Pergamon

Cement and Concrete Research, Vol. 26, No. 7, pp. 1131-1143, 1996
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0008-8846/96 $15.00 + .00

PII S0008-8846(96)00074-9

THE INTERACTION OF CALCIUM NITRATE AND A CLASS C FLY ASH DURING HYDRATION

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(Refereed)
(Received June 1, 1995; in final form April 10, 1996)

ABSTRACT

Different analytical techniques were used to study the hydration of a Class C fly ash in the presence of various concentrations of calcium nitrate. Calcium nitrate was found to accelerate the hydration of calcium aluminate phases in relationship to dosage. Hydration mechanisms were modified resulting in altered products. The new products consisted of calcium aluminate hydrate and nitrate. Evidence suggested that the modified nitrate-hydrates competed with or inhibited the formation of calcium aluminate sulfates hydrates.

Introduction

Fly Ash is routinely used as a mineral admixture to improve the economics and performance of concrete in many applications. The incorporation of fly ash often leads to an extension of setting times, particularly in colder environments. This retardation of set can be offset by making use of chemical admixtures. Calcium chloride is a common set accelerating admixture but the Cl^- anion can lead to severe corrosion of rebar in concrete. Calcium nitrate has been one of the leading nonchloride accelerators used in place of calcium chloride.

Limited information, however, is available on the chemical interaction of calcium nitrate with cementitious material such as Class C fly ash. Class C fly ash is self cementing and hardens without the addition of activating chemicals similar to cement. This setting is primarily due to the hydration of crystalline and amorphous calcium aluminate phases (1-4). This study focused on the impact that calcium nitrate dosed at various concentrations, had on the hydration of a particular Class C fly ash.

Experimental

A fly ash sample obtained from the Fayette Power Project in LaGrange, Texas was used. The ash's chemistry, as given below, is typical for a Texas ASTM - C 618 Class C fly ash.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	H_2O	LOI	+325 sieve	S. G.
34.5	20.6	5.4	26.2	5.8	1.9	0	0.3	11.9	2.75

X-ray diffraction and thermal analysis found the material to contain tricalcium aluminate, anhydrite, quartz, calcium hydroxide and magnetite as minor constituents. Appropriate solutions of calcium nitrate were mixed with 20 grams of the ash at a w/s = 0.5, 1 and 5 to represent different test conditions. Molar concentrations were adjusted so that $Ca(NO_3)_2$ was dosed at a rate of 2.5, 5 and 10% by weight of ash for all slurries.

After mixing the samples were sealed in plastic vials. Immediately before testing, subsamples were removed and acetone washed to stop hydration prior to analysis by differential scanning calorimetry (DSC), X-ray diffraction (XRD), and fourier transform infrared analysis (FTIR). Details of these analytical techniques were reported elsewhere (5).

Results and Discussion

Fly Ash Hydration Analysis by Calorimetry. Analysis of the fly ash slurries at w/s of 1 by a semi-adiabatic calorimetry clearly showed that calcium nitrate influenced hydration kinetics. This test was performed at a w/s of 1 to more clearly resolve different rates of heat evolution produced by varying nitrate concentrations. The time to reach maximum heat evolution is presented in Table 1.

The control reaction reached an initial peak corresponding to a 2°C temperature increase within 10 minutes followed by an approximate 30 minute dormant period and then an additional temperature rise of 1°C to a peak temperature of 3°C. Reactions with $Ca(NO_3)_2$ solutions produced much higher heat evolution at a greatly accelerated rate. The dormant stage was effectively by-passed with the major peak overlapping the dissolution peak to a point where resolution was not possible. From Table 1 it can be seen that nitrate provided additional acceleration with increasing concentration, although asymtopically.

Hydration Kinetics. The hydration kinetics in relation to the conditions tested are presented in Figure 1. Degree of hydration is represented by total peak area of endothermic DSC peaks (all less than 400°C) versus times ranging from 10 minutes to 3 days. Figure 1 presents results for

TABLE 1

Results of Semi adiabatic Calorimetry

Admixture	wt % $Ca(NO_3)_2$	Time to Peak (min)	Peak Temp. (C°)
Control Peak 1	0	10	2
Control Peak 2	0	41	3
0.6095 M NO_3	2.5	10	8
1.219 M NO_3	5.0	8	8.3
2.438 M NO_3	10	7	11

calcium nitrate solutions with Class C ash at a w/s of 0.5. This condition reflects the most probable mix for field applications. The nitrate solution markedly increased the extent of hydration as well as the rate.

The increased hydration due to the addition of calcium nitrate is considered to be either a result of the admixture catalyzing existing reactions to produce more hydration products at a faster rate, or due to admixture/ash interactions that lead to new or modified products and thus provide for additional hydration. Understanding of how hydration products were modified by the use of this admixture required more extensive analysis.

Details of Hydration Process. A more thorough analysis of hydration was made from DSC curves of hydrated Class C ash in Figure 2. Thermal gravimetric analysis proved that each DSC peak for all dosages corresponded with a weight loss, and was thus probably associated either with hydration or free moisture.

The appearance of two endotherms approximately at 50 and 70°C is noteworthy because these temperatures are very low for dehydration. It was determined that the peaks were not due to residual acetone. The growth of these peaks suggested they were a result of some form of undefined hydration process and weakly adsorbed water.

Referring to the control in (Figure 2a), it is observed that after 30 minutes the only evidence of hydration is a nearly non-existing exothermic peak at 131°C. After three hours this peak began to grow and shifted to over 140°C. New peaks at 50°C, 80°C and 280°C had also grown to a significant size at three hours. These peaks continued to increase with time with the 50°C and 145°C peak dominating at 24 hours. (The 50°C peak at 1 day appears lower, however this was traced to excessive sample drying.)

Figure 2b presents the hydration with the addition of 2.5% calcium nitrate. The accelerating effect of the salt is evident from the larger size of the two endotherms at 30 minutes. A new

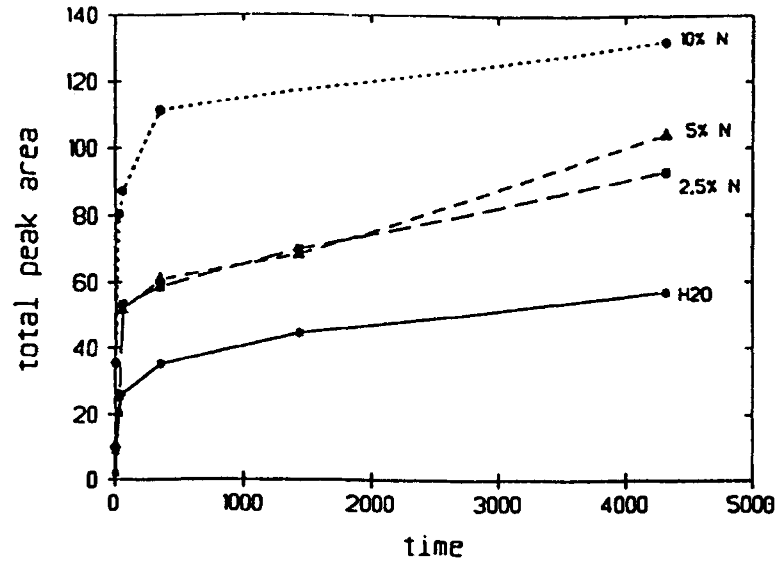

FIG. 1.
Hydration of a Class C ash with different concentrations of calcium nitrate.

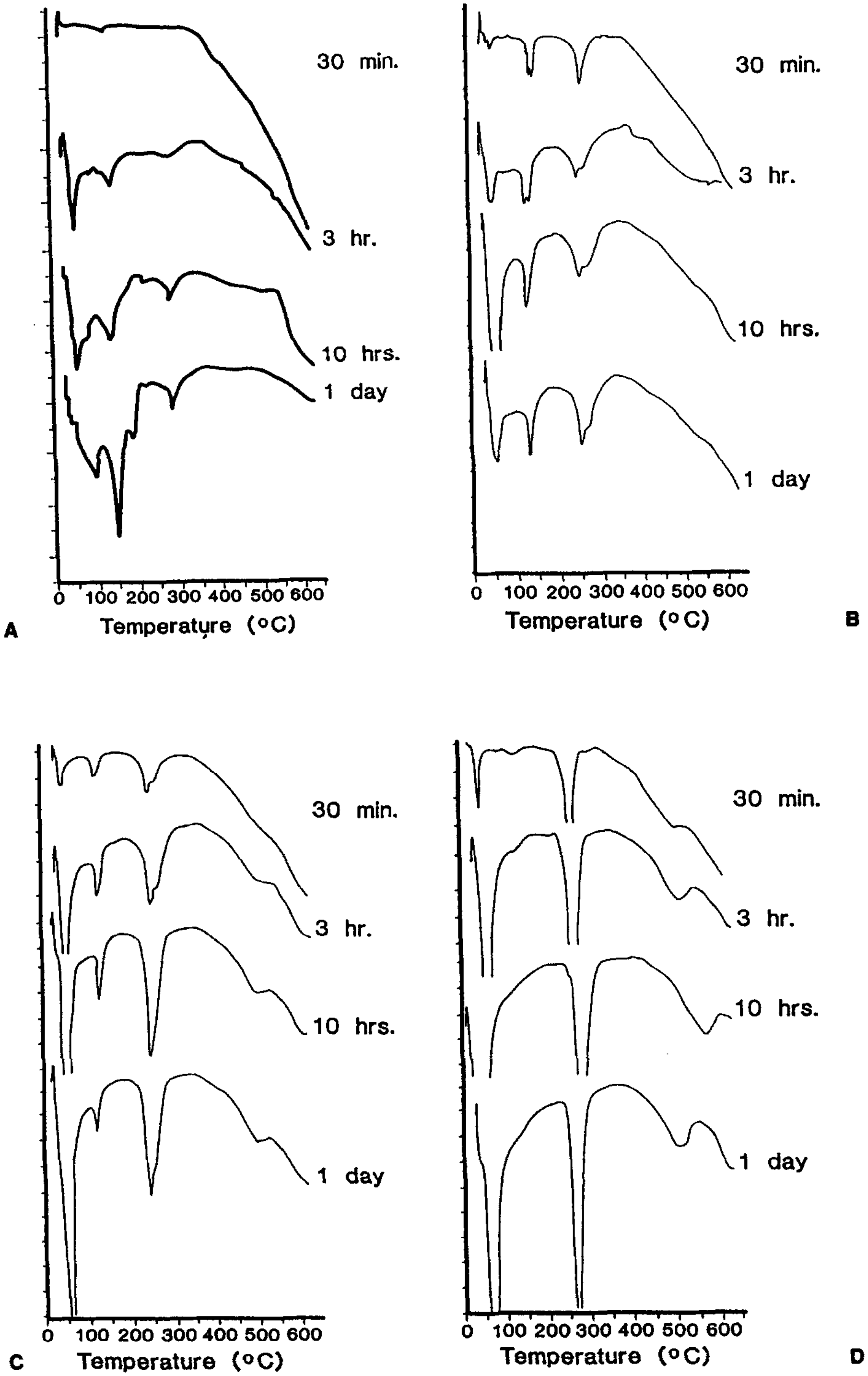

FIG. 2.

DSC analysis of hydrated fly ash with: a) water, b) 2.5% calcium nitrate, c) 5% calcium nitrate, d) 10% calcium.

peak at ~ 135°C appears just below the ~ 148°C peak forming a doublet, and a new higher temperature peak at ~ 260°C appears. Although all peaks continues to grow with time, the lower temperature doublet remains larger than the higher temperature peaks. The growth of the 135°C portion of the doublet occurs more rapidly than the growth of the 148°C peak growth at all stages. The original peak at 280°C for hydration with H_2O also slowly becomes apparent as a shoulder on the 260°C peak.

The addition of 5% calcium nitrate (Figure 2c) continues to accelerate peak growth. The 135°C side of the doublet now completely overshadows the higher temperatures side and appears to go through a maximum at 10 hours and then begins receding. Under these conditions the 250°C endotherm becomes larger than the 135°C peak. The presence of the 280°C peak is barely discernible as a shoulder on the 250°C endotherm. A new peak near 490°C now appears and grows with time.

Ten percent calcium nitrate seen in Figure 2d accelerates the existing growth even more. The 135°C peak now basically disappears by 10 hours. The 250°C is much larger with no indication of a higher temperature shoulder. The highest temperature peak at ~ 500°C is now larger and continues growing.

The major peaks between 120-150°C for the hydration reaction with H_2O are in a region typically assigned to a variety of hydration products such as $C_6A\bar{S}_3H_{32}$, C_2AH_8, and $C\bar{S}H_2$ (6-8). Peaks in the region of 250 to 280°C are likewise associated with a number of hydrates including C_4AH_{19}, $C_4A\bar{S}H_{12}$, AH, and $K_2SC\bar{S}H$ (9,10).

Additional testing was felt necessary to better identify peak origins. Infrared analysis of the ash hydrated in H_2O is provided in Figure 3a. Comparison of the spectra over the time frame studied displays the hydration progress by the growth of H_2O bands at 3500 and 1630cm^{-1}. The major peak associated with sulfate, interestingly, appears to shift from over 1200cm^{-1}, at 30 minutes to ~ 1160cm^{-1} by 24 hours. The cause of this phenomenon can be attributed to the incorporation of gypsum (1240cm^{-1}) into the calcium aluminate sulfate AFt (1166cm^{-1}) phase (16). This data suggests that the Class C ash contains calcium aluminate capable of eventually reacting with gypsum to form AFt according to the following reactions:

$$C_3A + 3C\bar{S}H_2 + 26\,H \rightarrow C_6A\bar{S}_3H_{32} \; (\underline{11})$$

X-ray diffraction analysis confirmed this interpretation. Results in Figure 3b monitor the hydration of ash (w/s = 5) by XRD from 1 hour to 1 day. From these patterns the decrease of the peak representing C_3A, indicates the consumption of C_3A due to hydration. At 3 hours the appearance of a broad peak at 9.6Å can be traced to the growth of ettringite (14).

Hydration of a standard C_3A sample alone and in the presence of gypsum was also monitored to facilitate identification of fly ash thermal peaks. In Figure 4a, DSC results of C_3A hydration produces two growing peaks at ~ 135 and 280°C. C_3A is typically considered to undergo hydration to two metastable, hexagonal phases followed by conversion after 24 hours to a stable cubic phase, through:

$$2C_3A + 27\,H_2O \rightarrow C_2AH_8 + C_4AH_{19} \rightarrow 2C_3AH_6 + 15H \; (\underline{12})$$

X-ray diffraction analysis of this sample (Figure 4b) shows C_3A hydrating to form C_2AH_8 and C_3AH_6. Characteristic peaks for C_4AH_{19} are not clearly visible, although it should be mentioned that several of the major peaks for this species overlap with the C_2AH_8 peak. The possible absence of C_4AH_{19} might indicate that C_2AH_8 is produced, preferentially to or is relatively more stable than C_4AH_{19} under the higher water/solids and calcium hydroxide undersaturated

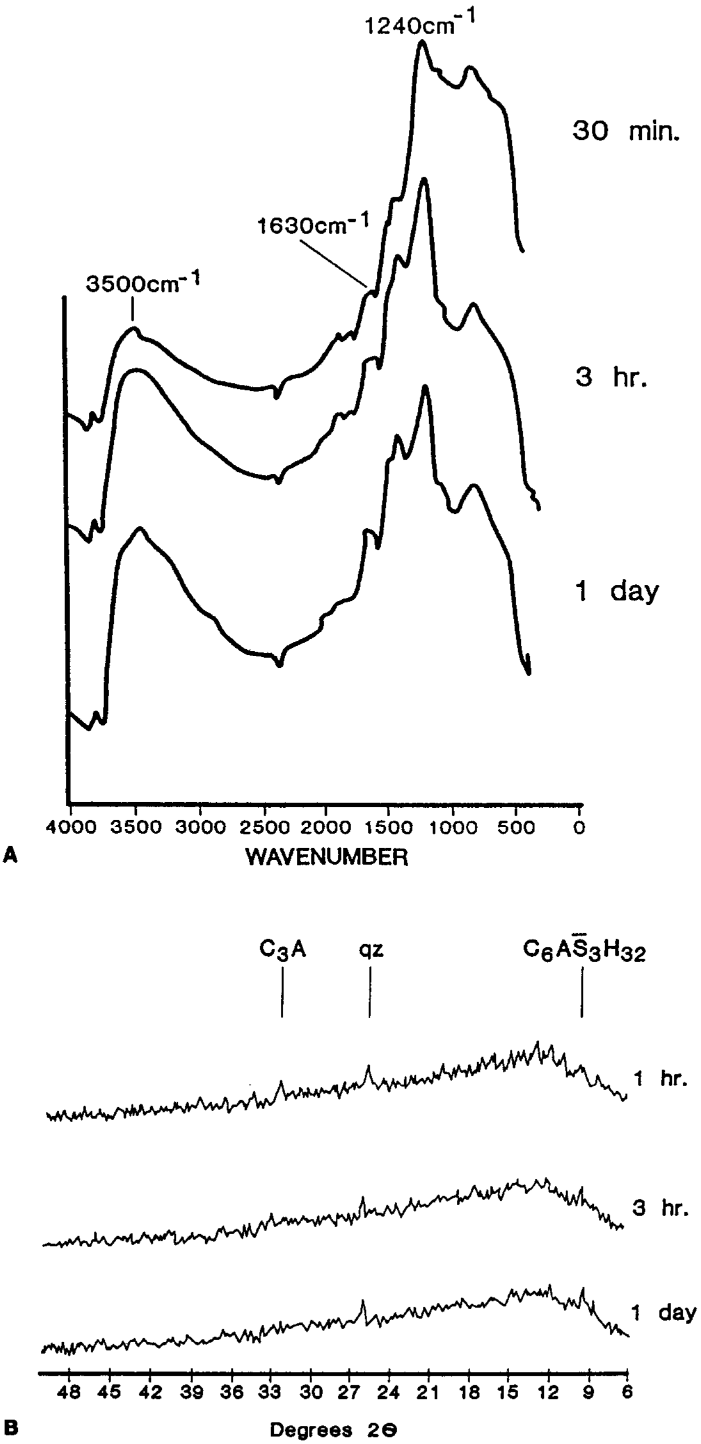

FIG. 3.

Analysis of Class C fly ash hydrated without calcium nitrate: a) by FTIR, for 30 minutes to 1 day b) by XRD for 1 hour to one day.

conditions tested. Another explanation could be that C_4AH_{19} does exist but is too poorly crystallized for XRD determination. Previous DTA studies at a more traditional water/solids ratio of 0.5 reported endotherms near 170°C, 250°C and 320°C for C_2AH_8 C_4AH_{13-19} and C_3AH_6 respectively (10). Results from previous thermal gravimetric analysis had shown that C_3AH_6 produced a sharp weight loss at just over 275°C (12). Therefore, the 135°C peak detected in this

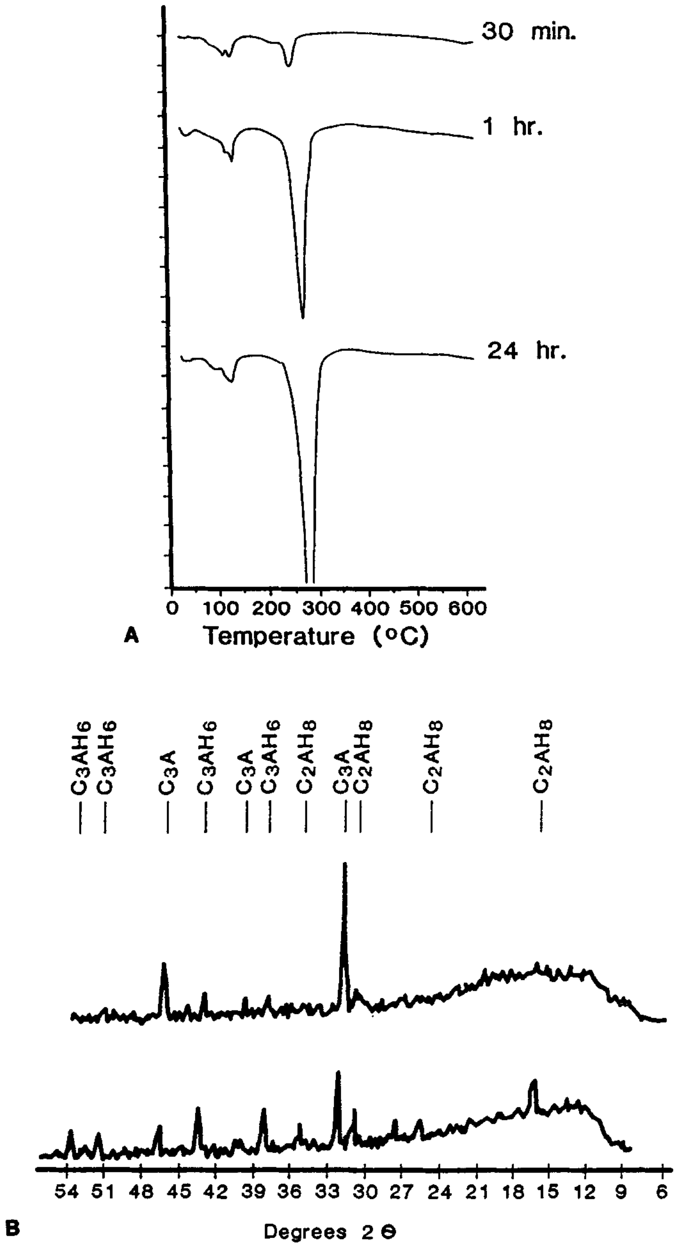

FIG. 4.
Analysis of tricalcium aluminate hydrated with water: a) DSC, b) XRD.

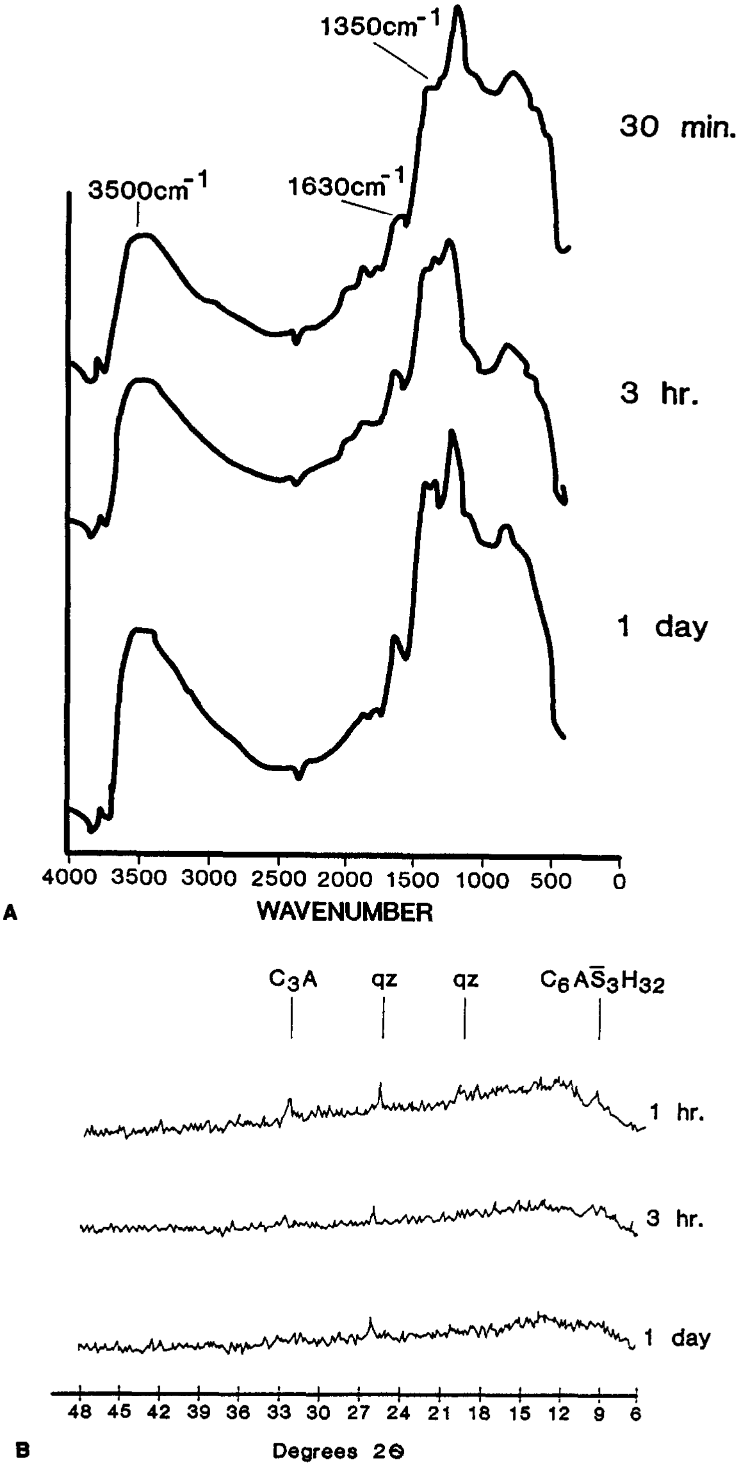

FIG. 5.
Analysis of Class C fly ash hydrated with 2.5% calcium nitrate: a) FTIR, b) XRD.

experimentation was assigned to C_2AH_8 while the 280°C peak was considered to represent C_3AH_6. It should be emphasized that thermal peaks very close to these temperatures were also present as a result of fly ash hydration.

Differential Scanning Calorimetry results (Figure 5a) for analysis of C_3A plus 5% gypsum at w/s = 5 initially produced the expected hydration peak at 260°C as well as a sharp peak at 120°C due to gypsum (9). After further hydration has occurred, a 146°C peak dominates the thermal curve. This development is the result of gypsum being consumed to form AFt. XRD analysis confirmed this to be the case. (Figure 5b)

Affects of Nitrates on Hydration. The addition of calcium nitrate causes some notable modification to the basic hydration process in terms of kinetics and products formed. The addition of 2.5% calcium nitrate (Figure 2b) not only accelerates the growth of existing peaks but promotes the development of two new endothermic peaks at 130°C and 250°C. The 130°C peak appears to compete with the previously noted $C_6A\bar{S}H_{32}$ peak at 140°C and dominates with time. The new 250°C peak appears much stronger than the 280°C calcium aluminate hydrate (C_3AH_6) endotherm initially, but with time these two peaks become nearly equal in size. It is important to note that for fly ash hydration in the absence of $Ca(NO_3)_2$ the lower temperature 130/140°C doublet is larger than the 250/280°C doublet.

The existence of the two new peaks is not a simple result of the presence of residual calcium nitrate. A dry mixture of Class C ash and 5% $Ca(NO_3)_2 \cdot 4\ H_2O$ produced only two peaks: a low temperature doublet at ~ 50°C and a higher temperature endotherm (~ 500°C) due to decomposition of $Ca(NO_3)_2$ (13). The peaks observed during fly ash hydration are absent.

FTIR analysis of the 2.5% calcium nitrate samples (Figures 5a) mark the progress of hydration, with a gradual increase in the presence of a nitrate species as exhibited by the growing IR band at (~ 1350cm^{-1}) (13). Thus, nitrate is present even though the strong 490°C decomposition endotherm is not observed for these reaction conditions. The IR band representing sulfate in this material occurs at a wavenumber greater than 1200cm^{-1} for all times tested, however at 30 minutes there is a faint suggestion of a shoulder at ~ 1160cm^{-1} indicative of AFt at early stages which corroborates well with XRD analysis for the same time frame. (Figure 5b)

Detection of AFt by both FTIR and XRD only at early stages of hydration substantiates thermal evidence of the growing emergence of a new species with a endotherm at 130°C which eventually obscures and possibly suppresses the formation of the AFt endotherm (140°C).

Results for the 5% addition of calcium nitrate (Figure 2c) suggest that increasing dosages of nitrate enhance the growth of both the 130°C and 250°C endotherms. The fact that the 250°C peak now becomes dominant implies that addition of nitrate accelerates growth of this species greater than the 130°C endotherm. The 140°C endotherm is basically nonexistent at this dosage. The presence of an increasing amount of physically bound nitrate is indicated by the growth of the endotherm at 470°C. Infrared analysis noted an increase in the characteristic nitrate band. Contrary to the previous sample (2.5% $Ca(NO_3)_2$), FTIR and XRD failed to detect the presence of AFt at any time tested. The two new endothermic peaks at 130°C and 250°C occurred as shoulders to peaks considered to represent calcium aluminate hydrates.

From the thermal curve for 10% calcium nitrate addition (Figure 2d) one observes that the 130°C peak is detectable only up to 3 hours. The 250°C peak now completely dominates the spectra with no sign of a peak at 280°C and the nitrate peak at 490°C is much more prominent. Data from IR analysis marked the progress of hydration and the growth of the nitrate peak. After three hours the sulfate peak had shifted from 1200cm^{-1} to 1160cm^{-1} where it remained. This corresponded to a time when the 130°C endotherm basically disappears. The IR data indicates the presence of AFt, however DSC analysis show no characteristic peak at 140°C.

X-ray diffraction data for this sample was similar to previous patterns with two notable exceptions. First, the low angle, diffuse peak apparent after 3 hours shifted from 9.6 to 8.9Å and secondly, a new peak at 2.90Å appears. While the 2.90Å peak is in the region of a major peak for both C_2AH_8 and C_3AH_6 the major peaks for the calcium aluminate hydrate monosulfate ($C_4A\bar{S}H_{12}$) are given as: 8.92Å; 2.87Å, and 4.46Å (14). Thus, the presence of new peaks at 2.90 and 8.9Å could be representative of the AFm species. This agreed with IR data because AFm also exhibits a typical sulfate band near 1160cm^{-1} (16). The endothermic peak for the AFm species occurs at much higher temperatures than AFt, typically at 185°C or higher (9). Although no thermal peak is visible at 185°C it is conceivable that the peak is overlapped by the broad 250°C peak.

The formation of AFm typically occurs subsequent to AFt formation and is associated with an excess availability of calcium aluminate. The reaction can be written as:

$$C_6A\bar{S}_3H_{32} + 3\,(C_2AH_8) \rightarrow 3(C_4A\bar{S}H_{12}) + AH_3 + 17\,H_2O \quad (11)$$

However, in the presence of an excess of calcium aluminate there may not be enough sulfate ions available to form ettringite. In these cases, the monosulfate is known to form first through

$$C_3A + C\bar{S}H_2 + 10H \rightarrow C_4A\bar{S}H_{12} \quad (16)$$

It appears that an increasing dosage preferentially promotes hydration of the 250°C species to a point such that at 10% addition, the 130°C species is eliminated. In the absence of the 130°C species the reaction of calcium aluminate with sulfate is possible, however, under these accelerated conditions the excess calcium aluminate hydrates react so fast with sulfate that the primary product is AFm in lieu of Aft.

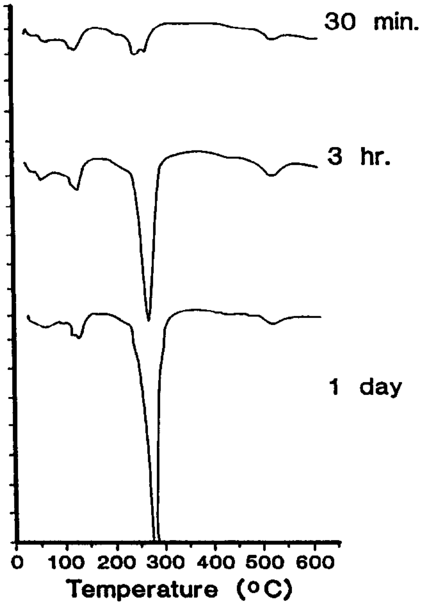

FIG. 6.
DSC analysis of tricalcium aluminate hydrated with 5% calcium nitrate.

Results of Special Tests. The nature of the new products was further investigated by performing several special tests. Several DSC curves for the reaction of a C_3A standard with 5% calcium nitrate are presented in Figure 6. In this test the nitrate addition lead to a doublet (250/270°C) only at the earliest stage of hydration. After 3 hours the 270°C endotherm appeared larger and stronger. This fact suggested that for pure C_3A the nitrate has only a brief altering effect.

A temperature profile of Class C ash reacted with 5% nitrate (Figure 7) was used to better characterize the peaks at 130 and 250°C. FTIR data after temperature ramping to 170°C (after the 130°C endotherm) found not only a loss in H_2O but also a lowering of the NO_3^- peak at $1351cm^{-1}$. After heating to 300°C (after the 250°C endotherm) the $1640cm^{-1}$ H_2O peak largely disappears and the nitrate peak is not only seriously depleted but shifts to $1358cm^{-1}$. Finally at 600°C (after the 490°C endotherm) the NO_3^- peak is completely removed. From this data it can be inferred that the endotherms at 130°C and 250°C are due to species that involve the NO_3^- anion. The shift from 1351 to $1358cm^{-1}$ possibly indicates the existence of two forms of nitrate,

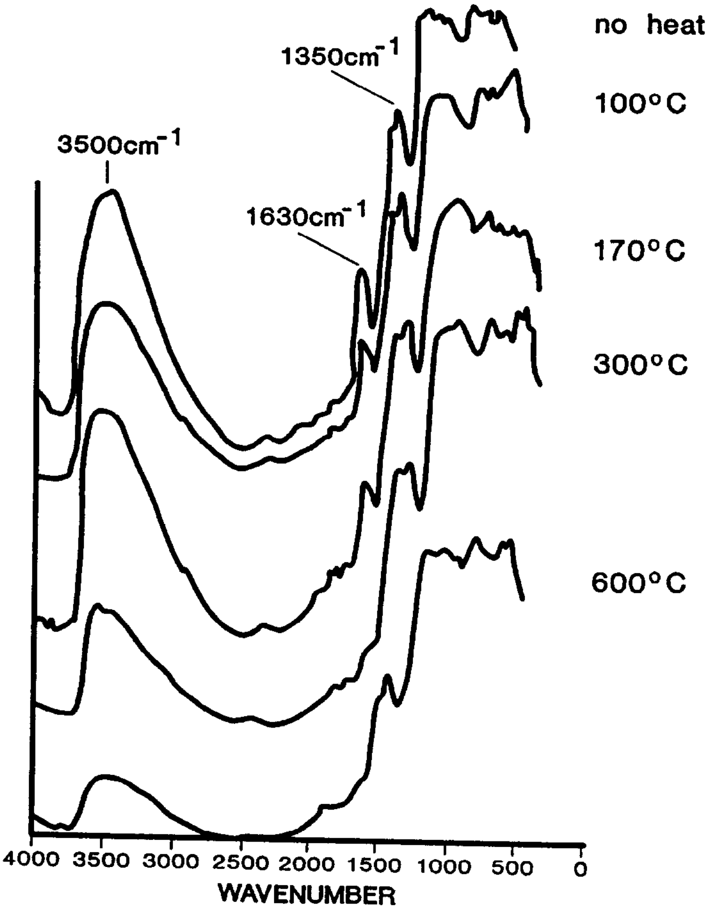

FIG. 7.
FTIR analysis of Class C ash reacted with 5% calcium nitrate after heating to various temperatures.

one which is chemically bonded to the surface represented by the 130 and 250°C endotherms and the other physically trapped as calcium nitrate represented by the 490°C peak. The proximity of the lower temperature endotherms to peaks representative of calcium aluminate hydrates and calcium aluminate hydrate sulfates suggests that nitrate modified calcium aluminate hydrates such as the double salt $C_3A \cdot 3Ca(NO_3)_2 \cdot H_{11\text{-}13}$ may be forming. X-ray diffraction data for compounds of this nature are available (14), however this study found no peaks characteristic of nitrate compounds. This is not surprising, however, given the poorly crystalline nature of the hydrate products.

Conclusion

Based on these findings the hydration process for Class C ash at w/s of 5 results in the production of calcium aluminate hydrates. C_3A plays an important role in the formation of these products. These materials initially react to form calcium aluminate hydrates which are probably similar to C_3AH_6 and C_2AH_8 and possibly C_4AH_{19}. DSC endotherms at ≈ 135 and 280°C represent the calcium aluminate hydrates C_2AH_8 and C_3AH_6 respectively. Eventually (at about 3 hours) these hydrates react with sulfate present in the ash to produce AFt represented by an endotherm at ≈ 140°C.

The addition of calcium nitrate results in the appearance of three new endotherms at ~ 130°C, ~ 250°C, and ~ 490°C. The proximity of the two lower temperature peaks to the previously described hydrates suggest they represent substituted calcium aluminate nitrate hydrates. The peak at 490°C is simply due to a decomposition of physically included calcium nitrate. A temperature profile analysis by FTIR confirmed that the 130°C and 250°C peaks each represent nitrate bearing hydrates.

At low dosages, (2.5%) the nitrate-modified calcium aluminate hydrates compete with the production of AFt and the 130°C nitrate modified hydrate peak eventually dominated the AFt endotherm. FTIR and XRD analysis of these samples support these conclusions.

Higher dosages of calcium nitrate (5%, 10%) tend to preferentially enhance the production of the higher temperature 250°C nitrate modified hydrate. At 10% addition the 250°C species completely dominates with little formation of the 130° substituted hydrate. In the absence of the inhibiting 130°C species, the calcium aluminate hydrate is apparently again free to react with sulfate. However, under these accelerated conditions, the high concentration of available calcium aluminate leads to the formation of calcium aluminate monosulfate $C_6A\bar{S}_3H_{32}$.

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