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Thermal stability of ettringite in alkaline solutions at 80 °C

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Abstract

The thermal stability of synthetic ettringite was examined in NaOH solutions up to 1 M after 12 h of heat treatment at 80 °C, with or without the coexistence of C_3S in the system. Ettringite was found to convert to the U phase, a sodium-substituted AFm phase, over the heat treatment in the absence of C_3S. The presence of C_3S, leading to C-S-H formation, prevents the U phase formation and results in the conversion of ettringite to monosulfate. Sulfate ions generated from ettringite decomposition mostly remain in the solution, but some is incorporated into C-S-H. During subsequent storage at room temperature, the majority of monosulfate slowly converts back to secondary ettringite under moist conditions, using the supply of sulfate ions from the solution and C-S-H. The observations support the current mechanism of delayed ettringite formation (DEF).

Keywords: Delayed ettringite formation (DEF); Stability; Ettringite; $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$

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1. Introduction

1.1. Background

The stability of ettringite has received renewed interest associated with controversies over the mechanism of delayed ettringite formation (DEF), which leads to deterioration of hardened concrete or other cementitous materials. The thermal decomposition of primary ettringite during heat curing above certain temperatures and subsequent recrystallization as secondary ettringite during cooling and storage under moist conditions are considered essential mechanisms involved in DEF-related expansion [1].

In comparison with other related phases, ettringite has been reported to be relatively stable over a wide range of temperatures [2–16]. Ettringite is the most insoluble phase in the CaO-SiO_2-$CaSO_4$-H_2O system [2]. The phase relations in the CaO-SiO_2-$CaSO_4$-H_2O system are influenced by temperature and pH of the system, which alter equilibrium and overall kinetics of the system. The pH range in which ettringite is stable has been reported to be between 9 and 13.4 in previous studies [17,18]. It is, however, generally agreed that the stability of the AFm phase increases as temperature and/or pH of the system increase.

Damidot and Glasser [2] studied the phase changes in the CaO-Al_2O_3-$CaSO_4$-H_2O system in alkaline environment using Na_2O to control pH of the system. In their computer-based calculations, calcium monosulfoaluminate (hereafter referred to as monosulfate) is confirmed to be metastable at 25 °C, although in reality, monosulfate usually forms in cement-based systems due to hydration being a dynamic process. Monosulfate becomes increasingly stable at the expense of ettringite as temperature and/or pH increases. An increase in temperature extends the range of sulfate concentration in which hydrogarnet and monosulfate are stable and decreases that of ettringite.

At the end of heat treatment in DEF-susceptible pastes, sulfate ions are distributed between C-S-H, pore solution, and AFm phases [1]. The sulfate adsorbed by C-S-H is probably in the form of SO_4^{2-}, perhaps balanced by Ca^{2+} [1]. The adsorption of sulfate ions by C-S-H is completely reversible and is enhanced at higher pH, temperature, and ionic strength [19]. Thus, adsorbed sulfate can be slowly released during subsequent storage in moist conditions at room temperature [20–24]. The driving force for such a release is the chemical concentration gradient between the sulfate incorporated in C-S-H and in pore solution. Therefore, the sulfate release should occur as the sulfate in the pore solution is consumed in secondary ettringite formation, triggered by decrease in pH of the system [25].

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Glasser et al. [26,27] performed quantitative analyses of the chemical balances during thermal cycles and proposed a hypothesis of the mechanism involved in DEF-related expansion. Because the concentration of soluble aluminate in the solution is notably low compared with that of sulfate, it limits the potential for direct precipitation of ettringite by a through-solution process away from a source of aluminate. Therefore, the presence of host AFm phase, providing a rich source of Ca and Al ions, favors the nucleation of secondary ettringite crystals, which then grows as sulfate ions become available through diffusion. The ettringite that forms from AFm phase in this way is occluded in "dense inner C-S-H products" and gives rise to expansive pressure. This is consistent with the observations by Scrivener et al. [28,29] that following the heat curing of cement paste at 80 °C, the majority of aluminate and sulfate ions are intimately mixed with the C-S-H gel, in which ettringite reforms as dispersed microcrystals during subsequent storage under moist conditions.

1.2. Scope of the present study

The reversible conversion between ettringite and monosulfate is hence an essential process that governs expansive behavior of cement systems associated with DEF. Therefore, the stability of calcium sulfoaluminate phases, particularly ettringite and monosulfate under conditions in which DEF-related expansion favorably occurs must be examined for a better understanding of the DEF-related issues. Instead of dealing with complex cement systems, applying simplified systems consist only of synthetic pure materials enables us to obtain basic information on the ettringite stability with respect to DEF-related reactions. The coexistence of C_3S in such conditions is considered important, as significant interaction between ettringite and C-S-H have been suggested. In the present study, the thermal stability of ettringite in various NaOH solutions was examined during 12 h of heat treatment at 80 °C, a temperature known to trigger DEF in practice. The effect of the presence of C_3S on the ettringite stability and its long-term stability at room temperature were also examined.

2. Experimental

2.1. Synthesis of ettringite

Under nitrogen atmosphere at room temperature, 0.08 mol of $Ca(OH)_2$ was added to 0.02 mol/l of $Al_2(SO_4)_3$ solution and stirred for 24 h. The resulting precipitate was removed by vacuum filtration. After rinsing with D.I. water and ethanol, the precipitate was dried in a desiccator under nitrogen atmosphere at 13% R.H. The white powder-like compound obtained was identified as ettringite ($3CaO.Al_2O_3.3CaSO_4.30.9H_2O$) by X-ray diffraction (XRD) and thermogravimetric (TG) analysis. A trace of a monosulfate was detected in the XRD pattern by its primary peak at 9.9° 2-theta.

2.2. Heat treatment

After passing through a sieve with 300-μm openings, 5 g of synthetic ettringite was mixed with 10 ml of D.I. water or various concentrations of NaOH solutions up to 1 M. These slurries were heated at 80 °C in sealed bottles for up to 12 h in an oven. Subsequently, the solid was separated from the solution by centrifuging, and then, precipitates were rinsed with D.I. water and ethanol. The samples were dried in a desiccator under a nitrogen atmosphere at 13% R.H. Selected samples were dried at either 11% R.H. over saturated LiCl solution or 100% R.H. over water [30].

A mixture of 1.25 g ettringite and 3.75 g (C_3S) was also used as a starting material. Selected samples were stored for up to 10 months at room temperature after 12 h of heat treatment.

2.3. Characterization

XRD patterns of the precipitates were obtained using a Rigaku DmaxII diffractometer (Rigaku, Lowell, MA) at a scan rate of 2° 2 theta/min using CaKα radiation generated at 40 kV and 40 mA. For scanning electron microscopy (SEM) observations, a JSM-5400LVS microscope (JEOL, Tokyo, Japan) was operated with an accelerating voltage of 10 kV in high vacuum mode. The SEM samples were prepared with gold coating using a JEC-550 sputter coater on carbon tapes and aluminum holders. Selected samples were analyzed by ^{27}Al, ^{23}Na, and ^{29}Si MAS nuclear magnetic resonance (NMR) spectroscopy using a Unity/INOVA 500 spectrometer (Varian, Palo Alto, CA). NMR samples were spun at 5 kHz in a 7-mm-diameter zirconia rotor for silicon and at 8–10 kHz in a 5-mm-diameter Kel-F rotor for aluminum and sodium with an appropriate background processing. TG analysis was carried out using NETZSCH Simultaneous Thermal Analyzer STA 409 (NETZSCH, Selb, Germany) at 5 °C/min from room temperature to 1000 °C in an inert gas. The compositions of the filtrates were analyzed for S, Al, and Ca by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer Plasma II Emission Spectrometer (Perkin-Elmer, Norwalk, CA).

3. Results

3.1. Thermal stability of ettringite in alkaline solutions

Fig. 1 shows the XRD patterns of ettringite heat treated at 80 °C in various alkaline solutions. Ettringite was observed to be stable after 12 h of heat treatment in D.I. water. New peaks appear in the pattern as the alkali concentration increases, corresponding to the formation of U phase, a

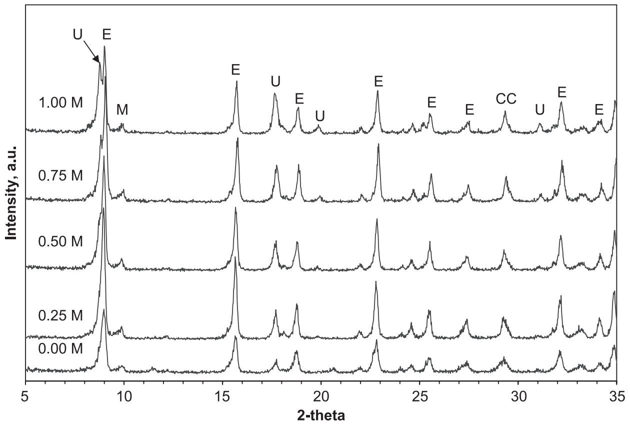

Fig. 1. XRD patterns of ettringite, heat treated for 12 h in various concentrations of NaOH solutions (E: ettringite; U: U phase; M: monosulfate, CC: calcium carbonate).

sodium-substituted AFm phase. Although complete decomposition of ettringite was not observed the degree of conversion from ettringite to the U phase increases with increases in the alkali concentration. Small calcite peaks were also observed from carbon dioxide impurity in the system. SEM observation shows a needle-like morphology of the synthetic ettringite (1–4 µm in length) in Fig. 2a. During the 12 h of heat treatment in 1 M solutions, this ettringite morphology changed to fine stubby prisms less than 1 µm in length, as shown in Fig. 2b and c. Hexagonal plate-like crystals (2–5 µm in diameter) appear to be the U phase.

Subsequently, ^{27}Al NMR spectroscopy analysis was carried out after 12 h of heat treatment in various alkali solutions (Fig. 3A). The peak seen at 13.2 ppm is associated with ettringite while the peak at 10.6 ppm is assigned to the U phase. The gradual appearance of the U-phase peak with increase alkali concentrations agrees with the XRD analysis. The conversion of ettringite to the U phase was quantitatively analyzed by calculating the area ratios of the peaks at 13.2 ppm and 10.6 ppm as shown in Fig. 3B. The conversion of ettringite to the U phase occurs in alkaline solutions as low as 0.25 M but not in D.I. water. The degree of the conversion is nearly proportional to the alkali concentration, and approximately 40% of ettringite completely converted to the U phase in 1 M solutions. The maximum conversion appears to complete within the first 4 h of heat treatment.

Dosch and zur Strassen [31] have suggested the composition of U phase as follows:

$$\{\mathrm{Ca_4Al_{2(1-x)}(OH)_{12}[SO_4]}\}^{6x-}\{y\mathrm{Na_2SO_4}\cdot 6x\mathrm{Na}\cdot \mathrm{aq}\}^{6x+}$$

To confirm the U phase formation with the proposed composition, ^{23}Na NMR spectroscopy analyses were carried out on the samples heat cured in 1 M solutions for 12 h. The spectrum of the specimen dried at 11% R.H. (Fig. 4) shows a broad peak composed of at least two peaks, indicating that multiple Na sites exist in the sample. Although one Na site could appear in two split peaks due to quadrupolar coupling, this is probably not the case [32]. On the other hand, the sample exposed to 100% R.H. exhibits a sharp and distinct peak at −1.01 ppm in Fig. 4. This indicates that Na ions weakly bonded to the surface of the solid phases or the interlayer of the U phase structure, which shows solution-like behavior in the saturated atmosphere. The broad peak(s) overlapping this peak may be attributed to one or more Na sites that have relatively strong bonds in the U phase structure. Due to the large differences in atomic size and charge, it is unlikely that Na ions substitute for Al ions in the main layer of the U phase. However, there is no further

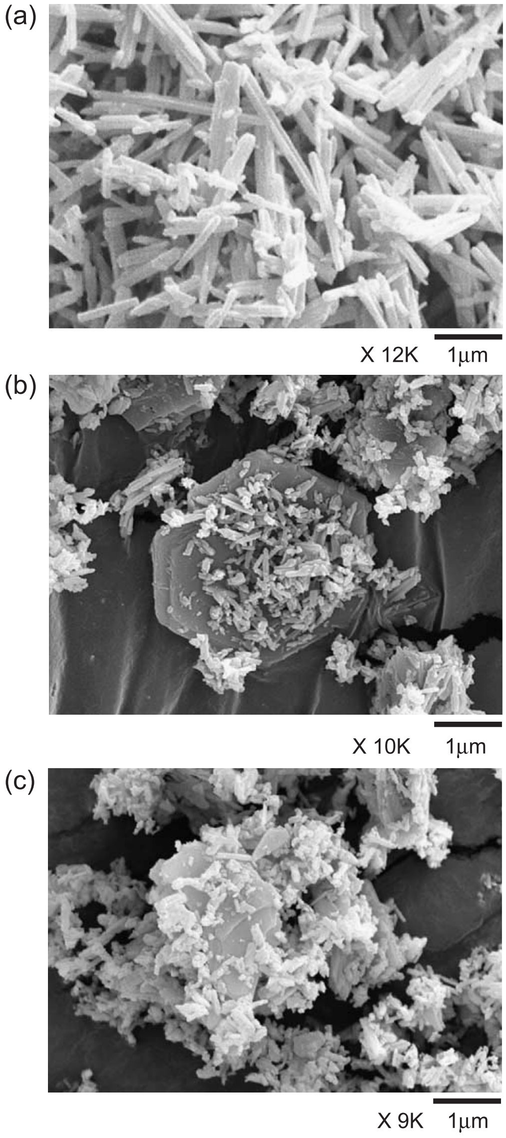

Fig. 2. SEM micrographs of synthetic ettringite (b) and that heat treated for 12 h in 1 M NaOH solution (b and c).

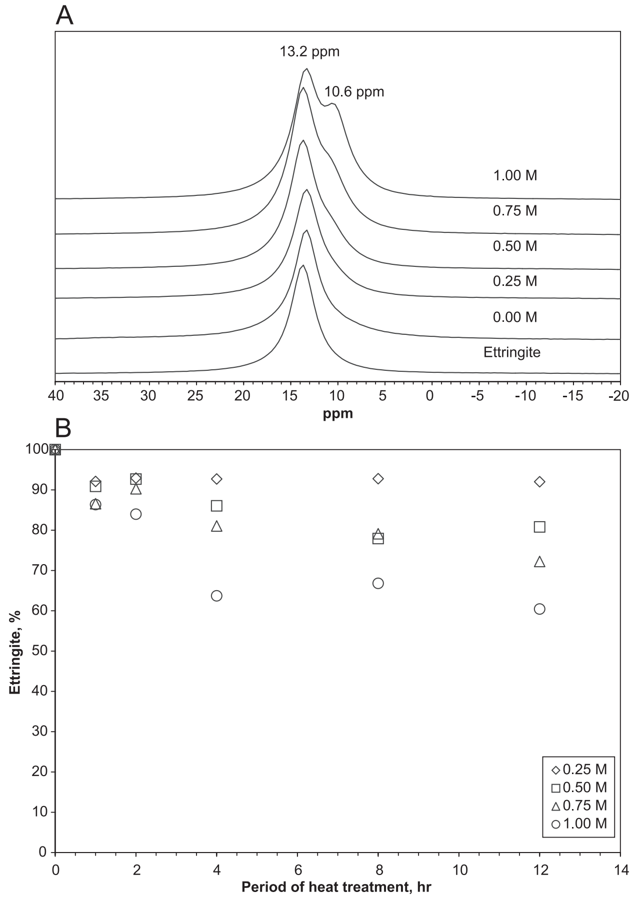

Fig. 3. ^{27}Al NMR spectroscopy of ettringite, heat treated for 12 h in various concentrations of NaOH solutions: (A) representative spectra and (B) quantitative changes in amount of ettringite.

evidence that this Na site exists in the interlayer, as in the suggested composition.

The compositions of filtrates were analyzed for SO_4^{2-}, Ca^{2+}, and $Al(OH)_4^-$, as shown in Table 1 (expressed as SO_3, CaO, and Al_2O_3). The sulfate concentrations increase with increases in alkali concentrations, corresponding to the degree of U phase formation, at the expense of ettringite. The low-aluminum concentrations indicate that the decomposed portion of ettringite has almost fully converted to the U phase, regardless of the alkali concentration. The calcium concentrations are also low due to the formation of calcite, observed by XRD.

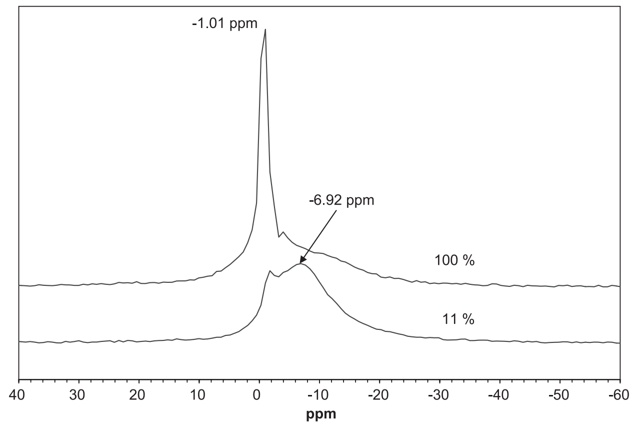

Fig. 4. ^{23}Na NMR spectra of ettringite heat treated for 12 h in 1 M NaOH solution followed by drying over 11% R.H. or kept at 100% R.H.

Table 1
Composition of storage solutions of ettringite heat treated for 12 h

Concentration (M)			
NaOH	SO_3	CaO	Al_2O_3
0.00	1.49e – 02	1.80e – 02	2.00e – 04
0.25	3.41e – 02	1.68e – 04	4.82e – 03
0.50	6.80e – 02	5.40e – 04	4.62e – 03
0.75	7.25e – 02	5.84e – 04	1.68e – 03
1.00	1.28e – 01	6.05e – 04	3.05e – 03

3.2. Effect of the coexistence of C_3S on the stability of ettringite in alkaline solutions

Fig. 5 shows XRD patterns of the mixture of ettringite and C_3S heat treated at 80 °C in various alkaline solutions for 12 h. In the presence of C_3S, ettringite converts to monosulfate, not to the U phase. A higher degree of conversion was observed as the concentration of alkali increases. This was confirmed by ^{27}Al NMR spectroscopy (Fig. 6A), where the ettringite peak at 13.2 ppm is replaced by the monosulfate peak that appears at 10.6 ppm with an increase in the alkali concentration. Conversion occurs quickly within the first several hours of the heat treatment at any concentrations. Quantitative analyses (Fig. 6B) indicate that approximately 20% of ettringite converts to monosulfate in D.I. water, while complete conversion was observed in 0.75 and 1 M solutions. Apparently, the coexistence of C_3S prevents

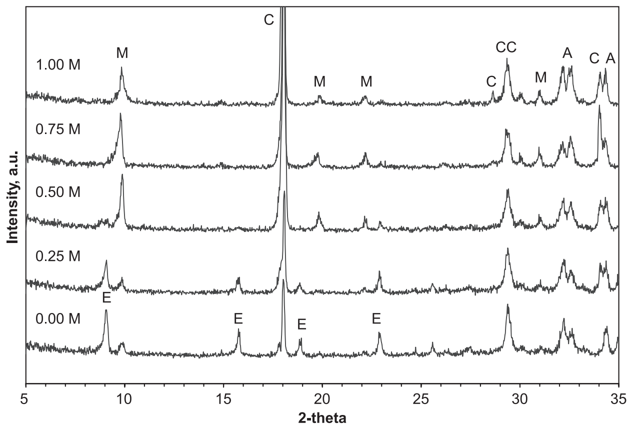

Fig. 5. XRD patterns of ettringite mixture with C_3S, heat treated for 12 h in various concentrations of NaOH solutions (E: ettringite; M: monosulfate; A: alite, C_3S; C: calcium hydroxide; CC: calcium carbonate).

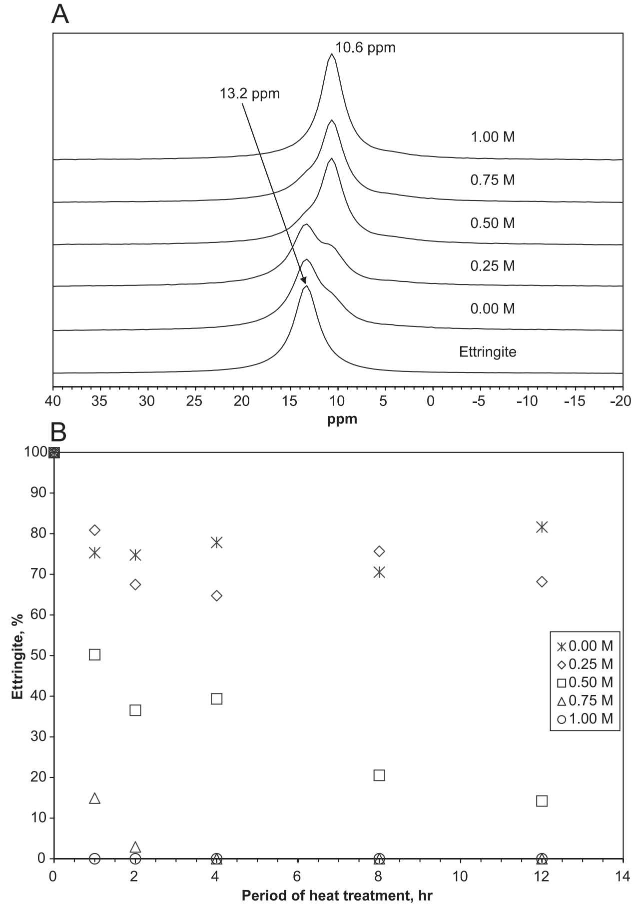

Fig. 6. ^{27}Al NMR spectra of ettringite mixture with C_3S, heat treated for 12 h in various concentrations of NaOH solutions: (A) representative spectra and (B) quantitative changes in amount of ettringite.

Na ions from participating in the U-phase formation; perhaps, Na^+ coadsorbs with SO_4^{2-} in C-S-H.

C_3S hydration was confirmed by the appearance of calcium hydroxide peaks in the XRD patterns, but unhydrated C_3S peaks still remain, regardless of the alkali concentration. SEM observation after the heat treatment shows hexagonal plate-like morphologies (3–6 μm in diameter) of monosulfate and calcium hydroxide crystals mixed with C-S-H. ^{29}Si NMR spectroscopy (Fig. 7) also confirmed C_3S hydration. Peaks at -78.5 and -84.4 ppm are attributed to Q^1 and Q^2 species of C-S-H. The appearance of a small Q^2(1Al) peak at -82.0 ppm indicates incorporation of a small amount of Al ion into the C-S-H structure [33,34]. Such tetrahedrally coordinated Al ions in the C-S-H structure have been reported to be observed at 40–80 ppm in ^{27}Al NMR spectroscopy also [35]. This peak however, could not be observed here due to overlapping with the spinning side band of octahedrally coordinated Al ions.

ICP-AES analyses of the filtrates (Table 2) show the aluminum concentrations to be below detection limits in many cases. This is in agreement with Glasser et al. [26] and consistent with the low solubility of calcium sulfoaluminate hydrates. Increases in alkali concentration were observed, as would be expected, from the formation of $Al(OH)_4^-$. Most of the sulfate ions released by ettringite decomposition remain in the solution at all alkali concentrations. Calcite formation resulted in low-calcium concentrations.

3.3. Long-term stability of ettringite in alkaline solutions in the presence of C_3S

Fig. 8 shows XRD patterns of the mixture of ettringite and C_3S stored for 3 months at room temperature after the heat curing. The monosulfate peaks observed after the heat treatment completely disappear, and small ettringite peaks appear again after storage. The secondary ettringite formation is independent of the initial concentration of alkali. Further hydration of C_3S, accompanied by additional C-S-H formation, was suggested by a decrease in unhydrated C_3S peaks and an increase in calcium hydroxide peaks (compare Fig. 5). XRD patterns after 10 months of storage are very similar to those after 3 months. Ettringite peaks became slightly sharper, and the calcium hydroxide peaks increased in intensity. SEM images show needle-like morphology of secondary ettringite crystals and hexagonal plate-like morphology of calcium hydroxide crystals.

^{27}Al NMR spectra after the 10 months of storage also show peaks of secondary ettringite at 13.2 ppm, as shown in Fig. 9. A peak at approximately 10 ppm, observed as a shoulder on the dominant ettringite peak, indicates the presence of a residual amount of monosulfate not detected by XRD. The peak at 4.66 ppm is attributed to an unidentified Al-bearing phase, newly formed during the storage. Although quantitative analysis was not accurate due to the large difference in the area ratios, the amount of secondary ettringite formed does not appear to vary with alkali concentration.

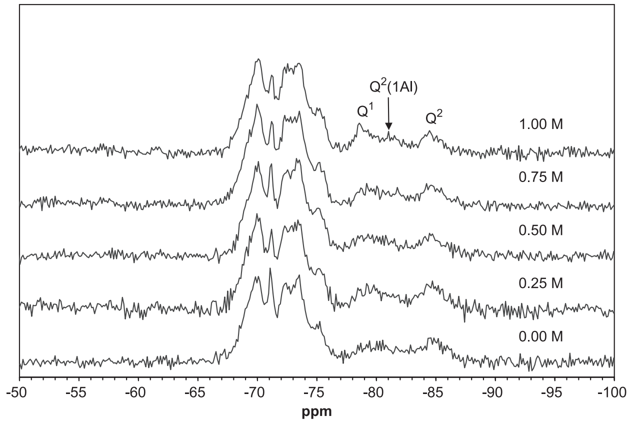

Fig. 7. ^{29}Si NMR spectra of ettringite mixture with C_3S, heat treated for 12 h in various concentrations of NaOH solutions.

Table 2
Composition of storage solutions of ettringite mixture with C_3S, heat treated for 12 h, followed by 10 months of storage at room temperature

Concentration (M)						
NaOH	SO_3		CaO		Al_2O_3	
	12 h	10 months	12 h	10 months	12 h	10 months
0.00	1.50e – 03	N.D.	2.22e – 03	4.69e – 04	N.D.	N.D.
0.25	3.71e – 02	1.90e – 03	3.14e – 03	3.04e – 05	N.D.	4.82e – 06
0.50	1.26e – 01	7.80e – 03	7.05e – 04	4.99e – 05	N.D.	1.08e – 04
0.75	1.76e – 01	2.40e – 02	1.28e – 03	9.55e – 04	1.19e – 05	1.36e – 04
1.00	1.69e – 01	4.98e – 02	8.96e – 04	1.48e – 04	1.07e – 04	2.11e – 04

N.D. = not detected.

^{29}Si NMR spectra show the absence of residual unhydrated C_3S peaks in Fig. 10, indicating its complete hydration. It may be noted that the peak at -84.4 ppm due to Q^2 species in the C-S-H structure decreases as the alkali concentration increases. This suggests a higher degree of silicate polymerization in C-S-H at lower alkali concentrations. Despite the development of Q^1 and Q^2 peaks with C_3S hydration, the peak of $Q^2(1Al)$ species is still recognizable. This indicates that Al ions incorporated in the C-S-H structure during the heat treatment remain after 10 months of storage. ICP-AES analyses of filtrates (Table 2) show decreases in sulfate concentrations due to the secondary ettringite formation during the storage. The calcium concentrations further decreased due to calcite formation during the prolonged storage.

4. Discussion

It has been shown that in the presence of Na ions, ettringite converts only to the U phase (a sodium-substituted AFm phase) incorporating the Na ions. The formation of U phase has been reported as a hydration product of OPC in 2 and 4.5 M NaOH solutions [36], OPC with 25 wt.% of Na_2SO_4 [37], and synthesized C_3A, C_3S, and Na_2SO_4 in 3 M NaOH solution [38]. Clark and Brown [39] also reported the U phase as the dominant hydration product of C_3A and gypsum in 0.5 M of NaOH solution at 50 °C and above. Our NMR studies show that conversion to the U phase occurs in as low as 0.25 M of NaOH solution and that the degree of ettringite decomposition increases nearly in proportion to the NaOH concentration. Ghorab and Kishar [8] also studied the thermal stability of ettringite in up to 1 M NaOH solutions at up to 100 °C, although neither the U-phase formation nor the ettringite stability was observed. This may be due to the presence of carbonate in the decomposition process of ettringite, which leads to monocarbonate formation. Although the U-phase composition has not been clearly established, ^{23}Na NMR spectroscopy analyses suggest that Na species appear to be incorporated in the interlayer of the U phase structure, but with some, as yet, undetermined substitution between the layers.

The major influence of the coexistence of C_3S is to prevent the U-phase formation in favor of monosulfate. Perhaps, Na ions are adsorbed by C-S-H in preference to U-phase formation; the lower degree of C-S-H polymerization in high NaOH concentrations is consistent with this hypothesis. Not all sulfate ions are taken up by C-S-H, and the greater proportion remains in the solution. However, in the mixtures studied, the proportion of ettringite is much

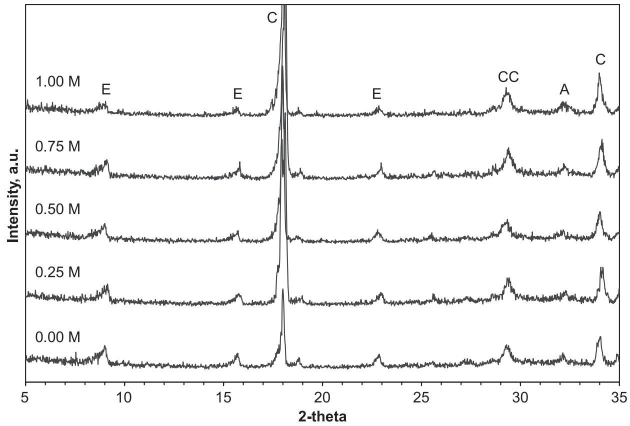

Fig. 8. XRD patterns of ettringite mixture with C_3S, heat treated for 12 h in various concentrations of NaOH solutions followed by 3 months of storage at room temperature (E: ettringite; A: alite, C_3S; C: calcium hydroxide; CC: calcium carbonate).

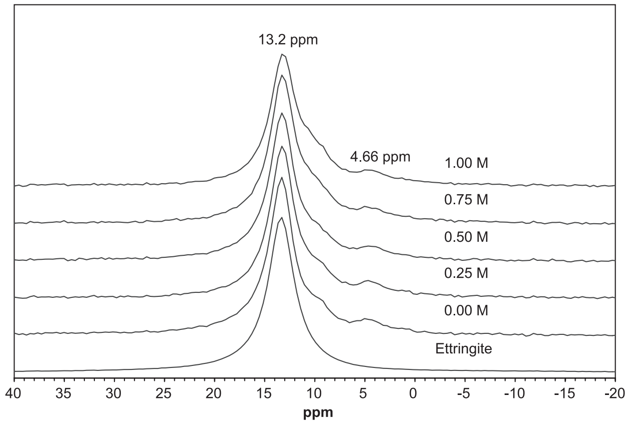

Fig. 9. ^{27}Al NMR spectra of ettringite mixture with C_3S, heat treated for 12 h in various concentrations of NaOH solutions followed by 10 months of storage at room temperature.

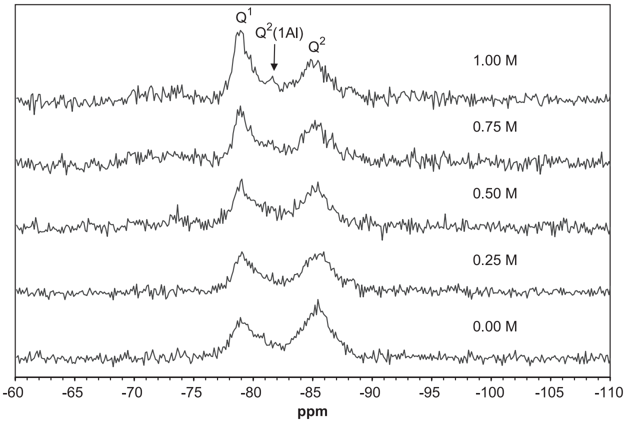

Fig. 10. ^{29}Si NMR spectra of ettringite mixture with C_3S, heat treated for 12 h in various concentrations of NaOH solutions followed by 10 months of storage at room temperature.

higher in relation to C-S-H than it would be in a typical Portland cement paste. In this latter case, C-S-H may act as a more significant reservoir of adsorbed sulfate. The distribution of SO_4^{2-} between C-S-H and pore solution requires further study.

In the presence of C_3S, secondary ettringite formation occurred during 3 months of prolonged storage, as observed in DEF-related expansions. Between 3- and 10-month storage, the amount of secondary ettringite formed slightly increased and became better crystallized. These observations confirm the importance of monosulfate as the precursor of secondary ettringite, as suggested by Glasser et al. [26]. Although this system consists only of pure components and does not simulate the complexity of real cementitious materials, the observations are also in a good agreement with the current view of DEF in mortar systems [1].

5. Conclusions

In the absence of C_3S, ettringite converts to U phase, a sodium-substituted AFm phase, during heat treatment at 80 °C in NaOH solutions at 0.25 M and above. In this compound, Na ions most likely are incorporated into the interlayer of the U-phase structure. The degree of conversion increases in nearly direct proportion to the alkali concentration but is limited to about 40%. The major influence of adding C_3S, which concomitantly forms C-S-H, is to prevent the U phase formation and results in a complete conversion of ettringite to monosulfate in above-0.5 M NaOH solutions. Ettringite quickly converts to monosulfate during the heat treatment, while C_3S slowly hydrates and forms C-S-H. Sulfate ions generated from ettringite decomposition mostly remain in the solution, but some are incorporated into C-S-H, probably by adsorption, as SO_4^{2-} together with a counter ion (which could be Na^+ or Ca^{2+}). During the subsequent storage at room temperature, the majority of monosulfate slowly converts back to ettringite, drawing on the supply of sulfate ions in the system. The observations are consistent with the current hypotheses of DEF mechanisms in Portland cement pastes.

Acknowledgements

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