

## Effect of Coexisting Materials on Secondary Ettringite Formation

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### 1 Introduction

The expansion mechanism of the hardened cement paste due to secondary ettringite formation is not clear. 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 monosulfate (Ms) sample in conjunction with coexisting materials such as calcium-silicate-hydrates (C-S-H).

### 2 Materials and Methods

The Ms was prepared from C<sub>3</sub>A and CaSO<sub>4</sub>. C-S-H (having C/S ratios of 0.80, 1.00 and 1.50), calcium hydroxide (CH), hydrogarnet (HG), amorphous silica (AS), Al-substituted C-S-H (C-A-S-H) and silica stone powder (SSP) were used as the coexisting materials in this work.

The Ms was combined with each coexisting material at a mass ratio of 1:1. And the CH and AS were mixed simultaneously so that the C/S ratio was either 1.00 or 1.50 and the mixture was combined with the Ms. 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 and cured at 20 °C for 1 d. These specimens were dried at 20 °C and 11% RH.

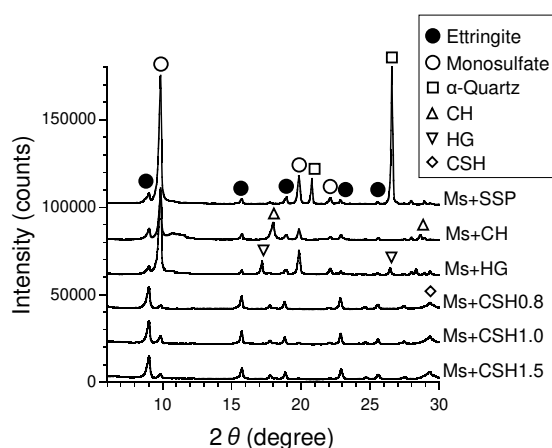
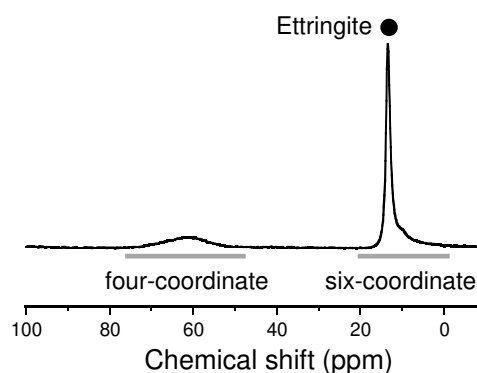
Powder XRD was used for the identification and quantification of hydration products. The pH and ionic composition of the liquid phase after mixing were also measured. Solid state <sup>27</sup>Al nuclear magnetic resonance (NMR) was employed to determine the chemical state of Al.

### 3 Results

Figure 1 shows the XRD patterns of Ms samples with each coexisting material after mixing with the sodium sulfate solution. The diffraction peaks due to Ms almost disappeared while those resulting from ettringite increased when C-S-H was added to the Ms.

In all cases, the pH was in the range of 11.57 to 13.29, which is associated with the stable formation of ettringite. The Ms+CSH1.5 had the highest Ca<sup>2+</sup> concentration, and almost the same value was obtained from the Ms+CSH0.8, Ms+CSH1.0 and Ms+CH. Thus, the promotion of secondary ettringite formation due to the presence of C-S-H is not completely explained by the effects of the pH and Ca<sup>2+</sup> concentration of the liquid phase.

Figure 2 shows the <sup>27</sup>Al NMR spectra of Ms with CSH0.8 after mixing. The sample containing C-S-H generated a broad peak corresponding to four-coordinate Al. This peak is


**Figure 1.** XRD patterns.

**Figure 2.**  $^{27}\text{Al}$  NMR spectrum of Ms+CSH0.8.

also generated by C-A-S-H, in which Al is substituted for Si in the silicate chains of C-S-H (Pardal *et al.*, 2012). Therefore, 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.

These results suggest that the presence of four-coordinate Al is closely related to 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. 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.

## 4 Conclusions

The conclusions derived from this study can be summarized as follows.

- Upon mixing Ms samples containing C-S-H with a sodium sulfate solution, the amount of secondary ettringite is increased compared other coexisting materials.
- The  $^{27}\text{Al}$  NMR results confirm that C-A-S-H is formed in samples made with C-S-H. 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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