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HYDROTHERMAL REACTIONS OF FLY ASH WITH $Ca(OH)_2$ AND $CaSO_4{\cdot}2H_2O$

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ABSTRACT

Hydrothermal reactions of fly ash were investigated. Variations in reactivity depended on the presence of added $Ca(OH)_2$ or $CaSO_4 \cdot 2H_2O$. Isothermal calorimetry determined the kinetics of the reactions between fly ash and these compounds. Fly ash was activated by these calcium salts and activation influenced hydration rates as determined by the rates of heat evolution. X-ray diffraction analysis determined the phases formed as a result of hydrothermal treatment. Calcium silicate hydrate, tricalcium aluminate hydrate and ettringite were observed. The mechanical properties developed by hydrothermal treatment demonstrates that hazardous ashes could be consolidated to be handled. Alternatively, non-hazardous ashes can be reacted to form useful products. © *1997 Elsevier Science Ltd*

Introduction

Because of the large amount of fly ash generated annually, there is continuing interest in establishing ways in which it may be used. It is well known that fly ash demonstrates satisfactory performance when intermixed with Portland cements. However, only a small proportion of ash is utilized in this way. Recently there is growing concern that certain fly ashes may be hazardous. Therefore, identification of further means to facilitate the use of fly ash and avoid the need to dispose of it as hazardous waste are desirable. To achieve these goals it is essential to establish the nature of the phases that form in the presence of selective additives and assess whether these phases are capable of sequestering hazardous species. Fly ashes reacted with suitable additives have been reported to produce new types of cementitious materials (1,2). A potentially attractive process involving reacting with activators, which may offer the benefits of facilitating waste immobilization and forming useful products, is hydrothermal treatment.

It is a common view that the primary reaction of fly ash in cement, the pozzolanic reaction, occurs to an appreciable extent only after one or more weeks. In the pozzolanic reaction, amorphous silica from the fly ash reacts with $Ca(OH)_2$ produced during the hydration of the cement. Reaction produces an amorphous calcium silicate hydrate (C-S-H) as follows:

$$SiO_2 + 1.7Ca(OH)_2 + 2.3H_2O \Rightarrow CaO_{1.7}SiO_2 \cdot 4H_2O \qquad (1)$$

Because the pozzolanic reaction is much slower than the reactions which occur during cement hydration, the fly ash behaves more or less as an inert material, primarily serving as nuclei for precipitation of $Ca(OH)_2$ and C-S-H originating from the cement hydration (3,4). Farry et al. (3) reported the duration of the period before the onset of the pozzolanic reaction depends on the alkalinity of the pore solution. Highly alkaline solutions are more capable of solubilizing silica by breaking Si-O bonds in the glassy, silica-rich portions of fly ash. In order to maintain active hydration of the fly ash, it is necessary to supply hydroxyl ion. Roy and Silsbee (5) have shown that the hydroxyl ions, which can be derived from the fly ash alone, are frequently insufficient. This is particularly true of low-lime fly ashes.

The formation of an appropriate hydrate structure on the surface of the fly ash particles also assists in promoting fly ash hydration. The conditions of formation, morphologies, and crystallinities of such hydrates depend largely upon hydroxyl ion concentration (6). The increase in SiO_2 solubility with increasing pH has been illustrated with reference to the quaternary system CaO-Na_2O-SiO_2-H_2O (7). It has been demonstrated empirically that the presence of $Ca(OH)_2$ will markedly increase the solubility of SiO_2 in fly ash (8) thereby making it available to undergo the pozzolanic reaction illustrated in EQ. 1. However, both the composition and the crystallinity of calcium silicate hydrate vary depending on the temperature at which it is formed. These variations are likely to influence the ability of the hydrates to sequester hazardous constituents in an ash. Regarding mechanical property development, Jiang and Roy (9) suggested that well crystallized hydrated calcium silicates may form under hydrothermal conditions and form strong networks with superior mechanical properties.

The principle underlying activation by gypsum is based on the ability of the sulfate ions to react with the alumina, the latter being one of the principal components in fly ash. This results in dissociation of the glass structure (10). It was suggested that the reaction between sulfate and fly ash also may lead to a dense hydrate structure and higher strength (1).

Effects of curing temperature on the properties of cements blended with fly ash have been reported in the literature (8,12,13). The results reveal that low calcium fly ash reduces the heat evolution when used as a partial replacement for cement (8,12). Although $Ca(OH)_2$ exhibits retrograde solubility, the rates of hydration of Portland and blended cements increased with increasing temperature (13). The solubility of the SiO_2 present in fly ash was found to increase with increasing temperature (14). Because of the large difference in the solubilities of SiO_2 and $Ca(OH)_2$, it is likely that the ability of SiO_2 to enter solution is rate limiting (15). Therefore, enhancing SiO_2 solubility accelerates the rate of reaction.

Heat evolved during early hydration was measured for both activated and unactivated ash. To establish the nature of the temperature dependent phenomena accompanying hydration, analyses of the variations in solution chemistry were carried out, and the hydration products were identified by X-ray diffractometry. Finally, the effects of activators and temperature on splitting strengths were established.

Experimental

Two fly ashes were used: class F fly ash (B25) and class C fly ash (B75). The compositions of the ashes used are provided in Table 1.

TABLE 1

Compositions of Fly Ashes (Wt %)

Oxide	Class F Ash	Class C Ash
SiO_2	50.2	36.9
Al_2O_3	27.0	17.5
Fe_2O_3	13.8	5.9
CaO	1.8	26.1
MgO	0.8	5.9
Na_2O	0.2	1.9
K_2O	2.5	0.5
SO_3	---	2.1

Class F fly ash has a low lime content (less than 10%), is a pozzolanic material, and requires an external source of $Ca(OH)_2$ to develop mechanical properties associated with the formation of C-S-H. Class C fly ash has a high lime content (>10%), is hydraulic, and will develop mechanical properties in the absence of an external source of $Ca(OH)_2$. The ashes were reacted for 24 hours at 25°, 60°, 80°, 100°, and 180°C under saturated steam pressure using tubular pressure vessels.

Calorimetric studies were performed to test reactivities of the activated and unactivated ashes by determining rates of heat evolution. In isothermal calorimetry, heat evolved during reaction is conducted across thermopiles which surround the calorimetric cell. The heat output is thereby converted to a voltage output which is recorded against time. Applying a known thermoelectric coefficient allows the rate of heat evolution to be determined. In the method used, approximately three grams of water were inoculated into an equivalent mass of reactant powders that had been placed in a gold-plated copper sample cup and placed within the calorimeter cavity. The cups were sealed with plastic film to minimize evaporation of water. Each reactant was allowed to equilibrate separately to the appropriate temperature prior to mixing. The water was equilibrated in a syringe and, when equilibration had been achieved, the plastic film was penetrated and the water injected over the reactants. The rates of heat evolution, dQ/dt in mWatts, were measured and recorded using a computer data acquisition system. Integration of the areas under the rate curves allowed calculation of the total heats evolved. A trapezoid integration was utilized for such analyses. Calorimetric data were obtained at 25°, 38°, and 60°C.

X-ray diffraction analyses were performed on a Scintag automated X-ray diffractometer interfaced with a microVAX computer. Variations in solution pH were measured with an Orion 920 pH meter that utilized an automatic temperature-compensating probe. The splitting strength was measured on an Instron physical testing machine. The splitting strength was calculated using the expression: $S.S. = 2P/(\pi dt)$, where d is the diameter and t the thickness. The morphologies and chemical compositions of the hydrates were determined by using scanning electron microscopy (SEM) and energy-dispersion X-ray (EDX) spectrometry.

Results and Discussion

Kinetics of Reaction

Reactivity of class F fly ash with $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$. The heat evolved during the hydrothermal reactions of class F fly ash and that evolved when the ash reacted with 10wt.% $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$ were measured. Reactions at 25°, 38°, and 60°C were investigated and the rates of heat evolution during the first hour after mixing are shown in Figure 1. Reaction at elevated temperatures provided sufficient thermal activation to significantly accelerate the reactions. However, only single heat evolution peaks, which occur immediately after mixing, were observed. Calorimetric curves characteristic of cement reactions are typically characterized by two heat evolution peaks. One occurs immediately after mixing the solid and liquid reactants and is termed a "mixing peak". Mixing peaks are primarily associated with wetting, initial dissolution, and establishment of critical degrees of supersaturation. The total area under the mixing peak represents the total heat evolved during this initial period.

Following the mixing peak is a main reaction peak. The two peaks may be well resolved and temporally separated by an induction period. During the induction period, the rate of reaction becomes very low. This behavior is typical of the manner in which heat is evolved in the reactions of tricalcium silicate in cement (16). Alternatively, the mixing and main reaction peaks may overlay one another and not be readily resolved. Finally, the presence of a single peak may be indicative of a reaction which is diffusionally controlled. Only a single heat evolution peak, as shown in Figure 1, was observed regardless of the temperature when

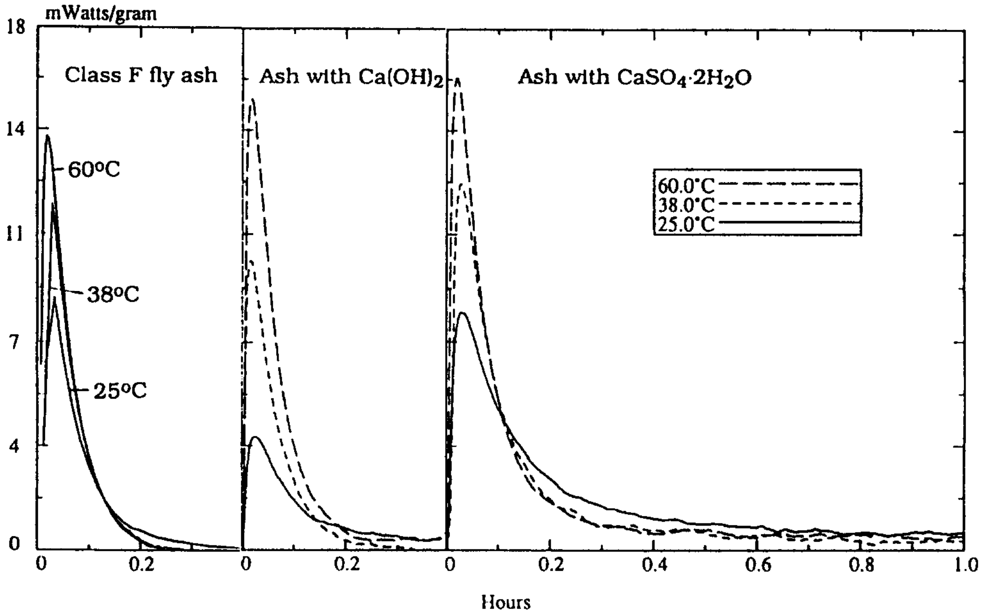

FIG. 1.

Calorimetric curves showing rates of heat evolution of class F fly ash and mixtures of this ash with $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$ during the first hours of hydration at different temperatures.

low-lime fly ash reacted. The peaks appeared between ~3 and 5 minutes and may be regarded as mixing peaks. Although the extent of heat evolution increased with increasing temperature, it can be concluded that the low-lime ash exhibits a relatively low reactivity at temperatures of 60°C and below. This is illustrated by the fact that the activators were relatively ineffective in promoting heat evolution; the extent of heat evolution was the greatest when $CaSO_4 \cdot 2H_2O$ is added even though its presence will not facilitate the pozzolanic reaction shown in EQ 1. Although they underwent reaction at elevated temperatures, specimens prepared for mechanical testing exhibited very low strengths. Therefore, mild hydrothermal treatment of low-lime ash in the presence of $Ca(OH)_2$ or $CaSO_4 \cdot 2H_2O$ did not appear to accelerate the formation of cementing phases, such as C-S-H, by a mechanism which is different from the diffusionally controlled pozzolanic reaction. However, under

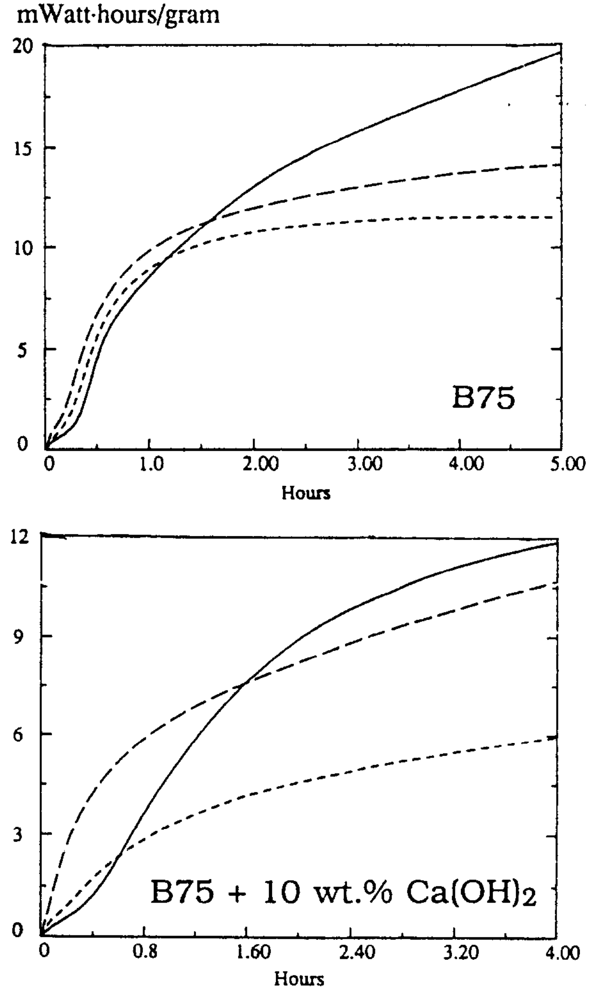

FIG. 2.

Calorimetric curves showing the total heat evolved as a function of time (a) for class C fly ash, (b) for class C fly ash with $Ca(OH)_2$.

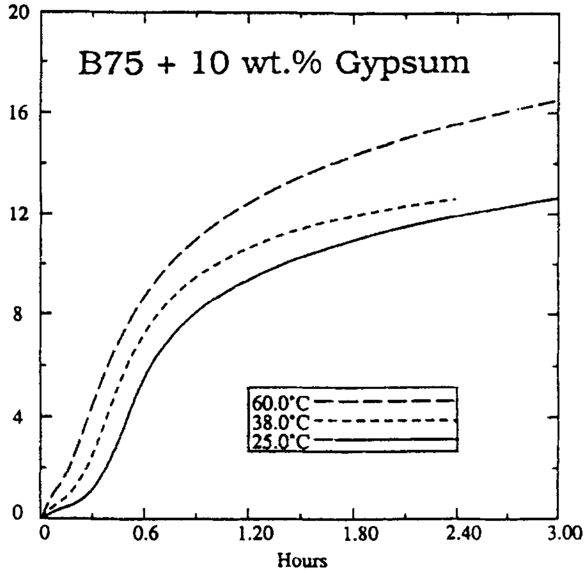

FIG. 2 (continued).
Calorimetric curves showing the total heat evolved as a function of time (c) for class C fly ash with $CaSO_4 \cdot 2H_2O$ during the first several hours of hydration at different temperatures.

hydrothermal treatment at higher temperature low-lime ash becomes very active as will be subsequently described.

Reactivity of class C fly ash. The high-lime fly ash exhibited direct cementitious activity. The rates of heat evolution during the first 3 hours of reaction of class C fly ash at 25, 38, and 60°C show two peaks separated by induction periods. This thermal behavior is very similar to that observed during the hydration of Portland cement (13,17). The total heats evolved in 5 hours are shown in Figure 2a. The data in the figure show that reaction at 60°C initially occurred at a more rapid rate but evolved less total heat than reaction at 25°C.

Class C ash + $Ca(OH)_2$. Figure 2b compares the heat evolution characteristics of mixtures of the ash and 10 wt.% $Ca(OH)_2$ at 25°, 38°, and 60°C. The induction period had disappeared at 60°C and the reaction proceeded continually after the first peak. Comparing the heat evolved during the reaction of the ash in the absence of $Ca(OH)_2$ to that in its presence demonstrates that $Ca(OH)_2$ did not provide an effective means of activating this ash during this initial period. The addition of $Ca(OH)_2$ resulted in a reduction in the total heat evolved reducing the amount liberated by about one half. This result shows that hydration of high-lime ash was highly thermally activated and much more calcium silicate hydrate formed at 60°C than at the lower temperatures (as X-ray diffraction analyses will illustrate).

Class C ash + $CaSO_4 \cdot 2H_2O$. Heat evolution during the reaction of mixtures of the ash and 10 wt.% $CaSO_4 \cdot 2H_2O$ are shown in Figure 2c. Heat evolution in the presence of $CaSO_4 \cdot 2H_2O$ was generally comparable to that in the absence of an additive. However, the kinetics of these reactions appeared more well behaved than those previously discussed. Reaction at higher temperature increased the amounts of heat evolved during the mixing peak, shortened the induction period and increased the total heat evolution. The addition of $CaSO_4{\cdot}2H_2O$ will not result in the pozzolanic reaction represented in Eq. 1. Rather, the origin of heat evolution is the result of the formation of a calcium sulfoaluminate hydrate i.e., ettringite, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$. Ettringite formation in the class C fly ash is the result of the lime and the alumina in the ash reacting with the added $CaSO_4{\cdot}2H_2O$. Such reaction would be limited in the class F fly ash because of its low lime content. Based on an analysis of the hydration behavior in the system $3CaO{\cdot}Al_2O_3$-$CaSO_4{\cdot}2H_2O$, it has been observed that ettringite formation is diffusionally controlled (18,19). In such a system ettringite forms on the surfaces of the $3CaO{\cdot}Al_2O_3$ grains and promotes the formation of an underlying layer of hydrous alumina. The latter acts as a diffusional barrier. As a consequence, ettringite formation is not highly thermally activated. However, Figure 2c illustrates that the rates of reaction during the first 4 hours were accelerated and the heat release was significantly increased at higher temperatures. This suggests that formation of an effective hydrous alumina diffusional barrier does not occur when fly ash is the alumina source.

Solution Chemistry. Figure 3 shows the variations in solution pH as a function of temperature when the ashes or the ash-activator mixtures were reacted with water at a water-to-solid weight ratio of 2.67. Slurries of the ash and the ash-activator mixtures were hydrothermally treated at 25, 60, 100 and 180°C for 24 hours. The pH values were obtained after the slurries were cooled to 25°C.

Figure 3a shows the variations in pH in slurries containing class F fly ash; 3b shows those in class C ash slurries. The extent of reaction at 25°C was negligible for all compositions. Class F ash maintained a neutral pH regardless of the thermal treatment, whereas class F ash-$CaSO_4{\cdot}2H_2O$ mixtures showed a nominal decrease in pH with reaction at temperatures above 60°C. The pH of a saturated $Ca(OH)_2$ solution (ca 12.6) was maintained in mixtures of class F ash and $Ca(OH)_2$ when these were treated at 25° and 60°C. When these mixtures were treated at 100° and 180°C, solutions having pH values of about 11 were produced. A reduction of the pH to a value below 12.6 indicates the consumption of the $Ca(OH)_2$ initially present. The pozzolanic reaction forming C-S-H is responsible for such a reduction and that establishment of the same pH value indicates the extents of reaction were comparable at both temperatures.

As would be expected from its CaO content, the pH of a slurry containing class C ash was above 12 indicating the ash to be highly basic. This pH was maintained after treatment at 25°

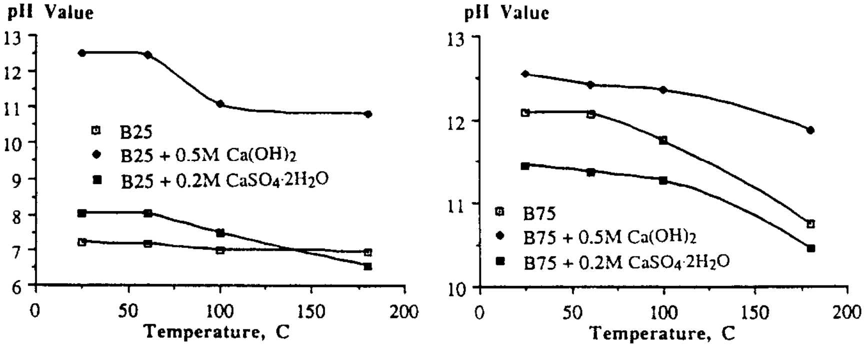

FIG. 3.

The variations in solution pH for (a) class F fly ash with activators (b) class C fly ash with activators at different temperatures.

and 60°C indicating minimal reaction at these temperatures. The pH decreased as a result of treatment at 100° and 180°C reaching a value near 11 at the higher temperature. This is comparable to the value reached in the class F ash and this pH may be near that at the invariant point between hydrous silica and C-S-H (20). It was also observed that the surface area produced after fly ash reacted with $Ca(OH)_2$ increased significantly between 60° and 100°C (21). This is consistent with the formation of C-S-H.

Hydrothermal treatment of mixtures of class C ash and $CaSO_4{\cdot}2H_2O$ also resulted in the decrease of pH as the temperature of treatment increased. Except when the treatment was carried out at 180°C, a mixture of C-S-H and ettringite formed. Because the formation of both consumed available lime, the pH of the solutions were reduced as compared to those when $Ca(OH)_2$ was added. Indeed, the pH values measured in the ash-$CaSO_4{\cdot}2H_2O$ slurries were also always more acidic than that of the ash slurry.

Regardless of the cementing compound formed (C-S-H or ettringite), reaction in the range of temperature from 60° to 100°C is important because such temperatures are relatively easily achieved using waste heat from utilities. Thus the opportunity exists to remediate hazardous ash by treatment at these temperatures.

Hydration Products Formed. The phases formed during the hydration of fly ash with $Ca(OH)_2$ and $CaSO_4{\cdot}2H_2O$ were determined by X-ray diffraction (XRD). The XRD patterns obtained indicated that temperature and compositional variables resulted in the formation of variety of phases. When class F fly ash was hydrothermally treated at temperatures up to 180°C, only quartz and mullite (which were present in the untreated ash) were detected. No other discernible crystalline phases were observed. Class C fly ash showed much higher reactivity. C-S-H was observed in SEM micrographs after treatment at temperatures up to 180°C. Figure 4 shows that a large amount of ettringite was formed when class C fly ash was hydrothermally treated at temperatures up to 80°C. Stellerite, $Ca_2Al_4Si_{14}O_{36}{\cdot}14H_2O$, then was observed at 100°C. This indicates that limit of thermal stability of ettringite is below this temperature.

A number of crystalline phases were formed when the class F fly ash reacted with $Ca(OH)_2$ or $CaSO_4{\cdot}2H_2O$. Calcite was observed after the treatment of mixtures of class F fly ash and $Ca(OH)_2$ regardless of temperature. Calcium sulfate anhydrite, $CaSO_4$, was observed after treating ash-$CaSO_4{\cdot}2H_2O$ mixtures at 110° and 180°C. Unreacted fly ash could be observed due to the presence of quartz and mullite peaks after reactions with $Ca(OH)_2$ and $CaSO_4{\cdot}2H_2O$ at all temperatures. The presence of C-S-H cannot be confirmed by the X-ray diffraction; it is poorly crystalline and its main peak is masked by the main calcite peak. Moreover, the C-S-H from fly ash is reported as less crystalline than the C-S-H from ordinary Portland cement (22). The C-S-H which formed during reaction of class F fly ash with 10 wt.% $Ca(OH)_2$ for 24 hours at 100°C fully surrounded the ash particles. The Ca/Si ratio of this C-S-H is 1.4, as determined by EDX. This value falls in the range of values between 1 and 1.50 reported by Regourd (22). The presence of such C-S-H coatings surrounding the fly ash particles is consistent with a diffusionally controlled rate of reaction as previously discussed.

X-ray diffraction analyses of the products of hydrothermal treatment of class C ash have shown that the silica-containing and alumina-containing phases originally present react with $Ca(OH)_2$. Calcium aluminate hydrates formed at temperature below 100°C are of interest because they are believed to act as hosts for incorporation of hazardous species. In addition, a large amount of ettringite was formed in the mixture of this ash with $CaSO_4{\cdot}2H_2O$ at temperatures up to 80°C. Figure 5 shows that, although ettringite is stable up to 80°C, it decom-

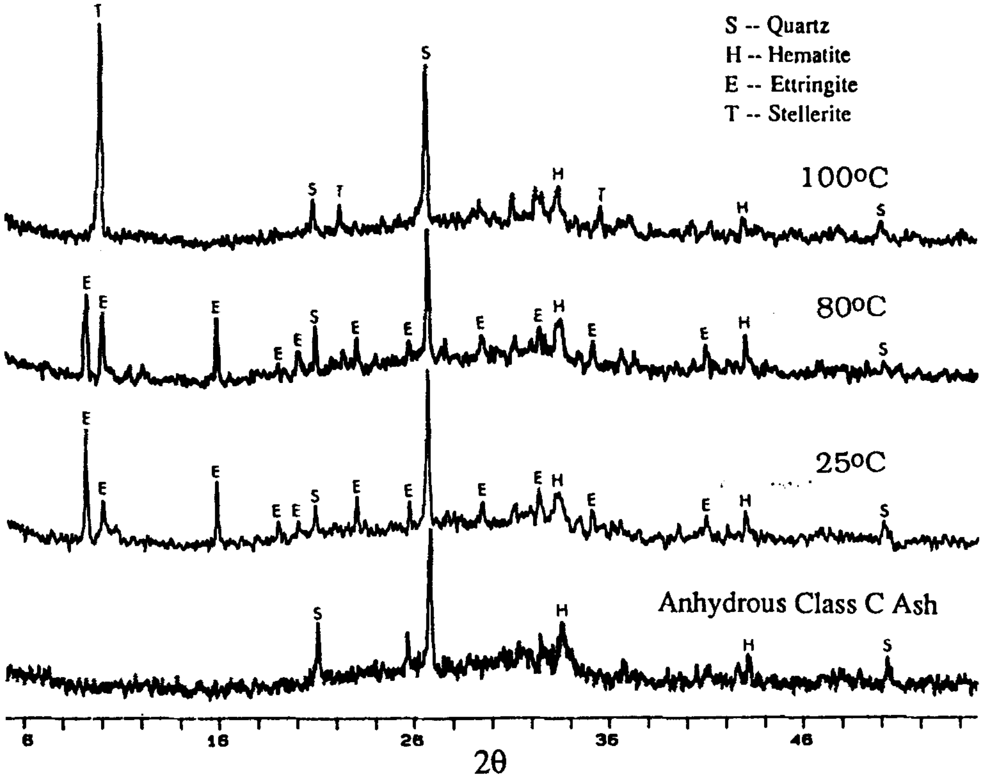

FIG. 4.
XRD of class C fly ash hydrothermally treated at different temperatures for 24 hours.

poses at higher temperatures. Ettringite exists in equilibrium with calcium aluminate hydrates. The proportion of the two depends on the availability of sulfate. Therefore, the absence of calcium aluminate hydrates and the presence of unreacted gypsum in the patterns shown in Figure 5 suggest that 10% $CaSO_4 \cdot 2H_2O$ is sufficient to fully consume all the available alumina in this ash in the formation of ettringite. As with C-S-H formation, ettringite formation provides the opportunity to produce cementitious materials. The mechanical properties of the materials are discussed in the following section.

Mechanical properties. If fly ashes are to be used for a variety of technological applications, it is important they develop suitable mechanical properties. To establish mechanical property development, cylindrical samples of the fly ash were fabricated, subjected to hydrothermal treatment for 24 hours at 25°, 60°, 80°, 110°, and 180°C, and then tested in flexure. Because of the poor reactivity of class F fly ash, strength data could not be obtained after hydrothermal treatment of the ash itself or of ash mixtures. However, the values obtained from class C fly ash show that reasonable strength values can be realized by hydrothermal treatment in the presence of $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$, Figure 6. At a minimum, the development of mechanical properties in this range show that hazardous ashes can be consolidated to be handled. Alternatively, non-hazardous ashes could potentially be reacted to form useful products.

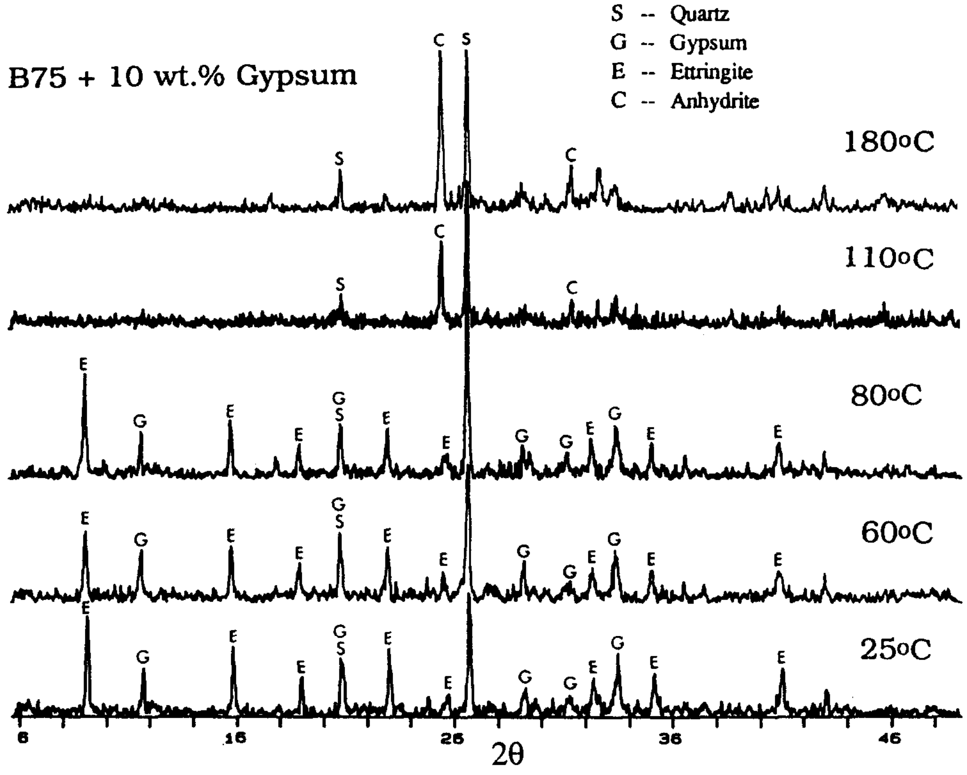

FIG. 5.
XRD of class C fly ash with 10 wt.% $CaSO_4 \cdot 2H_2O$ hydrothermally treated at different temperatures for 24 hours.

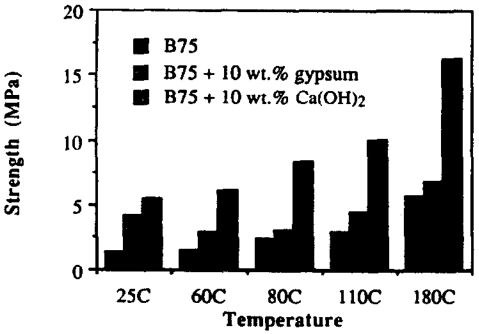

FIG. 6.
Splitting strengths of class C fly ash reacted with activators at different temperatures.

Conclusions

The low-lime ash studied did not undergo significant reaction when subjected to short-term hydrothermal treatment. Such ashes are well known to slowly undergo the pozzolanic reaction with the formation of calcium silicate hydrate. Present findings are consistent with a diffusionally controlled reaction which is not strongly thermally activated. Alternatively, the high-lime fly ash studied exhibited direct cementitious activity with water, showed pozzolanic reactivity, and ettringite formed when reaction occurred in the presence of $CaSO_4 \cdot 2H_2O$.

Reaction of high-lime ash was sluggish at 25°C. Reaction occurred more rapidly at elevated temperature with significant reaction occurring during 24 hours at 60°C. A variety of products were formed in the hydrothermal reactions of high-lime ash and ash-$Ca(OH)_2$ or ash-$CaSO_4 \cdot 2H_2O$ mixtures. Principal cementing phases formed were calcium silicate hydrate, calcium aluminate hydrate and ettringite. C-S-H formed during hydrothermal treatment of high lime ash regardless of the presence of added $Ca(OH)_2$. However, C-S-H formation was more extensive when $Ca(OH)_2$ was added. Significant ettringite formation was observed only when $CaSO_4 \cdot 2H_2O$ was admixed and only at temperatures of 80°C and below. Reasonably high strengths can be achieved from high-lime fly ash with $CaSO_4 \cdot 2H_2O$ and $Ca(OH)_2$ additions indicating that hazardous ashes could be consolidated to be handled and landfilled.

Acknowledgement

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