Effect of Coexisting Materials on Secondary Ettringite Formation

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Abstract. *The expansion of cement paste can occur as a result of secondary ettringite formation due to attack by sulfates. It has been proposed that this expansion is affected by coexisting hydration products such as calcium-silicate-hydrates (C-S-H), although the mechanism has not yet been clarified. The present study experimentally examined the effects of coexisting materials on secondary ettringite formation. Synthesized monosulfate and coexisting materials such as C-S-H were mixed with a sodium sulfate solution. The secondary ettringite proportion was markedly increased by the presence of C-S-H, and calcium-aluminate-silicate-hydrates (C-A-S-H) containing four-coordinate Al were formed in these samples. It is evident that ettringite is likely to form from four-coordinate Al, and that C-S-H promotes secondary ettringite formation because it transitions six-coordinate Al derived from the monosulfate to four-coordinate Al by substituting Al in the Si chains.*

Keywords: *Sulfate Attack, DEF, Secondary Ettringite Formation, Coexisting Materials, C-S-H.*

1 Introduction

Expansion due to sulfates is typically referred to as either external or internal sulfate attack, depending on the sulfate source. Internal sulfate attack after high temperature curing is also referred to as delayed ettringite formation (DEF) (Collepardi, 2003). Both external and internal sulfate attack are attributed to secondary ettringite formation in the cement paste.

Ettringite has the composition $C_6A\bar{S}_3H_{32}$ and is formed from tricalcium aluminate (C$_3$A) in Portland cement or from aluminum in supplementary cementitious materials during the early stages of hydration. Ettringite is subsequently converted to a monosulfate (Ms) form having the formula $C_4A\bar{S}H_{12}$ as the sulfate ion concentration in the liquid phase decreases. When sulfate ions are supplied to the hardened cement paste they react with the Ms to reform so-called secondary ettringite. However, the mechanisms which can explain all expansions due to secondary ettringite formation in a unified manner has not yet been proposed.

It has been suggested that the expansion due to secondary ettringite formation is affected by the properties of hydration products coexisting with the ettringite, such as calcium-silicate-hydrates (C-S-H). Taylor *et al.* (2001) proposed the DEF expansion mechanism in a mortar. According to this mechanism, ettringite may have a greater degree of expandability when it is formed in the outer C-S-H near the boundary between two C-S-H phases (outer C-S-H and inner C-S-H) than when it is formed in the outer C-S-H far from the boundary.

The goal of the present study was to experimentally examine the effects of coexisting materials on secondary ettringite formation. This was accomplished using a synthesized Ms sample in conjunction with coexisting materials such as C-S-H. The Ms and other materials were mixed and hydrated using a sodium sulfate solution, followed by analysis.

2 Methods and Materials

2.1 Preparation of Materials

The Ms was prepared from a suspension of a 1:1 molar mixture of C_3A, which was prepared by calcining of $CaCO_3$ and Al_2O_3, and $CaSO_4$ in deionized water, at a water to solid mass ratio of 10:1. The solid and aqueous phases were separated after curing at 20 °C for 14 d.

C-S-H, calcium hydroxide (CH) and hydrogarnet (HG) were used as the coexisting materials in this work. Because silica stone does not react at ambient temperature and pressure, silica stone powder (SSP) was also used for the purposes of comparison with other coexisting materials. In addition, amorphous silica (AS) and Al-substituted C-S-H (C-A-S-H) were used in verification experiments. Three C-S-H samples having different CaO to SiO_2 molar ratios (C/S ratio) (of 0.80, 1.00 and 1.50) were synthesized by reacting mixtures of CH, ethyl silicate and deionized water for 2 d at 40 °C, after which the solid and aqueous phases were separated by vacuum filtration. HG was synthesized via the reaction of C_3A with deionized water at a water to solid mass ratio of 1:1. Samples were cured for 28 d at 40 °C, after which the solid phase was separated by vacuum filtration. C-A-S-H was synthesized based on the method of Pardal *et al.* (2009). The CH, AS and SSP (purity > 96%) used in this work were all commercially-available products.

These materials were dried under 110 °C in a drying oven (defined as 0% RH), and subsequently crushed into particles smaller than 90 μm. The H_2O to SiO_2 molar ratios of C-S-H having the C/S ratios of 0.8, 1.0 and 1.5 dried at 110 °C were 0.63, 0.67, 0.82, respectively.

2.2 Mixing with a Sodium Sulfate Solution

The mixing proportions of the Ms and the coexisting materials are summarized in Table 1. Herein, the C-S-H and C-A-S-H specimens are termed CSH0.8, CSH1.0, CSH1.5, CASH0.8, CASH1.0 and CASH1.4, where the numerical portion of the name gives the C/S ratio. The effects of the chemical composition of the mixture were assessed by simultaneously

Table 1. Specimen proportions.

Sample name	Powder composition (mass%)										
	Ms	CSH 0.8	CSH 1.0	CSH 1.5	CH	HG	SSP	AS	CASH 0.8	CASH 1.0	CASH 1.4
Ms+CSH 0.8	50	50	–	–	–	–	–	–	–	–	–
Ms+CSH 1.0	50	–	50	–	–	–	–	–	–	–	–
Ms+CSH 1.5	50	–	–	50	–	–	–	–	–	–	–
Ms+CH	50	–	–	–	50	–	–	–	–	–	–
Ms+HG	50	–	–	–	–	50	–	–	–	–	–
Ms+SSP	50	–	–	–	–	–	50	–	–	–	–
Ms+AS	50	–	–	–	–	–	–	50	–	–	–
Ms+(CH+AS)1.0	50	–	–	–	27.61	–	–	22.39	–	–	–
Ms+(CH+AS)1.5	50	–	–	–	32.46	–	–	17.54	–	–	–
Ms+CASH 0.8	50	–	–	–	–	–	–	–	50	–	–
Ms+CASH 1.0	50	–	–	–	–	–	–	–	–	50	–
Ms+CASH 1.4	50	–	–	–	–	–	–	–	–	–	50

combining CH and AS with the Ms. In these trials, the CH and AS were mixed so that the C/S ratio was either 1.00 or 1.50 and the mixture was combined with the Ms at a mass ratio of 1:1.

Each mixture of the Ms and the coexisting materials were mixed with a 0.5 M sodium sulfate solution at a liquid to powder mass ratio of 2:1. They were manually mixed for 3 m and transferred into a plastic bottle and cured at 20 °C for 1 d.

After the curing, the samples were broken into small pieces and immersed in acetone for 2 d to prevent further hydration. These specimens were subsequently placed under vacuum to remove the acetone and stored in a vacuum desiccator in the presence of silica gel for 2 d. The samples were crushed into particles smaller than 90 μm and dried at 20 °C and 11% RH using a saturated LiCl solution in a vacuum desiccator until the sample mass no longer changed.

2.3 Analysis

Powder XRD was used for the identification and quantification of hydration products after mixing with the sodium sulfate solution.

For the measurement of the pH and ionic composition of the liquid phase, a Ms specimen together with coexisting materials were mixed with a 0.5 M sodium sulfate solution at a liquid to powder mass ratio of 3:1. After mixing, each sample was placed in a plastic bottle and then cured at 20 °C for 1 d, after which the solid and liquid phases were separated by centrifugation. The pH of the liquid phase was measured using a glass electrode pH meter and the concentrations of Na^+, Ca^{2+} and SO_4^{2-} ions in the liquid phase were analyzed.

Solid state ^{27}Al nuclear magnetic resonance (NMR) was employed to determine the chemical state of Al in each sample after mixing with the sodium sulfate solution. The ^{27}Al magic angle spinning (MAS) NMR experiments were performed with a ECA800 operating at 18.79 T with a 3.2 mm probe and a spinning frequency of 20 kHz. ^{27}Al spectra were recorded with a 0.6 μs pulse width and a recycle delay of 1 s between scans.

3 Results

3.1 Formation Characteristics of Secondary Ettringite

Figure 1 shows the XRD patterns of Ms samples with each coexisting material after mixing with the sodium sulfate solution. SSP does not react at ambient temperature and pressure, and so does not contribute to secondary ettringite formation. The ettringite peaks of the Ms+CH and Ms+HG were not increased in intensity as compared with Ms+SSP. Thus, when CH and HG coexist (that is, even when the Ca and Al necessary for the formation of the secondary ettringite are supplied), there was almost no secondary ettringite formation. In contrast, the diffraction peaks due to Ms almost disappeared while those resulting from ettringite increased when C-S-H was added to the Ms.

3.2 Effects of pH and Calcium Leaching

The pH values and ionic compositions of the liquid phases after mixing with the sodium sulfate solution are provided in Table 2. In all cases, the pH was in the range of 11.57 to 13.39, which is associated with the stable formation of ettringite (Stark and Wicht, 2003; Shimada et al., 2005). The Ms+CSH1.5 had the highest Ca^{2+} concentration, and the values for the Ms+CSH0.8 and Ms+CH were especially close. The pH of the Ms+CH was higher than that
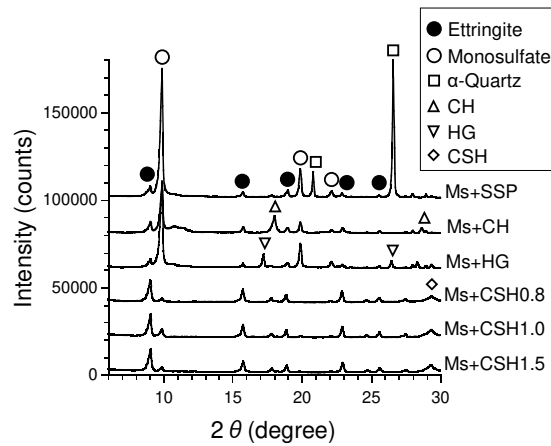
Figure 1. XRD patterns of monosulfate specimens with coexisting materials after mixing with a sodium sulfate solution.

Table 2. pH values and ionic compositions of the liquid phases.

	pH	Na^+ (mol/L)	Ca^{2+} (mol/L)	SO_4^{2-} (mol/L)
Ms	12.38	1.81	0.01	0.35
Ms+SSP	12.54	1.13	0.02	0.38
Ms+HG	12.43	1.11	-	0.34
Ms+CH	13.39	1.09	0.04	0.05
Ms+CSH0.8	11.68	0.78	0.04	0.24
Ms+CSH1.0	12.60	0.88	0.06	0.28
Ms+CSH1.5	11.57	0.86	0.12	0.13

of the Ms+CSH0.8, although the amount of secondary ettringite in the latter material was significantly greater than that in the former. Kunther *et al.* (2015) reported that of the extent of Ca^{2+} leaching decreases with decreases in the C/S ratio of the C-S-H, such that the supersaturation of ettringite in the pore solution decreases and expansion of the mortar is suppressed. This suggests that a higher Ca^{2+} concentration in the liquid phase will promote secondary ettringite formation. However, the results of this study show large differences in the extent of secondary ettringite formation, even when the Ca^{2+} concentration in the liquid phase is constant. Moreover, although the Ca^{2+} concentration of the liquid phase was slightly higher in the case of the Ms+CSH1.0 compared with the Ms+CSH0.8, and both pH values were in the range required for ettringite to be stable, the amount of secondary ettringite in the latter material was greater. Thus, the promotion of secondary ettringite formation due to the presence of C-S-H is not completely explained by conventional theories regarding the effects of the pH and Ca^{2+} concentration of the liquid phase.

3.3 Effects of Ca and Si-Based Materials

Si in the C-S-H is thought to have played an important role in secondary ettringite formation in the present work. Figure 2 shows the XRD patterns of Ms specimens with added Ca and Si-based materials after mixing with the sodium sulfate solution. For comparison, the XRD patterns generated by the Ms+SSP, Ms+CH, Ms+CSH1.0 and Ms+CSH1.5 are also provided

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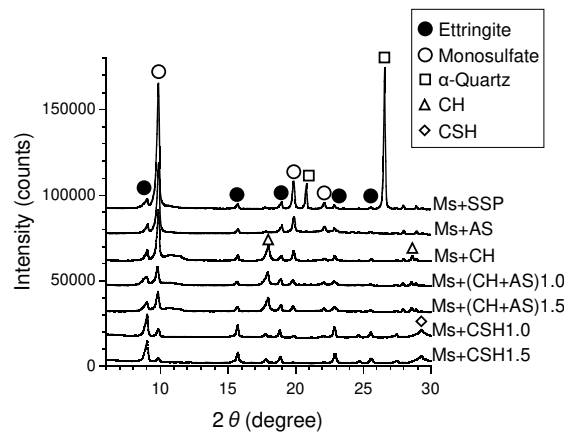
Figure 2. XRD patterns of monosulfate specimens with added Ca and Si
after mixing with a sodium sulfate solution.

in the figure. These patterns demonstrate that the Ms diffraction peaks produced by the Ms+AS were slightly less intense than those in the Ms+SSP pattern. When both CH and AS were present, the Ms peaks were further decreased. Therefore, it appears that the simultaneous addition of both Ca and Si promoted the dissolution of the Ms. Conversely, the ettringite peaks did not increase significantly even when both CH and AS coexisted. Thus, even when the chemical composition in the sample is the same as that of C-S-H, the amount of secondary ettringite is greatly increased only when C-S-H is present.

3.4 Evaluation of the Chemical State of Al

The chemical state of Al, which is an important constituent element of both Ms and ettringite, was investigated using ^{27}Al NMR. Figure 3 shows the ^{27}Al NMR spectra of Ms specimens with each coexisting material after mixing with the sodium sulfate solution. For all coexisting materials, two peaks corresponding to six-coordinate Al appeared. These two peaks are attributed to Ms and ettringite (Skibsted *et al.*, 1999; Andersen *et al.*, 2004). The Ms+HG also generated a HG peak close to the ettringite peak (Cuesta *et al.*, 2017). In the case of the sample without C-S-H, a six-coordinate Al peak produced by the Ms is clearly present. In contrast, the spectra obtained from the samples with C-S-H contain a significantly reduced Ms peak along with a much more intense ettringite peak. Thus, these ^{27}Al NMR data also demonstrate that the coexistence of C-S-H promoted secondary ettringite formation.

Moreover, each of the three samples containing C-S-H generated a broad peak corresponding to four-coordinate Al. This peak is also generated by C-A-S-H, in which Al is substituted for Si in the silicate chains of C-S-H at pairing and bridging sites (Richardson, 2004). Because the bridging sites in the silicate chains are increased as the C/S ratio decreases, Al is more readily substituted for Si at these sites (Pardal *et al.*, 2012; Renaudin *et al.*, 2009). It is therefore apparent that, in samples containing C-S-H, the Si in the silicate chains were substituted with Al released by dissolution of the Ms to generate C-A-S-H.

3.5 Effect of the Presence of C-A-S-H

Figure 4 presents the XRD patterns of Ms specimens with added C-A-S-H after mixing with the sodium sulfate solution, along with the patterns of the C-S-H samples for comparison

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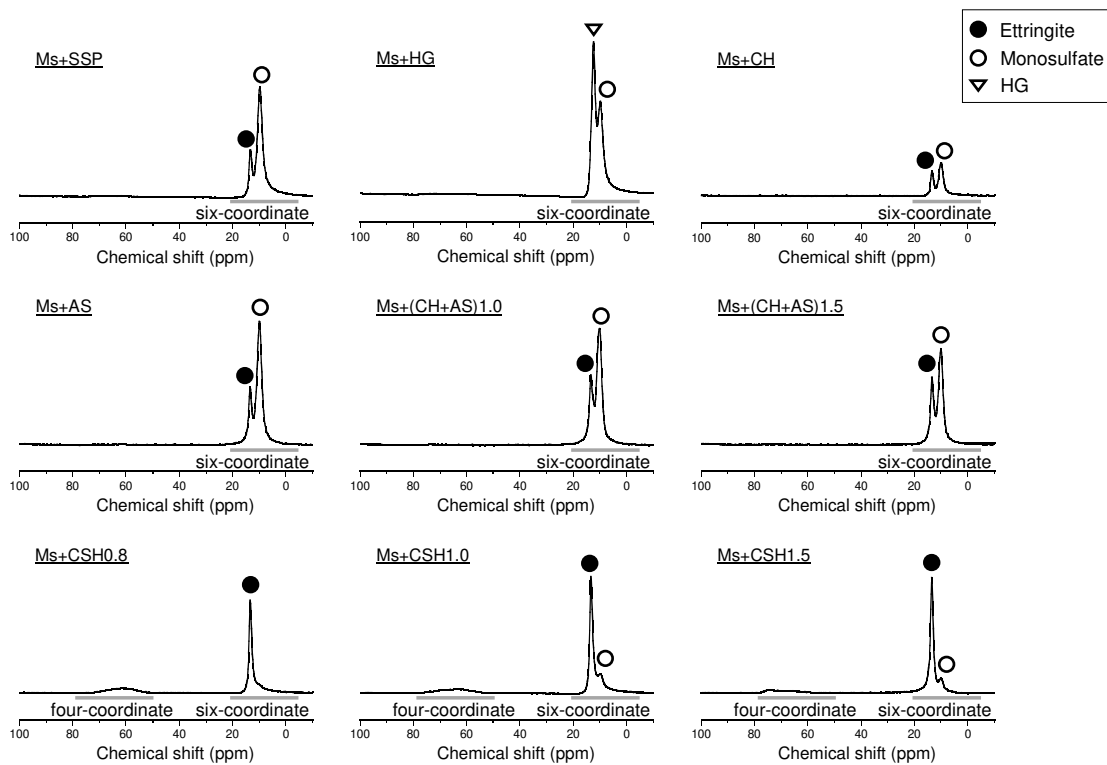
Figure 3. ^{27}Al NMR spectra of monosulfate specimens with coexisting materials after mixing with a sodium sulfate solution.

purposes. The Al/Si ratio in the C-A-S-H was 0.05. These data confirm that the Ms+CASH generated more intense Ms peaks than the Ms+CSH at equivalent C/S ratios. In addition, although the ettringite peaks were less intense than those generated by the samples containing C-S-H, these peaks were more intense compared with those generated by samples with other coexisting materials. Therefore, in the case of the Ms+CASH, the reaction of the Ms did not proceed as readily, although the ettringite peak was relatively high. These results suggest that C-A-S-H contributed to the formation of secondary ettringite by supplying Al.

Figure 5 provides the ^{27}Al NMR spectra of Ms samples with C-A-S-H after mixing with the sodium sulfate solution. These spectra confirm that the peak ascribed to six-coordinate Al in the Ms was more intense than those generated by specimens made with C-S-H. The samples with C-A-S-H as the coexisting material also produced six-coordinate Al peaks corresponding to ettringite that were comparable to those obtained from the C-S-H samples.

The combined XRD and NMR data suggest that the presence of C-A-S-H promoted secondary ettringite formation primarily by consuming four-coordinate Al in the C-A-S-H.

4 Discussion

This work demonstrates that only the presence of C-S-H markedly increased the amount of secondary ettringite in the samples. The ^{27}Al NMR spectra show that four-coordinate Al appeared only in samples in which C-S-H coexisted with the Ms, and this Al is attributed to the C-A-S-H (Richardson, 2004). Samples containing C-A-S-H were mixed with the sodium sulfate solution and examined by XRD and ^{27}Al NMR. The level of ettringite was found to be
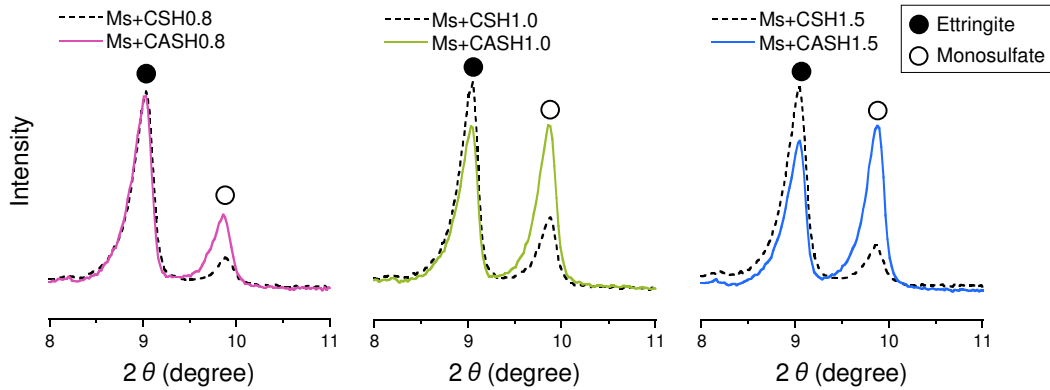
Figure 4. XRD patterns of monosulfate specimens with C-S-H or C-A-S-H
after mixing with a sodium sulfate solution.
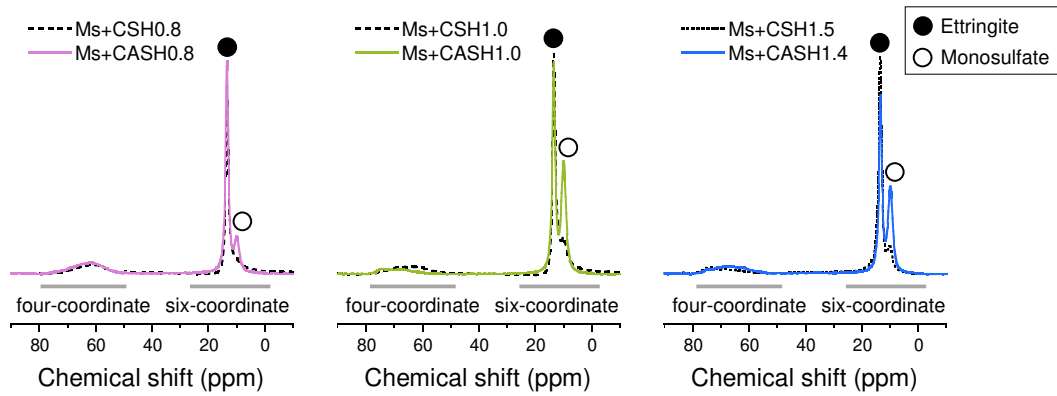
Figure 5. ^{27}Al NMR spectra of monosulfate specimens with C-S-H or C-A-S-H
after mixing with a sodium sulfate solution.

equal to that in samples containing C-S-H, although the Ms peaks were not deceased.

These results suggest that the presence of four-coordinate Al is closely related to se
condary ettringite formation, hence we assessed the Al coordination numbers in the samples.
In the absence of coexisting materials, or when materials other than C-(A)-S-H coexist with
the Ms (that is, when four-coordinate Al is not present), ettringite having six-coordinate Al is
directly formed from Ms having the same six-coordinate Al. Under such conditions, the
formation of secondary ettringite does not readily proceed.

In the case that C-S-H is present, Al released from the Ms is substituted into the silicate
chains in the C-S-H. As a result, C-A-S-H is formed with four-coordinate Al. If a sufficient
concentration of sulfate ions is available, ettringite is more likely to be formed from four-
coordinate Al than from the six-coordinate Al in the Ms. That is, the presence of C-S-H
promotes secondary ettringite formation by changing the Al coordination number.

As such, ettringite is likely to be formed from four-coordinate Al, and C-S-H promotes
secondary ettringite formation by substituting Al into the silicate chains and converting six-
coordinate Al to four-coordinate. On the other hand, using SCMs is beneficial to decrease
sulfate attack, while the production of C-A-S-H is increased with the amount of added SCMs.
Based on the results of the present study, ettringite is likely to be formed when SCMs are used,

however; the expansion is actually suppressed. Because of that, the expansion due to secondary ettringite formation may be related not only to the amount of ettringite but also to the location of ettringite formation.

5 Conclusions

The purpose of this study was to investigate experimentally the effects of coexisting materials on secondary ettringite formation. The conclusions can be summarized as follows.

- When monosulfate and C-S-H are mixed with a sodium sulfate solution, the amount of secondary ettringite is increased in comparison with other coexisting materials.
- The ^{27}Al NMR results confirm that C-A-S-H containing four-coordinate Al is formed in samples made with C-S-H. In addition, when C-A-S-H is added to the monosulfate, secondary ettringite is generated at a comparable level to that found in the C-S-H samples, although the monosulfate remains intact. It appears that ettringite is likely generated from four-coordinate Al, and that C-S-H promotes secondary ettringite formation as a result of transitioning six-coordinate Al to four-coordinate Al by substituting Al in the Si chains.

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