HYDRATION AND MICROSTRUCTURE DEVELOPMENT OF PORTLAND CEMENT BLENDED WITH BLAST FURNACE SLAG

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Abstract

This paper deals with the hydration process and the microstructure changes of Portland cement blended with blast furnace slag. The hydration process indicated by heat release was measured using a thermometric isothermal conduction calorimeter. The microstructure of hydration products and the morphology of C-S-H, CH, and unhydrated particles were examined by means of Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX). The influence of factors, like water/cement ratio, curing age, and the amount of blast furnace slag on the hydration and microstructure was studied in detail. The results show that the microstructure of Portland cement blended with blast furnace slag is different compared to Portland cement paste.

Keywords: Hydration, Microstructure, Blast furnace slag, Portland cement

1. INTRODUCTION

In recent years, nanotechnology has been introduced in cement chemistry. This seems promising in view of the development of new production processes with higher energy efficiency, a reduction of the use of natural raw materials and less production of waste, thus contributing to sustainable development in the construction industry.

The possibility to manipulate the nanostructure and microstructure, and hence the connectivity of phases in cement-based materials by changing the composition of the powder (cement and cement replacements), opens the way to design new and improved materials with predefined (transport) properties. This potential may stimulate the use of active and/or inert fillers, such as blast furnace slag and limestone powder, through which a less energy-demanding and environment-friendly building material is obtained.
Blast furnace slag is a by-product of metallurgical furnaces producing pig, iron, steel, copper, nickel, and lead. It is formed as a liquid at 1350-1550 °C in the manufacture of iron. Granulated blast-furnace slag (GGBFS) is a non-metallic product consisting essentially of silicates and aluminosilicates of calcium and magnesium. If cooled sufficiently rapidly to below 800 °C, it forms a glass which is a latent hydraulic cement [1]. The GGBFS containing CaO, SiO$_2$, MgO and Al$_2$O$_3$ in roughly 7.88:7.39:3:1 [2]. The hydration of Portland cement-granulated slag mixes is much complex than that of Portland cement, since both constituents react with the water. If blast furnace slag is placed in water alone, it dissolves to a small extent, but a protective film deficient in Ca$^{2+}$ is quickly formed, and inhibits further reaction [1]. Reaction continues if the pH is kept sufficiently high. The pore solution of a Portland cement is a suitable medium since the presence of OH$^-$ ions supplied from calcium or sodium hydroxide, sodium silicate or sodium carbonate. These alkalis act as the necessary activators for GGBFS hydration in a slag-cement system. So that, for a given slag, the rate of reaction maybe limited by the rate at which the necessary ions are supplied by the clinker or taken up by its hydration products [1]. There are two reaction stages of BBGSF and Portland cement system were proposed in the literature [3]. During the early stage, GGBFS reacts with alkali hydroxides. Subsequent reactions occur primarily with Ca(OH)$_2$. The continued hydration of GGBSF and Portland cement results in the formation of three regions of hydration in slag-cement at the early stages. These are i) the cement paste, where Portland cement hydration takes place, ii) the GGBSF particles, where the two hydration products are formed. iii) an intermediate transition zone, where the two hydration products can interact [3].

In order to model the hydration process and the microstructural properties of GGBFS cement, the hydration kinetics and stoichiometry are necessary. In this contribution, the hydration kinetics was examined by thermometric isothermal conduction calorimeter. The microstructure of hydration products and the morphology of CSH, CH, and unhydrated particles was examined by SEM and Energy Dispersive X-ray Analysis (EDXA). The factors, like water/cement ratio, the amount of blast furnace slag on the pore solution was studied.

The results of this study will provide solid input data for the simulation of hydration and development of microstructure of Portland cement blended with blast furnace slag.

2. EXPERIMENTAL PROGRAM

2.1 Materials and mixtures

2.1.1 Portland cement and blast furnace slag

The materials used in this study were prepared with Portland cement I 52.5 blended with Blast furnace slag. The blast furnace slag was provided by ORCEM Company. The chemical composition and the morphology were analyzed by EDXA, and listed in Table 1 and shown in Figure 1. A high content of silica, magnesium and aluminates can be found in the Blast furnace slag.
Table 1. The chemical and physical properties of cement and Blast furnace slag

<table>
<thead>
<tr>
<th></th>
<th>CEM I 52.5 (%)</th>
<th>Blast furnace slag (%)</th>
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<tbody>
<tr>
<td>CaO</td>
<td>59.61</td>
<td>40.77</td>
</tr>
<tr>
<td>SiO₂</td>
<td>23.55</td>
<td>35.44</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.65</td>
<td>12.98</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.05</td>
<td>0.53</td>
</tr>
<tr>
<td>MgO</td>
<td>2.84</td>
<td>7.99</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.74</td>
<td>0.49</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.61</td>
<td>0.21</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.16</td>
<td>0.1</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.53</td>
<td>0.052</td>
</tr>
<tr>
<td>Total</td>
<td>96.74</td>
<td>98.56</td>
</tr>
<tr>
<td>C₃S</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂S</td>
<td>59.0</td>
<td>-</td>
</tr>
<tr>
<td>C₃A</td>
<td>12.60</td>
<td>-</td>
</tr>
<tr>
<td>C₄AF</td>
<td>8.01</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>9.40</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 1: The morphology and chemical composition pattern by EDX.
The Blaine value of blast furnace slag and CEM I 52.5 are 460 m²/kg and 420 m²/kg respectively. The average particle size of blast-furnace slag is slightly smaller than that of Portland cement CEM I 52.5. The density of GGBFS and CEM I 52.5 are 2.88 g/cm³ and 3.15 g/cm³ respectively.

2.1.2 Mix proportion
GGBFS content varied from 0% up to 100% by weight of Portland cement. Two different water/powder ratio (w/p=0.3 and w/p=0.4) were tested.

2.2 Experiments
2.2.1 Isothermal hydration tests
The rates of heat evolution of the mixes were measured in a Thermometric isothermal conduction calorimeter (TEM Air 314), using 10 g samples and appropriate amounts of mixing water. Measurement of the rate of heat evolution $q$ (in J/g) proceeds continuously starting immediately after water addition.

2.2.2 SEM image observation
In the experiments, the distribution of the phases (the capillary pore, CSH gel, CH, blast furnace slag and unhydrated cement) were identified by using Scanning Electron microscopy (SEM) image analysis. In order to obtain high quality images, the samples were prepared carefully, this including epoxy impregnation, cutting, grinding (on the middle-speed lap wheel with p320, p500 and p1200 sand papers) and polishing (on a lap wheel with 6, 3, 1, and 0.25 µm diamond pastes for about 2 minutes each). The images are obtained using a BSE detector in water vapour mode. In order to get a high contrast image for image analysis, a low acceleration voltage of about 20 kV was used. The physical size of the region in each image is 263 µm in length and 186 µm in width when a magnification of 500X is used. The image size is 1728×1027 pixels, so the resolution is 0.152 µm per pixel. More details can be found in [4].

3. RESULTS
3.1 Isothermal conducted calorimetric test
The results of the rate of heat evolution at first 50 hours are plotted in Figure 2. It can be observed that two different mixtures show very similar pattern. The shoulder of the first peak becomes more and more wide with the increase of the GGBSF content and moves to earlier times as the GGBFS content is increased. The shoulder is attributed to the hydration of the slag component, resulting from the liberation of CH from the hydration of alite [5-6]. Only the samples with 90% GGBFS shows a second peak after the first peak of heat release at early time around 5 hours, this agrees with the experiments published by [5-7]. Pure GGBSF paste almost does not have heat release. This is due to the absence of alkali in the fresh pure GGBSF paste solution.

The cumulative heat release of mixes at first 90 hours are plotted in Figure 3. If comparing the samples with 100% of GGBFS and 90% of GGBFS, it can be found that only 10% of cement can activate the GGBFS very much. Calculations show that 75% of the heat was produced by GGBFS in both mixtures of w/c 0.3 and w/c 0.4.

It was assumed that the hydration of the Portland cement fraction in GGBFS/Portland cement blends remain essentially independent of the slag/cement ratio, then by subtracting a proportion neat Portland cement contribution from the total heat evolved, it is possible to get
an indication of the progress of the hydration of the slag fraction. Figure 4 is a plot of the cumulative heat release from the GGBFS fraction against GGBFS content. The values of the two mixtures are similar to each of the GGBFS fraction studies, indicating similar reaction progress, independent of the quantity of cement content. From the plot, it can also be found that a dramatic decrease of heat release from GGBFS occurs from 50% to 90%.

Figure 2: Rate of the heat evolution for the mixtures of w/p=0.4 and w/p=0.3 with different GGBFS content.

Figure 3: Cumulative heat release for the mixtures of w/p=0.4 and w/p=0.3 with different GGBFS content.
3.2 SEM observation results

3.2.1 Morphology
Backscatter images of two mixes with 30% and 50% GGBFS content are shown in Figure 5 and Figure 6. The addition of GGBFS changes the microstructure much compared with the Portland cement paste.

Figure 5: BSE image of sample with w/p = 0.40, 30% and 50% GGBFS.

Figure 6: BSE image of sample with w/p = 0.40, 30% and 50% GGBFS.
From Figures 5-7, a porous gap around 1 μm can be found between unhydrated GGBFS particles and matrix. This differs from the observation of pure Portland cement paste, where a dense hydration product forms around the unhydrated cement particles [8-10]. All images show that there are no dense products found from the hydration of GGBFS. From EDXA analysis, the hydration product around GGBFS is almost the same as the hydration product around unhydrated cement particles. This suggests that the hydration product of GGBFS forms so call lower density CSH gel [8-10]. The dense CSH gel normally formed around unhydrated cement is also not present clearly in the Portland cement/slag hydration system. This is clearer from the high magnification image in Figure 7.

Less hydration products of Ca(OH)₂ can be found near the unhydrated GGBFS particles. This can be explained by GGBFS consuming most of the OH⁻ ions.

![Figure 7: The morphology of hydration system of sample with w/p =0.30 with 50% GGBFS at different magnification. (left: X = 1000, X: magnification = 2000).](image)

### 3.2.2 Phase distribution and degree of hydration

The phase distribution (pore, C-S-H, CH, undrated slag and unhydreted cement) of two mixtures with 30% and 50% of GGBFS content were analyzed from backscatter scanning electron microscopy images. The results are listed in Table 2. The results are the average value of a total number of 12 frame images, captured for each sample in order to guarantee a 95% degree of confidence [4].

<table>
<thead>
<tr>
<th></th>
<th>w/c</th>
<th>pore</th>
<th>CSH</th>
<th>CH</th>
<th>slag</th>
<th>cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%GGBFS w/p0.3</td>
<td>0.38</td>
<td>17.63</td>
<td>60.38</td>
<td>5.88</td>
<td>8.34</td>
<td>7.88</td>
</tr>
<tr>
<td>50%GGBFS w/p0.3</td>
<td>0.46</td>
<td>17.69</td>
<td>56.56</td>
<td>5.13</td>
<td>15.34</td>
<td>5.14</td>
</tr>
<tr>
<td>30%GGBFS w/p0.4</td>
<td>0.49</td>
<td>20.23</td>
<td>54.68</td>
<td>17.25</td>
<td>4.64</td>
<td>3.14</td>
</tr>
<tr>
<td>50%GGBFS w/p0.4</td>
<td>0.57</td>
<td>16.31</td>
<td>58.56</td>
<td>11.01</td>
<td>10.60</td>
<td>3.43</td>
</tr>
</tbody>
</table>

From the analysis of phase distribution, it is possible to calculate the degree of hydration $\alpha(t)$ [-] of the individual pozzolanic materials from the volume of the remaining unhydrous pozzolanic material. The individual degree of hydration is the ratio of the volume of pozzolanic material that has reacted at time $t$ relative to the original volume of pozzolanic material.
Similarly, the overall degree of hydration of the blended cement system can be defined as the ratio of the total volume of pozzolanic materials that have reacted at time $t$ relative to the original volume of pozzolanic materials:

$$\alpha_{(t)\text{overall}} = \frac{V_{(t=0)\text{total volume of individual pozzolanic materials at } t=0} - V_{(t)\text{total volume of unhydrous pozzolanic materials at time } t}}{V_{(0)\text{total volume of individual pozzolanic materials at } t=0}}$$  \(2\) 

The total volume of individual pozzolanic material can be obtained according to the w/p ratio and the ratio of blended materials. The calculation results are listed in table 3.

### Table 3. Degree of hydration of individual components at curing age of 3 months

<table>
<thead>
<tr>
<th></th>
<th>slag</th>
<th>cement</th>
<th></th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>w/c</td>
<td>t = 0</td>
<td>t = 3 month</td>
<td>Degree ofhydration</td>
<td>t = 0</td>
<td>t = 3 month</td>
<td>Degree ofhydration</td>
<td>Overall degree ofhydration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30%GGBFS w/p0.3</td>
<td>0.42</td>
<td>16.63</td>
<td>0.50</td>
<td>35.48</td>
<td>7.88</td>
<td>0.78</td>
<td>0.68874</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50%GGBFS w/p0.3</td>
<td>0.60</td>
<td>27.46</td>
<td>0.44</td>
<td>25.1</td>
<td>5.14</td>
<td>0.80</td>
<td>0.61035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30%GGBFS w/p0.4</td>
<td>0.57</td>
<td>14.34</td>
<td>0.68</td>
<td>30.59</td>
<td>3.14</td>
<td>0.90</td>
<td>0.82684</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50%GGBFS w/p0.4</td>
<td>0.80</td>
<td>23.71</td>
<td>0.55</td>
<td>21.67</td>
<td>3.43</td>
<td>0.84</td>
<td>0.69083</td>
<td></td>
<td></td>
</tr>
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</table>

From table 2 and table 3, it can be seen that the sample with w/p 0.3 GGBFS produced more CSH than others. After 3 month curing, only 40% to 70% of GGBFS was hydrated. However, the cement shows a much high degree of hydration, at least 80% of cement was hydrated. Sample with w/p 0.4, 30% of GGBFS content shows highest hydration degree. 90% of cement and 68% of GGBFS were hydrated. The overall degree of hydration reaches to 80%. This is due to the high w/c ratio (0.57) and less GGBSF content. The sample with high w/c provides sufficient water for cement hydration, the result of high degree of cement hydration also provide more OH⁻ ion for GGBFS hydration.

The overall degree of hydration is different even if the samples have the same w/p ratio. High GGBFS content samples show a lower overall degree of hydration. This is in agreement with the heat release curve as shown in Figure 3.

### 4. CONCLUSIONS

With this research, the hydration and the microstructure of Portland cement blended with blast furnace slag was investigated. Following conclusions can be drawn:

1. Isothermal conducted calorimetric test shows that only 10% of cement is sufficiently already activate the reaction of the GGBFS very much. The chemical reactions of GGBFS are independent of the quantity of cement content.
2. The microstructure of Portland cement blended with blast furnace slag is different than that of Portland cement paste. A porous gap about 1 μm can be found between
unhydrated GGBFS particles and matrix. No dense products can be found from the hydration of GGBFS.

3. Dense C-S-H gel is not present clearly in Portland cement blended with GGBFS system.

4. The degree of hydration of blended cement systems and the degree of hydration of each individual phase can be examined from the phase percentage of each individual component. Through this method, it was found that the hydration of Portland cement in the blended system are much high than that of pure Portland cement paste. The degree of hydration of GGBFS is much lower than the overall degree of hydration of blended system.

5. From this paper it was confirmed that blending of Portland cement with GGBFS, the hydration and the microstructure can be changed.

ACKNOWLEDGEMENTS

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REFERENCES