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Identification and characterisation of thaumasite by XRPD techniques

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Abstract

X-ray powder diffraction (XRPD) data analysis techniques (full pattern fitting and Rietveld refinement) have been evaluated as a means of characterisation of thaumasite. For the first time, these XRPD methods, which employ the whole of the powder pattern rather than just a few reflections, have been used to study systems containing thaumasite. Structure refinement by Rietveld methods, using synchrotron data, produced a crystal structure model of thaumasite suitable for use in the analysis of thaumasite in cements. The use of these techniques in the analysis of cement systems containing thaumasite is discussed. An example of the use of Rietveld refinement in quantification of a sample containing thaumasite is given. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Full pattern fitting; Rietveld refinement; Thaumasite; X-ray powder diffraction

1. Introduction

Thaumasite [1], $Ca_3Si(SO_4)(CO_3)(OH)_6.12H_2O$, is a naturally occurring mineral which is also found in cements as a consequence of sulphate attack [2,3]. The similarity of its crystal structure to that of ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$, has led to confusion in the past. This paper describes part of a project in which modern methods of X-ray powder diffraction (XRPD) data analysis, such as full pattern fitting and Rietveld refinement, are being evaluated as a means of identifying the exact nature of ettringite, thaumasite and other related phases, as well as their solid solutions, in cementitious systems.

2. X-ray powder diffraction techniques

Full pattern fitting [4] and Rietveld refinement [5] are both least squares minimisation techniques, in which a refinable model is used to produce a calculated data set which is then fitted to the experimental data. The model is adjusted in an iterative procedure until a good fit of observed and calculated data is achieved.

Full pattern fitting is used to obtain accurate unit cell dimensions and intensity measurements [4]. The calculated data is produced from a model which includes the Miller indices of the reflections present in the diffraction pattern, approximate unit cell dimensions, instrumental and sample-dependent effects. Relative intensities, unit cell parameters, 2θ corrections and peak profile coefficients are refined so as to produce the best fit to the experimental data. No information on atom types and positions within the crystal structure is required or obtained. An early use of this technique, in which real Portland cement systems were quantified by fitting to standard patterns for the phases present, was made by Gutteridge [6].

Rietveld refinement is a structure refinement technique[5]. The calculated pattern in this case is based on refinable models for the crystal structure (unit cell dimensions, atomic parameters), instrumental effects and specimen-dependent characteristics. A reasonably good starting model for the crystal structure is required in order to ensure that the refinement leads to a global minimum. The main problem in the application of the technique is the difficulty in determining the peak profile function in order to resolve overlapping reflections, particularly for patterns obtained on laboratory instruments. For synchrotron data, the contribution to the peak shape and width due to instrumental effects can be described quite simply. This, combined with the high intensity and superior resolution, makes radiation particularly important in Rietveld studies of substances like thaumasite which produce a large number of

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potentially overlapping reflections. Rietveld refinement has been used in quantification of alite and belite [7,8] and in structure refinement of the phases present in anhydrous cements [9,10].

This work concerns the application of these techniques to thaumasite, in order to evaluate their potential use in the analysis of cementitious systems containing thaumasite. Both of these techniques are now capable of simultaneous refinement of several phases, meaning that their application to cement systems is possible. The techniques enable quantification of a sample using the whole of a powder pattern. Considering thaumasite itself, these techniques are capable of detecting variations in the crystal structure caused by solid solution effects. Full pattern fitting provides information on unit cell dimensions which vary with deviations in composition. In Rietveld refinement, the effects of changing composition can be allowed for by incorporating these changes into the crystal structure model. Other atom types can be included and atomic occupancy factors can be refined. Both of these techniques are currently being used in studies of the solid solution between ettringite and thaumasite, in another aspect of this work.

3. Materials

The thaumasite used in this study was prepared, using reagent grade materials, by mixing a solution of 13.40 g CaO in 890 cm^3 10% w/w sucrose solution with one of 16.90 g $Na_2SiO_3.5H_2O$, 8.45 g Na_2CO_3 and 11.30 g Na_2SO_4 in 40 cm^3 distilled water. The mixture was stored at 4°C for 6 months. The solid produced was filtered by suction filtration, washed with distilled water followed by acetone, and dried at room temperature and pressure. Repeated preparations following this method showed that periodic agitation of the mixture during the reaction time is required to ensure that thaumasite is produced.

4. Experimental

Laboratory XRPD data for thaumasite was collected using a Philips PW1050 diffractometer with CuKα radiation, driven by a Hiltonbrooks control system. High resolution powder diffraction data was collected on Station 2.3 at CLRC Daresbury Laboratory's Synchrotron Radiation Source (SRS) using a beam size of 2 × 15 mm and an X-ray wavelength of 1.4 Å.

Pattern fitting was carried out, with conventional laboratory data, using the in-house BESTFIT software developed by Adam [11]. The thaumasite standard pattern [12] was used to provide Miller indices of the reflections and initial unit cell parameters. It was also necessary to refer to a calculated pattern based on the single crystal structure determination [1] in order to include several weak reflections which did not appear on the standard pattern; the thaumasite standard pattern is not assigned a high quality mark in the powder diffraction file.

The PROFIL [13] package was used for Rietveld refinement of thaumasite, using synchrotron data. The Edge and Taylor structure determination [1] was used as a starting model for the crystal structure. The 2θ-zero error, scale factors, unit cell dimensions, peak shape and width parameters and atomic positions were refined. Constraints were applied to the lengths of the C–O and S–O bonds of the CO_3^{2-} and SO_4^{2-} groups in order to produce a model which is chemically reasonable.

The refined model obtained was used to quantify the crystallinity of a separate sample of thaumasite. This is achieved by adding 50% w/w corundum (Al_2O_3) to the sample before XRD analysis. The quantification was carried out using the Rietveld refinement software GSAS [14] (general structure analysis system), with data obtained using a sealed tube X-ray source.

5. Full pattern fitting

A section of the graphical output of the pattern fitting for thaumasite is illustrated in Fig. 1. The unit cell parameters calculated by this procedure are $a = 11.054(3)$ Å, $c = 10.410(3)$ Å. These are in close agreement with previously published values for thaumasite[15] ($a = 11.06$ Å, $c = 10.42$ Å).

Full pattern fitting is a very reliable way of determining unit cell parameters, even in mixtures containing several phases. The technique is able to account for errors in 2θ measurements, i.e. zero error and sample height corrections, so that even very slight variations (±0.005 Å) in unit cell parameters in mixtures can be detected without the need for an internal standard[4].

6. Rietveld refinement

The fit of observed and calculated data for the Rietveld refinement of thaumasite, using synchrotron data, is shown in Fig. 2. The difference profile shows that the observed and calculated data are in good agreement; the differences between them are little above the noise level of the observed data. The R_{wp}-factor for this refinement (a measure of the quality of the fit) is 13.6%. The refined crystal structure is given in Table 1. Thaumasite has a hexagonal structure (space group $P6_3$). The structure is based on columns of composition $[Ca_3Si(OH)_6.12H_2O]^{4+}$ with

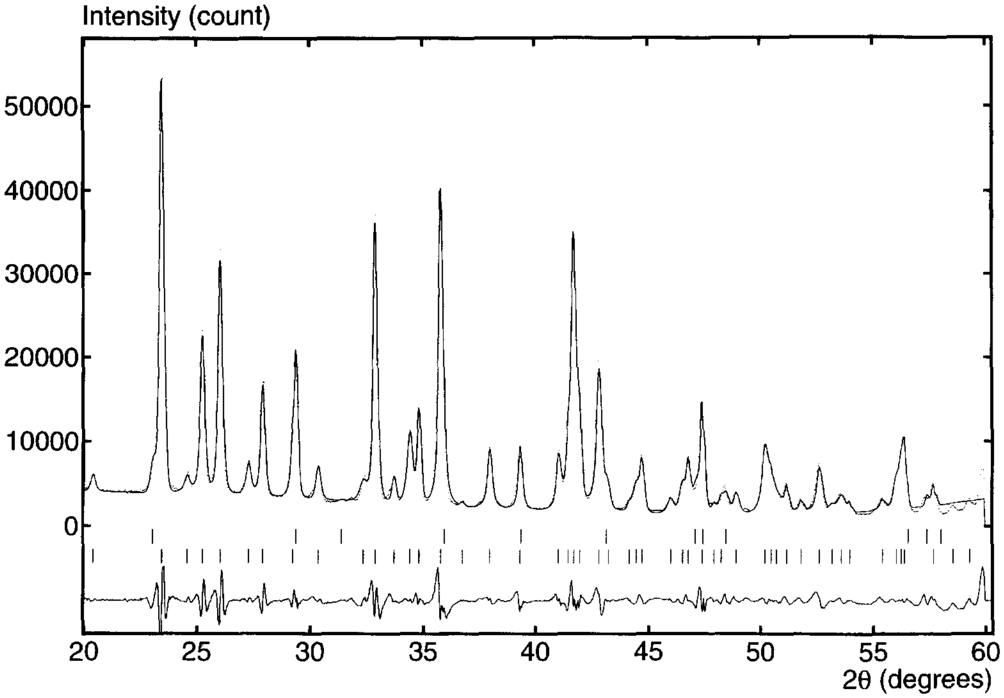

Fig. 1. Pattern fitting for thaumasite. Main plot: observed data—dotted line; calculated data—solid line. Lower plot: difference profile. Markers along horizontal axis indicate reflection positions: lower markers—thaumasite; upper markers—calcite.

the sulphate and carbonate groups distributed in an ordered arrangement along the channels between the columns.

It was decided to allow the C and O atoms of the CO_3^{2-} group to move independently of each other, since the single crystal structure determination by Edge and Taylor [1] suggests that the CO_3^{2-} group in thaumasite deviates from the usual planar shape. These results show a similar deviation from coplanarity to that reported in the literature. The O–C–O angle obtained by this refinement is 119(2)°, compared to the literature value [1] of 118(1)°.

As Rietveld refinement is a purely mathematical process, it is important to make sure that the final model produced makes physical and chemical sense. The bond lengths of the crystal structure model were examined at various stages in the refinement procedure. Bonds which deviate significantly from their expected range of values[16] can be constrained. This constraint takes the form of an approximate value for the bond length, along with an associated error, and is treated as an experimental observation in the refinement. In this refinement, the S–O bonds of the sulphate group were constrained to 1.49 ± 0.04 Å, while the C–O bonds of the carbonate group were constrained to 1.29 ± 0.01 Å. These constraints were successful in ensuring that the refinement converged to a chemically reasonable crystal structure model.

The bond lengths for the final model are compared to those for the Edge and Taylor crystal structure determination [1] in Table 2. The bond lengths of this model all lie within their expected ranges. In contrast with the Edge and Taylor paper, which noted that the $Si(OH)_6^{2-}$ group in thaumasite is somewhat asymmetrical, this refinement shows that the Si–O distances are quite similar. This is in agreement with a later single crystal structure refinement [17], which found that the Si–O distances were equal. The Ca–O bonds are generally longer than those in the Edge and Taylor structure model, although two are quite short [Ca(1)-O(4) and Ca(1)–O(8a)].

This model is suitable for use in the analysis of cement pastes containing thaumasite, provided that crystal structure models exist for the other phases of interest present. If no structural data is available for a phase present, reflections from it can be eliminated from the refinement procedure by excluding certain regions of the X-ray diffraction pattern. However, since thaumasite and systems containing it usually produce complicated XRD patterns with a large number of overlapping reflections, the use of excluded regions is likely to remove a considerable amount of information from the refinement. The refined scale factors for each phase present provide a means of quantitative phase analysis of the cement, using the whole pattern rather than just a few strong reflections. In GSAS, the scale factor is proportional to the number of unit cells of the phase present in the sample. The weight ratios of the phases present can therefore be calculated directly. If an internal standard is incorporated, it is also possible to determine the amount of non-crystalline material present in a sample.

This method was used to quantify the crystallinity of another thaumasite sample from the same batch. Calculated powder patterns for thaumasite and corundum confirmed that the strongest reflections from each phase have similar absolute intensities, making corundum a suitable choice of internal standard for this purpose. Ideally, the overlap of reflections from the two phases should be as small as possible also. Fig. 3 shows the fit of observed and calculated data for this mixture. It can be seen that the 100% thaumasite reflection (at ~9°2θ) is much weaker than the 100% corundum reflection (~35°2θ), thus indicating that

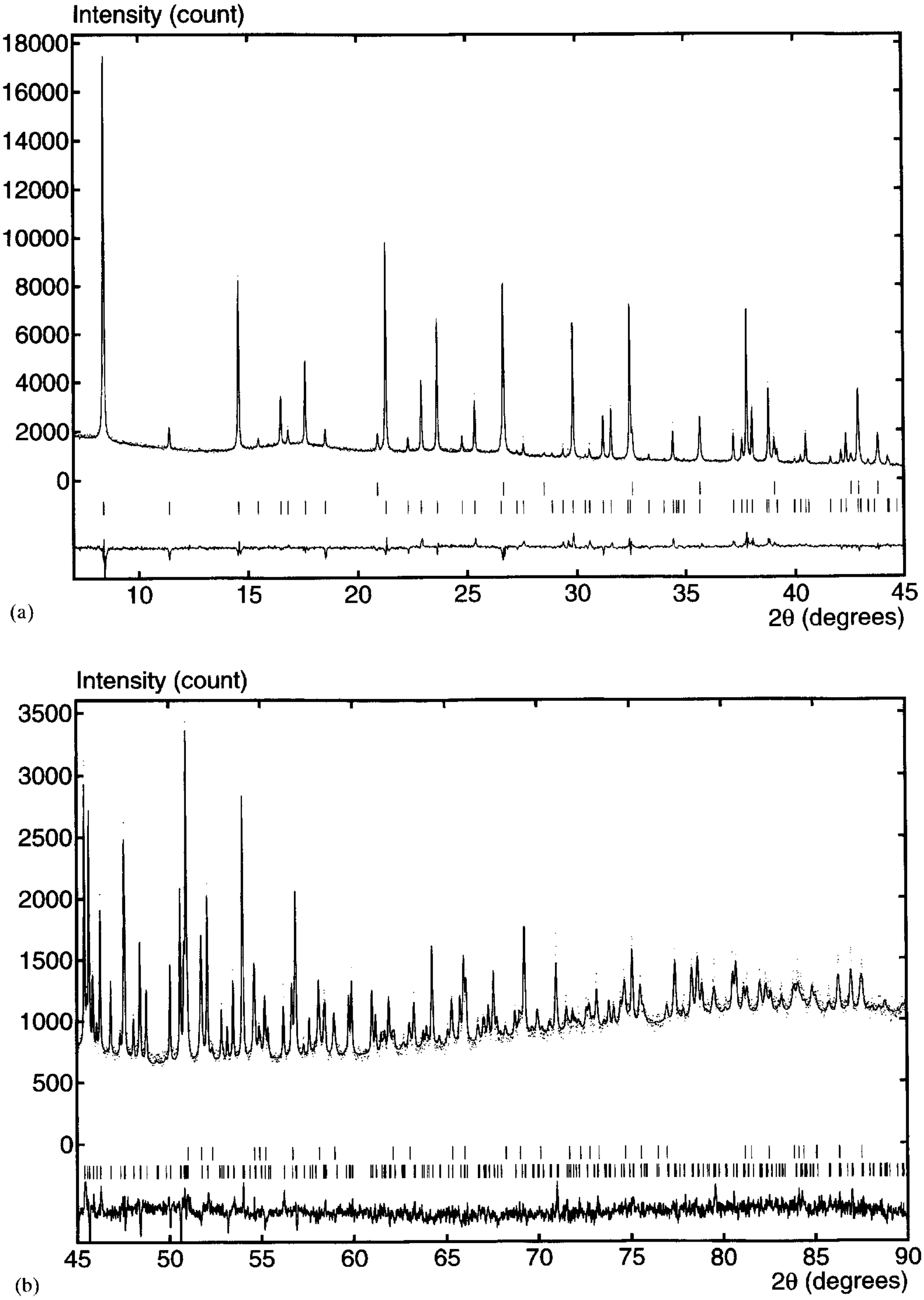

Fig. 2. Rietveld refinement of thaumasite. Main plot: observed data—dotted line; calculated data—solid line. Lower plot: difference profile. Markers along horizontal axis indicate reflection positions: lower markers—thaumasite; upper markers—calcite.

there is a significant amount of poorly crystalline material in the sample. The results of the refinement showed that 14.0±0.5 weight-% of the sample is thaumasite.

7. Conclusions

Previous X-ray diffraction studies of thaumasite in cement and concrete have been confined to qualitative analysis and to quantification based on a few reflections in the pattern [2,3]. A novel application of methods which employ the whole of the powder pattern to systems containing thaumasite has been described here. The techniques of full pattern fitting and Rietveld refinement have been shown to be a useful tool in characterising these systems. The development of methods of quantification of thaumasite and related phases using the whole of the powder pattern, using these techniques, is now possible.

Table 1
Refined crystal structure of thaumasite

		Fractional co-ordinates		
		x	*y*	*z*
Ca(1)		0.1982(6)	−0.0073(10)	0.2512(28)
Si(1)		0	0	0.0026
C(1)		1/3	2/3	0.474(8)
S(1)		1/3	2/3	−0.0267(28)
O(1)	H_2O	0.4030(25)	0.2393(24)	0.2349(36)
O(2)		0.2579(21)	0.3992(22)	0.258(4)
O(3)		0.0047(32)	0.3480(34)	0.057(4)
O(4)		0.0155(24)	0.3480(35)	0.419(5)
O(5)	CO_3^{2-}	0.2037(16)	0.627(4)	0.464(4)
O(6)	SO_4^{2-}	0.1960(19)	0.624(4)	0.0407(39)
O(7)	OH^-	0.1367(33)	0.1344(31)	0.095(4)
O(8)		0.1340(32)	0.1216(30)	0.393(4)
O(9)		1/3	2/3	0.8289(33)

Table 2
Bond lengths for thaumasite (in Å)

Bond	Edge and Taylor model	Refined model
Within SiO_6 octahedra		
Si(1)–O(7)	1.835(7)	1.78(4)
Si(1)–O(8)	1.731(7)	1.82(4)
Within CaO_8 polyhedra		
Ca(1)-O(1)	2.45(3)	2.532(21)
Ca(1)-O(2)	2.50(2)	2.515(27)
Ca(1)-O(3)	2.43(1)	2.57(5)
Ca(1)-O(4)	2.40(1)	2.32(5)
Ca(1)-O(7a)	2.46(1)	2.57(5)
Ca(1)-O(7b)	2.48(1)	2.54(4)
Ca(1)-O(8a)	2.44(1)	2.39(5)
Ca(1)-O(8b)	2.46(1)	2.506(39)
Within SO_4^{2-} group		
S(1)-O(6)	1.47(1)	1.518(39)*
S(1)-O(9)	1.48(2)	1.50(4)*
Within CO_3^{2-} group		
C(1)-O(5)	1.29(1)	1.276(37)*

NB: Bonds that were constrained to their expected values are indicated by *. Expected interatomic distances[16] are Ca–O 2.29–2.82(±5), S–O 1.44–1.53(±4), and C–O 1.15–1.43.

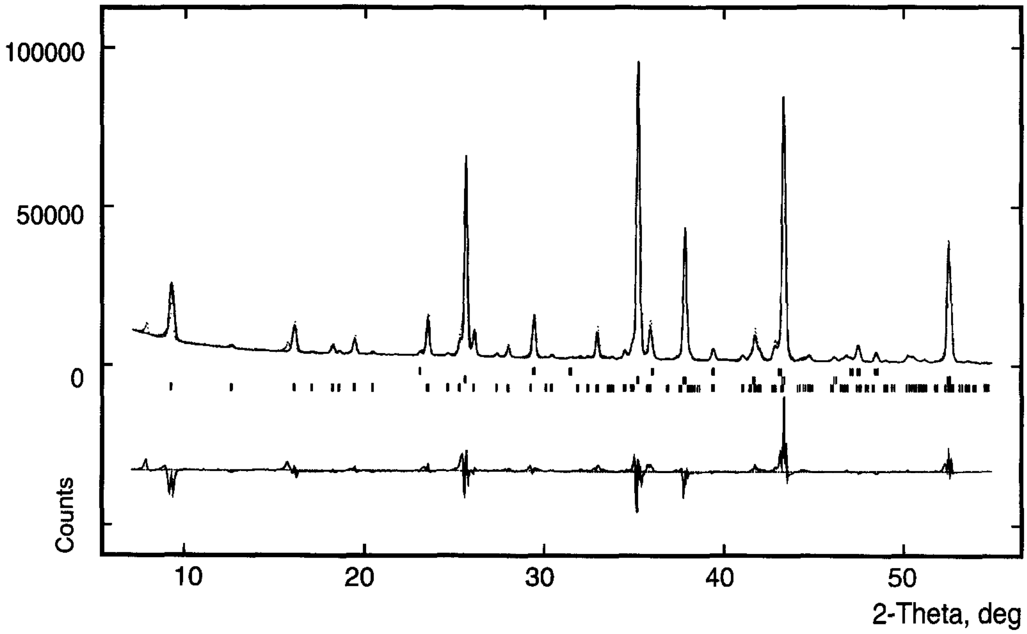

Fig. 3. Quantification of sample containing thaumasite. Main plot: observed data—dotted line; calculated data—solid line. Lower plot: difference profile. Markers along horizontal axis indicate reflection positions: lower markers—thaumasite; centre markers—corundum; upper markers—calcite.

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