

# Effect of Competing ion on the Solidification of Cr<sup>3+</sup> and Cr<sup>6+</sup> During the Formation of Ettringite

J.-W. Ahn, K.-S. You, D.-Y. Han, K.-H. Cho  
*Korea Institute of Geoscience and Mineral Resources,  
Daejeon, South Korea*

**Abstract.** In this study, the degree of the substitution of Cr<sup>3+</sup> and Cr<sup>6+</sup> into the ettringite structure has been investigated to extent the immobilization potential of ettringite in the field under specific conditions. Aqueous suspension containing calcium hydroxide, alumium sulfate, CrCl<sub>2</sub>(trivalent chromium) and CrO<sub>3</sub>(hexavalent chromium) was subjected to ultrasound irradiation under atmospheric pressure to investigate their effects on synthesis of Cr-ettringite. In the result, the substitution of Cr<sup>3+</sup> into Al site takes place in ettringite structure in solution with Cr<sup>3+</sup>, and monosulfate/friedel' salt phase is also formed by occurrence of extra Al ion in solution. However, in the case of Cr<sup>6+</sup>, owing to a higher affinity of sulfate anion to form ettringite than that of Cr<sup>6+</sup>, most of Cr<sup>6+</sup> did not substituted into the crystal structure of ettringite.

## 1. Introduction

Ettringite(Ca<sub>6</sub>[Al(OH)<sub>6</sub>]<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•26H<sub>2</sub>O) is hydration product of calcium aluminate minerals, and its crystals have two distinct structural components; Columns, {Ca<sub>6</sub>[Al(OH)<sub>6</sub>]<sub>2</sub>•24H<sub>2</sub>O}<sup>6+</sup>, and Channels, {(SO<sub>4</sub>)<sub>3</sub>•2H<sub>2</sub>O}<sup>6-</sup>. The columns consist of Al(OH)<sub>6</sub> octahedral alternating with triangular groups of edge-sharing CaO<sub>8</sub> polyhedral. Column alignment is along the c-axis of a trigonal-hexagonal unit cell. The eight oxygens in the polyhedral come from Ca coordination with four OH ions shared with the Al(OH)<sub>6</sub> octahedral and from coordination with four H<sub>2</sub>O molecules. The hydrogen atoms on the water molecules form the cylindrical surface of the columns. The channels contain four sites per formula unit of the column structure which contains six calcium atoms.[1~3] Three of these sites are occupied by SO<sub>4</sub><sup>2-</sup> and one by two

H<sub>2</sub>O molecules.

Ettringite possesses the ability to behave as a host for metallic pollutants that immobilize both cationic and anionic waste ions through sorption, phase mixing and substitution; the ions available for substitution are Ca<sup>2+</sup>, Al<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup> and OH<sup>-</sup>. [4, 5] Reportedly, the octahedral site of Al on ettringite can be easily substituted with Ti, Cr, or Mn, which have similar ionic radii and polyhedral sites of Ca<sup>2+</sup> with Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Co<sup>3+</sup>, and tetrahedral site of SO<sub>4</sub><sup>2-</sup> with CrO<sub>4</sub><sup>2-</sup>, AsO<sub>4</sub><sup>3-</sup>. Organic molecules are known to become a solid solution by entering into voids arranged as tunnels located within a structural body. [6, 7]

In this study, in particular, the degree of the substitution of Cr<sup>3+</sup> and Cr<sup>6+</sup> into the ettringite structure has been investigated to extent the immobilization potential of ettringite in the field under specific conditions

## 2. Experimental Procedure

The molar ratio of the samples added to make the suspension was Ca(OH)<sub>2</sub> : Al(SO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O = 6 : 1 with 500ml of a fixed volume of distilled water. The suspension was then mixed for 30 min. by an agitator during the dropping of 50 ml of 1mol NaOH to adjust the pH. An ultrasonic apparatus with a frequency of 20kHz with 200W of power was used to project an ultrasonic wave for 2 hr. After 120 min. of wave projection, the temperature of the suspension was 80 . The tip of an ultrasonic generator was placed 10mm off the bottom of the vial. When the ettringite was synthesized, an aqueous suspension was filtered through in order to collect products. These were then dried for 5 hr at 50 . The molar ratio of the samples added to make the suspension was Ca(OH)<sub>2</sub> : Al(SO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O : CrCl<sub>3</sub> = 6 : 1 : 0.005 and Ca(OH)<sub>2</sub> : Al(SO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O : CrO<sub>3</sub> = 6 : 1 : 0.003 with 500ml of a fixed volume of distilled water. First, 0.005 mol CrCl<sub>3</sub> was added to the distilled water, and then it was mixed in order to dissolve it completely using an agitator for 30 min., during a dropping of 50 ml of 1mol NaOH to adjust the pH. And In this study, CrCl<sub>3</sub> powder was also directly added to the beaker to yield a molar ratio ranging from 0.3 to 1.0 to investigate the effect of Cr<sup>3+</sup> substituted on the change of ettringite crystal structure.

After collecting the synthesized powders, they were analyzed with XRD, FT-IR, ICP, and SEM. An X-RAY diffractometer system, (RU-200,

Rigaku, Japan) was used with CuK $\alpha$  set at 30kV, 40mA, and at a scan speed of 5°/degree per min to evaluate them from 5 to 60°/degree. A Fourier Transform-Infrared Spectrophotometer (MB104, BOMEM, Germany) was employed with KBr pellets at 4000cm<sup>-1</sup>~500cm<sup>-1</sup>. These measurements were taken 12 times. A GBC SDS-270 device (GBC Scientific Equipment Pty. Ltd., Australia) was used as an ICP, and utilized the unique optical emission spectrum of Cr by triggering a plasma ignition followed by the detection of residues of the Cr ion from that spectrum. A SEM (Scanning electron microscope) (JSM-528DLA, JEOL, Japan), at A 5000x multiplying factor, was used to confirm the formation of ettringite and monosulfate

### 3. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns for the synthesized products. Ettringite powder was obtained from the ratio: Ca(OH)<sub>2</sub>:Al(SO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O = 6 : 1 mol preparation. It showed the characteristic peak pattern of ettringite, as analyzed by an XRD peak. Moreover, the XRD peaks of Cr(III)-ettringite and Cr(VI)-ettringite showed a relatively low intensity, while ettringite synthesis was also confirmed by analyzing the 2 $\theta$ /degree value. However, the XRD data for Cr(III)-ettringite showed monosulfate and friedel's salt peaks as well as an ettringite peak.

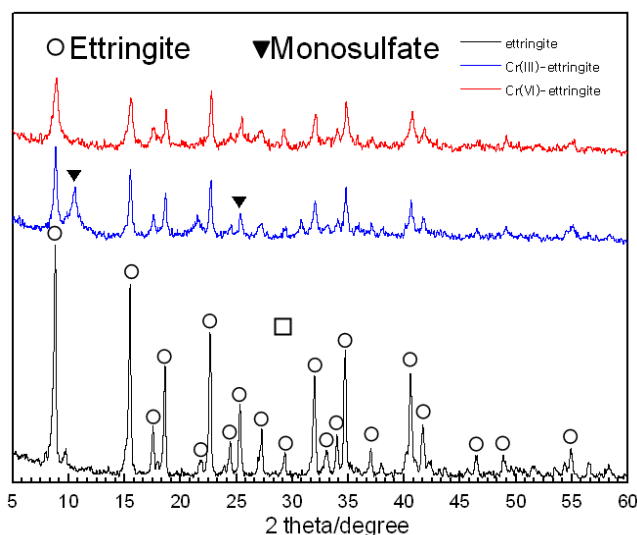


Figure 1. X-ray diffraction patterns of ettringite synthesized in different solution

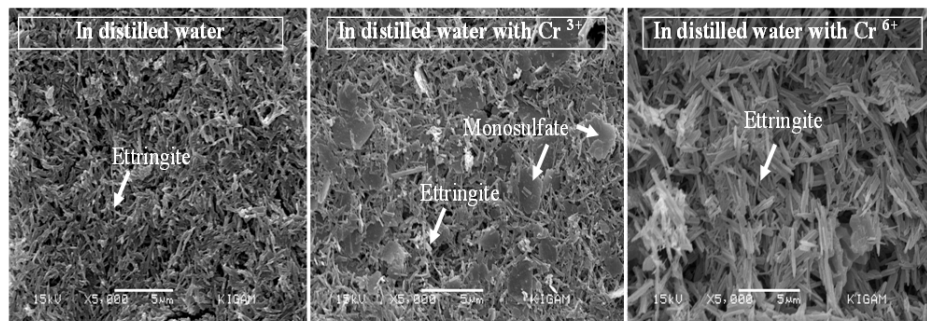


Figure 2. Morphologies of ettringite synthesized in different solutions

Fig. 2 shows the morphologies for the synthesized products. Ettringite powder obtained from distilled water and a  $\text{Cr}^{6+}$  solution appeared to have an ordinary column-type crystal structure. Ettringite powder obtained from a  $\text{Cr}^{3+}$  solution showed, and a plate-type monosulfate was also observed. A FT-IR analysis showed that all of these had the general spectrum of ettringite, as shown in Fig. 3. Peaks caused by  $3700\text{cm}^{-1}\sim 3600\text{cm}^{-1}$  of free O-H,  $3500\text{cm}^{-1}\sim 3400\text{cm}^{-1}$  of O-H stretch,  $1700\text{cm}^{-1}\sim 1600\text{cm}^{-1}$  of O-H bending, and  $1200\text{cm}^{-1}\sim 1100\text{cm}^{-1}$  of Al-O-H bending are known as the general pattern of typical ettringite. A peak for  $\text{Cr}^{6+}$  was found at  $886\text{cm}^{-1}$  or  $867\text{-}902\text{cm}^{-1}$  and for  $\text{Cr}^{3+}$ , at  $750\text{-}850\text{cm}^{-1}$ ,  $798\text{cm}^{-1}$ . The origin of the adsorption peak caused by  $\text{Cr}^{6+}$  in above graph could not be discerned; however, for  $\text{Cr}^{3+}$ , there was an adsorption peak at approximately  $785\text{cm}^{-1}$ , which was caused by the Cr-O stretch.

Table 1 shows the amount of chrome substituted in an ettringite crystal by a deduction of the residual amount from the initially added amount of chrome. This reveals that the residue of  $\text{Cr}^{3+}$  in the solution decreased by 99.92% after the reaction, while that of  $\text{Cr}^{6+}$  decreased only by 28.28%. The results here elucidate that  $\text{Cr}^{3+}$  is substituted most during the reaction, while in the case of  $\text{Cr}^{6+}$ , a large amount of chrome ions are detected in the solution after the reaction. These results indicate that a fixed quantity of  $\text{Cr}^{6+}$  is only substituted into the ettringite crystal, and that most of this does not participate in the reaction.

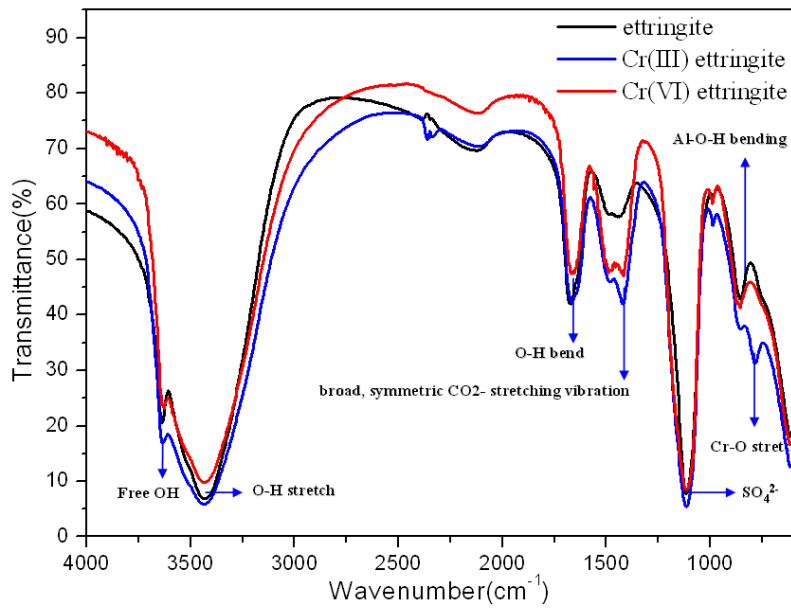


Figure 3. FT-IR spectrum of ettringite synthesized in different solutions

Fig.4. shows the XRD peak of the synthetic product of the hydration reaction. Generally, it showed the main peak of ettringite, but addition to  $\text{CrCl}_3$  showed relatively low and broad intensity. The similarity in the results showed that the two compounds have similar crystal lattices

Table 1. The residual amount of chrome after ettringite is produced in the solution

	Dosage amount of chrome ion(mg/Kg)	Residual amount of chrome ion(mg/kg)
$\text{CrCl}_3$ ( $\text{Cr}^{3+}$ )	300	0.26
$\text{CrO}_3$ ( $\text{Cr}^{6+}$ )	300	240

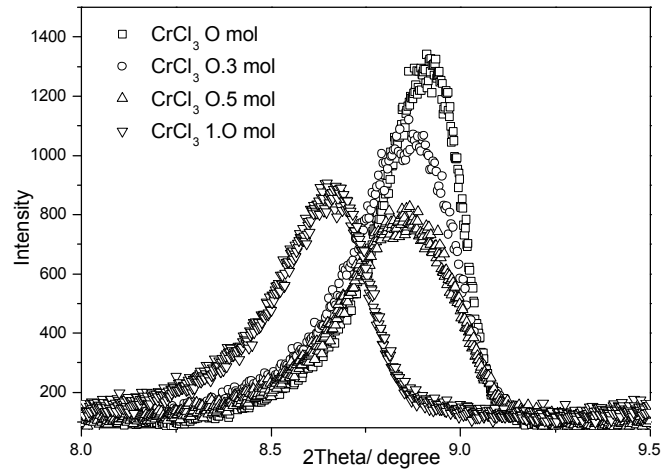


Fig. 4. X-ray Diffraction peak of ettringite in different  $\text{CrCl}_3$  input

The change of ettringite structure from X-Ray Diffractometry was calculated: The  $2\theta$  peak of ettringite corresponds to the 100 peak and thus essentially measures the width of the ettringite crystals. The peak broadening observed in the XRD patterns can be used to calculate the average size of the ettringite crystals [5] according to the Scherrer formula.

$$L = \frac{K\lambda}{B \cos \theta_B}$$

Where,  $L$  = thickness of crystallite

$K$  = constant dependent on crystallite shape

(0.89)

$\lambda$  = x-ray wavelength

$B$  = FWHM (full width at half max)

$\theta_B$  = Bragg Angle

Table 1. Calculation of crystal structure value in different  $\text{CrCl}_3$  input by calculate the Bragg formula and Scherrer formula.

Molar of Cr	(100) $2\theta$	$d_{(100)}$	FWHM	$L_{(100)}$
0 mol	8.88 °	9.94 Å	0.218	1354 Å
0.3 mol	8.84 °	9.99 Å	0.266	1036 Å
0.5 mol	8.83 °	10.01 Å	0.291	934.7 Å
1 mol	8.63 °	10.23 Å	0.25	821 Å

It was confirmed that the  $d_{(100)}$  of pure-ettringite is 9.94 Å. In addition, we were able to confirm that the  $d_{(100)}$  of Cr(III)-ettringite increases up to 10.23 Å by  $\text{CrCl}_3$  1.0 mol. The increase of lattice parameter can explain how the  $\text{Al}^{3+}$  site ( $\text{Al}^{3+}$  ion radius: 0.51Å) in the ettringite structure is substituted in the  $\text{Cr}^{3+}$  atom ( $\text{Cr}^{+3}$  ion radius: 0.65Å) by  $\text{CrCl}_3$  input.

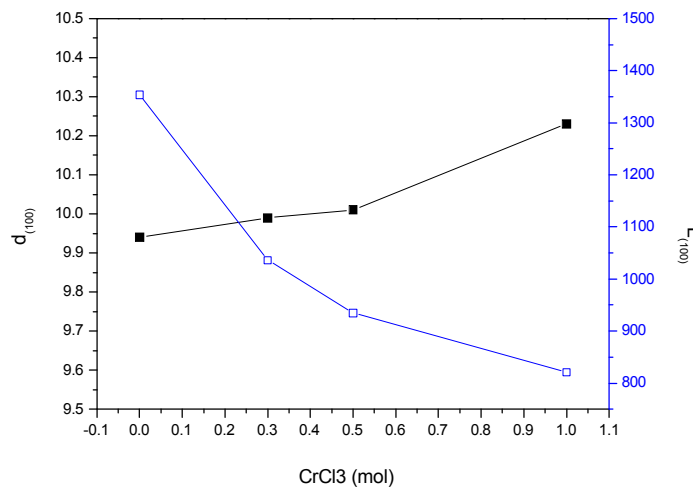


Fig. 5. Change of  $d(100)$  and  $L(100)$  according to the amount of  $\text{Cr}^{3+}$

Figure 6 shows the changing morphology of synthetic ettringite according to the quantity of  $\text{Cr}^{3+}$  increased. Thus, it was determined that the aspect ratio of ettringite was decreased. It is likely that during hydration in chloride solutions, the sulfate is readily exchanged by the chloride ions, which would explain the high concentration of  $\text{CrCl}_3$ . A Cl ion entered the ettringite structure, replacing the  $\text{SO}_4^{2-}$  ion and also modifying the morphology of the ettringite, forming thick stubby crystals instead of the usual elongated crystals.

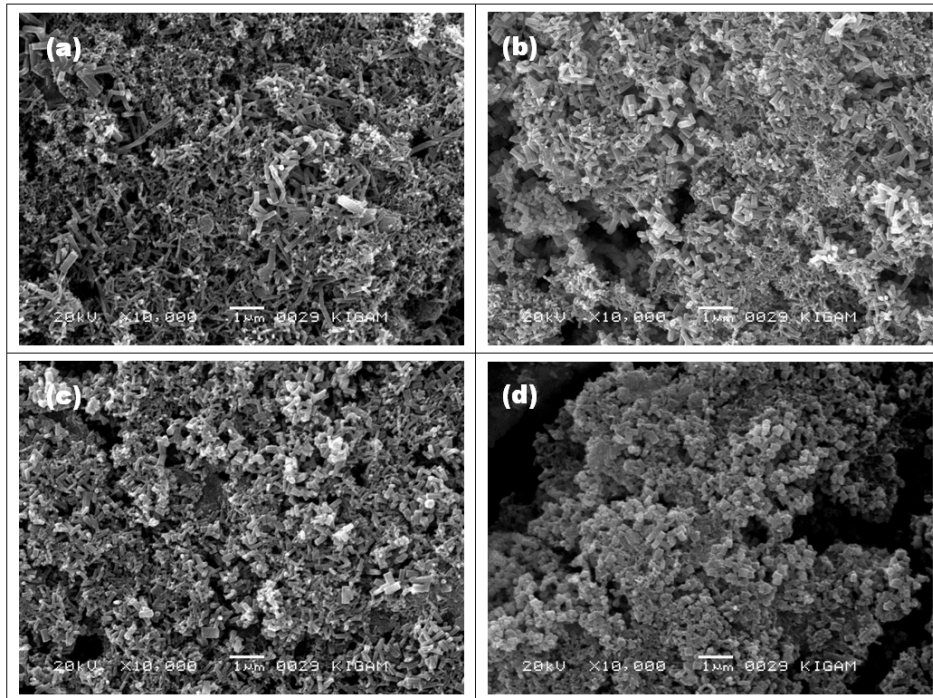


Fig. 6. the changing morphology of synthetic ettringite by different  $\text{CrCl}_3$  input

(a) 0 mol. Cr (b) 0.3 mol  $\text{Cr}^{3+}$  (c) 0.5 mol  $\text{Cr}^{3+}$  (d) 1 mol  $\text{Cr}^{3+}$

#### 4. Conclusions

1. Ettringite containing column and channel structure has advantage to stabilize heavy metal.
2. In solution with  $\text{Cr}^{3+}$ , the substitution of  $\text{Cr}^{3+}$  into Al site takes place in ettringite structure, and monosulfate/friedel'salt phase is also formed by occurrence of extra Al ion in solution.



3. Sulfate in the solution shows higher affinity to form ettringite than that of  $\text{Cr}^{6+}$  and sulfate is preferentially incorporated in ettringite.
4. Depending on the quantity of Ettringite with a containing column and channel structure has useful applications for heavy metal. Depending on the quantity of  $\text{Cr}^{3+}$  added, the  $2\theta$  value of face (100) is changed,
5. It was confirmed that ettringite can behave as a host for metallic pollutants to immobilize  $\text{Cr}^{3+}$  ions through substitution

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