1: Equivalent mortar mix proportions for a concrete grade C45

<table>
<thead>
<tr>
<th>Mortar</th>
<th>Cement (kg/m³)</th>
<th>ggbs (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Free water (kg/m³)</th>
<th>Added water (kg/m³)</th>
<th>w/b</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC45</td>
<td>455</td>
<td>-</td>
<td>1505</td>
<td>232</td>
<td>242</td>
<td>0.51</td>
</tr>
<tr>
<td>20GGBS45</td>
<td>385</td>
<td>96.00</td>
<td>1476</td>
<td>231</td>
<td>241</td>
<td>0.48</td>
</tr>
<tr>
<td>35GGBS45</td>
<td>319</td>
<td>171</td>
<td>1470</td>
<td>230</td>
<td>240</td>
<td>0.47</td>
</tr>
<tr>
<td>50GGBS45</td>
<td>261</td>
<td>260</td>
<td>1439</td>
<td>229</td>
<td>238</td>
<td>0.44</td>
</tr>
<tr>
<td>70GGBS45</td>
<td>163</td>
<td>380</td>
<td>1419</td>
<td>228</td>
<td>237</td>
<td>0.42</td>
</tr>
</tbody>
</table>

2.1 Materials
Single batches of Portland cement and ggbs were used throughout. The fine aggregate was a very fine sand with 81% of the particles passing through the 600 μm sieve. All aggregate was oven-dried before use and allowance was made for absorption when calculating batch weights for mixing.

2.2 Mixing, Casting, Curing and Testing of Concrete Specimens
The materials were weighed and placed in a 0.1 m³ capacity horizontal pan mixer in the order: coarse aggregate, cement, ggbs, sand, and then the water. The mortar was mixed for 5 minutes, cast into 50 mm steel cube moulds, and then externally compacted using a vibrating table. The specimens were wrapped with a polythene sheet and immediately placed in curing tanks set at 20, 30, 40 and 50°C. They were only demoulded just prior to testing for compressive strength.

The specimens for adiabatic curing were placed in a computer controlled water curing tank. The water temperature of the curing tank was set so that it would follow the internal adiabatic temperature history of a mortar specimen curing in the tank. The specimens in the tank were either demoulded just prior to testing or after 5-days when they were transferred to a constant temperature cabinet or curing tank. The ones placed in a temperature cabinet were wrapped in damp hessian and polythene sheet until they were tested.

2.3 Adiabatic Temperature Measurements
The adiabatic temperature rise due to hydration of cement is defined as the temperature rise which will occur if fresh concrete or mortar is stored in a perfectly insulated environment, i.e. one from which no heat loss can occur. To achieve this state it is necessary either to heavily insulate the concrete/mortar or to ensure that the environment in which the concrete/mortar is
stored is at the same, or nearly the same, temperature as the concrete/mortar. The latter approach was adopted in this research programme.

In addition to the mortar cubes, an 150mm mortar block was cast in a steel mould lined with 20 mm expanded polystyrene for insulation and heavy duty polythene to prevent moisture loss. The specimen was then placed in the water curing tank, with two copper/constantan thermocouples embedded into the mortar using a hole in the top of the mould. Two more copper/constantan thermocouples were used to monitor the water temperature of the curing tank. The thermocouples were all connected to a computer which was set to activate the heating element of the tank when the temperature difference between the water in the tank and the concrete was 1°C. There was no temperature drop observed after the maximum had been reached and from this it was deduced that the conditions were near-adiabatic.

2.4 Determination of Activation Energies
Activation energies have been determined according to ASTM Standard C1074-98 [5]. This standard recommends that tests are performed on mortar specimens and the results applied to the concrete under investigation. The mix proportions, shown in Table 1, have been derived from those of a concrete of Grade C45. Each mortar had the same water-binder ratio as the concrete. The sand/binder ratio was equal to the coarse/binder ratio of the concrete. The 50 mm mortar cubes were mixed and cast into moulds using a similar procedure to the 100 mm concrete cubes. They were wrapped in cling film immediately after casting and placed in water baths maintained at four different temperatures, 20, 30, 40 and 50 °C. Additional specimens were wrapped in damp hessian and polythene sheeting and cured at 10 °C in a cooler incubator.

The compressive strength of three replica mortar cubes was determined at a time when it was estimated that the mortar had achieved a strength of at least 4 MPa, e.g., 6 hours for specimens cured at 50 °C. Subsequent tests were carried out at ages that were approximately twice the age of the first test. For example, if the time of the first test was 12 hours, successive compressive tests were performed at 1, 2, 4, 8, 16, and 32 days. Sufficient mortar cubes were cast for at least six testing ages.

3. Results and discussion

3.1 Strength Development of Isothermally Cured Mortar Mixtures
A high curing temperature accelerates the strength development of both the neat Portland cement and ggbs mortars, as can be seen from Figure 1. The strength development from using ggbs was observed to be slower than from using neat Portland cement at the standard curing temperature of 20 °C. However, an elevated curing temperature had a greater influence on the strength development of cubes using ggbs. Higher early age curing temperatures appear to have significant detrimental effect on the later age strength development of particularly the Portland cement mix while a lesser effect for mortar mixtures with ggbs.
3.2 Determination of “apparent” activation energies.
Activation energies can be determined from the strength development of 50 mm mortar cubes cured at 10, 20, 30, 40 and 50 °C. Several functions have been proposed to relate concrete strength to either the maturity index or time after casting [4, 6-12], e.g., the Three Parameter Equation (TPE) suggested by Freiesleben Hansen and Pedersen [4]:

\[ S = S_\infty e^{\left(\frac{\tau}{M}\right)^\alpha} \]  

where:
- \( S_\infty \) = limiting strength
- \( \tau \) = characteristic time constant,
- \( \alpha \) = shape parameter

The activation energy was determined by plotting the logarithm of the characteristic time constant (\( \tau \)), versus the reciprocal absolute temperature of the water bath. The slopes of the lines, shown in Figure 2, were multiplied by the gas constant, \( R = 8.3144 \text{ J/mol-K} \), to obtain the activation energies which were for PC = 34.88 kJ/mol, 20GGBS45 = 42.71 kJ/mol, 35GGBS45 = 43.58 kJ/mol, 50GGBS45 = 45.34 kJ/mol and 70GGBS45 = 49.65 kJ/mol. The higher activation energies found with increasing ggbs content confirm that higher curing temperatures increase the strength development considerably more than when using neat Portland cement.

3.3 Strength Predictions Using Maturity Functions
Numerous maturity functions have been proposed but the two most commonly used are the Nurse-Saul function and Freiesleben Hansen and Pedersen’s expression for equivalent age [4]. The latter is based on the Arrhenius equation.
The Nurse-Saul maturity model:
\[ M = \sum (T - T_0) \cdot \Delta t \]  
(2)

assumes a linear relationship:
\[ k_{NS} = a \cdot (T - T_0) \]  
(3)

where:  
- \( M \) is the Nurse-Saul maturity (°C·days),  
- \( T \) is the average temperature (20 °C for standard curing) over the time interval \( \Delta t \) (°C),  
- \( T_0 \) is the datum temperature (°C),  
- \( \Delta t \) is the time interval (days),  
- \( k_{NS} \) is the rate constant,  
- \( a \) is a constant.

The datum temperature is the temperature below which it is assumed that no strength gain will occur, taken as -11 °C in this work which is the average of what is recommended in the literature, i.e. between -10 °C and -12 °C [13-15]. The relationship between strength and maturity is assumed to be independent of temperature history, and can therefore be

Figure 2: Natural logarithms of the rate constant (k) versus the reciprocal of absolute temperature.
determined at a reference temperature. An equivalent age, $t_e$, can be defined as the age at the reference temperature at which the concrete has the same strength as at a time $t$:

$$
t_e = \frac{\sum (T - T_0)}{(T_r - T_0)} \cdot \Delta t
$$

where:

- $t_e$ is the equivalent age at the reference temperature (days),
- $T_r$ is the reference temperature (°C).

Freiesleben Hansen and Pedersen’s expression for equivalent age [4], based on the Arrhenius equation, is:

$$
t_e = \sum_0^t e^{-8 \left[ \frac{1}{273 + T} + \frac{1}{273 + T_r} \right]}
$$

where:

- $t_e$ = equivalent age at the reference curing temperature
- $T$ = average temperature of concrete (°C) during time
interval $\Delta t$,

$T_r =$ reference temperature, $^\circ$C

$E =$ apparent activation energy, J/gmol,

and

$R =$ universal gas constant, 8.3144 J/gmol-K.

The Nurse-Saul function requires the temperature history, in this case the curing temperature – see Figure 3 for adiabatic temperature histories, of the mortar in order to calculate the maturity index according to Equation 2. The equivalent age $t_e$ at time $t$ was calculated using Equation 3. The value of equivalent age obtained, $t_e$, was then substituted for $t$ in Equation 1 with constants $S_f$, $W$ and $D$, as previously determined for the strength data obtained for the mortar cured at 20 $^\circ$C and the estimated strength was thus obtained.

![Figure 4: Estimated adiabatic strengths based on the Nurse-Saul (NS) and Arrhenius (Arr) based functions.](image)

The Arrhenius function required the apparent activation energies of all mortars which were determined according to ASTM C107 [5] method. The equivalent age $t_e$ at time $t$ was calculated using Equation 5. The specified reference temperature, $T_r$, used was 293 K (20 $^\circ$C). $T_a$ being the average temperature, in Kelvin, of mortar during time interval $\Delta t$ was none other than the curing temperature. The value of equivalent age obtained, $t_e$, was then substituted for $t$ in Equation 1 with constants $S_f$, $\tau$ and $\alpha$, as previously determined for the strength data obtained for the mortar cured at 20 $^\circ$C (see Table 2). The estimated strength was thus obtained.
The Nurse-Saul function estimated the adiabatic early age strengths of Portland cement relatively well but underestimated the ones for ggbs. This appeared to increase with increasing ggbs content, see Figure 4. This is because the Nurse-Saul function assumes that the concrete or mortar strength gain rate varies linearly with temperature irrespective of whether ggbs or other SCMs are used or not. Ggbs has been shown to be more temperature sensitive, as indicated by its higher activation energy, than Portland cement. The Nurse-Saul function overestimated later-age strengths beyond eight and sixteen days for Portland cement and ggbs mixes respectively. This increased with increasing age and appears to be due to the inability of this function to account for the detrimental effect high early age temperatures have on the ultimate strength.

The strength estimates from the Arrhenius function, see Figure 5, were accurate for very early ages, i.e. up to one and two days, for both Portland cement and ggbs mixes. This is because the Arrhenius function considers that the strength gain rate varies exponentially with temperature. However, this is also the reason that it overestimates strengths beyond the first couple of days. If the strength estimates of the Arrhenius function are correct then the detrimental effect of high curing temperature starts from early age and is simply more pronounced in long term. There are indications that the cross-over effect for ggbs mixes occurs at later ages than Portland cement mixes.


The early age strength of “equivalent” mortars of concretes with similar 28-day strengths and cured at 20 °C (68 °F) have been shown to be adversely affected by high levels of ggbs in the total binder. However, the acceleration of the strength development of ggbs mortars with high early age curing temperature has also been shown to be greater than neat Portland cement mortars. If these improved strengths are to be exploited for precast work, then:

(a) The expected or required early age curing temperature should be modeled, e.g., using finite element analysis software. Heat of hydration values, obtained from adiabatic tests, will be needed as input.

(b) The strength development at these elevated curing temperatures should be predicted using maturity functions.

The detrimental effect of a high early age curing temperature on the strength development has been shown to affect the strength predictions of maturity functions. This detrimental effect needs to be incorporated into maturity functions for a more accurate strength prediction from 24 to 48 hours for Portland cement and ggbs mortars.

Acknowledgements

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Physical Sciences Research Council, UK (GR/R83880/01), for the financial support received for the equipment.

References

Abstract

Working group 2 of the RILEM TC 238-SCM organized a round robin test to compare the protocols of different laboratories to determine the degree of reaction of two slags, a calcareous and a siliceous fly ash in binary mixes with Portland cement. The techniques used were: selective dissolution, analysis of the differences in portlandite content from thermogravimetric analysis, X-ray diffraction with PONKCS (partial or no known crystal structure) refinement, and scanning electron microscopy with image analysis. As each laboratory followed their own protocols, the collective assessment of the results provided an idea of the maximum inter-laboratory variability, which should be universally valid. This study assesses the accuracy and precision of the four techniques investigated and with respect to each of the materials studied.

1. Introduction

Working group 2 of the RILEM TC 238-SCM: Hydration and microstructure of concrete with supplementary cementitious materials (SCMs) carried out a comparison of the practices in six European laboratories (named A-F) to determine the degree of reaction of slag and fly ash in composite cements. The quantification of the degree of reaction of SCMs in hydrated cement is challenging and each of the currently available methods has both advantages and disadvantages. The abovementioned committee have recently summarized those techniques in [1], but the actual inter-laboratory performance has never been tested. This paper presents general results of this study and a full paper is in preparation.
2. Materials

The materials used in this study were portland cement PC, slag S1 and slag S2, siliceous fly ash SFA, calcareous fly ash CFA, and quartz Q inert filler. The chemical and phase composition of the raw materials are shown in Table 1. The two slags studied were > 99% amorphous. The particle size distributions of the raw materials were measured by laser diffraction using a Malvern MasterSizer S and are presented in Figure 1.

Table 1: Chemical and phase composition [wt.-%] of the raw materials measured by XRF and by XRD-Rietveld refinement respectively.

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</table>

Figure 1: Particle size distributions measured by laser diffraction.

The study was carried out on paste samples: PC + 40 wt.-% slag and 30 wt.-% fly ash. Reference samples contained PC and 40 wt.-% and 30 wt.-% of quartz inert filler. The powders were mixed with water (water/binder ratio 0.4) using a laboratory mixer at 1600 rpm. The pastes were seal-cured for 1, 7, 28 and 90 days at 20 °C. After curing, discs of around 2-3 mm thickness and 33 mm diameter were cut from the paste cylinders. To stop hydration these discs were kept for 7 days in isopropanol and then 7 days in vacuum desiccator. One
laboratory prepared the samples, which were then sealed in vacuum bags and distributed to the participants. Before experiments, the participants removed by gentle grinding the outer layer of the samples, which may have carbonated.

3. Methods

Below basic information is given on the techniques used. Details will be presented in the full publication. Each participating laboratory could choose the techniques to apply and follow their own protocols.

Selective dissolution for fly ash and its cements was carried out using HCl + salicylic acid + methanol, similarly to the European standard CEN/TR 196-4 (2007). The residue of raw fly ashes in salicylic acid + HCl was: for SFA 98-99 wt.-% and for CFA 70-80 wt.-%. Such low residue of CFA made it unacceptable for the determination of the degree of reaction by this method. The calculation of the degree of reaction of SFA was done according to [3].

Selective dissolution of slags and slag cements was carried out using EDTA+TEA+DEA water solution. The residue of slags in EDTA+TEA+DEA was 90-95 wt.%, which is rather low but still acceptable. The degree of reaction of slag in the PC-S pastes was computed according to [2].

Calculation of the degree of reaction of SCMs based on the portlandite difference was carried out on data from thermo-gravimetric measurements on PC-SCM and PC-quartz samples. The latter were used to account for the filler effect of SCMs. One laboratory computed the degrees of reaction of the SCMs following the procedure of Pane and Hansen [4]. The others followed a mass-balance approach, in which Ca required from portlandite and Si coming from the SCM to form C-S-H are balanced. The Ca/Si ratio of the C-S-H needed for this calculation was measured by SEM-EDS point analysis.

SEM – image analysis was carried out on polished sections of epoxy-impregnated paste discs coated with ~15 nm of conductive carbon. Unreacted slag was quantified using BSE images and EDS maps of Mg (lab B) or Mg, Ca, Si (lab E). Unreacted fly ash was segmented using high quality EDS maps of Al, Si and Ca as in [8]. The degree of reaction of the SCMs was computed from the difference between initial and measured amount of SCMs.

X-ray powder diffraction measurements were carried out on raw SCMs and on ground pastes with CuKα radiation (source at 45 kV, 40 mA) and angles 5-70 °2θ. Rietveld refinement was carried out on the background, the unit cell parameters and the Lorentzian peak broadening. Amorphous phase models for PONKCS were prepared based on the scans of raw materials and included in the refinement to quantify the amount of unreacted SCMs.

4. Results

Figure 2 presents the results of the four techniques studied, in which the points correspond to the mean degree of reaction and the whiskers show min-max values. The global mean was
calculated as an average of means. This presentation was chosen, as elaborate statistics on the small data set available would be misleading.

![Figure 2: Comparison of the degrees of reaction measured by the four techniques studied.](image)

The main observation from Figure 2 is that the precision of the determination of the degree of reaction of SCMs in hydrating cement pastes is quite low, mostly around ± 10 %, and at best around ±5 %.

Selective dissolution based on EDTA for slag cements underestimated the reaction compared to the global mean. Selective dissolution of siliceous fly ash pastes done with salicylic acid + HCl seemed to work fairly well, but failed completely for the calcareous fly ash pastes.

The degrees of reaction calculated from the portlandite difference were in the low range too. This technique is sensitive to the portlandite content measured since the reaction of slags and calcareous fly ashes consumes little portlandite. Imprecise determination or an estimation of the Ca/Si of the C-S-H may lead to further errors.

SEM-IA was able to measure the reaction of all the SCMs studied, but tended to overestimate the degrees of hydration of slags. This may have been due to unresolved fine particles, which regards the fly ashes too although not observed in the results of this study.
By far the largest variations were observed for the XRD-PONKCS. For PC-SFA the results of the different laboratories were much more comparable, but this is because the degrees of reaction were lower. There is no strict protocol of how model amorphous phases should be prepared and refined. Further, a correct definition of the background is challenging and an overlap between the contribution of the SCM and the C-S-H may hinder correct refinement.

5. Conclusions

The precision of the determination of the degree of reaction of SCMs was assessed by a round robin test of six laboratories. The results indicated that it is generally impossible to determine the degree of reaction of SCMs with precision better than ± 10 %, and at best ± 5 %. As each laboratory followed its own protocols these results are expected to be universally applicable.

As for each of the techniques studied: The degrees of reaction were systematically low for the selective dissolution and this technique failed for calcareous fly ash. Calculations based on portlandite difference may be very sensitive to the portlandite content measured and the Ca/Si ratio of the C-S-H. SEM-image analysis could tackle all the SCMs studied, but may overestimate the degrees of reaction due to unresolved fines. XRD-PONKCS had rather low accuracy and seems very sensitive to the way it is carried out. An improved, strict and careful protocol should be prepared and verified before this method is more widely used.

References

EFFECT OF TESTING CONDITIONS ON THE LOSS ON IGNITION RESULTS OF ANHYDROUS GRANULATED BLAST FURNACE SLAGS DETERMINED VIA THERMOGRAVIMETRY

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Abstract
A key property influencing the quality of a blast furnace slag (GBFS) used in cements and concretes is the loss on ignition (LOI), which is associated with the amount of moisture and carbonates present. Both EN and ASTM standards describe determination of the LOI of GBFS, and thermogravimetric analysis (TGA) is also a valuable test which provides information that can be related to the LOI. However, the final mass loss obtained by TGA is influenced by the testing conditions including nature and flowrate of the gas used, the sample mass and heating rate, and there is no existing standard method for TGA of SCMs. As part of the efforts of RILEM TC 238-SCM, this study assesses the effect of the gas environment and gas flowrate on the observed mass loss from a GBFS, determined via TGA in nitrogen, argon or air atmospheres using different gas flowrates, and without correction for oxidation of sulfides to sulfates. Significant mass changes occur between 800–1000 °C independent of the gas used, and are more notable under an oxidising atmosphere and at low gas flowrates. These results elucidate that it is required to standardise TGA testing parameters for analysis of GBFS to enable collection of meaningful results by this technique.

1. Introduction

Most modern concretes contain supplementary cementitious materials (SCMs) such as granulated blast furnace slag (GBFS), a by-product derived from the iron making industry, as partial replacements of Portland cement. The growing interest in the utilisation of SCMs is mainly associated with their environmental benefits, and the enhanced performance developed by blended concretes, compared with those without additions [1, 2]. However, as some SCMs are wastes or by-products from different industrial practices, it is imperative to ensure their accurate physical and chemical characterisation to determine suitability for use as building materials. One of the tests used to assess the quality of slags is the loss on ignition (LOI), used to identify pre-hydration or weathering which can affect slag reactivity and thus impact the
performance of the concretes produced. The LOI of GBFS can be determined according to the standardised testing method EN 196-2 [3] which specifies to ignite the sample in an oxidising atmosphere at 950 ± 25°C to assure that the carbonates and water present in the sample are completely removed, and that oxidation of any iron, manganese or sulfides takes place. Similarly, ASTM C114 [4] specifies to ignite the sample at 950 ± 50°C. In both standards the procedure to correct the LOI values due oxidation of sulfides is specified.

Thermogravimetric analysis (TGA) of construction materials including gypsum [5] and fly ashes [6] has been identified as a faster method for determination of mass loss upon heating. However, results from TGA are strongly influenced by the testing conditions such as the geometry of the cell and balance, the nature and flow rate of the gas environment used, the amount of sample tested, and the heating rate used, among other parameters. As there is no existing standardised method for TGA of SCMs, variation among different laboratories are identified, which can lead to misleading results regarding the quality of a given SCM.

As part of the efforts of working group 1 (WG1) of RILEM TC 238 SCM, the present study assesses the effect of the nature and flowrate of the gas environment on the measured mass loss of a blast furnace slag, as determined via TGA coupled with mass spectrometry. Anhydrous slag samples were tested in nitrogen, argon and air atmospheres using gas flowrates of 20, 40, 60 and 100 mL/min. Complementary in-situ heating X-ray diffraction of the slag was conducted in air, to elucidate potential formation of crystalline solid reaction products via the interactions of sulfate species forming in the slag at high temperatures.

2. Experimental programme

2.1. Material and tests conducted

An anhydrous GBFS supplied by RILEM TC 238-SCM, whose chemical composition is shown in Table 1, was used in this study. Its loss on ignition, determined according to BS EN 196-2, was 0.84%.

Table 1. Chemical composition of the GBFS as determined by X-ray fluorescence. The entry reported as “SO₃” is the oxide equivalent of the total sulfur content, which was determined to be present 8.5% as sulfate and 91.5% as sulfide. Data provided by RILEM TC 238-SCM.

<table>
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<th></th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
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</table>

TGA of all samples was carried out in a Perkin Elmer TGA 4000 instrument coupled with a Hiden mass spectrometer. 40 mg of sample was tested from 30°C to 1000°C at a heating rate of 10°C/min. Commercial-grade argon, nitrogen or air were used as sample purge gases, at varying flowrates between 20 and 100 mL/min.

To determine the potential formation of sulfate-rich phases upon heating of the GBFS, in-situ heating X-ray diffraction (XRD) experiments were carried out in a D5000 Siemens diffractometer with Cu-Kα radiation and a nickel filter. Samples were heated from room
temperature to 1050 °C at a heating rate of 10 °C/min. Measurements were taken at room temperature before heating, 750 °C, 850 °C, 950 °C, 1050 °C during heating, and 30 °C after cooling down from 1050 °C. The XRD scans were acquired with a step size of 0.02° and a counting time of 2 s/step from 5° to 55° (2θ). The temperature was held constant while each diffractogram was collected.

3. Results and discussion

3.1. Thermogravimetric analysis

Fig 1 shows significant differences in the thermograms as a function of the type of gas and the gas flowrate used. Between 30°C and 200°C only minor mass changes were identified in all the samples, independent of the testing conditions. Notable differences in the mass loss were observed between 200°C and 650°C depending on the type of gas used. For samples tested in argon (Fig 1A), at gas flowrates between 20 and 60 mL/min minor differences were detected; however, an increased rate of gas flow (100 mL/min) led to a higher mass loss within this range of temperatures than was observed at lower gas flowrates. When using nitrogen (Fig 1B), an increased mass loss was observed at lower gas flowrates, although no significant differences in the mass loss were identified when using 40 and 60 mL/min of gas. Variations in the mass loss were not observed in this range of temperatures when testing the samples in air.

The most significant mass changes observed under all testing conditions took place between 650°C and 1000°C, a temperature range of significant relevance when comparing to determination of LOI according to different standard methods. For samples tested in argon (Fig 1A) at gas flowrates below 60 mL/min, a slight mass gain is observed between 650°C and 930°C, followed by a significant increase in mass up to 1000°C. This was more notable in the samples tested at the lower gas flowrates. Conversely, using 100 mL/min of argon induced a slight mass reduction at higher temperatures of testing. Comparable results were identified for samples tested in nitrogen (Fig 1B), however, greater mass loss is observed at higher gas flowrates. In samples tested under 60 and 100 mL/min of nitrogen, mass gains above 900°C were not identified. It appears likely that these mass increases in the presence of lower flowrates of ‘non-oxidising’ gases may be related to the insufficient purging of oxygen from the furnace – whether entering due to improper furnace sealing, released from the slag in mass loss processes then reabsorbed at higher temperature, or from other sources – but confirmation of this theory would require further investigation using a broader range of slags and other specimens.

For specimens tested in air (Fig 1C), a two stage mass gain is observed, independent of the gas flowrate used. The first mass gain took place between 650°C and 930°C, and the second from 930°C to 1000°C. There is a clear consistency in the ranges of temperatures at which the mass gain was observed across the different testing conditions, not just for samples tested in air, but also for samples tested in argon and nitrogen. This indicates that similar phenomena are governing the mass gain of this GBFS at high temperatures, independent of the gas and flowrate used during testing. All of the TGA tests showed a maximum mass loss at a
temperature just below 700°C, reaching a value of around 1% which was significantly greater than the measured LOI of the slag.

![Fig 1. TGA results, as a function of the gas flowrate, of anhydrous GBFS tested under (A) argon, (B) nitrogen and (C) air at flowrates as marked, and (D) enlargement of the thermograms in air, highlighting ranges of temperatures used to determine LOI in EN and ASTM standards](image)

The mass loss values of the slag at 950°C determined by TGA (uncorrected for any mass gain due to oxidative reactions) are reported in Table 2, where it can be seen that the type of gas and the gas flowrate used during testing strongly influence the measurements. For all gases used, a high gas flowrate gives an increase in the mass loss. Slight differences were identified in the mass loss values obtained when using nitrogen or argon at the different gas flowrates; however, when using air (which is specified as the gas environment in the standardised LOI tests), the mass loss values were four to five times lower than the values obtained when using nitrogen or argon, due to the oxidative processes taking place in the presence of this gas atmosphere. The temperature at which the mass loss is determined influences significantly the measured mass change, as shown in Fig 1D, and this variability is greater when adopting the range of temperatures recommended by ASTM compared with that stipulated in the EN standard. In conducting that LOI test, the absolute change in mass recorded at 950°C was in fact a gain of 0.31%, with the application of the EN 196-2 sulfide oxidation correction.
(subtraction of 1.15% in this case) yielding the underlying loss value of 0.84%. This value is within the range of the results obtained when testing the slag in air and using a gas flowrate higher than 60 mL/min (Table 2).

Table 2. Mass loss at 950°C of the anhydrous GBFS determined by TGA*

<table>
<thead>
<tr>
<th>Type of gas</th>
<th>Gas flowrate (mL/min)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>0.83 ± 0.23</td>
<td>1.07 ± 0.22</td>
<td>1.25 ± 0.08</td>
<td>1.94 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.68 ± 0.16</td>
<td>1.49 ± 0.01</td>
<td>1.83 ± 0.02</td>
<td>2.25 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>0.26 ± 0.24</td>
<td>0.29 ± 0.24</td>
<td>0.53 ± 0.22</td>
<td>0.59 ± 0.21</td>
<td></td>
</tr>
</tbody>
</table>

* Range of the residual weights (%) obtained at 950 ± 25°C; no correction for sulfide oxidation applied

3.2. Mass spectrometry

Fig 2 shows the measurement of the evolution of oxygen concentration during TGA of a GBFS, as a function of the gas type and flowrate. When using Ar or N₂ as purging gases, a significant reduction in O₂ was observed with an increase in the gas flowrate. In both of these cases negligible contents of O₂ were detected when using gas flowrates of 60 and 100 mL/min. Therefore, it is unlikely that mass changes under these testing conditions are associated with oxidation reactions of reduced species in the GBFS. However, at lower flowrates (20 and 40 mL/min argon, 40 mL/min nitrogen), a sharp dip in O₂ concentration is observed at 900°C, which corresponds closely to the sharp increase in mass in Fig.1 in these samples, and thus provides further weight to the identification of this mass increase as being related to an oxidative process. Conversely, negligible changes in O₂ concentrations are identified when using air as the purge gas, between the different gas flowrates assessed, where the oxygen content of the purge gas is registered in the mass spectrometer.

![Mass spectra of O₂(g) detected during TGA of an anhydrous GBFS when using (A) argon, (B) nitrogen or (C) air, as protective gases](image)

Fig 2 shows mass spectroscopy measurements of H₂S(g) and SO₂(g) during heating of samples tested using a low gas flowrate (20 mL/min). When using an N₂ gas environment,
H₂S(g) is the predominant sulfur-containing gas up to 800°C. At higher temperatures, a significant drop in the concentration of this gas is observed, consistent with the increase in SO₂(g) concentration. Similar results were identified when using dry air, where an initially low concentration of H₂S(g) was detected at temperatures below 200°C, followed by a significant increase in its concentration at temperatures between 200 and 800°C. This elucidates that at temperatures relevant for LOI determination the complete oxidation of sulfide has not taken place, even when testing GBFS in air.

Fig 3. Mass spectroscopy results for H₂S(g) and SO₂(g) detected during TGA of anhydrous GBFS using 40mg of sample, and 20 mL/min of (A) N₂ or (B) air

The mass spectroscopy results for H₂O(g) and CO₂(g) (Fig 4) indicate that the mass losses observed in the thermograms below 700°C (Fig 1) correspond to dehydration (between 30°C to 500°C) and decarbonation (between 250°C to 700°C) of the GBFS. Independent of the type of gas and the gas flowrate used, these reactions took place in the same temperature ranges.
For all the testing conditions assessed, an increased gas flowrate reduced the concentration of H$_2$O(g) released from the GBFS. Only minor differences in the concentration of CO$_2$ were identified as a function of the gas flowrate, indicating that the decomposition of carbonates present in the GBFS is not affected significantly by the nature of the gas environment used during TGA. Hence, the nature of gas and its flowrate during TGA of GBFS have a negligible effect on the quantified amounts of carbonates.

3.3. In-situ heating XRD

Fig 5, presenting X-ray diffractograms collected in situ during heating of GBFS in air, shows that GBFS crystallisation starts taking place between 850°C and 950°C and involves the formation of a transient phase wollastonite-2M (CaSiO$_3$, powder diffraction file (PDF) #43-1460), followed by the formation of akermanite (Ca$_2$MgSi$_2$O$_7$, PDF# 35-0592), as well as another polymorph of monocalcium silicate (CaSiO$_3$, PDF# 34-0612) and kilchoanite (Ca$_6$(SiO$_4$)(Si$_3$O$_{10}$), PDF# 46-1479).

Formation of sulfur-rich crystalline phases was not identified; however, the range of temperatures at which crystallisation of the GBFS was identified is consistent with the second mass gain observed by TGA (Fig 1), corresponding to the oxidation of S$^2-$ species (Fig 5). This indicates that the structural changes taking place in the GBFS glass at the point of crystallisation are also increasing the mobility of sulfur-containing species, because the
capacity of the glass to host sulfides is much greater than its potential degree of incorporation into any of the crystalline phases identified in Fig 5.

![Fig 5. In-situ heating X-ray diffractograms (Cu Kα radiation) of an anhydrous GBFS](image)

4. Conclusion

This study provides evidence that the testing conditions adopted during TGA for characterisation of SCMs, such as GBFS, strongly influence the ability to determine mass loss, and thus potentially to calculate LOI values, from those data. Therefore, the application of this technique needs to be standardised so that samples are evaluated under similar TGA testing conditions, and results for different slags across different laboratories can be compared. It is noted that a limitation of this study has been that the small sample masses studied (40 mg in each case) precluded the accurate measurement of sulfate content of the slags after heating, and so the corrections for oxidation of sulfide to sulfate which are specified in standard LOI determinations could not be implemented.

Upon heating the GBFS undergoes three main processes: (i) the removal of evaporable water (30°C - 500°C), (ii) decomposition of carbonate species (300°C - 750°C), and (iii) oxidation of sulfides (>750°C). The mass changes associated with each of these reactions depend on the type of gas and gas flow rate used during testing. When the ‘inert’ gases argon or nitrogen were used, a minimum gas flowrate of 60 mL/min (approximately double the usual recommended flowrate for this instrument) was required to eliminate oxygen gas and
consequently hindered the mass gains associated with the oxidation of the sulfides present in the GBFS. If determination of pre-hydration and/or weathering of the slag is desirable, it may be recommended to conduct LOI analysis at 750°C to minimise the convoluting effects of higher-temperature oxidation processes, which appear also to be linked to the onset of slag glass devitrification as identified by XRD.

The gas flowrate does not have a significant impact on the measured mass loss in an air environment, hence comparable results are obtained over a wide range of gas flowrates, although the mass loss values were up to three times lower than those reported when using nitrogen or argon as protective gases. The temperature selected to determine the LOI, within the allowable variation in standard test methods, may significantly affect the results obtained as the main mass changes in GBFS are observed between 900°C and 1000°C. Considering the high sensitivity of TGA, it is recommended to specify a narrower range of temperatures to determine LOI, than is stipulated in the EN and ASTM standards, to reduce variability of LOI results across laboratories.

Acknowledgments

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References

INFLUENCE OF SCM ON PORE SOLUTION COMPOSITION

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Abstract
The pore solution is an essential but often overlooked part of hydrated cements. The composition of the cement pore solution reflects the ongoing hydration processes and determines which solid phases are stable and may precipitate, and which phases are unstable and may dissolve. The study of the cement pore solution therefore contributes to the understanding of the mechanisms as well as of the kinetics of cement hydration. This contribution reviews the impact of supplementary cementitious materials (SCMs) on the pore solution composition of blended cements. An extensive literature survey is used to document the effect of the addition of SCMs (blast furnace slag, fly ash and silica fume) on the pore solution. The collected literature data are compared to thermodynamic simulations. The performance and current limitations of thermodynamic modelling of blended cement hydration are demonstrated and discussed in view of future progress.

1. Introduction
This paper is an output of the work of working group 3 (Hydration product assemblage and microstructure of SCM blended cements) of the RILEM TC 238-SCM. It aims to contribute to the understanding of the reaction mechanisms and kinetics of supplementary cementitious materials (SCMs) in combination with Portland cement by reviewing their impact on the liquid phase of cement paste. The composition of the liquid phase reveals which hydrate phases are stable and can thus (potentially) precipitate. Therefore the analysis of the pore solution is very useful for the thermodynamic modelling of hydrating cements. An extensive literature survey was carried out and information on chemical composition of the components, the mixture proportions of the pastes and the concentrations of hydroxide ions, sodium, potassium, calcium, sulfate, silicon and aluminium in the pore solution were summarised in a database. The findings and the database were published in [1].
To compare the general trends of the pore solution composition only the data measured between 20 to 23 °C were considered and the composition is restricted to pastes containing plain Portland cements (PC) and fly ash (FA), ground granulated blast furnace slag (GGBS) or silica fume (SF). Ternary blends were excluded and the water/binder ratio was limited to w/b < 1.0.

The changes in pore solution composition over time including the effect of type and amount of SCM in the blend are discussed in [1]. A summary and some examples are presented in this paper. To gain an understanding of the underlying mechanisms the effect of SCMs on the liquid composition and solid phase assemblage calculations were performed using thermodynamic modelling with the Gibbs free energy minimization program GEMS. Details on the thermodynamic database and the calculations are given in [1].

2. Methods

The experimental data included in this study were determined on cement pastes with practical w/b ratios (below 1.0). During the first hours of hydration the liquid phase can be separated by vacuum filtration or centrifugation. After hardening the pore solution has to be obtained by using a high pressure device. The extraction and the analysis of cement pore solutions should be carried out with caution. Detailed guidelines to the extraction and analysis of pore solution are given in [1].

3. Experimental results on pore solution composition in the course of hydration

The cement pore solution composition changes over time. To illustrate the influence of the SCMs, the trends in ionic concentrations in plain Portland cement pore solutions were analysed statistically. The average and the 95 % range of pure Portland cement pore solutions are shown in the following figures and are compared to reported pore solution compositions of cements blended with GGBS, FA and SF respectively. Since the w/b ratio has an impact on the alkali and hydroxide concentrations the discussion for these ions is limited to cements of w/b ratios of 0.4 - 0.5. The main components Ca, S, Al and Si are less affected by the w/b ratio. Therefore all cement pastes with w/b < 1 were considered for these elements. Exemplarily the concentrations of hydroxide, calcium and aluminium are shown in the following paragraphs.

3.1 Effect of SCMs on the alkalinity of the pore solution

Alkali concentrations in the pore solution depend strongly on the total alkali content of the cement and the SCM which is used. Blast furnace slags, fly ash and silica fume normally contain less alkali compounds than Portland cement clinker, which leads to lower alkali concentrations in blended cements.

Fig. 1 shows the hydroxide concentrations in the course of time that result from the lower alkali concentrations in the three different types of blends. In case of GGBS also reduced sulfur species can lower the pH of GGBS blend pore solutions. A decrease of the alkali
concentrations with time can be observed which is related to the reaction of the SCMs, which results in the formation of C-S-H with a lower Ca/Si ratio, where more alkalis are bound.

Due to the higher reaction degree of silica fume the blending of Portland cement with silica fume is most effective to lower the alkali and hydroxide concentrations in the pore solution. The strong pozzolanic reaction increases the amount of C-S-H formed and leads to the formation of C-S-H phases with lower Ca/Si ratio. At very high SF replacement levels portlandite is completely consumed, low Ca/Si C-S-H is present and more alkalis are bound. In the case of fly ash, different trends can be observed depending on the amount of alkalis present in the fly ash.

Fig. 1: Hydroxide concentration in the pore solution of blended cement pastes compared to the 95 % range of pure CEM I pastes with a w/c ratio of 0.4 to 0.5, [1]
3.2 Effect of SCMs on calcium concentration

The calcium concentrations in the pore solution are shown in Fig. 2 and 3. For GGBS and FA no significant differences compared to pure CEM I pastes are observed.

For silica fume the concentrations of calcium and sulfate in the pore solution are often out of the range of pure CEM I pastes. One would expect that calcium concentrations are reduced once portlandite is depleted, but instead they increase at high replacement ratios, because the pH-value decreases significantly. The solubility product of C-S-H for the reaction shown in equation (1), from [2] for low Ca/Si C-S-H, indicates that a decrease of the hydroxide concentration leads to an increase of calcium and/or silicon concentration.
\[
\frac{2}{3} \text{Ca}^{2+} + \text{Si(OH)}_2^+ + \frac{4}{3} \text{OH}^- + \frac{7}{8} \text{H}_2\text{O} \leftrightarrow (\text{CaO})_{0.67}\text{SiO}_2(\text{H}_2\text{O})_{1.5} \quad K_{sp} = 10^{-10.38} \tag{1}
\]

Fig. 3: Calcium concentration in the pore solution of blended cement pastes with SF compared to the 95 % range of pure CEM I pastes, [1]

3.2 Effect of SCMs on aluminium concentration

For GGBS and SF the concentrations of aluminium in the pore solution are in the same range as for pure CEM I pastes (see Fig. 4). For FA a slightly different trend is observed: the concentrations seem to increase over time. This trend has been related to the reaction of fly ash, which contains more aluminium than PC [3]. Unfortunately there is no data available for very long hydration times (> 365 d) to confirm this trend. Furthermore it has to be considered that the concentrations are very low. Typical detection limits of aluminium are indicated in the Fig. 4. Some authors apparently reached a higher analysis precision, nevertheless the scatter of the chemical analysis is high in that concentration range and changes that might occur are difficult to detect.
4. Thermodynamic modelling

Thermodynamic modelling is used to calculate the effect of the quantity of FA and SF on the pore solution composition and the hydrate assemblage. The results are compared with experimental data from literature. The chemical composition of the PC, FA and silica fume used in the calculations is given in [1]. The kind and amount of hydrates formed during the hydration of the Portland cements and the blended cements were calculated by assuming complete reaction of the PC and a limited reaction of the SCM, as the SCM reacts more slowly than PC. The degree of reaction (DoR) of fly ash and silica fume has been estimated based on literature data (refer to [1] for details).
For fly ash experimental data for a blending of up to 60 wt.-% fly ash were available. The results for a hydration stage of 12 years from [4] were chosen for this paper. The degree of fly ash reaction was 25 – 50 % depending on the fly ash content. The experimental results and the results of the thermodynamic modelling are presented in Fig. 5.

The effect of blending silica fume into Portland cement on pore solution composition is shown for a silica fume content of up to 35 wt.-% of the binder for ≥ 150 days of hydration (see Fig. 6). Based on experimental results the degree of reaction of the silica fume was assumed to be 80 % regardless of the replacement level [1].

Fig. 5: Comparison between collected experimental pore solution data (points) and modelled pore solution compositions (lines) and solid phase assemblage as a function of the fly ash fraction in the blended cement, [1].
Fig. 6: Comparison between collected experimental pore solution data (points) and modelled pore solution compositions (lines) and solid phase assemblage as a function of the silica fume fraction in the blended cement, [1].

The main effect of the presence of fly ash and silica fume on the pore solution after longer reaction times is the lowering of the alkali and hydroxide concentrations which is in good agreement with the experimental data.

The thermodynamic modelling predicts less portlandite if PC is replaced by fly ash. Above 40 wt.-% of fly ash a complete consumption of portlandite and the formation of C-S-H with lower Ca/Si ratio is predicted. In hydration studies, generally a decrease of the Ca/Si ratio of the C-S-H and lowering of the portlandite content is observed but not a complete depletion of portlandite [3, 4, 8]. The resilience of portlandite in hydrating fly ash-PC blends has been explained by the inhomogeneity of the microstructure and the lack of water.
The predicted changes in the solid phase composition are mirrored in the calculated decrease of calcium concentrations at higher replacement ratios. In parallel an increase of the silicon concentration is predicted, which could not be verified due to a lack of experimental silicon measurements.

Beyond portlandite depletion lower calcium and higher aluminium and silicon concentrations result in the formation of strätlingite (2CaO·Al₂O₃·SiO₂·8H₂O) instead of monocarbonate. Ettringite and hydrotalcite are predicted to be stable over the explored range of blending. Slightly decreasing volume fractions are related to the dilution of the Portland cement component. The aluminium and sulfate concentrations are controlled by the solubility of ettringite and thus increase as the calcium concentration and pH-values decrease.

The decrease of the alkaline and hydroxide concentrations is much stronger in the presence of silica fume as shown in Fig 6. As for fly ash, the thermodynamic modelling predicts the decrease of the portlandite content if PC is replaced by silica fume. Above 20 wt-% of silica fume the absence of portlandite and the formation of more C-S-H with lower Ca/Si ratio is predicted. Again the portlandite depletion marks the significant decrease of the alkali concentrations and of pH-values. The modelling predicts lower alkali and hydroxide concentrations than in the case of fly ash, as more C-S-H is predicted to form, which increases the alkali binding. The general decrease of the alkali and hydroxide concentrations predicted by the thermodynamic model agrees well with the experimental data, although the calculations overestimate the alkali and hydroxide concentrations at higher replacement levels.

As for fly ash, the calculations predict a decrease of calcium and an increase of silicon, aluminium and sulfate concentrations, which is however not confirmed by experimental data. However, overall the modelled trends show a good agreement with the available experimental data from literature, especially considering the differences in materials and experimental methods.

5. Summary and outlook

The collected experimental data on pore solution composition of pure Portland cement pastes and pastes with SCMs show considerable scatter because of the use of different raw materials, water to cement ratios and analytical methods. Nevertheless, following common trends are observed concerning the impact of SCMs on the cement pore solution:

- The alkalinity of the pore solution decreases with increasing replacement of PC by SCMs. SF is most effective in reducing the alkali concentration of the pore solution. The decreased alkali concentrations in the pore solution lead to reduced OH⁻ concentrations. In the case of GGBS negatively charged sulfur species such as sulfide or thiosulfate can additionally decrease the OH⁻ concentrations of the pore solution. The trends in the experimental data are in line with modelled OH⁻ concentrations for FA and SF blended cements.
- Calcium and sulfate concentrations are not significantly affected by GGBS or FA blending. According to the thermodynamic model calcium concentrations tend to
decrease at high FA replacement levels (> 60 wt.-%) when portlandite is depleted. The depletion has not been observed in experimental studies.

Blends with SF deviate from the thermodynamic model at high replacement ratios (> 30 wt.-%) and low pore solution pH. Contradictory to the modelling results the experimental data indicate an increase of calcium and a decrease in sulfate concentrations.

Reported measured silicon and aluminium concentrations are few. Therefore some of the very low measurements given in literature may not be reliable. The available data do not show changes in the silicon and aluminium concentrations of GGBS and SF blends compared to pure PC pastes, whilst for FA blends the aluminium concentration tends to increase over time and with an increasing replacement ratio. The latter observation is reproduced by thermodynamic modelling that predicts rising aluminium (and silicon) concentrations beyond portlandite depletion.

In general the comparison between experimental and modelled trends shows a good agreement. Some discrepancies, such as noted for Ca and Si concentrations in low pH, high SF cements, indicate that the currently used C-S-H model can be improved further. In addition, not only potassium and sodium, but also many other ions including aluminium, iron, chloride, sulfate or carbonate can be taken up by the C-S-H phase, which was not considered in the present model.

The effect of elevated temperature is also an important topic, especially for massive concrete structures. At the moment, only a few studies concerning this topic exist (e. g. [3, 6, 7]).

References

Abstract
A critical loading ratio is reached at 50% of concrete ultimate load. Beyond this point the presence of micro cracks exerts a big influence on the chloride transport. For compression the strain distribution in the sample developed micro-cracking system that is more or less homogeneously distributed in the sample. Therefore it is expected the same chloride profile regardless of the position. When combined splitting tensile load and chloride attack are acting on concrete, the main micro-crack system is located on the loading plane. This contributes to regular and alike shaped chloride profiles if they are taken from planes that are kept parallel to the splitting one. Prismatic samples (100 x 100 x 400 mm) made of OPC binder were exposed to a 3% by weight sodium chloride solution while maintaining a loading ratio equal to 60 % of the maximum capacity. Cubic samples (side = 150 mm) made of OPC and 50% BFS had similar chemical exposure while applying a permanent splitting tensile load corresponding to 65 % of their breaking capacity. After the exposure, ground layers were obtained from the samples to determine the total chloride ingress into the concrete by means of potentiometric titration and the effect of the load on the chloride ingress was assessed.

1. Introduction
One distinguishing feature presented by hardened concrete is its porosity. The nature of openings in cement paste depend on different conditions. For instance, the type of cement and binder along with their physical and chemical characteristics shape the porous nature of this material. Furthermore other conditions such as water/binder ratio, hydration time, curing temperature, and aggregate/paste ratio also outline the nature of this more or less changeable assembly. Micro-structure can be modified in time due to external factors of chemical and physical nature. Some of them can be considered aggressive and affect the durability of concrete. In contrast others help to improve the pore system. Concretes at field sites commonly have their voids partly occupied by solutions. Water containing salt can enter the
concrete pores by capillary absorption. This process is also called convection. The penetration magnitude of convection will be governed by other material features for example the size of the pores, existence of cracks and initial saturation degree. Once harmful salts have gone into the pore system they can travel further inside through diffusion, the degree of salt ingress is captured in the so-called diffusion coefficient. It depends not only on voids volume and size and amount of saturation, but also on the physicochemical nature of the cement or binder gel and its interaction with the aggressive ions in solution. Movement of ions into concrete is also influenced by cycles of wetting and drying, pressure and temperature. These factors contribute to the complexity of ionic transportation into the concrete.

The volume of pores in concrete is always changing, sometimes due to an on-going paste hydration and another time it is modified by its deterioration. It also can be considerably modified by an applied load to the concrete. Consequently it is probable that the movement of deleterious ions into concrete by convection and diffusion may be altered by the type and magnitude of the load applied to it. Chloride movement produced by convection and diffusion is depressed when a slight compressive load is applied to concrete. Contrarily an opposite effect is observed when the applied load exceeds a certain limit. Usually when 30 or 50 % of the concrete’s full compressive capability is surpassed, some micro cracks are created. These fresh pathways give an increase to the chloride intrusion. Under direct tensile load the rate of chloride infiltration surges gradually as the load is increased. While in splitting tensile loading, a critical stress has to be surpassed in order to increase the chloride transport into concrete.

The proposition of this research is not only to analyse the chloride ingress into loaded concrete from a physical point of view. Conversely the high chemical interaction that chloride ions have with cementitious binders it is well known. In order to compare these influences, concretes made of ordinary Portland cement (OPC), high sulfate-resistant cement (HSR) and OPC with 2 replacement levels of blast furnace slag (BFS) were exposed to a 3% sodium chloride solution while maintaining concrete specimens under permanent compressive and splitting tensile loads.

2. Experimental investigation

2.1 Materials and preparation of specimens

Five types of concrete mixes –S0, S50, S70, HSR, and S0-b– were prepared for the experiment. The mix composition are presented in table 1.

Aggregates consist of silica gravel and natural sand with a nominal maximum size of 16 mm. Three different binders were used. A Portland type I 52.5 cement with no special property for durability. Another type I 52.5 N cement but with high sulphate resistance (HSR) property. Blast furnace slag addition was utilized to replace part of the OPC in amounts of 50 and 70 % by weight. Characteristics of binders are shown in table 2.
A high range water reducer (Polycarboxylate based) was employed in amounts between 0.2 – 0.4 % by weight of binder in order to plasticize the fresh mix to obtain a slump between 160 – 210 mm before casting the samples.

Cubical samples of 150 mm side were moulded for the splitting test setups with mix designation S0, S50, S70, and HSR. The specimens were stored after casting for 7 days at 20±2 °C and RH = 95%, the cubes were then demoulded and stored for an additional 21 days at 20±2°C and 60±5% RH.

Concrete prisms of square section (100 x 100 mm²) and a height of 400 mm were cast for the compression test setup. They were stored 28 days after demoulding in a moist chamber at 20 ± 2 °C and RH>95%.

Table 1: Mix proportions of concrete.

<table>
<thead>
<tr>
<th>Designation</th>
<th>w/b ratio</th>
<th>Water (kg/m³)</th>
<th>CEM I (kg/m³)</th>
<th>CEM I (HSR) (kg/m³)</th>
<th>BFS (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Gravel (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>0.451</td>
<td>156</td>
<td>345</td>
<td>0</td>
<td>0</td>
<td>771</td>
<td>1085</td>
</tr>
<tr>
<td>S50</td>
<td>0.451</td>
<td>156</td>
<td>173</td>
<td>0</td>
<td>173</td>
<td>771</td>
<td>1084</td>
</tr>
<tr>
<td>S70</td>
<td>0.453</td>
<td>154</td>
<td>102</td>
<td>0</td>
<td>238</td>
<td>759</td>
<td>1067</td>
</tr>
<tr>
<td>HSR</td>
<td>0.451</td>
<td>157</td>
<td>0</td>
<td>347</td>
<td>0</td>
<td>774</td>
<td>1090</td>
</tr>
<tr>
<td>S0-b</td>
<td>0.450</td>
<td>166</td>
<td>369</td>
<td>0</td>
<td>0</td>
<td>840</td>
<td>1025</td>
</tr>
</tbody>
</table>

Table 2: Binder properties

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>CEM I 52.5 N</th>
<th>CEM I 52.5 N HSR</th>
<th>BFS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mineral phase (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃S</td>
<td>57.49</td>
<td>57.71</td>
<td>-</td>
</tr>
<tr>
<td>C₂S</td>
<td>10.81</td>
<td>18.45</td>
<td>-</td>
</tr>
<tr>
<td>C₄AF</td>
<td>13.12</td>
<td>12.32</td>
<td>-</td>
</tr>
<tr>
<td>C₃A</td>
<td>7.90</td>
<td>2.50</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Chemical composition (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>63.37</td>
<td>63.90</td>
</tr>
<tr>
<td>SiO₂</td>
<td>18.90</td>
<td>21.62</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.74</td>
<td>3.53</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.31</td>
<td>4.05</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.34</td>
<td>2.40</td>
</tr>
<tr>
<td>MgO</td>
<td>0.89</td>
<td>1.82</td>
</tr>
</tbody>
</table>
2.2 Experimental setup

For the splitting load setup 3 cubes representing each mix of S0, S50, S70, and HSR were tested at the age of 28 days. The strength properties of the materials as well as the corresponding load utilized for the experiment at 65% of their maximum capacity are shown in table 3.

Table 3: Average splitting loads for 3 cubes (150 mm side) and permanent applied load

<table>
<thead>
<tr>
<th>Sample #</th>
<th>28 days Ave. max. Load kN</th>
<th>Var. Coeff. %</th>
<th>28 days Splitt. Strength MPa</th>
<th>65% of max. Permanent load kN</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>145.5</td>
<td>1.9</td>
<td>4.1</td>
<td>94.6</td>
</tr>
<tr>
<td>S50</td>
<td>142.5</td>
<td>4.9</td>
<td>4.0</td>
<td>92.6</td>
</tr>
<tr>
<td>S70</td>
<td>124.0</td>
<td>1.8</td>
<td>3.5</td>
<td>80.6</td>
</tr>
<tr>
<td>HSR</td>
<td>168.7</td>
<td>1.8</td>
<td>4.8</td>
<td>109.6</td>
</tr>
</tbody>
</table>

Before the salt plus load exposure 2 cubes representing each mix were vacuum saturated. Afterward the cube’s faces were covered with black silicon plus aluminium foil leaving only two parallel opposite faces without this application. One of the faces will serve to attach one flexible reservoir of 640 cm³ capacity which will contain a circulating 3% sodium chloride solution. On the other face, a similar capacity reservoir will be placed, but only with saturated Ca(OH)₂ solution whose function is to keep the sample saturated, provide calcium ions in case of leaching and to check for any unexpected chloride filtration.

The reservoir with the attacking salt solution is connected to an 8 litres stock solution tank provided with an aquarium pump with capacity to pump the solution at a flow rate of 23 l/h.

The cubes are subjected to a permanent splitting stress by 2 opposed and coaxially aligned plywood strips 160 mm in length, 25 mm wide and 3 mm of thickness and are placed in the middle axis of the loading face. The wooden strips rest between the metal plates of a mechanical rig and the loading faces of the cubes as shown in figure 1. The load is transferred by an hydraulic jack which is connected to a pressurized cylinder which contains a nitrogen/oil mixture.

For the compressive loading setup 2 prism were tested for uniaxial compression at the age of 28 days. The obtained average strength result is shown in table 4. Afterward 2 prism were loaded coaxially until reaching 60 % of the reference maximum load as shown in figure 2. The same type of loading rig was used as the one utilized for the splitting test setup. After the prisms were loaded they were exposed to a 3% sodium chloride solution. The salt solution was recirculated trough a rectangular section reservoir of 80 mm width by 160 mm length and 50 mm depth which was attached to the middle part of the exposed face. The solution was pumped from an eight liter capacity stock solution using an small aquarium pump.
After a certain time of the combined attack exposure, the samples were taken out from their respective rigs. Subsequently, they were subjected to profile grinding starting from the chloride exposed face.

The powder for chloride determination was obtained by a diamond drilling bit of 10 mm in diameter. The drilling head was fixed on a rotating vertical shaft. The sample was placed on a horizontal moving table capable of providing 2 controlled perpendicular displacements.

The sampling ground surface consists of a groove whose long axis is oriented parallel to the splitting plane or to the prism’s axis. This consists of an indentation 25 mm long, 10 mm wide, and 1 – 2 – 3 or 4 mm depth. Usually, the first layers close to the exposed surface were ground at 1 mm depth interval. Subsequently, the depth's intervals were increased. After reaching the final depth, the obtained groove was cleaned with pressurized air and filled with epoxy, thus it can be used for further chloride exposure.

The sampling for the profiles exposed to compression were taken with the groove axis always oriented parallel to the prism axis at any location of the exposed surface. This was done considering the homogeneous strain distribution in that surface. On the contrary, the sampling for the splitting tensile exposure were taken at parallel planes located at 0 – 20 – 40 mm away from the splitting plane within the exposed surface.

The obtained powdered layers were treated with nitric acid to extract the total chloride content. The utilized procedure is described in EN 14629 “Determination of chloride content in hardened concrete”. This was done by potentiometric titration with a 0.01 M silver nitrate solution.

Figure 1. Setup for combined chloride attack plus splitting tensile loading.

Afterward, the obtained chloride penetration profiles were analysed and an error function solution was applied to Fick’s second law in order to obtain the apparent diffusion coefficient and the modelled chloride surface concentration.
Table 3: Compressive loads for 2 prisms (100x100 mm, h = 400 mm) and permanent load

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Ave. Load (100%)</th>
<th>Var. Coeff.</th>
<th>Compr. Strength</th>
<th>60% of Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0-b</td>
<td>568.9 kN</td>
<td>1.1 %</td>
<td>56.9 MPa</td>
<td>341.4 kN</td>
</tr>
</tbody>
</table>

Figure 2. Setup for combined chloride attack (2 prism), plus compressive loading.

2.3 Results and discussion

2.3.1 Micro crack observation for concretes under splitting tensile loading

In order to investigate the nature of micro cracking in concrete exposed to the combined attack, samples were taken from all concrete specimens for thin section microscopy. Special care was taken in order to obtain a rectangular section centered around the splitting plane and perpendicular to it as shown in figure 3 left.

The concrete slices of rectangular shape (width = 30 mm, depth = 50 mm) were then impregnated with fluorescent epoxy under vacuum and finally the sample was polished to obtain a 25 μm thickness of concrete for microscopic observation.
Under the microscope a main crack oriented parallel to the splitting plane was observed as shown in figure 4. The crack width is variable and can reach an opening close to 100 μm at the surface but it narrows with concrete depth. The crack is typically seen to run along some smooth texture aggregates, it jumps from aggregate to aggregate traversing the paste and also fracturing some irregular shaped stones. This main crack may tend to subdivide into smaller branches as the depth increases. A very fine network of microcracks (crack width between 1 – 4 μm) was also noticed connected perpendicularly to this main crack shaft.

![Figure 4. Micro cracking details under fluorescent light (grey tones left), showing fine crack network (red arrows) perpendicular to the main crack. Detail of micro cracking pattern (right). For S70 after 30 weeks chloride exposure.](image)

The intensity of cracking seems to be different according to the binder type. For the pure Portland cements S0 and HSR the same cracking pattern was found, but in their case it seems that the developed micro-cracks are filled again by a self-healing product sometime after their formation. That is why in these 2 types of concretes, the crack interior appears somehow blurred. On the contrary the S50 and S70 types of concrete shown a very clean micro-cracked pattern where it is easy to verify even 1 μm sized microcracks.

### 2.3.2 Micro-crack observation for concrete under compressive load

A slice of concrete of similar dimension as the samples representing the splitting test was taken for microscopy observations. The sample was taken perpendicular to the exposed face as shown in figure 3.

Figure 5 shows the typical micro crack network and its orientation. Some of the cracks develop with a sub-parallel orientation forming a small angle (25 degrees approximately) with the exposed surface. Another set of micro-cracks intersect the latter forming an internal angle of 108° approximately. This pattern is not always constant and some irregular orientation has also been observed. The width of the micro-cracks is finer than the one observed in the splitting test. The widest showed an average width of 8 – 10 μm and they are reduced to reach 1 - 3 μm openings.
2.3.3 Obtained chloride profiles for concrete under compressive load

Chloride transport in concrete under compressive loading remains more or less homogeneous as long as a critical loading ratio is not surpassed. This critical loading is reached when micro cracking starts to be the main factor in chloride transport within the concrete. It is mostly agreed [1] that the critical loading ratio for concrete under compression is reached at nearly 50% of the ultimate or highest load. Beyond this point it is assumed that the micro cracking pattern starts to enhance the chloride transport within the concrete.

There has been some agreement about the lower limit for the micro crack size beyond which the chloride diffusion coefficient is increased. According to several researchers (Ismail 2004, Francois 2005, Djerbi 2008) this lower limit would be 30 μm, while others (Yoom et al 2014) (Maes M. 2015), place this critical limit at 12 and 10 μm respectively. Afterwards the diffusion coefficient is increased until an upper limit is reached and beyond that, the chloride diffusion in the crack is just like dispersion of chloride in plain water. The upper size limit has been set by (Ismail, Francois, Kato and Djerbi) in a range between 75 and 125 μm.

It would be very simple to point out that the penetration of chloride ions through a cement matrix can be explained only with the known model of Fick's second law. Chloride ions are chemically active, as is the hydrated cement paste. At the beginning chlorides penetrate through the outermost layers of concrete. These layers are usually enriched with cement paste. This zone is more porous and the dominant transport here is by convection. After the convection zone and in non cracked paste, chlorides leave the aggressive solution reacting chemically with hydrated cement products. They are also physically adsorbed on the huge specific surface of CSH that acts as filter for these ions, decelerating the chloride ingress.

The presence of microcracks alters the delicate balance and therefore the ability of healthy cement paste to delay chloride entrance. It has been observed in this study that the effect promoted by microcracking has similar characteristics as if the convection zone is gradually increased over time.
Figure 6 shows a typical chloride penetration profile when concrete has been subjected to a combination of compressive stress and chloride solution exposure.

Figure 6. Acid soluble chloride content penetration after 8, 19 and 34 weeks, for S0-b exposed to 60% permanent compressive stress ratio and 3% chloride solution. Dashed vertical lines show the expansion of the convection zone ($\Delta x$) with time.

As seen in Figure 6, the layers obtained within the convection zone show a deviation towards lower values in the chloride content. Those points deviate from the normal fitting obtained at higher depths. The convection zone is a region with micro-cracks presence and where an aggressive solution is interacting with the paste. That provokes a reduction in the chloride adsorption capacity of CSH. Therefore unexpected low chloride points are seen in this region.

Considering the movement of the convection zone the expression shown in equation (1) is proposed:

$$C(x, t) = C_i + (C_{s\Delta x} - C_i) \cdot (1 - \text{erf} \left[ \frac{x - \Delta x}{\sqrt{4Dt}} \right])$$

(1)

Where $C(x, t)$ is the total chloride concentration at depth $x$ ($x > \Delta x$) and exposure time $t$ (s), $\Delta x$ is depth of the convection zone (m), $C_{s\Delta x}$ is the surface chloride concentration (%) but measured at $\Delta x$, $C_i$ is the initial chloride concentration (%) in the concrete and $D$ is the apparent chloride diffusion coefficient ($\text{m}^2/\text{s}$) which is obtained by modelling the chloride profile in a given period.

Table 4: Depth of convection zone, modelled surface concentration (% by weight of concrete) and diffusion coefficient applying equation (1) to profiles from figure 6

<table>
<thead>
<tr>
<th>Time (weeks)</th>
<th>$\Delta x$ (mm)</th>
<th>Surf. Conc. at $\Delta x$ (%)</th>
<th>$D \times 10^{12}$ (m$^2$/s)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>5</td>
<td>0.151</td>
<td>2.779</td>
<td>0.998</td>
</tr>
<tr>
<td>19</td>
<td>9</td>
<td>0.116</td>
<td>0.958</td>
<td>0.977</td>
</tr>
<tr>
<td>34</td>
<td>17</td>
<td>0.117</td>
<td>0.583</td>
<td>0.974</td>
</tr>
</tbody>
</table>

To characterize the chloride penetration in micro-cracked concrete, it is important to consider both parameters being the depth of the convection zone which is changing with time ($\Delta x$).
and the diffusion coefficient obtained at $x > \Delta x$. Table 4 shows the calculated parameters obtained from the chloride profiles of figure 6.

2.3.4 Obtained chloride profiles for concrete under splitting tensile loading

It is perceived from the petrographic analysis that the microcracking pattern provoked by the 65% splitting strength ratio is more intense than that produced by the compressive test. This statement relates to the size and frequency of cracks found, which are larger and abundant in the indirect tensile test.

The shape of the chloride profile remains more or less alike as long as the ground profile is taken parallel to the splitting plane. Figure 7 shows the chloride profile obtained for S0 mix.

Several researchers have noticed an inner higher peak in the chloride profile of concrete subjected to carbonation [2,3]; some also found this behaviour in concretes exposed to drying-wetting cycles [4]. Others have also noticed this conduct in cracked concrete [5]. In our case it is believed that microcrack formation promotes a higher ingress of chloride ions into this zone. Afterwards chlorides encourage calcium leaching from CSH sites and reduces the binding capacity (physical or chemical) of this gel. Probably it also provokes a lowering of the pore solution pH, a condition very similar to the effect of paste carbonation. In such condition the chloride content is lowered from the concrete surface towards inner zones until a lowest value is reached. The lowest value of the chloride content in our test is reached between 2-5 mm from the exposed surface. Subsequently, there is an increase in the chloride content until a higher peak is reached at inner depths. In some type of binders like S0 shown in Figure 7, two peaks are formed at 30 weeks of exposure and the chloride content forms a plateau between them. The second peak is located where the bulk condition is reached and normal diffusion takes place afterwards. The more intense micro-cracking system found in splitting tensile exposure provoke more damage and lower binding capacity for chlorides. Consequently their obtained profiles were lower than those observed in compression and their diffusivities were larger.
To calculate the chloride penetration parameters for the splitting tensile tests, equation (1) is also employed. Table 5 presents the obtained parameters for the chloride profiles from S0 shown in Figure 7.

<table>
<thead>
<tr>
<th>Time Axis dev. Weeks</th>
<th>Axis dev. mm</th>
<th>Δx mm</th>
<th>Surf. Conc. at Δx (%)</th>
<th>D x 10^{12} m^2/s</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0</td>
<td>7</td>
<td>0.176</td>
<td>4.009</td>
<td>0.995</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>13</td>
<td>0.166</td>
<td>2.154</td>
<td>0.969</td>
</tr>
<tr>
<td>30</td>
<td>19</td>
<td>13</td>
<td>0.142</td>
<td>2.569</td>
<td>0.925</td>
</tr>
<tr>
<td>30</td>
<td>38</td>
<td>13</td>
<td>0.193</td>
<td>0.868</td>
<td>0.976</td>
</tr>
</tbody>
</table>

3. Conclusions

When the considered concretes are subjected to sustained compressive and splitting tensile load levels of 60 and 65 % respectively of the maximum load capacity micro-cracks are formed. It was observed that the micro-crack width in compression ranged from 1 to 10 μm. In the other hand splitting tensile tests provoked a wider microcrack system located on the splitting plane and it can reach up to 100 μm in width. A thinner microcrack pattern of 1 to 10 μm width is connected perpendicularly to the main splitting micro-crack system.

Chloride ions ingress into the microcrack system and alter the properties of the gel and the pore solution. The penetration profile seems to be very similar to that found after chloride intrusion in carbonated concrete or under the effect introduced by repetitive cycles of wetting and drying in concrete. The principal observed features on the chloride profile consist firstly in a zone of low chloride binding capacity located close to the exposed surface. Next there is the presence of a chloride content peak which usually progresses in time to deeper zones. Finally there is the normal diffusion profile which develops afterward in areas where the physical-chemical damage has not yet altered the concrete.

Acknowledgements

The financial help of the National Ecuadorian Secretary for Science and Technology “SENESCYT”, Ghent University and ESPOL are gratefully acknowledged.

References


[5] Chunhua Lu et al, Effect of Transverse Crack on Chloride penetration into Concrete Subjected to Dying-Wetting Cycles, 4th International Conference on the Durability of Concrete Structures, Purdue University, West Lafayette, IN, USA, 2014, 169-175.
APPLICABILITY OF NORDIC CLAYS AS SCM

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(1) SINTEF Building and Infrastructure, Trondheim, Norway

Abstract
Nordic clays are usually low in kaolin and rich in illite and smectite, unlike clays in tropical zones that are rich in kaolin. It has been shown that Nordic clays also perform well as SCMs in spite of their low kaolin content when calcined carefully. Furthermore, Nordic clays are also usually contaminated with inert quartz particles that does not seem to hamper the performance too much as they may potentially act as fillers. Sometimes the clays are contaminated with calcium carbonate that actually can be beneficial as it may react with pozzolanic products to form calcium carboaluminate hydrates leading to extra bound water and densification of the microstructure and thereby also increased strength. The performance of three Nordic clays as SCMs is documented by strength data of mortars when these calcined clays are partly replacing cement. For more clarity on the pozzolanic mechanism, one of the clays – 'marl' was studied in greater details. The results are discussed in terms of microstructural features as studied by XRD, thermal analysis and scanning electron microscopy. To further elucidate their applicability, the clays used are dug directly out of the ground without any purification prior to calcination. Social aspects of using "quick clay" that otherwise have to be removed before land exploration is also briefly discussed.

1. Introduction
Calcined clays have in the later years been recognized as a source of supplementary cementitious materials (SCMs) that are sufficiently large to serve the demand to make blended cements worldwide or to be used as cement replacement in concrete to make it more environmental friendly [1]. Pure metakaolin (off-white) from calcination of purified kaolin has been a well-established SCM [2] for years. Research in the later years has shown that impure clays contaminated by quartz and feldspars also function well as SCMs [3]. The research at SINTEF has been focused on calcined "marl" (or calcareous clay) natural occurring in Denmark that is rich in the clay mineral smectite and containing 20% calcium
carbonate [4-8]. Clays containing calcium carbonate cannot be used to produce other clay products like bricks or lightweight aggregates for concrete due to the decomposition to calcium oxide and formation of calcium hydroxide in reaction with moisture leading to so called "pop outs". Another benefit is that calcium carbonate surviving the calcination at < 850°C will react with the calcium aluminate hydrates formed by the pozzolanic reaction of the aluminates in the clay to calcium carbonato hydrates and stabilization of ettringite. These synergic reactions will lead to extra bound water, which further densify the microstructure and lead to higher strength as thoroughly documented for the limestone-fly ash analogue [9-11] as the chemical composition of siliceous fly ash is not very different from clay. After all the fly ash originates from the clay contaminations of clay in the coal burnt in the energy plants.

The above synergic reactions are also utilized in the limestone-calcined clay-cement project (www.lc3.ch) focusing on kaolinite rich clays often found in hot and humid countries like India, Thailand etc. The research at SINTEF focuses on Nordic clays often containing all three main clay minerals; smectite, kaolinite and illite, and are contaminated with substantial amounts of quartz or calcium carbonate. Smectite being a large group of specific clay minerals are often dominating.

2. Experimental

Two clays were selected from different parts of Norway. One taken from a road excavation at the Fosen peninsula in the county Trøndelag, (63°52' N-10°13' E) and one from an old clay field of a shutdown brick factory in the county Telemark (59°14' N-9°19' E). The oxide composition of the Telemark clay (old data from the brick factory) as obtained by X-ray fluorescence is given in Table 1 and compared to the composition of "marl" (calcareous clay) from Denmark (55°53' N-10°0' E) studied previously [7]. The two Norwegian clays were calcined at 850 °C in an electrical furnace at the laboratory for 2 days and milled down to a fine powder in a laboratory mill, while the "marl" was calcined in a gas fired rotary kiln and milled down as a larger batch.

Mortars were made with 20 % replacement of cement by weight for all the calcined clays and further replacements of up to 65% for the Danish "marl". One reference mortar was prepared with Ordinary Portland cement (CEM I). The consistency of fresh mortar was determined by using a flow table. The aim was to obtain a w/b ratio of 0.5 by varying the amount of superplasticizer. The flow of the mortars was within ± 5 % of the reference. The mortar mixes where cast in 40x40x160 mm moulds, demould after 1 day and stored at 90 % RH and 23 °C in 27 days. The strength was measured after 28 days of curing on 3 parallel prisms for the flexural strength and 5 for the compressive strength in accordance with the norm EN 196-1.

A Bruker AXS D8 Focus (θ/2θ configuration with Bragg-Brentano geometry), equipped with a LynxEye detector and a CuKα source (λ = 1.54 Å) was used for XRD measurements.

TG/DTG was performed with a Mettler Toledo apparatus (TGA/SDTA 851) under N2-atmosphere in the temperature range from 40 °C to 1100 °C with a heating rate of 10°C/min.

332
Backscattered electron images (BSE) was taken by a JEOL JXA-8500F Electron Probe Microanalyzer (EPMA) using an accelerating voltage of 15 kV.

3. Results and discussion

One requirement of pozzolans by for instance ASTM C618 is that the content of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$. However, this cannot be applied to such impure clays used in this study as it is first and foremost the clay mineral that is pozzolanic in nature. The Danish "marl" contained about 20% calcium carbonate (mostly as coccolith skeletons [3] pointing at marine origin), while the Norwegian clays contained substantial amounts of quartz considered inert. The bulk compositions of the clays in Table 1 demonstrated that all clays still pass the ASTM C618 criterion.

The XRD profile of Trøndelag clay in Fig. 1 clearly show a strong peak from quartz at $2\theta = 26.6^\circ$ (marked with Q). The main peaks assigned to the clay minerals smectite, illite and kaolinite are marked with S, I and K, respectively. After calcination the K and S peaks disappear and I peak slightly decreased in size, while a new peak indicated by question mark (?) appeared around $27.6^\circ 2\theta$, indicating that the clay had a too long retention time (2 days) at maximum temperature (850°C) forming a crystalline phase. The minerals of the Telemark clay was essential the same as in Trøndelag sample as seen from the XRD profiles in Fig. 2, but the quartz content was higher (18,000 vs. 8,000 counts for Q peak). The XRD profiles of "marl" before and after calcination [3] are shown in Fig. 3 for comparison.

Table 1 The elemental composition of dry Telemark clay and calcined "marl" given as oxides.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>K$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Telemark</td>
<td>64.6%</td>
<td>14.3%</td>
<td>1.7%</td>
<td>2.0%</td>
<td>5.3%</td>
<td>0.8%</td>
<td>4.1%</td>
</tr>
<tr>
<td>&quot;Marl&quot;</td>
<td>49.6%</td>
<td>18.1%</td>
<td>14.1%</td>
<td>2.9%</td>
<td>10.6%</td>
<td>1.0%</td>
<td>2.4%</td>
</tr>
</tbody>
</table>

Fig. 1 XRD of Trøndelag clay before (below) and after (above) calcination at 850°C.
The strengths of mortar with 20% calcined Nordic clays replacing cement after 28 days curing at 20°C are shown in Table 2. The relative compressive strengths of mortar with Trøndelag and Telemark clay were 96 and 93% of reference, respectively, while it was 107% for mortar with calcined "Marl". The strengths obtained for the Norwegian clays are promising considering the high content of quartz (the main quartz peak reached 8,000 and 18,000 counts by XRD for Trøndelag and Telemark clays, respectively) and that the resident time in the calcination chamber was too long. Fig. 4 illustrates the effect of temperature and retention time on the compressive strength of calcined clay-lime mortars cured at 50°C for 7 days [9].
clearly showing a drop in strength with too long retention time at 850°C and above. It is also known that different clay minerals also have different optimum calcination temperatures giving highest reactivity. The optimum calcination temperature for Ca- and Na-montmorillonite (belonging to smectite group of clay minerals) was assessed to 830°C [10]. The highest reactivity and pozzolanic activity of illite was obtained at 930°C [11], while kaolinite achieved highest reaction rates when calcined at 650°C [12]. In this case, all three clays are rich in smectite and illite clays, thus making them more comparable to each other.

Table 2 Strength of mortar with 20% calcined Nordic clays replacement

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average compressive strength ± standard deviation [MPa]</th>
<th>Average flexural strength ± standard deviation [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (Reference)</td>
<td>53.5±0.6</td>
<td>7.8±0.3</td>
</tr>
<tr>
<td>Trøndelag clay</td>
<td>51.5±0.5</td>
<td>7.2±0.1</td>
</tr>
<tr>
<td>Telemark clay</td>
<td>49.8±1.1</td>
<td>7.5±0.1</td>
</tr>
<tr>
<td>&quot;Marl&quot;</td>
<td>57.3±1.3</td>
<td>7.4±0.2</td>
</tr>
</tbody>
</table>

Nonetheless, a better understanding of what is happening in the reaction of these clays as pozzolanic binder is needed. Based on the differences in strength at 28 days, the calcined 'marl' sample was selected for further analysis to determine the mechanistic behaviour of smectite/illite rich clays as pozzolanic materials.

Fig. 4 Weight loss and compressive strength as a function of temperature (right) and retention time at different temperatures (left) for calcination of clay used in lime mortars cured at 50°C for 7 days. Repotted after [9].

The compressive and flexural strength development of mortar with 0, 20, 35 50 and 65 vol% replacement of cement with calcined 'marl' is given in Table 3 from 1 day until 2 years (730 d). The XRD profiles for corresponding paste with 35, 50 and 65 vol% after 2 years moist curing are shown in Fig. 5. Calcium hydroxide is still present in the paste with 35% calcined marl after 2 years while it was depleted for 50 and 65 vol% replacement already at 90 days [8].
Table 3 Compressive (upper number) and flexural (lower number) strength development for mortar with calcined marl replacing cement by volume

<table>
<thead>
<tr>
<th>Marl (vol%)</th>
<th>Average strength ± standard deviation [MPa] at ages [days]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 d</td>
</tr>
<tr>
<td>0</td>
<td>22.0±0.3</td>
</tr>
<tr>
<td>20</td>
<td>17.9±0.4</td>
</tr>
<tr>
<td>35</td>
<td>14.0±0.1</td>
</tr>
<tr>
<td>65</td>
<td>5.7±0.1</td>
</tr>
</tbody>
</table>

Figure 5: XRD pattern of pastes replaced with 35 (upper), 50 (middle) and 65% (lower) calcined marl and moist cured for 2 years. Peaks from ettringite, calcium hemicarbonate hydrate and monocarbonate hydrate are marked with E, HC and MC, respectively, while calcium hydroxide is marked with CH. Quartz and calcite are marked Q and CC, respectively.

The XRD profiles after 2 years (Fig. 5) show that ettringite (E) is stabilised on the expense of monosulphate due to reaction with carbonate as explained by De Weerdt et al [14-16], but another interesting feature is that higher cement replacement by calcined marl seems to stabilise calcium hemicarboaluminate hydrate (HC) over monocarboaluminate hydrate (MC), or something else with exact same peak position at about 11° 2θ (e.g. iron-substituted hemicarbonate).
As seen from Table 3, it is peculiar that the strength gain from 90 to 365 days, as well as from 1 to 2 years, is greater for mortar with the higher cement replacements by calcined marl with no calcium hydroxide present compared to the reference. Hence, no classical pozzolanic reaction is possible. There are four hypotheses that might explain the latter effect as also discussed by Justnes and Østnør [6]:

1) There are two types of CSH in the system. One with high C/S from hydration of cement and one with low C/S from the direct pozzolanic reaction between calcined marl and calcium hydroxide. The one with higher C/S has higher solubility of Ca\(^{2+}\) and is considered weaker mechanically than the one with lower C/S. Slowly the two different CSHs will equilibrate to an overall stronger CSH with intermediate C/S.

2) The solubility of Ca\(^{2+}\) from CSH with high C/S and pH is so high that one can have a direct further pozzolanic reaction with unreacted calcined marl.

3) The silicate anions of in particular CSH with low C/S will polymerize over time creating longer chain lengths of the CSH which may lead to even higher strength and release water.

4) When calcined marl reacts, both silicate and aluminate is released forming CSH and CAH, as well as possibly intermediate products like C\(_2\)ASH\(_8\). Crystalline CAH generally demands a higher atomic Ca/Al than amorphous CSH demand high Ca/Si, and CSH is more flexible in its Ca/Si. The craving for Ca by the aluminate could lead to the decalcification lowering the Ca/Si of the overall CSH that will adapt to that by increased polymerization of silicates (i.e. point 3 above). Inclusion of aluminate in the CSH structure (i.e. bridging of dimers) will also contribute to higher degree of polymerization of CSH. In total this may lead to a higher strength binder.

The compressive strengths of mortars are plotted in Fig. 6 against the mass loss of hydrates in corresponding pastes in range 105-450°C obtained by TG for 35, 50 and 65% cement replacement by calcined marl. It is interesting that all 3 mixes follow about the same line at early ages before they break off at different points corresponding to 90 days and give higher strength than expected from hydrate water supporting points 3 and 4 in the above discussion as CSH polymerization should give less bound water due to fewer –Si-OH end groups.

![Figure 6: Correlation of compressive strength and mass loss between 40 and 450°C](image)
Back scattered electron images of plane polished sections of mortar with 65% replacement of cement are shown in Fig. 7 after 90 and 2 years curing. The overview taken with 100x magnification shows a number of "black" spots across the sample at both ages, but clearly that the overall matrix is denser after 2 years compared to 90 days consistent with higher strength. A close-up of the dark spots in the lower part of Fig. 7 shows that there is material there and that they are not pores. The dark material is probably decalcified inner CSH supporting point 4 in the preceding discussion in explaining long-term strength increase without presence of calcium hydroxide. The material has generally a low Ca/Si and contains Mg and Al probably originating from the content in the alite producing the inner CSH in the first place. The composition of the dark material shown in the lower right image of Fig. 7 is according to EDS in atom%: 17.1 Si, 13.1 Ca, 6.6 Al, 5.6 Mg and 2.1 Fe. Inclusion of isolated weak micrograins in a strong and dense binder should not weaken strength or hamper durability.

Fig. 7: Mortar with 65 vol% cement replaced by calcined marl (M65) after 90 days (left upper and lower) and 2 years (right upper and lower) curing showing "dark-spots" consisting of partly decalcified inner products (low Ca/Si and containing Mg/Al from alite).
As discussed so far, the superior performance of the calcined "marl" as compared to the other Nordic clays in Table 2 may not only be due to shorter resident time at optimum temperature but also that about 20% of the 20% inherent calcium carbonate survived the calcination process. As it is essential for all aluminate containing SCM reactions, presence of 4% calcium carbonate of the calcined "marl" could react with calcium aluminate hydrates from the pozzolanic reaction as well as calcium monosulfoaluminate hydrates to form calcium carboaluminate hydrates and stabilize ettringite. This will lead to more chemically bound water, less porosity and thereby higher compressive strength. This synergetic reaction has been thoroughly studied for cement-fly ash-limestone systems [13-16] and is currently exploited in the ternary cement-metakaolin-limestone system in the LC3 project (www.lc3.ch). Thus, it is likely that the compressive strength of mortars with calcined Norwegian clays could have been increased further by combining them with limestone powder.

Looking specifically at the benefit of using clays, other than the fact that it is an abundant material, in some communities clay deposits may cause problems as they over time may become "quick clays" creating landslides with catastrophic results for people, housing and infrastructure. Several such landslides has occured in Norway over the years and the frequency may increase as the weather is supposed to be "wetter and wilder" as a result of global warming. Recently, the politicians of the community Hegra in Trøndelag county discussed openly if the should be pro-active and demolish two houses in a "quick clay" area and remove the clay before they developed the area further for residential purposes. A bold thought could then be to calcine the clay at site (mobile rotary kilns exist) and use it as SCM for the concrete in the property development rather than transport it away and deposite it somewhere else where it would have a negative local environmental impact.

4. Conclusion

Nordic clays rich in smectite and illite may be used as supplementary cementing materials when carefully calcined, even when they contain substantial amounts of quartz.

A content of calcium carbonate seems to be beneficial in terms of increasing strength and clays not containing it may be beneficiated by adding some limestone powder before or after calcination to improve the performance.

Explanation for continued strength increase in mortars with calcined clay as SCM even after calcium hydroxide is depleted is discussed in terms of microstructural changes other than classical pozzolanic reactions.

Calcination of problematic "quick clay" deposits at site during removal before developing the area for residential or infrastructure purposes and use it as SCM in the concrete for the subsequent construction is put forward as an alternative to long transport and deposit elsewhere negatively affecting the local environment.
References


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PRODUCTION OF CERAMICS USING BOTTOM ASH AND FLY ASH FROM A THERMAL POWER PLANT

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Abstract
The aim of this work was to investigate the possibility of the production of ceramics from fly ash (FA) and bottom ash (BA) produced at thermo-electric power plants. Ashes originating from the REK Bitola thermal power plant, which is located in the Republic of Macedonia, were used for this investigation. The physical and chemical properties of the ashes are analyzed and discussed. Using a powder processing technique, ceramic products were made with a variable ratio of the BA and the FA. It was found that the main processing factors which affected the physical and mechanical properties of these products are the amount of added fly ash, and the sintering temperature. It was also found that the greatest effect on the density, porosity, and mechanical properties of the products are the lower residual coal content in the fly ash compared to the bottom ash, the different geometry of the particles, the fineness of the powders, and the particle size distribution. The best values for bending strength and E-moduli were 31±1 MPa and 19±1 GPa. They were achieved in the case of the samples having a BA/FA ratio of 1:3 and an applied pressure of 100 MPa, with sintering at 1100°C.

1. Introduction

In the Republic of Macedonia the electricity is mainly produced in coal-fired thermal power plants [1], which, however, produce considerable amounts of solid wastes. During coal combustion its organic components are incinerated, but its inorganic components remain mostly in the plant's by-products [2]. The majority of the ash enters the gas flow, where it is then captured and recovered as fly ash, so can be disposed of as a dry by-product. On the other hand, bottom ash is removed from the water-filled hopper at the bottom of the boiler by means of high pressure water-jets, and then conveyed away by sluiceways for the dewatering process.
Only a small proportion of the generated bottom ash is utilized in the construction industry for making bricks and concrete blocks, or for blending with cement [3-8]. However various reports have indicated that there is a growing interest in recycling and new applications. According to [7], the highest level of utilization of coal bottom ash occurs in construction industry. Significant percentages are used either as an addition to concrete, in civil engineering applications, or in the production of cement [5].

The physical and chemical properties of such ashes are influenced by the different processes which occur during combustion [7]. In general, FA (fly ash) and BA (bottom ash) consist of silicates, carbonates, aluminate, ferrous materials and metalloids. The exact composition of bottom ash and fly ash varies according to the source of the raw coal, the size and type of the coal burner, and the burner's operating conditions [8]. With regard to its physical appearance, bottom ash is an angular material with a porous surface texture, ranging from fine gravel to coarse gravel, as opposed to the fine structure of fly ash [9]. The main objective of the study was to evaluate the possibility of producing ceramic products from bottom ash and fly ash derived from the lignite coal which is mostly found in Macedonian coal mines.

2. Materials and Methods

The as-received materials bottom ash (BA) and fly ash (FA) were collected from the REK Bitola thermal power plant, which is located in the Republic of Macedonia. The ashes were dried at 100-110°C in order to achieve constant weight.

Particle size distribution was determined by dry sieving using sieves +1mm – 63μm. Loss on ignition was determined after heating at a constant rate of 10°C/min, up to the isothermal process at 800°C for 2 hours. Specific gravity was determined by means of a gas pycnometer.

The morphology of the particles of different fractions was examined by a SEM JEOL JSM 5500LV microscope. The powders were coated with gold prior to examination. The coating was performed using BAL-TEC/SCD005 equipment with gold at a current of 35mA for 120s. Chemical composition were determined by XRF (ARL 9900XP).

The powders were milled by a ball mill with alumina grinding media and a milling time of 2 h. (BAMA2; FAMA2). Distilled water was added as a binder to the ash powder. Approximately 2.5g powder was uniaxially cold pressed at 100MPa using Weber Pressen KIP 100 equipment. The resulting compacted samples had average dimensions of 60mm x 5mm x 5mm. The green bars were dried for 24 h at room temperature, and then for 24 h at 110°C. The green density was calculated from weight and volume measurements of the unfired samples.

Sintering was performed in the laboratory furnace in an air atmosphere at temperatures of 900, 1100 and 1150°C, using a heating rate of 5°C/min, with 60 min of isothermal treatment, and then the samples were furnace cooled to room temperature. The bulk density of the sintered samples was determined by the water displacement method according to EN-993. Porosity was calculated from the measured relative density.
The bending strengths and E-moduli of the investigated samples were determined by means of a 3-point bending strength tester (Netzsch 401/3), with a span of 30mm and a 0.5mm/min loading rate.

3. Results and discussion

The chemical composition of the investigated BA and FA showed that their main components were: SiO\(_2\), Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), and CaO. The CaO content in the FA was higher than 10 % so that it could be characterized as fly ash type C. The bottom ash contained a greater amount of coal as was determined by the LOI, amounting to 48.7 wt%. This is a measure of the amount of volatile matter which would be released during sintering.

Table 1. Chemical compositions of the investigated BA and FA

<table>
<thead>
<tr>
<th></th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>K(_2)O</th>
<th>Na(_2)O</th>
<th>SO(_3)</th>
<th>MgO</th>
<th>TiO(_2)</th>
<th>LOI</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA (wt%)</td>
<td>33.46</td>
<td>9.11</td>
<td>2.81</td>
<td>1.33</td>
<td>0.51</td>
<td>0.47</td>
<td>/</td>
<td>0.29</td>
<td>48.7</td>
<td>99.06</td>
<td></td>
</tr>
<tr>
<td>FA (wt%)</td>
<td>50.33</td>
<td>18.59</td>
<td>7.71</td>
<td>13.76</td>
<td>1.41</td>
<td>1.44</td>
<td>3.05</td>
<td>/</td>
<td>2.60</td>
<td>99.96</td>
<td></td>
</tr>
</tbody>
</table>

From Table 2 it can be seen that the carbon content in the ashes varied depending on the different fractions obtained in the sieve analysis. The highest percentage of LOI can be observed in the case of the fraction with a particle size of +1.00mm, for both ashes. The specific gravity of fly ash has been reported to be related to the shape of its particles as well as its chemical composition. In general, the specific gravity of fly ash can vary between 1.3 and 4.8 g/cm\(^3\) [4]. The particle size distribution of both ashes is also presented in Table 2 The bottom ash particles were coarser than the fly ash particles, which is demonstrated by the fact that the highest percentage of the fly ash, i.e. 43.60 wt%, passed through the 0.063 mm sieve, whereas the amount of the medium particles of the bottom ash (-0.5 and -0.25mm) is around 50 wt %. In order to avoid the problem with packaging density which can occur due to the unburnt coal particles which are present in the coarser fractions, both of the ashes were mechanically activated for two hours, and for the further investigations the fraction of ashes passing through the 0.125 mm sieve (BAMA2; FAMA2) were taken.

Even in the case when ashes are obtained from the same coal source, in the same power plant, the physical and chemical properties can vary depending on the operational conditions, the firing temperature, and the handling of the ashes. The results of the performed SEM analysis are presented in Figure 1, from which it can be seen that in the case of sample BAMA2 the particles are angular-shaped with irregular geometry and different dimensions. The angular-shaped particles are mineral particles from the different phases present in the ash,while the popcorn-like particles belong to the coal particles present in the ash. In the case of sample BAMA2 the particle size ranged from 1 to 30 \(\mu\)m. According to [8], the shape of these particles is determined according to the different zones of the burner, where the bottom ash is removed. The SEM image obtained in the case of sample FAMA2, Figure 1, showed that the particle size of the fly ash was smaller than that of the bottom ash particles, as well as being more homogeneous. It is well known that the fly ashes contain a greater amount of spherical...
particles than the bottom ashes [8]. After mechanical activation of the FA some spherical particles with dimensions of between 2 and 20 μm can be seen.

Table 2. Particle size distribution, LOI, and specific gravity of the investigated BA and FA

<table>
<thead>
<tr>
<th>Size distribution [mm]</th>
<th>BA [wt%]</th>
<th>FA [wt%]</th>
<th>BA LOI [wt%]</th>
<th>FA LOI [wt%]</th>
<th>BA Specific gravity [g/cm³]</th>
<th>FA Specific gravity [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>7.53</td>
<td>0.6</td>
<td>86.07</td>
<td>86.96</td>
<td>1.42</td>
<td>/</td>
</tr>
<tr>
<td>-1 +0.5</td>
<td>20.02</td>
<td>2.20</td>
<td>29.23</td>
<td>59.90</td>
<td>1.81</td>
<td>1.63</td>
</tr>
<tr>
<td>-0.5 +0.25</td>
<td>37.74</td>
<td>9.10</td>
<td>11.85</td>
<td>6.48</td>
<td>2.32</td>
<td>2.14</td>
</tr>
<tr>
<td>-0.25 +0.125</td>
<td>20.17</td>
<td>18.90</td>
<td>13.18</td>
<td>1.62</td>
<td>2.51</td>
<td>2.05</td>
</tr>
<tr>
<td>-0.125+0.063</td>
<td>6.47</td>
<td>24.90</td>
<td>32.69</td>
<td>0.78</td>
<td>1.76</td>
<td>2.11</td>
</tr>
<tr>
<td>-0.063</td>
<td>7.46</td>
<td>43.60</td>
<td>34.54</td>
<td>1.10</td>
<td>2.05</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Figure 1. SEM micrographs of the activated bottom ash (top) and fly ash (bottom)

Consolidation of the powders was achieved by pressing and sintering of the BAMA2 and FAMA2 samples, and of the compacts with different ratios of BAMA2 and FAMA2, i.e.
BAMA2/FAMA2=1:1, BAMA2/FAMA2=1:2; BAMA2/FAMA2=1:3. Dense composites with different densities were obtained by varying the firing temperature from 900 to 1150°C, with one hour isothermal treatment at the final temperature. The density, porosity, water absorption, bending strength, and E-moduli of the compacts which were measured at the optimal sintering temperature are shown in Table 3.

Table 3. Density, porosity, water absorption, bending strength, and E-moduli of the ceramics which were sintered at 1100°C with a heating rate of 5°C/min

<table>
<thead>
<tr>
<th>Samples</th>
<th>Density [g/cm³]</th>
<th>Porosity [%]</th>
<th>Water Absorption [%]</th>
<th>Bending Strength [MPa]</th>
<th>E-moduli [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAMA2</td>
<td>1.234</td>
<td>31.78</td>
<td>29.89</td>
<td>6.94</td>
<td>3.85</td>
</tr>
<tr>
<td>FAMA2</td>
<td>1.959</td>
<td>8.05</td>
<td>11.98</td>
<td>46.48</td>
<td>30.37</td>
</tr>
<tr>
<td>BAMA2/FAMA2=1/1</td>
<td>1.67</td>
<td>21.62</td>
<td>18.25</td>
<td>23.39</td>
<td>12.80</td>
</tr>
<tr>
<td>BAMA2/FAMA2=1/2</td>
<td>1.735</td>
<td>14.30</td>
<td>16.59</td>
<td>27.13</td>
<td>16.12</td>
</tr>
<tr>
<td>BAMA2/FAMA2=1/3</td>
<td>1.852</td>
<td>10.77</td>
<td>14.08</td>
<td>31.39</td>
<td>18.55</td>
</tr>
</tbody>
</table>

From Table 3 it can be seen, as the proportion of FA was increased, a higher density of the sintered compacts was obtained, and thus also a lower porosity of the samples. The porosity of the BA compacts is considerably higher than that of FA compacts, since the BA had a higher residual coal content, which is eliminated as carbon gas which generates pores in the compacts during sintering. The addition of fly ash to the compacts also improved the mechanical properties of the compacts. The measured bending strength and E-modulus of the BAMA2/FAMA2=1:3 compacts was 31.39 MPa and 18.55 GPa, respectively.

The microstructure of the fractured surface on some of the obtained ceramic compacts is shown in Figure 2. Fig.2(a) presents the microstructure of the BAMA2 sample which was sintered at 1100°C, with a heating rate of 5°C/min. Fig 2(b) shows the microstructure of the compacts produced from FAMA2, which was sintered at 1100°C, with a heating rate of 5°C/min, whereas Figs. 2(c), (d), and (e) show the microstructure from samples BAMA2/FAMA2=1:1, BAMA2/FAMA2=1:2, BAMA2/FAMA2=1:3, which were fired under the same sintering conditions.

From Fig. 2(a) it can be seen that the fracture surface of the BAMA2 sample is rough, with open porosity, varying pore geometry and pore size. Most of the pores are interconnected resulting in pore diameters within the range 2 - 200 μm. The microstructure of the fractured surface of the ceramic samples obtained from the FAMA2 which was sintered at 1100 °C is homogeneous and smoother compared with BAMA2 ceramics sintered at the same temperature. The pores are more uniformly closed, and have dimensions between 5 and 20 μm. When the amount of fly ash is increased changes occur in the microstructure, as previously confirmed by the measured density and porosity of the compacts [Fig 2(c), (d), (e)]. Besides the above-mentioned lower residual coal content in the FA, another factor which has an effect on the microstructure is particle size. The smaller particle size of the FA is also
the reason for the lower porosity of the compacts, since the pores in the compacts are smaller when particles in the powder are smaller.

Fig 2. SEM images for the compacts which were sintered at 1100°C/1h, dT/dt = 5 °C/min

4. Conclusions
The results of the performed tests showed that when the FA content in the ceramic compacts was increased, their mechanical properties improved due to the increase in the density of the sintered compacts, and a consequent reduction in the porosity in the samples. This effect is
correlated with the three major differences when compared to bottom ash: (i) the lower residual coal content; (ii) the different geometry of the particles; and (iii) the fineness of the powder and the particle size distribution.

The experimental conditions for producing the ceramic which exhibited the optimal physical and mechanical properties were: a ratio of BAMA2/FAMA2=1:3, a sintering temperature of 1100°C with a 5°/min heating rate, and one-hour isothermal treatment at the final temperature.

The obtained data from the measured physical, chemical and mechanical properties show that ashes obtained in thermal power plants can potentially be used in civil engineering.

Acknowledgements

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References

ULTRA HIGH PERFORMANCE CONCRETE (UHPC) WITH LOW SILICA FUME CONTENTS AND LIMESTONE AGGREGATES

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Abstract

UHPC it’s the newest iteration of high Performance Concrete, it is characterized with a high compressive strength, a very high durability and high cost. The typical formulations commonly use costly aggregates such as fine powdered quartz and sand of that same material, bauxite, basalt, among others. These formulations typically require very high dosages of silica fume additions (25% in addition by weight of cement (woc)). In this work, UHPC mixes were made with regular limestone sand with a maximum size of 4.75 mm in replacement of the common quartz aggregates (both fine sand and powder). Mixtures contained additions of silica fume between 0 and 25% by woc. At a paste level, thermogravimetric analysis on silica fume/Portland cement and on silica fume/calcium hydroxide systems were performed to evaluate the potential pozzolanic reaction and as another way to determine the silica fume addition to maximize calcium hydroxide consumption. As a result of our experimental work, an UHPC with limestone aggregates was obtained with 5% of silica fume by woc and for a target minimum compressive strength of 150 MPa.

1. Introduction

The UHPC-class materials are cementitious based materials with an improved durability due to its discontinuous pore structure and compressive strength above 150 MPa [1]. In order to get these properties, the designers of UHPC usually support their designs in the guidelines made by Pierre Richards and Marcel Cheyrezy [2]. This type of mix design requires at least 800 kg/m³ of cement and 200 kg/m³ of silica fume, combined, these two cementitious materials together with the high prices of the commonly used siliceous aggregates, make the democratization of the material a very hard issue.

In these guidelines, it is stated that the water/cement ratio (w/c) should be 0.25 or less and that the addition of silica fume by woc is 25%. From the Powers Model we know that for w/c
ratios below 0.42 the cement is not completely hydrated [3], hence the calcium hydroxide is not the maximum that a gram of cement could produce, and therefore the addition of silica fume could be overestimated. Even Pierre Richard and Marcel Cheyrezy recognize in their work that the silica fume added in their design is more than the required amount to consume all the portlandite and part of it will remain entrapped within the cementitious matrix as a filler. In this regard, it was a main objective of our work to optimize the use of silica fume in UHPC and to characterize its reaction with portlandite.

Concerning the aggregates, they consist usually of two kinds, the coarser one is made from fine silica sand between 150 and 600 micrometers and the micro filler is a crushed quartz powder with an average size of 10 micrometers [4]. Despite these granulometric characteristics have been adopted by the technical and scientific community as a general rule, there have been several works that have replaced these aggregates by limestone or by recycled glass without strength loss [5]-[8]. Collepardi demonstrated that it was possible to replace the micrometric sand with a well graded 8 mm maximum size limestone [7]. In this study it was concluded that the compressive strength is not compromised by changing the type or size of aggregate, although the tensile properties can be reduced. In our University, this literature review encouraged the development of a new research line on UHPC made with limestone aggregates.

2. Experimental details

2.1 Materials

The materials used consisted of:

- Sulfate Resistant cement with a Blaine fineness of 3629 cm²/g, a density of 3.13 gr/cm³ and the following Bogue calculated phase composition (wt%): C₃S: 66.3, C₂S: 8.7, C₃A: 2.1, C₄AF:13.6, LOI: 2.6.
- Densified Silica fume (SF) with a BET-surface of 21.6 m²/g, a density of 2.20 gr/cm³ and the following chemical composition (wt %): SiO₂: 94.9, Al₂O₃: 0.76, Fe₂O₃: 0.05, CaO: 0.41, MgO: 0.36, K₂O:0.81, LOI: 2.3.
- Polycarboxylate based super plasticizer (SP) with a density of 1.12 gr/cm³ and an active agent content of 54.40%.
- Calcium hydroxide (CH) with a purity of 97.6%.
- Distilled water.
- Limestone sand with 4.75 mm maximum size, a density of 2.62 gr/cm³ and an absorption of 1.56 %.

2.2 Mixtures

The silica fume is a mineral admixture that is highly reactive, but that benefit comes with a high monetary price. This is why its addition should be taken with care. In order to estimate the optimum amount of silica fume, there were made two kinds of tests, a hydration-pozzolanic based test trough thermogravimetric analysis (TGA), and a strength based test.

Hydration-Pozzolanic activity quantification:
To characterize the pozzolanic reaction of the silica fume in an UHPC paste, 4 sets of pastes of cement-silica fume were made (Table 1), each paste had a constant w/c, but the silica fume/cement ratio (s/c) was variable from 0 to 0.25.

A silica fume-calcium hydroxide paste was made to assess the maximum calcium hydroxide consumption of the silica fume. The molar Calcium Hydroxide (CH)/Silicon Dioxide was 1.60 to ensure that enough CH could be available for the pozzolanic reaction to take place [9]. In this test, a gram of the paste contained 0.16 gr of silica fume, 0.30 gr of calcium hydroxide and 0.54 gr of distilled water.

<table>
<thead>
<tr>
<th>Table 1 : Pastes composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>SP dosage (gr/kg of cementitious material)</td>
</tr>
<tr>
<td>W/C ratio</td>
</tr>
<tr>
<td>S/C ratio</td>
</tr>
<tr>
<td>Water (kg/m³)</td>
</tr>
<tr>
<td>Silica fume (kg/m³)</td>
</tr>
<tr>
<td>Cement (kg/m³)</td>
</tr>
<tr>
<td>SP (kg/m³)</td>
</tr>
</tbody>
</table>

Strength based tests:

With the same basic paste design previously mentioned, four mortar mixes were made to determine the optimum addition of silica fume through the compressive strength (Table 2).

<table>
<thead>
<tr>
<th>Table 2: Mortars mix designs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>SP dosage (gr/kg of cementitious material)</td>
</tr>
<tr>
<td>W/C ratio</td>
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<td>S/C ratio</td>
</tr>
<tr>
<td>Water (kg/m³)</td>
</tr>
<tr>
<td>SP (kg/m³)</td>
</tr>
<tr>
<td>Cement (kg/m³)</td>
</tr>
<tr>
<td>Silica fume (kg/m³)</td>
</tr>
<tr>
<td>Sand (kg/m³)</td>
</tr>
<tr>
<td>Air (%)</td>
</tr>
<tr>
<td>Spread of mini cone (cm)</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
</tr>
</tbody>
</table>
2.2 Mixing of paste and mortar

**Paste**
The following procedure was used to mix the paste in a ASTM C 305 [10] planetary mixer:
- All ingredients were put together in the mixing bowl with almost 90 % of the water. The remaining 10 % of the water was used to dilute the SP and to wash its container.
- An initial mixing at low speed for four minutes was made to homogenize the materials. At the end of this period, the SP was added, followed by another minute of mixing. When the mix was not in a fluid state, mixing was continued for two additional minutes.
- Mixing was suspended and the sides and bottom of the bowl was scrapped.
- Finally, pastes were mixed at medium speed for three additional minutes.

**Mortars**
To produce the mortars, a UNIVEX planetary mixer with a bowl capacity of 14.21 liters was used. The mixing procedure was as follows:
- All ingredients were put together in the mixing bowl with almost 90 % of the water. The remaining 10 % of the water was used to dilute the SP and to wash its container.
- An initial mixing with a fixed speed of 190 rpm was made for four minutes to homogenize the materials. At the end of this period, the SP was added, followed by another minute of mixing. When the mix wasn’t in a fluid state, mixing was continued for two additional minutes.
- Mixing was interrupted and the sides and bottom of the bowl was scraped.
- Finally, mortars were mixed at 400 rpm for three additional minutes.

The flow cone spread test was made in accordance to ASTM C230/C230M but without vibration; it was used to assess a target spread of the mortar mixes. In this regard, SP was adjusted in each mixture to obtain a spread of 30 ± 1 cm.

2.3 Measurement of the pozzolanic reaction and cement hydration
The silica fume-cement pastes were casted in 50 mm steel cubic containers and demolded 24 hours after the mixing. Cubes were cured in lime water until the age of 200 days, after the end of their curing process they were grinded manually until all the powder passed the #100 sieve (149 micrometers), immediately the powders were submerged in an isopropyl alcohol bath for 24 hours to stop its hydration. After freezing the hydration, samples were dried in vacuum until constant weight.

Silica fume-calcium hydroxide paste was casted in a glass vial filled with distilled water and remained sealed until an age of 28 days after mixing. Conditioning and hydration freezing processes were the same as the ones used on cement-silica fume pastes.
Thermogravimetric analyses (TGA) were performed on a TGA 4000 Perkin Elmer analyzer with the following conditions:

- For the cement-silica fume pastes, 65 milligrams were used.
- For the silica fume-calcium hydroxide paste, 51 milligrams were used.
- The heating rate was 10° C/min with nitrogen flux of 20 ml/min up to a temperature of 1000°C.
- Two isotherms were applied, one at 28° C to ensure the stabilization of the sample weight at room temperature and another at 105° C for 10 minutes to obtain a stable value of the sample weight without capillary water.

From the TGA of the cement-silica fume pastes the following information was obtained with the average of two tests:

- Chemically bound water
- Amount of CH produced/consumed

The mass of CH consumed by the silica fume was determined with the silica fume/CH paste. To analyze the TGA results, the following equations were used, the first two were used for the cement-silica fume pastes, and the third one for calcium hydroxide-silica fume paste:

\[
\frac{w_n}{c_o} = \frac{M_{1000°C} - M_{105°C} - M_{CO2}}{M_{1000°C}} \\
\frac{CH}{c_o} = \frac{M_{H2O} \times 74.1}{1 - LOI_c + S_c - S_c \times LOI_s} \\
\frac{CHc}{s} = \frac{1 - LOI_s + \frac{CH}{s} \times (1 - \frac{H}{CH})}{M_{1000°C} - \frac{CH}{s} \times (1 - \frac{H}{CH})}
\]

Were:

- \(w_n/c_o\) = Amount of chemically bound water per gram of cement.
- \(M_{1000°C}\) = Mass at 1000°C
- \(M_{105°C}\) = Mass at 105°C
- \(M_{CO2}\) = Mass loss due to decarbonation of the CaCO3, usually between 650-800°C.
- \(LOI_c\) = Loss on ignition of the cement
- \(S_c\) = Silica fume/cement ratio
- \(LOI_s\) = Loss on ignition of the silica fume
- \(CH/c_o\) = Amount of calcium hydroxide per gram of cement
- \(CHc/s\) = Amount of calcium hydroxide consumed per gram of silica fume
- \(CH/s\) = Calcium hydroxide/silica fume ratio of the mix
H/CH= Amount of chemically bound water per gram of calcium hydroxide.
M$_{H_2O}$= Mass loss due to evaporation of water from the calcium hydroxide, usually between 400-450ºC.

2.4 Measurement of the compressive strength
The compressive strength was measured on 50 cm cubic specimens according to the ASTM C 109 standard [12]. Four ages were tested 3, 7, 28 and 56 days, each test consisted in the compression of 9 cubes.

3. Results
Figure 1 contains the TGA of all the analyzed pastes. Figure 2 shows the amount of chemically bound water per gram of each cement-silica fume paste calculated from the TGA’s with the equation (1). Figure 3 contains the amount of calcium hydroxide within each silica fume-cement paste calculated with the equation 2. Figure 4 shows the TGA of the silica fume-calcium hydroxide paste and Figure 5 shows the compressive strength of the mortars.
Figure 2. Chemically bound water per gram of cement vs silica fume/cement ratio

Figure 3. Calcium hydroxide per gram of cement vs silica fume/cement ratio

Figure 4. TGA of the silica fume-calcium hydroxide paste
4. Discussion

4.1 Termogravimetric analysis

From the results of chemically bound water shown on the Figure 2 it can be seen that the hydration of the cement is slightly reduced by the addition of the silica fume, this phenomenon has been previously mentioned [13]. The pozzolanic reaction of the silica fume produces a C-S-H with a CaO/H₂O of 1, this means that it uses only the water molecule of the calcium hydroxide to form its hydrates and does not bound chemically any additional water, although it needs 0.5 gr of the water adsorbed around the C-S-H by gr of reacted silica fume [14]. The adsorbed water around C-S-H needed for the pozzolanic reaction to take place has to come from the water required to hydrate the cement, so this could be a reason of the slight decrease of the chemically bound water per unit mass of cement that augments with a higher incorporation of silica fume.

The slope of the line in Figure 3 is 0.3. This value shows the consumption of calcium hydroxide per unit of silica fume added in a paste with water/cement of 0.25. From the information in Figure 4 and by using equation (3) the amount of calcium hydroxide consumed per unit of silica fume in a calcium hydroxide rich environment can be calculated. This value is 1.3 gr of CH/gr of silica fume. If the calcium hydroxide consumption can be taken as an indicator of the silica fume hydration, in the portland cement paste with w/c of 0.25 the hydration of the silica fume was reduced by 77% (in comparison to reaction in lime rich environment). For an SF addition of 25 % a reduction of the chemically bound water of 5 % per gram of cement was seen. This observation suggests that in the hydration process, the cement has a hydration priority indicating that the degree of hydration of both cementitious materials cannot be considered as equal as supposed [13].
4.2 Compressive strength of the ultra high performance concrete made with limestone aggregates

For all the ages with the exception of the s/c ratio of 0.25, an increase in compressive strength was observed as silica fume increased. For the mortar with s/c ratio of 0.25, the reduction in compressive strength can be attributed to the higher presence of undispersed high specific surface area powder as a result of the ineffective performance of the SP.

The target compressive strength of 150 MPa was reached in 28 days with the s/c ratio of 0.14, but the mix with the s/c ratio of 0.05 was close to meet the target strength at later age of 56 days. As it can be seen in Figure 5, for almost all the mortars, there is a negligible strength increment after an age of 28 days. This phenomenon could be attributed to the limestone aggregate that is known to have a lower performance in comparison with the siliceous aggregates.

The use of a micro filler with a similar size to the cement was not necessary to reach the characteristic/target strength of the UHPC. This could be attributed to the characteristic relative softness of the limestone aggregates that makes them having a high amount of micro powder that could fill voids within the cementitious matrix.

5. Conclusions

The pozzolanic reaction of the silica fume is heavily influenced by the hydration of the cement, having the cement priority to form its hydrated products. In the case of w/c of 0.25 (usually used in UHPC), the hydration of silica fume was reduced by 77% in comparison to its reaction in a lime rich environment.

The addition of larger amounts of silica fume in a UHPC may not be always good to improve compressive strength. There are other factors like the packing density and the strength limitations of the aggregates that are key aspects to obtain high strengths.

The production of UHPC was possible with limestone aggregates and with a much lower amount of silica fume than commonly used in this kind of mixes. An addition of 14 % of silica fume was enough to meet the required strength at 28 days and 5% was enough to meet the required strength at 56 days. These amounts are 44% and 80% lower than the common used value of 25%.

Acknowledgments

The authors wish to express their gratitude and sincere appreciation to the different organizations that contributed in the development of this project, to the Consejo Nacional de Ciencia y Tecnología de Mexico (CONACYT), and to the Facultad de Ingeniería Civil of the Universidad Autónoma de Nuevo León. The authors also want to thank Filiberto Marin from EUCOMEX, S.A. de C.V. and to Jose Alfredo Rodriguez Campos from HOLCIM México.
S.A. de C.V. for providing the high-range water-reducing admixture and the portland cement, respectively.

References

INTERNAL CURING OF HIGH PERFORMANCE CONCRETE WITH SUPERABSORBENT POLYMERS: EVALUATION OF DURABILITY

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(1) Universidad Autónoma de Nuevo León, Facultad de Ingeniería Civil, Monterrey, Nuevo León, México.

Abstract
Internal Curing (IC) has been proved to be an effective technique to mitigate autogenous shrinkage of High Performance Concrete (HPC). Among several agents that have been studied for IC, superabsorbent polymers (SAP) have higher absorption rates and retain the IC water until the relative humidity decreases. However, these agents could remain within the concrete as voids and can affect the durability. To evaluate the effect of SAP on the durability of HPC with silica fume, electrical resistivity and non-steady chloride migration coefficient tests were conducted. In this study, portland cement-silica fume mortars were made with and without SAP with a w/c ratio of 0.40 to determine the performance of internal curing in autogenous shrinkage, electrical resistivity and chloride diffusion coefficient. The silica fume addition was of 9.5% to consume all the calcium hydroxide produced by the portland cement and it was calculated by thermogravimetric analysis. Chemical shrinkage according to ASTM 1608 was measured to determine the required amount of IC water, according to through the hydration model of Powers, which is modified by Jensen.

1. Introduction
Nowadays, the use of super-absorbent polymers (SAP) is very common in the hygiene, agriculture, and recently in the concrete industry due to their high absorption rates and water retention capacity [8, 13, 15, 21, 23]. In concrete technology, SAP are more often commonly used as internal curing (IC) agents to provide additional water within the concrete to mitigate autogenous shrinkage during early age hydration [14, 17, 20]. Also, it is well known that internal curing is used to provide an adequate curing for HPC.

The major benefit attributed to IC in HPC is the improvement of durability because it mitigates autogenous shrinkage [4, 5, 15, 18, 20, 21, 22]. However, it becomes important to run other tests to confirm the improvement on durability because the increase of porosity when IC agents are added is common.
Surface Electrical Resistivity (SER) and Chloride Diffusion Coefficient (CDC) are widely considered important parameters to evaluate service life and durability of concrete exposed to marine environment. In particular, SER has the advantages of being a non-destructive technique to evaluate permeability, quality, a rapid indication of the concrete’s resistance to chloride ion penetration and durability [1]. Chloride diffusion coefficient is related with porosity, pore connectivity and pore solution composition of concrete, then, for concrete structures, is essential for service life prediction to determine a quantitative property as CDC to qualify the cementitious paste. [7, 11]. Then, to have a bigger picture of the durability of the structure, both parameters (CCD and SER) should be measured.

The AASHTO TP 95 [1] is one method to measure SER, it describes a procedure based on the Four-Point Wenner Array Probe Test, and has shown to be effective in qualifying the concrete structures. To calculate CDC, the method from NT Build 492 is the faster option and is based on Fick’s 2nd law in a non-steady state migration [14].

The aim of this study was to analyse if the mitigation of autogenous shrinkage through the implementation of IC is achieved, other durability parameters as SER and CCD should be improved in mortars with SAP as IC agent. Although only mortars were prepared; it is assumed that comparable conclusions derived from mortars may be also applicable to concrete.

2. Experimental details

2.1 Materials

The materials used in this study consisted of:

- Type V Ordinary Portland Cement according to ASTM C 150, with a Blaine fineness of 362.9 m²/kg and a loss of ignition (LOI) of 3.37%.
- Silica fume in dry powder with a BET-surface of 21.63 m²/g, a LOI of 2.63% and a 95% content of SiO₂.
- Crushed limestone fine aggregates from the metropolitan area of Monterrey, México.
- Apolyacrylamide-potassium polyacrylate SAP with an absorption of 25 g/g and desorption of 90% in pore solutions extracted from pastes of cement and silica fume (s/c = 0.095) with a w/c of 0.4.
- The calcium hydroxide Ca(OH)₂ used to determine chemical shrinkage of the silica fume has a purity of 97.6%.
- Superplasticizer (SP) based on polycarboxylates.

2.2 Mixtures design

All mixtures were designed based on the modification to the Hydration Powers Model made by Jensen for Portland Cement- Silica Fume (PC-SF) cementitious system [12, 16, 17] with an initial water/cement (w/c) ratio of 0.40. The model explains the two systems of hydration, namely a water-entrained open system with external curing water and a closed system isolated
from external water. It classified water in the cementitious pastes into three phases [12, 16, 17]:

- Chemically bounded water of cement (bw),
- Physically bound water (pw) between C-S-H layers
- Capillary water in the pores

Silica fume doesn’t bind water during the pozzolanic reaction but each gram of silica fume will physically absorb 0.5 g of water [16]. For this study, the following equations (1-5) from the model [14, 15] were taken to determine the amount of internal curing water and subsequently the amount of SAP.

\[
\begin{align*}
\text{w/c}_1 &= (bw + pw) \\
\text{w/c}_{\text{closed}} &= 0.42 + 0.5 \left( \frac{\text{c}}{\text{c}} \right) \\
\text{w/c}_{\text{min}} &= 0.42 + \left[ \text{P}_w \times (\text{C}_{\text{sem}} + \text{C}_{\text{sf}}) \right] + 0.5 \left( \frac{\text{c}}{\text{c}} \right) \\
\text{IC}_w &= (\text{Cem}) \left[ 0.42 + 0.5 \left( \frac{\text{c}}{\text{c}} \right) \right] - \left( \frac{\text{w}}{\text{c}} \right) \\
\text{IC}_s &= \left( \text{IC}_w / \text{abs} \right) / \text{des}
\end{align*}
\]

Where:

- w/c1 is the minimal w/c ratio for a cement hydration degree of 1 in a closed system
- w/c_{\text{closed}} is the minimum w/c for the hydration degree of 1 in a PC-SF closed system
- s/c is the silica/cement ratio
- w/c_{\text{min}} the minimum w/c to reach a hydration degree of 1 for a water-entrained system
- C_{\text{sem}} is the chemical shrinkage of the cement
- C_{\text{sf}} is the chemical shrinkage of the silica fume
- IC_w is the internal curing water, kg/m³
- Cem is the amount of cement, kg/m³
- w/c is the w/c ratio of the paste
- IC_s is the amount of SAP
- abs is the absorption of SAP
- des is the desorption of SAP

TGA were made in cement pastes with a w/c ratio of 0.40. (figure 1). This results were used to calculate the bw given in equation 6 and reported in table 1. Also, to calculate w/c1, the bw result was used and p_w was considered as 0.19 g/g of cement [12, 16, 17].

\[
b_w = \frac{M_{1000^\circ C} - M_{105^\circ C} - M_{\text{CO}_2}}{M_{1000^\circ C} / (1 - \text{LOI}_{\text{sem}})}
\]

(6)

Where:

- M_{1000^\circ C} mass at 1000°C of the sample, g
- M_{105^\circ C} mass at 105°C of the sample, g
- M_{\text{CO}_2} mass loss due to decarbonation of the CaCO₃, usually between 650-800°C.
- LOI_{\text{sem}} loss of ignition of the cement
Also, TGA were made in cement and silica fume-calcium hydroxide pastes (figures 1-2) to calculate the consumption of calcium hydroxide through equations 7-9 and consequently the S/C ratio [10].

\[
CH_{cem} = \left[ \frac{M_{1000 C}}{(1-LOI_{cem})} \right] \left[ \frac{CH_{of CH} - M_{H_2O}}{CH_{of CH} - M_{H_2O}} \right] (7)
\]

\[
CH_{SF} = \frac{CH_{of CH} - M_{H_2O}}{CH_{of CH} - M_{H_2O}} (8)
\]

\[
S/C = \frac{CH_{cem}}{CH_{SF}} (9)
\]

Where:
- \(CH_{cem}\) is the amount of calcium hydroxide produced per gram of cement
- \(CH_{SF}\) is the amount of calcium hydroxide consumed per gram of silica fume
- \(bw/CH\) is the amount of chemically bound water per gram of calcium hydroxide gram.
- \(M_{H_2O}\) = Mass loss due to evaporation of water from the calcium hydroxide, usually between 400-450°C.
- \(LOI_{SF}\) is the loss of ignition of the silica fume
- \(M_{Ca(OH)2}\) is the molar weight of the \(Ca(OH)_2\)
- \(M_{H_2O}\) is the molar weight of the \(H_2O\)

All TGA tests were performed in a Perkin Elmer TGA 4000 equipment, with the following specifications: Heat rate of 10°C/min, 65 mg of sample for each test, nitrogen was used as a purge gas with a flow rate of 20 ml/min and 10 minutes of isothermal heating at 28°C and 10 minutes at 105°C, respectively.

Fig 1. TGA of cement paste with 0.40 w/c ratio. Fig 2. TGA of silica fume-calcium hydroxide paste with Ca/Si ratio of 1.5
Prior to determine the IC water with equation 4, the w/c min needs to be calculated to know if the w/c of 0.40 will reach a hydration degree of 1 with the IC water. Therefore, chemical shrinkage of cement (Cs cem) and silica fume (Cs sf) were measured according to ASTM 1608 to calculate the w/cmin for an open PC-SF system given in equation 3.

All the parameters mentioned to the mixture design are given in Table 1-2. Mixture proportioning is given in Table 3. The amount of SP was 6ml per kg of binder to achieve an extensibility of 24cm.

Table 1. Hydration parameters of the cementitious materials from TGA and CS measurements

<table>
<thead>
<tr>
<th>Material</th>
<th>bw (g/g)</th>
<th>pw (g/g)</th>
<th>CS (ml/100g of material)</th>
<th>CH g/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>0.23</td>
<td>0.19</td>
<td>6.03</td>
<td>0.16</td>
</tr>
<tr>
<td>Silica fume</td>
<td>0</td>
<td>0.5</td>
<td>19.66</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 2. w/c ratios, s/c ratio, IC water and amount of SAP for the water entrained system

<table>
<thead>
<tr>
<th>w/c closed</th>
<th>w/c min</th>
<th>w/c</th>
<th>w/c closed – w/c</th>
<th>s/c</th>
<th>IC water (kg/m³)</th>
<th>SAP (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.47</td>
<td>0.39</td>
<td>0.40</td>
<td>0.07</td>
<td>0.095</td>
<td>33.8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 3. Mixtures design in grams per litre.

<table>
<thead>
<tr>
<th>Materials</th>
<th>s/c (g/l)</th>
<th>Cement (g/l)</th>
<th>Silica fume (g/l)</th>
<th>Water (g/l)</th>
<th>IC water (g/l)</th>
<th>SP (g/l)</th>
<th>AF (g/l)</th>
<th>SAP (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>0.095</td>
<td>500</td>
<td>47.5</td>
<td>232.64</td>
<td>0</td>
<td>3.28</td>
<td>1560.3</td>
<td>0</td>
</tr>
<tr>
<td>SAP</td>
<td>0.095</td>
<td>500</td>
<td>47.5</td>
<td>232.64</td>
<td>33.75</td>
<td>3.28</td>
<td>1468.2</td>
<td>1.5</td>
</tr>
</tbody>
</table>

2.3 Curing regime

All the mortars were standard cured under controlled temperature (23 ± 2°C) and a relative humidity ≥ 95%.

2.4 Standard mixing procedure

1. Materials were added in the following order: fine aggregates, cement, silica fume and water. For mixtures with SAP, this ingredient is added after silica fume and before the water and the mixture will rest within the bowl for 30 s until the mixing process continues.
2. Then, materials were mixed at a low speed for 4 minutes.
3. SP is added and mixing is continued at a low speed for 1 minute.
4. The mixer is turned off, within 30 s, the sides and bottom of the bowl are scraped.
5. The mixture is mixed for another 3 minutes at a high speed.
2.5 Durability parameters

The durability parameters measured from the mixtures consisted of:

- Autogenous shrinkage was measured in mortars according to ASTM 1698. 3 samples are used for each series. Average values of autogenous shrinkage are presented in Figure 3.
- Electrical resistivity was measured on mortars cylinders with a diameter of 100 mm and a height of 200 mm according to AASHTO TP 95 with a proceq-resipod device that operates on the Four-Point Wenner Array Probe Test. Results are presented in figure 4, each single result is an average of 3 tests.
- Accelerated chloride migration test according to NT Build 492 was used to calculate the non-steady chloride diffusion coefficient (equations 10-12). An electrical potential of 30 volts was applied for a time period of 96 hours.

\[
D_{\text{num}} = \frac{RT}{zFE} \left[ (X_d - \varphi \sqrt{X_d}) t \right] \quad (10)
\]
\[
E = \frac{(U-2)}{L} \quad (11)
\]
\[
\varphi = 2 \sqrt{\frac{RT}{zEF}} \text{erf}^{-1} \left[1-(2 \frac{C_d}{C_0})\right] \quad (12)
\]

Where: \(D_{\text{num}}\) is the CCD in a non-steady state migration, (m²/s); \(R\) is the gas constant, \(T\) is the average value of the initial and final temperatures in the anolyte solution; \(z\) is the absolute value of ion valence, for chloride, \(z = 1\); \(F\) is Faraday constant, \(U\) is the absolute value of the applied voltage, \(V\); \(L\) is the thickness of the specimen, \(m\); \(X_d\) is the average value of the penetration depths, \(m\); \(t\) is the test duration, seconds; \(C_d\) is the chloride concentration at which the colour changes, \(C_d \approx 0.07\) N for OPC concrete and \(C_0\) is chloride concentration in the catholyte solution, \(C_0 \approx 2\) N.

3. Results

3.1 Mixtures

Fresh stage properties for all the mortars are presented at table 4. Extensibility was the same for all the mixtures. However, the substitution of sand by SAP leded to an increase in the air content and subsequently to a decrease in the unit weight.

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Extensibility (cm)</th>
<th>Air content (%)</th>
<th>Unit weight (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>24</td>
<td>1.4</td>
<td>2359</td>
</tr>
<tr>
<td>SAP</td>
<td>24</td>
<td>2.1</td>
<td>2283</td>
</tr>
</tbody>
</table>

3.2 Autogenous shrinkage

Results of autogenous shrinkage for the mixtures are shown in figure 3. Mixtures with SAP presented an autogenous shrinkage lower than 55µm/m at 28 days, while the value of the
mixture without SAP reached 345 $\mu$m/m at 28 days. The drying effect was negligible, which was verified by measuring the initial and 28 day weight for both mixtures, the difference in weight was less than 0.01%, which is the maximum value established by the specification.

The lower autogenous shrinkage presented by the mixture with SAP (55 $\mu$m/m at 28 days) is a clear evidence of the effectiveness of the equations used to estimate the required amount of internal curing water to mitigate autogenous shrinkage through the incorporation of SAP in a PC-SF based material.

### 3.3 Durability parameters

The development of surface electrical resistivity was made to an age of 14, 28, 75 and 114 days and is presented in figure 4, results show that SAP with IC water could decrease surface electrical resistivity by 32% compared to the reference mixtures for an age of 114 days. Factors found to affect the resistivity of cementitious materials are w/c ratio, supplementary cementitious materials, polymeric admixtures, air-void system, aggregate type, and degree of consolidation [1]. In this work, almost all factors for both mixtures are kept identical, other than that the air-voids were introduced by SAP and the final w/c ratio is increased by IC water. Therefore, the water-filled pores due to IC water increased the conductivity of concrete.

Farzanian et al. [8] studied the effect of SAP on the electrical resistivity of concretes without IC water and without silica fume; the results exhibited that SAP improved the electrical resistivity for mixtures with w/c ratio of 0.40 and a SAP addition of 0.3% by mass of cement; however, the initial w/c ratio of each mixture was reduced by the absorbed water of SAP that was retained until certain time; therefore, the improvement of electrical resistivity could be attributed to the reduction of the final w/c. Comparing the results from this study to the one from Farzanian et al. [8], it is assumed that the addition of SAP without IC water can lead to an enhancement of the electrical resistivity in cement pastes and with IC water electrical resistivity worsens.
Results of CDC are presented in the Table 5 with standard deviations and coefficients of variation. Regarding to the reference mixture, CCD is increased by 38 % in mixtures with SAP. These results are closely correlated with the decrease observed for the surface electrical resistivity.

Table 5. CDC of the mortars with and without SAP.

<table>
<thead>
<tr>
<th>Mixes</th>
<th>CDC (10^-12 m^2/s)</th>
<th>Standard deviation (10^-12 m^2/s)</th>
<th>Coefficient of Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>1.46</td>
<td>0.06</td>
<td>4.4</td>
</tr>
<tr>
<td>SAP</td>
<td>2.01</td>
<td>0.14</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Hasholt M. and Jensen O. [9] measured the CDC in concrete with SAP at different ages with and without IC water. The authors discussed that SAP without extra water enhance the CDC in all w/c ratios used. Also, they conclude that the improvement of SAP with IC water in the chloride ingress within concretes depends on the increase of the hydration degree. Gehlen C. [13] calculated CDC in concrete with SAP for different w/c ratios, in his results, SAP improved CDC just in some concretes. The results of CDC showed large differences in the performance of SAP and no certain conclusion were made on the performance of SAP.

Bagheri A. et al. [2] were made tests of electrical resistance and CDC in concretes with a w/b ratio of 0.38 and a cement weight replacement of 10% by silica fume. They presented CDC results of concretes with Silica Fume of 4 x 10^-12 at 180 days and the mixtures with only cement had a CDC about 13 x 10^-12, this results showed a silica fume performance 3 times better than the reference. Also, electrical resistance results showed a similar behaviour as CDC results, the concretes with silica fume had an electrical resistivity above 42 kohm.cm at 180 days and without silica fume was about 5.5 kohm.cm. Added to this, Dotto J. et al. [6] measured the electrical resistivity in concretes with a w/b ratio of 0.50 and a silica fume addition of 0, 6 and 12%. They conclude that the addition of 6% of SF increases the electrical...
resistivity of concrete by 2.5 times and 12% of SF increases it by 5 times. Clearly the silica fume enhance the durability properties of concrete referring to electrical resistivity and CDC. Thus, why the silica fume was added in this study.

The differences in the results from [2,6,8,9,13] and from this work, allow to take into consideration three possible phenomena:

1. The internal curing water added to the mortars in this work mitigates the autogenous shrinkage but the IC water could be overestimated because some theoretical values were used to calculate the IC\textsubscript{water}.
2. A silica fume addition in concretes enhance the CDC and electrical resistivity with or without internal curing.
3. Results of electrical resistivity and CDC reflects a weaker performance for mixtures with SAP due to the voids left after desorption of SAP. There is a probability that in low w/c ratios with silica fume, surface electrical resistivity and CDC are more influenced by the incorporation of micro fillers than by a higher hydration of the cement.

However, more experimental work should be done to prove these considerations and also to understand the mechanisms how SAP affects the electrical resistivity and CDC.

4. Conclusions

From the aforementioned results and discussions, the following conclusions can be drawn for the specific portland cement-silica fume mortars evaluated in this study:

1. The Power’s model modified by Jensen to calculate the required amount of SAP and the dosage of internal curing water has proven to be effective in terms of mitigating the autogenous shrinkage of cementitious materials up an age of 28 days.
2. Even though autogenous deformation was practically eliminated, electrical resistivity and chloride migration coefficient presented an opposite behaviour. These results are attributed to a higher porosity and a probable higher final water/binder ratio in the mortars with SAP. It could be useful to compliment these results with an accelerated carbonation test to observe the gas diffusion and calculate the hydration degree.
3. Seems to be enough the use of silica fume without internal curing for durability performance of concrete according to electrical resistivity and CDC results. However, complementary studies should be done with another type of cement, curing regime, w/c ratio and SAP without internal curing water.

Acknowledgment

The authors wish to express their gratitude and sincere appreciation to the different organizations that contributed in the development of this project, to the Consejo Nacional de Ciencia y Tecnología of Mexico (CONACYT), and to the Facultad de Ingeniería Civil of the Universidad Autónoma de Nuevo León. The authors also want to thank Filiberto Marin from EUCOMEX, S.A. de C.V. and Jose Alfredo Rodríguez Campos from HOLCIM México S.A.
de C.V. for providing the high-range water-reducing admixture, and the portland cement, respectively.

References

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DO SUPPLEMENTARY CEMENTITIOUS MATERIALS AND BLENDED CEMENTS INDEED INCREASE CRACKING POTENTIAL OF CONCRETE?

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Abstract
The results of standard restrained shrinkage ring tests demonstrate that introduction of supplementary cementitious materials (SCM) in concrete mixes and reduction of clinker content in the cement do not necessarily reduce the cracking potential. These results are contradictory with findings of other authors demonstrating that binary and ternary cementitious binders, in spite of their higher autogenous shrinkage potential, often exhibit later autogenous cracking ages than the control Portland cement mix. The reasons of this contradiction are hereby analysed.

1. Introduction
Cracking of concrete occurring at early age has numerous negative influences on the performance and durability of structures made of plain and reinforced concrete. Shrinkage is considered as the most important driving force for the early age cracking. However, several additional factors control the probability of cracking: among these are degrees of restraint, creep and the rate of tensile strength development. Restraint influences the level of shrinkage-induced stress, creep determines the stress relaxation, while tensile strength defines the probability of cracking at a given stress. Shrinkage deformation, in turn, may have a different origin. Researchers often distinguish between autogenous, drying, carbonation and thermal shrinkages. By definition, shrinkage deformations are characteristic of unloaded concrete occurring as a result of chemical reactions (such as cement hydration or carbonation), and changes in thermal and hygral conditions (either inside concrete – such as self-desiccation or temperature changes due to hydration heat, or outside – due to the climate changes.

The total deformation of an early age concrete is even more complicated to model, because it is not clear whether the different shrinkage components are additive each to the other, and in relation to creep deformation. Curing conditions complicate the early-age cracking phenomena even further. Considering the variety of factors affecting cracking sensitivity,
restrained shrinkage tests seem to be the most reasonable approach to estimate the cracking potential of concrete, because restrained shrinkage tests actually take into account the combination of most of the factors listed.

Three different types of restrained shrinkage testing methods (bar, slab and ring specimen) are available. A detailed review and analysis of pros and cons of the longitudinal (uniaxial), plate and ring testing arrangements is available in [1]. Among these testing methods, in spite of its limitations (such as insufficient restraining for large size of specimens and lack of capturing the heat effects on cracking) researchers are increasingly using the ring test due to the relative simplicity of its setup and the ease of implementation. Additionally, for common size specimens, the ring test can provide sustained and sufficient restraint against some rigid core to induce the cracking.

The guiding principle behind this test is quite simple: a concrete ring is cast around a restraining core and is allowed to shrink against it. Because of the drying shrinkage restrained by the internal rigid core, the concrete develops tensile stresses in the circumferential direction $\sigma_t$ and may crack, provided these stresses are sufficiently high. For the analysis purpose, the ring specimen has the advantage of being axisymmetric. The work [2] presents analytical solution for both radial $\sigma_r$ and tangential $\sigma_\theta$ stresses in terms of the shrinkage strains, the elastic properties of the concrete and steel, and the ring geometry, as shown in Figure 1.

![Figure 1. Scheme of the restrained ring test](image)

\[
\sigma_r / \varepsilon_s E_0 = -\left[ r_2^2 / r_2^2 - r_1^2 / r_1^2 \right] k / 2 \tag{1}
\]

\[
\sigma_\theta / \varepsilon_s E_0 = -\left[ r_1^2 / r_1^2 + r_2^2 / r_2^2 \right] k / 2 \tag{2}
\]

\[
k = \frac{e(1 + \mu_\sigma) + 1 - \mu_\sigma}{e(1 + \mu_\sigma) + (1 - \mu_\sigma)(r_1^2 / r_2^2)} \tag{3}
\]
where:

- \( r \) - radius of the point where stress is calculated;
- \( TV \) and \( r_v \) - circumferential and radial stresses, respectively, at a radius \( r \); \( r_i \) and \( r_e \) - internal and external radii; \( e_{sh} \) - shrinkage strain; \( E_0 \) and \( E_i \) - elasticity moduli of the concrete and the core material, respectively; \( \mu_0 \) and \( \mu_i \) - Poisson ratios of the concrete and the core material, respectively.

2. Standard restrained shrinkage ring tests

The ring test is now considered the most popular method to assess the cracking potential of concrete. Concrete, that is cast around a steel ring, which serves often as a restraining rigid core, is cured in sealed conditions for one day, then demoulded from the external side surface and exposed to drying in a laboratory under well-controlled thermal and hygral conditions.

There are two main standard methods for testing cracking potential of concrete using the ring geometry, AASHTO T 334-08 [3] and ASTM C1581/C1581M-09a [4], which are well-known for researchers and engineers dealing with design, testing and quality control of concrete. The differences between the AASHTO and ASTM standards is minor and is related to the ring geometry. The test arrangement consists of a concrete ring with inner diameter of 300 or 330 mm (in AASHTO and ASTM standards, respectively), thickness of 75 or 38 mm (in AASHTO and ASTM standards, respectively) and height of 150 mm (in both standards), and the restraining core made of steel ring with a wall thickness of 12 or 13 mm (in AASHTO and ASTM standards, respectively). Strain gauge is attached to the inner surface of the steel ring and enables to calculate stresses in the steel as well as the age of cracking. The ASTM standard also includes a recommendation for interpretation of the results (Table 1).

<table>
<thead>
<tr>
<th>Net Time-to-Cracking, ( t_{cr} ), days</th>
<th>Average Stress Rate, ( S ) (MPa/day)</th>
<th>Potential for Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ( &lt; t_{cr} \leq 7 )</td>
<td>( S \geq 0.34 )</td>
<td>High</td>
</tr>
<tr>
<td>7 ( &lt; t_{cr} \leq 14 )</td>
<td>( 0.17 \leq S &lt; 0.34 )</td>
<td>Moderate-High</td>
</tr>
<tr>
<td>14 ( &lt; t_{cr} \leq 28 )</td>
<td>( 0.10 \leq S &lt; 0.17 )</td>
<td>Moderate-Low</td>
</tr>
<tr>
<td>( t_{cr} &gt; 28 )</td>
<td>( S &lt; 0.10 )</td>
<td>Low</td>
</tr>
</tbody>
</table>

As we can see from this table, concrete can be classified onto four different categories by cracking potential, from low to high. The net time-to-cracking criterion seems to be the most important. The second criterion, average stress rate, is especially important, when concrete does not crack during the test, and when the test is terminated. In these cases, the rate of tensile stress development at the time is expected to provide a basis for comparison of the materials.

Due to the experimental scatter, different category of cracking potential, the net time-to-cracking and the rate of tensile stress development, is sometimes assigned to the same
concrete by different criteria. To solve this uncertainty, the integrated criterion as a ratio between the stress rate and time-to-cracking was introduced later on [5]. The integrated criterion of cracking sensitivity was shown as being more reliable for the classification than the individual ones.

The restrained ring test method has been primarily used to evaluate cracking potential of concrete and the effectiveness of different types of material additives and different types and volume fractions of fibres in controlling cracking of mortar and concrete. The procedure of restrained shrinkage ring tests can be used to determine the effects of variations in the proportions and material properties of mortar or concrete on cracking due to both autogenous and drying shrinkage, and deformations caused by heat of hydration.

It is widely accepted that the ring test method is useful for determining the relative likelihood of early-age cracking of different cementitious mixtures and for aiding in the selection of cement-based materials that are less likely to crack under restrained shrinkage. Actual cracking tendency in service, as correctly stated by the ASTM standard, depends on multiple variables including type of structure, degree of restraint, rate of property development, construction and curing methods, and environmental conditions [4]. Paragraph 4.4 of this standard states that the restrained ring test can be used to determine the relative effects of material variations such as aggregate source, aggregate gradation, cement type, cement content, water content, supplementary cementing materials (SCM), or chemical admixtures. In other words, the ring test is considered by the authors of both AASHTO and ASTM standards and by the scientific and engineering community as well-suitable method for estimation of the crack potential of concrete containing different SCM. Accordingly, several authors tried to use this test method in their research and published the results, which will be reviewed hereafter. The goal of the present analysis is to have a deeper look into these studies, which in several cases provided controversial results.

3. Effect of fly ash

Using the uniaxial restrained test, Breitenbucher and Mangold (1994) [6] found that when the cement content of the concrete was lower than 340 kg/m$^3$, fly ash did not significantly influence the cracking tendency of concrete exposed to drying at 1 day during the first 4 or 5 days.

Hossain, Fonseka, & Bullock (2008) [7] studied restrained shrinkage cracking of low water to binder ratio mortar containing UFFA and regular fly ash. The ring specimens used in this study were slightly different from the standard AASHTO version of the rings. One of the deviations was changing the evaporation conditions: the specimens were sealed till the age of 24 hours, and thereafter placed in a constant temperature (21 °C) and RH (50%) room to allow drying from top and bottom surfaces of the ring. In this case, moisture is assumed to be lost more uniformly along the radial direction. The authors concluded that mortars containing two different types of UFFA exhibited slightly delayed cracking (at the age of 11 and 15 days, respectively), than mortar containing regular fly ash (12 days) and reference mortar (9.5 days). In other words, the differences were minor. Moreover, the question as to how
introduction of this type of SCM actually influences the cracking sensitivity remained in fact unanswered, because no comparison was made with rings made of reference mortar.

Qiao, McLean and Zhuang (2010) [8] applied restrained shrinkage test by AASHTO standard. In particular, two types of concrete were tested: reference mix (concrete made at water to cement ratio of 0.4) and the mix, in which 20% fly ash (by the total mass of the cementitious materials) replaced Portland cement. The authors removed outer forms at age of 8 hours and exposed the concrete to drying at standard environment. The results (Table 2) clearly show that concrete containing fly ash cracks earlier than the corresponding concrete without FA.

Table 2. Time to cracking of concrete specimens, with and without fly ash [8]

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Reference concrete</th>
<th>Concrete with 20% FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.1</td>
<td>4.8</td>
</tr>
<tr>
<td>2</td>
<td>17.6</td>
<td>7.8</td>
</tr>
<tr>
<td>3</td>
<td>10.9</td>
<td>3.3</td>
</tr>
</tbody>
</table>

However, these results contradict those obtained by Riding et al. (2008) [9], which used a different test method (uniaxial restrained cracking frame) for similar concrete mixtures made at water to binder ratio of 0.42 with 20% FA replacement and showed that all fly ashes lowered the early-age cracking risk of concrete. FA concrete had a lower tensile strength development than the control mixture. Given an equal stress development, the FA concrete should crack sooner than the control mixture. In reality, the cracking tendency for FA concrete was lower, because the stresses were reduced by a lowered thermal strain (caused by lowered heat of hydration) and increased early-age creep. In sum, lower cracking risk of FA concrete was a result of the combination of factors, such as creep, lower heat of hydration, modulus development, and tensile strength gain, all of which depend on the testing procedure.

4. Effect of silica fume

Altoubat and Lange (2001) [10] studied the effect of water to binder ratio. These authors built and applied the uniaxial restrained shrinkage apparatus based on the system suggested in [11]. Their compositions are presented in Table 3. The mixes were cured in sealed conditions and on the next day exposed to air-drying at the room temperature of T=23°C and air relative humidity RH=50%. The shrinkage-induced stresses for these compositions are shown in Figure 2.

The mixture of water to binder ratio of 0.32 (HPC-0.32) included SF. Figure 2 shows that its addition resulted in an accelerated growth of shrinkage stresses and earlier cracking. This finding was not completely new: similar data about higher cracking risk of concrete incorporating SF was reported earlier. The adverse effect of SF on cracking sensitivity of concrete was experimentally studied by Krauss and Rogalla (1996) [12], which noted that restrained shrinkage rings (AASHTO PP34-99) contained SF cracked 5-6 days earlier than similar specimens without SF.
The authors of NCHRP Report 410 “Silica Fume Concrete for Bridge Decks” published in 1998, Whiting and Detwiler, stated: “Cracking tendency of concrete is influenced by the addition of silica fume only when the concrete is improperly cured” [13]. The authors of this report concluded that curing period was extremely important with regards to the age at which of cracking. They attentively analyzed the data obtained by Krauss and Rogalla [12], concluding that specimens (especially those containing silica fume) cured for 7 days took significantly longer to crack than those cured for 1 day only (Table 4).

Table 3. Proportions of concrete mixtures, slump and time of cracking [10]

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Water to binder ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>Coarse aggregate, kg/m³</td>
<td>974.1</td>
</tr>
<tr>
<td>Fine aggregate, kg/m³</td>
<td>622.8</td>
</tr>
<tr>
<td>Cement, kg/m³</td>
<td>533.1</td>
</tr>
<tr>
<td>Silica fume (SF), kg/m³</td>
<td>117.0</td>
</tr>
<tr>
<td>Water, kg/m³</td>
<td>208.0</td>
</tr>
<tr>
<td>High-range water-reducing admixture, mL/m³</td>
<td>954.8</td>
</tr>
<tr>
<td>Slump, mm</td>
<td>40</td>
</tr>
<tr>
<td>Time of cracking, hours</td>
<td>69.5</td>
</tr>
</tbody>
</table>

Table 4 clearly shows that mixtures containing silica fume and cured sealed for 1 day (according to the existing standard procedures of the restrained ring test by both AASHTO and ASTM) cracked earlier than the reference mixtures. However, had silica fume concrete mixtures been given 7 days of continuous moist curing, there would then be almost no association between the content of silica fume and the cracking. This tendency is especially characteristic of high-strength concrete made at water to binder ratio lower than 0.45. Therefore, in their report, Whiting and Detwiler [13] strongly recommend that agencies must ensure that the minimum moist curing period of 7 days is specified for all bridge-deck...
construction projects where silica fume concrete is to be used. This recommendation is consistent with the practical suggestion of Schmitt and Darwin (1995) [14] to apply fog sprays or keep concrete moist after the placement for 7 days continuously, when silica fume is used.

As far as longer curing period is concerned, Krauss and Rogalla [12], Altoubat and Lange [10] and others have found that concrete cured for extremely extended periods (even up to 60 days) typically cracked at similar or shorter periods of drying in restrained ring tests. It seems that the longer curing increases the stiffness of the concrete and lessens the creep so that higher stresses develop upon subsequent drying.

Table 4. Time to first crack, days [12]

<table>
<thead>
<tr>
<th>Water to binder ratio</th>
<th>Silica fume content</th>
<th>Curing for 1 day</th>
<th>Curing for 7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 6% 9%</td>
<td>0 6% 9%</td>
<td></td>
</tr>
<tr>
<td>0.45</td>
<td>33 19 17</td>
<td>33 25 30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>36 14 18</td>
<td>35 20 46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27 17 11</td>
<td>38 19 28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27 13 16</td>
<td>40 20 28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22 23 20</td>
<td>33 16 31</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>24 14 14</td>
<td>30 17 27</td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>24 17 30</td>
<td>36 49 51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26 12 17</td>
<td>24 18 14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22 23 11</td>
<td>34 25 34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24 18 22</td>
<td>18 21 55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31 10 14</td>
<td>50 56 52</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>25 16 18</td>
<td>32 31 39</td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>35 13 11</td>
<td>53 29 67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>43 12 13</td>
<td>29 57 32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22 14 18</td>
<td>32 17 53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24 28 28</td>
<td>28 37 66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35 17 21</td>
<td>32 64 30</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>31 17 18</td>
<td>34 39 48</td>
<td></td>
</tr>
</tbody>
</table>

5. Effect of slag

Darquennes et al. (2006) [15] observed a significant difference in cracking potential tested by the AASHTO standard ring test between concrete mixtures made of slag cements (CEM III/A 42.5; CEM III/B 42.5) and concrete made of Portland cement (CEM I 42.5) at water to binder ratios 0.44 – 0.48. Even after several months, no cracking of rings made in Portland cement was observed whatsoever, while all the rings made of slag cement concrete indeed cracked. These authors thus suggested that slag cement concrete is more prone to early age cracking than Portland cement concrete.

These authors also refer the study conducted by Lokhorst in Delft University of Technology, The Netherlands (1998) that estimated cracking potential of concretes made of Portland...
cement and slag cement CEM III/B 42.5 at slightly higher water to binder ratio (0.5) using uniaxial restrained shrinkage test method and obtained similar results.

Bouasker et al. (2014) [16] studied the effect of the partial replacement of Portland cement (PC) with blast furnace slag (BFS) and/or limestone filler (LF) on cracking potential of concrete. Their results seem to be contradictory: on one hand, the authors found that the combination of PC, BFS and LF in binary and ternary binders yielded, in most cases, a delay of the cracking time compared to the corresponding binary binder paste; on the other hand they concluded that the best results in terms of crack delay were obtained for the binders with the lowest concentration of slag.

Darquennes et al. (2011) [17] attempted to estimate the effect of slag content in cement on the evolution of free autogenous shrinkage and cracking sensitivity of concrete exposed to uniaxial restraint in sealed conditions, when one of the main driving forces of cracking was assumed to be autogenous shrinkage. Three cements were used in this experimental program: a Portland cement CEM I 52.5 N and two blended cements: CEM III/A 42.5 LA and CEM III/B 42.5 HSR LA, which contained 42% and 71% of slag, respectively. The authors stated that from the evolution of the elasticity modulus, compressive strength and autogenous shrinkage, one could conclude that the slag cement concretes, especially CEM III/B, are more prone to crack under restrained conditions than the Portland cement concrete. On the other hand, the cracking susceptibility of the slag cement concretes was delayed in comparison with the Portland cement concrete. The authors explained this unexpected behavior due to the slower hydration kinetics of slag cement, the larger capacity of slag cement concrete to relax tensile stresses and the expansion of the slag cement matrix at early age. Based on these findings, the authors concluded that autogenous deformation is not the major factor controlling cracking behavior.

6. Effects of different SCM and their combinations
The work published by Subramaniam et al. (2005) [18] dealt with evaluating the shrinkage cracking concerns in concrete containing ultrafine fly ash (UFFA) with mean particle size of 3 µm (UFFA mix) and silica fume (SF mix) as cement replacements. The compositions studied in this work are shown in Table 5.

Table 5. Mixture proportions and cracking time [18]

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Reference</th>
<th>UFFA mix</th>
<th>SF mix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine aggregate, kg/m³</td>
<td>755.9</td>
<td>755.9</td>
<td>755.9</td>
</tr>
<tr>
<td>Coarse aggregate, kg/m³</td>
<td>1,133.80</td>
<td>1,133.80</td>
<td>1,133.80</td>
</tr>
<tr>
<td>Cement, kg/m³</td>
<td>404.2</td>
<td>366.3</td>
<td>363.2</td>
</tr>
<tr>
<td>Silica fume, kg/m³</td>
<td>0</td>
<td>31.85</td>
<td>0</td>
</tr>
<tr>
<td>UFFA, kg/m³</td>
<td>0</td>
<td>0</td>
<td>37.3</td>
</tr>
<tr>
<td>Water, kg/m³</td>
<td>161.7</td>
<td>159.2</td>
<td>160.2</td>
</tr>
<tr>
<td>Water/binder ratio</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Aggregate volume</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
</tr>
<tr>
<td>The average age of cracking obtained from three specimens, days</td>
<td>10.00</td>
<td>5.33</td>
<td>12.33</td>
</tr>
</tbody>
</table>
The authors used the standard ASTM ring test method [4] to assess the restrained shrinkage cracking potential. The experimental results obtained by the authors indicated that replacement of cement with UFFA produces improvement in the potential for restrained shrinkage assessed using the ring test without a significant influence on the strength. Although the authors did not address the adverse effect of silica fume introduction on cracking sensitivity of concrete in this publication, their results are quite confirmative to what was found in the previous studies.

Ray et al. (2012) [19] used AASHTO ring test method to study the cracking sensitivity of concrete containing three different SCM combinations: slag + silica fume, fly ash + silica fume, and metakaolin, at different water to binder ratios (0.30; 0.35 and 0.40) and at two types of coarse aggregates: crushed limestone and river gravel. They found that concrete with gravel generally cracked 2–8 days later compared to that with limestone. For concrete made at lower water to binder ratios, the cracks occurred earlier. Finally, for concrete with different SCM combinations, only slight differences among the specimens were found on the cracking onset. Unfortunately, the comparison with reference mixtures was not made. In view of this, the question whether introduction of SCM into concrete mixtures influences their cracking potential was unanswered.

Kovler et al. (2012) [20] reported recently the results of a systematic evaluation of cracking sensitivity, addressing the major parameters in concrete technology, especially for the high end of concrete quality. The cracking potential of concrete was evaluated using the standard ASTM ring test [20] method. All types of specimens were demolded after one day and exposed to lab environment at 21°C/60%RH. The concrete compositions are given in Table 6. The variables studied in this work were, in particular: the type of cement in the 0.33 water to cement ratio concretes (Portland cement CEM I 52.5 N, Portland – fly ash cement CEM II/A-V 42.5 N or blast furnace slag cement CEM III/B 42.5 N), and the type of mineral additive, which was used to replace part of the cement (61 of the 567 kg/m³ cement): metakaolin (MK), coal fly ash (FA) or silica fume (SF).

The results of the tests are shown in Figure 1. They indicate the higher sensitivity to cracking of the blast furnace slag cement concrete. As far as the effect of mineral additives is concerned, significant difference was found in the cracking sensitivity. Although the shrinkage and strength curves were similar for these concretes, the mixtures with mineral additives showing greater sensitivity than the reference concrete made of Portland cement CEM I. Within these concretes, the fly ash concrete was less sensitive than the ones with metakaolin and silica fume. The latter concrete was found the most sensitive to cracking, which is consistent with the results obtained by Krauss and Rogalla [12] and other authors. Slag (in the CEM III/B 42.5 N cement) and fly ash (added to the concrete mix) increased cracking potential, but to an extent, which is much smaller than that of metakaolin and silica fume.

The enhanced sensitivity to cracking of concrete made with SCM can be explained by insufficient curing of the material, when the concrete microstructure was not developed enough to resist cracking. It has to be emphasized that this study (like many other studies of
this kind) was conducted strictly following the requirements of the ASTM standard C1581. It is very possible, that a prolongation of the curing period, for example till one week or even longer (it means a deviation from the standard requirements), would mitigate the cracking potential of concrete made with SCM. Indeed, like other mechanical properties of concrete (strength, modulus of elasticity, visco-elastic properties etc.), which are all dependent on the initial curing (under either wet or sealed conditions); cracking sensitivity is also expected to be dependent on this important factor. If the goal of testing is to evaluate cracking potential of concrete mixtures having different kinetics of hardening (like concretes with and without SCM), it would be worth slightly modifying the existing AASHTO and ASTM standards, introducing the recommendation to apply different curing periods, before drying commencement. At least, two different curing periods are recommended: 1 and 7 days.

Table 6. Concrete compositions [20]

<table>
<thead>
<tr>
<th>Cement</th>
<th>Mineral additive</th>
<th>Content (kg/m³)</th>
<th></th>
<th></th>
<th></th>
<th>Mineral Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cement</td>
<td>Mix</td>
<td>Water</td>
<td>Sand</td>
<td>Gravel</td>
</tr>
<tr>
<td>CEM I 52.5 N</td>
<td>-</td>
<td>567</td>
<td>167</td>
<td>572</td>
<td>1145</td>
<td>-</td>
</tr>
<tr>
<td>CEM II/A-V 42.5 N</td>
<td>-</td>
<td>567</td>
<td>167</td>
<td>572</td>
<td>1145</td>
<td>-</td>
</tr>
<tr>
<td>CEM III/B 42.5 N</td>
<td>-</td>
<td>567</td>
<td>167</td>
<td>572</td>
<td>1145</td>
<td>-</td>
</tr>
<tr>
<td>CEM I 52.5 N</td>
<td>Metakaolin</td>
<td>506</td>
<td>167</td>
<td>508</td>
<td>1145</td>
<td>61</td>
</tr>
<tr>
<td>CEM I 52.5 N</td>
<td>Silica fume</td>
<td>506</td>
<td>167</td>
<td>472</td>
<td>1145</td>
<td>61</td>
</tr>
<tr>
<td>CEM I 52.5 N</td>
<td>Fly ash</td>
<td>506</td>
<td>167</td>
<td>503</td>
<td>1145</td>
<td>61</td>
</tr>
</tbody>
</table>

Figure 3. Cracking potential of concretes with different types of cement and SCM [20]
7. Conclusions
The AASHTO and ASTM standard restrained shrinkage ring tests are very popular among researchers and engineers for determining the relative likelihood of early-age cracking of different cementitious mixtures. However, the test results for concrete containing SCM often contradict those obtained by other test methods. In fact, concrete compositions with SCM have different kinetics of hardening, creep, heat of hydration, elasticity modulus and tensile strength gain. In other words, “higher” cracking risk of concrete containing SCM seems to be a result of the combination of factors, such as creep, lower heat of hydration, modulus development, and tensile strength gain, which all depend on the testing procedure. The standard ring tests, in particular, require curing period of 1 day only for all kinds of concrete, but this requirement does not reflect the typical features of SCM-based concrete (slower setting and early strength development, need in longer keeping moisture because of slower hydration). If the goal of testing is to evaluate cracking potential of concrete mixtures having different kinetics of hardening (like concretes with and without SCM), it is recommended to modify the existing AASHTO and ASTM standards, applying at least two different curing periods: 1 and 7 days.

Acknowledgements
The author is thankful to Prof. Arnon Bentur and Dr. Semion Zhutovsky from the Technion – Israel Institute of Technology, for the opportunity to openly discuss the experimental results, excellent team-work atmosphere and a long-term cooperation in the numerous research projects related to the development of modern methods of testing cracking potential of concrete.

References
REPLACEMENT OF CEMENT WITH WASTE CERAMIC POWDER IN CEMENTITIOUS COMPOSITES: RESULTS OF A PRELIMINARY INVESTIGATION

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(4) Queen’s University of Belfast, Northern Ireland, UK

Abstract
This study presents the results of a preliminary study aiming at assessing the feasibility of using waste ceramic powder as a partial replacement of cement in cement based mortars. The aim is to improve the sustainability footprint of concrete and cement based construction materials in the precast industry. Ceramic powders from two different sources have been employed, respectively coming from crushed bathroom waste fixtures and from foundry residuals. Two different cement replacement volume percentages have been considered, respectively 10%, 30%. Effects of the replacement on the workability and on the compressive and flexural strength development have been considered, up to longer curing periods in the region of three months. This is aimed at establishing if there is any potential for pozzolanic activity. The study is prodromal to investigating durability characteristics, including plastic and restrained shrinkage cracking potential. The results of the study provide an interesting insight into the possibility of using this kind of wastes as a concrete constituent, thus reducing the demand for raw cement and the burden on the landfills for disposing of such kind of invading waste.

1. Introduction
As concrete is the second largest used material worldwide, after water, the “concrete community” can significantly contribute to increasing the sustainability signature of our current “life-style” and, in particular, the construction sector as a whole. This actually continues to represent, despite the well-known negative economic trends, a significant share of the gross domestic product in both developed and emerging countries. At the same time, Construction and Demolition (C&D) activities are, according to recent estimates, 75% of the waste due to all human activities.

It has been claimed that one of the most significant environmental burdens of the whole life
cycle of concrete is represented by the production of Portland cement. This is mainly due to the depletion of natural resources (limestone, clay etc.) and the high energy necessary for the production of clinker. It is thus evident that any effect to reduce the demand for cement or towards a clinker-free cement or alternative binders, such as geo-polymers, has a high sustainability value.

With reference to the first concept, the use of cement substitutes, with mere “inert filler” function or featuring either pozzolanic and/or cementitious additions (fly ashes, silica fume, ground granulated slag etc.) is now a well consolidated practice in the cement and concrete industry. This is well documented noting the benefits in terms of improved performance, fresh state behaviour, matrix compactness, strength, and durability.

The aforementioned cement substitutes are by-products or waste materials from activities other than construction “proprie dicta”, ranging from quarrying to electric power to steel production. Such advances invite novel research activities aimed at assessing the feasibility of using such materials as cement replacement or substitutes. There is a tremendously wide variety of waste products available from a wide range of human activities. Examples ranging from agriculture to C&D wastes (recycled concrete aggregates for the production of recycled aggregate concrete). These are gaining wider and wider popularity and acceptance in standards and structural design codes worldwide.

In this framework, it is worth remarking that a conspicuous share of the C&D waste (54% according to recent estimates) is represented by ceramic materials (blocks, tiles, electrical insulation, bathroom fixtures), to which waste from the medical sector (anatomical and dental prostheses) and the ceramic production sector (up to 2% of the total production, depending on the degree of automation and quality control) have to be added. It would be of the foremost interest and importance to assess the feasibility of employing such a waste in a suitable form as a replacement/substitute either for cement and/or of natural aggregates in the production of concrete and cementitious composites [1].

Using ceramic waste in concrete production has been increasingly attracting researchers and practitioners in the last decade, both as replacement of cement [2-4] and as a raw material for the production of alternative clinkers and cements [5-7]. Pozzolanic activity of the waste has been confirmed, which has led to setting some upper bounds on the ceramic-to-cement replacement ratios (35%), in order to limit the negative effects on strength development. This is due to both later hydration of the pozzolana as well as to the lower availability of calcium hydroxide necessary to activate the same pozzolanic reaction. Incorporation of the waste into cement and concrete was also effective in limiting the leaching of toxic substances such as zinc, boron and zirconium, normally employed for surface glazing of tiles and ceramic artifacts.

Coarser ceramic waste particles were also used as a replacement of natural fine aggregates in the concrete, highlighting their potential as internal curing agents [8-10].

Moreover, because of the generally higher fineness that both waste ceramic powder and fine aggregates feature with respect to cement and river sand, higher matrix compactness could be
achieved, with reduced pore sizes. This also resulted in improved durability vs., e.g., chloride attack.

In this study, the feasibility has been investigated of partially replacing cement with ceramic powder originating from waste bathroom fixings. In the interest of simplicity, reference has been made to cement pastes and mortars, formulated from Self Compacting Concrete (SCC) mixes, in which up to 30% by volume of cement has been replaced with ceramic powder. Since the mere replacement of cement with ceramic powder results in a modification of the actual w/c ratio, an alternative mix-design strategy has also been adopted, in which fixed w/c and ceramic-to-cement replacement ratios have been input as the optimization variables.

Results, in terms of compressive and flexural strength of the investigated pastes and mortars seem to confirm that ceramic powder can be effectively incorporated into concrete without detrimental outcome on the mechanical properties.

2. Experimental program: materials and tests

The employed ceramic waste powder comes from disposed bathroom fixtures; its composition, analysed by means of XRD, is shown in Figure 1. As a matter of fact the results of the analysis show peaks in correspondence of the diffraction angle characteristics of quartz (SiO$_2$) as well as of aluminium composites, i.e. corundum (Al$_2$O$_3$) and sillimanite (Al$_2$SiO$_5$).

![XRD analysis](image)

Particle size analysis with laser diffraction method was also performed (Figure 2). The powder has a significant fraction of sub-micron (nano)-sized particles; moreover, more than
90% of the particles have a diameter lower than 10 μm. This would result in increased matrix compactness.

Its effects as cement replacement has been investigated with reference to cement pastes and mortars, formulated from SCCs, the composition of which is listed in Tables 1 and 2. Two different volume percentage replacements have been investigated, equal to 10% and 30%. For the latter, an “alternative” composition has been also proposed, which also keeps the w/c weight ratio unaltered, by suitable scaling of the dosage of all constituents.

Mini-slump flow tests were first performed, employing a frustum of cone 50 mm high and with major/minor diameters respectively equal to 100 mm and 70 mm.

With each mix, beam specimens 40x40x160 mm have been cast, these are tested in bending and compression according to EN 197-1. Tests have been performed at 1, 3, 7, 28, 56 and 84 days, also to assess potential pozzolanic activity, if any.

![Figure 2. Cumulative particle size distribution](image)

Until testing, specimens were cured in a moist room at 20°C and 95% RH. For each testing age three specimens were cast; the data-base will hence consist of three flexural strength and six compressive strength values for each mix at each testing age (a compression test is performed on each beam-half, after breaking the specimen in bending). Mercure Intrusion Porosimetry (MIP) tests have been performed on 28 d mortar samples.
Table 1. Mix. Composition of investigated cement pastes and mortars (dosages in kg/m³).

<table>
<thead>
<tr>
<th>Mix-code</th>
<th>PCEM- ref</th>
<th>PCER-10</th>
<th>PCER-30</th>
<th>PCER-30wc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>1632</td>
<td>1468</td>
<td>1142</td>
<td>1325</td>
</tr>
<tr>
<td>Ceramic</td>
<td></td>
<td>105</td>
<td>316</td>
<td>374</td>
</tr>
<tr>
<td>Water</td>
<td>461</td>
<td>461</td>
<td>461</td>
<td>374</td>
</tr>
<tr>
<td>Superplasticizer</td>
<td>14.2</td>
<td>14.2</td>
<td>14.2</td>
<td>23.3</td>
</tr>
</tbody>
</table>

Table 2. Mix. Composition of investigated cement pastes and mortars (dosages in kg/m³).

<table>
<thead>
<tr>
<th>Mix-code</th>
<th>MCEM - ref</th>
<th>MCER-10</th>
<th>MCER-30</th>
<th>MCER-30wc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>875</td>
<td>788</td>
<td>613</td>
<td>689</td>
</tr>
<tr>
<td>Ceramic</td>
<td></td>
<td>57</td>
<td>170</td>
<td>190</td>
</tr>
<tr>
<td>Water</td>
<td>247</td>
<td>247</td>
<td>247</td>
<td>194</td>
</tr>
<tr>
<td>Superplasticizer</td>
<td>7.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>1205</td>
<td>1205</td>
<td>1205</td>
<td>1205</td>
</tr>
</tbody>
</table>

3. Experimental program: results and discussion

Results of mini-slump flow tests on mortars, shown in Table 3, this highlights that the substitution of cement with ceramic powder slightly affects, or better moderately improves, the mortar flowability, provided the water/powder ratio was kept constant. For the mixture obtained by scaling the dosage of constituents in order to keep the w/c ratio constant, similar flowability could be obtained only by increasing the dosage of superplasticizer in tandem. Because of its smaller particle size, waste ceramic powder is able to provide a lubricant effect to the cement, as is common for extra-finely ground cement substitutes. Interestingly, the addition of ceramic powder also seems to result into slightly less dispersed values of the mini-slump flow diameter, most likely because of the higher particle fineness and hence higher specific surface. This favours absorption of some extra water contributing to the increase in the mixture robustness.

Table 3. Slump-flow diameters of investigated mortars (12 data for each mix).

<table>
<thead>
<tr>
<th>Mix-code</th>
<th>MCEM-ref</th>
<th>MCER-10</th>
<th>MCER-30</th>
<th>MCER-30wc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av. diam. (mm)</td>
<td>298</td>
<td>333</td>
<td>322</td>
<td>297</td>
</tr>
<tr>
<td>Std. dev. (mm)</td>
<td>36</td>
<td>17</td>
<td>14</td>
<td>10</td>
</tr>
</tbody>
</table>

In Figure 3 a-b the time evolution of compressive strength for pastes and mortars is plotted. It can be observed that for low ceramic to cement replacement volume ratios, the likely pozzolanic activity of the former is able to compensate at quite later ages, the effects of cement reduction and proportional increase of the w/c ratio. For higher ceramic to cement replacement ratios, the aforementioned negative effects could only be overcome, by keeping the w/c ratio constant. The sole pozzolanic activity of the ceramic is not able to provide a
products (portlandite), necessary for its activation. In the case of mortars, these negative effects are strongly reduced, also because of the “stabilizing” effect provided by the fine aggregate. This accounting for about 46% of the mortar volume fraction, and thus leading to hypothesize that this effect could be even less evident in a concrete mix, if the paste volume fraction becomes even lower. The same statements hold firm with reference to flexural strength (Figure 4 a-b). Quite surprisingly, after an almost constant trend for intermediate ages, the flexural strength seems to decrease for longer age, always more dramatically for cement pastes than for mortars. This could be partially explained with progressive stiffening and embrittlement of the composites with aging, which makes more difficult the sectional redistribution of bending stresses.

MIP test results (Table 4) show that the ceramic powder, thanks to its fineness and despite its slower reaction and the lower availability of cement, is able to guarantee not only an unaltered total porosity but also lower average and median pore radii. The increase in W/C is also unaffected. This would all contribute towards an improved durability, the potential hazard vs. aggressive substances being correlated to the pore radius.

Table 4. MIP test results on mortars.

<table>
<thead>
<tr>
<th>Mix-code</th>
<th>MCEM-ref</th>
<th>MCER-10</th>
<th>MCER-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total porosity %</td>
<td>21.59</td>
<td>20.88</td>
<td>23.26</td>
</tr>
<tr>
<td>Av. pore radius (µm)</td>
<td>0.0184</td>
<td>0.0143</td>
<td>0.0109</td>
</tr>
<tr>
<td>Median pore radius (µm)</td>
<td>0.0264</td>
<td>0.0201</td>
<td>0.0142</td>
</tr>
</tbody>
</table>

4. Conclusions

In this study a preliminary assessment has been performed of the feasibility of replacing cement with a waste ceramic powder obtained from disposed bathroom fixture in cement pastes and mortars.

Results have confirmed that the decrease of strength due to the reduction of cement content can be partially overcome at later ages by the likely pozzolanic activity of the ceramic, but can also be effectively tempered designing the mix composition so to keep constant the water to cement ratio.

Negative effects on the fresh state performance can be easily overcome by suitably adjusting the SP dosage. Stabilizing effects of fine aggregates in mortars have been also highlighted, which leads to hypothesize that good results are going to be obtained with reference to concrete mixtures, with the further presence of coarse aggregates.

This prodromal study, which seems to confirm literature findings about the upper bound for cement replacement ratio, is going to be completed with durability investigation, in order to pave the way for the use of sustainable concrete incorporating waste ceramic powder for building engineering applications.
Figure 3. Time evolution of compressive strength for investigated cement pastes (a) and mortars (b).
Figure 4. Time evolution of flexural strength for investigated cement pastes (a) and mortars (b).

Acknowledgements
The authors wish to acknowledge the financial support and funding received from the European Union, as this research is part of the FP7-PEOPLE-2012-IAPP project “EiroCrete: Development of sustainable, lower carbon, pre-cast concrete infrastructure”. This work actually represents the summary of the activity performed by the authors during reciprocal secondments. The authors also acknowledge the cooperation of Mr. Eduardo Ballesteros Ribera, Mr. Héctor David Méndez Figueroa, Mr. Alex Pellegri and Mr. Lorenzo Sgubbi in performing the experimental tests and reducing the data, in partial fulfilment of the requirements for the respective achievement of their MSEng and BEng in Civil Engineering at Politecnico di Milano.
References


PERMEABILITY OF AMBIENT CURED FLY ASH GEOPOLYMER CONCRETE BLENDED WITH ADDITIVES

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Abstract
Fly ash geopolymer concrete is a low-emission alternative building material to ordinary Portland cement (OPC) concrete. Previous studies mostly reported the properties of heat cured geopolymer concrete. However, heat curing is a costly and energy-intensive process which is not always feasible for cast-in-situ concreting. This study presents the effects of different mixture parameters on the permeability properties of geopolymer concrete cured in ambient condition. Low-calcium fly ash was blended with small percentages of additives such as blast furnace slag, OPC and hydrated lime in order to enhance setting and overcome the need for heat curing. The results of different mixtures were compared with those of control geopolymer and OPC concrete. The results of ambient cured geopolymer samples were also compared with those of heat cured samples. It was found that the volume of permeable voids (VPV) of geopolymers modified with different additives remained unaffected, despite achieving higher strength as compared to the control concrete. Sorptivity of the mixtures depended on the type and amount of the additives present in the mixture. The results show suitability of the fly ash blends for ambient-cured geopolymer concrete of strength and permeability similar to those of OPC concrete and heat-cured geopolymer concrete.

1. Introduction

In the advent of finding alternate binders for concrete, the geopolymer or alkali activated binder has been a potential alternative to ordinary Portland cement (OPC) [1]. Geopolymer, which is an inorganic polymer, is produced from various alumino-silicate materials reacted by alkaline solutions. By-product materials like fly ash, blast furnace slag and materials of geological origin such as metakaolin are generally used as the alumino-silicate sources for producing geopolymers [2]. Hence geopolymers can play a substantial role in green concrete technology by reducing the use of cement, a major contributor of greenhouse gases, by utilizing various by-product materials [1]. Studies conducted over the last decades indicated
potential benefits of fly ash based geopolymer over OPC concrete [3, 4]. It has been reported
that, low calcium fly ash based geopolymer concrete achieved excellent mechanical and
durability properties, when cured in high temperature [5, 6, 7].

Despite the superior resistance of the low-calcium fly ash geopolymer concrete in various
severe environments [8, 9, 10], according to Kong et al. [11] and Sindhunata [12], the fly ash
gegopolymer paste contains higher proportion of pores of the mesopore sizes. However, Ma et
al. [13] reported that the pore structure of alkali activated fly ash (AAF) with high silica
content as an activator significantly differs from that of cement paste. The development of the
pore structure of AAF with time is considerably slower than that of cement paste that is more
pronounced with increased curing age. Yet, the water permeability of AAF is higher than that
of cement paste (w/c = 0.4), especially at later ages. Increase of both silica and alkali content,
and heat curing time resulted in a lower porosity and a finer pore system.

In the study of Olivia et al. [14], heat-cured fly ash based geopolymer concrete exhibited low
water absorption and sorptivity. A water/binder ratio and well-graded aggregate are some
important parameters that influence the water penetrability of low-calcium fly ash
geopolymer concrete. It was found that water absorption and VPV, sorptivity and water
permeability were less when water/binder ratio was low, and aggregate was well graded. They
classified the studied mixture as a concrete of average quality according to water permeability
coefficient values.

It is noted that most of the studies on the durability of fly ash geopolymer concrete are
reported for heat cured or steam cured specimens. However, heat curing is not always
practicable in cast-in-situ applications. Hence a series of study has been conducted and
reported geopolymer concrete mixtures suitable for ambient curing condition [15, 16, 17].
The amount of calcium content in the fly ash was found to have significant impact on the
resulting hardened geopolymer [18, 19]. The amount of internal and external calcium in the
fly ash was found to have significant impact on the resulting geopolymer [20]. While addition
of calcium bearing additives accelerate setting and provide significant strength development
for ambient curing condition, it is also necessary to investigate the durability properties of
these geopolymer concrete. Report on durability properties of ambient cured geopolymer is
scarce in literature. This study aimed to investigate the permeability parameters of low-
calcium fly ash geopolymers modified with additives such as ground granulated blast furnace
slag, OPC and calcium hydroxide that can be cured in ambient condition without elevated
heat. Fly ash was replaced partially with these additives to accelerate the setting of the
geopolymers at ambient condition. The effects of these additives on the volume of permeable
void and sorptivity of concrete are compared with those of control geopolymer and OPC
concrete.

2. Experimental program

2.1 Materials

A low-calcium fly ash (Class F as per ASTM C 618), sourced from a Western Australian
power plant, was used as the primary binder. The additives were commercially available
ground granulated blast furnace slag (GGBFS), ordinary Portland cement (OPC) and hydrate
lime [Calcium hydroxide, Ca(OH)₂]. The chemical compositions of fly ash, GGBFS and OPC are given in Table 1. Laboratory grade calcium hydroxide was used which contained about 99% pure anhydrous Ca(OH)₂. A combination of sodium hydroxide (NaOH) and sodium silicate (Na₂SiO₃) solutions was used as the activator solution. Sodium silicate solution was prepared in the laboratory by mixing 97-98% pure NaOH pellets with normal tap water. Sodium silicate solution, collected from a local producer, has the mass ratio of SiO₂ to Na₂O of 2.64 (SiO₂ = 30.1%, Na₂O = 11.4% and water = 58.5%). Natural sand with nominal maximum size of 1.18 mm was used as fine aggregate along with locally available granite coarse aggregate of 20 mm, 10 mm and 7 mm sizes.

Table 1: Chemical composition of fly ash, GGBFS and OPC.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>P₂O₅</th>
<th>TiO₂</th>
<th>LOI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash (%)</td>
<td>53.71</td>
<td>27.2</td>
<td>11.7</td>
<td>1.9</td>
<td>-</td>
<td>0.36</td>
<td>0.54</td>
<td>0.30</td>
<td>0.71</td>
<td>1.62</td>
<td>0.68</td>
</tr>
<tr>
<td>GGBFS (%)</td>
<td>29.96</td>
<td>12.25</td>
<td>0.52</td>
<td>45.45</td>
<td>-</td>
<td>0.31</td>
<td>0.38</td>
<td>3.62</td>
<td>0.04</td>
<td>0.46</td>
<td>2.39</td>
</tr>
<tr>
<td>OPC (%)</td>
<td>21.1</td>
<td>4.7</td>
<td>2.7</td>
<td>63.6</td>
<td>2.6</td>
<td>0.5</td>
<td>-</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*Loss on ignition

Table 2: Control geopolymer and OPC concrete mixture proportion (kg/m³).

<table>
<thead>
<tr>
<th>CA*</th>
<th>Sand</th>
<th>Fly ash</th>
<th>Additive</th>
<th>OPC</th>
<th>SSb</th>
<th>SHc</th>
<th>Water</th>
<th>SPd</th>
<th>w/s</th>
<th>w/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>F00</td>
<td>1209</td>
<td>651</td>
<td>400</td>
<td>0</td>
<td>-</td>
<td>114.3</td>
<td>45.7</td>
<td>0</td>
<td>0</td>
<td>0.202</td>
</tr>
<tr>
<td>OPC (%)</td>
<td>1054</td>
<td>740</td>
<td>-</td>
<td>-</td>
<td>366.4</td>
<td>-</td>
<td>172.2</td>
<td>0</td>
<td>-</td>
<td>0.47</td>
</tr>
</tbody>
</table>

*Coarse aggregate; bSodium Silicate; cSodium Hydroxide; dSuperplasticizer; eWater to solid ratio

2.2 Mixture proportions

Six geopolymer mixtures using fly ash blended with additives (GGBFS, OPC and Ca(OH)₂), one control concrete with fly ash alone as the binder (F00) and one OPC concrete were prepared. Table 2 shows the mixture proportions of the control fly ash geopolymer (F00) and OPC concrete. Mixtures S10 and S15 were designed by replacing fly ash with 10% and 15% GGBFS respectively. Mixtures P05 and P10 were mixed with OPC as 5% and 10% of the total binder respectively. Mixtures C02 and C03 were designed with 2% and 3% Ca(OH)₂ respectively. All the geopolymer mixtures were activated with a combination of sodium silicate (SS) and 14M sodium hydroxide (SH) solution with a SS/SH ratio of 2.5. The alkaline activator solution was added as 40% of the total binder. To compare with similar grade geopolymer mixtures, an OPC concrete mixture was designed in accordance with the ACI guideline [21].

2.3 Casting and curing of samples

Prior to the actual mixing, the alkaline solution was prepared by mixing the sodium hydroxide and sodium silicate solutions together and left in room temperature to cool down. Concrete was mixed in a laboratory pan mixer. The mixtures were cast in cylindrical (100 mm diameter and 200 mm depth) moulds for compressive strength and permeability tests. The moulds were
filled in two layers and compacted using a vibrating table. After casting, the moulds were left in curing room (about 23°C and 70±10% RH). The samples were de-moulded after at least 24 hours and stored in the same environment of curing room. The control mixture F00 was de-moulded after 3 days. The OPC mixture was cured under water until 28 days of age.

Another batch of samples was cured at 60°C for 24 hours immediately after casting. After curing, the moulds were cooled down to room temperature and de-moulded after cooling. The samples were then stored in curing room (about 23°C and 70±10% RH) until tested.

2.3 Test methods
The volume of permeable void (VPV) in concrete was determined in accordance with AS 1012.21 [22]. The capillary suction property of concrete was tested with the sorptivity test. Testing for water sorptivity was based on the method ASTM C 1585 - 13 [23]. The tests were done at 28 days for both ambient cured and heat cured samples. Separately prepared ambient-cured paste samples of mixtures F00, S15, P10 and C03 were tested for porosity by using the mercury intrusion porosimetry test.

3. Results and discussions

3.1 Compressive strength
Compressive strength of the mixtures at 7 days and 28 days for different curing conditions are shown in Fig. 1. The strength at 28 days varied in the range of 35 MPa to 45 MPa when cured in ambient condition (23°C and 70±10% RH). Inclusion of the additives improved compressive strength of ambient cured geopolymer concretes from the early age. As usual, curing in higher temperature (24 hours at 60°C) enhanced the strength immediately after curing. Heat cured specimens gained 58 to 72 MPa compressive strength at 28 days. The OPC concrete mixture cured under water resulted in strength of 46.5 MPa at 28 days. These results are consistent with strength development of geopolymer concrete presented in previous studies [16, 17].

![Fig. 1: Compressive strength of concrete cured in (a) ambient condition (23°C) and (b) high temperature (60°C).](image-url)
3.2 Volume of permeable voids (VPV)
Permeability properties of different mixtures were determined by the volume of permeable volume test and sorptivity test. Samples cured in ambient condition (23°C) and in high temperature (60°C for 24 h) were tested separately.

Fig. 2 compares the VPV values of all the mixtures. It can be seen that the variation of VPV is very small for the geopolymer mixtures. Apparently, inclusion of additives within the studied limit made no significant difference in the VPV as compared to fly ash-only geopolymer concrete. Increasing the percentage of additive slightly decreased the value of VPV of the mixture modified with GGBFS and OPC.

3.3 Sorptivity
Fig. 3 compares the initial sorptivity coefficients of all the mixtures subjected to ambient and heat curing conditions. The values for ambient cured specimens indicate that fly ash based geopolymer having 10% GGBFS (S10) as additive resulted almost similar sorption as control concrete (F00). However, sorption was higher when OPC or calcium hydroxide was added with fly ash. Sorptivity values decreased when additive content increased in the mixtures.
According to recommended typical values of sorptivity for various performances of concrete by Papworth and Grace [24], the geopolymer concrete mixtures can be classified as “very good”, as the co-efficient of sorptivity values are less than $129.1 \times 10^{-4}$ mm/sec$^{1/2}$.

### 3.4 Discussion

When the samples were heat cured after casting, both the VPV and the sorptivity values decreased for the blended fly ash geopolymer concrete samples as compared to ambient cured samples. However, slightly higher values were observed for the control fly ash geopolymer that was heat cured. This is possibly due to different morphology of binder gel present in the mixtures. In normal room temperature curing, the geopolymer binder tends to react slowly and have more pores filled with pore solution. On the other hand, heat curing, although accelerates the reaction kinetics, leaves more empty pores that can absorb water.

**Table 3: Porosity of the ambient cured paste samples.**

<table>
<thead>
<tr>
<th></th>
<th>F00</th>
<th>S15</th>
<th>P10</th>
<th>C03</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore diameter (µm)</td>
<td>0.140</td>
<td>0.010</td>
<td>0.009</td>
<td>0.008</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>18.18</td>
<td>16.40</td>
<td>18.21</td>
<td>20.66</td>
</tr>
</tbody>
</table>

The percentage of an additive present in the mixture is found to influence the permeability properties of geopolymer concrete, as an increased amount of additive decreases both the VPV and sorptivity. Table 3 shows the porosity results of some selected paste mixtures cured in ambient condition. It is clear that inclusion of additives decrease the pore size as compared to control mix (F00). However total porosity decreased when GGBFS was added 15% of total binder and no improvement of porosity is observed when 10% OPC and 3% CH was added. Similar trend was also observed by the VPV and sorptivity results of the corresponding concrete samples. Inclusion of additives more than that used in this study is likely to enhance the absorption resistance further; however, that might require refining the mixture proportions to obtain reasonable setting time as well as workability [16, 17].

It was shown in previous studies that, inclusion of additives (GGBFS and OPC) produced calcium silicate hydrate (CHS) in addition to geopolymer gel and make apparently a denser matrix [16, 17, 25]. However, the beneficial effect of reduced amount of micropores is superficial when small amount of additive was used with fly ash and cured at room temperature. Higher sorption properties of the OPC and Ca(OH)$_2$ blended mixtures can be attributed to the presence of more interconnected pores and higher porosity, although achieving smaller pore size. Zhu et al. [26] reported that, at the constant liquid/solid of 0.7, substitution of 20–40% fly ash by slag did not change the porosity too much but reduced the sizes of pores and also increased the tortuosity. However, at high temperature the interconnectivity of pores is believed to be reduced by the concentrated binder formation.

The result of OPC concrete is compared with the geopolymer mixture of same grade, S15. It can be noted that the value of sorptivity of OPC concrete is less than that of ambient cured mixture S15. However, VPV value of the OPC mixture is slightly higher than that of S15.
(Fig. 2 and 3). Overall, it appears possible to obtain geopolymer concrete of similar permeation properties to OPC concrete by adjusting the additive content as well as other mixture variables.

4. Summary

Geopolymer concrete samples were prepared using low calcium fly ash as the principal binder. Ground granulated blast furnace slag, ordinary Portland cement and hydrated lime were used as additives in order to enhance the early-age properties when cured at ambient temperature. The effects of the additives were investigated on the permeability properties of the ambient cured (23°C) and heat cured (60°C) concrete specimens.

Fly ash geopolymer concrete blended with GGBFS, OPC or Ca(OH)₂ achieved higher 28-day compressive strength as compared to control concrete cured in ambient condition (23°C). The permeability, measured in terms of the volume of permeable voids and sorptivity, is influenced by the types and amount of the additives.

The volume of permeable void of the blended fly ash geopolymer concrete showed no significant difference as compared to that of the fly ash-only geopolymer specimen. Sorptivity of the specimens was decreased when GGBFS was included up to 15% of the total binder. Blending with OPC and Ca(OH)₂ with fly ash in the studied range caused no improvement of permeability resistance.

Heat cured specimens achieved lower value of VPV and sorptivity than the ambient cured specimens.

Finally, the results indicate that fly ash geopolymer concrete can be modified with additives to enable ambient curing and achieve similar permeability properties of similar grade OPC concrete.

References


Sonma, K. and Bunrongjaroen, W., Effect of external and internal calcium in fly ash on geopolymer formation, in 35th International Conference on Advanced Ceramics and Composites, Daytona Beach, Florida (2011).


SINTERING OF CERAMICS BASED ON MECHANICALLY
ACTIVATED FLY ASH

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(2) Friedrich-Schiller-Universität Jena, Germany
(3) Goce Delcev University, Shtip, Macedonia

Abstract
This paper presents the results for the influence of the mechanical activation on the properties of the sintered fly ash compacts. By varying the time of mechanical activation (short time of 10, 20 and 30 min) and temperature of sintering: 1050, 1100 and 1130 °C/60 min a spectrum of properties was obtained, but as an optimal defined was the mechanical activation of 20 min prior to the sintering at 1130°C.

1. Introduction

Solid waste (fly ash and bottom ash) generated from the thermal power plant during the combustion of coal to produce electricity presents the global problem from the environmental point of view. Part of the generated fly ash is successfully used in the cements production [1], but also the possibilities to incorporate fly ash into ceramics matrices like in tiles [2] and bricks [3], in the production of mullite [4] as well as in geopolymers [5] are widely reported. Fly ash presents valuable low cost material due to its chemical composition consisting mainly of SiO₂, Al₂O₃, CaO, Fe₂O₃. Physical properties of fly ash depend on the burning conditions and the type of coal. The shape of the fly ash particles are mostly spherical with specific surface area from 250 to 600m²/kg. As far as it is very fine material it is usually used as raw material with no pre-treatment [6, 7]. By increasing the geometrical factor of activity – specific surface area and reducing the particle size distribution the consolidation of the powder is favored, usually at lower temperatures.

This paper presents the results obtained from the investigation realized by pre-treating the fly ash i.e. thermal treatment (600°C) and mechanical activation for short period of time (10, 20 and 30 min). Also, the influence of the pretreatment on the final properties and the microstructure is discussed.
2. Materials and methods

Fly ash used in this investigation was obtained from the thermal power plant REK Bitola, Republic of Macedonia, derived from lignite combustion. X-Ray Fluorescence (model ARL 990XP) was used for determination of the chemical composition of fly ash. The loss of ignition (LOI) was determined by calcination of pre-dried samples at 900°C/2h. Residual coal contained in the ashes was determined from the mass loss after 2 hours at 600°C. Particle size distribution of the fly ash was determined by sieving analyses (Retsch AS200) and the specific gravity was calculated using the pycnometer method.

The morphology of the fly ashes during the investigation was followed by scanning electron microscopy (Leica S 4401) coupled with EDS, which was used for determination of chemical composition of particular fly ash particles.

The thermal properties of the pressureless prepared fly ashes compacts were determined using a heating microscope (Leitz Wetzlar) in the temperature interval of RT-1400°C, in air atmosphere with a heating rate of 10 °C/min. Dilatometry (NETZSCH 402E) was used to follow the shrinkage of the pressed fly ash samples during sintering from RT to 1130°C.

In order to increase the structural and geometrical activity of the fly ash, mechanical activation was applied in vibro mill. Mechanical activation was applied for a short time (period of 10, 20 and 30 min) in order to follow the obtained properties on the sintered fly ash compacts. The fly ash samples in this investigation were assigned as: TFA for thermally treated fly ash at 600°C, and TFA-MA10, TFA-MA20 and TFA-MA30 for the fly ash samples thermally treated and mechanically activated for 10, 20 and 30 min prior to the sintering.

Fly ashes were consolidated by uniaxial pressing (P = 45 MPa) using 8% water as a binder. The compacted green samples were dried at 105°C for 10 hours prior to the sintering. The sintering of the TFA samples was realized at 1050, 1100, 1150 and 1200°C, but for the mechanically activated fly ashes (TFA-MA10, TFA-MA20 and TFA-MA30), the sintering was realized at three different temperatures: 1050, 1100 and 1130°C using chamber furnace. The applying heating rate was 10°C/min. The isothermal treatment at final temperature was 60 min. The cooling to RT was not controlled.

Water displacement method according to EN-993 was used for determination the bulk density. Porosity was calculated from the relative density.

The bending strength and E-modulus of the sintered fly ash compacts were determined with the 3-point bending strength tester (Netzsch 401/3) with 30mm span and 0.5mm/min loading rate. Instron testing machine (model 1126) with a crosshead speed of 0.5 mm/min was used for the compressive strength test. Three samples were used for determination of the mechanical properties and the average values were reported as the result.
3. Results and discussion

The chemical composition of the investigated fly ash is presented in the Table 1. According to the CaO which is 11.49 wt.% this fly ash can be classified as C class fly ash according to the ASTM C618 definitions. The free CaO was not detected. Residual (unburned) coal contained in the fly ash was 2.75 wt.%.

Table 1: Chemical composition of fly ash

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>SO$_3$</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>54.74</td>
<td>20.29</td>
<td>6.76</td>
<td>11.49</td>
<td>2.46</td>
<td>1.57</td>
<td>0.93</td>
<td>0.93</td>
<td>3.12</td>
</tr>
</tbody>
</table>

It is evident from the chemical composition presented in Table 1 that silica (SiO$_2$) and alumina (Al$_2$O$_3$) are the main oxides, but besides them, fly ash has a significant amount of calcium oxide (CaO) and iron oxide (as ferric). The integral content of SiO$_2$ comes from SiO$_2$ - quartz, CaAl$_2$Si$_2$O$_8$ – anorthite and NaAlSi$_3$O$_8$ – albite and according to the XRD the presence of Fe$_2$O$_3$ - hematite, CaSO$_4$ - anhydrite and an amorphous phase was also determined [8].

Fly ash belongs to the relatively fine materials and according to the granulometric composition, Table 2, almost 50% of fly ash particles are less than 63μm. The specific gravity of the fly ash is 2.17g/cm$^3$.

Table 2: Granulometric composition of as received fly ash

<table>
<thead>
<tr>
<th>Diameter, (mm)</th>
<th>Fly ash, (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>-1.0+0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>-0.5+0.25</td>
<td>7.6</td>
</tr>
<tr>
<td>-0.25+0.125</td>
<td>18.0</td>
</tr>
<tr>
<td>-0.125+0.063</td>
<td>25.2</td>
</tr>
<tr>
<td>-0.063</td>
<td>47.1</td>
</tr>
<tr>
<td>Σ</td>
<td>100</td>
</tr>
</tbody>
</table>

The morphology of fly ash is presented in Figure 1. Figures 2-4 and Table 3 present the morphology and the chemical composition (microprobe analysis) of the Fe$_2$O$_3$, needle SiO$_2$ and amorphous silica (diatomite). Typical fly ash cenospheres are presented in Figure 3 and the rough surface particle presents hematite.

In the present investigation, in order to reduce the sintering temperature of fly ash, mechanical activation during short period of time (10, 20 and 30 min) was performed. Morphology of the
TFA particles and after mechanical activation (TFA-MA10, TFA-MA20 and TFA-MA30) are presented in Figures 5-8. It is evident that by increasing the time of mechanical activation the particles reduced their dimension. After 10 min of milling, part of the particles remain their start dimensions, but the biggest part of the particles changed their dimension and morphology. The dimension of the particles, TFA-MA10, varied from 2 to 50 μm, but for the TFA-MA20 and TFA-MA30 the particles sized distribution varied from 1 to 30 μm and 1 to 20 μm, respectively.

The thermal characteristics of pressure less prepartd fly ash samples before (TFA) and after mechanical activation (TFA-MA10, TFA-MA20 and TFA-MA30) are presented in Table 4.
Table 3: Chemical composition of the particular fly ash particles – needle quartz, hematite and diatomite

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Needle quartz, (wt.%)</th>
<th>Hematite sphere, (wt.%)</th>
<th>Diatomite, (wt.%)</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>98.12</td>
<td>1.75</td>
<td>95.48</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.56</td>
<td>0.13</td>
<td>1.62</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.35</td>
<td>97.07</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>0.22</td>
<td>0.35</td>
<td>0.37</td>
</tr>
<tr>
<td>MgO</td>
<td>0.18</td>
<td>0.13</td>
<td>0.01</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.06</td>
<td>0.11</td>
<td>0.20</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.33</td>
<td>0.07</td>
<td>0.70</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.09</td>
<td>0.02</td>
<td>0.53</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.05</td>
<td>0.15</td>
<td>0.04</td>
</tr>
<tr>
<td>MnO</td>
<td>0.01</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.04</td>
<td>0.08</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Figure 5. Morphology of TFA (bar 10μm)  
Figure 6. Morphology of TFA-MA10 (bar 10μm)  
Figure 7. Morphology of TFA-MA20 (bar 10μm)  
Figure 8. Morphology of TFA-MA30 (bar 10μm)
Table 4: Thermal characteristics of fly ash before (TFA) and after different time of mechanical activation (TFA-MA10, TFA-MA20 and TFA-MA30)

<table>
<thead>
<tr>
<th>Type of fly ash</th>
<th>Significant shrinkage, °C</th>
<th>Softening temperature, °C</th>
<th>Melting temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFA</td>
<td>1220±10</td>
<td>1260±10</td>
<td>1360±10</td>
</tr>
<tr>
<td>TFA-MA10</td>
<td>1160±10</td>
<td>1220±10</td>
<td>1350±10</td>
</tr>
<tr>
<td>TFA-MA20</td>
<td>1150±10</td>
<td>1210±10</td>
<td>1340±10</td>
</tr>
<tr>
<td>TFA-MA30</td>
<td>1145±10</td>
<td>1215±10</td>
<td>1345±10</td>
</tr>
</tbody>
</table>

The region of sintering of fly ash before mechanical activation, TFA, is 1220 - 1260±10°C, but it is reduced with the increase of the time of mechanical activation. The sintering regions for the mechanically activated fly ashes are: 1160 - 1220 ±10°C for TFA-MA10, 1150 - 1210±10°C for TFA-MA20 and 1145 - 1215±10 for TFA-MA30. The particle size of fly ash decreased during the mechanical activation and this results in the decrease of the melting temperature from 1360±10°C for the starting fly ash (TFA) to 1345±10°C for fly ash mechanically activated for 30 min (TFA-MA30).

After the consolidation of the fly ash powders by pressing, the shrinkage of the consolidated samples during sintering was followed by dilatometry. The dependances of the shrinkage with temperature in the polythermal part of sintering for the fly ash before (TFA) and after mechanical activation (TFA-MA10, TFA-MA20 and TFA-MA30) are presented in Figure 9. The shrinkage of TFA started at 400°C and continues slightly up to 1100°C, reaching the total shrinkage of 2.61mm at 1130°C. The shrinkage for mechanically activated fly ash samples (TFA-MA10, TFA-MA20 and TFA-MA30) starts at a temperature 730°C and up to the temperature of 1050°C it showed slight shrinkage followed by rapid shrinkage up to the temperature of 1130°C. Mechanically activated TFA-MA20 sample showed maximal shrinkage of 4.72mm.

Sintered fly ash compacts were characterized from physical (density and porosity) and mechanical (bending strength, E-modulus and compressive strength) aspect. The properties of the sintered fly ash compacts are presented in Table 5.

Generally, by increasing the sintering temperature and the time of mechanical activation the density and mechanical properties increased, but the porosity decreased for all sintered fly ash samples (TFA, TFA-MA10 TFA-MA20 and TFA-MA30).
Figure 9. Shrinkage /temperature dependence in polythermal part of sintering for: TFA, curve [1]; TFA-MA10, curve [2]; TFA-MA20, curve [3] and TFA-MA30, curve [4].

Table 5: Physical and mechanical properties of sintered TFA, TFA-MA10 TFA-MA20 and TFA-MA30 samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>T, °C</th>
<th>Density, g/cm³</th>
<th>Porosity, %</th>
<th>E-modulus, GPa</th>
<th>Bending strength, MPa</th>
<th>Compressive strength, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFA</td>
<td>1050</td>
<td>1.25</td>
<td>47.01</td>
<td>2.17</td>
<td>1.71</td>
<td>2.49</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>1.29</td>
<td>46.89</td>
<td>1.88</td>
<td>2.67</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>1.46</td>
<td>44.07</td>
<td>6.73</td>
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<td>8.32</td>
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<td></td>
<td>1200</td>
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<td>21.34</td>
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<td>32.30</td>
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<td>11.44</td>
<td>19.47</td>
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<td>1.62</td>
<td>38.98</td>
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<td>48.04</td>
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</tbody>
</table>

TFA compacts have low values for mechanical properties (up to 8.32 GPa compresive strenght for the sample sintered at 1150°C) except the compacts sintered at 1200°C. The values for mechanical properties are almost 3 to 4 times higher as the sintering temperature.
increased from 1150 to 1200°C. The comparable microstructures for the sintered TFA compacts at 1150 and 1200°C are presented in Figures 10 and 11. The effect of the different degree of sintering is evident. At temperature of 1150°C, part of the fly ash particles lost their individuality and the appearance of the liquid phase among the spherical fly ash particles is evident. Liquid phase sintering is favoured at 1200°C.

The presented results for the mechanically activated fly ashes (TFA-MA10, TFA-MA20 and TFA-MA30), Table 5, showed that the properties increased significantly after 10 min of mechanical activation (in comparison to TFA) and there are no significant changes of the properties for 20 and 30 min of mechanical activation (TFA-MA20 and TFA-MA30). The values of density, porosity and mechanical properties have no significant differences for all fly ash compacts sintered at 1050 and 1100°C, but the rapid changes of the values occurs for the fly ash compacts sintered at 1130°C. The microstructures of the fly ash compacts (TFA-MA10, TFA-MA20 and TFA-MA30) sintered at maximal temperature of 1130°C are presented in Figures 12 - 14.
Intragranular pores with dimensions from 3 to 8 μm are present in the microstructure of the TFA-10 compact (Figure 12) and also local appearance of liquid phase is evident. The bigger quantity of liquid phase is typical for the TFA-MA20 (Figure 13) where the biggest part of the grains are covered with the liquid phase. The pores with dimensions from 4 to 8 μm are present between particular grains and non-coherent layer of the liquid phase. By increasing the time of mechanical activation to 30 min, sample TFA-MA30, the coherent part of liquids phase (Figure 13) transforms to inherent layer (Figure 14). The dimensions of the grains are from 3 to 50 μm.

4. Conclusion

In this investigation by varying the process parameters (short time of mechanical activation: 10, 20 and 30 min and sintering temperatures: 1050, 1100 and 1130°C) a spectrum of properties is achieved. The defined optimal conditions in this investigation were a sintering temperature of 1130°C and 20 min of mechanical activation prior to the sintering.

The obtained fly ash compacts pre-treated at 600°C and mechanically activated for 20 min prior to the sintering at 1130°C has the following properties: density: 2.34g/cm³; porosity:11.46%; E-modulus: 48.04 GPa; bending strength: 79.90 MPa and compressive strength - 78.48 GPa. The compacts can be potentially used for construction purposes.

Acknowledgement

The financial support from DAAD, Germany is gratefully acknowledged and also to COST Action TU1301. www.norm4building.org.
References

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INVESTIGATION OF THE EFFECT OF PARTIAL REPLACEMENT OF PORTLAND CEMENT BY FLY ASH ON CARBONATION USING TGA AND SEM-EDS

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Abstract
The aim of this paper is to investigate the effect of partial replacement of Portland cement by fly ash on the phase changes upon carbonation and the resulting CO₂-binding capacity. Two mortars with water-to-binder ratio 0.55 and two different binders, Portland cement (CEM I) and Portland fly ash cement (CEM II/B-V) were cured sealed for 14 days at 20°C and subsequently exposed to accelerated carbonation (20°C, 60% RH and 1.5% CO₂) for 4 weeks. The changes in the phase assemblage upon carbonation were studied by TGA and SEM-EDS. TGA allowed the quantification of changes in Portlandite and calcium carbonate content. SEM-EDS was used to investigate changes in the C-S-H composition and the microstructure. It was observed that both binders formed similar amounts of carbonates upon accelerated carbonation, even though their CaO content differed. This could be attributed to differences in the reaction degree of the Portland clinker and a larger contribution to the uptake of CO₂ by C-S-H for the fly ash containing cement. Hence care should be taken when applying the CaO content as a measure for the CO₂-binding capacity.

1. Introduction
Carbonation is the spontaneous reaction of CO₂ present in the air with the cement paste, which causes, among others, a drop in the pH of the pore solution. Once the carbonation front reaches reinforcement, embedded steel is no longer passivated and corrosion may start depending on the exposure [1]. Carbonation-induced corrosion is one of the major causes of premature deterioration of reinforced concrete structures [2].

Carbonation is a stepwise reaction which causes gradual changes in the cement paste. First CO₂ is dissolved in the pore solution and carbonic acid is formed. Then the carbonic acid reacts with Ca ions from the different cement phases and calcium carbonate (CC₄ ) is formed. Portlandite (CH) is the first to react, followed by monosulphate (AFm) and ettringite [3].
Calcium silicate hydrate (C-S-H) decalcifies gradually once CH is consumed until it becomes silica gel \([4, 5]\). Additionally, unhydrated phases as alite and belite can be carbonated \([6]\).

Replacing Portland cement partially with fly ash results in changes of the overall CaO content and the phase assemblage such as consumption of CH by the pozzolanic reaction, and lowering of the Ca/Si ratio of the C-S-H \([7]\). This affects the CO2-binding capacity of the resulting binder \([3, 8]\).

The most common way to identify carbonation in concrete is to spray a freshly split surface with a pH indicator (EN 13295 \([9]\)). It is a simple, non-expensive and reliable method to determine the carbonation depth \([10]\). However, pH indicators do neither reveal information about the changes in the phase assemblage nor the microstructure upon carbonation.

The authors used thermogravimetric analysis (TGA) to quantify the content of CH and CC on homogenized profile ground samples and scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) to investigate differences in morphology and elemental composition upon carbonation on polished sections. The aim was to investigate the effect of partial replacement of Portland cement by fly ash on the phase changes upon carbonation and the resulting CO2-binding capacity. In this paper, two mortars with water-to-binder ratio 0.55 and two binders, Portland cement (CEM I) and Portland fly ash cement (CEM II/B-V), exposed to accelerated carbonation (20°C, 60% RH and 1.5% CO2) were investigated.

The present study is part of a PhD project on carbonation of Portland fly ash cement. The final aim of the project is to improve the understanding of the mechanisms affecting the service life of concrete structures with Portland fly ash cements. Both the initiation period (carbonation) and the propagation period (corrosion) are considered.

2. Experimental

Figure 1 provides an overview of the experimental techniques and the sampling undertaken on mortar prisms.

2.1 Mortar samples

Mortar prisms 40 x 40 x 160 mm with two binders were investigated. The binders were: CEM I containing 4% limestone powder and CEM II/B-V containing 30% fly ash and 4% limestone powder. Table 1 presents the chemical composition of the binders determined by XRF. Clinker with similar mineralogy was used for both cements. The mortar composition (water-to-binder ratio 0.55) was 450 g binder, 1350 g standard CEN sand (dmax 2 mm) and 247.5 g water per batch. The mortars were mixed according to EN 196 \([11]\). The prisms were stored in the moulds covered with a plastic wrap at 20°C for 24 hours after casting. Then, they were demoulded, wrapped in plastic and stored at 20°C for 13 days in a sealed container.
Table 1: Chemical composition of the investigated binders determined by XRF [% by mass]

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>P$_2$O$_5$</th>
<th>K$_2$O</th>
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<tr>
<td>CEM I</td>
<td>20.4</td>
<td>4.8</td>
<td>3.4</td>
<td>61.7</td>
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<td>3.5</td>
<td>0.2</td>
<td>0.9</td>
<td>0.5</td>
</tr>
<tr>
<td>CEM II/B-V</td>
<td>29.5</td>
<td>10.8</td>
<td>4.5</td>
<td>44.6</td>
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<td>3.2</td>
<td>0.4</td>
<td>1.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

2.2 Exposure
Fourteen days after casting, the mortar prisms were exposed for four weeks to accelerated carbonation conditions: 20 ± 0.5°C, 60 ± 1.5% RH and 1.45 ± 0.1% CO$_2$. Note that the short curing period only allows for a limited degree of reaction of the fly ash [7, 13].

2.3 Methods
TGA was performed on profile ground samples. To study carbonation as a one dimensional phenomenon, the lateral sides (10 mm on each) were removed by dry cutting before profile grinding, see Figure 1. The right (R) and top (T) side were studied. The outer 0-1 mm step was omitted as different paste content was expected. The grinding steps were 1 mm for the first 10 mm and 2 mm-steps for the rest of the sample. The TGA was performed with a Mettler Toledo TGA/DSC 3+, on samples of approximately 300 mg loaded in aluminum oxide crucibles. The samples were heated from 40 to 900°C at a rate of 20°C/min while the oven was purged with N$_2$ at 50 ml/min. The weight loss of the samples was monitored as a function of the temperature. The amounts of CH and CC were calculated according to equation (1). However, the exact boundaries were taken from the derivative curve:

$$CH\% = \frac{W_{400°C} - W_{50°C}}{W_{50°C}} \times \frac{74}{18} \times 100\%; \quad CC\% = \frac{W_{50°C} - W_{550°C}}{W_{550°C}} \times \frac{100}{44} \times 100\%$$ (1)

Polished sections were prepared according to [12]. All polished sections were carbon coated. Images were taken in back scatter electron (BSE) mode using a Quanta 400 ESEM from FEI operated at high vacuum mode at an accelerating voltage of 20 kV. SEM-EDS point analysis was performed using a JEOL JXA – 8500F Electron Probe Micro analyzer and a Hitachi S-3400N equipped with an Oxford EDS at an accelerating voltage of 15 kV. The following elements were analysed: Al, Ca, Cl, Fe, K, Na, Mg, S, and Si. The points were manually selected avoiding sand grains and unreacted fly ash and clinker grains.
3. Results

3.1 TGA

Figure 2 presents an example of both mass loss and derivative curve for a sound sample (dark) and a carbonated sample (grey) determined by TGA for both CEM I (left) and CEM II/B-V (right) mortar after 2 weeks curing and 4 weeks of exposure. It can be seen that the carbonate peak for the carbonated sample (450-850 °C) has broad shoulders extending from temperatures as low as 450°C up to 850°C. This could relate to the decomposition of different CC polymorphs which decompose at lower temperatures compared to calcite. However, XRD analysis reported in [10] did not indicate the presence of polymorphs such as vaterite or aragonite. The broadness of the carbonation peak is therefore attributed to large amount of CC present and to the variation in crystallinity of the CC formed. The carbonation of CH has been observed to result in more crystalline CC which decomposes at higher temperatures. Carbonation of C-S-H, on the other hand, results in microcrystalline CC of which the decomposition starts at temperatures as low as 450 °C [13]. This is in agreement with the results presented in Figure 2 where the decarbonation peak related to more crystalline CC at about 800 °C seems to be larger for the carbonated CEM I mortar compared to the CEM II/B-V one, as more of the CC originate from CH carbonation for the former compared to the latter. Note that the AFm peak at about 200 °C disappears upon carbonation.

![Figure 2: TGA (solid) and DTG (dotted) of sound sample (black), and carbonated sample (grey). Left: CEM I sample. Right: CEM II/B-V sample.](image)

Figure 3 shows the CH and CC profiles determined by TGA on profile ground powder. The horizontal axes indicate the depth inwards, with the origin at the exposed surface. The outer 4-6 mm for CEM I and 6-8 mm for CEM II/B-V are affected by carbonation. Carbonation is associated with a decrease in the CH content and an increase in the CC content. The amount of CC seems to be stable in the carbonated zone, and both binders appear to form comparable amounts of CC upon carbonation. Except for the first measurement on the top side of the CEM I mortar prism (depth 1-2 mm) which indicates a higher amount of CC compared to the other measurements. However, this might be due to a higher paste content at the top surface caused by e.g. instability in fresh state.
In the non-carbonated mortar, the amount CH seems to be stable for both binders. The CH content in the CEM II/B-V (about 4%) is notably lower than for the CEM I mortar (about 7%). This lower content is expected both due to the dilution of clinker by the fly ash (dilution effect: 7%·66/96=4.8%) resulting in less clinker to form CH, as well as the pozzolanic reaction of the fly ash consuming part of the CH formed by the clinker (difference between measured CH content in the CEM II/B-V, 4%, and the diluted content due to fly ash, 4.8%: the 0.8% is consumed by the pozzolanic reaction).

It should be noted that for profile grinding in the case of TGA, the content of the different phases is homogenized over the depth of the step (1 or 2 mm). Gradual variations in the CH and CC content, between 4-6 mm for CEM I and 6-8 mm for CEM II/B-V, could therefore be partially due to spatial variations in the carbonation depth as stated in [10].

3.2 SEM-EDS
Figure 4 shows BSE images of the carbonated side of CEM I and CEM II/B-V after 2 weeks curing and 4 weeks of exposure.
Figure 4: BSE image of side of mortar samples. Left: CEM I. Right: CEM II/B-V (scale indicates 500 μm).

A remarkable difference between the two mortars is the presence of lots of unhydrated cement particles (brighter particles size 10-20 μm) in the CEM I mortar and the near absence of them in the CEM II/B-V mortar. This indicated that the degree of hydration of the cement clinker is considerable higher in the CEM II/B-V mortar compared to the CEM I mortar. The explanation for this might be the higher effective water to clinker ratio in the CEM II/B-V mortar. The observation indicates that unhydrated cement grains resist carbonation within the period of exposure.

It should be noted that SEM-BSE imaging is not the most recommended technique to detect carbonation [10]. Detection of the carbonation is far more efficient using optical microscopy with cross polarized light on thin sections, as calcium carbonate crystals formed upon carbonation change the colour of the cement paste from dark brown to bright opaline colours. Nevertheless, one can distinguish between carbonated and non-carbonated paste in BSE images, tracing CH, as indicated in Figure 5. In the carbonated paste CH can no longer be observed. The presence or absence of CH is, however, difficult to identify, especially for the CEM II/B-V sample containing a lower amount of CH.

Figure 6 shows SEM-EDS dot-plots for carbonated and non-carbonated paste of the mortars. During an EDS point analysis the elements in a certain volume are analysed, e.g. 1 μm³. This volume comprises generally a mixture of phases. In order to be able to identify phases the results are expressed in ratios. Hence if a mixture of phases is analysed, the result should lie in between the ideal stoichiometry of these phases.

The SEM-EDS analyses of the non-carbonated pastes indicate the presence of hydration phases such as AFm, CH and C-S-H. The C-S-H composition of the two binders seems to be slightly different. The Ca/Si ratio of the CEM I mortar seems to be 1.8 (Si/Ca = 0.56) compared to 1.55 (Si/Ca = 0.65) in the case of CEM II-B/V. The C-S-H of the CEM II-B/V also seems to have a slightly higher Al/Si ratio compared to CEM I, respectively 0.14 versus 0.09. These findings are in agreement with [14, 15].
Figure 5: Identification of carbonated and non-carbonated paste in BSE images of CEM I mortar based on presence or absence of CH (scale indicates Left - 500 µm, Right – 100 µm). CH with its typical grey tone is indicated with arrows.

Upon carbonation the data points move to lower Si/Ca ratios. The majority of the points gather around a Si/Ca ratio of 0.25 and an Al/Ca ratio of 0.05. This is contradictory to what is expected. Carbonation results in decalcification of the C-S-H and hence in an increased Si/Ca ratio [5]. However, as mentioned before during SEM-EDS point analysis a volume comprising a combination of phases is analyzed. The lower Si/Ca ratio might indicate a consistent intense intermixing between decalcified C-S-H and CC.

Due to the fine intermixing, EDS on smaller volumes e.g. combined with TEM is required in order to differentiate between the calcite and the decalcified C-S-H and the Ca/Si ratio of the decalcified C-S-H [13]. Alternatively, other techniques e.g. Si NMR could be used as in [5].

4. Discussion

From Figure 3 it can be seen that both binders, CEM I and CEM II/B-V seem to bind comparable amounts of CC in the carbonated cement paste, being slightly higher in the case of CEM I binder. This is unexpected as CEM I has a considerably higher CaO content compared to CEM II/B-V (see Table 1). Calculations of CO₂-binding capacities of binders are commonly related in one way or another to the CaO content of the cement [3, 8, 16].

Hence, one would expect considerably higher amounts of CC in the carbonated zone of the CEM I mortar compared to the CEM II/B-V mortar. However, in this investigation it was observed that even though the CaO content in the Portland cement was 40% higher than in the fly ash cement, the amount of CC was only about 10% higher in the Portland cement sample upon carbonation. Thus it seems that other factors should be considered when estimating the binding capacity of a given concrete/mortar.
Figure 6: SEM-EDS point analysis of non-carbonated (Left) and carbonated (Right) paste expressed as molar ratios of Si/Ca versus Al/Ca. The ideal composition of ettringite (AFt), monosulphate (AFm), and portlandite (CH), as well as the assumed composition of C-S-H for the different binders is marked.

In order to understand this apparent discrepancy, the origin of the CC was estimated. Figure 7 presents the different contributions for the carbonated section at 1-2 mm depth. To be able to calculate the different contributions, the CC and CH content of the non-carbonated samples (depth 12-14 mm) were determined by TGA. These samples contained CC due to minor limestone additions to the binders (L). The CC originating from the carbonation of CH were calculated based on the amount of CH in the non-carbonated samples (CC=100/74 CH). The remaining amount of CC was assumed to originate from carbonation of C-S-H. For the CEM I a larger part of the formed CC originates from the carbonation of CH compared to CEM II/B-V. This can be expected as CEM II/B-V contains less CH compared to CEM I due to both dilution of Portland clinker and the pozzolanic reaction of the fly ash.

Figure 7: Estimated origin of carbonates (CC) for carbonated samples. CH and L content taken from sound sample (depth 12-14 mm) and total CC content from carbonated sample.
The CEM II/B-V seems to bind more CO₂ through carbonation of C-S-H compared to CEM I. Based on the results presented two potential explanations can be put forward for the similar CO₂-binding capacity of the two binders even though their CaO contents differ:

- First, the degree of reaction of the clinker is considerably higher in the CEM II/B-V mortar compared to the CEM I (Figure 4). This results in an increased CO₂-binding capacity relative to the clinker content for the CEM II/B-V mortar compared to the CEM I mortar, as the unreacted clinker grains do not seem to have carbonated.
- In addition, the CEM II/B-V binder seems to bind more CO₂ during the carbonation of the C-S-H compared to CEM I (Figure 7). This might be both due to differences in the amount of C-S-H formed and due to the binding capacity of the C-S-H for the two mortars. In the CEM II/B-V mortar, potentially more C-S-H can have formed due to the combination of higher reaction degree of the clinker and the pozzolanic reaction of the fly ash. The binding capacity of the C-S-H will also be influenced by the composition of the non-carbonated and the carbonated C-S-H. With the applied techniques, we are neither able to quantify the amount of C-S-H formed nor to identify the Ca/Si ratio of the carbonated C-S-H. Therefore, we cannot at present quantify the contributions of the before named effects on observed difference in CO₂-binding in the C-S-H for the two mortars.

Even though both binders seem to have a similar CO₂-binding capacity, their carbonation rate is very different. As Figure 3 shows that CC was found at greater depth for the CEM II/B-V mortar compared to the CEM I for the same accelerated carbonation conditions. This indicates the CO₂-binding capacity is not a rate limiting factor for carbonation. Additional investigations are needed to identify the parameters determining the carbonation rate i.e. porosity.

5. Conclusions

- The TGA results show that the CEM I mortar contains more CH than the CEM II/B-V mortar, as expected. The TGA also reveals that both binders, CEM I and CEM II/B-V, bind a similar total amount of CO₂ upon accelerated carbonation. As both binders, CEM I and CEM II/B-V, differ considerably in CaO content, respectively 62 and 45%, the CO₂-binding capacity can therefore not be related to the CaO content of the binders.
- SEM-EDS analyses indicate that both binders form similar reaction products upon carbonation, i.e. finely inter-mixed decalcified C-S-H with calcium carbonate. The BSE images reveal a large difference in the reaction degree of the clinker in the two binders. The partial replacement of Portland cement by fly ash leads to a near to complete reaction of the clinker whereas lots of unreacted clinker grains were observed for the pure Portland cement. The unreacted clinker did not seem to carbonate.
- CEM II/B-V has a similar CO₂-binding capacity compared to CEM I, which can be explained by a higher degree of reaction of the clinker and a larger contribution of C-S-H to the uptake of CO₂ for the CEM II/B-V mortar compared to CEM I.
Acknowledgements

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References

EFFECTS OF WASTE GLASS AND ACTIVATING SOLUTION ON TUNGSTEN MINING WASTE ALKALI-ACTIVATED BINDERS

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Abstract
Increasingly more research is being directed towards the valorisation of waste materials as precursors for synthesizing alkali-activated binders. In this paper, varying blends of waste tungsten mine tailings (TMT) and waste glass (WG) are activated using a combined sodium hydroxide and sodium silicate alkali solution. The activating solution itself is also varied in terms of the quantities of sodium silicate and sodium hydroxide to determine their effect on reactant formation and mechanical strength. The results show that WG effectively provided additional source reactive silica, contributing to the formation of reaction products and thus making a significant improvement to the compressive strength. The TMT-WG alkali-activated binder was found to have a low activating solution demand and produced the highest compressive strength when a low Na2SiO3/NaOH activating solution combined with a low activator/precursor ratio was used.

1. Introduction
The negative environmental impact of Portland cement [1] has resulted in a quest for sustainable construction which has put the construction industry under immense pressure from governments and the public. More recently the concern about the environmental issues of mining and quarrying waste is emerging. While mining and quarrying processes are used for extracting minerals which are essential for energy, construction, infrastructure and manufacturing, their extraction has damaging effects on the environment and public perception. Mining and quarrying activities in the EU generates approximately 735 million tonnes of waste which contribute to 30% of the total waste generation by economic activity [2]. Another waste material that has not received appreciable attention is glass waste. It is estimated that 18 million tonnes of it were produced in 2012 in the EU, and only 35% of it was recycled [3].

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Alkali-activated binders (AABs) have been studied in significant detail over the last 40 years [4–6]. Typically, they are cement-free construction materials which pose a number of benefits including high strength with rapid setting, good durability and high resistance to chemical attack [8–10]. They are produced by combining an aluminosilicate precursor, in this study, TMT and WG, with a highly alkali solution. Typical aluminosilicate sources include industrial waste by-products (fly ash, slag), metakaolin, etc. Alkali-activation can be considered to consist of a five-stage process: (1) dissolution of solid aluminosilicate source by silicate species in activating solution, (2) rearrangement and exchange among dissolved species, (3) gel nucleation (C-(A)-S-H or N-A-S-(H) gel), (4) solidification and hardening, (5) ongoing gel evolution.

AABs are still a relatively new technology and the advancements made in this field are incremental compared to Portland cement. In particular, tungsten mine tailings (TMT) are one type of aluminosilicate precursor which has had little research coverage. Preliminary studies have been conducted on the transformation of TMT into AABs and has shown promising results from an environmental, technical and economic point of view [11, 12]. As for waste glass, its high SiO₂ content and amorphous structure has also led researchers’ experimenting with its incorporation into AABs. Christiansen et.al. [13] obtained excellent mechanical strength results blending waste glass and metakaolin, showing off the high potential for the utilisation of waste glass.

Previous research has established that SiO₂ is highly soluble in alkaline solutions making the SiO₂/Na₂O molar ratio an important parameter of AABs [7] while the composition and dosage of the activating solution also plays a critical role in controlling the gelation process [14]. The first stage of the paper is a brief report on the effects of increased replacement of TMT with WG. In the second stage of the paper, a systematic study of the effects of the individual NaOH and Na₂SiO₃ components of a multi-compound alkali activator is reported and the results will be used to delimitate the level of activating solution required for successful alkali-activation. Scanning electron microscopy (SEM) is used to characterize the hardening process and structural composition of the final products while crushing tests at specific ages are made to determine the mechanical strength.

2. Experimental

2.1. Materials

The materials used in this investigation include TMT, WG, sodium hydroxide (NaOH), and sodium silicate (Na₂SiO₃). The TMT were received in powder form from the Panasqueira mine in Portugal, and the WG was donated from the local authority. TMT and WG were dried, milled and sieved to a mean particle size of 96 and 26 μm respectively. Table 1 shows the chemical composition of the TMT and the WG. The activating solution was prepared by dissolving 99% pure sodium hydroxide pellets in de-ionized water to make a 10M solution and combining it with sodium silicate with a SiO₂/Na₂O = 3.23 (8.60 wt.% Na₂O, 27.79 wt.% SiO₂, 63.19 wt.% H₂O, 0.4 wt.% Al₂O₃).
Table 1 Chemical composition of TMT and WG as determined by SEM-EDS

<table>
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<tr>
<th>Chemical compound</th>
<th>TMT (%)</th>
<th>WG (%)</th>
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</tr>
<tr>
<td>MgO</td>
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</table>

3. Methods and characterization

3.1. Mixture design
The first stage of the study involved testing the effect of TMT replacement with WG. Three combinations were considered with the first containing 20 wt.% WG (80TMT20WG), the second, 30 wt.% (70TMT30WG) and the third, 40 wt.% (60TMT40WG). An AAB using TMT only was also prepared for comparison purposes. For the first stage of the study, a preliminary mix ratio with satisfactory workability was obtained using activator/precursor (a/p) and sodium silicate/sodium hydroxide (ss/sh) wt.% ratios of 2.7 and 4.0, respectively, and thus remained constant. During the second stage of the study, the TMT-AAB with a WG replacement that provided the highest compressive strength at 28 days from the first stage of the study was used to investigate the effect of the a/p ratios, as shown in Tables 2 and 3, respectively.
Table 2 Composition of TMT-WG AAB synthesized with different NaOH/Precursor ratio

<table>
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<tr>
<th>Mix</th>
<th>a/p (wt.%)</th>
<th>NaOH/precursor (wt.%)</th>
<th>H₂O/precursor (wt.%)</th>
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<td>0.156</td>
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<td>0.26</td>
<td>0.04</td>
<td>0.171</td>
</tr>
<tr>
<td>3</td>
<td>0.28</td>
<td>0.06</td>
<td>0.186</td>
</tr>
<tr>
<td>4</td>
<td>0.3</td>
<td>0.08</td>
<td>0.201</td>
</tr>
<tr>
<td>5</td>
<td>0.32</td>
<td>0.1</td>
<td>0.217</td>
</tr>
<tr>
<td>6</td>
<td>0.34</td>
<td>0.12</td>
<td>0.232</td>
</tr>
</tbody>
</table>

Table 3 Composition of TMT-WG AAB synthesized with different Na₂SiO₃/Precursor ratio

<table>
<thead>
<tr>
<th>Mix</th>
<th>a/p (wt.%)</th>
<th>Na₂SiO₃/Precursor (wt.%)</th>
<th>H₂O/Precursor (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.22</td>
<td>0.16</td>
<td>0.143</td>
</tr>
<tr>
<td>8</td>
<td>0.25</td>
<td>0.19</td>
<td>0.162</td>
</tr>
<tr>
<td>9</td>
<td>0.28</td>
<td>0.22</td>
<td>0.181</td>
</tr>
<tr>
<td>10</td>
<td>0.31</td>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td>11</td>
<td>0.34</td>
<td>0.28</td>
<td>0.219</td>
</tr>
</tbody>
</table>

3.2. TMT-AAB production

To produce the TMT-AAB, firstly the TMT and WG at selected proportions were mixed in the dry state for five minutes, forming the precursor materials. The NaOH and Na₂SiO₃ were mixed for 5 minutes at 700rpm. The activator solution was added to the precursor materials, and the resulting paste was stirred for 5 minutes. Prismatic polystyrene foam moulds of 40x40x160 mm were filled with the AAB and sealed in a plastic bag to prevent moisture loss during curing. The specimens were placed in a temperature and humidity controlled environmental chamber for curing at 80°C. The samples were removed from the oven after 24 hours, demoulded and left in a laboratory condition of approximately 25°C and 50 %R.H for curing until the test age.

3.3. Strength testing

Compression strength tests on were measured at 1, 3, 7 and 28 days at 144 kN/min according to BS EN 196.
3.4. SEM analysis
For the characterization and analysis of the surface morphology and microstructure of the TMT-AAB, a Zeiss Supra 35VP type scanning electron microscope was used with 20 kV energy, combined with secondary and backscatter electrons. All samples were tested in a state where the alkali activation process has been stopped using the combined water and solvent extraction protocol developed by Chen et al. [15].

4. Results and discussion

4.1. Stage I
Results from the SEM imaging show the amorphous product formation in the 100TMT sample (Fig. 1). Sites of (Fe, Mg)-N-A-S-H alkalinisation products (P1) are bridged together with branch-like formations of the same composition (shown in Fig. 1a). The same reaction products in Fig.1b can be seen merging with the quartz particles from the TMT. The muscovite crystals in the raw TMT were found to have undergone some thermal decomposition at its source due to their striated appearance and lack of a laminated structure, however according to XRD analysis (not shown here), had not reached a state of dehydroxylation. Fig. 1c shows a muscovite crystal (Ms) regaining its laminated structure upon rehydroxylation due to the uptake of hydroxyl ions from the activating solution.

Figure 1 (a) branch-like product formations (b) reaction product and quartz (c) muscovite crystal in the 100TMT sample at 1-day

Fig. 2 clearly shows that the TMT-AAB obtained improved compressive strength with an increase of WG. In fact, a 20 wt.% increase in WG from a 20 wt.% to 40 wt.% replacement level raised the 28-day compressive strength by 90% to 41MPa. Fig. 3 shows how the 60TMT40WG sample (3a) compared to the 70TMT30WG sample (3b) exhibited more regions dominated by reaction products, identified as amorphous gel-like formations (3c). This figure also shows how particles of WG are partially transforming into amorphous reaction products supporting the idea that an increased replacement of WG provides a means of increasing reactive silica and thus increasing the Si/Al ratio without resorting to using the more costly and less sustainable soluble silica found in the Na2SiO3 solution. The 60TMT40WG sample structure appears to contain fewer voids while the reaction products appear denser and have more continuity i.e. are not comprised of isolated regions like in the 70TMT30WG sample. By the age of 28 days, many large particles of SiO2 chemical
composition were found embedded in the AAB matrix; however it was difficult to establish whether they came from the TMT or WG. Nonetheless, it can be inferred that the increased WG content not only supplied reactive silica to the mix but may have also contributed to strengthening the AAB as an inert filler. Fig.4 shows the Energy Dispersive X-ray (EDX) spectra for the 1-day reaction products in the 100TMT sample (P1) and the 60TMT40WG sample (P2). The distinction between the spectra is firstly the increased intensity of the main silicon peak at 1.7keV (4.5K for P1 and 14.4K for P2) which is likely due to the contribution of amorphous silica from the WG. Secondly, the presence of calcium compounds, which in another study have been shown to improve the mechanical properties of alkali-activated binders [16] is also believed to contribute to the increased mechanical strength of the 60TMT40WG sample due to the formation of a calcium-containing N-A-S-H gel.

![Figure 2 Effect of WG substitution on TMT-AAB compressive strength](image)

Figure 2 Effect of WG substitution on TMT-AAB compressive strength

![Figure 3 (a) 70TMT30WG at 28-days (b) 60TMT40WG at 28-days (c) amorphous reaction products at 1-day](image)

Figure 3 (a) 70TMT30WG at 28-days (b) 60TMT40WG at 28-days (c) amorphous reaction products at 1-day
4.2. Stage II

The results of the 60TMT40WG-AAB compressive strength with varying a/p ratios are presented in Fig. 5. Fig. 5a shows the effect of an increased a/p ratio due to NaOH and constant Na₂SiO₃, while in Fig. 5b, it is vice versa. The general trend observed from both series of specimens is that the compressive strength declines with an increase in a/p ratio. The results also reveal that increased quantities of the activating solution in the AAB have a more adverse impact on the strength development when NaOH is the varying component rather than the Na₂SiO₃ which although also impacts the strength, is much more subtle in effect.

For specimens with an activator of varying NaOH, the highest 28-day compressive strength achieved is for an a/p ratio of 0.26. Any increase of NaOH in the activator thereafter reduces the compressive strength across all ages. The 60TMT40WG-AAB appears to be able to develop a compressive strength as high as 60MPa, which although occurs at the lowest ss/sh ratio, i.e., containing more sodium hydroxide (indicated in Fig. 5 by the dotted lines), this is compensated by the fact that the a/p ratio is only 0.22. In fact, the mixture with the latter a/p ratio contains 27% less activator than the best performing 28-day specimen from the NaOH varying series. The latter results indicate that a low a/p ratio combined with a low ss/sh ratio is preferential for the development of high compressive strengths. It is theorized that the WG component of the mix was able to provide sufficient reactive silica for the formation of reaction products and thus possesses the capacity to partially replace the Na₂SiO₃ component of the activating solution, thus imparting ability for TMT/WG AABs to develop high strengths with a lower demand for alkali solution. This property is very beneficial considering that the activating solution is the most expensive component of alkali-activated binders.
Figure 5 Effect of varying (a) NaOH ad (b) Na₂SiO₃ in the activator/precursor ratio

In both series, however, the lowest a/p samples did suffer from a so-called ‘balling’ effect due to the low H₂O/precursor ratio and thus required more compaction (Fig.6a). The increase in H₂O/solid content has previously been shown to contribute to the reduction of fly ash AAB compressive strength due to crystallisation of the otherwise amorphous reaction products [17], however in samples prepared in this study, no products of zeolitic nature were observed for the highest H₂O/precursor ratio of 0.232. Instead, at the latter ratio, the activating solution was observed to bleed, covering the sample surface and mould, as shown in Fig.6b. Unlike in concrete where the excess bleed water can evaporate without affecting the mechanical strength, the loss of activating solution AABs is detrimental to the hardening and thus contributes to the lower mechanical strength observed in this study. Samples in the 0.26-0.28 range provided the most satisfactory flow and workability (Fig.6c).
5. Conclusion

AABs made of varying ratios of TMT and WG were investigated with regard to activator/precursor ratios. It was found that a replacement of up to 40 wt.% with WG provided an additional source reactive silica, contributing to the formation of reaction products and thus making a significant improvement to the compressive strength due to the development of a denser microstructure. Conversely, larger SiO₂ particles were found to remain unreactive, establishing themselves as inert fillers.

TMT-WG AAB was found to have a low activating solution demand and produced the highest compressive strength when a combination of a low Na₂SiO₃/NaOH activating solution with a low activator/precursor ratio was used. It is believed that through the release of soluble silica from the WG fraction, the Na₂SiO₃ component of the activating solution may be reduced, providing a more sustainable means of activation. Further research into the fineness modulus of both TMT and WG will be investigated to determine if reactivity could be further improved.

Acknowledgement

Partial finance support from the European Commission Horizon 2020 MARIE Skłodowska-CURIE Research and Innovation Staff Exchange scheme through the grant 645696 (i.e. REMINE project) is greatly acknowledged. The first author thanks, Brunel University London for providing a bursary and Thomas Gerald Gray Charitable Trust for the tuition fee to support his PhD study.

References

2–9, 2013.


**PERFORMANCE OF ALUSILICA AS MINERAL ADMIXTURE IN CEMENTITIOUS SYSTEMS**

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(2) Technical University of Denmark, Lyngby, Denmark

**Abstract**

This paper presents a preliminary study of the effect of alusilica (ALS) as a mineral admixture on the fresh properties and development of mechanical properties of cementitious systems. Cement was substituted with ALS with the ratio of 10% during grinding or blended during mixing. The produced ALS-substituted powder was studied by scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX). Flow of the fresh mortar, air content and mechanical properties of the hardening mortar were measured. The results show that the inclusion of ALS in the mortar as a mineral admixture resulted in a higher air content and lower flowability in comparison with the reference mortar. Mortar with ALS substitution, exhibited a lower compressive strength as compared to the reference mortar. This can be accounted for by the higher air content. By appropriately adjusting the flow of the fresh mortar, it is believed that ALS can be a useful cement substitution.

1. **Introduction**

Today supplementary cementitious materials, such as silica fume, fly ash and blast furnace slag are widely used in concrete. In many cases supplementary cementitious materials have an origin as problematic industrial waste products, but when these materials are properly utilized in concrete they may become very valuable through improvement of concrete properties and they may also lead to an overall reduction in CO₂ emissions.

Alusilica (ALS) is an industrial by-product from the production of aluminium fluoride (AlF₃). ALS consists of mainly amorphous silicon dioxide, a chemical compound which is known to be useful as mineral admixture in concrete. The ALS also contains some fluorides (~5 wt%), notably in the form of aluminium fluoride, which may cause problems in cementitious systems [1]. However, this fluoride can be made chemically inert through a simple reaction with CaO. ALS can potentially be used as a mineral admixture in concrete. A preliminary
investigation took place as a BSc project in 2015 with encouraging results but also with a number of issues which needed further investigation [2].

In this paper the effect of ALS as a mineral admixture on the fresh properties and development of mechanical properties of cementitious systems is examined. A more detailed description of the investigation is given in [3].

2. Materials

Aalborg Portland cement clinker and gypsum (CaSO₄·2H₂O) are used. The mineral composition of the cement clinker is listed in Table 1. ALS is provided by the company Alufluor, Sweden. In the original by-product form, the ALS contains some fluoride, mainly as aluminum fluoride. To avoid free fluorides the ALS has been further processed by mixing it with CaO in hot water. This makes the fluoride precipitate as calcium fluoride (CaF₂) which is inert in cementitious systems. The composition of raw and fluoride stabilized ALS is measured by X-ray fluorescence (XRF) and the result is shown in Table 2. The moisture content in the fluoride stabilized ALS is 4.8%. The ALS is dried to a constant mass at 105°C before use. CEN standard sand and demineralized water is used.

Table 1: Mineral composition of white Portland cement clinker.

<table>
<thead>
<tr>
<th>Component</th>
<th>C₃S</th>
<th>C₂S</th>
<th>C₃A</th>
<th>C₄AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt%)</td>
<td>77</td>
<td>16</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2: Composition of raw and fluoride stabilized ALS according to XRF.

<table>
<thead>
<tr>
<th>Content (wt%)</th>
<th>F</th>
<th>Al</th>
<th>SiO₂</th>
<th>Ca</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw ALS</td>
<td>4.9</td>
<td>2.1</td>
<td>85</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>Fluoride stabilized ALS</td>
<td>6.2</td>
<td>1.9</td>
<td>73</td>
<td>8.7</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Mix proportions are given in Table 3. The water/binder-ratio is 0.5 and binder/sand-ratio = 1:3 for all mixes. The level of substitution was 10% ALS relative to the total binder mass. Three binders are investigated:

1) Reference (co-ground clinker and gypsum),
2) ALS-substituted, co-ground (co-ground clinker, gypsum and ALS),
3) ALS-substituted, blended (co-ground clinker and gypsum, subsequently blended with ALS).

Table 3: Mix proportions of mortars [g].

<table>
<thead>
<tr>
<th>Component</th>
<th>Clinker (95%) + gypsum (5%)</th>
<th>ALS</th>
<th>CEN-standard Sand</th>
<th>Demineralized Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>450</td>
<td>0</td>
<td>1350</td>
<td>225</td>
</tr>
<tr>
<td>ALS-substituted</td>
<td>405</td>
<td>45</td>
<td>1350</td>
<td>225</td>
</tr>
</tbody>
</table>
3. Methods

The clinker and gypsum were initially crushed with a jaw crusher followed by disc milling (particle size < 0.5 mm) and subsequently mixed homogeneously. Further grinding was done by ball milling. For each 1 hour ball milling the Blaine specific surface by a HMK-C1 Blaine Finesseness Air Permeability Apparatus and the sieve residue at the 50 μm sieve was measured [4]. After ball milling of the reference binder for 4 hours, the specific surface area, S, was 358 m²/kg, which is in the desired range 300-400 m²/kg. Therefore, the total ball milling time, 4 hours, was used for the rest of the batches. The specific surface and 50 μm sieve residue of the co-ground clinker and gypsum are listed in Table 4. For ALS-substituted, co-ground the same ball milling time as for reference is used since this would imply the same energy input during processing.

Table 4: The specific surface and 50 μm sieve residue of co-ground clinker and gypsum

<table>
<thead>
<tr>
<th>Grinding batch</th>
<th>Reference</th>
<th>co-ground ALS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Specific surface (m²/kg)</td>
<td>358</td>
<td>380</td>
</tr>
<tr>
<td>50 μm sieve residue (%)</td>
<td>0.39</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Mixing was done in a 20 l epicyclic mixer. For ALS-substituted, blended, cement and ALS were initially dry mixed for 5 min. For the other two mixes no initial mixing of the binder was relevant. A low mixer speed (140 ± 5 min⁻¹) was used during addition of the water to the binders. After 30 s of paste mixing, the sand was added during the subsequent 30 s. The mixer was switched to high speed (285 ± 10 min⁻¹) and mixing was continued for another 30 s. The mixer was stopped for 90 s to remove the mortar adhering to the walls of the bowl and mixing was subsequently continued at the high speed for a further 60 s.

Immediately after mixing the flow table test was done according to ASTM C1437-15 [5]. Casting was done in standard mortar molds 4×4×16 cm³ and cured in a room with 95% RH, 21°C. The mortar samples were demolded 1 day after casting, and the air content of each sample was determined by weighing over and under water. Subsequently, the mortar samples were immersed in lime saturated water (19°C) until further testing [6]. The mechanical testing was in general in accordance with EN 196-1 [7]. Mechanical properties were measured at 1, 2, 3, 7, 14, 28, 56 and 112 days. Scanning electron microscopy and energy dispersive X-ray analysis (element mapping) were performed on some of the powder materials in order to examine to what extent the ALS agglomerates were broken by the co-grinding process.

4. Results and analysis

Table 5 lists the results of consistency of fresh mortar measured by flow table and air content of hardened mortars. Fig. 1 shows the relationship between flow value and air content by weighing of the three mortars. Clearly ALS substitution of cement leads to a lower flow percentage (defined in [5]) and a higher air content, most likely due to the stiffer mortar which more easily encapsulates air during mixing and which is less likely to release it again during casting and vibration.
Table 5: Test results for fresh and hardened mortars.

<table>
<thead>
<tr>
<th></th>
<th>Reference</th>
<th>ALS-substituted, co-ground</th>
<th>ALS-substituted, blended</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow percentage (%)</td>
<td>124</td>
<td>103</td>
<td>61</td>
</tr>
<tr>
<td>Air content by weighing (%)</td>
<td>0.86</td>
<td>2.20</td>
<td>4.87</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.33</td>
<td>2.26</td>
<td>2.19</td>
</tr>
</tbody>
</table>

Fig. 1. Air content vs. flow percentage of fresh mortars.

The flexural strength of mortars is shown in Fig. 2. Taking into account the fluctuations on the individual measurements and the measurements as a time series, there does not seem to be a marked difference in the flexural strength between the three mixes. There may be a slight tendency towards a lower flexural strength of the mortar with ALS-substituted, blended, and perhaps a slight tendency towards a higher flexural strength of the mortar with ALS-substituted, co-ground, but the effect, if any, is minor.

The compressive strength of mortars is shown in Fig. 3. It can be seen that the samples ALS-substituted, co-ground and blended have a lower compressive strength throughout the considered time range. Compared with the reference mortar the reduction in compressive strength of samples with co-ground and blended ALS at 28 days were 11% and 15% respectively. The strength reduction for samples with ALS-substituted, co-ground is less pronounced than for samples with ALS-substituted, blended. This may have several explanations including a better dispersion of co-ground ALS and thus better reactivity of the ALS and better pore filling in between the cement particles. Also breakage of ALS agglomerates and dispersion of the particles may enable them to better act as nucleating sites and thus improve the hydration progress of the cement [8].
Another important factor concerns the observed, different air contents, which seem to be related to the differences in workability, and apparently strongly influenced by the presence and form of ALS present in the mortar. It is known that an increase in air content of 1% leads to a reduction in compressive strength by 5% [9]. Therefore, by taking the factor of air
content into consideration, the results of compressive strength can be corrected for differences in air content. Such corrected results are shown in Fig. 4. This comparison is relevant as it will be possible to correct the workability of the different mortars by means of plasticizer adjustment, and thus most likely eliminate the differences in air content. For the corrected results in Fig. 4 it is seen that the strength reduction by ALS substitution apparently can be fully accounted for by the extra air in the samples.

![Image of Fig. 4](image_url)

**Fig. 4.** The effect of ALS substitution by co-grinding and blending on the compressive strength of hardening mortars. The results are corrected for the influence for air content.

SEM images were captured to investigate if the ALS agglomerates were broken by the co-grinding process, see Fig. 5 and Fig. 6. As seen from Figure 5 (top left), the ALS powder consist of agglomerates of particles mainly in the size range from a few micrometer to about 50 μm. Relative to the ALS powder, the cement particles are slightly finer. From the EDAX maps it is possible to identify main components in the ALS co-ground system: C₃S (high Ca, some Si), C₂S (medium high Ca, some Si), C₃A (high Ca, some Al), ALS (no Ca, high Si), gypsum (high S). All ALS particles found in Fig. 6 (brightest intensity in the Si map and “no” intensity in the Ca map) are in the size range of a few micrometer. In the SEM image of ALS, Fig. 5, a multitude of particle sizes from micrometer size to about 50 μm is found. A comparison of Fig. 5 and Fig. 6 thus clearly shows that in the ALS co-ground binder the ALS agglomerates have been broken down to particle sizes of a few micrometer. The ALS particles appear to be well dispersed in the cement system. These microscopic observations are in accordance with the measured differences regarding flowability and air contents – and further the mechanical properties – between the co-ground and blended ALS-substituted mortars.
Fig. 5. SEM images of the different powders. Top left: ALS as received (i.e. after fluoride stabilization). Scale bar is 50 μm. Top right: Cement, i.e. ground cement clinker with gypsum. Bottom left and right: Cement with co-ground ALS at two different magnifications: the scale bar on left image is 50 μm, and 20 μm on the right image.
Fig. 6. Identical view fields by SEM (bottom left) and four EDAX mappings of the produced ALS-substituted powder. The elements analyzed for are written above each EDAX map. Height of the view field (image height) is approximately 40 μm.
5. Conclusions

The following conclusions can be drawn based on the present laboratory investigation.
1. The fluoride in the ALS seems within the tested regime to be effectively bound as CaF$_2$ and does apparently not disturb the cementitious reactions.
2. Co-grinding of ALS and cement clinker (and gypsum) leads to a finer dispersion of ALS in the cementitious system and breaks up ALS agglomerates from about 5-50 $\mu$m size to about 1-5 $\mu$m size.
3. The inclusion of ALS in the mortar as a mineral admixture with the substitution ratio of 10% of cement mass resulted in a higher air content and a corresponding reduction in the flow compared with the reference mortar. Compared with blending ALS during the mixing, mortar containing co-ground ALS was closer to the reference mortar considering these properties.
4. The addition of ALS did not affect the flexural strength significantly at the investigated hardening times 1 to 122 days.
5. Mortars containing 10% ALS by cement mass exhibited a lower compressive strength compared with the reference mortar. At 28 days the strength reduction is 11% for ALS-substituted, co-ground and 15% for ALS-substituted, blended. Apparently the strength reduction can be accounted for by the increased air content, i.e. it is expected that it by simple means will be possible to incorporate ALS in cementitious systems without strength loss.

Acknowledgements

The project has been carried out in cooperation with the company Alufluor (Helsingborg, Sweden), and MSc Ebbe Skyum Jøns. We are thankful for fruitful discussion with them.

References

MITIGATION OF EARLY AGE SHRINKAGE IN SELF-CONSOLIDATING PASTE SYSTEMS USING SUPERABSORBENT POLYMERS

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(1) NUST Institute of Civil Engineering (NICE), National University of Sciences and Technology (NUST), Islamabad, Pakistan.

Abstract
This research reports the effects of super absorbent polymers (SAPs) on linear early age shrinkage response of self-compacting cement paste systems (SCPs) containing fly ash (FA) and marble powder (MP) as secondary raw materials (SRMs) also called supplementary cementitious materials (SCMs). The results show that the use of powdered super plasticizer (SP) increased the early age shrinkage of self-consolidating paste systems (SCPs) without SRMs while the use of SAPs in SCPs induces some early expansion in all of the studied formulations. SAPs were also successful internal curing agents for the mitigation of early shrinkage of SCPs especially those containing fly-ash. In another side investigation by the authors, it was observed that SAPs work more efficiently in cement based systems without super plasticizer.

1. Introduction

Structural Engineers are mainly interested in the amount of total shrinkage of a cement based formulation and not in the individual contributions of several simultaneously operative mechanisms. Therefore, most building codes only specify the maximum permissible limit of total shrinkage of cementitious systems. This study focuses on the use of Super Absorbent Polymers (SAPs) as internal curing agents to mitigate the total shrinkage in self-compacting cementitious systems with mineral admixtures. In cement paste systems having mineral admixtures and low water-cement ratio (w/c < 0.36) early age cracking due to the early shrinkage damages the strength, durability and aesthetics of the hardened concrete. This contraction of the cement paste can be a result of several parallel operating shrinkage mechanisms including autogenous shrinkage, thermally-induced shrinkage, drying shrinkage due to loss of water to the surrounding and shrinkage due to carbonation [1]. Drying shrinkage and thermally induced shrinkage are hard to control using an internal curing agent but the self-desiccation shrinkage can be mitigated.
During cement hydration, the hydration products precipitate in the water filled spaces between the solid particles causing the remaining water to form menisci and exert hydrostatic tension forces. In parallel a drop in the internal relative humidity takes place. Therefore without the presence of an internal curing agent or extra water, the cement pastes experience shrinkage causing cracking. Several methods to avoid cracking due to self-desiccation have been studied by researchers using light weight aggregate [2] which makes it difficult to control the consistency of the paste and also reduces strength significantly. Researchers have used some other materials for internal curing in which the water entrainment occurs physically, chemically and through unbound water using micro-encapsulations but the use of SAPs and LWA is reported to be the most practical [3].

Some SAPs have the ability to absorb and hold liquids up to 1500 times their weight depending on the pH, ionic composition, temperature and relative humidity of the liquid. However, the value of absorption capacity is generally within the range of 20-50 g/g of the weight of SAPs in cementitious environment due to its ionic composition [4]. This unique ability of SAPs makes them useful in many industrial applications of concrete in the sense that it not only mitigates the early age autogenous shrinkage and hence total shrinkage but it may also increases the freeze thaw resistance [5], help to modify the rheology of fresh concrete [6] and aid self-healing of concrete systems [7].

SAPs take up the water from the cement-water formulations during the mixing stage to form water-filled inclusions which supply water to the cement matrix when the internal relative humidity drops through capillary pressure developing in the pore fluid due to emptying of pores [8] and osmotic pressure [9]. This loss of water causes the SAPs particles to shrink; leaving a void in the matrix [10]. Therefore extra water is to be added to take care of water absorption of SAPs. The amount of extra water required, in the presence of SAP, for a given w/c ratio was calculated using Power’s Theorem [11] and is equal to 0.18 times the basic (w/c) for (w/c)_b < 0.36. This water is referred to as the “extra water” throughout the paper and the initial water available for cement hydration is called the “basic water”.

2. Experimental

2.1 Materials

Bestway Ordinary Portland Cement 52.5 R, a suspension-polymerized covalently cross-linked acrylamide/acrylic acid copolymer as super absorbent polymer (SAP), class F German fly ash (FA) and locally available marble powder (MP) were used. A PCE based powdered superplasticizer, Melflux 2651-F by BASF was used to achieve the target flow of (30 ± 1) cm measured by Hagerman’s cone of 6x7x10 cm^3 dimensions. This target gives good flow indices and shortened flow times enabling better self-consolidation.

Scanning Electron Microscopy (SEM) along with EDX technology was used to determine the dry particle size and chemical composition of SAP respectively. Due to suspension polymerization the individual SAP particle is spherical [4], see figures 1 and 2.
X-Ray Florescence test was used for chemical characterization of all the powders including cement, fly-ash and marble powder and results are shown in Table 1. Analysis was carried out on Axios Advanced WD- XRF PANalytical for all the major elements using pressed pellet.

Table 1 Chemical Characterization of Powders

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>MP E.879</th>
<th>CEM E.880</th>
<th>E.878 (FA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>8.32</td>
<td>19.19</td>
<td>59.06</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.00</td>
<td>0.29</td>
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2.2 SCP Formulations and Sample Preparation

A total of twenty formulations were studied for shrinkage response of cement pastes. The amount of extra water required for absorption by SAPs was determined using Power’s Theorem [11]. To define the initial (dry) state, all the SAPs were kept in a desiccator with silica gel for at least 24 hours prior to use as improper initial state may induce error up to 0.25 g/g of SAPs when exposed to moist conditions (RH ≥ 50%) [12]. More than 50% of the swelling occurs within first five minutes of mixing [12] so it was decided to use 5 minute wet mixing in 5 liter Hobart Mixer. After 1 minute of dry manual mixing of formulation ingredients in a plastic jar, these were added to the Hobart Mixer containing the required mixing water. The mixes received 90 s of slow mixing (145 rpm) after which mixing was stopped for 30 s and the inside of the mixer bowl was cleaned. Thereafter, the mixes received 210 s of fast mixing (285 rpm). Table 2 shows the composition of formulations where \((w/c)_t = (w/c)_b + (w/c)_e\), \((w/c)_t\) is the total mixing water, \((w/c)_b\) is the basic water and \((w/c)_e\) is the entrained water.
2.3 Absorption Capacity of SAP

A sieve method was used to measure the absorption capacity of SAPs using three different liquids (de-ionized water, tap water and cement slurry) to study the effects of ionic composition variation and pH on the absorption capacity of SAPs. The cement slurry was obtained by adding 400g of water to 40g of cement and subsequent filtration. 1g of SAP was added to 200g of liquid and stirred magnetically for 30 minutes. The resulting mixture was filtered through sieve 100 (150 μm). The excess of liquid was removed by rubbing a soft sponge at the bottom of the sieve until, when held vertically, no flow of the gel was observed. It is difficult to remove all the inter particle water by a sponge, therefore the reported absorption capacity of SAP may be higher than the one measured in developed countries by highly skilled professionals where necessary equipment is easily available.

Absorption Capacity was calculated using equation (1) reported in [13]

\[
St = \frac{(At + B) - (B + W1)}{W1}
\]  
(1)

Where  
St = swelling at time t (g/g)  
At = Weight of swollen SAP at time t (g)  
B = Weight of sieve (g)  
W1 = Weight of dry SAP

Table 3 shows the absorption capacity of SAPs in different types of liquids.
The cement slurry was assumed to represent the environment within the cement mix thus an absorption capacity of 22 g/g was used to calculate required SAP percentage. The same value of absorption capacity was used for SCPs containing FA and MP as it has been reported that the amount of mixing water absorbed by SAPs is independent of the mix composition [1].

3. Results

3.1 Super Plasticizer Demand

The Super Plasticizer demand was determined by Hagerman’s Cone measuring 6x7x10 cm³. SP dosage was adjusted by trial and error until the target flow of (30 ± 1) cm was achieved. To further assess the flow characteristics of the self-compacting cement pastes, T₃₀ cm time was recorded. Table 4 shows the results.

<table>
<thead>
<tr>
<th>Serial</th>
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<th>SP (%)</th>
<th>Spread (cm)</th>
<th>T₃₀ (s)</th>
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<td>2</td>
<td>Plain Cement @ 27% W/C</td>
<td>0.120</td>
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<td>Cement + 0.186% SAP @ 27% W/C</td>
<td>0.250</td>
<td>30.4</td>
<td>22.10</td>
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<td>4</td>
<td>Cement + FA + 0.186% SAP @ 27% W/C</td>
<td>0.263</td>
<td>30.7</td>
<td>19.73</td>
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<td>5</td>
<td>Cement + FA + MP + 0.186% SAP @ 27 W/C</td>
<td>0.270</td>
<td>29.5</td>
<td>21.56</td>
</tr>
</tbody>
</table>

3.2 Early Age Shrinkage Response of SCP Systems

The fresh SCPs were placed in a modified version of German Classical “Schwindrinne” channel apparatus measuring 4x6x25 cm² interfaced with computer software at 20-25 °C laboratory temperature and were covered with plastic sheet to avoid water escape from surface. As pointed out earlier, the total shrinkage was of interest so this apparatus gives total shrinkage and the protocol for a closed system at isothermal conditions was not possible with this apparatus. The recording of the shrinkage response was started after 10 minutes of mixing.
for all the formulations and was carried out for the first 72 hours only. The resulting early
shrinkage response of the formulations is plotted against time along with the final Vicat
setting time of respective SCP formulations which marks the end of setting and the start of
hardening processes. The results are shown in Figures 3-6.

![Figure 3: Shrinkage response of SCPs @ 0.27 W/C](image)

![Figure 4: Shrinkage response of SCPs @ 0.30 W/C](image)

![Figure 5: Shrinkage response of SCPs @ 0.35 W/C](image)

![Figure 6: Shrinkage response of SCPs @ 0.40 W/C](image)

### 3.3 Calorimetry of SCP Systems

F-CAL 8000 field calorimeter was used for calorimetric measurement in order to observe the
hydration kinetics of the SCPs. The apparatus was switched on and was allowed to log
temperature data for at least one hour prior to the addition of sample so that it can get
acclimatized. Calorimetric measurement starting time, of each respective formulation placed
in the channel, was established at the time when mixing water was added to the dry mixed
ingredients of the formulation. The fresh SCP weighing 700-800 grams was then added to the
channel of the calorimeter having a poly-ethylene bag inside and temperature of the SCP was
recorded for 72 hours. The results are shown in figures 7-10.
3.4 Strength of SCP Systems

The fresh SCPs were cast into the prism moulds measuring 40x40x160 cm³ as per DIN 196. The prisms were demolded after 24 hours and were placed in a curing tank for the required period of water curing. These were then taken out and surface dried, before performing strength test. The flexural and compressive strengths were measured at ages of one, three and twenty eight days using a dual chamber machine capable of testing flexural and compressive strength. The results are shown in figures 11-12.
3.5 Vicat Setting Times of SCPs
A Vicat apparatus was used to determine the initial and final setting times of SCP formulations so that the effect of retardation or acceleration imparted by chemical and mineral admixtures could be observed. The results are shown in figure 13 which demonstrates that SP, SAP and FA cause delay in setting of the self-compacting pastes while the use of MP speeds up the setting process.

![Figure 13 Initial and Final Setting Times of SCP Formulations](image)

4. Discussion

4.1 Super Plasticizer Demand of SCP Systems
SAP addition in the SCP mixes causes a significant increase in the SP content required to attain the target flow because SAPs arrest considerable amount of water from the fresh SCP formulations resulting in lower basic w/c ratio and the flow. The addition of SRMs do not significantly affect the SP demand, especially at higher w/c ratios due to the abundant availability of water.

4.2 Setting Times and Calorimetry of SCP Formulations
SP seem to increase the setting time and delay the hydration peak due to their inherent retarding nature. The addition of SAP in the SCP formulations also delays both, the setting time and calorimetric peak. It may be possible that SAP also takes up Ca$^{2+}$ ions while absorbing water, thus slowing down their built-up in the SCP mix and delaying the hydration process [4]. The reduction in the peak value can be explained using general retarding effects. The same effect was observed on setting time and calorimetric response by the addition of FA, as FA particles are also well known Ca$^{2+}$ ion sinks. These may cause reduced calcium ion concentration in the first few hours delaying the CH and CSH formation resulting in retardation and lowering of the peak temperature [14]. FA-MP blend addition accelerates the hydration process denoted by early setting times and early hydration peak, compared to SCP containing only FA as SRM. This may be attributed to cohesive nature and rough particle texture of MP particles.
4.3 Linear Early Shrinkage of SCP Systems
Taking the plain cement samples as control, the use of SP increased the shrinkage probably because of de-flocculation of cement particles produced increased heat of hydration. The samples were covered with plastic sheet to avoid rather easy escape of heat and water, however, the sample in this equipment may not have a perfect closed system at isothermal condition, a requirement for the measurement of autogenous shrinkage. The use of SAPs reduces the total early shrinkage significantly by acting as internal curing agents. The effects are more prominent in samples with lower w/c ratios as the shrinkage in these samples is more influenced by the self-desiccation phenomenon that can be effectively mitigated by an internal curing agent. SAPs are more effective in absence of SP, potentially they have some interaction which reduces the effectiveness of SAPs. The use of FA also reduces the overall shrinkage of the SCP formulations because FA particles not only delay the hydration process but also encourage the growth of expansive species like CH [14] which aid in reducing the shrinkage. The lesser shrinkage in SCP containing FA can also be explained through dilution effect. At 0.30 w/c without any SRM at 72 hours the shrinkage reduction caused by SAPs is about 40% when compared with the self-compacting plain paste. Although, with only 10% replacement of cement by FA, almost 100% of the early shrinkage at 72 hours was mitigated. The addition of FA-MP blend may increase, decrease or show no effect on the shrinkage response of SCP formulation containing only FA as a SRM.
Initial expansion is observed in all the formulations having SAP. This was also observed by Lura et al [15] and was attributed to the size of SAP particles especially in the range of 125-160 μm. This expansion may also be explained through the re-absorption of bleed water by the SCP formulation and the crystallization pressure of calcium hydroxide [16]. Further studies are required to completely understand this phenomenon.

4.4 Strength of SCP Systems
Reduction in both, compressive and flexural strengths by 16% and 12% respectively was observed by the addition of SAPs at twenty eight day, when compared with the control SCP. This may be because the strength of the cement pastes is greatly influenced by the size of the largest defect/void in the matrix [17] and SAPs tend to shift porosity towards macro-pores. The experts believe that the used technique might overestimate the absorption capacity of SAPs resulting in higher basic and lower entrained w/c ratio, further reducing strength. Although, the use of SRMs show promising potential in countering this effect, as by only 10% of cement replacement by FA it was possible to regain 33% of the lost compressive strength at 28 days.

5. Concluding Remarks
1. Internal curing by means of SAP has been found to be successful in mitigating total early age shrinkage also in self-compacting cement pates with or without SRMs with pronounced effects at low water-cement ratios.
2. SAP seems to work better in combination with FA to mitigate total early age shrinkage of self-compacting paste systems possibly due to delayed setting of systems using FA and simultaneous supply of internally entrained water.

3. SAPs seem to cause early age expansion in all the SCP samples and further studies are required to fully understand this mechanism.

4. The addition of SAP reduces both flexural and compressive strength of the self-compacting cements pastes to some extent; an effect which has been largely offset by using suitable SRMs or their combinations at optimum replacement level.

5. Delay in setting time was observed in all the samples containing SAP as they, along with water, may take up the dissolved calcium ions causing slow built up of their concentration resulting in delayed hydration process.

Acknowledgements

The authors are grateful to Prof. O. M. Jensen for supplying SAP used in this investigation and also for his valuable comments on the results. He has been a source of continuous inspiration and prompt guidance. Thanks are also due to DAAD for providing F-Cal 8000 Field Calorimeter and modified Schwindrinne Shrinkage Apparatus to NICE/NUST under an International Research Project. NUST/HEC is appreciated for a possible travel grant. The help extended to us by Hassan Arif and Sohaib Z. Gondal is also appreciated.

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<td>Yibing Zuo 253</td>
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Concrete with Supplementary Cementitious Materials

Edited by
Ole Mejlhede Jensen, Konstantin Kovler and Nele De Belie

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This volume contains the proceedings of the MSSCE 2016 conference segment on "Concrete with Supplementary Cementitious Materials" (SCM). The conference segment is organized by the RILEM technical committee TC 238-SCM: Hydration and microstructure of concrete with supplementary cementitious materials. TC 238-SCM started activities in 2011 and has about 50 members from all over the world. The main objective of the committee is to support the increasing utilisation of hydraulic and pozzolanic industrial by-products, natural resources and societal waste to obtain more sustainable, less CO₂-intensive binders for the construction industry. The TC serves as a knowledge platform where fundamental science and practical expertise are gathered to create a horizontal overview of the research area and to implement and promote the dissemination of more integrated generic approaches into the scientific community. One of the main challenges of the TC is to deal with SCM variability and binder diversification.

The present conference segment deals with theory, modeling, and results from experimental investigations with relation to the use of SCMs in concrete. The topics covered include characterization of SCMs, SCM reactivity in blended cements, cement-SCM interaction, SCM-admixture interaction, hydration products, pore solution composition, effect of SCM on fresh concrete, hardened concrete with SCM, SCM influence on microstructure and durability of concrete with SCM. All these topics have relation to the aforementioned RILEM technical committee 238-SCM. The conference segment is attended by more than 40 presenters from university, industry and practice representing 30 different countries. Hopefully, it will contribute to synthesis of research on concrete with SCMs and promote knowledge transfer from academia to practice. All contributions have been peer reviewed.

The event "Materials, Systems and Structures in Civil Engineering 2016", 15-29 August 2016, Lyngby, Denmark, is scientifically sponsored by RILEM. The event is hosted by the Department of Civil Engineering at the Technical University of Denmark and is financially sponsored by a number of independent foundations and organizations.

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