

# Density functional theory study of the crystal structure and infrared spectrum of Ettringite

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## INTRODUCTION

The hardened cement paste is a porous material which is intended to be used for the containment of radioactive waste in future deep nuclear waste repositories. The contact of cement with water is a possible hazard due to the dissolution/precipitation processes at the surface of the solid phases leading to transport of chemical species by diffusion and to chemical reactions modifying the local equilibrium. The understanding of the hydration mechanisms and properties of cement paste components is crucial in materials science. However, the description of cement system is difficult because it is a complex multi-component assemblage and requires the knowledge of the properties of the individual solid phases and the use of appropriate methods for modelling. Among the individual components, ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 27\text{H}_2\text{O}$ ) (Hartman & Berliner, 2006) is an important product occurring during the hydration of Portland cements. It is also the main product resulting from hydration of special binders such as calcium aluminate cements blended with calcium sulphates. The main purpose of this work is the accurate theoretical description of ettringite towards its use in the modelling of its surface reactivity. From the computed structure, the analysis of the mineral surfaces should allow to correlate the structural properties of surface OH groups with their acidity by determining the density of  $\equiv \text{AlOH}$  and  $\equiv \text{CaOH}$  groups and the corresponding acidity constants. The first step in this study is the computation of the crystal structure of this phase, the associated X-ray diffraction patterns and infrared spectrum to evaluate the accuracy of the model.

## METHODS

### Experimental

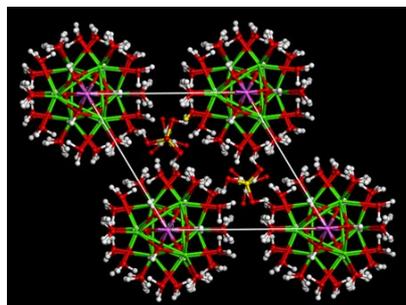
The experiments were performed with a crystalline powder sample of ettringite synthesized in our laboratory (CIEMAT). The synthesis was performed by mixing  $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$  solutions inside an anoxic glove box. The final solution was diluted in a solution of NaOH, sealed in a polyethylene bottle, heated and stirred. The precipitate was filtered, dried and stored at room temperature in a desiccator. The powder X-ray diffraction (XRD) pattern of ettringite was collected by using a Philips X'Pert-PRO diffractometer, in the range from 2 to 80 °2 $\theta$ . The Fourier-transform infrared (FTIR) spectrum of ettringite was recorded by using a Nicolet iS50 spectrometer with a DTGS KBr detector on KBr-pressed discs in transmission technique. All spectral manipulations were carried out using Omnic 9 software. The identity of the material was confirmed using XRD analysis.

### Theoretical

The crystal structure and infrared spectrum of ettringite were modeled employing CASTEP program (Clark et al., 2005), a component of the Materials Studio program suite. The theoretical treatment employed is based on Periodic Density Functional Theory using plane wave basis sets and pseudopotentials (Payne et al., 1992). The computations were carried out using the Perdew-Burke-Ernzerhof (Perdew et al., 1996) density functional complemented with Grimme's dispersion correction. The specific pseudopotentials utilized were norm-conserving pseudopotentials. The unit-cell parameters and atomic positions were optimized by means of the BFGS technique. A plane wave kinetic energy cut-off parameter of  $\epsilon = 900$  eV and a Monkhost-Pack  $k$ -mesh of  $2 \times 2 \times 2$  were employed. The software REFLEX was used to derive the X-ray powder diffraction patterns. The computation of the infrared spectrum of ettringite was performed by means of density functional perturbation theory.

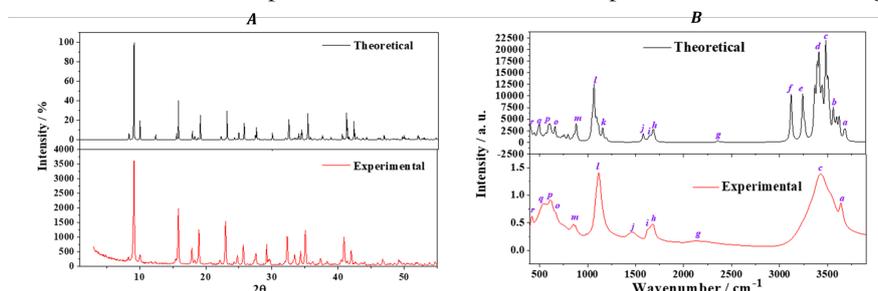
## RESULTS

The computed crystal structure of ettringite is shown in Figure 1. The crystal structure of ettringite (Hartman & Berliner, 2006) contains columns with formula  $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]^{3+}$ , expanding along the direction of  $c$  axis which are composed of  $\text{Al}(\text{OH})_6$  octahedra alternating with triangular groups of edge-sharing  $\text{CaO}_8$  polyhedra. Four of the oxygen atoms coordinating the Ca atom are from  $\text{H}_2\text{O}$  molecules, which form the cylindrical surface of the column (see Fig. 1). The columns delimitate channels containing sulfate ions and zeolitic water. The different columns are linked through the sulfate ions via hydrogen bonds.



**Fig 1.** Computed crystal structure of ettringite from  $[100]$ . Color code: Ca-green; Al -violet; O-Oxygen; S-Yellow; H-hydrogen.

The computed unit cell parameters,  $a=b=11.21 \text{ \AA}$  and  $c=21.14 \text{ \AA}$  ( $P31c$  space group), are in excellent agreement with the experimental ones  $a=b=11.17 \text{ \AA}$  and  $c=21.35 \text{ \AA}$  (Hartman & Berliner, 2006). From the structure of ettringite calculated theoretically, the X-ray powder pattern was derived. The resulting pattern is compared with the experimental one in Figure 2A. As it can be observed, both patterns are highly consistent. The five main reflections are observed at  $2\theta=9.15, 15.85, 22.98, 18.95$  and  $35.02^\circ$  which may be compared with the experimental positions at  $2\theta=9.12, 15.83, 23.16, 19.14$  and  $35.36^\circ$ . The infrared spectrum determined theoretically compared with the experimental infrared spectrum is shown in Figure 2B. Both spectra are in good agreement. However, the six high frequency bands found in the theoretical spectrum are not resolved in experimental one, showing only a broad band.



**Fig 2.** (A) Computed and experimental X-ray diffraction patterns of ettringite; (B) Computed and experimental infrared spectra.

## CONCLUSIONS

The agreement in the X-ray diffraction pattern and IR spectra gives a strong support to the computed structure and to the methods employed for its determination. Therefore, they may use with confidence for the study of the surface properties and reactivity of ettringite.

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