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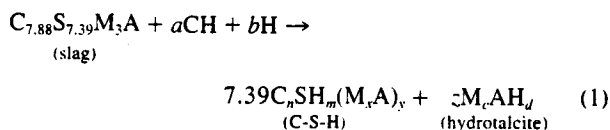
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The stoichiometry of the reaction between ground granulated blast furnace slag (GGBFS) having an empirical formula of $C_{7.88}S_{7.39}M_3A$ and calcium hydroxide (CH) was investigated. Scanning electron microscopy (SEM) was used to determine the slag consumption as well as the Ca/Si ratio in calcium silicate hydrate (C-S-H) products. A tentative stoichiometric ratio of 2.6 mol of CH consumed per mole of slag reacted was determined using two methods. By combining consumption data determined separately for slag and CH a molar stoichiometry of 2.79 was found. Similarly, by directly determining the Ca/Si ratio in the C-S-H gel product, a range for the molar stoichiometry between 1.65 and 3.42 was found. Finally, a comparison of the stoichiometry of the slag/CH reaction was made with slag/portland cement hydration. The basic features of both appear similar. In the C-S-H gel around slag grains, a calcium-to-silica ratio of 1.3 to 1.4 was found for both slag/CH and slag/cement systems.

I. Introduction

GROUND granulated blast furnace slag (GGBFS) is a glassy amorphous waste material formed as a byproduct from the production of steel and iron. GGBFS has successfully been used with portland cement to produce cement blends that are more economical, more environmentally friendly, and, in some cases, have performance advantages.[1] However, a thorough understanding of the hydration mechanism and kinetics has not been fully developed.

GGBFS from Holnam, Inc.,* containing CaO (C), SiO_2 (S), MgO (M), and Al_2O_3 (A) in roughly 7.88:7.39:3:1 molar proportions was used to study the hydration process in the presence of calcium hydroxide (CH). A proposed chemical reaction for the slag/CH reaction is as follows:

$$C_{7.88}S_{7.39}M_3A + aCH + bH \rightarrow$$
$$\text{(slag)}$$

$$7.39C_nSH_m(M_xA)_y + cM_cAH_d \quad (1)$$
$$\text{(C-S-H)} \qquad\qquad \text{(hydrotalcite)}$$

where $a = 7.39n - 7.88$, $b = 7.39(m - n) + 7.88 + dz$, $y = (1 - z)/7.39$, $z = (3 - x)/(c - x)$, and if $x > 3$ then $c < 3$ or $x < 3$ then $c > x$.

The name "hydrotalcite" is used here generically to describe a hydrotalcite-type phase with the generic empirical formula $M_cA\bar{C}_\alpha H_d$ wherein hydrotalcite is the specific mineral $[Mg_{0.75}Al_{0.25}(OH)_2](CO_3)_{0.125}(H_2O)_{0.5}$ or $M_6A\bar{C}H_{12}$. The *carbonate* ($\bar{C} = CO_2$) content is omitted in Eq. (1) and subsequently for simplicity since the amount of substitution is not known. Similarly, the notation C-S-H indicates a C-S-H phase that may or may not contain substituted M and A. Where chemical compositions relate to a mixture of C-S-H and one or more other phases that cannot be individually discerned by conventional X-ray microanalysis, the term "C-S-H gel" will be used. Finally, while prior research has shown that M likely does not enter the C-S-H phase to any significant extent, it was included a priori so that a comprehensive and unbiased analysis for the slag/CH system could be made.

The stoichiometry of reaction (1) was studied and a comparison of this reaction to slag hydration in the presence of portland cement was made. Analyses done on portland cement/slag blends and on alkali activated and unactivated slag were used as controls for comparison since considerable prior data exist for these systems. Thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and X-ray diffraction (XRD) were the primary analytical methods used.

II. Literature Review

No reports could be found on the reaction of slag in the sole presence of calcium hydroxide. The stoichiometry of slag hydration in the presence of portland cement, however, has been studied by a number of investigators. The principal findings include formation of hydration rims around slag particles,[2] reduction of the Ca/Si ratio in the bulk C-S-H gel,[3] likely formation of hydrotalcite ($M_{4.06-6.32}AH_x$),[4] partial accommodation of M and A within the micro- or nanostructure of the C-S-H phase[5] and uptake of sulfate ($\bar{S}$) by Afm phases.[6] Katoite ($C_3AS_\alpha H_\beta$, $\alpha < 1.5$) has also been suggested as a slag product, but is less documented than the former mentioned species.

Taylor[5] states that the hydration products of slag are principally the same as that of ordinary portland cement (OPC), although the C-S-H formed in slag-cements has a lower Ca/Si ratio (1.55) than C-S-H formed in OPC (1.7). Using oxide mass percents determined by Pietersen and Bijen,[7] a 1.4 Ca/Si ratio was computed for C-S-H formed directly around slag grains. The following rules, suggested by Taylor,[5] were used in the present study to propose reaction (1):

(1) Assume the slag Mg enters a hydrotalcite-type phase with an assumed Mg/Al ratio, e.g., 2.5.

(2) Assume that the slag SiO_2 (S) and Al_2O_3 (A) enter a $C_xSH_yA_z$ phase for which x and z must be assumed, e.g., Ca/Si = 1.55, Al/Ca = 0.09.

(3) Assume that the remaining A enters an Afm phase along with the S^{2-} released from the slag.

(4) Consume CH and reduce the Ca/Si ratio in the bulk C-S-H produced as the result of clinker hydration.

While a number of investigators have observed or proposed hydrotalcite as a Mg-bearing product of slag hydration, there are varied findings concerning the microstructure of the product. A pure form of hydrotalcite has not been observed although the presence of hydrotalcite has been verified by numerous researchers.[3,8,9,10] Prior research indicates that the Mg and Al form a hydrotalcite phase that exists as an intimate microscale mixture within the C-S-H gel with at least some of the remaining Al from the slag being directly incorporated into the nanostructure of the C-S-H phase wherein Al may be replacing Si.[11,12] Wang and Scrivener[13] report that hydrotalcite forms around the rims of the hydrate product. Richardson *et al.*[12] state that the inner C-S-H gel products formed around slag grains in cement systems have higher concentrations of Mg and Al than the outer C-S-H gel. Song[14] reports the formation of hydrotalcite, but only found evidence by XRD at high degrees of hydration for alkali-activated systems using 1.0*M* NaOH solution (pH $\approx$14).

III. Experimental Procedure

(1) Materials and Sample Preparation

Slag provided by Holnam, Inc., and one source of reagent-grade CH from Mallinkrodt were used. Type I portland cement from Holnam, Inc., was also used. The chemical compositions for all solid reagents are given in Table I. All water used was boiled deionized water stored in glass jars. A 0.10*M* NaOH solution (pH $\approx$13.0) was used for preparation of NaOH-activated samples.

All samples prepared for TGA and SEM testing were mixed and sealed in 14 mL glass vials. Slag-to-CH mass ratios of 0/100, 80/20, 90/10, 95/5, and 100/0 and slag-to-cement ratios of 100/0, 30/70, and 0/100 were used. Slag/CH samples were reacted at 15°, 25°, 35°, and 50°C for between 0 and 32 days. Slag/cement samples were reacted at 35°C for 32 days. A water-to-solids mass ratio of 0.55 was used. All samples were mixed by hand in a

consistent manner. After mixing, samples were held at their respective temperatures in a water bath. To prevent carbonation reactions with CO_2 in the air, all materials were stored in a CO_2-free glove box in sealed containers and all sample preparations were performed within the glove box.

(2) Thermogravimetric Analysis (TGA)

Samples were heated in a platinum pan to 1000°C at 10°C/min with an isothermal hold of 45 min at 100°C. The furnace was purged at 50 mL/min with nitrogen to prevent carbonation and exposure to oxygen. The initial dried mass of solids was determined by using the stable mass after the isothermal time at 100°C, at which point virtually all of the evaporable water had been liberated.

To calculate the mass loss of CH, an approximation procedure, given by Taylor,[5] which utilizes leading and trailing derivative lines and mass loss curve inflection as the midpoint for estimation of the mass loss, was used. The nonevaporable water loss between 100° and 1000°C was determined by subtracting the water associated with CH from the total mass loss. A small correction was also made for the mass loss observed for the unhydrated slag. All mass losses were referenced to the final ignited mass.

(3) Scanning Electron Microscopy (SEM)

Hydrated samples were crushed using an isolated, hand-held piston[15] that produced small thin flakes. These flakes were immediately D-dried under a vacuum measuring less than 13.3 Pa (10^{-1} torr) for 8 h to remove any unbound water and to stop the hydration process. The flakes were then immersed in acrylic resin for 24 h and were then cured at 70°C, polished, and carbon coated for SEM backscattered electron analysis.

Typical SEM setup parameters were an accelerating voltage of 20 kV, a probe current of 5 nA, and a collection time of 30 to 45 s.

Table I. Composition of Various Solid Materials

	Slag (mass%)	Cement (mass%)		CH (mass%)
SiO_2	37.83	20.68	$Ca(OH)_2$	96.80
Al_2O_3	8.70	4.76	$CaCO_3$	2.60
Fe_2O_3	0.21	2.18	Cl	0.03
CaO	37.63	63.94	Fe	0.02
MgO	10.40	3.81	Mg and alkali as sulfates	0.70
SO_3	3.18	2.48	Sulfur compounds as SO_4	0.07
Na_2O	0.05	0.07	Heavy metals as Pb	0.0002
K_2O	0.42	0.65		
TiO_2	0.52	0.030		
P_2O_5	0.02	0.20		
Mn_2O_3	0.55	0.07		
SrO	0.04	0.05		
ZnO	0.01	0.03		
Loss on ignition	1.13	0.92 (gain)		
Total	100.13	99.21[+]		
Sulfide sulfur	1.15	0.002		
Sulfate ion as SO_3	0.22	2.47		
Total as SO_3	3.18	2.48		
Water-soluble alkalies				
$\quad Na_2O$	0.03	0.01		
$\quad K_2O$	0.02	0.36		
$\quad Na_2O$ equivalent	0.04	0.25		
Other parameters				
$\quad$ Blaine (m^2/kg)	582	387		
$\quad$ Specific gravity	2.87	NA		
$\quad$ Molecular weight[‡]	1167	NA		

[+]Not including loss on ignition. [‡]The slag molecular mass was normalized to the alumina content using the following calculation:

$$MW^{slag} = \sum_i \frac{x_i MW_i}{x_A}$$

where x_i = the mole fraction of oxide component, x_A = mole fraction of Al_2O_3.

Conditions varied as necessary to establish good images or EDS spectra collection. EDS spectra were quantified, using the slag as a calibration standard, the composition of which was previously determined using EDS and a traceable calibration standard.

SEM was also used to compute volume fractions of different phases.[16] By converting the volume fraction of slag in a reacted sample to mass of slag, the amount of slag consumed was determined by subtracting the amount of slag in the reacted material from the original amount of slag in the unreacted material. Extents of reaction for slag were thereby directly measured using SEM as well as indirectly computed (inferred) using TGA CH consumption data.

(4) X-ray Diffraction (XRD)

Samples were prepared for XRD using a conventional powder diffraction sample preparation technique with back-loaded cavity mounts. All samples were tested using 40 kV, 40 mA, steps between 0.02°/s to 0.04°/s, and 2θ values ranging from 10° to 75°.

IV. Results and Discussion

(1) Ca/Si Ratio in C-S-H and Stoichiometry of Reaction

The Ca/Si ratio of the C-S-H product for the slag/CH reaction was estimated by two independent methods. Blends containing 80% slag and 20% CH were reacted for 32 days at 35°C. EDS was used to directly measure the Ca/Si ratio. Spectra were collected at various locations in the hydrate phase and quantified as previously described. Table II summarizes the range of values found for an 80% slag/20% CH sample hydrated at 35°C for 32 days. On the average, the Ca/Si ratio around slag grains was found to be 1.29 with a standard deviation of 0.15 and 1.53 with a standard deviation of 0.16 in the paste. These values result in a range for the stoichiometric coefficient a between 1.65 and 3.43, i.e., for n = 1.29, $a = 7.39n - 7.88 = 1.65$.

CH and slag consumption provided another independent way of computing n and a. SEM X-ray maps were used to determine the amount of slag consumed and TGA was used to compute the amount of CH consumed. The two values were then combined to predict the stoichiometry of the C-S-H product and reaction. This method provided a bulk estimate of the parameters a and n for comparison to the local values computed above using EDS spot analysis.

Backscattered electron images and X-ray maps for Ca, Mg, and Si were collected at 500× magnification (Fig. 1). Ranges for the intensity values of different elements were found for the unreacted slag phase. These intensity ranges for Mg, Si, and Al for the slag phase were then used to identify and convert slag regions to white, leaving all other areas black. In this way, a binary (black and white) image was generated from a normal gray-scale backscattered electron image. The area fraction of the now white residual slag phase was computed. For the sample illustrated in Fig. 1, the residual slag phase calculated in this way was found to be 14.91%. This is equal to the volume fraction of the residual slag remaining in the sample. By knowing the original total volume of the sample and the specific gravity of all the original phases, the mass of slag remaining was determined. The amount of slag consumed was then

found by difference, the mass of slag remaining subtracted from the original mass of slag. Using the mass loss of CH over the temperature range from 370° to 450°C the amount of CH consumed was calculated using a material balance. For the 80% slag/20% CH sample reacted at 35°C for 32 days, 7.21 g of CH was consumed per 100 g of starting solids as determined by TGA. The stoichiometric coefficient a and the empirical formula coefficient n were then estimated to be 2.79 and 1.44, respectively, by combining the slag and CH consumption values. These values are in good agreement with the spot analysis ranges of 1.65 to 3.43 and 1.29 to 1.53 values for a and n, respectively, estimated using EDS data. Based on these results the stoichiometric coefficient a was estimated to be roughly 2.6 and the Ca/Si ratio roughly 1.42.

With the Ca/Si ratio in the C-S-H (n) and the molar stoichiometric coefficient for CH (a) defined, the remaining questions concern water consumption and the fates of Mg and Al in the reaction.

(2) Fate of Mg and Al

A series of experimental samples including activated and unactivated 80% slag/20% CH mixtures were prepared. Activated and unactivated 100% slag and 30% slag/70% portland cement were also prepared as controls. This series was analyzed using SEM/EDS so that various hydration environments could be compared. These samples were reacted for 32 days at 35°C. Since a considerable database for activated and unactivated slag and slag/cement systems already exists, such were used here as control benchmarks to ensure that the techniques and procedures used in this study were consistent with prior results for known systems. Only then could reliable comparisons be made for the results of the present slag/CH system.

The gross microstructure of the C-S-H gel in slag/CH systems forms hydration rims at the surface of the slag grains and little or no C-S-H gel is found precipitated elsewhere in the system (see Fig. 2). Similar hydration rims were also found in products formed from slag/cement systems (see Fig. 3). In comparison, the microstructure and chemistry of product formed from pure slag hydration are considerably different. Figure 4 illustrates that both alkali-activated (0.1M NaOH) and unactivated slag hydration produces what appears to be a finely distributed hydrate phase with Ca/Si ratio between 1.1 and 1.2 with the higher values found for the alkali-activated system. Richardson and Groves found similar results for alkali-activated 100% slag hydration.[17]

EDS spot analyses collected for the samples listed in Table II and the Ca, Mg, and Al contents quantified as described above were used to plot the Mg/Ca versus Al/Ca ratios, in the fashion described by Taylor[5] and others[3] (see Fig. 5). Plotting Mg/Ca versus Al/Ca parameterizes the stoichiometric relationship between Mg, Al, and Ca. Initially, all of the Mg and Al was assumed to appear in one of two forms, either $C_nSH_m(M_xA)_y$ or M_xAH_d, in the C-S-H or hydrotalcite, respectively. If these *phases* exist as an intimate microscale mixture with a local hydrotalcite molar composition f, then it can be shown that the slope of the Mg/Ca versus Al/Ca plot is equal to the Mg/Al ratio in the hydrotalcite and that Mg/Al = $c/2$. A plot of the Mg/Ca versus the Al/Ca ratio for the samples listed in Table II illustrates that the hydrotalcite M/A

Table II. Atomic Ratios for C-S-H Gel in Slag/CH and Slag/Cement Systems Hydrated at 35°C for 32 days

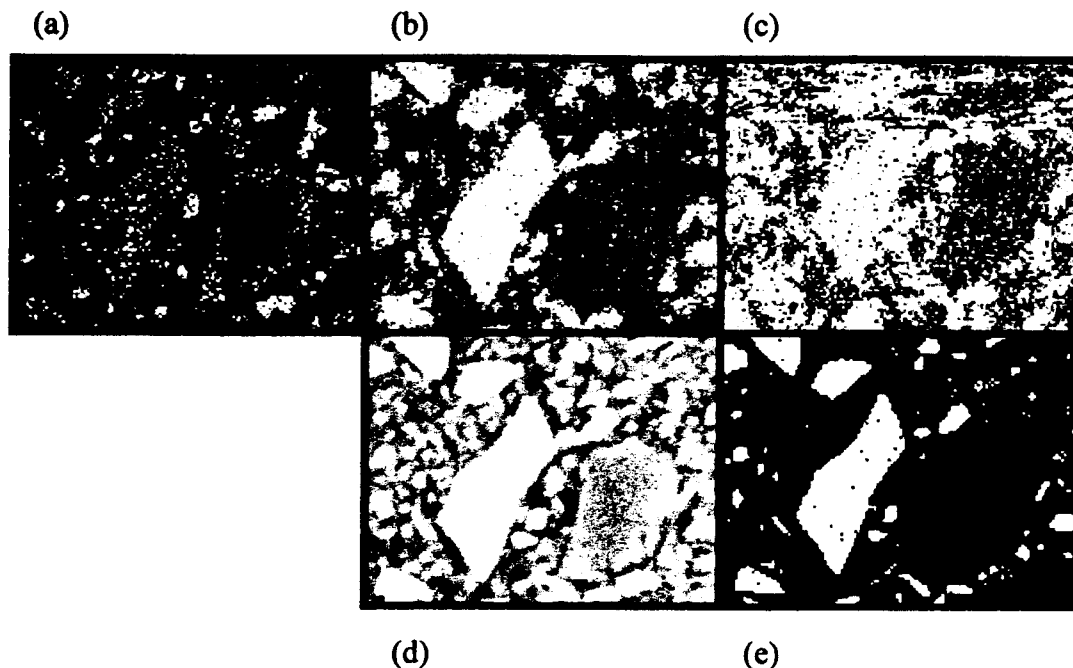| Sample	Mg/Ca	Al/Ca	Ca/Si	Number of points
Slag	0.34 (0.09)[†]	0.25 (0.05)[†]	1.07 (0.09)[†]	11
Alkali-activated slag	0.41 (0.09)	0.29 (0.06)	1.20 (0.29)	11
80% slag/20% CH				
Around slag grain	0.39 (0.16)	0.23 (0.04)	1.29 (0.15)	14
In paste	0.21 (0.04)	0.17 (0.03)	1.53 (0.16)	5
30% slag/70% cement				
Around slag grain	0.51 (0.43)	0.28 (0.18)	1.53 (0.23)	22
Around cement grain	0.08 (0.04)	0.08 (0.02)	1.67 (0.06)	5

[†] σ in parentheses.

Fig. 1. Element maps for an 80% slag/20% CH sample reacted at 35°C for 32 days: (a) Ca, (b) Si, (c) Mg, (d) backscattered, and (e) binary.
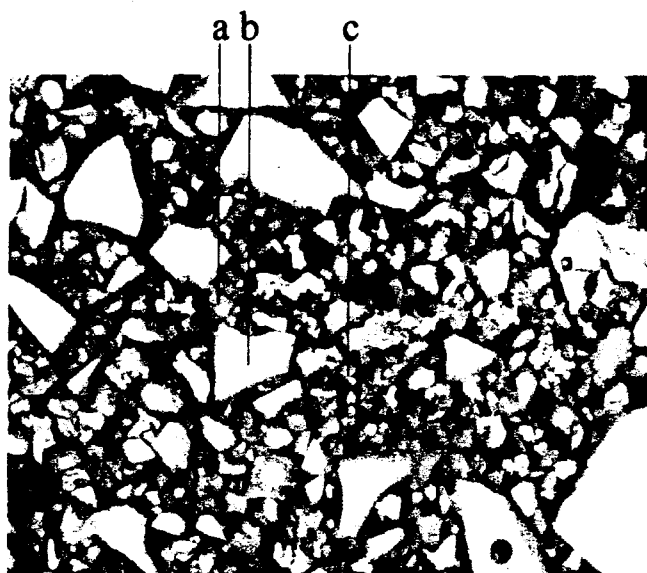

Fig. 2. Backscattered electron image for 80% slag/20% CH sample reacted at 35°C for 32 days showing location of EDS spot analysis: (a) hydration rim on slag particle, (b) unhydrated slag, and (c) fully hydrated slag.
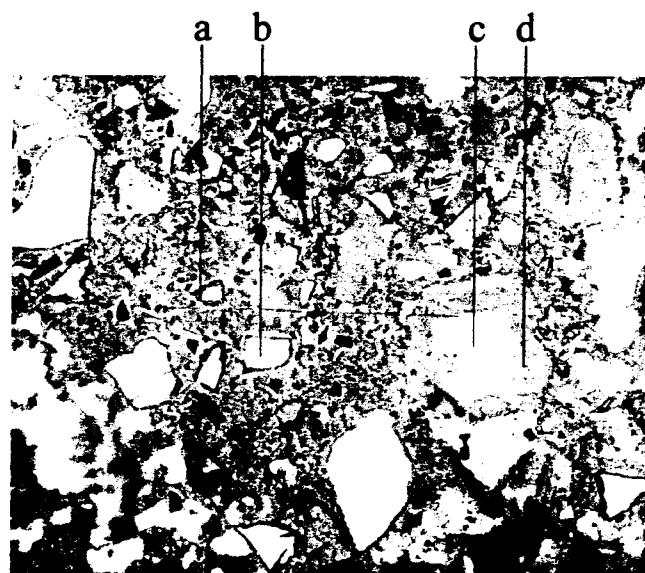

Fig. 3. Backscattered electron image for 30% slag/70% cement sample reacted at 35°C for 32 days showing location of EDS spot analysis: (a) hydration rim on slag particle, (b) unhydrated slag, (c) unhydrated clinker, and (d) hydation rim on clinker.

molar ratio, c, is nominally constant regardless of the environment in which the slag was hydrated, having a value of roughly 4.6 ($c = 2 \times 2.3 = 4.6$) when the Mg/Al ratio is 2.3. This Mg/Al ratio is well within the range reported by other investigators, 1.92 to 4.35, for hydrated slag/cement pastes.[3,13,17] These results suggest that the overall stoichiometry for slag hydration produces nominally the same form of hydrotalcite regardless of the system chemistry: activated, unactivated, portland cement blended, or in the presence of CH. X-ray diffraction evidence also supports these findings in that the same hydrotalcite phase was identified in both slag/CH and slag/cement samples. Hydrotalcite was identified by peaks at roughly 11.3°, 22.6°, and 39.3° 2θ. It is also notable that the basal peak has a pronounced low-angle tail extending to about 16°. A distinct monosulfate pattern identified by peaks at 20°, 30.5°, and

56.4° 2θ was found only in the slag/cement system, although the small amount of Al in the slag may account for the absence of these peaks. C-S-H at about 30° was pronounced in both patterns.

The value of x, the empirical formula constant for Mg in the C-S-H, was shown to be uniquely zero since the x-intercept, the Al/Ca ratio, is positive. This indicates that there is no Mg substitution in the C-S-H nanostructure since the Al substitution level is positive when the local Mg/Ca ratio falls to zero. This finding is expected since Mg is too small to be easily accommodated within the C-S-H structure. The Al/Ca ratio when the Mg/Ca ratio is zero was thus used to determine the empirical formula constant y where the x-intercept (from Fig. 5) = $2y/n$ = Al/Ca ratio in the C-S-H product. The Al/Ca ratio in the C-S-H product was found to be roughly 0.07 from which $y = 0.046$ was determined.
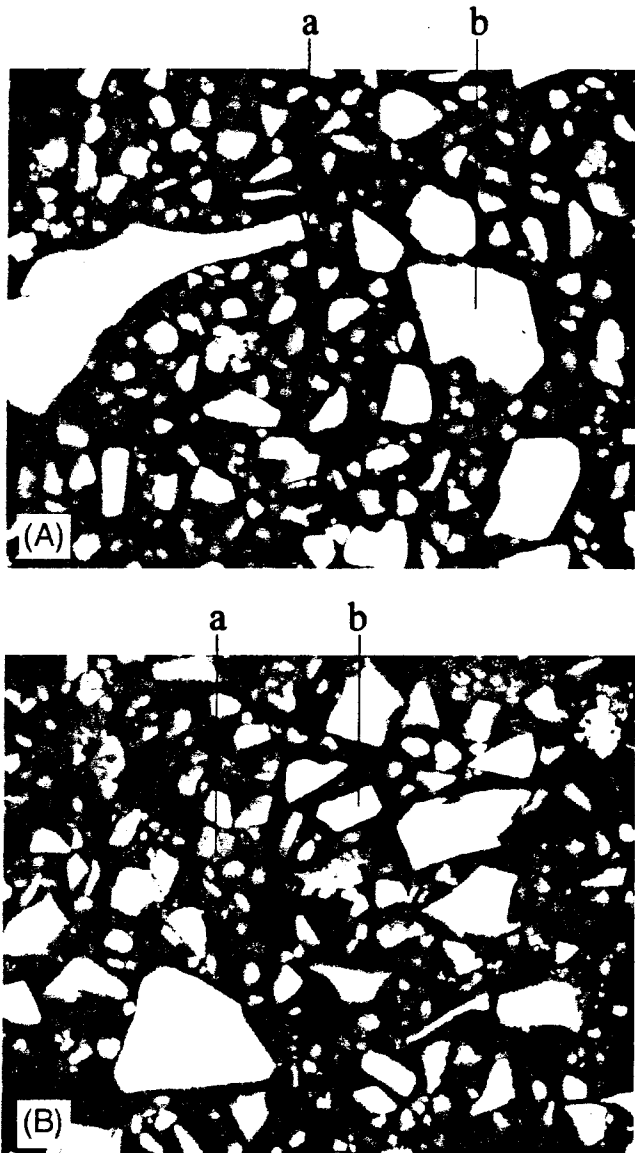
Fig. 4. (A) Backscattered electron image for 100% slag sample reacted at 35°C for 32 days: (a) hydration product and (b) unhydrated slag. (B) Backscattered electron image for 100% slag sample alkali activated with pH 13.0 NaOH solution reacted at 35°C for 32 days: (a) hydration product and (b) unhydrated slag.

Fig. 5. Mg/Ca versus Al/Ca atomic ratio spot analysis for samples reacted at 35°C for 32 days: (a) slag hydration, (b) alkali-activated slag hydration with pH 13.0 NaOH solution, (c) 80% slag/20% CH, (d) 30% slag/70% cement, and (e) Al/Ca = 0.068 + 0.434(Mg/Ca).

These values are in general agreement with results reported by Harrisson *et al.*, who found an Al/Ca ratio of roughly 0.09 for slag/cement pastes.[3]

The Al/Ca versus Si/Ca ratios for the same series of samples were also plotted (see Fig. 6). In this case, lines representing mixtures of CH + C-S-H, Afm + C-S-H, and C-S-H gel around slag grains are plotted along with the experimental results. This figure illustrates several important features that clearly distinguish the differences in C-S-H gel product when slag is hydrated in various environments. C-S-H gel product around slag grains is bounded by two lines representing C-S-H gel formed in systems containing a source of CH such as portland cement or added CH and C-S-H gel formed from pure hydrated slag and are designated as type I and type II, respectively. Data collected for the control portland cement/slag blends show the characteristic range of products defined by the CH + C-S-H and Afm + C-S-H lines, a Si/Ca ratio of about 0.62 (Ca/Si = 1.6), and an Al/Ca ratio of roughly 0.07. The experimental slag/CH systems have similar Si/Ca ratios, with Si/Ca values within a broad band between roughly 0.6 and 0.8 (1.25 ≤ Ca/Si ≤ 1.7). It is notable, however, that virtually no points from the slag/CH sample lie on the Afm +
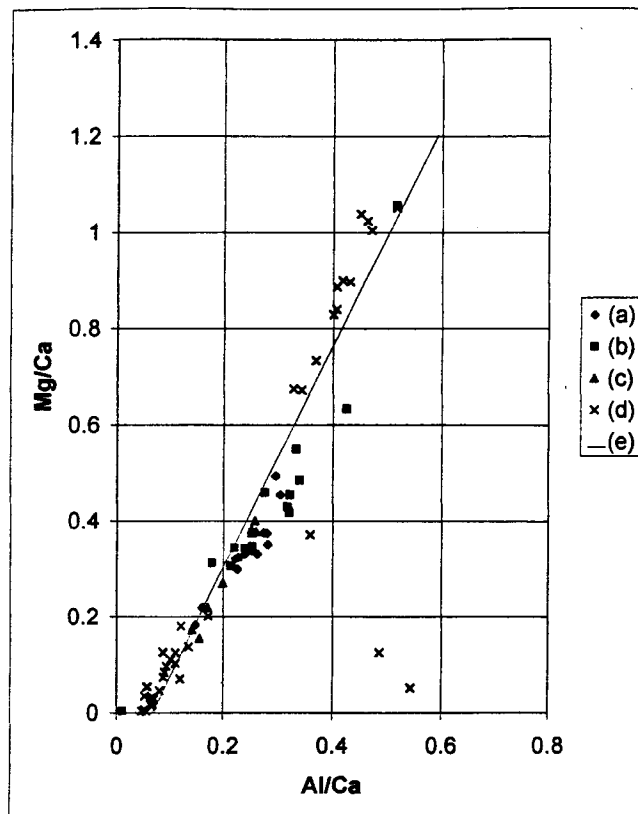
C-S-H line, suggesting that little or no Afm is present. Alkali-activated and unactivated slag control samples were found to have a considerably higher Si/Ca ratio of nominally 0.95 consistent with that reported by Richardson.[11]

The more recent work of Richardson (1999) suggests, however, that the Al/Ca content for slag and slag–cement systems increases as the Si/Ca ratio increases per the following equation:[11]

$$Si/Ca = 0.4277 + 2.366(Al/Ca)$$

The present data support Richardson's findings, yet there are several possible interpretations. Figure 6 clearly shows that the C-S-H gel of slag and alkali-activated slag does not have an Al/Ca ratio below about 0.25 while the Si/Ca ratio is on the order of 1. This point lies on Richardson's line, which is also plotted in Fig. 6. Data for the slag/CH system also fall on this line with its somewhat higher Si/Ca ratio as compared to cement–slag systems. For the slag/CH system an Al/Ca ratio of about 0.12 would be expected for the apparent Si/Ca ratio of 0.7 (Ca/Si = 1.42). Figure 5, however, indicates that in slag and slag–CH systems, the C-S-H gel is never observed in the absence of Mg. Since it is unlikely that Mg substitutes into the C-S-H phase, it is more likely that in these systems the gel is always associated with some hydrotalcite-type phase. Since the Mg/Ca versus Al/Ca relationship for slag, slag/CH, and slag cement are nominally collinear, and since this line projects through Al/Ca = 0.07, as expected, then it may be that the apparent higher Al/Ca is due only to the presence of hydrotalcite-like phase in all analysis. For this reason, a value of Al/Ca = 0.07 was used in the proposed stoichiometry, yet a higher value of 0.12 may also be suggested per Richardson's interpretation.

The value for the stoichiometric coefficient *z* was estimated by satisfying the Al element balance for reaction (1): 1 = 7.39*y* + *z*. The value of *z* was found to be 0.66. The resulting stoichiometric
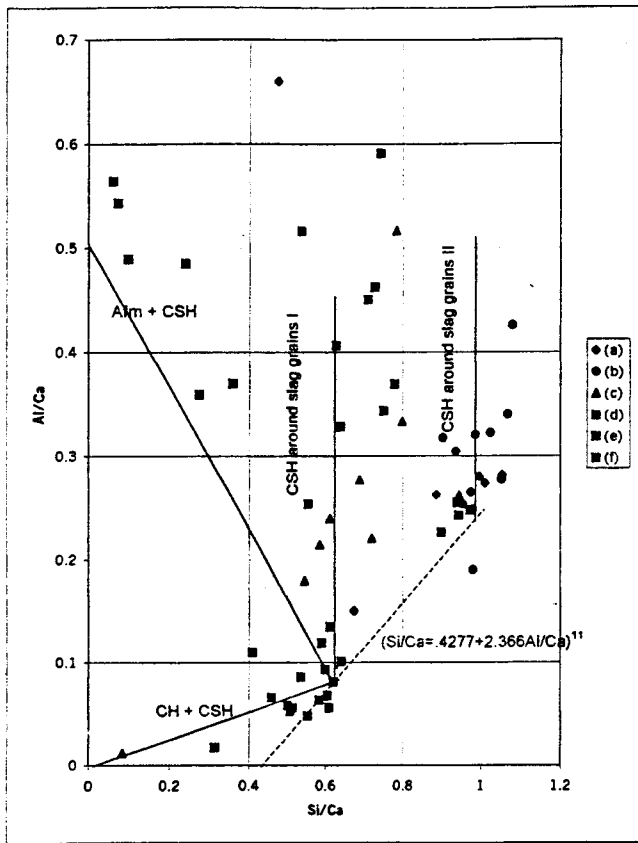
Fig. 6. Al/Ca versus Si/Ca atomic ratio spot analysis for samples reacted at 35°C for 32 days from Table II: (a) slag hydration. (b) alkali-activated slag hydration with pH 13.0 NaOH solution, (c) 80% slag/20% CH. (d,e,f) from three different 30% slag/70% cement samples. Slag grains in systems containing CH or cement are referred to here as "I" and slag grains in systems without CH or cement are referred to here as "II."

coefficients and empirical formulas result in complete accommodation of Al by either the C-S-H nanostructure or the hydrotalcite. This is further supported by the experimental evidence that suggests an absence of Afm phase for slag/CH samples. A Mg balance using $z = 0.66$ and $c = 4.6$ shows that Mg is fully accounted for by the hydrotalcite phase and no additional Mg-bearing phases are required.

Consistent with the findings of others,[8,9,17] it appears that some of the Mg and Al from the slag concentrates within the core of fully hydrated slag grains and that the C-S-H gel formed around the slag grains is richer in Mg and Al than that formed elsewhere in the slag–cement system. This finding is consistent with that of Richardson et al.[12] wherein they report Mg and Al enrichment in hydrated slag grains. If all of the Mg and Al is accommodated in the C-S-H and hydrotalcite phases, then one would expect the Mg/Al ratio of the hydrotalcite phase to be greater than 3/2 (M/A > 3 for this slag) since some of the aluminum would be incorporated into the C-S-H nanostructure. Higher Mg/Al ratios are possible and suggested by the findings of the present EDS studies and those of other researchers.[3,12,17]

(3) Hydration Water

Blends containing a weight ratio of slag/CH of 100/0, 95/5, 90/10, and 80/20 were reacted at 15°, 25°, 35°, and 50°C for between 0 and 32 days. The nonevaporable water content for each sample was determined. While water uptake measurements depend on the level of dehydration before assay,[5] an effort was made to estimate the stoichiometric coefficient b by combining CH consumption and nonevaporable water data derived from TGA measurements and material balance calculations. In the following analysis. M and A were lumped into the gel hydrate. Similarly,

sulfur-bearing phases were ignored in this analysis. The following bulk reaction stoichiometry was used:

$$C_{7.88}S_{7.39}M_3A + 2.6CH + bH \rightarrow 7.39C_{1.42}SH_{m'}(M_3A)_{1/7.39} \quad (2)$$
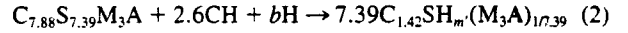
By plotting the grams of CH/grams of slag versus the grams of nonevaporable water/grams of slag, the ratio of the grams of CH/grams of nonevaporable water was found, e.g., the slope of the line. Figure 7 illustrates this relationship for 95% slag/5% CH mixtures hydrated at 15° and 50°C for up to 32 days. By applying the stoichiometric ratio 2.6 mol of CH/7.39 mol of hydrate, the moles of water per mole of hydrate product, m', was calculated. In turn $b = 7.39m' - 2.6$, the stoichiometric coefficient for the water in the C-S-H, was computed for samples prepared at various reaction temperatures and slag/CH ratios (Table III).

Furthermore, the linearity of the CH consumption versus nonevaporable water plots was shown, thereby verifying that CH consumption is directly related to hydrate product formation and that the stoichiometry of the hydrate product does not vary as a function of degree of hydration. It can be seen, however, that the amount of water of hydration appears to be dependent on the slag/CH ratio and the temperature of hydration, varying between 1.10 and 1.74. This range of values for the stoichiometric coefficient of nonevaporable water in the C-S-H gel is consistent with a value of 1.5 reported and determined by Song[13] for the hydration of GGBFS. Song reports water contents ". . . dried at 105°C then ignited at 1005°C." In the present study, all samples were dried at 100°C then ignited to 1000°C. By comparison, hydrated C_3S pastes have been shown to have water stoichiometries in the range of 1.3 to 1.52 when assayed in a similar fashion.[18] Comparison to hydrated portland cements is more difficult since reported values typically include water associated with CH decomposition as well.
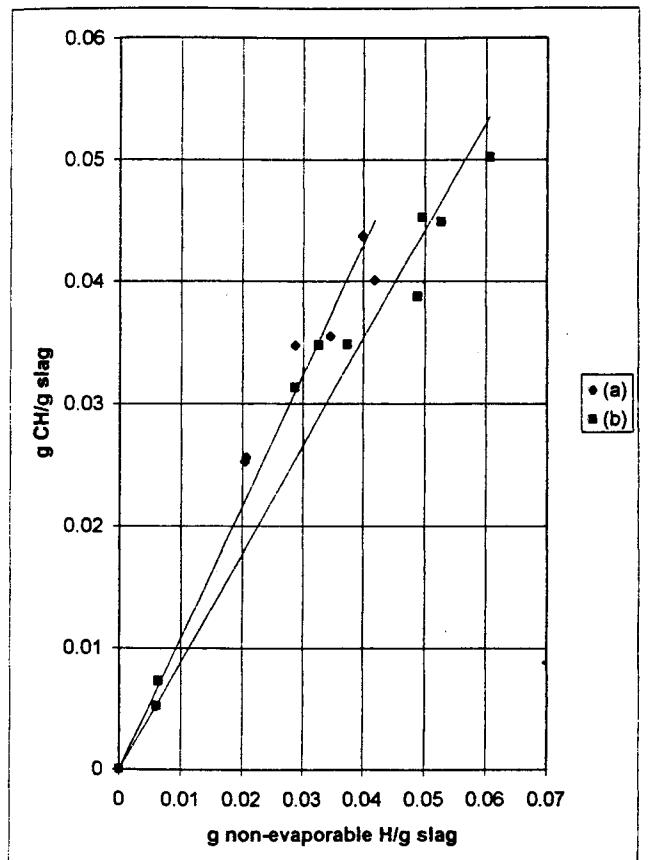

Fig. 7. CH consumption (g of CH/(g of slag)) vs nonevaporable water content (g of water/(g of slag)) for (a) a 95% slag/5% CH sample reacted at 15°C for 0 to 32 days and (b) a 95% slag/5% CH sample reacted at 50°C for 0 to 32 days.

Table III. Stoichiometric Coefficients m and b for Various Slag/CH Ratios and Temperatures

Slag/CH	Stoichiometric coefficient m values			
	15°C	25°C	35°C	50°C
80/20	1.10	1.06	1.27	1.25
90/10	1.18	1.28	1.39	1.33
95/5	1.40	1.55	1.74	1.70

Slag/CH	Stoichiometric coefficient b values			
	15°C	25°C	35°C	50°C
80/20	5.39	5.11	6.67	6.55
90/10	5.99	6.78	7.60	7.16
95/5	7.62	8.75	10.14	9.87

(4) Overall Reaction Stoichiometry

Using the best nominal values for the stoichiometic coefficients, the following final chemical reaction was written and proposed for hydration of slag in the presence of CH.

$$C_{7.88}S_{7.39}M_3A + 2.6CH + bH \rightarrow$$

$$7.39C_{1.42}SH_mA_{0.046} + 0.66M_{4.6}AH_d \quad (3)$$
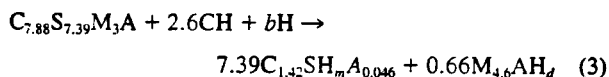
where $7.39m + 0.66d = b$ exclusive of other hydrates that may include $\bar{S}$ and M and depending on the temperature and composition of the mixture as sown in Table III.

V. Conclusions and Recommendations

For hydrated slag/CH samples the calcium-to-silica ratios of C-S-H have been shown to vary with regard to where in the microstructure the C-S-H forms. An average value for the Ca/Si ratio of 1.35 was determined by direct measurement using SEM/EDS and by combining CH and slag consumption data measured using TGA and SEM image analysis. The bound water demand was also estimated to be roughly 12 g of H_2O/(g of slag). Mg and Al were found in association with the C-S-H gel. A hydrotalcite-type phase was identified by XRD as a product of hydration in both slag/CH and slag/cement systems. An analysis of the Al/Ca and Mg/Ca ratio shows that virtually no Mg is incorporated into the C-S-H nanostructure and that hydrotalcite associated with the C-S-H gel can account for the total Mg content of the paste. The addition of slag to cement was found to lower the average Ca/Si ratio (≈ 1.5 to 1.6) of the C-S-H gel in the paste on the whole but does not appear to affect the C-S-H gel near calcium silicate clinker particles (≈ 1.7). Ca/Si ratios around slag grains in slag/cement systems were found to be similar to those around slag

grains in slag/CH (1.3–1.5) systems. From this observation. it is concluded that the C-S-H gel formed around slag grains in the slag/CH system is very similar to or nearly the same as that formed around slag grains in the cement system.

Finally. while the major product of hydration. the C-S-H gel. has been shown to be nominally equivalent for slag hydration in the CH system compared to slag hydration in the presence of portland cement, considerable work must be done to validate this finding. Further studies that directly quantify the extent of reaction of slag in cement mixtures would be of particular interest.

References

[1]"Ground Granulated Blast-Furnace. Slag as a Cementitious Constituent in. Concrete." ACI 233R-95, *ACI Manual of Concrete Practice. Part I.* American Concrete Institute. Farmington Hills, MI. 1999.

[2]R. Kondo and S. Ohsawa. "Studies on a Method to Determine the Amount of Granulated Blast Furnace Slag and Rate of Hydration in Cements," *Proc. Int. Symp. Cem. Chem.. 5th,* 4, 255–69 (1969).

[3]A. M. Harrisson. N. B. Winter. and H. F. W. Taylor. "Microstructure and Microchemistry of Slag Cement Pastes," *Mater. Res. Soc. Symp. Proc.,* 85, 213–22 (1987).

[4]G. Mascolo and O. Marino. "A New Synthesis and Characterization of Magnesium-Aluminum Hydroxides," *Mineral. Mag..* 43 [329] 619–21 (1980).

[5]H. F. W. Taylor. *Cement Chemistry.* 2nd Ed. Thomas Telford Publishing. London. U.K., 1997.

[6]R. S. Gollop and H. F. W. Taylor. "Microstructural and Microanalytical Studies of Sulfate Attack. IV. Reactions of a Slag Cement Paste with Sodium and Magnesium Sulfate Solutions." *Cem. Concr. Res..* 26. 1013–29 (1996).

[7]H. S. Pietersen. "Reactivity of Fly Ash and Slag Cement"; Ph.D. Thesis. Ch. 8. Delft University of Technology. Delft. Netherlands. 1993.

[8]A. P. Barker. "An Electron Optical Examination of Zoninig in Blast-Furnace Slag Hydrates. Part I. Slag Cement Pastes at Early Age," *Adv. Cem. Res..* 2 [8] 171–79 (1989).

[9]Q. L. Feng. E. E. Lachowski. and F. P. Glasser. "Densification and Migration of Ions in Blast-Furnace Slag–Portland Cement Pastes," *Mater. Res. Soc. Symp. Proc..* 136. 263–72 (1989).

[10]H. Tanaka. Y. Totani. and Y. Saito, "Fly Ash. Silica Fume. Slag and Other Mineral By-products in Concrete"; pp. 963 in *Publication SP—American Concrete Institute.* No. 79, Vol. 2. Edited by V. M. Malhotra. American Concrete Institute. Detroit. MI. 1983.

[11]I. G. Richardson. "The Nature of C-S-H in Hardened Cements," *Cem. Concr. Res..* 29 [8] 1131–47 (1999).

[12]I. G. Richardson. A. R. Brough. G. W. Groves. and C. M. Dobson. "The Characterization of Hardened Alkali-Activated Blast Furnace Slag Pastes and the Nature of the Calcium Silicate Hydrate (C-S-H) Phase." *Cem. Concr. Res..* 24 [5] 813–29 (1994).

[13]S. D. Wang and K. Scrivener. "Hydration Products of Alkali Activated Slag Cement." *Cem. Concr. Res..* 25. 561–71 (1995).

[14]S. Song. "Hydration of Ground Granulated Blast-Furnace Slag"; Ph.D. Thesis. p. 142. Northwestern University. Evanston. IL. 1998.

[15]C. Ferraris: personal communications, 2000.

[16]P. E. Stutzman and D. P. Bentz: personal communications, 2000.

[17]I. G. Richardson and G. W. Groves. "Microstructure and Microanalysis of Hardened Cement Paste Involving Ground Granulated Blast Furnace Slag." *J. Mater. Sci.* 27 [22] 6204–12 (1992).

[18]A. Hinrichs and I. Odler. "Investigation of the Hydration of Portland Blast-Furnace Slag Cement: Hydration Kinetics." *Adv. Cem. Res..* 2 [5] 9–13 (1989). ☐