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# Kinetics of Reaction of Calcium Hydroxide and Fly Ash

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*The alkali activated reaction kinetics of a Type-F fly ash with calcium hydroxide (CH) and water has been investigated at temperatures between 25 and 60 C. Thermogravimetric analysis (TGA) was used to determine CH consumption and production of hydrates (nonevaporable water) as a function of hydration temperature and time for various CH/fly ash ratios. The results indicate that the reaction rate, reaction stoichiometry, and activation energy are dependent on the CH/ash ratio. The reaction rate was also found to be a function of the extent of reaction of both CH and fly ash phases. Various kinetic models were considered including those proposed by Knudsen and Avrami. These, however, were found to have limited applicability. A model is suggested that provides a broader fit to the observed data.*

**Keywords:** fly ash; hydration; pozzolan.

## RESEARCH SIGNIFICANCE

The use of waste materials in portland cement concrete is increasing as mounting environmental concerns focus on accumulating stockpiles of industrial by-products. These waste materials include fly ash from coal combustion and slag from blast-furnace operation, and have the potential for being a major constituent of high-quality concrete. Incorporating such materials into concrete, however, presents several technical challenges; not all waste streams are the same, chemically or physically, and the effect of these materials on cement hydration and the way they participate in the hydration process is not fully understood.

Developments in the past 10 years on the modeling of cement hydration has led to microstructural models based on cellular automata that have been shown to mimic real portland cement systems.<sup>1</sup> More recently, Bentz and Remond<sup>2</sup> have incorporated fly ash phases into these models. In an effort to better understand the effects of blending components such as fly ash and other waste materials, it is necessary to develop accurate kinetic descriptions and parameters that reflect the interaction between such materials, portland cement, and possibly aggregate and external species such as sulfate, alkali, and carbonate. In the present work, a model system is used to study the reaction between a Class F fly ash and calcium hydroxide (CH)\* in an effort to elucidate kinetic features of this reaction and to extract a reasonable activation energy for the apparent hydration process.

## LITERATURE REVIEW

Existing microstructural models represent cement hydration as a complex series-parallel network of chemical reactions.<sup>1</sup> Presently, cellular automata-based models scale the rates of reactions according to a single kinetic parameter, an activation energy of 80,000 J/mol, which is based on the pozzolanic re-

action of silica fume—for example, the reaction of S with CH and water.<sup>3,4</sup> The present study focuses on accurate measurement of the activation energy of the ash-CH reaction.

There is an extensive body of information in the literature concerning fly ash. Among these are Helmuth's<sup>5</sup> 1987 comprehensive review and annual reviews appearing in *Cements Research Progress* under "Blended and Modified Cements."<sup>6</sup> A number of investigators have reported the apparent effect of fly ash on portland cement hydration by observing heat evolution. Ma et al.<sup>7</sup> report calorimetric results for 17% ash blended portland cement at temperatures ranging between 10 and 55 C. In their study the ash used contained 3.53% CaO. The results illustrate the classic effect of Class F fly ash to retard hydration. Their results, however, also indicate that heat liberation is retarded more at higher temperatures. Takemoto and Uchikawa observed that early age hydration could be retarded while later stages accelerated.<sup>8</sup> Such changes in the dormant stage as well as the rate of reaction during Stage III hydration have been reported by other investigators with varying results.<sup>9</sup> Various studies offer insights into complex behaviors such as combined acceleration and retardation. Yamazaki has shown that fine particles such as fly ash can actually promote hydration by physical means.<sup>10</sup> The addition of fine particles open the floc structure providing more space for precipitation of clinker hydrate products and thus tend to accelerate hydration. This accelerating effect may compete with other mechanisms that have been shown or are suggested as possible retarding influences. Three primary theories have been proposed to explain the observed effect of fly ash on reaction rates.

1. Fine particles promote nucleation and growth of various phases including CH and ettringite. This promotes C-S-H formation and stimulates reaction rates;<sup>10</sup>

2. Fly ash may contain water soluble organic species that inhibit CH precipitation and so inhibit the onset of Stage III hydration;<sup>9,11</sup> and

3. Aluminate rich fly ash phases consume Ca<sup>++</sup> to form AFt phases during early ages, thereby retarding the formation of Ca rich surface layers on clinker phases that are necessary to initiate Stage III hydration.<sup>12</sup>

These three theories most likely are not independent. The dominant mechanism is not known, yet some evidence exists to suggest that Theory (2), organic inhibition, is less likely than Theory (3) as an explanation for inhibition of Stage III hydration. Fajun, Grutzeck, and Roy<sup>13</sup> report that water washed fly ashes are not as retarding, yet they appear to suppress the rate of reaction to varying extents. One strongly retarding Class F ash was shown to inhibit onset of

\*Cement chemist's notation is used as shorthand for chemical formulas as follows: Ca(OH)<sub>2</sub> = CH, SiO<sub>2</sub> = S, CaO = C, Al<sub>2</sub>O<sub>3</sub> = A, Fe<sub>2</sub>O<sub>3</sub> = F, H<sub>2</sub>O = H, S = SO<sub>3</sub> and C = CO<sub>2</sub>.

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Stage III hydration nominally by 4 h. After water washing, the same ash inhibited onset by approximately 2 h. For a Class C ash, washing had virtually no effect on inhibition, but diminished the maximum rate of heat evolution by a factor of two. Wash water leachate from the washing process was found to have virtually no effect on cement hydration. They suggest that surface aluminate phases responsible for influencing early age rates of hydration and retardation are modified by the washing process. Furthermore, one may also suggest that their result demonstrates that soluble organic species—inhibitors—are not responsible for inhibition, or else leachates should inhibit hydration. Their study also suggests that ash either inhibits  $\text{Ca}^{++}$  production or consumes  $\text{Ca}^{++}$  produced at an early age. They propose that  $\text{Ca}^{++}$  consumption by active aluminates in the ash reduce the buildup of Ca rich layers on clinker particles, which are necessary to initiate Stage III hydration, thereby resulting in retardation.

Ogawa et al.<sup>14</sup> offer a detailed microstructural blueprint of the hydration process involving  $\text{C}_3\text{S}$  and fly ash. Their model describes calcium silicate hydrate (C-S-H) formation reactions that occur at the surface of the ash with sequential buildup and rupture of surface layers due to osmotic forces established across the growing hydrate layers. They postulate that more rapidly diffusing aluminates escape the particle and precipitate away from the ash surface. More recently, Shi<sup>15,16</sup> and Katz<sup>17</sup> offer similar microstructural details for the CH/fly ash system.

The most obvious effect of pozzolanic materials is the reduction of CH content, as observed at long curing times. A number of authors have observed the pozzolanic reaction of fly ash in the presence of portland cement by monitoring the CH content as a function of time.<sup>18</sup> Taylor reports that the Ca/Si ratio for the  $\text{C}_3\text{S}$ -fly ash reaction is approximately 1.4 in mature samples.<sup>19</sup> At early ages, however, Helmuth<sup>5</sup> reports that for portland cement-fly ash mixtures, the early pozzolanic reaction does not reduce the amount of calcium hydroxide, but instead reduces the Ca-Si ratio of the calcium silicate hydrate. Prior studies have also focused on the use of the pozzolanic activity index (PAI) with lime test method, ASTM C 311.<sup>20</sup> This method infers pozzolanic activity through strength measurements for hydrated lime/fly ash mixtures. Numerous investigators have used this or similar methods as a basis for evaluating the reactivity of fly ashes, but none infer an activation energy from their data.<sup>21-24</sup>

## PROCEDURES AND MATERIALS

### Reaction of ash with calcium hydroxide

Fly ash was reacted with CH and water at nominal CH/ash mass ratios of 75/25, 50/50, 25/75, and 12.5/87.5 for 1, 2, 5,

and 16 d at 25, 40, 50, and 60 C, respectively, to establish early age hydration rates. Pastes containing the desired ratio of solids were prepared by combining 50 g of the solid components with 40 mL of pH 13.4 NaOH solution to yield a 0.8 liquid-to-solids ratio. A solution pH of 13.4 was selected based on the report by Fraay, Bijin, and Haan,<sup>25</sup> which suggests that the pozzolanic reaction does not proceed at an appreciable rate below an initial pH of 13.2. Samples were mixed by hand at room temperature until the paste was smooth, free of clumps, and visibly homogeneous. A 60 mL syringe was filled with the paste and one dram glass jars with twist on lids were filled nearly to the top by expelling paste through the syringe. Lids were tightly sealed to prevent water or air exchange and the samples were placed in temperature controlled water baths at their respective temperatures.

### Stopping hydration

The standard procedure outlined by Hobbs,<sup>26</sup> Section B, was used to displace water and dry samples. Hydrated samples were crushed into fragments ranging in size from individual ash and CH grains to agglomerates of nominally 1 mm. The crushed material was slurried with roughly 50 mL of anhydrous methanol and immediately filtered. An additional 50 mL of methanol was passed through the resulting cake. The cake was then dried at 105 C overnight.

### Raw materials

A single source of fly designated as 9703 was obtained from the American Coal Ash Association (ACAA).<sup>\*</sup> Chemical analysis is provided by ACAA and is tabulated in Table 1. Additional physical properties were determined including specific surface area and particle size distribution. Surface area analyses were performed by the National Institute of Standards and Technology (NIST) Powder Characterization Laboratory in the NIST Ceramics Division using an automated BET gas absorption system<sup>27</sup> (Table 1). Particle size distributions were estimated using a particle settling technique and were also done by the NIST Powder Characterization Laboratory.<sup>27</sup> The results are summarized in Table 2.

**Chemical reagents**—Reagent Grade NaOH and CH (Malenckrodt AR) were used in all cases. The particle size distribution for the CH was also determined using a laser light scattering particle size analyzer. The data are listed in Table 2. As-received CH was characterized by thermogravimetric analysis (TGA). The powder was found to contain approximately 1%  $\text{H}_2\text{O}$  that is completely volatilized by 200 C and small amounts of carbonate (1.99%).

### Reaction rates

Material balances were used to determine the amount of non-evaporable water and the amount of CH consumed by reaction.

**CH consumption**—From TGA analysis, the mass percent water associated with CH was estimated by approximating the mass loss due to CH decomposition at temperatures roughly between 400 and 500 C. The amount of  $\text{CO}_2$  was determined similarly by estimating the mass loss due to  $\text{CO}_2$  between 500 and 700 C. Approximations use the procedure suggested by Taylor<sup>28</sup> that utilizes leading and trailing derivative lines and mass loss curve inflection as the midpoint for estimation of the weight loss. Using this procedure,

<sup>\*</sup>Certain products or organizations are identified to more fully describe the analytical procedures or origin of materials. In no case does this imply endorsement by the National Institute of Standards and Technology, nor does it mean that they are the best available for the purpose.

**Table 1—Chemical and physical analysis of fly ash**

Chemical analysis	Value, %
SiO <sub>2</sub>	55.3
Al <sub>2</sub> O <sub>3</sub>	26.4
Fe <sub>2</sub> O <sub>3</sub>	7.4
TiO <sub>2</sub>	1.2
CaO	3.1
MgO	1.6
Na <sub>2</sub> O	0.4
K <sub>2</sub> O	2.9
SO <sub>3</sub>	0.5
P <sub>2</sub> O <sub>5</sub>	0.1
BaO	0.1
MnO	< 0.1
SrO	0.1
Total carbon	1.0
Other	0.3
Total	100.4
Physical analysis	Value
pH	11.3
Multipoint BET surface area, m <sup>2</sup> /g	1.31
Specific conductivity, m-mhos	595
Available alkalis, %	0.73
Evaporable water, %	0.21
Loss on ignition, %	1.65
Retention on No. 325 sieve, %	23.90
Specific gravity	2.25
Soundness, %	-0.036
Pozzolan activity index	
Water required, % control	98
Strength at 7 days, % control	83

weight loss was taken as the difference between leading and trailing tangents projected to the vertical line drawn through the midpoint.

The amount of CH consumed was computed by subtracting the CH remaining from the initial CH in the sample. The initial CH was estimated by material balance. All material balances were computed for 100 g of starting materials ( $M^{feed}$ ) on a dry basis for simplicity

$$CH_{actual}^{feed} = \left[ \frac{CH_{gross}^{feed}}{CH_{gross}^{feed} + Ash_{gross}^{feed}} \right] \quad (1)$$

$$(1 - f_{CH\ moisture}^{feed} - f_{CH\ carbonate}^{feed}) M^{feed}$$

The fraction of CH moisture ( $f_{CH, moisture}^{feed}$ ) was taken to be 1% and the fraction CH carbonate ( $f_{CH, carbonate}^{feed}$ ) was taken to be 1.99%, both as determined by TGA. The subscript gross is used herein to identify mass quantities that have not been corrected for purity. The amount of CH remaining is given by

$$CH_{remaining}^{sample} = \quad (2)$$

$$\left[ f_{CH\ as\ water}^{sample} \frac{74}{18} + f_{CH\ as\ CO_2}^{sample} \frac{74}{44} \right] M^{sample}$$

**Table 2—Particle size analysis**

Cumulative mass, %	Diameter, mm	
	CH	Fly ash
10	13.756	43.08
25	11.582	34.17
50	7.565	26.72
75	6.135	20.00
90	5.111	10.53

The addition of the term  $f_{CH\ as\ CO_2}^{sample}$  is included because it was determined that the majority of CO<sub>2</sub> evolved was due to CH carbonation. The factors 74/18 and 74/44 convert the fraction of mass loss as H<sub>2</sub>O and CO<sub>2</sub> into CH.

The final mass of the sample ( $M^{sample}$ ) was determined by using the total nonevaporable solids in the feed as a tie-component (component mass that does not change through the system). This includes nonevaporable components of both the ash and the CH

$$M_{nonevaporable}^{feed} = M_{nonevaporable}^{sample} \quad (3)$$

$$M_{nonevaporable}^{feed} = (1 - f_{evaporable}^{sample}) M^{sample} \quad (4)$$

$$M_{nonevaporable}^{feed} = (1 - f_{evaporable}^{feed}) M^{feed} \quad (5)$$

$$M^{sample} = M^{feed} \left[ \frac{1 - f_{evaporable}^{feed}}{1 - f_{evaporable}^{sample}} \right] \quad (6)$$

where  $f_{evaporable}^i$  is the fraction of  $i$  that is evaporable up to 105 C, and  $i$  = feed or sample. Finally, the amount of CH consumed ( $CH_{consumed}$ ) can be computed

$$CH_{consumed} = CH_{actual}^{feed} - CH_{remaining}^{sample} \quad (7)$$

where  $CH_{actual}^{feed}$  and  $CH_{remaining}^{sample}$  are the mass of CH in the feed and remaining in the hydrated sample, respectively.

An extent of reaction for CH was defined as the mass reacted divided by the mass initially

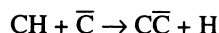
$$\alpha_{CH} = \left( \frac{CH_{consumed}}{CH_{actual}^{feed}} \right) \quad (8)$$

where  $\alpha_{CH}$  is the extent of reaction for CH.

**Nonevaporable water production (hydrate formation)**—The amount of hydrates formed was estimated by determining the amount of nonevaporable water (water removable above 105 C). The mass loss due to waters of hydration between 25 and 1000 C was determined after samples had initially been equilibrated at 105 C post-methanol quench. These were stored in sealed vials until TGA assays were performed. The amount of hydrates formed  $H$ , decomposable between 25 and 1000 C, were then estimated by

$$H = M^{sample} (f_{nonevaporable}^{sample} - f_{carbonate}^{sample} - f_{CH}^{sample} \Phi f_{carbonate}^{sample}) \quad (9)$$

where  $\phi$  is a coefficient that corrects for the amount of water evaporable up to 1000 C associated with carbonate formation. TGA of carbonated CH samples consistently show a low temperature water-loss to carbonate-loss ratio on the order of 0.4. This is consistent with calcium carbonate formation stoichiometry wherein, presumably, the water of carbonation remains weakly absorbed



The ratio of  $\text{H}_2\text{O}/\text{CO}_2 = 18/44 = 0.409$ .

Raw data for CH consumed and nonevaporable water generated for 1, 5, and 16  $d$  are summarized in Table 3.

### X-ray diffraction (XRD)

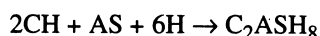
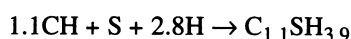
Samples were prepared for X-ray diffraction (XRD) using a conventional powder diffraction sample preparation technique with back-loaded cavity mounts. Standard  $\text{CuK}\alpha$  radiation was used. All samples were tested using 40 kV (40 mA) steps between 0.02 to 0.04 degrees per s, and  $2\theta$  values ranging from 5 to 45 degrees.

## ANALYSIS AND DISCUSSION

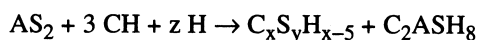
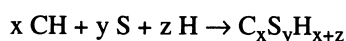
### Stoichiometry of reaction

The stoichiometry of the CH-fly ash interaction was estimated from the asymptotic CH consumption value obtained for the reaction of samples containing an excess of CH, that is,  $\text{CH}/\text{ash} = 75/25$ , at 60 C. Under these conditions, the limiting consumption was estimated to be roughly 1.12 g CH/g fly ash. While it would be ideal to gather similar data at lower temperatures and different ratios of CH/ash, it becomes somewhat impractical because reaction rates and transport effects limit the extent of reaction. Mechanical stimulation via grinding has been used; however, this is thought to alter the product chemistry. Extensive XRD analysis shows essentially identical products forming regardless of temperature or CH/ash ratio.<sup>29</sup> At this time, a single value of consumption appears justifiable, yet further validation of this critical assumption should be done.

By comparison, Bentz<sup>2</sup> suggests the following two pozzolanic reactions for fly ash



If the fly ash silicate and aluminate phases are allocated between a S silicate glass and an AS (aluminosilicate glass) phase as Bentz suggests, then in every mole of the fly ash used in this research there are 0.6 mol pozzolanic silica and 0.2 mol aluminosilicate glass. By material balance, this corresponds to a consumption of 1.04 mol CH per mole of fly ash. The limiting mass ratio, upon complete reaction, is 0.79 g CH/g ash. Similarly, Helmuth<sup>5</sup> suggests the following pozzolanic reactions



Helmuth suggests that a fly ash with reactive S and A of 50 and 30%, respectively, will for a complete reaction have a mass ratio of 0.83 g CH/g fly ash, assuming that  $x/y = 1$ . This

**Table 3—Raw data for CH consumption and hydrate formation**

Nominal CH/ash	Time $d$	Temperature, C	Raw amounts (g/100 g starting solids)	
			$\text{CH}_{\text{consumption}}$	Total nonevaporable $\text{H}_2\text{O}$
12.5/87.5	1	25	0.82	2.98
25/75	1	25	0.43	3.01
50/50	1	25	2.31	3.05
75/25	1	25	6.54	3.52
12.5/87.5	1	40	1.02	3.22
25/75	1	40	1.87	2.73
50/50	1	40	5.63	4.41
75/25	1	40	6.83	4.12
12.5/87.5	1	50	2.64	3.47
25/75	1	50	3.11	3.48
50/50	1	50	4.44	5.39
75/25	1	50	10.29	5.63
12.5/87.5	1	60	3.08	4.21
25/75	1	60	6.32	4.91
50/50	1	60	11.00	7.31
75/25	1	60	14.55	6.34
12.5/87.5	5	25	1.77	3.59
25/75	5	25	1.60	4.39
50/50	5	25	5.03	4.95
75/25	5	25	7.55	5.29
12.5/87.5	5	40	3.35	4.90
25/75	5	40	6.20	6.15
50/50	5	40	11.06	7.54
75/25	5	40	11.01	7.06
12.5/87.5	5	50	7.97	7.48
25/75	5	50	13.99	9.73
50/50	5	50	17.04	9.32
75/25	5	50	16.40	9.16
12.5/87.5	5	60	9.10	7.60
25/75	5	60	16.40	10.7
50/50	5	60	18.67	9.77
75/25	5	60	23.62	11.13
12.5/87.5	16	25	2.60	4.27
25/75	16	25	5.96	4.85
50/50	16	25	7.46	6.64
75/25	16	25	9.65	7.74
12.5/87.5	16	40	9.52	7.49
25/75	16	40	17.38	11.20
50/50	16	40	18.69	11.25
75/25	16	40	18.54	11.76
12.5/87.5	16	50	10.62	8.53
25/75	16	50	19.86	11.80
50/50	16	50	23.59	12.17
75/25	16	50	22.40	13.99
12.5/87.5	16	60	11.05	7.95
25/75	16	60	19.52	11.56
50/50	16	60	23.61	11.93
75/25	16	60	26.33	14.02

ratio is very similar to the experimental fly ash, which has 55.3 and 26.4%, respectively. Using the experimental ash composition, this analysis yields a limiting ratio of 0.87 g CH/g fly ash. A C/S ratio in the C-S-H of one is, however, low for the calcium-rich CH environment in which the experiments

were run. If  $x/y = 1.3$ , for example, the limiting ratio becomes 0.95 g CH/g fly ash. This limiting analysis is generally in good agreement with the observed value of 1.12 g CH/g fly ash. Furthermore, closer agreement is likely if the aluminate product contains hydrogarnet ( $C_3AH_6$ ) or hydrogrossular phases such as katoite ( $C_3AS_0.5H_0.5$ ,  $\alpha < 1.5$ ), because they contain C/S ratios greater than 2.0 in comparison to the stratlingite ( $C_2ASH_8$ ) suggested by Helmuth. Such products have been identified and will be discussed as follows. Based on the limiting stoichiometry of reaction, the extent of ash reaction was defined

$$\alpha_{ash} = \alpha_{CH} \frac{f_{CH}}{f_{Ash}} \frac{1}{\epsilon} \quad (10)$$

where  $f_{Ash}$  and  $f_{CH}$  are the initial fraction ash and CH in the sample, respectively, and  $\epsilon$  is the mass stoichiometry ratio grams of CH consumed per gram of fly ash reacted ( $\epsilon = 1.12$ ).

### Rate analysis

Reaction rates in cement systems are typically analyzed using the Avrami,<sup>30</sup> Knudsen,<sup>31</sup> or similar equations or combinations, because they encompass reaction- and diffusion-controlled mechanisms typical of cement hydration processes.

Avrami:

$$-\ln(1 - (\alpha - \alpha_N)) = k_A(t - t_N)^{n_A} \quad (11)$$

Knudsen:

$$\alpha = \frac{k_K(t - t_o)^{n_K}}{1 + k_K(t - t_o)^{n_K}} \quad (12)$$

where

- $t$  = time;
- $t_o$  = initial time, Knudsen (typically the induction time for cements);
- $t_N$  = initial time, Avrami;
- $\alpha$  = extent of reaction at any time  $t$ ;
- $\alpha_N$  = extent of reaction at  $t_N$ ;
- $k_A$  = Avrami reaction rate parameter;
- $k_K$  = Knudsen reaction rate parameter;
- $n_A$  = Avrami reaction exponent; and
- $n_K$  = Knudsen reaction exponent.

These expressions, however, are only applicable for a single reacting solid phase or when rates depend only on the extent of reaction of a single solid phase.

The hydration of low calcium fly ash requires the presence of not only the fly ash phases and water, but also calcium hydroxide. Reactions involving two solid phases may exhibit rate dependence upon one, both, or neither surfaces depending on the rate-controlling mechanism. Such a rate expression must go to zero as either or both phases reach full extent of reaction. The simplest form of rate expression having the desired functional form is given by

$$\frac{d\alpha_1}{dt} = k(1 - \alpha_1)^n(1 - \alpha_2)^m \quad (13)$$

where  $\alpha_1$  and  $\alpha_2$  are extents of reaction for Phases 1 and 2, respectively,  $n$  and  $m$  are the reaction orders,  $k$  is the reaction

rate constant, and  $d\alpha_1/dt$  is the rate of reaction of Phase 1. Similar expressions are typically used to describe various reaction rate-controlled processes.

To discern the functional dependence of the reaction rate for the CH/fly ash reaction, it was necessary to run experiments wherein the CH/ash ratio in the starting materials was varied. In this way, dependence of the rate on relative amounts of ash and CH surface and extent of reaction of both phases could be discerned.

Observation of the raw CH consumption data and reaction rates computed thereof illustrate the complex behavior of this reaction (Fig. 1 and 2). Several features are notable:

1. The rate of CH consumption and the rate of hydrate formation are functions of the CH/ash ratio. In particular, there is more hydrate formed and more CH consumed per gram of starting ash per unit time when the mixtures contain more CH. Figure 1(a) and (b) illustrate this effect for samples reacted at 40 and 60 C, respectively;

2. In addition, the rates of reaction are also a function of both the extent to which CH and ash are reacted (Fig. 2(a) and (b)); and

3. The reaction rates exhibit an inflection as a function of CH/ash at a CH/ash ratio in the neighborhood of 50/50. Figure 2 illustrates this observation for samples reacted at 60 C. This is particularly evident for higher temperatures.

Since both CH and fly ash are consumed as the reaction progresses, the extent of reaction for both vary with time. Experimentally, it is impossible to hold either constant as the reaction progresses for a single experiment. By running a series of experiments with varying CH/ash initial compositions, however, it is possible to measure instantaneous rates at constant extents of reaction for either constant ash extent ( $\alpha_{Ash}$ ) or CH ( $\alpha_{CH}$ ) extent. To locate rates at constant  $\alpha_{Ash}$ ,  $\alpha_{Ash}$  was plotted versus time for various CH/ash ratios at constant temperature. Rates of reaction were then determined for various  $\alpha_{Ash}$  values by computing the derivative at points on the  $\alpha_{Ash}$  versus time curve for various CH/ash values. The respective  $\alpha_{CH}$  values were determined using the following relationship between  $\alpha_{Ash}$  and  $\alpha_{CH}$

$$\alpha_{CH} = \alpha_{Ash} \frac{f_{Ash}\epsilon}{f_{CH}} \quad (14)$$

Figure 2 illustrates rates determined by this method. From these plots it can be seen that the rate of reaction depends upon both the extent of reaction for CH ( $\alpha_{CH}$ ) and the CH/ash ratio because, as seen from Fig. 2(a), the rate of reaction was found to increase with increasing CH/ash ratio at constant  $\alpha_{CH}$  and decrease with increasing  $\alpha_{CH}$  at constant CH/ash ratio. The dependence on  $\alpha_{Ash}$ , however, is more difficult to discern. At low  $\alpha_{CH}$ , the rate of reaction was shown to increase with increasing CH/ash ratio at constant  $\alpha_{CH}$ , despite increasing  $\alpha_{Ash}$ . It appears that either the reaction is independent of ash extent—zero order in ash surface—or the apparent effect of ash extent is overwhelmed by the affect of increasing CH content (increasing CH surface area in the system) when  $\alpha_{CH}$  is low. For higher values of  $\alpha_{CH}$ , however, the rates exhibit a maximum, decreasing for increasing  $\alpha_{Ash}$  as the CH/ash ratio increases above the maximum, and decreasing for decreasing  $\alpha_{Ash}$  as the CH/ash ratio decreases below the maximum. These complex behaviors suggest that the rate of CH consumption per gram of ash is not only dependent on the extent of reaction of both the CH and ash

phases, but also dependent on the relative amount of CH and ash in the system. In either case, the initial strategy for rate analysis was to assume that the form of the rate expression was first order with respect to both CH and fly ash extent, for example,  $n = m = 1$  in Eq. (13). This left only the dependence on the reaction constant  $k$  to be determined. If the assumed rate dependence is correct, the rate constant  $k$  should be a function of temperature only.

Reaction rates were analyzed by integration of the following rate expression

$$\frac{d\alpha_{CH}}{dt} = k(1 - \alpha_{CH})(1 - \alpha_{Ash}) \quad (15)$$

Because the extent of ash reaction is proportional to the extent of CH reaction,  $\alpha_{Ash}$  could be eliminated by using Eq. (14), resulting in the following differential equation with only one dependent variable:  $\alpha_{CH}$

$$\frac{d\alpha_{CH}}{dt} = k(1 - \alpha_{CH})(1 - a\alpha_{CH}) \quad (16)$$

where  $a$  is the proportionality constant  $f_{CH}/f_{Ash}/\epsilon$  relating  $\alpha_{CH}$  to  $\alpha_{Ash}$ . Upon integration, the following relationship between  $\alpha_{CH}$  and time is found

$$\frac{1}{a-1} \ln \frac{1 - \alpha_{CH}}{1 - a\alpha_{CH}} = kt \quad (17)$$

To determine the rate constant  $k$ , a fitting routine was used that minimized the squared error in predicted and experimental extents of reaction  $\alpha_{CH}$  as a function of  $k$ . The rate constant  $k$  was determined in this way for  $\alpha_{CH}$  versus time curves at each temperature and for each CH/ash ratio. The  $\alpha_{CH}$  versus time plots for experimental data and for Eq. (17) are shown in Fig. 3 for 50 C. On the average, the equation simulates observed trends over the entire range of CH/ash ratios, however, the absolute fit is better for the higher temperature data.

The computed reaction rate parameters were analyzed using an Arrhenius plot, that is,  $\ln(k)$  versus  $1/T$ , (Fig. 4(a)). Good linearity for the Arrhenius analysis is noted with  $r^2$  values greater than 0.95 for all but the CH/ash = 75/25 data set (Fig. 4). The resulting apparent activation energies over a temperature range from 25 to 60 C (298 to 333 K), however, were found to vary as a function of CH/ash ratio (Fig. 4(b)), dipping to a minimum for CH/ash = 0.5. This observed change in activation energy is most likely the result of increased diffusion resistance at CH/ash = 1 (50% CH).

Since the stoichiometry of the reaction consumes roughly 1.12 g of CH per g of ash  $\epsilon = 1.12$  the porosity of reacted CH-ash samples will be minimized at a CH/Ash ratio of approximately 1. This is consistent with the observed inflection in rates at a CH/ash ratio of 1, as shown in Fig. 2(b), and with the observed decrease in activation energy at the same ratio.

Ideally, plots of  $\ln(k)$  versus  $1/T$  for any CH/ash ratio should be colinear. Good colinearity was found for low CH/ash ratios. At the higher ratios, however, lower  $k$  values were found with minimum values occurring at a ratio of 50/50. This deviation is consistent with the observed decrease in activation energy at a CH/ash ratio of 50/50. This result suggests that while the assumed rate expression offers a

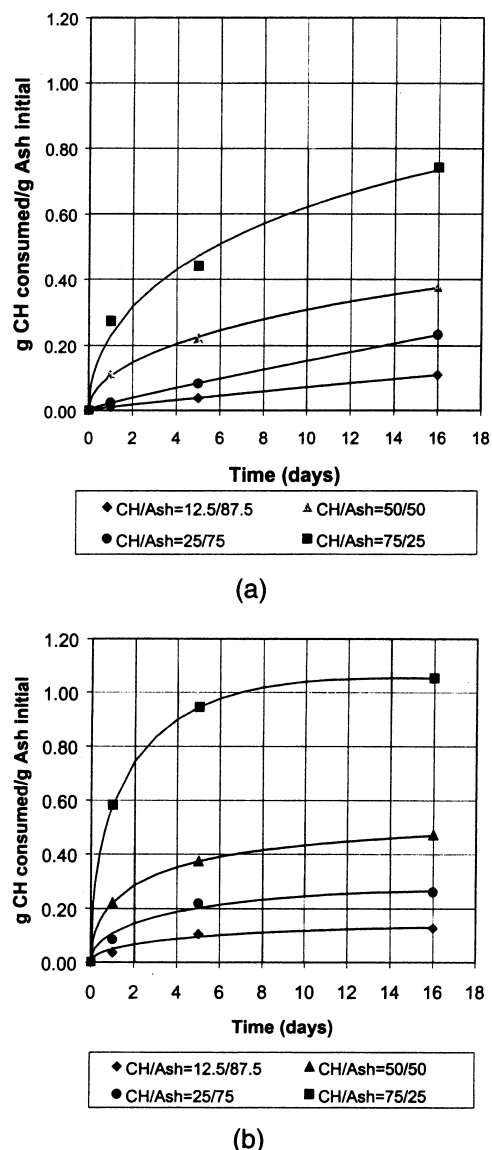


Fig. 1—Mass of CH consumed per unit mass of fly ash as function of time for various CH/ash ratios: (a)  $T = 40$  C; and (b)  $T = 60$  C.

good overall fit to the data and predicts observed trends, fundamentally, it does not adequately account for changes in transport conditions between reactant surfaces with changes in CH/Ash ratio, nor does it account for particle size and size distribution effects. These factors likely account for less than adequate fit for some data sets.

While Eq. (17) appears to have the correct global mathematical form,  $d\alpha/dt$  going to zero as either  $\alpha_{CH}$  or  $\alpha_{Ash}$  approaches unity and the effect of CH/ash ratio embodied in the  $k$  value, it is without mechanistic interpretation at this time. Furthermore, similar behavior was found when the Avrami and Knudsen equations were used despite the mathematical limitations previously discussed. Assuming that the reaction rate is only dependent on  $\alpha_{CH}$  and using only the data for CH/ash mixtures for which CH is the limiting reagent, it was found that the Avrami and Knudsen equations provide a reasonable fit giving similar values for the activation energy for CH/ash values of 12.5/87.5, 25/75, and 50/50 (Table 4). To achieve a good fit, however, it was found that both the Avrami and Knudsen exponent must be

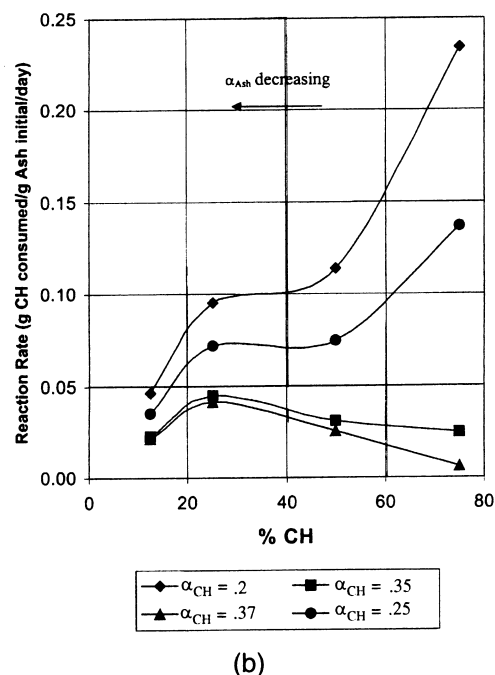
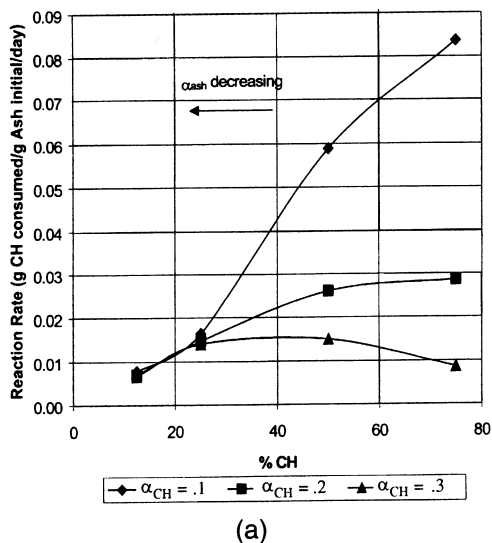


Fig. 2—Rate of CH consumption per unit mass of fly ash per day as function of CH/ash ratio at various constant extent of CH reaction values: (a)  $T = 40^\circ\text{C}$ ; and (b)  $T = 60^\circ\text{C}$ .

changed from  $n = 1$  to  $n = 0.5$  for the CH/ash ratio of 50/50. While physical interpretations have been assigned to specific Avrami exponents, they seem only weakly plausible in this application, but should be taken into consideration. The Avrami coefficient is usually determined from the equation

$$n_A = (P/S + Q) \quad (18)$$

where  $P = 1$  if the product forms as fibers, needles, or spines;  $P = 2$  if the product forms as sheets, flat plates, or foils; and  $P = 3$  if the product forms as polygons.<sup>32</sup>  $S$  is a growth rate constant;  $S = 1$  if the growth is controlled by the interface or phase boundary; and  $S = 2$  if the growth is controlled by diffusion.  $Q$  is the nucleation rate;  $Q = 0$  for zero nucleation rate, and  $Q = 1$  for constant nucleation rate. The observed shift in exponent from 1 to 0.5 tends to support an increase in transport resistance and may be consistent with a change

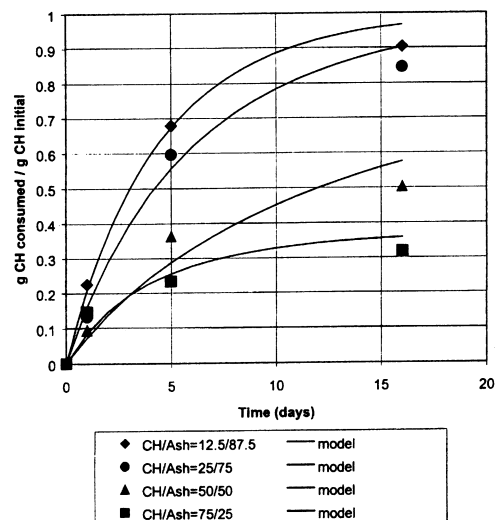


Fig. 3—CH consumption per unit mass of fly ash, experimental data, and kinetic model prediction for various CH/ash ratios at  $50^\circ\text{C}$ .

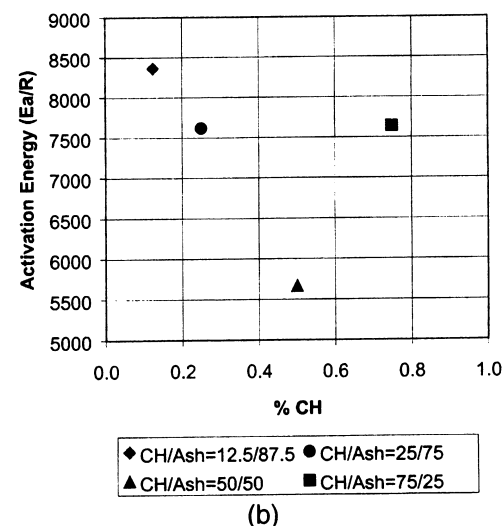
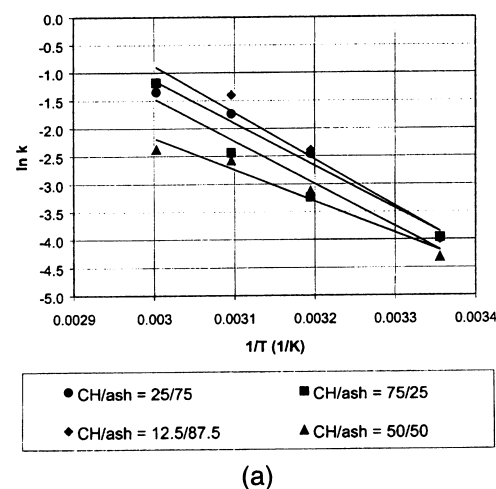


Fig. 4—(a) Arrhenius analysis for various CH/ash ratios; and (b) activation energy as function of CH/ash ratio.

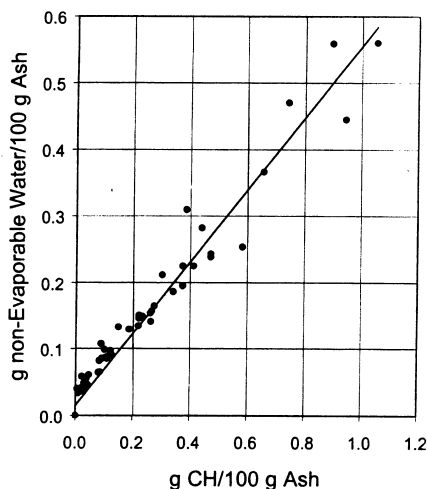
from reaction to diffusion control as  $S$  goes from 1 to 2. This shift is also consistent with and indicated by the reduction in apparent activation energy for CH/ash = 50/50.



**Table 4—Summary of kinetic parameters**

CH/ash	$d\alpha_{CH}/dt = k(1 - \alpha_{CH})$ $(1 - \alpha_{Ash}) E_a/R, r^2$	Avrami $n_A = 1$ $E_a/R, r^2$	Avrami $n_A = 0.5$ $E_a/R, r^2$	Knudsen $n_K = 1$ $E_a/R, r^2$	Knudsen $n_K = 0.5$ $E_a/R, r^2$
12.5/87.5	8400 (0.96)	8300 (0.97)	N/A	7400 (0.96)	N/A
25/75	7600 (0.98)	7500 (0.98)	N/A	7000 (0.97)	6900 (0.97)
50/50	5700 (0.96)	N/A	4400 (0.94)	N/A	5000 (0.95)
75/25	7600 (0.94)	N/A	5600 (0.99)	N/A	N/A

Note: N/A = not applicable.



**Fig. 5—Nonevaporable water content per unit mass of sample versus CH consumed per unit mass of sample.**

While Knudsen's equation has a fundamental basis in that it explicitly accounts for particle size and size distribution effects, it assumes a mathematical form for both the size distribution and the rate expression that have no physical interpretation other than mathematical convenience and consistency with the observed data. A point of interest is that the Avrami equation was found to fit the data better at the lower temperatures, while the Knudsen equation best fits the higher temperature data. This result is similar to published results that show the Avrami equation predicts early stage reaction and low extents of hydration, while the Knudsen is designed to predict later or the full reaction curve.<sup>28,29</sup> At lower temperatures, the extent of reaction is very low while at the higher temperature, the reaction has reached a level high enough to give the representative shape of the complete reaction curve. Even with the restrictions already set forth, it appears that neither of these models could predict a complete set of hydration curves for this reaction without changing the equation's rate basis, for example,  $d\alpha_{CH}/dt = f(\alpha_{CH})$  when CH is the limiting reagent and  $d\alpha_{CH}/dt = f(\alpha_{Ash})$  when ash is the limiting reagent.

Unless the rate basis is changed, neither the Avrami or Knudsen approaches are able to predict rates when ash is the limiting reagent (CH/ash = 75/25). Because  $\alpha_{CH}$  does not approach one when ash is the limiting reagent,  $d\alpha_{CH}/dt = k(1 - \alpha_{CH})$  cannot go to zero. Under these conditions, it is only appropriate to model  $d\alpha_{Ash}/dt = k(1 - \alpha_{Ash})$  or  $d\alpha_{CH}/dt = k(1 - \alpha_{Ash})/a$ . With this change in basis made, again a value for the activation energy was found for  $n_A = 0.5$ , and again the value is greater than that for CH/ash = 50/50, which is consistent with other findings in this study. In either case,  $k$  was found to depend on the CH/ash ratio, indicating that this approach is empirical.

By comparing the Avrami and Knudsen approaches to Eq. (17), it was confirmed that only a rate expression that

has explicit dependence on both the ash and CH extents of reaction can adequately predict the full range of rate behaviors observed. While the Avrami and Knudsen equations yield similar activation energies, it is necessary to change the rate basis as the CH/ash ratio moves from CH limiting to ash limiting further demonstrating that the observed rate is dependent on both CH and ash extents of reaction.

### Controls and other confirming results

It was assumed in these analyses that CH consumption is a direct indicator of hydrate formation. To confirm this assumption, the amount of hydrate formed was determined by measuring the nonevaporable water content of reacted samples. The mass of nonevaporable water per gram of sample was plotted versus the mass of CH consumed per gram of sample for each temperature, CH/ash ratio, and reaction time (Fig. 5). A linear relationship was found confirming that CH consumption is directly proportional to hydrate product formation with an average H/CH molar ratio of approximately 2.2 given by the slope of the line defined by the data. A more detailed analysis reveals that scatter in this plot is not due to experimental error, but rather is a systematic variation in the H/CH molar ratio as a function of temperature and CH/ash ratio. Figure 6 shows that the H/CH molar ratio varies between approximately 2.1 to 3.65 depending upon the temperature and relative amounts of CH and ash in the starting sample. To establish an estimate of the average H/C ratio in the hydrate product, it is necessary to multiply the H/C ratio by the fraction C in the product that comes from an external CH source. If 100% of the C supplied by the ash is incorporated into the hydrate products (100% of the 3.1% of Ca) then, by material balance, the average H/C ratio becomes 2.14.

XRD was used to investigate phases formed. Along with C-S-H, as indicated by broad diffraction peak at roughly 29 2 $\theta$ , monosulfate and hydrogarnet (phases related to  $C_3AH_6$ ) were the other major hydrate phases detectable by XRD. Monosulfate was noted by its characteristic peak at roughly 10 2 $\theta$ .<sup>33</sup> Hydrogarnet or one of the hydrogarnet family of phases such as katoite is detectable by XRD by its peak at approximately 17.5 2 $\theta$ , which is convoluted with a major portlandite peak at 18.32 2 $\theta$ . Katoite is likely because characteristic peaks at 32.5 and 40 2 $\theta$  are also present. These patterns are shown in Fig. 7 for a comparison of CH/ash ratios of 75/25, 50/50, 25/75, and 12.5/87.5 reacted for 5 d at 60 C. Based on these phases, it would be reasonable to observe H/C ratios between 1.24 ( $C_{1.7}SH_{2.1}$  as reported by Young and Hansen)<sup>34</sup> and 2 (for  $C_3AH_6$ ), depending on the relative amounts of these phases and the degree to which the sample has been dried.

To further confirm that material balance-based nonevaporable water analysis actually represents hydrate product formation, XRD intensities at 28.99 = 2 $\theta$  ( $d$ -spacing of 0.306 nm) were compared to measured nonevaporable water values. C-S-H-type hydration products are known to produce XRD scattering in the 29 2 $\theta$  region, and so intensities in this region of the XRD

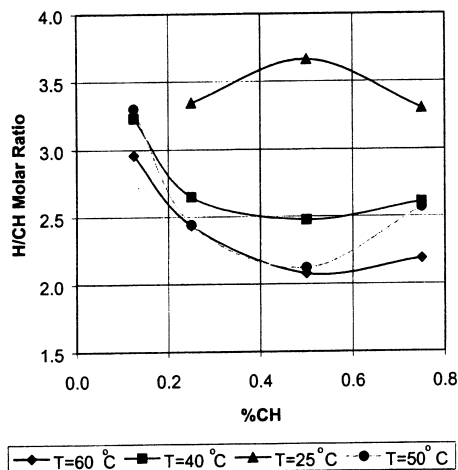


Fig. 6—H/CH molar ratio as function of initial CH/ash ratio and hydration temperature.

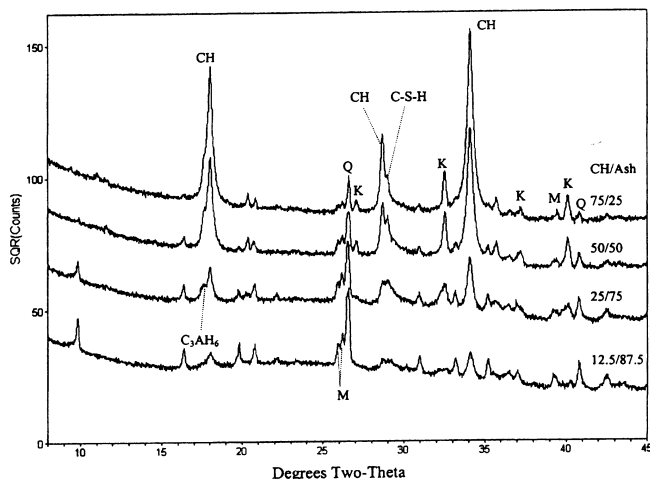


Fig. 7—XRD patterns for samples of CH/ash = 50/50 hydrated for 5 days at 60 C (CH = calcium hydroxide; C-S-H = calcium silicate hydrate; K = katoite;  $C_3AH_6$  = hydrogarnet; M = mulite; and Q = quartz).

pattern should correlate with nonevaporable water content measured by TGA. XRD patterns in this region overlap with a peak for CH at 28.69 2 $\theta$  and thus intensities at 28.99 2 $\theta$  were determined by peak fitting. Figure 7 summarizes XRD data for 5-day samples reacted at 60 C for CH/ash ratios of 75/25, 50/50, 25/75, and 12.5/87.5. Figure 8 illustrates excellent qualitative agreement between XRD intensities thus determined and nonevaporable water content confirming material balance results.

A number of control experiments were also run to verify that the observed results previously described are indeed the result of the interaction between the ash and CH and not some form of self-reaction in the NaOH solution. CH samples were soaked in deionized water and in pH 13.4 NaOH solution for 1, 5, and 19 days at 25, 40, 50, and 60 C. No reaction was noted as indicated by no change in CH content as measured by TGA. There was also no difference between samples as a function of either time or temperature, thus indicating that no reaction is occurring as the result of exposure to the either water or pH 13.4 NaOH solution.

A similar experiment was conducted for the fly ash. Samples of fly ash were soaked for 19 days in pH 13.4 NaOH solution (Fig. 9). Clearly, there is self-reaction

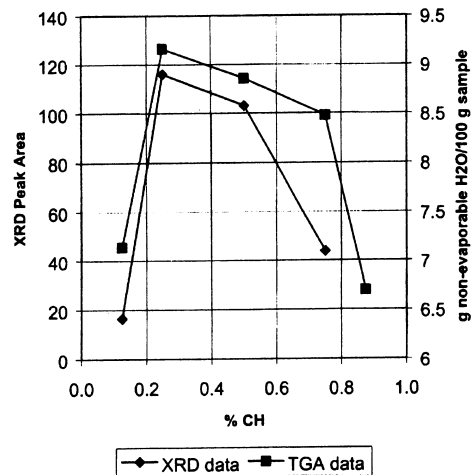


Fig. 8—Comparison of XRD C-S-H peak area at 28.99 C 2 $\theta$  and nonevaporable water content measured by TGA.

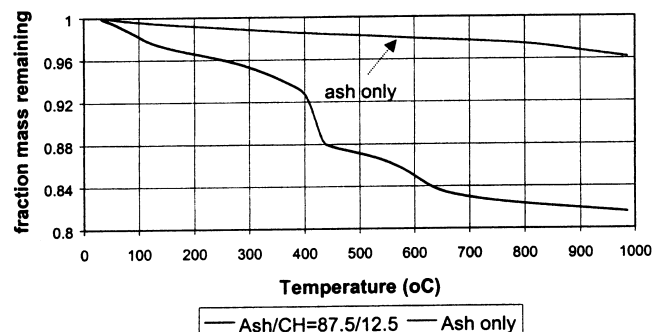


Fig. 9—TGA of hydrated ash sample and hydrated CH/ash mixture at 60 C in pH 13.4 NaOH.

Table 5—pH of supernatant for various CH/ash mixtures with 13.2 NaOH solution

CH/ash		Day 1	Day 4	Day 15
T = 25 C	100/0	13.18	13.00	12.91
	50/50	13.22	13.08 (12.85)*	12.98 (12.83)*
	0/100	13.21	13.07	12.96
T = 50 C	100/0	12.83	12.66	12.63
	50/50	12.93	12.72	12.65
	0/100	12.93	12.64	12.55

\*Values in parentheses for expressed pore solution.

shown. When compared, however, to the 16-day samples containing ash and CH at the same temperatures, it was found that self-reaction is considerably less than that observed when CH is present in the system. In all experiments the hydrate formed by self-reaction was lumped in with that formed with externally added CH, because deconvolution would add to the errors already caused by carbonate and moisture subtraction routines.

Reaction rates for through-solution reactions involving  $Ca^{++}$ , siliceous and aluminate bearing ions are sensitive to pH. Because the pH of ash is known to be lower than the pH of the NaOH solutions used, while it is thermodynamically unlikely, it is conceivable that the pH may not be constant from one mixture to the next. This could result in changes in observed reaction rates as a function of CH/ash ratio. To verify that the pore solution pH was not a function of CH/ash ratio, a series of experiments were run wherein the pH of the pore solution was measured as a function of time, tempera-

ture, and CH/ash ratio. The results, shown in Table 5, illustrate that while the pH does evolve with time and is a function of temperature, the pH does not change as a function of CH/ash ratio, and thus it is safe to assume that the pH of the system is set by the pH of the NaOH solution.

Finally, Taylor and Turner, and Beaudoin et al. suggest that the use of methanol to quench hydration may cause undesirable interactions when using TGA to quantify residual CH.<sup>28,35</sup> This, however, is particularly the case when quantifying small amounts of CH hydration byproduct. To demonstrate that the use of methanol had no significant effect in the present experiments, TGA data for as received CH and methanol washed CH were compared. No differences were noted.

## SUMMARY OF RESULTS

A method for determining the apparent activation energy for the pozzolanic reaction of low CaO containing fly ash is suggested. The technique involves reacting CH/ash pastes in simulated pore solution at fixed temperatures and times. The apparent activation energy for CH consumption is on the order of 69 kJ/g-mol. All experiments were conducted in a pH 13.4 NaOH solution. Preliminary data suggests that the stoichiometry of the hydrate phase depends upon the CH/ash ratio and that the rate of CH disappearance and the rate of hydrate formation is a function of CH content. Considerable work is yet required to describe these observations with mechanistic arguments. Microstructural data, as well as more detailed XRD and calorimetric studies, are suggested.

A single fly ash was investigated by reaction in pH 13.4 NaOH solution to mimic pore solution pH at later stages of hydration, as noted by other investigators. Similar studies should be conducted in the absence of NaOH (pH approximately 12.7 for CH) and at other pH values and with other cation and anions present in solution, that is,  $K^+$  and  $SO_4^{2-}$ . Ashes with various amounts of aluminate and CaO phases should then be studied to understand the effect of chemical composition on reactivity. Finally, comparison of model-predicted performance and performance in portland cement systems would be useful.

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