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Scientific paper

Effects of Pre-Drying and 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. Drying conditions may also influence secondary ettringite formation because the structure of the monosulfate is changed. The present study experimentally examined the effects of monosulfate pre-drying conditions and coexisting materials on secondary ettringite formation. Synthesized monosulfate samples dried under varying conditions and with coexisting materials such as C-S-H were mixed with a sodium sulfate solution, and the amount of secondary ettringite was found to increase following drying under 0% or 11% relative humidity. The secondary ettringite proportion was also markedly increased by the presence of C-S-H, regardless of the pre-drying conditions, 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.

1. Introduction

The deleterious effects of sulfates on concrete have attracted increasing attention because they can affect the long term durability of concrete structures (JSCE 2003). Expansion due to the action of 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) (Collepari 2003). Both external sulfate attack and internal sulfate attack are attributed to secondary ettringite formation in the cement paste. Ettringite has the composition $C_6A\bar{S}H_{32}$ and is formed from tricalcium aluminate (C_3A) 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 expansion mechanism of the hardened cement paste due to secondary ettringite formation is not clear regardless of external or internal sulfate attack.

Heinz and Ludwig (1986) studied the mechanism associated with the expansion of cement paste due to secondary ettringite formation, and proposed that this occurs due to the crystal growth pressure imparted by secondary ettringite locally generated around the aggregate. Famy (1999) proposed an expansion mechanism in which the cement paste expands uniformly due to secondary ettringite formation. The former is known as the crystal growth pressure theory, while the latter is termed the paste expansion theory. Although these two theories have been discussed for some time, the secondary ettringite formation and expansion mechanisms have not yet been clarified.

It has been suggested that the expansion of cement paste 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). Observations using microscopy have shown that the C-S-H phase can be classified as inner or outer C-S-H (Goto *et al.* 1976). Inner C-S-H refers to material that grows within the boundaries of the clinker grains, occupying the regions associated with anhydrous phases. In contrast, outer C-S-H forms outside the clinker grain boundaries in the water-filled space. In general, inner C-S-H has a more compact and amorphous structure, while outer C-S-H has been found to form bundles of fibers radiating from the cement grains (Taylor 1997). The schematic diagram of the mechanism suggested by

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Taylor *et al.* (2001) for expansion of the paste in a mortar due to DEF is shown in Fig. 1. 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 than when it is formed in the outer C-S-H far from the boundary. The relationship between the CaO/SiO₂ molar ratio (the C/S ratio) of the C-S-H and the proportional change in length of mortar specimens made using cement and silica fume after exposure to a sodium sulfate solution has been investigated (Kunther *et al.* 2015). The expansion of mortar having a low C/S ratio in the C-S-H is evidently suppressed as a result of the decreased supersaturation of ettringite in the pore solution with decreases in the amount of calcium leached from the C-S-H.

The authors previously reported that the proportional length change of a paste comprising cement and blast furnace slag and cured in a solution of sodium and magnesium sulfates increases along with the amount of secondary ettringite generated in the cement (Sato *et al.* 2014). It is believed that the secondary ettringite generated from the cement coexists with C-S-H having a high C/S ratio, while the secondary ettringite produced from the blast furnace slag coexists with C-S-H having a low C/S ratio. These results suggest that expansion due to the appearance of secondary ettringite is affected by the properties of the C-S-H that is present along with the ettringite. However, because hardened cement pastes contain many hydration products in addition to C-S-H, it is difficult to directly determine the effects solely of C-S-H on secondary ettringite formation.

The structure of the Ms and the physical properties of the C-S-H, such as density and specific surface area, also change with the drying conditions (Baquerizo *et al.* 2014; Suda *et al.* 2011). Therefore, it is possible that the secondary ettringite formation is affected by both the drying conditions and the physical properties of the hydration products.

As described above, secondary ettringite formation

causes expansion regardless of external or internal sulfate attack. In the present study, the authors aimed to assess the ambient environmental conditions when secondary ettringite is formed. The goal of the present study was to experimentally examine the effects of the Ms pre-drying conditions as well as 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 dried under different conditions and subsequently mixed and hydrated using a sodium sulfate solution, followed by analysis of the secondary ettringite. This study was conducted assuming the secondary ettringite formation in the outer C-S-H structure close to the inner C-S-H.

2. Methods and materials

2.1 Preparation of the Ms

The primary precursor in the synthesis of the Ms was C₃A, which was prepared from reagent grade CaCO₃ and Al₂O₃ (Kanto Chemical Co., Inc.), combined at a 3 : 1 molar ratio. This mixture of CaCO₃ and Al₂O₃ was calcined three times in a muffle furnace at 1400°C for 3 h and the composition of the resulting C₃A was confirmed by powder X-ray diffraction (XRD). The Ms was prepared from a suspension of a 1 : 1 molar mixture of C₃A and CaSO₄ in deionized water, at a water to solid mass ratio of 10 : 1, held under N₂ to prevent carbonation. The mixture was cured at 20°C for 14 d, after which the solid and aqueous phases were separated by vacuum filtration.

2.2 Preparation of coexisting materials

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 SiO₂ molar ratios (of 0.80, 1.00 and 1.50) were synthesized by reacting mixtures of CH, ethyl silicate (reagent grade, Kanto Chemical Co., Inc.) and deionized water for 2 d at 40°C, after which the solid and aqueous phases were separated by vacuum filtration. The concentrations of Ca and Si in the aqueous phase were determined by EDTA titration and spectrophotometry, respectively.

HG was synthesized via the reaction of C₃A 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). In this process, C₃A was dissolved in deionized water and stirred for 10 d, following which the C₃A-saturated solution was separated by vacuum filtration. The Ca concentration of the saturated solution was

Fig. 1 Schematic diagram illustrating the suggested mechanism for expansion of the paste in a mortar expanding due to DEF by Taylor *et al.* (2001).

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	100	—	—	—	—	—	—	—	—	—	—
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

adjusted by adding CH. C-S-H samples having C/S ratios of 0.80, 1.00 or 1.40 obtained by the above method were added to C₃A-saturated solutions and mixed by manual shaking. The mixtures were allowed to stand for 30 d, after which the solid and aqueous phases were separated by vacuum filtration. The CH (reagent grade, Kanto Chemical Co., Inc.), AS (reagent grade, Kanto Chemical Co., Inc.) and SSP (purity > 96%, SAN-EI SILICA Co., Ltd.) used in this work were all commercially-available products.

2.3 Pre-drying conditions

The Ms and the coexisting materials were dried under three different conditions. These included heating at 110°C in a drying oven (defined as 0% relative humidity (RH)) as well as storage at 20°C and 11% RH (using a saturated LiCl solution) or at 20°C and 66% RH (using a saturated NaNO₂ solution), both in a vacuum desiccator. The Ms and the coexisting materials were dried under these conditions until these mass no longer changed. To prevent carbonation of the Ms and the coexisting materials during storage, each desiccator contained a quantity of soda lime. After drying, each material was crushed into particles smaller than 90 µm.

2.4 Mixing proportions of the Ms and the coexisting materials

The mixing proportions of the Ms and the coexisting materials are summarized in **Table 1** and the experimental conditions are provided in **Table 2**. 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 Ms pre-drying conditions on secondary ettringite formation were examined using a sample consisting of pure Ms. The effects of the coexisting materials were determined by mixing these materials with the Ms, all dried under the same conditions at a mass ratio of 1 : 1. In the case of trials with AS and C-A-S-H, only material that had been pre-dried at 0% RH was used. The effects of the chemical composition of

Table 2 Experimental conditions.

Sample name	Pre-drying condition		
	RH0% (110°C)	11% RH	66% RH
Ms	○	○	○
Ms+CSH 0.8	○	○	○
Ms+CSH 1.0	○	○	○
Ms+CSH 1.5	○	○	○
Ms+CH	○	○	○
Ms+HG	○	○	○
Ms+SSP	○	○	○
Ms+AS	○	-	-
Ms+(CH+AS) 1.0	○	-	-
Ms+(CH+AS) 1.5	○	-	-
Ms+CASH 0.8	○	-	-
Ms+CASH 1.0	○	-	-
Ms+CASH 1.4	○	-	-

the mixture were assessed by simultaneously 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.

2.5 Mixing with a sodium sulfate solution

The Ms dried at each condition or each mixture of the Ms and the coexisting materials as noted in Section 2.4 were mixed with a 0.5 M sodium sulfate solution at a liquid to powder mass ratio of 2 : 1. Depending on the types of sulfate solutions used for mixing, the behavior of secondary ettringite formation may change due to changing cation. However, in this study, a sodium sulfate solution was used in order to obtain a high Na⁺ concentration assuming the inside of the hardened cement paste. According to ASTM C 1012-04 (Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution), immersion in a 0.352 M (5 mass%) sodium sulfate solution is specified in order to promote sulfate expansion of mortar specimens. The authors therefore considered a 0.5 M sodium sulfate solution to be a high sulfate concentration sufficient to form ettringite in the samples. In each case, the mixture of the

Ms and each coexisting material was added to the sodium sulfate solution and they were manually mixed for 3 min to obtain a homogeneous paste that was subsequently transferred into a plastic bottle and cured at 20°C for 1 d.

2.6 Pretreatment and drying conditions

After curing at 20°C for 1 d, the samples described in Section 2.5 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.

2.7 Analysis

(1) XRD

Powder XRD was used for the identification and quantification of hydration products before and after mixing with the sodium sulfate solution. XRD data were acquired using an Aeris instrument (PANalytical, Almere, Overijssel, the Netherlands) with Cu-Kα radiation at a tube voltage of 40 kV and tube current of 15 mA, with a step width of 0.02°, scan rate of 6.5°/min, and 2θ range from 5 to 70°. α-Al₂O₃ was mixed with each sample at 10 mass% as an internal standard and Rietveld analysis was performed using the Topas 4.2 software package (Bruker AXS Inc., Billerica, Massachusetts, USA). The amount of amorphous phase in each specimen was calculated based on the equation (Jones *et al.* 2000)

$$G = \frac{100 \cdot (A - R)}{A} \cdot \frac{100}{100 - R} \quad (1)$$

where G is the proportion of the amorphous phase (%), R is the nominal proportion of α-Al₂O₃ (%) and A is the experimentally determined proportion of α-Al₂O₃ (%).

(2) FT-IR

The bonding state of the atoms in the Ms after pre-drying were assessed using Fourier transform infrared (FT-IR) spectroscopy. Spectra were acquired with a FT/IR-4600 instrument (JASCO, Hachioji, Tokyo, Japan) using the KBr pellet method in the transmission mode, with a sample to KBr mass ratio of 1 : 200. Spectra were recorded over the range of 400 to 4000 cm⁻¹, adding 16 scans, at a resolution of 4 cm⁻¹.

(3) SEM

The morphology of each hydrate, including the secondary ettringite formed in samples containing various coexisting materials along with the Ms, was examined using scanning electron microscopy (SEM). SEM was performed with a SCM-7001F instrument (JEOL, Aki-shima, Tokyo, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS) attachment (X-MAX^N, Oxford Instruments, Abingdon, Oxfordshire, UK). Prior to

observations, powder samples were dried at 11% RH after being mixed with the sodium sulfate solution. After D-drying for 12 h, each specimen was attached to a sample holder using carbon tape, and a carbon coating was applied. During the SEM observations, a secondary electron image of the powder sample was obtained with an accelerating voltage of 15 kV. The hydration products were also determined by obtaining the chemical composition of each sample based on an EDS analysis.

(4) Heat liberation rate measurements

During cement hydration, a rapid exothermic peak is typically observed immediately after water injection when the hydration heating rate is measured using a conduction calorimeter. This is due to the formation of ettringite in association with the hydration of C₃A (Sakai 2012). In the case that secondary ettringite is formed from the Ms, an exotherm should also appear immediately after water (or solution) injection. Therefore, to investigate the effects of coexisting materials on secondary ettringite formation, the heat liberation rates obtained from Ms specimens with coexisting materials were assessed after mixing with the sodium sulfate solution.

A conduction calorimeter IC-20 (Tokyo Riko Co., Ltd., Nishitokyo, Tokyo, Japan) specially designed for initial hydration heat measurement was employed and was placed in the test apparatus prior to mixing the powder sample and the solution. This allowed the heating rate to be measured while injecting the solution and stirring the mixture inside the apparatus (Sakai 2012; Ichinose *et al.* 2008). These trials used a solid sample dried at 0% RH together with a 0.5 M sodium sulfate solution, at a powder to solution mass ratio of 1 : 3. The mixture components were left to stand for approximately 6 h such that they were in equilibrium with the ambient temperature (20°C). After equilibration, the solution was injected into the powder and the mixture was stirred for 2 min. Heating rate measurements were initiated from the moment of injection and continued for 60 min.

(5) pH value and ionic composition of the liquid phase

Both the pH and ionic composition of the liquid phase were determined following the addition of the sodium sulfate solution. In these trials, a Ms specimen together with coexisting materials dried at 0% RH 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 at 4000 rpm for 10 min. The pH of the liquid phase was measured using a glass electrode pH meter and the concentrations of Na⁺, Ca²⁺ and SO₄²⁻ ions in the liquid phase were analyzed by ion chromatography (ICS-1100, Thermo Fisher Scientific, Waltham, Massachusetts, USA).

(6) Solid state ^{27}Al NMR

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 ECA800 (JEOL RESONANCE, Akishima, Tokyo, Japan) 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 Effects of pre-drying conditions on secondary ettringite formation

(1) Prior to mixing with the sodium sulfate solution mixing (after pre-drying)

Figure 2 shows the XRD patterns of the synthesized Ms specimens dried at 0%, 11% and 66% RH prior to mixing with the sodium sulfate solution. Each of the samples generated Ms peaks at 2θ values of 10° , 20° and 22° , in agreement with previously reported results (Baquerizo *et al.* 2014). In addition, the Ms dried at 66% RH generated diffraction peaks attributed to ettringite at $2\theta = 9^\circ$, 16° , 19° and 23° . Prior work has shown that ettringite is transformed into metaettringite along with an amorphous phase when dried at approximately 110°C (Zhou *et al.* 2004). However, the authors have confirmed that drying at 11% RH does not lead to decomposition of the ettringite (Nozawa *et al.* 2016). The pattern in **Fig. 2** confirms that ettringite was not present in the sample dried at 11% RH, and so provides evidence that the Ms was produced as a single phase, as intended. It has been reported that ettringite peaks are present in the XRD pattern of Ms dried at 84% RH (Baquerizo *et al.* 2014). Based on these data, it appears that ettringite is formed during drying at elevated humidity levels (such as 66% RH).

Figure 3 presents the FT-IR spectra of Ms specimens dried at 0%, 11% and 66% RH. All three samples generated peaks due to the degenerate bending and stretching vibrations (ν_4 and ν_3) of SO_4^{2-} near 600 and 1100 cm^{-1} , respectively (Lane 2007). Both peaks show a tendency to divide into two as the pre-drying humidity is decreased. The splitting of the vibrational spectra of highly symmetric bonds, such as those in SO_4^{2-} , suggests that the local symmetry is decreased (Murata and Yamashita 1991). Because the Ms has a structure in which SO_4^{2-} ions and H_2O molecules are positioned between layers of $[\text{Ca}_2\text{Al}(\text{OH})_6]$, the H_2O molecules between the layers desorb upon drying at an RH of 11% or less, leading to changes in the local structure of the adjacent SO_4^{2-} .

(2) After mixing with the sodium sulfate solution

Figure 4 shows the XRD patterns acquired from Ms samples dried at 0%, 11% and 66% RH after mixing with the sodium sulfate solution. As was also observed in **Fig. 2**, diffraction peaks due to ettringite were generated by

the sample dried at 66% RH, and there were almost no changes in these peaks after the addition of the sodium sulfate solution. However, in the case of specimens dried at 0% and 11% RH, (which did not contain ettringite after pre-drying), the diffraction peaks due to Ms decreased in intensity and ettringite peaks appeared. These data confirm that secondary ettringite was formed in these two materials. These FT-IR data demonstrate that a low

Fig. 2 XRD patterns of monosulfate specimens dried under various conditions.

Fig. 3 FT-IR spectra of monosulfate specimens dried under various conditions.

Fig. 4 XRD patterns of monosulfate specimens dried under various conditions after mixing with a sodium sulfate solution.

pre-drying humidity decreases the local symmetry of SO_4^{2-} ions in the Ms. Therefore, as the pre-drying humidity decreases, the structure of the Ms is liable to collapse, such that the generation of secondary ettringite is likely to follow mixing with the sodium sulfate solution.

3.2 Effects of coexisting materials on secondary ettringite formation

(1) Morphology of hydration products

Figure 5 provides secondary electron images of Ms specimens with coexisting materials after mixing with the sodium sulfate solution. These images were acquired using samples dried at 0% RH. Magnifications of $3500\times$ and $10,000\times$ were employed for samples with SSP and for those with all other materials, respectively. In the case of the pure Ms (without any coexisting materials), plate-like Ms crystals are observed, surrounded by rod-like ettringite crystals. Conversely, because SSP reacts only minimally at ambient temperature and pressure, residual Ms and sparse rod-like ettringite crystals are seen in the image of the Ms+SSP sample, similar to the pure Ms. Even the Ms+CH and Ms+HG show no significant changes in the degree of secondary ettringite formation. However, those samples containing C-S-H (Ms+CSH0.8, Ms+CSH1.0 and Ms+CSH1.5) did not contain plate-like Ms at any C/S ratio, while numerous rod-like ettringite crystals mixed with C-S-H were generated over each specimen. These observations suggest that the amount of secondary ettringite was greatly increased upon adding C-S-H to the Ms.

(2) Formation characteristics of secondary ettringite

Figure 6 shows the XRD patterns of Ms samples with each coexisting material after mixing with the sodium sulfate solution. As discussed in Section 2.2, SSP does not react at ambient temperature and pressure, and so does not contribute to secondary ettringite formation. Therefore, the XRD patterns of specimens made with the other coexisting materials were compared with that of the

Ms+SSP. Under all drying conditions, the ettringite peaks of the Ms+CH and Ms+HG were not increased in intensity. 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. As noted in Section 3.2 (1), the Ms dried at 11% RH tended to form secondary ettringite, and this process was greatly enhanced when C-S-H was present. As also described above, the material dried at 66% RH did not readily form secondary ettringite although, as was the case for the other drying conditions, a significant increase in the diffraction peaks due to ettringite occurred in the case that C-S-H was present.

Figure 7 shows the amounts of secondary ettringite as determined by Rietveld analysis of the XRD data. In the case of the sample dried at 66% RH, the proportion of ettringite prior to mixing with the sodium sulfate solution was subtracted from the amount of ettringite after mixing. These results demonstrate that the specimens dried at 11% and 0% RH (which are likely to generate secondary ettringite) and the 66% RH material (in which secondary ettringite is unlikely to form), showed increases in ettringite when C-S-H was present. Thus, the addition of C-S-H to the Ms significantly increases secondary ettringite formation regardless of the pre-drying conditions. As discussed in the Introduction, the location of secondary ettringite formation is related to its expandability. In the present study, solely the addition of C-S-H to the Ms dramatically increased the production of secondary ettringite. Therefore, the presence of C-S-H is considered to be an important factor affecting secondary ettringite formation and expansion, rather than the location at which the secondary ettringite is formed.

(3) Heat liberation rate at the point of mixing with the sodium sulfate solution

Figure 8 plots the variations in the heat liberation rates over time following mixing of the Ms and coexisting

Fig. 5 SEM images of monosulfate specimens with coexisting materials after mixing with a sodium sulfate solution.

materials with the sodium sulfate solution, based on using material dried at 0% RH. The heat liberation data here represent the calories released per 1 g of sample per 1 h. In each case, a peak ascribed to secondary ettringite formation is observed immediately after the start of mixing. All the plots also converge after 60 min. Based on these results, it appears that the reaction proceeded satisfactorily and reached equilibrium after one day, at which point additional analyses (such as XRD) were

carried out.

The sample consisting solely of the Ms produced the largest heat liberation peak due to secondary ettringite formation. The peak obtained from the Ms+SSP sample (which contained half the amount of Ms) was approximately half the height. Thus, as expected, the SSP had no effect on secondary ettringite formation. The peak generated by the Ms+CH was almost equal to that produced by the Ms+SSP. In contrast, in the case of the Ms+CSH,

Fig. 6 XRD patterns of monosulfate specimens with coexisting materials after mixing with a sodium sulfate solution.

Fig. 7 Amounts of secondary ettringite formed after mixing with a sodium sulfate solution.

Fig. 8 Heat liberation rates as functions of time during mixing with a sodium sulfate solution.

the peak area was increased and the peak resulting from the Ms+CSH1.5 was also greater compared with that for the Ms+CSH1.0. As described above, these heat liberation data agree with the results obtained from the XRD/Rietveld analysis.

(4) 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 3**, based on using the sample dried at 0% RH. In all cases, the pH was in the range of 11.57 to 13.29, which is associated with the stable formation of ettringite (Stark and Wicht 2003; Shimada *et al.* 2005). The pH obtained from the Ms+CH sample was as high as 13.29 and it has been reported that the upper pH limit at which ettringite is stable can be 13 or higher in the presence of alkali. In this study, Na^+ was present in abundance in the samples, and so it is considered that this pH range was suitable for the formation of ettringite in all samples.

The Ms+CSH1.5 had the highest Ca^{2+} concentration, and almost the same value was obtained from the Ms+CSH0.8, Ms+CSH1.0 and Ms+CH. The values for the Ms+CSH0.8 and Ms+CH were especially close. As noted above, the pH of the Ms+CH was higher than that 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.

(5) 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. Therefore, Ms samples with added AS and with both CH and AS were mixed with the sodium sulfate solution and compared with samples made with C-S-H. **Figure 9** shows the XRD patterns of Ms specimens with added Ca and Si-based materials after mixing with the sodium sulfate solution, based on drying at 0% RH. Note that the samples in which both CH and AS were added were mixed so that the C/S ratios were 1.0 or 1.5. For com-

Table 3 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

parison, the XRD patterns generated by the Ms+SSP, Ms+CH, Ms+CSH1.0 and Ms+CSH1.5 are also provided 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.

Figure 10 plots the relationship between the proportion of the Ms reacted and the amount of secondary ettringite as determined by Rietveld analysis. A clear correlation is evident. In addition, when either CH or AS were present, the proportion of Ms reacted was low,

Fig. 9 XRD patterns of monosulfate specimens with added Ca and Si after mixing with a sodium sulfate solution.

Fig. 10 The amount of secondary ettringite as a function of the proportion of the monosulfate reacted.

while the presence of both increased the amount of Ms reacted and so also increased the amount of secondary ettringite. However, comparing the samples with both CH and AS to those with C-S-H, the proportion of Ms reacted and the amount of secondary ettringite are markedly increased in the C-S-H specimens. 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.

(6) 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 11** shows the ^{27}Al NMR spectra of Ms specimens with each coexisting material after mixing with the sodium sulfate solution. Regardless of the drying conditions and 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 Ms+SSP, Ms+HG, Ms+CH, Ms+AS and Ms+(CH+AS), 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). **Figure 12** shows the ^{27}Al NMR spectra of Ms together with C-S-H following drying at 0% RH and after mixing with the sodium sulfate solution (40 - 90 ppm). Here, as the C/S ratio increases, the four-coordinate Al peak is shifted from the position corresponding to the bridging site to the position corresponding to the pairing site, representing the same trend as previously reported based on work with C-A-S-H. 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.

(7) Effect of the presence of C-A-S-H

As discussed in Section 3.2 (6), C-A-S-H was formed in samples containing C-S-H. Because C-A-S-H contains the Al necessary for secondary ettringite formation, it is likely that this component serves as a source of Al and

Fig. 11 ^{27}Al NMR spectra of monosulfate specimens with coexisting materials after mixing with a sodium sulfate solution.

contributes to increases in the amount of secondary ettringite. To examine this effect, samples were made with synthesized C-A-S-H and compared with those containing C-S-H.

Figure 13 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 purposes. The Al/Si ratio in the C-A-S-H was 0.05, and samples dried at 0% RH were used. 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

Fig. 12 ^{27}Al NMR spectra of monosulfate specimens with C-S-H dried at 0% RH after mixing with a sodium sulfate solution (40-90 ppm).

materials (Fig. 6). 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 14 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, regardless of the Ms drying conditions. The promotion of secondary ettringite formation in such samples could not be explained solely based on the pH and Ca^{2+} concentration of the liquid phase or the chemical composition (the Ca and Si content). 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 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 secondary ettringite formation, hence we assessed the Al coordination numbers in the samples. Figure 15 shows a conceptual diagram of the effect of the Al coordination number on secondary ettringite formation. 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. One factor affecting this process is that the Ms (which has a lamellar structure) and the ettringite (which has a column structure) are completely different in terms of their crystal morphology.

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, which has a completely different crystal structure from ettringite. That is, the presence of C-S-H promotes secondary ettringite formation by changing the Al coordination

Fig. 13 XRD patterns of monosulfate specimens with C-S-H or C-A-S-H after mixing with a sodium sulfate solution.

Fig. 14 ^{27}Al NMR spectra of monosulfate specimens with C-S-H or C-A-S-H after mixing with a sodium sulfate solution.

Fig. 15 Conceptual diagram of the effect of the Al coordination number on secondary ettringite formation.

number. Furthermore, in the case that C-A-S-H is initially added, it is considered that Al derived from the Ms is substituted for Si in the silicate chains after the four-coordinate Al in the C-A-S-H is consumed by secondary ettringite formation. For this reason, ettringite was formed in the same amount as in the samples containing C-S-H despite the fact that much of the original Ms remained.

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. In future, it would be helpful to investigate the effect of the Al coordination number on secondary ettringite formation using substances with four or five-coordinate Al other than C-S-H and C-A-S-H.

5. Conclusions

The purpose of this study was to investigate experimentally the effects of pre-drying conditions and coexisting materials on secondary ettringite formation. The monosulfate and coexisting materials were dried at 0%, 11% and 66% RH. After pre-drying, the monosulfate and coexisting materials were mixed with a sodium sulfate solution and XRD, FT-IR, SEM, heat liberation rate and ^{27}Al NMR data were acquired. The conclusions derived from this study can be summarized as follows.

- (1) When the monosulfate is dried at a low relative humidity and mixed with a sodium sulfate solution, the amount of secondary ettringite is increased.
- (2) Upon mixing monosulfate samples containing C-S-H with a sodium sulfate solution, the amount of secondary ettringite is increased in comparison to the results obtained with other coexisting materials, regardless of the pre-drying conditions. This is the first-ever experimental evidence for this effect.
- (3) The promotion of secondary ettringite formation due to the presence of C-S-H cannot be explained by either the pH or Ca^{2+} concentration of the liquid phase or by the chemical composition (the Ca and Si content).

- (4) 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.

It would be helpful to investigate the expansion characteristics of the secondary ettringite generated in the samples mixed with C-S-H, which is assumed to be the outer C-S-H close to the inner C-S-H, in future. Although the experimental conditions of the present study are different from the conditions of real concrete structures, the results obtained from this study are completely new insights concerning the behavior of secondary ettringite formation. We believe that, by accumulating such knowledge, the complicated mechanism of expansion due to secondary ettringite formation will be clarified, and it will lead to the proposal of a method to suppress the expansion of real concrete structures.

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