Effect of Alkali on the Hydration of Blast Furnace Slag in the Presence of Calcium Hydroxide

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Abstract
Model systems containing blast furnace slag (BFS) and calcium hydroxide (CH) were used to gain insights into the hydration of BFS and the interaction between BFS and CH. The effect of alkali, sodium hydroxide (NaOH) and water glass (sodium silicate), on hydration rate and product stoichiometry was studied. Samples were hydrated at 30, 40 and 50 °C for between 1 and 32 d. The effect of alkali was studied by comparing samples hydrated with pure water, .1, 1 and 2 M sodium hydroxide and 3 wt% waterglass (3 wt% Na2O equivalents on a total solids basis). Thermal analysis was used to determine the extent of conversion of the CH and quantitative energy dispersive spectroscopy (EDS) was used to determine the chemical composition of various phases. The presence of NaOH was found to retard (slow) early age hydration rates. A number of possible mechanisms are considered and explored including suppression of Ca⁺² concentration due to the common ion effect, modification of the Ca/Si ratio in the hydration product and changes in the water content of the hydrate gel. Evidence in support of all three mechanisms was found although some appear to be time dependent. At early ages the Ca/Si ratio appears to vary with solution molarity, while at later ages it does not. TGA/DTG analysis suggest that the gel phase may evolve differently in the presence of strong alkali concentrations as evident by the thermal stability of the apparent gel. Gel formed in strong alkali solution also appears to imbibite more water.

1. Introduction
More than 21 million tons of BFS are produced in the United States each year [1]. The composition of this by-product of steel making varies considerably, however, the major components are MgO, Al₂O₃, SiO₂, and CaO. Water-cooled slag is routinely blended with cement. The concrete made this way has properties similar to that made with pure Portland cement but at a lower cost per unit volume. Replacement of a portion of the cement with BFS often results in lower early strengths. The strength of blends at ages of 3 to 6 months formed by replacing up to 20 % BFS, however, often exceeds the strength of pure Portland cement concrete. None-the-less, variability in slag composition, the restrictiveness of some specifications, the inadequacy of test methods and the need to develop additional durability and engineering performance data limit utilization of BFS in the United States.

2. Literature
A considerable body of literature exists on the hydration of blast furnace slag with Portland cement. It is generally agreed that the C₆S₇MₓAl glass in slag, reacts with water and by-product
CH from Portland cement hydration to form a C-S-H gel similar to that formed when clinker phases hydrate [1]. The slag derived C-S-H gel in hydrate rims surrounding unreacted slag particles usually has a lower C/S ratio than that typical of clinker hydration [2]. The slag derived gel also contains A in about the same proportions found in hydrated ordinary Portland cement and the M fraction of the slag ends up forming a hydrotalcite-like phase (M₆ACH₁₂ with M₆ACH₁₂ is hydrotalcite) [1].

Surprisingly few publications have investigated the reaction between BFS and CH. Among these is the 1974 work of Abo-El-Enein, et al. [3] who investigated the unactivated reaction between slag and CH in an 80% slag/20% CH mixture at 20 °C between 6 hours and 180 days. More recently, Richardson et al. [4] determined the Ca/Si ratio in the C-S-H gel product for model BFS/CH systems. SEM and TGA were used to establish reaction stoichiometries by independent methods from which they proposed the following composite reaction stoichiometry:

\[
C_{7.88}S_{7.39}M_{3}A + 2.6 \text{ CH} + b \text{ H} \rightarrow 7.39 C_{1.42}SH_{m}A_{0.046} + 0.66 M_{4.6}AH_{d}
\]

Richardson et al. [3] also compared the stoichiometry of the slag/CH reaction with slag/Portland cement and found that the basic features appeared similar. Model systems containing 80% slag/20% CH and 70% Portland cement/30% slag were studied at 35 °C for 32 d. They found that the C-S-H gel formed around the slag particles had Ca/Si ratio of 1.3 to 1.4 for both the slag/CH and slag/cement systems. The gel composition, however, varied with regard to where in the microstructure the C-S-H formed, although, the C-S-H gel was found to be nominally equivalent for slag hydration in the CH system compared to slag hydration in the presence of Portland cement.

Biernacki et al. [5] investigated the kinetics of slag hydration with calcium hydroxide. Using the kinetic model developed by Knudsen [6], they found activation energies of 14.5, 17.9, and 22.6 kJ/mol for three different slag/CH ratios hydrated for between 0 and 32 d at temperatures between 15 °C and 50 °C. They concluded that CH substantially activates the hydration of slag and found no appreciable effect of alkali in a .1 M NaOH solution. Upon analysis of data presented by Battagin [7] for slag/Portland cement hydration, they also found that the rate and activation energy for slag hydration was nominally independent of the system, Portland cement or CH when 20% CH was present in the starting mixture. Battagin hydrated mixtures of 50% slag/50% high early strength Portland cement at temperatures between 23 and 80 °C. He determined the fraction of slag reacted using a selective dissolution method [8] and presented the descriptive results without formal kinetic analysis.

Song [9] investigated the NaOH activated slag hydration process. She found that the maximum rate of heat evolution increased with solution molarity and the length of the induction period decreased, both suggesting that NaOH activates BFS hydration. Fernandez-Jimenez and Puertas [10] explored the effect of waterglass (sodium silicate solution) on slag hydration. For alkali systems with an effective Na₂O content between 3 and 5 wt. %, they found a complex behavior wherein at constant temperature, the rate of hydration increased with increasing alkali content up to a point and then decreased again. The optimal concentration, however, was a function of temperature and could only be approximated from their data.

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3. Experimental

3.1 Materials

Type 1 Portland cement and ground granulated blast furnace slag. Holcim Ltd. were used, the composition of which can be found elsewhere [4]. Waterglass (sodium silicate solution) and sodium hydroxide were used as activators. The concentrations of sodium hydroxide solutions used were 0.1, 1, and 2M 0.15 corresponding to 1.5 and 3.0 wt % Na₂O equivalents respectively on a cement basis. Three wt % Na₂O equivalents on a cement basis were used for waterglass cases. Waterglass is a sodium silicate solution containing 29.2% SiO₂, 9.10% Na₂O and 61.7% water by weight. The as received waterglass was diluted and NaOH added to obtain the desired solution concentrations. Solutions containing the desired activator concentrations were prepared in a CO₂ free glove box, Table 1. A SiO₂ / Na₂O ratio of 1.55 was used for the waterglass solutions.

Table 1. Activators used.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Waterglass (wt %)</th>
<th>NaOH (wt %)</th>
<th>Water (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.0</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td>0.1 M NaOH (0.15 % Na₂O)</td>
<td>0.0</td>
<td>0.39</td>
<td>99.61</td>
</tr>
<tr>
<td>1 M NaOH (1.5 % Na₂O)</td>
<td>0.0</td>
<td>3.9</td>
<td>96.1</td>
</tr>
<tr>
<td>2 M NaOH (3.0 % Na₂O)</td>
<td>0.0</td>
<td>7.8</td>
<td>92.2</td>
</tr>
<tr>
<td>Waterglass (3 % Na₂O)</td>
<td>31.84</td>
<td>4.00</td>
<td>64.16</td>
</tr>
</tbody>
</table>

3.2 Sample Hydration

BFS and CH were mixed together in a mass ratio of 80:20. Since CH reacts with carbon dioxide that is present in the atmosphere to form calcium carbonate, the slag and CH were mixed in a glove box purged with nitrogen. Pastes were then formed by combining the solids and the solutions at a liquid to solid ratio of 0.5. The pastes were placed in sealed vials and submerged in a water bath at a temperature of 30, 40 or 50 °C and left to react for 1, 2, 4, 8, 16 or 32 days. After this duration, the samples were taken out of the water bath, crushed to smaller pieces, and dried for 24 hours under vacuum at 105 °C. The dried samples were stored in glass tubes with screw caps in a desiccator. Table 2 summarizes the experimental matrix performed for the activated and the unactivated solutions.

Table 2 Experimental matrix

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>16</th>
<th>32</th>
</tr>
</thead>
<tbody>
<tr>
<td>30, 40, 50 Activated</td>
<td>0.1 M +BFS + CH</td>
<td>0.1 M +BFS + CH</td>
<td>0.1 M +BFS + CH</td>
<td>0.1 M +BFS + CH</td>
<td>0.1 M +BFS + CH</td>
<td>0.1 M +BFS + CH</td>
</tr>
<tr>
<td>30, 40, 50 Activated</td>
<td>1 M +BFS + CH</td>
<td>1 M +BFS + CH</td>
<td>1 M +BFS + CH</td>
<td>1 M +BFS + CH</td>
<td>1 M +BFS + CH</td>
<td>1 M +BFS + CH</td>
</tr>
<tr>
<td>30, 40, 50 Activated</td>
<td>2M +BFS + CH</td>
<td>2M +BFS + CH</td>
<td>2M +BFS + CH</td>
<td>2M +BFS + CH</td>
<td>2M +BFS + CH</td>
<td>2M +BFS + CH</td>
</tr>
<tr>
<td>30, 40, 50 Activated</td>
<td>3 % waterglass +BFS + CH</td>
<td>3 % waterglass +BFS + CH</td>
<td>3 % waterglass +BFS + CH</td>
<td>3 % waterglass +BFS + CH</td>
<td>3 % waterglass +BFS + CH</td>
<td>3 % waterglass +BFS + CH</td>
</tr>
<tr>
<td>30, 40, 50 Unactivated</td>
<td>water +BFS + CH</td>
<td>water +BFS + CH</td>
<td>water +BFS + CH</td>
<td>water +BFS + CH</td>
<td>water +BFS + CH</td>
<td>water +BFS + CH</td>
</tr>
</tbody>
</table>

3.3 TGA Procedures

The samples were analyzed using TGA. Samples were heated to a temperature of 105 °C and held isothermal for one hour and then heated to 1000 °C and held for 15 minutes. The heating rate was 10 °C/min. The TGA was purged with nitrogen at 10 sccm.
3.4 ESEM Imaging and Chemical Microanalysis using EDS

15 to 20 flakes of the hydrated materials were crushed to form a coarse powder. The coarse powder was then mixed with resin and hardener on a glass plate until a dense viscous paste was formed. A thin layer (about 3 to 4 mm) of paste was placed in the bottom of a mold. The resin layer was degassed in a vacuum chamber for about 20 minutes and allowed to cure on the bench top overnight. Additional resin was placed atop the set film and allowed to fully cure. After curing, the mold was ground and polished using standard methods. Fragile porous partially hydrated samples prepared by this technique were well infiltrated by the resin and could be polished adequately.

Samples were analyzed using ESEM. A backscattered image was first obtained of the desired area. Compositional data were then obtained using energy dispersive spectroscopy (EDS). Quantitative spot compositions for Si, Ca, Fe, Mg, K, S and Al on an oxide equivalent weight basis were developed. The following microscope parameters were used: electron accelerating voltage of 20 kV, spot size of 4.4 mm, dead time of 35 counts/s, working distance of 10 mm and partial pressure of water vapor of 0.80 torr. Standard-based ZAF calibration of EDS was performed using the known BFS composition for standardization [4].

4. Results and Discussion

The mass of CH consumed was determined for samples reacted with different concentration activators at different temperatures and times. The amount of CH consumed was calculated using the procedure described elsewhere by Biernacki, et al. [11]. TGA overlays for different temperatures and different concentration of activator were used to analyze and compare treatments. Solubility of CH and the “common ion” effect is described and used to interpret the kinetic behavior of the BFS/CH/NaOH system. Based on the results obtained, insights on the influence of activators in BFS systems were obtained.

The extent of CH reaction, $\alpha$, where $\alpha=$amount of CH reacted/amount CH initially, was plotted as a function of time for various conditions including activator concentration, temperature and activator type. Figures 1a through c illustrate the effect of activator type and concentration at the three different temperatures 30, 40 and 50 °C respectively. Increasing the concentration of NaOH from zero to 2 M clearly inhibits reaction at all temperatures while waterglass appears to dramatically accelerate CH consumption. The effect of NaOH, however, is not linear in that the extent of reaction does not decrease proportional to the increase in NaOH solution strength. This is clearly illustrated by Figures 1b and c wherein the extent of reactions are virtually the same for both 1 M and 2 M NaOH cases at both 40 and 50 °C while for .1 M they are less than for pure water. This effect is also a function of temperature as seen by distinctly different behavior at 30 °C. At this lowest temperature, the extents of reaction continue to decrease with increasing NaOH concentration, Figure 1a.

When grouped by temperature, four figures are produced, one for each of four treatments, water, .1 M, 1 M and 2 M NaOH, Figures 2a through d respectively. Waterglass is excluded from this analysis since only one temperature was studied. When water is used as the mix solution, the rate of reaction appears to increase with temperature, as expected and demonstrated by increasing extents of reaction with increasing temperature, Figure 1a. As the concentration of NaOH increases, however, the temperature sensitivity decreases. Temperature sensitivity appears to decrease in the order pure water to .1 M to 1 M solution and then increase somewhat for 2 M NaOH solution. This suggests a possible minimum in temperature sensitivity as a function of NaOH concentration.
A close examination of the thermogravimetric analysis (TGA) and differential thermalgravimetric (DTG) curves reveals a rather complex and possibly unexpected behavior. While TGA-based quantification of the CH remaining lead to the conclusion that NaOH inhibits CH consumption, Figures 1a through c and 2a through d, comparison of entire TGA curves reveals that the non-evaporable water content of hydrated slag/CH mixtures increases with increasing NaOH solution molarity, Figures 3a and b. Since the CH consumption decreases with increasing NaOH solution concentration, it would be expected that likewise, the amount of non-evaporable water would also decrease as solution concentration increases. Inspection of Figures 3a and b demonstrate that non-evaporable water, particularly between 105 and 375 °C, increases with increasing solution concentration. This leads to a number of possible explanations including: 1. the Ca/Si ratio of the CSH gel decreases as the solution molarity increases, 2. the hydrate products formed incorporate more water as the solution molarity increases, 3. different hydrates or an altered ratio of hydrates which incorporate more water and a lower Ca/Si ratio are formed as the solution molarity increases, and 4. some combination of these mechanisms.

The TGA/DTG curves suggest that increasing the NaOH solution molarity may increase the rate of formation of a high water-bearing hydrate having rapid thermal decomposition at about 325 °C after one day of hydration. While both the 0.1 M and water samples exhibit weight loss at this temperature, a distinct DTG peak at 325 °C is noted only for the 1 M and 2 M samples. As hydration age increases, however, similar features develop for the water and .1 M samples in support of a hypothesis that would suggest that higher NaOH concentrations promote the production of a high water-bearing hydrate, but that it is not a unique product. Furthermore, at very early ages, the position of the CH decomposition peak is shifted toward lower temperature as the NaOH solution molarity increases. This rather striking observation has several possible explanations. It is well known in the thermal analysis literature that mass transfer effects can alter the thermal decomposition of materials. Since the CH decomposed in these experiments is residual reagent and not CH formed as a hydration product (by-product) it is interesting that the presence of NaOH would alter the thermal decomposition. This observation suggests that it is likely the structure of the early-age hydration product forming on or near the CH surface that is affecting the subsequent decomposition. It has already been established that less CH is consumed and that at very early age the hydration products contain a larger proportion of water as the NaOH concentration increases. These observations are also consistent with a hydrate gel microstructure that would permit more rapid mass transfer and hence permit a more rapid thermal decomposition of CH at a lower temperature for samples processed with higher NaOH solution concentrations as observed. Even at .1 M NaOH the CH peak is somewhat shifted towards lower temperatures. The effect of NaOH, however, decreases with hydration age. By 32 days, the CH thermal decomposition temperature is indistinguishable as a function of NaOH solution molarity.

Microscopy-based energy dispersive spectroscopy was performed on a large number of spots for samples reacted for four and 32 days at 30 °C. The data was analyzed by plotting the Al/Ca vs Si/Ca ratios in the manner previously illustrated by Richardson, et al. [2], Richardson, et al. [4] and others, Figures 4a and b. Samples reacted in water were compared to samples reacted in 2 M NaOH and 3 wt % waterglass solution, Figures 4a and b respectively. The resulting plots produce a band of points scattered about a nominally straight line that represents the linear combination of phase compositions for CH+C-S-H gel and C-S-H gel+slag. At four days the composition of the 2 M and water materials appear to be nominally the same, however, the waterglass sample has a distinctly lower aluminum content in the C-S-H gel phase, Figure 4a. TGA data indicates that more than twice as much CH is rapidly consumed when waterglass is used as the activator. The extremely low Al content of the waterglass-based C-S-H gel suggests that at early ages, this gel may be incorporating silicate from the

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silicate-rich, aluminum-lean waterglass solution rather than silicate produced from the
dissociation and dissolution of slag which would presumably produce a more aluminum rich C-
S-H gel product.

By 32 days, however, the relative composition of the hydrated samples changes. 2 M NaOH
and waterglass are now virtually indistinguishable, while the water sample suggests a lower Al
containing C-S-H gel. This observation is consistent with a mechanism wherein the alkali-
based activators promote dissolution of aluminates and enable slightly higher aluminum
association in the C-S-H gel.

Finally, the rate of reaction appears to be a function of the Ca$^{2+}$ ion concentration since NaOH
suppresses the rate of reaction. At 30 °C, the Ca$^{2+}$ falls by a factor of roughly six when the
NaOH concentration is increased from zero to .1 M and by another factor of 1,800 when the
concentration is increased to 1 M. The observed change in reaction rate, however, does not
decrease proportional to the Ca$^{2+}$ concentration since increasing the NaOH molarity likely
increases the silicate ion concentration which in-part may serve to offset the reduced Ca$^{2+}$
presence.

The apparent reduced temperature sensitivity with increasing NaOH molarity, however, is
somewhat more difficult to explain, Figure 2a through d. While the solubility of CH decreases
with increasing temperature, this effect is countered, when pure water is used, by the
temperature effect on reaction rate producing a net increase in observed rate of CH
consumption, Figure 2a. As the NaOH concentration is increased, however, the net apparent
effect of temperature is virtually zero. At this time a mechanistic explanation is not available.

5. Conclusions
Waterglass appears to aggressively consume CH at very early ages. At ages as young as 4
days, waterglass produced C-S-H gel tends to have lower A contents. At later ages, both the
C/S and A content are indistinguishable from that of samples prepared with strong NaOH
solutions. The presence of NaOH inhibits the reaction between BFS and CH at ages between
zero and 32 days. NaOH, however, appears to promote the formation of an early age high
water-bearing phase as suggested by TGA/DTG that has not been identified, but is not unique.
Although the water content of the early age hydrate of NaOH activated samples appears to be
different, the C-S-H gel C/S ratio does not. By 32 days, however, samples reacted in water
display a lower gel A content than either samples reacted with NaOH or waterglass.

6. Acknowledgements
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Figure 1. Extent of CH reaction as a function of time for various activator systems: (a) at 30 °C, (b) at 40 °C and (c) at 50 °C.
Figure 2. Extent of CH reaction as a function of time at various temperatures: (a) for water , (b) .1 M NaOH (c) 1 M NaOH and (d) 2 M NaOH.
Figure 3a. TGA and DTG curves for samples reacted for 1 d with different NaOH solution concentrations.
Figure 3b. TGA and DTG curves for samples reacted for 32 d with different NaOH solution concentrations.
Figure 4a. EDS spot analysis for samples reacted at 30 °C for four days.
Figure 4b. EDS spot analysis for samples reacted at 30 °C for 32 days.
7. References


