

# Investigation of the structure of ettringite by time-of-flight neutron powder diffraction techniques

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## Abstract

The crystalline structure of ettringite,  $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ , was investigated using high-resolution time-of-flight neutron powder diffraction techniques. The powder diffraction data were subjected to Rietveld crystal structure refinement. The resultant ettringite crystal structure confirmed the positions of Ca, Al, and S atoms while permitting a more precise determination of the locations of O and H atomic positions than in previous X-ray and neutron diffraction studies. A discussion of the ettringite hydrogen bonding network is presented, illustrating the role of hydrogen bonding in the stabilization of the ettringite structure.

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## 1. Introduction

Ettringite,  $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ , is an important mineral in the chemistry of cement at two very different time scales. During the early hydration stages of Portland cements, the formation of ettringite is important for controlling the rate of set of the highly reactive calcium aluminate phase,  $\text{Ca}_3\text{Al}_2\text{O}_6$  [1]. At the other temporal extreme, an understanding of ettringite is necessary to describe the destructive processes in mature cement pastes arising from sulfate attack [2] and delayed ettringite formation [3]. The crystalline structure of ettringite has been previously investigated by Berliner [4] using neutron powder diffraction techniques with a reactor-based instrument. Berliner's crystalline structural model consisted of a central column of aluminum and calcium coordination polyhedra with surrounding columns of sulfate tetrahedra and rigid water molecules in the  $P31c$  space group with  $a=1.11670(5)$  nm and  $c=2.13603(13)$  nm. Recent investigations into the formation of ettringite concomitant with the hydration of the calcium aluminate phase in the presence of gypsum, as well as a study of

the structural changes during the thermal decomposition of ettringite, using time-of-flight (TOF) neutron powder diffraction [5] revealed that the presently accepted description of the ettringite crystalline structure [4] was inadequate. To resolve the discrepancies in the structural model, phase-pure ettringite was synthesized and subjected to structural investigation using TOF neutron powder diffraction techniques.

TOF neutron diffraction employs a pulsed neutron beam from an accelerator driven neutron source. Neutrons diffracted from the specimen are captured in an array of detectors that simultaneously record the scattering angle and flight time of the scattered neutron. These two quantities allow the momentum transfer of the scattering process to be determined. Pulsed neutron diffraction instruments provide improved instrumental resolution at large momentum transfers or, equivalently, small d-spacings.

## 2. Experimental

### 2.1. Ettringite synthesis

Two different synthesis methods were employed. Boiled deionized  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  were used in both synthesis methods to preclude the incorporation of impurity ions into the ettringite structure. Additionally, the syntheses were conducted in a sealed

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glove box with an inert nitrogen atmosphere to eliminate the influence of  $\text{CO}_2$  on the reactions.

In the first method, denoted as Struble's method [6], ettringite was synthesized by dissolving 0.06749 moles of  $\text{Ca}(\text{OH})_2$  in 400 cc of a 10 wt.% sucrose solution in  $\text{H}_2\text{O}$ . A separate solution of 0.01125 moles of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  in 50 cc of  $\text{H}_2\text{O}$  was also prepared. After magnetically stirring both solutions, they were combined and stirred further to ensure proper mixing of the reactants. The ettringite precipitate was vacuum-filtered and rinsed with  $\text{H}_2\text{O}$  several times to remove any sucrose or unreacted material. Following the final rinse, the ettringite was vacuum-filtered and allowed to dry over a saturated solution of  $\text{LiCl}$  (11% RH) in  $\text{H}_2\text{O}$ .

Ettringite obtained by Struble's method was crushed to a fine powder and was characterized using X-ray diffraction, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). X-ray diffraction analysis of the ettringite showed the material to be nearly phase-pure with a trace amount of calcite but no indications of residual  $\text{Ca}(\text{OH})_2$  or  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ . SEM revealed acicular crystals characteristic of the ettringite crystalline habit [7]. TGA exhibited weight-loss curves similar to those reported by other researchers [4,7]. For neutron powder diffraction examination, it is necessary to substitute deuterium for hydrogen in the ettringite structure to eliminate the large incoherent scattering background signal that would otherwise be present due to the hydrogen. Attempts to deuterate the ettringite by soaking it in  $\text{D}_2\text{O}$  for a period of several weeks proved unsuccessful, as evidenced by preliminary neutron scattering measurements.

To overcome the difficulties in producing a well-deuterated ettringite encountered with Struble's method, a second synthesis method, denoted as direct-synthesis, was employed. The direct-synthesis method eliminated the use of sucrose and used  $\text{D}_2\text{O}$  in lieu of  $\text{H}_2\text{O}$ .  $\text{Ca}(\text{OH})_2$ , contaminated with trace amounts of calcite, was heated for a period of 24 h at 1000 °C, resulting in pure  $\text{CaO}$ . The  $\text{CaO}$  was reacted with  $\text{D}_2\text{O}$ , forming a moist  $\text{Ca}(\text{OD})_2$  paste which was subsequently dried over a saturated solution of  $\text{LiCl}$  in  $\text{D}_2\text{O}$ . The dried  $\text{Ca}(\text{OD})_2$  was crushed into a fine powder and characterized using X-ray powder diffraction. The ettringite synthesis then proceeded by creating one solution of 0.07884 moles of  $\text{Ca}(\text{OD})_2$  in 650 cc of  $\text{D}_2\text{O}$  and another consisting of 0.01314 moles of anhydrous aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , in 150 cc of  $\text{D}_2\text{O}$ . The two solutions were both magnetically stirred to ensure proper mixing. The aluminum sulfate solution was added to the  $\text{Ca}(\text{OD})_2$  solution and the resultant mixture was magnetically stirred for a period of 24 h. The ettringite precipitate was vacuum-filtered and dried over a saturated solution of  $\text{LiCl}$  in  $\text{D}_2\text{O}$ .

Ettringite obtained by the direct-synthesis method was crushed into a fine powder and subjected to X-ray diffraction, SEM, and TGA investigations. In contrast to the sample obtained by Struble's method, X-ray diffraction showed a phase-pure ettringite with no visible traces of calcite or other phases. SEM indicated an acicular crystalline habit, shown in Fig. 1, characteristic of ettringite [7]. The deuterated ettringite was subjected to neutron powder diffraction and exhibited a reduced background signal and a much improved signal-to-noise ratio.

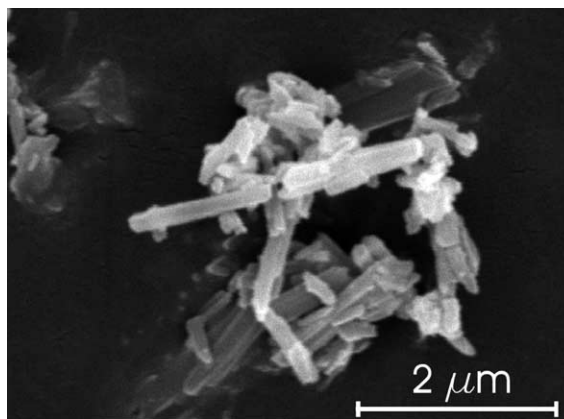


Fig. 1. SEM photograph of deuterated ettringite from the direct-synthesis method, demonstrating acicular crystalline habit.

## 2.2. TOF neutron powder diffraction

The direct-synthesis ettringite was investigated using the Special Environment Powder Diffractometer (SEPD) [8] at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory by placing the finely crushed ettringite powder into a vanadium sample can under a helium atmosphere. Once sealed, the sample can was placed in the instrument and data were collected at a temperature of 10 K. Data acquisition at low temperature minimizes the thermal motion of the atoms, permitting a precise determination of their equilibrium positions. The data acquisition exposed the sample to the neutron beam for a period of approximately 20 h to obtain data of sufficient statistical quality for Rietveld crystal structure refinement.

## 3. Discussion

### 3.1. Rietveld crystal structure refinement

The neutron powder diffraction data were subjected to Rietveld crystal structure refinement [9], denoted hereafter as structural refinement, using the *GSAS* [10] computer code as implemented in *EXPGUI* [11]. The structural refinement employs a non-linear least-squares fitting of a crystalline structural model to the diffraction data. The structural model is modified and compared to the data in an iterative fashion until close agreement between the model and the data is achieved. A detailed description of the Rietveld crystal structure refinement method is given by Young [12]. The initial positions for all atoms were taken to be those of Berliner's structural refinement [4]. The ettringite utilized for the experiment had deuterium in place of hydrogen, however in the discussion that follows, those sites that contain deuterium or hydrogen will be generically referred to as hydrogen sites for notational convenience. Initially, soft restraints, which apply stereochemical restrictions to the motions of atoms, were applied to the hydroxyl, water, and sulfate molecules. Soft restraints permit variation of a parameter, such as a bond length or bond angle, about a nominal or expected value but prevent non-physical distortions of known molecular identities within a crystal

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