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Transmission electron optical study of ettringite and thaumasite

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Abstract

Selected area electron diffraction studies of ettringite, carbonate ettringite and thaumasite have been made. Ettringite suffers severe dehydration effects in the electron microscope whereas carbonate ettringite and thaumasite are relatively stable and their *a* dimensions are close to those obtained by XRD. The *c* dimension of thaumasite is also preserved, but that of carbonate ettringite is reduced to less than half its XRD value by a symmetry change and slight longitudinal shrinkage of the calcium aluminate hydrate columns. This is believed to be the result of the stronger hydrogen bonding of apical water molecules in the columns by carbonate ions, which are not volatile in the conditions experienced in the electron microscope and which stabilises the structure.

Keywords: Ettringite; Thaumasite; Electron diffraction

1. Introduction

Ettringite and thaumasite have very similar crystal structures [1–5]. Thaumasite is hexagonal ($a = 11.054$ Å, $c = 10.401$ Å) with columns of $[Ca_3Si(OH)_6 \cdot 12H_2O]^{4+}$ and sulfate and carbonate ions in an ordered arrangement in channels between the columns. The Si is octahedrally coordinated by O. Ettringite is trigonal ($a = 11.234$, $c = 21.501$), Al replacing the Si in the columns and $3SO_4^{2-}$ and $2H_2O$ replacing $2SO_4^{2-}$ and $2CO_3^{2-}$. The columns are essentially similar, the difference in the *c* parameter and symmetry arising from ordering of the sulfate in ettringite, illustrated in Fig. 1. Solid solutions between the two phases exist in nature [6] and have been found in the products of the thaumasite form of sulfate attack [7,8] as well as in laboratory studies [9–11]. Solid solution between thaumasite and ettringite occurs by the replacement of Si by Al and of sulfate/carbonate by sulfate/water, although Si replacement may be independent of sulfate/carbonate replacement [11].

The similarity between the thaumasite and ettringite structures means that the XRD patterns are very similar. Rigorous analysis of these, however, does reveal the differences in the unit cells, but it has been shown in this work that electron diffraction is unable to distinguish the solid solutions. This is important when characterising morphologies in the electron microscope.

A study of solid solutions between thaumasite and ettringite, and sulfate–carbonate ettringite has been made by Barnett et al. [12]. In regions close to the end members, single phases were obtained, but, otherwise two solid solutions were observed. Rietveld analysis of XRD patterns showed that not only were there separate thaumasite-like and ettringite-like phases, but also that the unit cell parameters of each phase varied with composition. The two phase mixtures were found by TEM to have two distinct morphologies, stubby laths and acicular crystals and it was thought that the former might be ettringite and the latter thaumasite. EDX analysis in the TEM gave so much scatter that it was not possible to distinguish the solid solutions by composition, although IR data indicated the existence of a miscibility gap. (There are therefore also problems in distinguishing solid solutions by SEM/EDX.) In an attempt to determine whether the two morphologies did represent the two different solid solutions, an electron diffraction study was made in the thaumasite–ettringite series. Although the high water content of both phases makes them highly susceptible to beam and vacuum damage, useful SAED information can be obtained with careful work. As the diffraction patterns obtained from ettringite and thaumasite are different (ettringite is more susceptible to beam damage than thaumasite), it should be easy to distinguish them, but the results obtained indicated that

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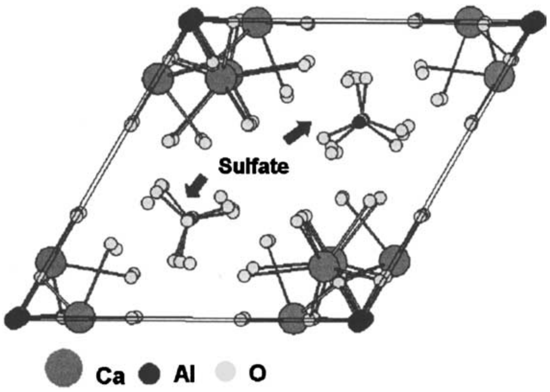

Fig. 1. [0 0 1] projection of ettringite structure showing stacks of sulfate ions rotated relative to one another. The unit cell is outlined. In thaumasite and carbonate ettringite, carbonate ions occupy sulfate sites.

both morphologies had thaumasite structures and it was not possible to distinguish the two solid solutions [13]. In this paper we describe further work on carbonate ettringite, $Ca_6Al_2(CO_3)_3(OH)_{12} \cdot 26H_2O$, which helps us to explain these apparently anomalous results.

2. Experimental

Solid solutions and carbonate ettringite were prepared by methods analogous to those described previously [12]. Selected area electron diffraction (SAED) patterns were obtained with a Jeol 200EX Temscan operating at 200 kV. Specimens were prepared by ultrasonically dispersing a portion of material in distilled water and drying a drop of the resulting suspension on a copper grid which had a carbon/aluminium support film. The aluminium provides a ring pattern superimposed on the SAED pattern of the specimen, which serves as an internal standard for d-spacings.

3. Results and discussion

Fig. 2a and b are SAED diffraction patterns of ettringite and natural thaumasite (Crestmore, CA), respectively. The ettringite pattern shows signs of considerable decomposition, c is reduced to between 0.982 and 1.054 nm in different crystals and a to 0.834 nm. (This indexing scheme is by analogy with the unit cell axes of normal ettringite and may not reflect the true cell. The patterns faded rapidly in the beam so a proper unit cell determination was not possible.) Many diffraction spots are missing or very weak and there is also considerable streaking. Occasionally there were also extra reflections incommensurate along a. This behavior was observed in several different preparations. Under vacuum, ettringite loses water step-wise [14,15] and the streaking and incommensuracy are consistent with the formation of domains, perhaps with differing water contents, parallel to c. The thaumasite pattern, on the other hand shows no sign of vacuum- or beam-induced damage, although the pattern faded in the beam over a few minutes. There is a regular array of spots and the unit cell parameters are in good agreement with those obtained by XRD [13]. The carbonate ettringite was even more stable in the TEM than thaumasite, and it remained crystalline long enough to permit tilting to find different zones, illustrated in Fig. 3, a $[1\bar{1}0]$ zone axis SAED pattern. This pattern tends to confirm the hexagonal symmetry of the partially dehydrated material. a is 1.080 nm, compared with 1.086 nm by XRD. Nevertheless, c is reduced from 2.125 to 1.048 nm, rather less than half the XRD value [16]. This reduction in c is largely brought about by the change from trigonal to hexagonal symmetry, which would exactly halve c, so that the column length is, in reality only slightly shortened.

Inspection of the structures of ettringite and thaumasite provides an explanation for the observed behavior.

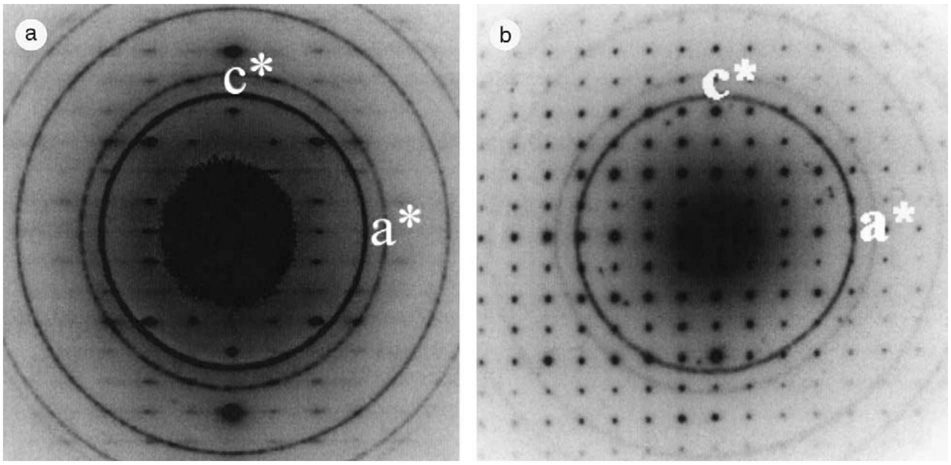

Fig. 2. (a) SAED pattern of ettringite showing severe damage and (b) thaumasite showing good preservation of structure. The rings are the Al internal standard.

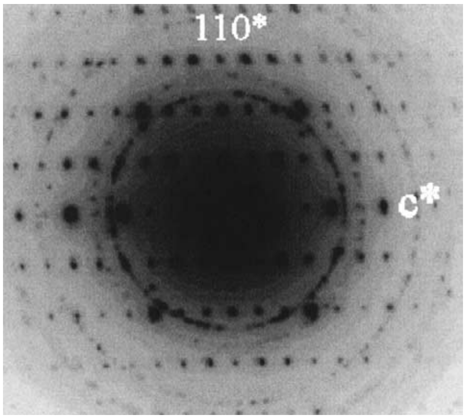

Fig. 3. SAED $[1\bar{1}0]$ zone axis pattern of carbonate ettringite. The rings are the Al internal standard.

In the case of ettringite, the first loss to occur in vacuum is that of the water molecules in excess of 30 per formula unit [14,15]. These are isolated molecules which lie in the space between the columns [1]. Disordering of the sulfate may also occur at this stage. Next to be lost are apical water molecules, down to 18 molecules remaining per formula unit, followed by the bridging hydroxyls that link the Al and Ca ions, indicated in Fig. 4. In the final stage the material becomes amorphous to X-rays. The trigonal symmetry can be lost during the second stage of the dehydration process. The range of values of c reflects differing extents of dehydration which cause varying degrees of shrinkage. These two factors can therefore explain the shrinkage of c to somewhat less than half its original value. Also, as the apical water molecules are lost, the columns may approach and even partially fuse. The value of a, 0.834 nm corresponds to a column repeat of about 0.72 nm if the assumption of a hexagonal or pseudohexagonal unit cell is correct. This value lies within the range expected if the columns fuse (the diameter of a fully hydrated column from apical oxygen to oxygen is 0.79 nm at 1 and 0.67 at 2, labelled in Fig. 4). One possible mechanism is for the waters at 1 to be lost completely and for fusion to occur by elimination of half the water molecules at 2. There is enough space to accommodate the sulfate groups and these may also join the columns together, with further elimination of water molecules at 2.

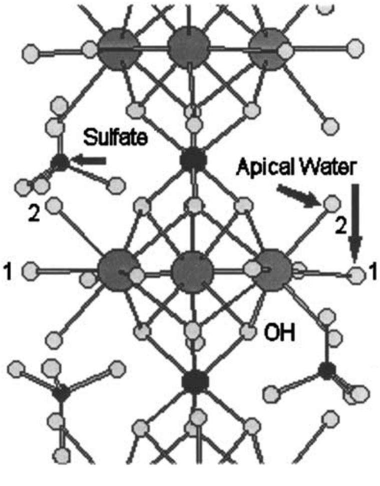

Fig. 4. [100] projection of ettringite structure showing apical water, hydroxyl and sulfate. The sulfate ions are not in the plane of the columns (see Fig. 1). Ca, Al and O atoms are coded as in Fig. 1.

In thaumasite both a and c are preserved, within experimental error, on dehydration, a is also preserved in carbonate ettringite, but c is slightly less than half. Again the loss of trigonal symmetry in the carbonate ettringite can be explained in terms of the loss of order in the inter-columnar ions. The higher thermal stability of thaumasite relative to ettringite has been attributed to the charge delocalisation away from the $Si(OH)_6$ [17], but this mechanism does not apply in ettringite. The preservation of a in both thaumasite and carbonate ettringite may be related to the higher charge density on the carbonate oxygens, 2/3-, compared with 1/2 on the sulfate oxygens. Bond distances between the apical water molecules and the carbonate oxygens are generally slightly shorter than those in the case of sulfate [18]. These two factors may increase the strength of the hydrogen bonding between the anions and the columns and so delay the water loss. Significant carbonate loss does not occur until the temperature exceeds 200 °C, by which time the material is amorphous [19]. The shrinkage of c in carbonate ettringite in addition to the symmetry-related halving, while the corresponding value of thaumasite is not affected in the vacuum of the microscope, suggests that the delocalisation mechanism suggested in [17], does confer extra stability to thaumasite. Nevertheless, the enhanced stability of the carbonate ettringite in the microscope relative to thaumasite suggests that the carbonate has the dominant effect.

4. Conclusions

This study has provided the explanation for the difference between XRD and SAED patterns obtained from the ettringite thaumasite system. It is shown that the ettringite structure is susceptible to shrinkage in the vacuum of the electron microscope; this does not occur with XRD. The presence of carbonate in ettringite hinders water loss and so prevents the movement of the columns along a and also reduces the shrinkage along c, compared with normal ettringite. It is this that results in the ettringite members of the solid solution series giving SAED patterns with a strong thaumasite-like character [12,13]. It is apparent that only partial substitution by carbonate is enough to stabilise the structure against dehydration. This highlights the importance of exercising caution when interpreting electron microscopical data on the products of degraded concrete.

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