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The formation of calcium sulfoaluminate hydrate compounds
Part II

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Abstract

The formation of ettringite ($3CaO \bullet Al_2O_3 \bullet 3CaSO_4 \bullet 32H_2O$) and monosulfate ($3CaO \bullet Al_2O_3 \bullet CaSO_4 \bullet 12H_2O$) from tricalcium aluminate ($3CaO \bullet Al_2O_3$), gypsum ($CaSO_4 \bullet 2H_2O$), and sodium hydroxide (NaOH) solutions were investigated by isothermal calorimetry and X-ray diffraction analyses. Tricalcium aluminate/gypsum mixtures with a molar ratio of 1:1 sulfate-to-aluminate were hydrated at constant temperatures from 30 to 90°C in deionized water and in 200 and 500 mM of sodium hydroxide (NaOH) solutions. Hydration in deionized water produced ettringite and monosulfate as the dominant crystalline phases, regardless of temperature. Complex assemblages of phases formed in 200 and 500 mM of sodium hydroxide; these included ettringite, monosulfate, and U-phase, at all temperatures. Calorimetry and X-ray diffraction data indicated that U-phase formation becomes the dominant reaction as sodium hydroxide concentrations increase. U-phase is the only AFm phase observed after hydration in 1.0 M of NaOH. The data also indicated that the presence of sodium cations promotes AFm formation.

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

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1. Introduction

This is the second of two papers examining hydration of tricalcium aluminate (C_3A)/gypsum mixtures in sodium hydroxide solutions. In Part I [1], a C_3A/gypsum mixture with a sulfate-to-aluminate ratio of 3:1 was hydrated in deionized water and 200 and 500 mM of NaOH solutions at temperatures between 40 and 80°C. That study found ettringite to be the dominant hydration product over the entire temperature range. The present study describes the results obtained when a C_3A/gypsum mixture with a sulfate-to-aluminate ratio of 1:1 was hydrated in deionized water and 200 and 500 mM of NaOH solutions at temperatures between 30 and 90°C.

As was discussed in Part I, ettringite ($3CaO \bullet Al_2O_3 \bullet 3CaSO_4 \bullet 32H_2O$) and monosulfate ($3CaO \bullet Al_2O_3 \bullet CaSO_4 \bullet 12H_2O$) are calcium sulfoaluminate compounds commonly found in concrete. The cement literature refers to ettringite as AFt and monosulfate as AFm, both terms being broad classifications for crystal structure types. It is generally accepted that ettringite and/or monosulfate formation in a hardened concrete can cause structural damage, cracking, and aggregate/paste debonding, due to the associated volumetric changes. Thus, calcium sulfoaluminate compounds are frequently observed in microstructures of damaged or deteriorated concrete. Because these compounds are common to concrete, sulfoaluminate compounds in the microstructure often exemplify concrete deterioration.

As described in Part I, precast concrete products are used in a wide variety of applications. The manufacture of these precast products is typically a continuous operation using steam curing to reduce curing times. Observed deterioration due to internal mechanisms in precast concrete structures has recently been the focus of scientific research [2]. The visually evident deterioration is termed "delayed ettringite formation" (DEF) [3]. The effects of temperature, curing rates, and cement composition have all been cited as a reason for deterioration due to sulfoaluminate compound formation [4]. The mechanistic phenomena by which DEF occurs are unresolved, but recent studies have linked alkali content of the cement paste and curing temperature to retardation of ettringite formation during initial curing [5–7].

As outlined in Part I, a variety of literature reviews are available that examine the causation of DEF and classic sulfate attack (from external sources) [8–10]. Many studies examined the effects of various ionic species on the formation of ettringite and/or monosulfate [11–15]. Substitution with chloride, carbonate, or alkali is common in AFm and AFt phases [16]. These studies typically indicate that the kinet-

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ics of hydration and the hydration products may change in response to the presence of electrolytes. For example, recent studies have shown a sodium-substituted AFm phase referred to as the "U-phase" can form in NaOH solutions [17–20]. 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 combined effects of alkali and temperature on kinetics. Two such studies are those by Brown and Bothe [5] and Ong and Diamond [21]. Brown and Bothe found that increasing alkali levels (KOH) retarded ettringite formation and at high concentrations (1.0 M KOH) formed syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$). Ong and Diamond found the addition of NaOH enhanced sulfate pore solution concentrations, but lowered hydroxyl and calcium ions in solution, again retarding ettringite formation. Therefore the hydration of tricalcium aluminate (C_3A) and gypsum at various temperatures in alkali concentrations typical of those in cements are examined in the present study.

2. Materials and methods

2.1. Experimental procedures

Isothermal calorimetry was performed using the experimental setup described by TenHuisen [22]. The same experimental procedure described in Part I was used, except that approximately 1.00 g of 1:1 molar ratio C_3A/gypsum mixture and 3.0 mL of solution 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 30, 40, 60, 80, and 90°C.

A Scintag 3100 system powder diffraction unit was used to examine the powders. All samples were analyzed at 2° 2θ per minute between 5 and 55° using Cu Kα radiation.

3. Results

3.1. Calorimetry

The rates of reaction and heat outputs for reactions of the C_3A/gypsum mixture hydrated in deionized water at constant temperatures between 30 and 90°C are shown in Figs. 1a and 1b, respectively. In general, the rate of hydration was observed to increase with increasing temperature, although the rate was slower at 80 than 60°C. Excluding the mixing peak, a single hydration peak, indicative of a single hydration event, characterized each of the reactions. As the temperature was increased this single hydration peak occurred at shorter times and could not be resolved from the "mixing" peak at 80°C. The durations of the hydration events decreased from 4 h at 30°C to approximately a half-hour at 60°C. The total heat evolved (Fig. 1b) was approximately 215 kJ/mole of Al_2O_3 at 30°C, with a maximum of 250 kJ/mole of Al_2O_3 for 60, 80, and 90°C. These total heats were slightly less than that found in Part I [1]; approximately 325 kJ/mole of Al_2O_3 on average, with a maximum of 370 kJ/mole of Al_2O_3.

Figs. 2a and 2b show rates of reaction and heat output curves for C_3A/gypsum mixtures hydrated in 200 mM of NaOH solutions between 30 and 80°C. The rates of the reactions again were observed to increase as the temperature was increased. The rate curves (Fig. 2a) were also characterized by single hydration peaks, which decreased in duration with increasing temperature. The durations of the reaction peaks were slightly longer than those observed in deionized water. As the temperature was increased, this single hydration peak overlapped the mixing peak at 90°C. The total heat evolved reached a maximum value of approximately 230 kJ/mole of Al_2O_3 at 60, 80, and 90°C, with a value of approximately 200 kJ/mole of Al_2O_3 reached at 30 and 40°C.

The rate curves shown in Fig. 3a for C_3A/gypsum mixtures hydrated in 500 mM of NaOH are again characterized by single hydration peaks and by increased reaction rates

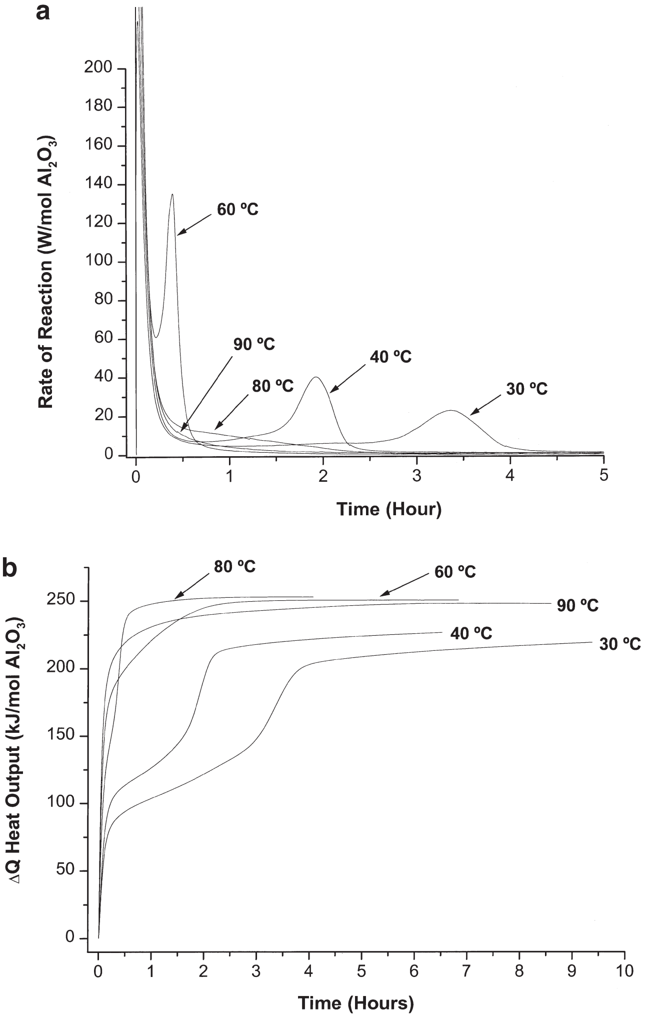

Fig. 1. (a) Rates of heat evolution when tricalcium aluminate and gypsum are hydrated in deionized water. (b) Total heats evolved when tricalcium aluminate and gypsum are hydrated in deionized water.

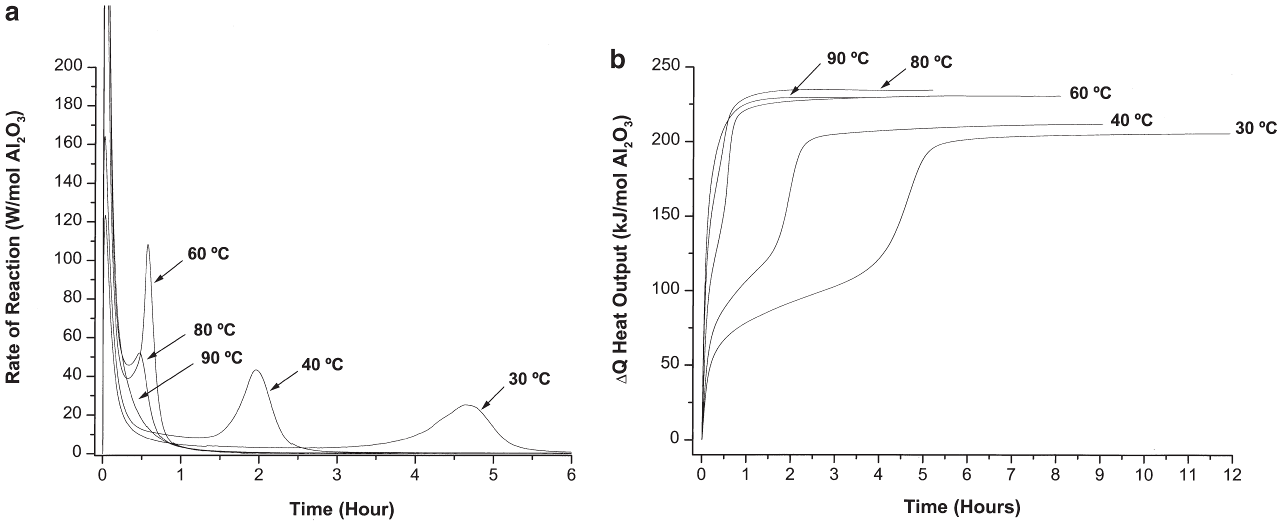

Fig. 2. (a) Rates of heat evolution when tricalcium aluminate and gypsum are hydrated in 200 mM of NaOH. (b) Total heats evolved when tricalcium aluminate and gypsum are hydrated in 200 mM of NaOH.

with increasing temperature. As with hydration in 200 mM of NaOH, the single hydration peak was lost in the mixing peak at 90°C. The duration of the hydration peaks also decreased with increasing temperature, but that duration was shorter than in deionized water or 200 mM of NaOH. The total heats evolved were similar to those of mixtures hydrated in 200 mM of NaOH, with a maximum of approximately 220 kJ/moles of Al_2O_3 reached at 60, 80, and 90°C. Thus, the maximum heat evolved decreased with increasing NaOH concentration.

3.2. XRD

As described in Part I [1], ettringite was the only hydration product formed in comparable solutions when the sulfate-to-aluminate ratio was 3:1. In a previous study, examining the hydration of monosulfate and gypsum in sodium hydroxide solutions, $Ca(OH)_2$ and U-phase were observed in phase assemblages together [23]. X-ray diffraction (XRD) patterns shown in Figs. 4, 5, and 6 indicate more complex crystalline phase assemblages formed in the present study. Ettringite, monosulfate, hydrogarnet ($3CaO \cdot Al_2O_3 \cdot 6H_2O$), U-phase, and carbonate-substituted AFm ($3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 32H_2O$) were all observed, while residual gypsum and calcium hydroxide ($Ca(OH)_2$) were not observed. The tricarbonate-substituted AFm phase was the only carbonate phase identified.

Monosulfate, ettringite, and hydrogarnet were observed in samples hydrated in deionized water. In general the primary diffraction peak for monosulfate increased with in-

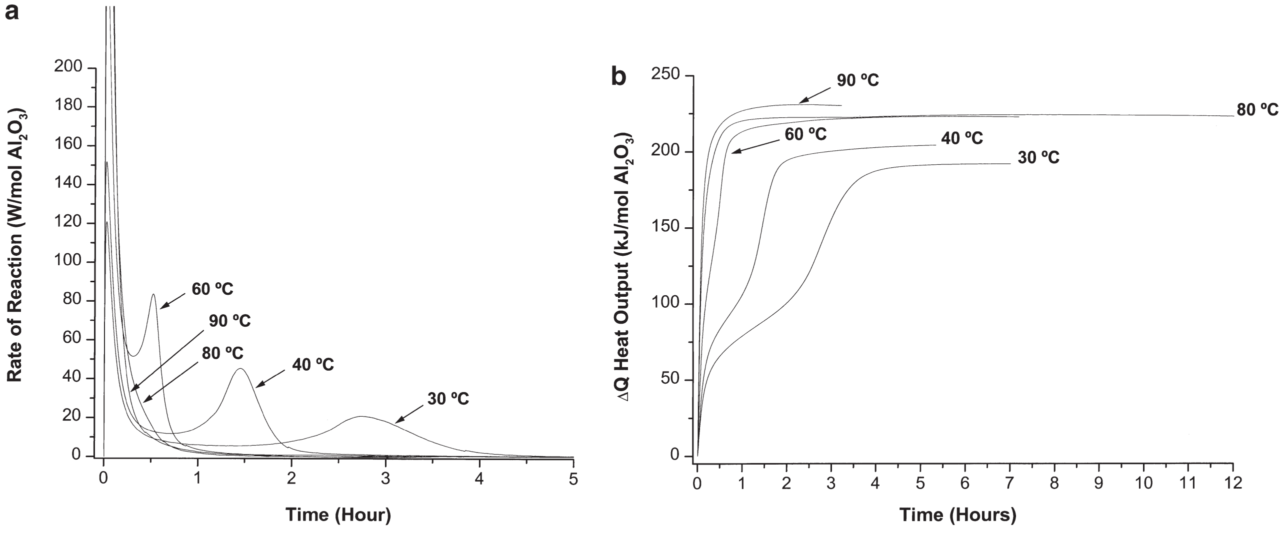

Fig. 3. (a) Rates of heat evolution when tricalcium aluminate and gypsum are hydrated in 500 mM of NaOH. (b) Total heats evolved when tricalcium aluminate and gypsum are hydrated in 500 mM of NaOH.

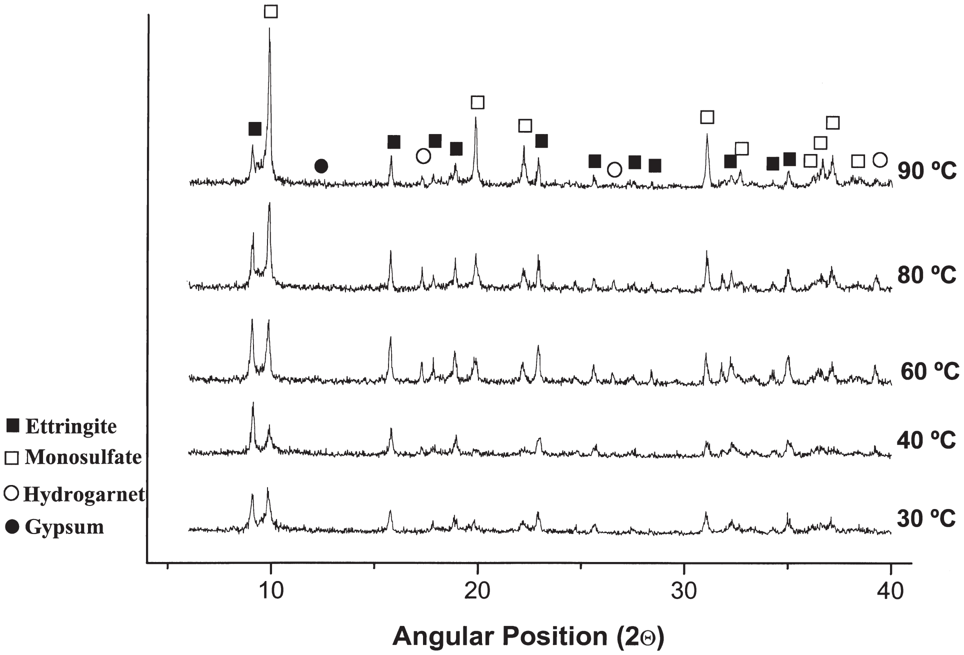

Fig. 4. XRD patterns obtained when tricalcium aluminate and gypsum are hydrated in deionized water.

creasing temperature, indicating an increasing amount of monosulfate. The hydrogarnet phase was most apparent in samples hydrated at 60 and 70°C. Samples hydrated at 60 and 70°C with approximately equal amounts of ettringite and monosulfate were observed in the diffraction patterns. Since this assemblage cannot coexist at equilibrium [24], complete reaction was not obtained.

Monosulfate, U-phase, carbonate-substituted AFm, and ettringite were the predominant phases observed in samples hydrated in 200 mM of NaOH. Trace amounts of hydrogarnet were also observed. The phase assemblage was quite complex and it was very difficult to establish the proportions of monosulfate and U-phase. The XRD data was complicated in that severe overlap of diffraction peaks from the

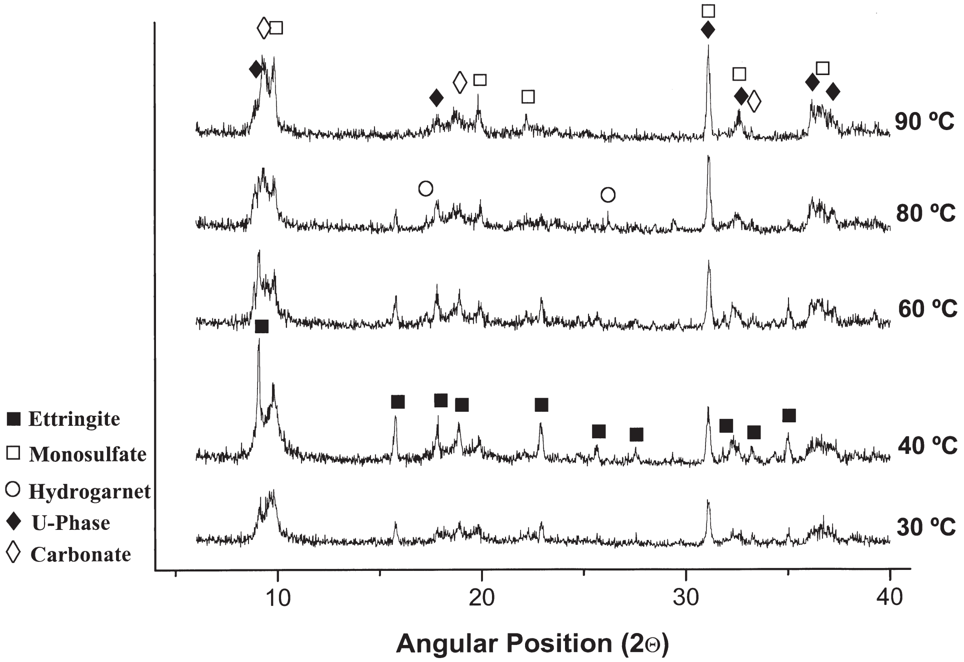

Fig. 5. XRD patterns obtained when tricalcium aluminate and gypsum are hydrated in 200 mM of NaOH.

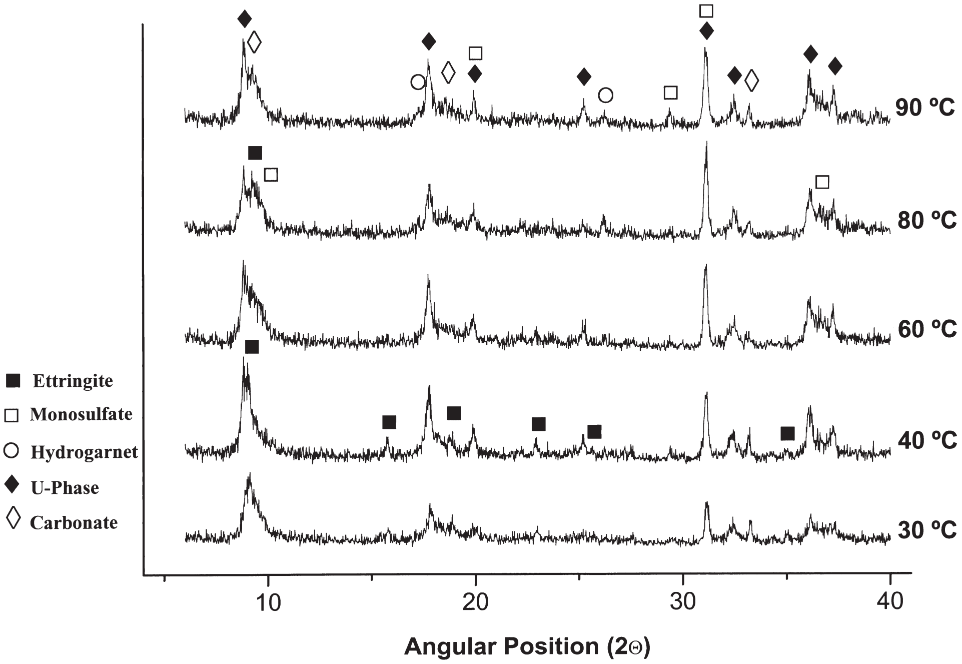

Fig. 6. XRD patterns obtained when tricalcium aluminate and gypsum are hydrated in 500 mM of NaOH.

various phases (ettringite, monosulfate, $Ca(OH)_2$, carbonate-substituted AFm, and U-phase) readily occurred. Care is needed in interpreting any of the diffraction patterns. However, the amount of AFm phase (monosulfate, U-phase and carbonate-phase) increased with increasing temperature. This is exemplified by the increasing intensity of the 1 1 0 (h, k, l) diffraction peak at 31.1° 2θ. The maximum amount of carbonate-substituted AFm phase was observed in samples hydrated at 80 and 90°C, while the maximum amount of ettringite was observed in samples hydrated at 40 and 60°C.

The predominant phases observed after hydration in 500 mM of NaOH are U-phase and carbonate-substituted AFm. Trace amounts of ettringite, monosulfate, and hydrogarnet were also observed. Again, calcium hydroxide and gypsum were not observed. The amounts of U-phase and carbonate-substituted AFm phase generally increased with increasing temperature, although less carbonate-phase was observed after hydration at 60°C than at 30 and 40°C. Carbonate-phase formation was a consequence of exchange with the atmosphere in our experimental setup. While the crystallization of carbonate-substituted AFm may exhibit a temperature dependence, the kinetics of its formation are unlikely to do so (any incidental CO_2 will be taken up). A maximum amount of ettringite was observed in samples hydrated at 40°C. Only trace amounts of the hydrogarnet phase were observed in samples hydrated at 80 and 90°C.

Fig. 7 shows an XRD pattern obtained after a tricalcium aluminate/gypsum mixture was hydrated in 1.0 M NaOH for 20 h at 50°C. U-phase, calcite ($CaCO_3$), and poorly crystalline gypsum were the only phases observed in the hydrated assemblage. Thus U-phase forms even in preference to carbonate AFm under these conditions.

4. Discussion

4.1. Phase behavior

The data illustrate the phase evolution when 1:1 molar ratio C_3A/gypsum mixtures are hydrated in deionized water and 200, 500, and 1.0 M of sodium hydroxide solutions. These observations are in contrast to analyses performed in Part I [1], where ettringite was the only phase formed. Thus the effects of sodium and sulfate ionic species on hydration differ depending on their relative concentrations. At the equivalent sodium concentrations, AFt formation is preferred at high sulfate concentrations, while at low sulfate concentration AFm formation is preferred. These results substantiate calculations made by Glasser et al. [15] and Damidot et al. [25], which indicate AFt may become more soluble with increased temperature and alkali pore solutions; although those studies indicate that sodium would not be incorporated into the solid phases. The above observations are also in accord with previous analyses performed using monosulfate as the precursor powder [23], where the U-phase was formed with increasing NaOH concentration (0.5 and 1.0 M). The observations also are consistent with a previous study of the hydration behavior of tetracalcium aluminoferrite (C_4AF) in magnesium sulfate solutions, where monosulfate, not ettringite, formed as the hydration product [26]. Thus the presence of a cationic species can accelerate AFm forma-

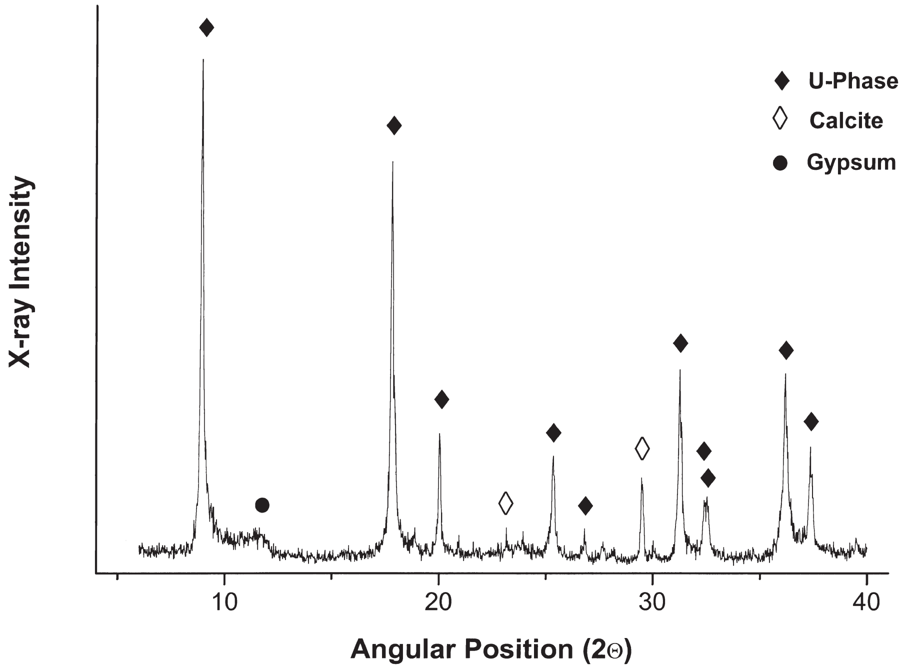

Fig. 7. XRD pattern obtained when tricalcium aluminate and gypsum are hydrated in 1.0M NaOH at 50°C.

tion and/or promote the stability of AFm in the assemblage. In the case of C_4AF hydration in $MgSO_4$ solutions, the magnesium cation facilitates the conversion of alumina from C_4AF to an AFm phase [27]. With hydration of C_3A/gypsum mixtures in NaOH solutions, the sodium cation is directly incorporated into an AFm phase, making it a constituent of a stable phase assemblage.

4.2. Kinetics

By examining the heat evolution curves, the rate controlling mechanism(s) for each solution can be assessed. The kinetics of the hydration reactions were fitted to an Arrhenius model ($k = \exp^{-}(Ea/RT)$) to permit calculation of the apparent activation energies. The logarithms of the reaction

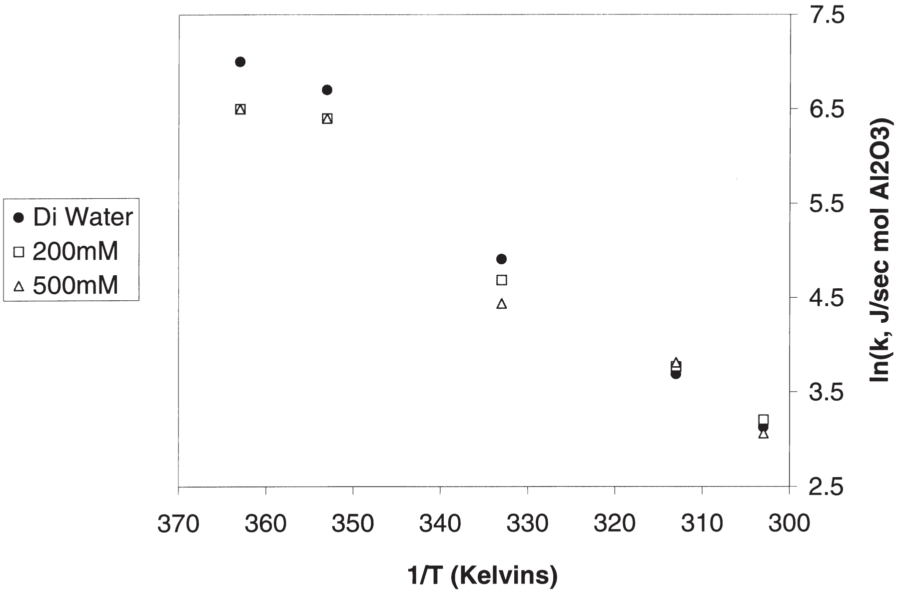

Fig. 8. Plot showing apparent activation energy when tricalcium aluminate and gypsum are hydrated in deionized water and 200 and 500 mM of NaOH.

Table 1
Kinetic results

Hydration solution	Apparent activation energy (kJ/mol Al_2O_3)	Predominant hydrated phase(s) observed by XRD
Deionized water	61.7	AFm, AFt
200 mM NaOH	53.1	AFm (U-phase, carbonate)
500 mM NaOH	54.3	AFm (U-phase, carbonate)

rates were obtained using the slopes of the total heat curves and are plotted vs. 1/*T* for each of the hydration solutions (Fig. 8). The results are summarized in Table 1.

The apparent activation energies reflect the temperature dependence of the rate of hydration. The apparent activation energies for 200 and 500 mM are almost identical and indicate that the reactions are very similar. The apparent activation energy for hydration in deionized water compares favorably (69.0 kJ/mol Al_2O_3) with previous analyses in Part I [1] of this study. The fit to the Arrhenius model is very good in every instance and indicates a first-order reaction is occurring. Because the hydration reactions show substantial changes with temperature, the rate-controlling mechanism appears to be an interfacial controlled process. The same conclusion was reached in Part I of this study and in a previous paper [23].

The hydration reactions indicate that AFm phases are more stable in increasingly alkaline solutions. Hydration in deionized water forms ettringite and monosulfate, while with small increases in alkalinity (200 mM of NaOH) U-phase, carbonate-substituted AFm, and monosulfate are the dominant phases. In 500 and 1.0 M of NaOH solutions U-phase becomes the dominant phase, replacing both monosulfate and carbonate-substituted AFm.

Increasing temperature in each hydration reaction increases the extent of AFm formation and promotes the formation of U-phase. In the 200-mM solution U-phase appears at 80 and 90°C and is not apparent in lower temperatures, while the extent of AFm phases increases with increasing temperature. In the 500-mM solution, the amount of U-phase increases with increasing temperature, while very little AFt phase appears at any temperature.

5. Summary

The hydration of a tricalcium aluminate/gypsum mixture with a 1:1 sulfate-to-aluminate ratio formed a complex phase assemblage. The data indicate the introduction of sodium cations in solution promote AFm formation at the expense of ettringite formation. Increasing temperature increases the extent of AFm formation. The data from Parts I and II indicate sulfate levels, which will allow ettringite formation, inhibit the formation of AFm phases. These findings are particularly important for precast, steam-cured concrete products. If AFt formation is suppressed by AFm formation during curing, then subsequent thermal fluctuations and/or cationic species migration could cause DEF and deterioration.

Acknowledgments

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