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The formation of calcium sulfoaluminate hydrate compounds
Part I

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Abstract

The formation of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) and monosulfate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$) from tricalcium aluminate ($3CaO \cdot Al_2O_3$) and gypsum ($CaSO_4 \cdot 2H_2O$) in sodium hydroxide (NaOH) solutions was investigated by isothermal calorimetry and X-ray diffraction analyses. Tricalcium aluminate/gypsum mixtures with a molar aluminate-to-sulfate ratio of 1:3 were hydrated at constant temperatures from 40 to 80°C in deionized water and 200 and 500 mM of NaOH solutions. Ettringite was the only crystalline phase ultimately formed between 40 and 80°C, regardless of whether hydration was carried out in deionized water or sodium hydroxide solutions. The rates of ettringite formation were retarded in sodium hydroxide solutions at all temperatures when compared to hydration in deionized water. The apparent activation energy for the conversion of the tricalcium aluminate/gypsum mixture to ettringite was observed to depend on the concentration of sodium hydroxide.

Keywords: Ettringite; Monosulfate; Durability; DEF; Hydration products

1. Introduction

Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) and monosulfate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$) are calcium sulfoaluminate compounds commonly found in concrete. Cement terminology also refers to ettringite as AFt and monosulfate as AFm; both terms are broad classifications for crystal structure types. If ettringite or monosulfate form while the concrete is still in a plastic state, the surrounding paste will simply accommodate this volumetric change. However, if ettringite forms after the concrete has set the ettringite formation can cause cracking and thus structural damage.

Deterioration observed in precast concrete structures has recently come under some scrutiny [1]. Precast concrete products are used in a wide variety of applications including decorative building motifs, highway barriers, and structural support members. The manufacturing of precast products is a continuous process and steam curing is frequently used to accelerate curing, so that 24-h batching operations can be achieved. The effects of temperature, curing rates, and cement composition have all been studied as underlying reasons for deterioration associated with ettringite formation [2]. Visually, deterioration is usually manifested as map cracking, spalling, and efflorescence. These visual manifestations are, in general, attributed to delayed ettringite formation (DEF). The mechanisms by which DEF can occur remains to be fully established, but recent studies suggest the alkali content of cement paste and steam curing temperature to be contributing factors [3–5].

The formation of ettringite and/or monosulfate may be caused by internal or external influences and examples of both mechanistic phenomena can be found in the literature [6–8]. The crystallization of sulfoaluminate compounds relies upon the movement of ionic species through water. In hardened concrete this ionic movement occurs in water-filled porosity. Because the specific ionic species in solution will determine the chemical reaction that takes place and the compound that is formed, many studies have examined the formation of ettringite and/or monosulfate and the interaction of various ionic species [9–13].

Taylor [14] lists 26 AFm phases structurally equivalent to monosulfate; most are formed with chloride, carbonate, or alkali substitutions. Recent studies have been performed on one such phase—a sodium-substituted AFm phase referred to as the "U-phase" [15–17]. This sodium-substituted AFm phase ($4CaO \cdot 0.9Al_2O_3 \cdot 1.1SO_3 \cdot 0.5Na_2O \cdot 16H_2O$) was first reported by Dorsch and zur Strassen in 1968 [18]. These recent studies examined the kinetics of U-phase formation and the deleterious effects it may cause in hardened

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concrete. In particular U-phase formation was found to cause expansion [15–17].

While much work has been done examining the formation of sulfoaluminate compounds and the interaction of various ionic species, only a few studies have examined the effects of alkali and temperature on formation kinetics. Brown and Bothe [3] showed that ettringite formation was retarded by concentrations of potassium hydroxide between 0.5 and 2.0 M. Ong and Diamond [19] have observed that during the initial stage of curing, pore solutions in concrete have ionic strengths that are much lower than those studied by Brown and Bothe [3]. Therefore the hydration of tricalcium aluminate (C_3A) and gypsum at various temperatures in “low” alkali concentrations are examined in the present study.

2. Materials and methods

C_3A was produced by mixing calcium carbonate with Alcoa “Hydral” alumina and firing at 1200°C for 2 h. Gypsum was produced by hydrating reagent grade hemihydrate ($CaSO_4 \cdot 1/2H_2O$). Phase purity of both precursors was qualified by X-ray diffraction (XRD) analysis. Isothermal calorimetry was performed using the experimental setup described by TenHuisen [20]. Approximately 1.00 g of 1:3 molar ratio C_3A/gypsum mixture and 3.0 mL of each solution concentration was used for each sample run. The solid sample and a syringe containing deionized water or NaOH solution were brought to thermal equilibrium at each experimental temperature before injection. Runs were carried out at 40, 50, 60, 70, and 80°C.

As the solution was injected onto the solid sample, heat output was measured by thermopiles, which completely surrounded the sample. Data points were collected at 0.1-s intervals. When no further heat output could be observed, the solids were removed from the calorimeter, washed with acetone, and allowed to air dry. These solids were ground in an agate mortar and pestle to a fineness of approximately 325 mesh.

A Scintag 3100 system powder diffraction unit was used to examine the powders. All samples were scanned at 2° 2Θper min between 5 and 55° by Cu Kα radiation. Analysis of the XRD data is complicated in that the ettringite pattern has diffraction peaks that overlap the primary diffraction peaks for monosulfate, $Ca(OH)_2$, and U-phase. This problem was overcome by examining the ratio of the primary (monosulfate, calcium hydroxide, or U-phase) peak and primary ettringite peak intensities and then determining where the ratio varied.

3. Results and discussion

3.1. Calorimetry

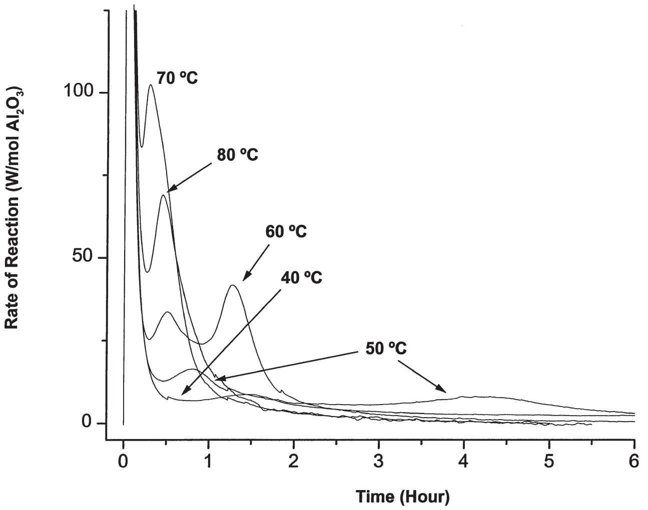

Fig. 1. Rates of heat evolved when tricalcium aluminate and gypsum are hydrated in deionized water.

Fig. 1 shows the rates of reactions of the C_3A/gypsum mixture hydrated in deionized water at constant temperatures between 40 and 80°C. In general, the rate of hydration increases with increasing temperature in any given solution. The hydration reactions are characterized by double exothermic peaks between 40 and 60°C, while at 70 and 80°C the reactions show only single peaks. The double heat peaks resolve two thermal events: mixing and hydration. At 70°C and higher, the hydration reaction (the initial peak) and the “mixing” peak overlap. The duration of the heat peaks vary from less than 1 h for hydration at 70 and 80°C to approximately 11 h for hydration at 40°C.

Fig. 2 shows rates of reaction for C_3A/gypsum mixtures hydrated in 200 mM NaOH solutions between 40 and 80°C. The reaction rates are observed to increase as the temperature increased. The rate curves are characterized by single

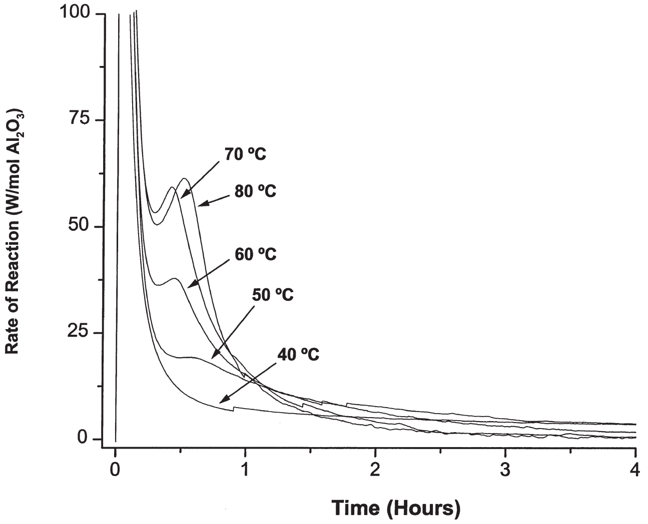

Fig. 2. Rates of heat evolved when tricalcium aluminate and gypsum are hydrated in 200 mM NaOH.

peaks that reach maxima before 1 h for hydration at temperatures greater than 50°C; no discernible peak is observed for hydration at 40°C. The maxima in the rate curves have decreased from those observed for hydration in deionized water.

The rate curves shown in Fig. 3 for C_3A/gypsum mixtures hydrated in 500 mM NaOH are again characterized by single hydration peaks; reaction rates are again observed to increase with increasing temperature. The peaks also reach maxima before 1 h at hydration temperatures above 50°C and a peak is not observed for hydration at 40°C. The maxima in the rate curves have decreased from those observed in 200 mM of NaOH solution.

The total heat evolved can be determined by integrating the rate curves. The maximum total heat evolved for each solution is shown in Table 1.

3.2. XRD analysis

XRD analyses of the solids retrieved after hydration in deionized water, and 200 and 500 mM NaOH at 80°C are shown in Fig. 4. XRD analyses of solids formed at lower temperatures were similar. Ettringite and gypsum are the only crystalline phases; monosulfate was not observed.

In general the diffraction patterns show only subtle differences with increasing sodium hydroxide concentrations. When hydration is carried out in sodium hydroxide solutions, the amounts of ettringite observed are relatively constant, regardless of temperature. Although ettringite and gypsum are the only crystalline phases observed, the amount of gypsum is observed to decrease in the 500-mM sodium hydroxide solution. These data are consistent with previous analysis [21]; this effect is due to increased gypsum dissolution, because of the higher solubility of sulfate in more concentrated NaOH solutions.

3.3. Phase assemblages

The observation of ettringite and gypsum as the only crystalline hydration products, irrespective of the hydration temperature or sodium hydroxide concentration, is in contrast to our analyses performed of the hydration of monosulfate and gypsum [21]. In that instance $Ca(OH)_2$ and the U-phase was formed with increasing NaOH concentrations (0.5 and 1.0 M). Present results indicate that an increased sulfate content enhances ettringite formation and suppresses U-phase formation. Experiments performed using a 1:1 sulfate-to-aluminate ratio showed U-phase formation in 200 and 500 mM NaOH [22]. The data discussed above illustrates the stability relationship between ettringite and U-phase. Ettringite forms at high sulfate levels; when the sulfate/aluminate ratio decreases, U-phase formation becomes favorable. Under the conditions in the present study, once ettringite is formed, it does not convert to the U-phase. However, the XRD patterns indicate either more ettringite is produced in deionized water than in the 200 or 500-mM solutions, or the ettringite produced is more crystalline. Since previous experiments [22] showed U-phase formation, the present XRD patterns are a further indication of the competition between ettringite and U-phase formation.

Table 1
Maximum total heat evolved

Hydration solution	Temperature	Q, kJ/mole of $A1_2O_3$
Deionized water	78°C	370
200 mM NaOH	80°C	310
500 mM NaOH	70°C	300

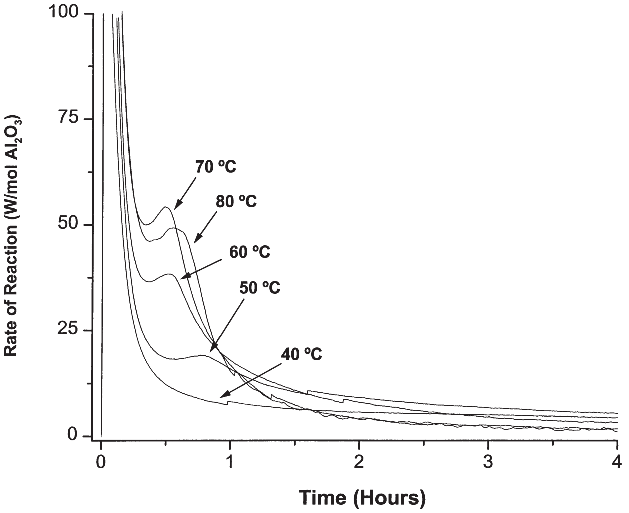

Fig. 3. Rates of heat evolved when tricalcium aluminate and gypsum are hydrated in 500 mM NaOH.

To ascertain the origin of the double heat peaks observed during hydration in deionized water, two experiments were performed at 60°C. Hydration was terminated after either 0.9 or 22 h; the solids were analyzed by XRD with the results shown in Figs. 5 and 6. Fig. 5 shows small amounts of ettringite and hydrogarnet ($Ca_3Al_2(OH)_{12}$) after 0.9 h of hydration (monosulfate may be present, but the data are inconclusive); gypsum is the dominant crystalline phase. Small

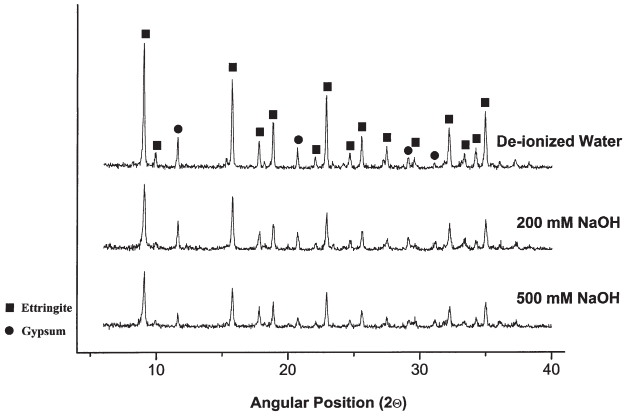

Fig. 4. XRD patterns obtained when tricalcium aluminate and gypsum are hydrated in deionized water and 200 and 500 mM NaOH at 80°C.

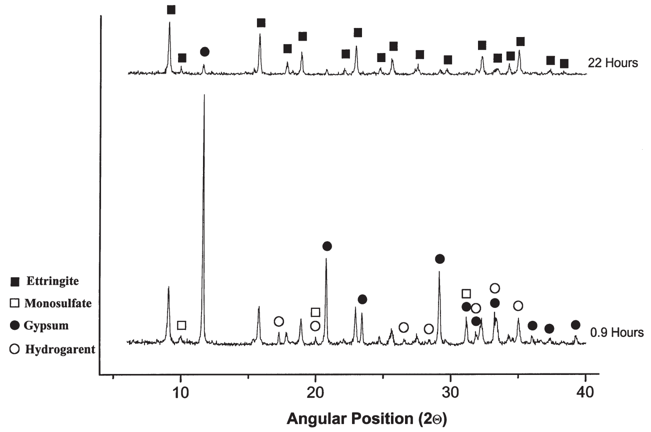

Fig. 5. XRD patterns obtained when tricalcium aluminate and gypsum are hydrated in deionized water at 60°C for 0.9 and 22 h.

amounts of gypsum remain after 22 h of hydration, but ettringite is the dominant crystalline phase. These data indicate the first and second hydration peaks, shown in Fig. 6, are due to competing reactions. The XRD pattern obtained at 0.9 h indicates the formation of hydrogarnet is competing with ettringite formation. However, by 22 h ettringite is the only hydrate present (except residual gypsum), indicating the complexity of the mechanistic path.

Consistent with our prior work [21] the data also indicate that the amount of gypsum dissolved into solution increases with increasing sodium hydroxide concentration. The dissolution of gypsum influences both the total heat evolved and the rate of the reaction [21] by retarding both. Although sodium hydroxide retards the overall extent of the reaction regardless of temperature, the final hydration product is essentially the same (ettringite). The enhanced dissolution of gypsum reduces the total heat output by 60 to 70 kJ. Retardation is also exemplified by the decreasing maxima of the second reaction peak with increasing NaOH concentration. Increased NaOH concentration also reduces the total heat evolved, suggesting that the extent of ettringite formation has been reduced.

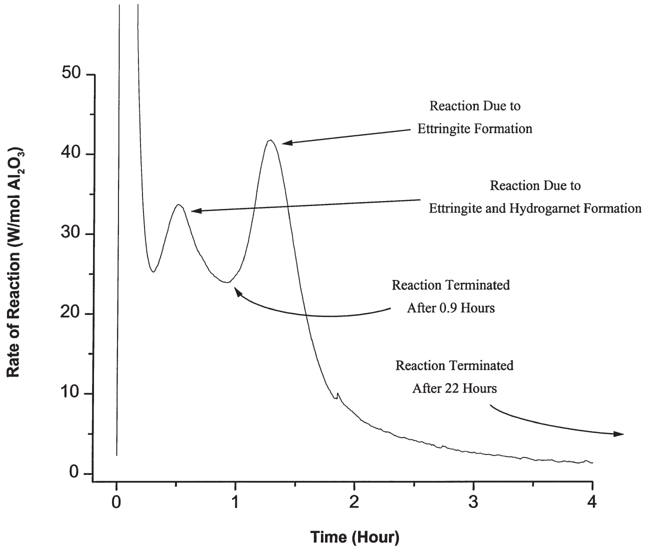

Fig. 6. Rate of heat evolved when tricalcium aluminate and gypsum are hydrated in deionized water at 60°C.

3.4. Thermodynamic calculation of phase stability

To establish how the phase assemblage is influenced by NaOH and sulfate in solution, the pH and the saturation indices (SI) for hydrogarnet (C_3AH_6), ettringite (AFt), gypsum (Gyp), calcium hydroxide (CH), monosulfate (AFm), and U-phase (AFm′) were calculated using the aqueous geochemical code PhreeqC [23]. Our intent in using the PhreeqC code is to observe the general trends of the phase assemblages at 40°C, not to compare the stable phase assemblages to the present data. The calculations were carried out at sulfate-to-aluminate ratios of 3:1 and 1:1, at NaOH concentrations of 200, 500, and 1.0 M, at a constant temperature of 40°C. $SI = 0.0$ indicates saturation, while a negative value indicates undersaturation. The PhreeqC code requires solubility products (k_{sp}) for the input/output phases. The solubility product values reported by Damidot and Glasser [24] and Reardon [25] for hydrogarnet, ettringite, and monosulfate formation at 25°C were used as input values. PhreeqC results using these k_{sp} values are shown in Tables 2 and 3. Because the solubility product values are not available for the above phases at 40°C, comparison between the observed phase assemblages and the calculated results should be viewed only for the trends.

While both sets of input data predict phase assemblages that are essentially the same, neither predicts the observed assemblages. Since the input data and PhreeqC predict equilibrium, these differences can be attributed to reaction kinetics and they indicate that the ettringite formed is metastable. At the 3:1 sulfate-to-aluminate ratio, calcium hydroxide and monosulfate are not observed, and are indicated by PhreeqC, while gypsum is observed. However, PhreeqC also indicates general trends: increased solubility of hydrogarnet with increased sulfate, a general decrease in gypsum solubility with increased sulfate, increased solubility of AFm

Table 2
Phase assemblage calculated using PhreeqC (Damidot and Glasser k_{sp} values)

Ratio of sulfate to aluminate	NaOH (mM)	pH	SI					
			C_3AH_6	AFt	Gyp	CH	AFm	AFm′
3:1	200	12.7	0.0	0.0	−2.7	0.0	−0.4	−0.7
	500	13.1	0.0	0.0	−2.7	0.0	−0.4	0.0
	1,000	13.3	−0.2	−0.7	−2.8	0.0	−0.8	0.0
1:1	200	12.8	0.0	0.0	−2.7	0.0	−0.4	−0.8
	500	13.1	0.0	0.0	−2.7	0.0	−0.4	0.0
	1,000	13.4	0.0	−1.2	−3.0	0.0	−0.8	0.0

Table 3
Phase assemblage calculated using PhreeqC (Reardon k_{sp} values)

Ratio of sulfate to aluminate	NaOH (mM)	pH	SI					
			C_3AH_6	AFt	Gyp	CH	AFm	AFm′
3:1	200	12.3	0.0	0.0	−3.1	0.0	−0.1	−0.6
	500	12.9	−0.8	0.0	−2.8	0.0	−0.6	−0.1
	1,000	13.2	−2.0	0.0	−2.4	0.0	−1.3	0.0
1:1	200	12.3	0.0	0.0	−3.1	0.0	−0.1	−0.7
	500	12.6	−0.1	0.0	−3.1	0.0	−0.1	0.0
	1,000	13.2	−1.2	−0.8	−2.9	0.0	−1.1	0.0

phases with increased alkali level, and a complex interplay between the formation of AFm phases and ettringite formation.

3.5. Hydration kinetics

The kinetics of the hydration reactions were fitted to an Arrhenius model to calculate the apparent activation energies as shown in Table 4.

There is a substantial difference between the apparent activation energies associated with the first and second reaction peaks when ettringite forms in deionized water. The first peak exhibits a lower apparent activation energy, indicating ettringite formation is less temperature dependent during this period. The apparent activation energy for the first peak is close to that observed for mixtures hydrated in sodium hydroxide, suggesting the reaction mechanisms may be similar.

4. Conclusions

The hydration of a tricalcium aluminate/gypsum mixture with a 3:1 sulfate-to-aluminate ratio produced ettringite as the sole reaction product regardless of NaOH solution concentration. The U-phase was not observed. However, the total heat of reaction decreased with increasing NaOH concentration. The phase assemblages observed were not those predicted by PhreeqC; a result indicative of slow reaction kinetics and the presence of a metastable phase assemblage.

Table 4
Hydration reactions fitted to an Arrhenius model to calculate the apparent activation energies

Hydration solution	Apparent activation energy (kJ/mol Al_2O_3)	Hydration phase observed by XRD
Deionized water (1st peak)	69	AFt
Deionized water (2nd peak)	107	AFt
200 mM NaOH	65	AFt
500 mM NaOH	67	AFt

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