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Prelyminary Communication

Crystal Structure Investigation of Calcium Aluminium Sulphate Hydrate- Ettringite

A. Bezjak and I. Jelenić

Research Department of the Association of Yugoslav Cement Producers,
Zagreb, Croatia, Yugoslavia

Received September 2, 1966

Calcium threesulphoaluminate hydrate — ettringite, the general formula of which is $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ occurs as natural mineral. This compound is, however, more important and better known as an ingredient of set Portland cement.

In the hydration of cement ettringite appears as reaction product between the calcium sulphate solution and the calcium aluminate solution. Consequently, it is very important to know the crystal structure of ettringite when studying the reaction mechanism of cement hydration as well as for the interpretation of chemical, physical and mechanical properties of set and hardened cement pastes.

In 1936 Bannister[1] first determined the cell dimension and the space group symmetry of ettringite. Swanson and co-workers[2] published somewhat more precise crystallographic data in 1958. According to their findings ettringite is hexagonal with $a = 11.23$ and $c = 21.44$ Å, the unit cell containing two formula units.

Among $hh\bar{2h}l$ reflections the diffraction pattern of ettringite shows only those with l — even. This condition limiting possible reflections is common in five hexagonal space groups. Swanson and co-workers proposed space group $D_{6h}^4 — P6_3/mmc$ and Bannister the group $D_{3d}^2 — P\bar{3}1c$.

Our results for cell dimension, space group symmetry and reflection intensities are in general agreement with the data of Swanson and co-workers. Our work on structural investigations was based on the presumption that ettringite has the D_{6h}^4 space group.

The crystal structure of ettringite was determined by X-ray powder data, as there were no single crystal specimens of ettringite available.

In the very beginning of the determination of the crystal structure of ettringite we calculated the three-dimensional Patterson synthesis taking into account 41 reflections. The interatomic vectors Ca-Al and Ca-Ca, *i. e.* the distances between the coordination polyhedra were determined from Patterson's synthesis. By analysing these vectors the positions of calcium and aluminium atoms were obtained.

According to the results from Patterson's synthesis calcium atoms are situated in special positions, *i. e.* in the vertical mirror plane of symmetry.

As every unit cell contains four aluminium atoms, these must be situated in three-fold axes with regard to the space group symmetry. This special position of Al-atoms is confirmed also by Patterson's synthesis.

Positions of SO_4^{2-} groups, OH^- groups and H_2O molecules were defined by trial and error method.

The atom parameters which were thus determined served to give the general feature of ettringite structure according to which Ca-atoms are surrounded by three OH^- groups and three water molecules. Bond lengths Ca-OH and Ca-OH_2 are between 2.33 and 2.44. OH^- groups and OH_2 molecules which surround the Ca-atoms form distorted octahedra. Al-atoms are also enclosed in distorted octahedra formed by three OH groups and three water molecules.

Bond lengths Al-OH and Al-OH_2 are 1.90 and 2.05 Å.

When first determining the atomic arrangement we thought one water molecule to be situated on the three-fold axis with coordinates $^1/_3$, $^2/_3$, z. A more precise analysis of intensities indicated, however, that the water molecules coordinates are 00Z, and that the distance between this molecule and the Ca-atoms is 2.70 Å. Judging from this distance we can assume that this water molecule also belongs to the coordination group around the calcium atom. If this assumption is arupted the coordination number for calcium is seven.

Fig. 1 shows an idealized projection of ettringite structure along c (001). In this structure Ca-atoms are surrounded by 3 OH^- groups and 4 H_2O molecules and Al-atoms by 3 OH^- groups and three water molecules. Coordination polyhedra about Ca-atoms are linked to the neighbouring Ca and Al polyhedra through common OH groups. These linked polyhedra form wavelike layers with formula $[Ca_6Al_2(OH)_{12} \cdot 26\,H_2O]_n^{6+}$. SO_4 groups are situated between these layers.

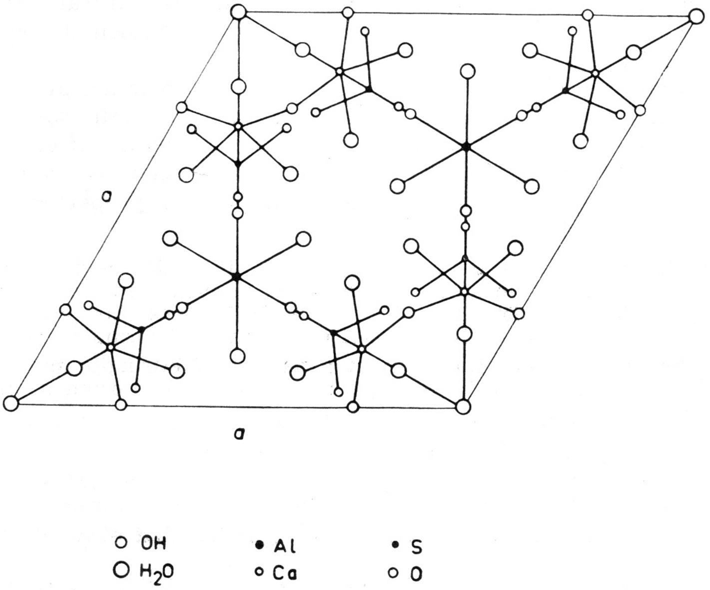

Fig. 1. Idealized projection of ettringite structure along c (001).

Oxygen atoms of SO_4 groups are located in two planes which correspond to two mirror planes belonging to space group D_{6h}^4 . The linkage of CaO_7 and AlO_6 polyhedra in wave-like layers is shown on Fig. 2. Each of the CaO_7 polyhedra is surrounded by two identical polyhedra and by one AlO_6 octahedron whilst each of AlO_6 octahedra is surrounded by three CaO_7 polyhedra.

The polyhedra are linked through OH groups while three water molecules of every coordination group share in the building of only one polyhedron.

Three neighbouring CaO_7 polyhedra have one water molecule in common. The oxygen atom of this fourth molecule is located above one side of the distorted octahedron.

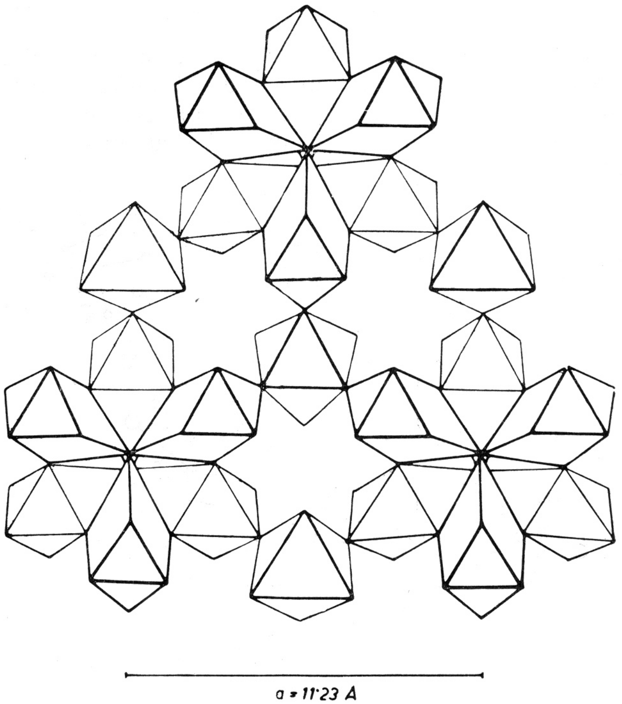

Fig. 2. Wavelike layers of linked Ca and Al polyhedra.

Accurate analysis of structural factors has shown that SO_4 groups deviate by 45⁰ from the position shown on the figure which presents an idealized structure (Fig. 3). Such a turned position does not correspond to space group $P6_3/mmc$ but rather to group $P\bar{3}1c$. There is a hydrogen bond between the O-atoms of SO_4^{2-} groups and O-atoms of H_2O molecules from the two neighbouring octahedral layers. The lengths of these hydrogen bonds are 2.70—2.74 Å. The final analysis of intensities has shown that positions of the water molecules are not completely in accordance with the symmetry $P6_3/mmc$ space group so that polyhedra about Ca-atom are distorted.

The coordination polyhedron around Ca in the idealized structure is a trigonal prism +1. In a non-idealized structure there is a polyhedron resembling an octahedron with a seventh group (octahedron +1).

The crystal structure investigation leads to the following formula: $[Ca_6Al_2(OH)_{12} \cdot 26H_2O](SO_4)_3$.

For $P\bar{3}1c$ space group the reflections $hk\bar{l}$ and $hk\bar{l}$ have an identical Bragg angle. Their intensities on the powder photograph overlap and can be determined only together.

In the present case refinement of the structure was not possible due to different values of F (hkl) and F $(hk\bar{l})$ structural factors.

Structure refinement is possible only from single crystal data or from the isomorphism of Ca and Cr aluminate threesulphate hydrate, the synthesis of which is under consideration.

The explained structure is in agreement with the behaviour of ettringite in the course of dehydration.

On the 7th Congress of International Union of Crystallography held in Moscow 1966, we were informed that Dr. J. W. Jeffery and his coworkers posses x-ray data for monocrystal specimen of ettringite. These data will enable a more precise determination of crystal structure.

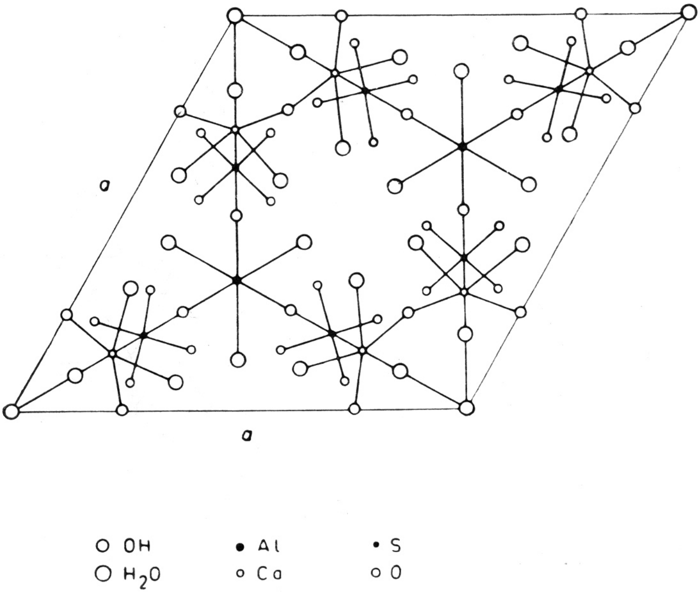

Fig. 3. Projection of ettringite structure along c (001).

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2. H. E. Swanson, H. T. Gilfrich, M. I. Cook, R. Stinchfield, and P. G. Parks, *U. S. Nat. Bur. Stand. Circ.* **529** No. 8 (1958) 3.

IZVOD

Određivanje kristalne strukture kalcijevog aluminijevog sulfat-hidrata — etringita

A. Bezjak i *I. Jelenić*

Na temelju Pattersonove i Fourierove sinteze određen je kristalokemijski motiv strukture etringita. Tačnom analizom intenziteta dokazano je da od 5 mogućih prostornih grupa etringitu pripada grupa D_{3D}^2 — $P\bar{3}1c$. Struktura etringita je slojevita. Slojeve čine međusobno povezani $Al(OH)_3(OH_2)_3$ i $Ca(OH)_3(OH_2)_4$ poliedri. SO_4 grupe su smještene između ovih slojeva.

ISTRAŽIVAČKI ODJEL
UDRUŽENJA PROIZVOĐAČA CEMENTA
ZAGREB

Primljeno 2. rujna 1966.