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Structure of calcium aluminate decahydrate (CaAl₂O₄·10D₂O) from neutron and X-ray powder diffraction data

Received 22 November 2006

Accepted 18 July 2007

Calcium aluminate decahydrate is hexagonal with the space group $P6_3/m$ and $Z = 6$. The compound has been named CaAl₂O₄·10H₂O (CAH₁₀) for decades and is known as the product obtained by hydration of CaAl₂O₄ (CA) in the temperature region 273–288 K – one of the main components in high-alumina cements. The lattice constants depend on the water content. Several sample preparations were used in this investigation: one CAH₁₀, three CAD₁₀ and one CA(D/H)₁₀, where the latter is a zero-matrix sample showing no coherent scattering contribution from the D/H atoms in a neutron diffraction powder pattern. The crystal structure including the positions of the H/D atoms was determined from analyses of four neutron diffraction powder patterns by means of the *ab initio* crystal structure determination program *FOX* and the *FULLPROF* crystal structure refinement program. Additionally, eight X-ray powder diffraction patterns (Cu $K\alpha_1$ and synchrotron X-rays) were used to establish phase purity. The analyses of these combined neutron and X-ray diffraction data clearly show that the previously published positions of the O atoms in the water molecules are in error. Thermogravimetric analysis of the CAD₁₀ sample preparation used for the neutron diffraction studies gave the composition CaAl₂(OD)₈·(D₂O)₂·2.42D₂O. Neutron and X-ray powder diffraction data gave the structural formula CaAl₂(OX)₈(X₂O)₂· γ X₂O ($X = D, H$ and D/H), where the γ values are sample dependent and lie between 2.3 and 3.3.

1. Introduction

The main hydraulic phase in high-alumina cements is CaAl₂O₄ (CA). However, high-alumina cements additionally contain the compounds Ca₁₂Al₁₄O₃₃ (C₁₂A₇), Ca₂FeAlO₅ (C₄FA), Ca₂Al₂SiO₇ (C₂AS) and Ca₂SiO₄ (C₂S) (Bensted, 2002; Guirado *et al.*, 1998). In the hydraulic reaction, CaAl₂O₄ forms the hydrate CaAl₂(OH)₈(H₂O)₂·4H₂O or CaAl₂O₄·10H₂O (CAH₁₀) at temperatures below 288 K. The phase has been known since 1933 as a decahydrate (Assarsson, 1933), but recently Guirado *et al.* (1998) suggested that the structural formula CaAl₂(OH)₈(H₂O)₂·1.84H₂O or CaAl₂O₄·7.84H₂O would be more appropriate.

CAH₁₀ is a metastable phase and transforms slowly to the stable garnet phase Ca₃Al₂(OH)₁₂ (C₃AH₆) and gibbsite, Al(OH)₃. This transformation is coupled with changes in volume which lead to fatal changes in the strength of concrete-containing CAH₁₀ as one of the main constituents, and this in turn results in the collapse of buildings (Guirado *et al.*, 1998). The recent crystal structure analysis of CAH₁₀ reported by Guirado *et al.* (1998) was based on X-ray powder diffraction data only. The derived model had a rather open structure with

channels where water molecules could be located, but no H atoms were found. In concrete, knowledge of the crystal structure and in particular the positions of the water molecules are of the utmost importance. The present investigation using neutron and supplementary X-ray powder diffraction data was aimed at finding a more complete structure of the compound, starting with the published structure and adding the positions of hydrogen/deuterium atoms. The results of these powder diffraction analyses on samples of nominal compositions $\text{CaAl}_2\text{O}_4 \cdot 10\text{D}_2\text{O}$, $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}_{0.64}(\text{D}_2\text{O})_{0.36}$ and $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ are reported below.

2. Experimental

2.1. Chemistry

Aluminium hydroxide, $\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ (Aldrich), and calcium carbonate, CaCO_3 (Merck p. a.), were used in the synthesis of CaAl_2O_4 at 1573 K. Details of the solid-state synthesis have been reported previously (Christensen *et al.*, 2004). Hydration of CaAl_2O_4 powder, sifted through a

0.11 mm sieve, was made at 277 K using distilled water or heavy water from the DR3 reactor at Risø National Laboratory, Denmark. The nominal composition of the heavy water is 99.7% D_2O , but it could be somewhat lower. A drop of detergent was added to the liquids in order to reduce the surface tension of water. This improved the moistening of the CA powder considerably. The detergent content of the liquids was less than 0.01% by volume. The CA liquid suspensions were stirred with a magnetic stirrer for *ca* 3 weeks. The mixtures contained typically 7.5 g of CA and 50 g of liquid. In total, five sample preparations of calcium aluminate decahydrate were made (*A*, *B*, *C*, *D* and *E*). Three of these preparations (*A*, *B*, *C*) were made with nominal 99.7% D_2O . One preparation was made with a liquid made from 39.6 g of nominal 99.7% D_2O and 66.7 g of H_2O (*D*), and one preparation was made with H_2O (*E*). All manipulations made with mixtures containing D_2O were performed in a glove-bag filled with dry nitrogen or with the mixtures kept in closed glass flasks.

The suspensions of calcium aluminate decahydrate in water were filtered on a glass filter and dried in a desiccator over silica gel. At low temperature (277 K), the reaction between the solid CaAl_2O_4 and water is slow, so CaAl_2O_4 is a potential impurity in the reaction products. At slightly higher temperatures the hydrated phase $\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ (C_2AH_8) is formed, which appears as an impurity in some of the samples. Classical chemical thermogravimetric analyses were made on samples taken from preparations *C*, *D* and *E*. In these analyses, a 0.7 g sample was kept in a platinum crucible at 1573 K for 2 h. These analyses gave the compositions $\text{CaAl}_2\text{O}_4 \cdot 8.28\text{D}_2\text{O}$, $\text{CaAl}_2\text{O}_4 \cdot 8.33(\text{H}_2\text{O})_{0.64}(\text{D}_2\text{O})_{0.36}$ and $\text{CaAl}_2\text{O}_4 \cdot 9.43\text{H}_2\text{O}$, respectively.

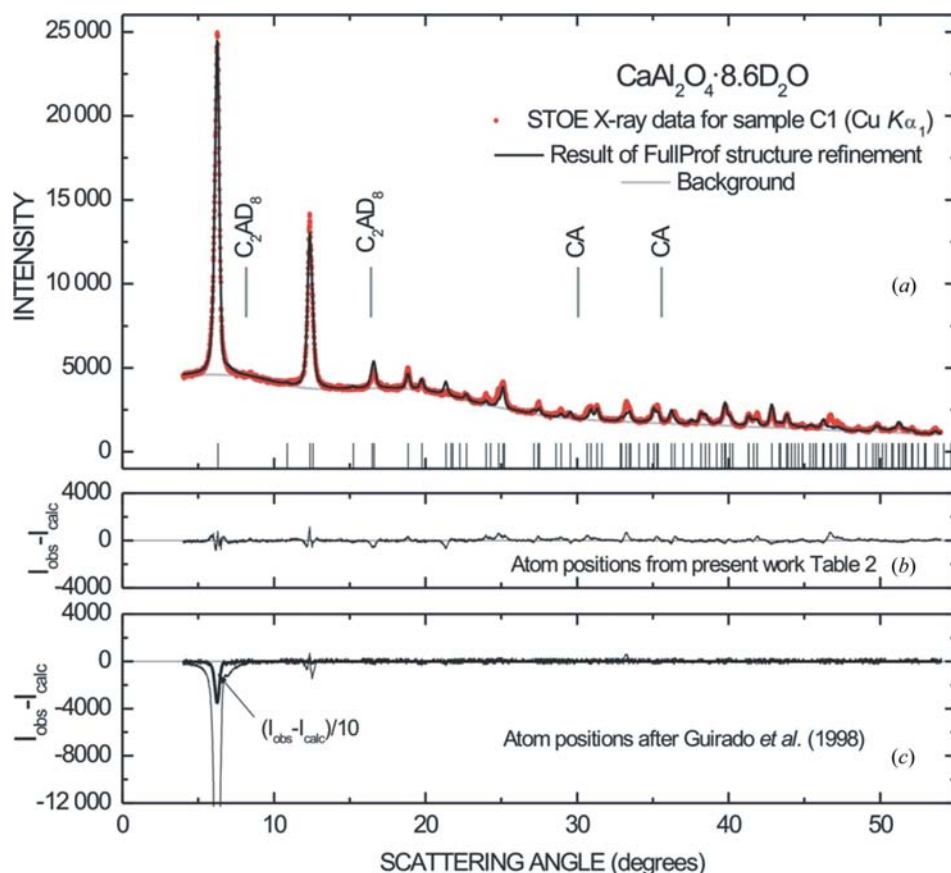
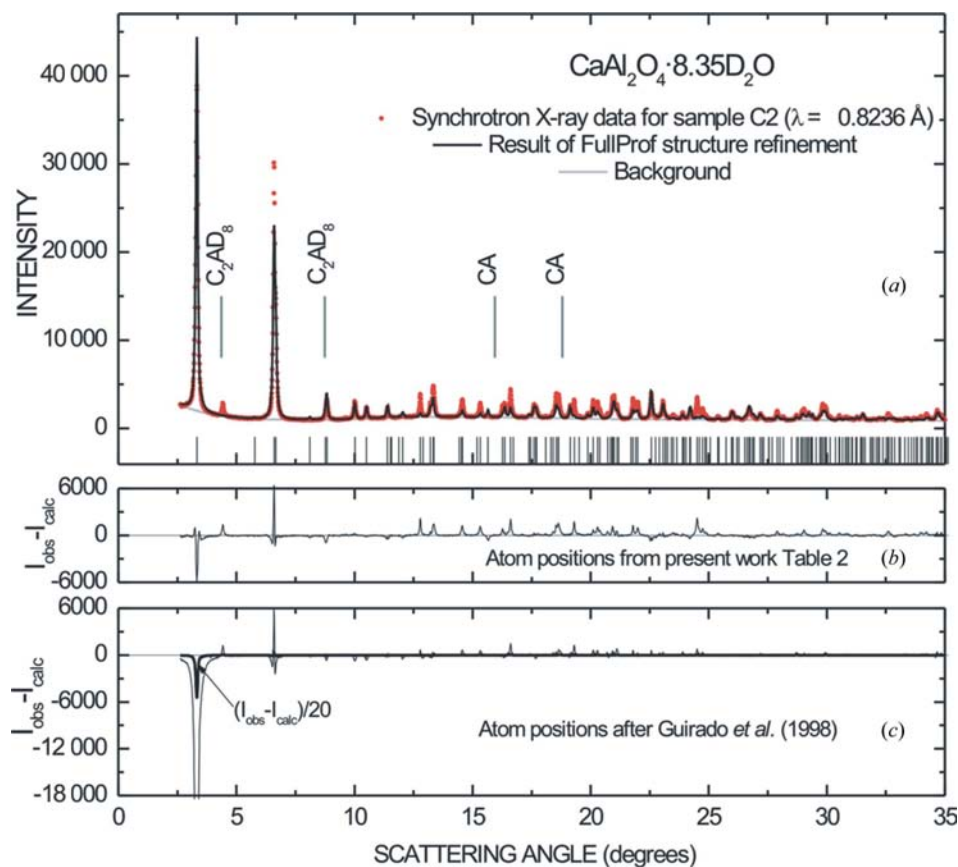


Figure 1

X-ray diffraction pattern for sample C1 obtained using a Stoe instrument in transmission mode with $\text{Cu } K\alpha_1$ radiation. The positions of the Bragg reflections are shown as vertical bars below the diffraction pattern. The vertical bars above the diffraction pattern indicate the positions of known impurity peaks (see §2.2). The difference between the measured diffraction data and intensities calculated from the atom positions given in the supplementary material are shown in (b). For details of the structure modelling and the *FULLPROF* refinement (see §§3 and 4). (c) shows the corresponding difference pattern based on the atom positions of Guirado *et al.* (1998) (see §3.2).

2.2. X-ray powder diffraction

X-ray powder diffraction patterns for phase identifications were measured at 300 K in transmission mode using a Stoe–Stadi powder diffractometer at the University of Aarhus, Denmark. Flat samples on tape were made from preparations *A1*, *B1*, *C1*, *D1* and *E1*. The radiation was $\text{Cu } K\alpha_1$ ($\lambda = 1.54059 \text{ \AA}$) and the diffractometer was calibrated with an external silicon standard ($a_{\text{Si}} = 5.43050 \text{ \AA}$). The position-sensitive


Figure 2

Synchrotron X-ray diffraction pattern for sample C2 obtained using the powder diffractometer at SLS/PSI in Switzerland using 0.8236 Å X-rays. For details see the caption to Fig. 1 and §§3.2 and 3.3.

detector covering 5° in 2θ was used in a step scan mode.

Additionally, samples (A2, B2 and C2) taken from the three preparations made with heavy water were used for synchrotron X-ray powder diffraction in order to obtain the most reliable information about impurities in the deuterated preparation selected for the subsequent neutron diffraction study. The synchrotron data were collected using the powder diffractometer at the SLS at PSI Villigen, Switzerland (samples A2 and C2), and the beamline X7A at NSLS, Brookhaven National Laboratory, USA (sample B2). These diffractometers have considerably higher intensity and somewhat better resolution than the Stoe instrument and showed several impurity peaks. The wavelengths for the synchrotron data were determined by intercalibrating the lattice parameters to the lattice parameters obtained from the Stoe diffraction data and were found to be 0.7057, 0.7100 and 0.8236 Å for samples A2, B2 and C2, respectively. All three samples were housed in glass capillaries of (0.3 and 0.4 mm) and rotated at 50 r.p.m. to randomize the crystallites.

The Cu $K\alpha_1$ and synchrotron X-ray powder patterns are all similar to the X-ray pattern of Guirado *et al.* (1998; ICSD #40-7150) and show strong peaks from $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ (ICDD card #12-0408) as expected, together with traces of peaks from CaAl_2O_4 (CA; ICDD card #23-1036) and $\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$

(C_2AH_8) (ICDD card #45-0564, crystal structure unknown). The strongest peaks from C_2AD_8 and CA are marked by vertical bars above the diffraction patterns in Figs. 1 and 2. The lowest-angle diffraction peak from C_2AD_8 is negligible in the Stoe diffraction pattern obtained for sample C1 (Fig. 1), but this and other impurity peaks are visible in the corresponding synchrotron X-ray pattern obtained for sample C2 (Fig. 2). The X-ray diffraction data from the other deuterated samples (A1, A2 and B1, B2) were similar. However, in the end the deuterated sample (C3) for the neutron diffraction was taken from sample preparation C, because the X-ray patterns from this sample have the weakest impurity reflections from C_2AD_8 and CA.¹

2.3. Neutron powder diffraction

Neutron diffraction powder patterns were measured with the HRPT diffractometer (Fischer *et al.*, 2000) at SINQ in PSI Villigen, Switzerland, using a wavelength of $\lambda = 1.8854$ Å. The patterns were measured in the 2θ range 4.0–164.8°

with steps of 0.1°. The C3 sample of nominal composition $\text{CaAl}_2\text{O}_4 \cdot 10\text{D}_2\text{O}$ was housed in a 10 mm diameter vanadium container and diffraction data sets were measured at 1.6 and at 79 K. The D3 and E3 samples of nominal compositions $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}_{0.64}(\text{D}_2\text{O})_{0.36}$ and $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ were housed in 8 mm diameter vanadium containers and diffraction data sets were measured at 1.6 K for sample D3 and at 1.6 and 300 K for sample E3. Impurities from C_2AH_8 and CA could not be identified in any of the neutron data.

3. Crystal structure solution

3.1. Determination of profile parameters, backgrounds and lattice parameters

In profile refinements of powder diffraction data the peak shapes are crucial. In the present study, pseudo-Voigt peak profiles were used for all patterns. The Gaussian part of the profile parameters (U , V , W) and asymmetry parameters for the Stoe data were determined from the data obtained for sample C1. These values were used when refining all the other

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: WS5055). Services for accessing these data are described at the back of the journal.

Table 1

Lattice parameters and agreement factors determined by *FULLPROF* refinement (Rodríguez-Carvajal, 1993) of the diffraction patterns from the samples *Ai*, *Bi*, *Ci*, *Di* and *Ei* (see §2.1 for details).

The indices *i* refer to the different types of radiation used to collect the diffraction data.

Sample	Radiation	Wavelength (Å)	Diffraction	<i>T</i> (K)	<i>a</i> (Å)	<i>c</i> (Å)	Refinement	χ^2_P	R^S_{wp}	R^S_{exp}	R^S_B
A1	X-ray, Cu $K\alpha_1$	1.54059	Stoe-Stadi powder	300	16.3323 (5)	8.2926 (4)	<i>FULLPROF</i>	17	28	6.6	18
A2†	Synchrotron X-ray	0.7057	SLS powder diffractometer, PSI	300	16.3422 (1)	8.2949 (1)	<i>FULLPROF</i>	14.6	36	4.5	20
B1	X-ray, Cu $K\alpha_1$	1.54059	Stoe-Stadi powder	300	16.3354 (5)	8.3144 (3)	<i>FULLPROF</i>	14.9	26	5.5	14.3
B2‡	Synchrotron X-ray	0.7100	X7A, NSLS, Brookhaven	300	16.328 (3)	8.330 (2)	<i>FULLPROF</i>	25	30	67	25
C1	X-ray, Cu $K\alpha_1$	1.54059	Stoe-Stadi	300	16.3411 (5)	8.3410 (3)	<i>FULLPROF</i>	11.5	20	7.0	12.6
C2†	Synchrotron X-ray	0.8236	SLS powder diffractometer, PSI	300	16.3433 (3)	8.2938 (2)	<i>FULLPROF</i>	10.6	32	5.8	23
C3	Neutron	1.8854	HRPT, SINO, PSI	1.6	16.3037 (4)	8.2760 (3)	<i>FULLPROF</i>	5.9	18	4.1	8.2
C3	Neutron	1.8854	HRPT, SINO, PSI	79	16.3062 (4)	8.2766 (3)	<i>FULLPROF</i>	5.3	17	4.1	8.2
D1§	X-ray, Cu $K\alpha_1$	1.54059	Stoe-Stadi powder	300	16.283 (3)	8.270 (4)	<i>FULLPROF</i>	29	42	7	32
D3 (1.6 K)	Neutron	1.8854	HRPT, SINO, PSI	1.6	16.3337 (6)	8.2836 (5)	<i>FULLPROF</i>	16	46	10.5	33
E1	X-ray, Cu $K\alpha_1$	1.54059	Stoe-Stadi powder	300	16.2823 (5)	8.3038 (3)	<i>FULLPROF</i>	19	24	10.8	19
E3 (1.6 K)	Neutron	1.8854	HRPT, SINO, PSI	1.6	16.280 (1)	8.327 (1)	<i>FULLPROF</i>	29	49	27	40
E3 (300 K)	Neutron	1.8854	HRPT, SINO, PSI	300	16.336 (1)	8.342 (1)	<i>FULLPROF</i>	15	38	11.9	34

† Diffraction pattern contaminated by many extra peaks. ‡ Poor peak-to-background ratio with a huge amorphous background bump from the SiO₂ glass capillary. § Increased step size, unreliable data.

Stoe diffraction patterns. For the synchrotron X-ray data the Gaussian parts of the profile parameters and the asymmetry parameters were determined from the individual patterns. The Gaussian part of the profile parameters for the neutron patterns was taken from the SINO web pages (The HRPT essentials, 2002; <http://sinq.web.psi.ch/sinq/instr/hrpt/manuals.html>). For the neutron data, the asymmetry parameters were determined for each pattern and found to be nearly equal. For all patterns the Lorentzian parts were composed by $X = 0$ and a sample-dependent Y value determined from the individual patterns. The background levels of the patterns were determined by *FULLPROF* (Rodríguez-Carvajal, 1993) in the profile-matching mode using interpolation between selected background points or a polynomial with six or 12 coefficients. For the neutron patterns, the low-angle part of the background (4–7°) had to be estimated manually because of the abrupt cut-off of the detector. The column χ^2_P in Table 1 serves as an indicator for the importance of the background and peak-profile modelling.

The neutron diffraction powder patterns of samples containing hydrogen (*D3* at 1.6 K and *E3* at 1.6 and 300 K) had, as expected, rather high backgrounds. For sample *E3* the peak-to-background ratio was so unfavourable that these patterns were excluded as input for the structure solution. However, the pattern with the best statistics (300 K) was later used in a *FULLPROF* model refinement (see §4.2). Unexpectedly, the backgrounds of the patterns for sample *C3* (1.6 and 79 K) were also surprisingly high. As great care was taken to avoid contamination of D₂O with H₂O in the preparations, the high backgrounds can possibly be ascribed to a considerable quantity of amorphous material in the samples. It has been reported that samples of CaAl₂O₄·10H₂O (CAH₁₀) do indeed contain considerable quantities of amorphous material (Guirado *et al.*, 1998).

Prior to the modelling and crystal structure refinements, all the X-ray diffraction patterns were indexed with the programs *DICVOL04* (Boultif & Louër, 2004) and *TREOR* (Werner *et al.*, 1985) on hexagonal cells. For the pattern obtained for sample *C2*, the former program gave $M(50) = 23.1$ and $F(50) = 125.8$ (the figures-of-merit are defined by Boultif & Louër, 2004) for a hexagonal cell with a volume of 1940.9 Å³, and $M(50) = 17.9$ and $F(50) = 96.0$ for the related orthorhombic cell with a volume of 970.1 Å³. The latter program gave $M(20) = 29$ for indexing of the hexagonal cell. Thus, there is convincing evidence that the unit cell is hexagonal. The d spacings of the indexed pattern and the observed intensities have been deposited.

The lattice parameters and agreement factors for all the diffraction patterns are listed in Table 1. The factor χ^2_P is the reduced chi-squared determined by *FULLPROF*, as defined by Rodríguez-Carvajal (1993), in the profile-matching mode (similar to the *ALLHKL* program by Pawley, 1981). R^S_{wp} , R^S_{exp} and χ^2_P are the conventional Rietveld factors with all non-excluded datapoints determined by *FULLPROF* in the structure refinement mode. See §4 and the *FULLPROF* manual for further details.

3.2. The reported crystal structure model

The reported structure solution of calcium aluminate decahydrate (Guirado *et al.*, 1998) gave the compound formula CaAl₂(OH)₈(H₂O)₂·1.84H₂O, corresponding to the overall formula CaAl₂O₄·7.84H₂O. Of the three possible space groups $P6_322$, $P6_3/m$ and $P6_3$, the structure was described in the hexagonal space group $P6_3/m$ with the unit-cell parameters $a = 16.387$ (2) and $c = 8.279$ (1) Å. The Ca atoms of the Guirado model are in special positions and the Al atoms are in general positions. The model has CaO₈ and AlO₆ coordination

Table 2

Number of free water molecules determined by the *FULLPROF* refinement of all the diffraction datasets.

Samples *Ai*, *Bi* and *Ci* are from deuterated sample preparations. Samples *Di* and *Ei* are from the zero matrix and the hydrogenated preparations, respectively. The indices *i* refer to the different types of radiation used in the diffraction data collection, where *i* = 1, 2 and 3 are for Cu *Kα*₁ X-rays, synchrotron X-rays and neutrons, respectively. See §§4.1 and 4.2 for further details.

Sample	Number of (H/D) ₂ O molecules per site			Number of free water molecules
	W #6, 6(<i>h</i>)	W #7, 12(<i>i</i>)	W #8, 12(<i>i</i>)	
A1	2.8 (1)	3.86 (7)	8.14 (7)	2.47 (2)
A2	1.57 (8)	6.11 (7)	5.89 (7)	2.26 (2)
B1	3.43 (8)	4.56 (7)	7.44 (7)	2.57 (2)
B2	4.5 (3)	6.9 (2)	5.1 (2)	2.74 (8)
C1	3.70 (8)	4.94 (6)	7.06 (6)	2.62 (2)
C2	2.1 (1)	7.0 (1)	5.0 (1)	2.35 (3)
C3	2.5 (1)	5.53 (7)	6.47 (7)	2.42 (2)
D1	(7.7)	(8.7)	(3.3)	(3.3)
D3	7.7 (3)	8.7 (3)	3.3 (3)	3.3 (1)
E1	4.1 (1)	7.4 (1)	4.6 (1)	2.68 (2)
E3	5.6 (4)	5.0 (4)	7.0 (4)	2.9 (1)

polyhedra with ring-shaped units of three edge-sharing Ca(OH)₆(H₂O)₂ polyhedra, and zigzag chains of AlO₆ octahedra along the *c* axis of the structure.

The Guirado structure was solved using direct methods which, however, were unable to locate the positions of the Al atoms. Hence the Al-atom positions were estimated from crystallochemical considerations. The profile refinement of the X-ray powder data quoted reliability values of $R_p^S = 0.167$, $R_{wp}^S = 0.180$, $R_B^S = 0.086$ and $\chi_S^2 = 3.5$. The first reflection in the reported X-ray powder pattern is the strongest reflection. The second peak has an intensity of approximately 50% of the first peak, whereas all the remaining reflections are weak; each with intensities less than 5% of the first strong reflection. In the published work (Guirado *et al.*, 1998), the first strong reflection was excluded from the refinement, which, as will be shown below, resulted in erroneous positions of the water molecules. The reported difference plot shows an acceptable agreement between the observed and calculated patterns. However, the difference plot for the first very strong reflection of the pattern is omitted (see Guirado *et al.*, 1998; Fig. 2).

3.3. Comparison with the Guirado structure model

Several complete X-ray powder diffraction patterns from the present investigation were used to test the published Guirado model described above by means of *FULLPROF* (Rodríguez-Carvajal, 1993). None of them could be modelled satisfactorily. As examples of this, Figs. 1 and 2 show the diffraction data obtained for samples C1 and C2. Figs. 1(c) and 2(c) show the difference patterns obtained in a refinement of the same datasets using atom coordinates and temperature factors of the Guirado model (Guirado *et al.*, 1998). The scale factors were chosen to match the second peak (101 and 200) and the zero-point, unit-cell parameters and profile parameters were determined as described in §3.1. The figures

Table 3

Shortest distances (Å) between the atoms in the crystal structure of CaAl₂O₄·8.42D₂O.

Standard uncertainties are for Ca—O bonds 0.017–0.040 Å, for Al—O bonds 0.016–0.020 Å and for O—D bonds 0.020–0.050 Å.

Al—O1	1.887	O6—O7	3.752
Al—O2	2.024	O6—O8	3.199
Al—O3	1.937	O6—O9	2.736
Al—O4	1.855	O7—O8	2.373
Al—O5	1.855	O7—O9	4.139
Al—O2'	1.930	O8—O9	2.620
O1—O2	3.888	O1—D1	1.040
O1—O3	2.379	O2—D2	1.073
O1—O4	2.660	O3—D3	1.076
O1—O5	2.730	O4—D4	1.074
O1—O2'	2.833	O5—D5	0.979
O2—O3	2.839	O2'—D2'	1.073
O2—O4	3.011		
O2—O5	2.707	O6—D61	1.108
O2—O2'	2.532	O6—D62	1.121
O3—O4	3.743	O7—D71	1.118
O3—O5	2.348	O7—D72	1.072
O3—O2'	2.807	O8—D81	1.038
O4—O5	2.633	O8—D82	1.098
O4—O2'	2.950		
O5—O2'	3.748	O9—D91	1.159
		O9—D92	1.028
Ca—Al	3.139		
Ca—O3	2.575	D71—D71'	0.606
Ca—O5	2.403	D72—D82'	1.300
Ca—O9	2.511		

illustrate clearly that it was ill-advised to exclude the first and strongest reflection in the refinements (Guirado *et al.*, 1998). The reliability values for Figs. 1(c) and 2(c) are $R_B^S = 0.75$, $\chi_S^2 = 362$ and $R_B^S = 0.78$, $\chi_S^2 = 798$, respectively. In contrast to Figs. 1(c) and 2(c), the difference patterns in Figs. 1(b) and 2(b) show much better agreement between observed and calculated diffraction patterns, in particular for the first Bragg peak. Here the latter patterns are determined when using the atom positions derived from the structure modelling and refinement to be described in §§3.4 and 4.

In fact, the reported Guirado model (Table 1 in Guirado *et al.*, 1998) has unrealistic displacement parameters for two, partly occupied O atoms representing water molecules not bonded to the framework structure. Not surprisingly, it was actually possible to fit the X-ray data equally well when excluding these O atoms of water molecules from the refinement. As a further test, the displacement factors were given the values of the O atoms of the framework structure, and their occupancies were refined. This gave negative values of the occupancy factors. Also, refinement of the neutron diffraction pattern obtained for sample D3 failed, although this pattern should have been adequately described by the Guirado model because sample D3 was prepared with a so-called zero-matrix mixture of H₂O and D₂O having a negligible scattering contribution to the Bragg reflections from the H/D atoms.

Owing to these failures, it was obviously necessary to find a more suitable crystal structure model before attempting a structure refinement, including all atoms and molecules.

Table 4

Bond angles ($^{\circ}$) between the atoms in the crystal structure of $\text{CaAl}_2\text{O}_4 \cdot 8.42\text{D}_2\text{O}$.

Standard deviations on angles are less than 2° .

O1—Al—O2	166.4	Al—O1—D1	114.4
O1—Al—O3	76.9	Al—O2—D2	134.3
O1—Al—O4	90.6	Al—O3—D3	100.5
O1—Al—O5	93.7	Al—O4—D4	113.6
O1—Al—O2'	95.8	Al—O5—D5	120.3
O2—Al—O3	91.5	Al—O2'—D2'	105.8
O2—Al—O4	101.8		
O2—Al—O5	88.4	D91—O9—D92	112.3
O2—Al—O2'	76.6		
O3—Al—O4	161.1	D61—O6—D62	108.5
O3—Al—O5	76.5	D71—O7—D72	113.1
O3—Al—O2'	93.1	D81—O8—D82	115.0
O4—Al—O5	90.4		
O4—Al—O2'	102.4		
O5—Al—O2'	163.9		

3.4. Model determination by the *ab initio* program FOX

The FOX program by Fèvre-Nicolin & Cerny (2004) is a model-building program working in direct space. The program builds crystal structure models from atoms, coordination polyhedra or molecules and compares the observed powder diffraction pattern with diffraction patterns calculated from the models.

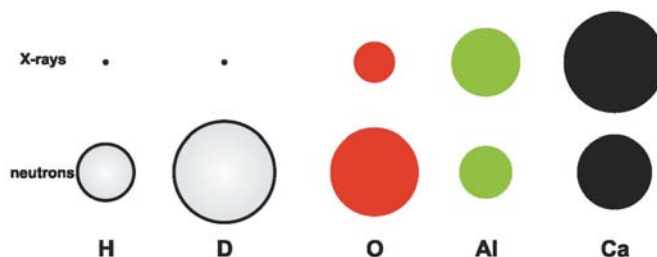
3.4.1. Preliminary simulations by FOX. The X-ray pattern obtained for sample C2 was used with the program FOX in attempts to solve the structure in the three possible space groups $P6_322$, $P6_3/m$ and $P6_3$. The reflections at $\sin \theta/\lambda$ larger than 0.17 are weak and in order to give these reflections an acceptable total weight, the pattern out to $\sin \theta/\lambda = 0.45$ was used. The AlO_6 octahedra were used in a rigid-body model with Al—O distances of 1.90 Å. At the start all the atoms were placed at the origin. In the space group $P6_322$ a model was found where the Ca atoms were placed statistically in 12 positions. This model was rejected. In the space group $P6_3/m$ the starting coordinates were those of the published structure. This calculation gave a packing of Ca atoms and AlO_6 octahedra similar to the published structure. However, this was not the case for the O atoms representing the water molecules in the large channels. In the space group $P6_3$ the starting model contained one Ca atom, two AlO_6 octahedra with the Al—O distances 1.90 Å, and four O atoms, representing water molecules. The derived model had six AlO_6 octahedra arranged in a ring. A similar model has previously been suggested for the structure of CAH_{10} , but not confirmed in a refinement of the model (Richard *et al.*, 1995). A refinement of the present data using the model of Richard *et al.* was not successful, because the model could not refine to positions where the AlO_6 octahedra were forming a network.

Thus, also the FOX simulations established that the space group is $P6_3/m$, in agreement with previous findings and hence the FOX model described above for the space group $P6_3/m$ was used as an input model for the FULLPROF program (Rodríguez-Carvajal, 1993) in a structure refinement of the synchrotron X-ray powder diffraction pattern of sample C2. The calculated intensities for the two first and strongest

reflections are extremely dependent upon the positions of the O atoms in the large channels formed by the framework structure. During the FULLPROF refinement these atoms moved rather far away both from the starting positions and the Guirado positions. Convergence could not be achieved, but the refinement seemed to settle with reliability values considerably lower than the values calculated from the published atomic coordinates (see §3.3).

3.4.2. An independent determination of the Ca, Al and O atoms by FOX simulation. In order to find an independent model for the $P6_3/m$ space group a FOX simulation of a combined set of diffraction patterns was made. The choice of patterns was two representative X-ray patterns, Stoe A1 and synchrotron data C2 and the neutron diffraction pattern without contribution from H or D atoms, D3. The reasoning for this choice of datasets can be illustrated by considering the relative scattering powers for the different elements in the structure and the type of radiation used. From Fig. 3 it is obvious that the contribution from the Ca and Al atoms will dominate the X-ray diffraction patterns, while the contribution from the O and Ca atoms dominates the neutron pattern of the zero-matrix sample D3. Therefore, it was supposed that the simulation of the combined data could give a better estimate of the oxygen positions than that provided by the X-ray data alone.

The published nominal composition of the compound is $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ (Assarsson, 1933) or in an ionic form $\text{CaAl}_2(\text{OH})_8 \cdot 6\text{H}_2\text{O}$. According to Guirado *et al.* (1998) five OH ions are part of the AlO_6 octahedra and one atom is bonded to the Ca ion as part of a water molecule in the framework composed of $\text{CaAl}_2(\text{OH})_8(\text{H}_2\text{O})_2$. The maximal number of water molecules in the channels is thus four. The starting configuration was chosen to be one Ca atom, one AlO_6 octahedron and four O atoms all placed in the origin. As in the previous FOX simulations the AlO_6 octahedra were used in a rigid-body model with constrained distances and angles. As before, the Ca atoms, one O atom and the AlO_6 octahedra converged quickly towards the positions of the Guirado model with two almost coinciding O atoms in nearest-neighbour canted octahedra (eventually replaced by one shared O atom). However, the positions of the O atoms of the water molecules in the large channels were quite different from both the Guirado model and the previous attempts by

**Figure 3**

Relative scattering powers of the Ca, Al, O, D and H atoms. The areas of the circles are proportional to N^2 (N = atomic number) and b^2 (b = neutron scattering amplitude) for X-rays and neutrons, respectively. The circle sizes are comparable within a row but not between rows.

FOX simulation (§3.4.1). Furthermore, the agreement to the diffraction pattern of sample *D3* was poor presumably because the *FOX* simulation weighted the X-ray patterns more than the neutron pattern, which is not optimal for determining the oxygen position.

3.4.3. Determination of the water O atoms by *FOX* simulation. A final attempt to find the O atoms of the water molecules was made by a *FOX* simulation using the Ca atom and the AlO_6 coordination polyhedra of Guirado *et al.* (1998) as the starting positions, and the diffraction patterns of sample *D3* only (zero matrix). Five additional O atoms were placed in the origin at the start of the simulation. The simulation quickly converged and showed that indeed only four loose O atoms (not fully occupied) were needed in agreement with the findings of Assarsson (1933). One of these O atoms was attached to Ca as part of the framework structure composed of the CaO_8 and AlO_6 coordination polyhedra. The three other O atoms were accommodated in the large channels parallel to the *c* axis.

Subsequently, individual *FULLPROF* refinements (Rodríguez-Carvajal, 1993) of the X-ray diffraction patterns for samples *A1* and *C2*, and the neutron pattern of sample *D3* were carried out. The atom coordinates of Ca, Al and O were those found by the *FOX* simulation. Only a scale factor and the occupancies of the three 'loose' O atoms were refined. The background and the instrumental parameters were deter-

mined as described in §3.1 and kept fixed during the *FULLPROF* crystal structure refinement. The results of these refinements established that this crystal structure model was adequate as a starting model to find the positions of the H/D atoms.

3.4.4. Determination of the D atoms by *FOX* simulation. Once the positions of the Ca, Al and O atoms were established it is obvious (see Fig. 3) that the neutron diffraction patterns of sample *C3* and/or *E3* would be the best to determine the positions of the D or H atoms. Since the peak-to-background ratio of the pattern of the hydrogenated sample was very poor, only the diffraction pattern of the deuterated sample *C3* taken at 79 K was used. The starting configuration of this final *FOX* simulation was the atom coordinates determined in §3.4.3. The O atoms of the AlO_6 shared octahedra were replaced by OD groups and the O atoms at the remaining four oxygen sites were replaced by D_2O molecules with appropriate constraints on atom distances (OD distance 1.1 Å) and angles (Al–O–D and D–O–D angle 110°). Two O atoms of the OD ions and one of the D_2O molecules had *z* coordinates equal to 1/4 [$6(h)$ site]. Consequently, the *z* coordinates of the corresponding D atoms were fixed at 1/4. As a start, only the D atoms were allowed to move. Once the simulation seemed to converge, the O atoms were set free with additional bounds on the Al–O and Al–D distances, and after a few more cycles, a reasonable agreement between the model and the observed diffraction

pattern of *C3* was achieved. The positions of the D atoms in the OD groups and in the four water molecules determined by the *FOX* simulation agree well with the positions found when using packing considerations.

This final *FOX* simulation confirmed the previous result (§3.4.3), *i.e.* part of the framework structure, that one of the D_2O sites is fully occupied and that three other D_2O molecules accommodated in the large channels parallel to the *c* axis are only partially occupied.

4. Crystal structure refinement using *FULLPROF*

The complete crystal structure model derived in §3.4.4 was now used as an input structure for the *FULLPROF* (Rodríguez-Carvajal, 1993) refinement of the neutron diffraction patterns of sample *C3* (see §4.1). Soft constraints were applied with Al–O distances from 1.88 to 1.92 Å, Ca–O distances from 2.52 to 2.58 Å, O–D distances of 1.08–1.12 Å and D–D distances in the water molecules of 1.78–1.82 Å. The displacement factors were fixed to $B = 1$ for the Ca, Al and O atoms and to $B = 2$ for the D atoms.

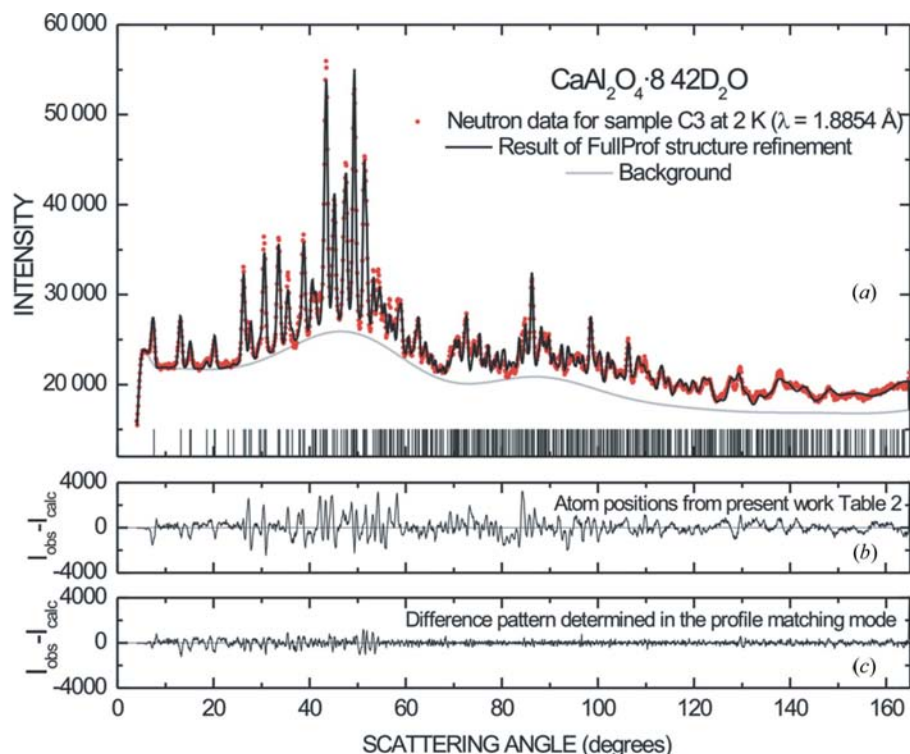


Figure 4 Neutron diffraction pattern for sample *C3* obtained at the HRPT neutron powder diffractometer at SINQ/PSI in Switzerland using 1.8854 Å neutrons. The positions of the Bragg reflections are shown as vertical bars below the diffraction pattern. (b) and (c) show the corresponding difference patterns obtained by *FULLPROF* in the structure refining mode and in the profile-matching mode, respectively (see §4 and *Appendix A*).

4.1. FULLPROF refinement of the deuterated sample C3

The refinement of the C3 diffraction patterns obtained at 1.6 and 79 K were first carried out individually, which (within the experimental accuracy) resulted in identical sets of atom coordinates. Therefore, the final refinement of the C3 neutron diffraction data was a combined refinement using the multi-pattern option of *FULLPROF*, where the two sets of scale factors and lattice parameters varied independently while the atom coordinates and site occupancies were constrained to have the same values at both temperatures. Individual backgrounds were used but they were the same within experimental accuracy. Further details of the final refinement procedure are outlined in *Appendices A1* and *A2*.

The atomic coordinates and occupancies for the final *FULLPROF* refinement (*Appendix A2*) of the neutron diffraction patterns of sample C3 have been deposited. The corresponding number of water molecules is listed in Table 2. Some selected interatomic distances and angles are listed in

Tables 3 and 4. The corresponding *d* spacings and the observed and calculated intensities have been deposited. Fig. 4 shows the diffraction pattern obtained for sample C3 at 1.6 K (filled circles). The model calculation using the refined structure is shown as the black curve in Fig. 4(a). The difference between observed data and the model calculation is shown in Fig. 4(b). Fig. 4(c) shows the corresponding difference pattern obtained by *FULLPROF* in the profile-matching mode. The patterns for sample C3 at 79 K are similar.

The crystal structure of $\text{CaAl}_2\text{O}_4 \cdot 10\text{D}_2\text{O}$ nominally determined based on the atom coordinates given in the supplementary material is illustrated in Fig. 5. The upper part of the figure shows the *ab* plane projection of one unit cell. The lower part of the figure shows a projection on the *ac* plane of two unit cells in the *c* direction and one unit cell in the *ab* plane. It should be noted that some single D atoms visible in the crystal structure drawings are in fact bound to O atoms lying outside the limits of the drawing.

4.2. FULLPROF refinement of the hydrogenated and zero-matrix samples

Once the *FULLPROF* refinement of sample C3 had converged, the atom positions given in the supplementary material were used to refine the scale factors and occupancies of the free water molecules of the different samples taken from all the synthesized preparations using the diffraction patterns obtained by neutron and $\text{Cu } K\alpha_1$ or synchrotron X-ray radiation. Only the scale factors and the occupancies of water molecules in the large channels (D_2O^6 , D_2O^7 and D_2O^8) were refined. The atom coordinates and the displacement factors were fixed at the values quoted in the supplementary material. The number of water molecules are summarized in Table 2 and the corresponding *R* factors are listed in Table 1.

The reliability factors for the structure fits listed in Table 1 are quite large in particular for the datasets obtained by X-ray and synchrotron radiation. There may be several factors which could explain this. Firstly the impurity phases play a more dominant role in these diffraction patterns than in the neutron patterns where they are not even visible and most probably hidden in the background. A second reason could be that the structural parameters given in the supplementary material were derived for the fully deuterated sample at low temperature while the X-ray and synchrotron data were all measured at ambient temperature. Thirdly, the sample contains different amounts of free water molecules in the large channels and this may affect the actual positions of these molecules. Finally, it is also plausible that the atom positions could depend somewhat on the hydrogen isotope in the actual sample.

In order to test this latter speculation a structure refinement was made of the neutron diffraction data obtained for the hydrogenated sample E3 at 300 K, for which the statistics were much better than for the corresponding dataset obtained at 1.6 K. Despite the fact that the E3 datasets have very poor peak-to-background ratios, the 300 K data for E3 were used for this test because the neutron diffraction pattern of the

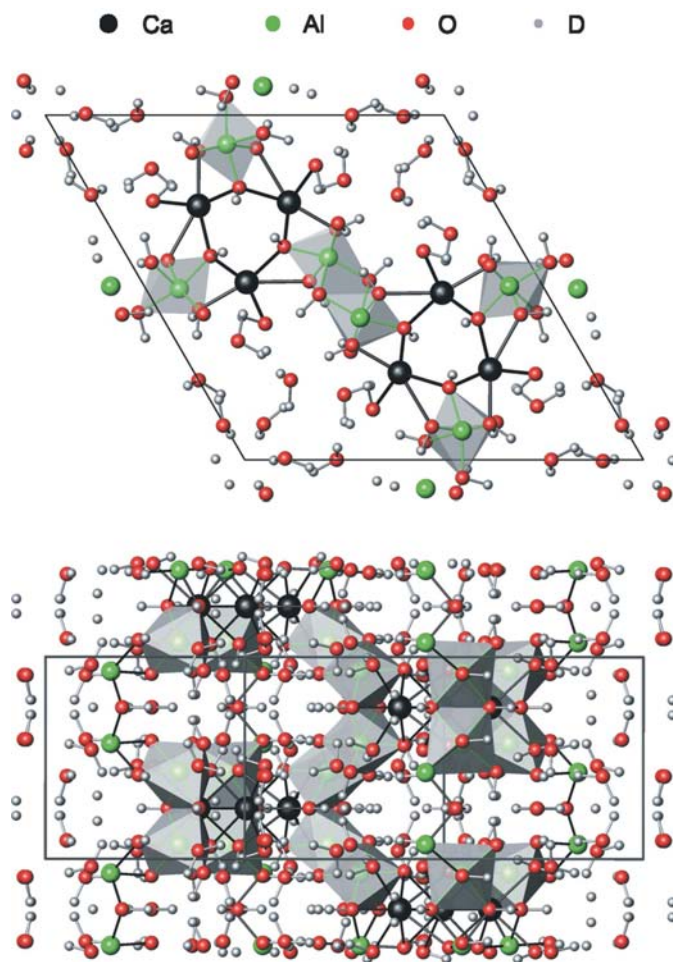


Figure 5

The crystal structure of $\text{CaAl}_2\text{O}_4 \cdot 10\text{D}_2\text{O}$ determined from neutron diffraction data obtained for sample C3 at 1.6 and 79 K. The upper part of the figure shows the *ab* plane projection of one unit cell. The lower part of the figure shows a projection on the *ac* plane of two unit cells along the *c* direction and one unit cell in the *ab* plane. The Ca, Al, O and D atoms are shown as spheres of decreasing size.

Table 5

Shortest distance (Å) between the atoms in the crystal structure of $\text{CaAl}_2\text{O}_4 \cdot 9.00\text{H}_2\text{O}$.

Standard uncertainties are for Ca—O bonds 0.020–0.030 Å, for Al—O bonds 0.020–0.030 Å and for O—H bonds 0.020–0.030 Å.

Al—O1	1.904	O6—O7	3.812
Al—O2	1.840	O6—O8	3.258
Al—O3	1.842	O6—O9	2.585
Al—O4	1.897	O7—O8	2.649
Al—O5	1.920	O7—O9	4.063
Al—O2'	1.853	O8—O9	2.430
O1—O2	3.738	O1—H1	1.115
O1—O3	2.402	O2—H2	1.087
O1—O4	2.862	O3—H3	1.052
O1—O5	2.543	O4—H4	1.084
O1—O2'	2.726	O5—H5	1.112
O2—O3	2.703	O2'—H2'	1.087
O2—O4	2.591		
O2—O5	2.747	O6—H61	1.101
O2—O2'	2.603	O6—H62	1.115
O3—O4	3.732	O7—H71	1.114
O3—O5	2.567	O7—H72	1.095
O3—O2'	2.664	O8—H81	1.076
O4—O5	2.630	O8—H82	1.075
O4—O2'	2.753		
O5—O2'	3.771	O9—H91	1.076
		O9—H92	1.108
Ca—Al	3.550		
Ca—O3	2.592	H71—H71'	1.501
Ca—O5	2.387	H72—H82'	1.440
Ca—O9	2.535		

zero-matrix sample *D3* reveals no information about the hydrogen positions. The starting parameters for the structure refinement were the atom coordinates given in the supplementary material, and eventually all the atom coordinates were refined. However, when considering Fig. 3 it is obvious that the atoms cannot be included in the refinement in the same order as that used for the refinement of the deuterated sample *C3* (Appendix A). After a few trials, the following scheme was adopted. First the O atoms of the Al coordination polyhedra were refined to convergence, then the Ca atom, the H atoms of the Al coordination polyhedra, the water molecule of the framework structure and the Al atom were included one by one and each refined to convergence with a steady improvement of the reliability factors. Finally, the coordinates of the water molecules were refined, while all the other atom coordinates remained fixed at the values reached. Throughout this refinement the sum of the occupancies of the 12(*i*) site water molecules (H_2O^7 and H_2O^8) was constrained to 12.

The result of this refinement of sample *E3* at 300 K is listed in Tables 5 and 6, and the supplementary material. The reliability factors for refinement of the diffraction pattern of sample *E3* at 300 K improved from $R_p^S = 0.45$, $R_B^S = 0.40$, $R_F^S = 0.25$ and $\chi^2 = 10.5$ using the coordinates given in the supplementary material (Fig. 6c) to $R_p^S = 0.29$, $R_B^S = 0.18$, $R_F^S = 0.106$ and $\chi^2 = 4.2$ using the coordinates given in the supplementary material (Fig. 6b). As before, R_p^S is the conventional Rietveld *R* factor. The number of channel water molecules changed from 5.6 (4), 5.0 (4) and 7.0 (4) to 6, 5.8 (3) and 6.2 (3) for H_2O^6 , H_2O^7 and H_2O^8 , respectively, corresponding to a change in the total amount of free water molecules from

Table 6

Bond angles (°) between the atoms in the crystal structure of $\text{CaAl}_2\text{O}_4 \cdot 9.00\text{H}_2\text{O}$.

Standard deviations on angles are less than 2°.

O1—Al—O2	173.7	Al—O1—H1	98.7
O1—Al—O3	79.7	Al—O2—H2	123.4
O1—Al—O4	97.7	Al—O3—H3	110.0
O1—Al—O5	83.4	Al—O4—H4	103.5
O1—Al—O2'	93.0	Al—O5—H5	95.6
O2—Al—O3	94.4	Al—O2'—H2'	107.7
O2—Al—O4	87.8		
O2—Al—O5	93.8	H91—O9—H92	112.4
O2—Al—O2'	89.6		
O3—Al—O4	172.9	H61—O6—H62	110.3
O3—Al—O5	86.0	H71—O7—H72	106.8
O3—Al—O2'	92.3	H81—O8—H82	114.5
O4—Al—O5	87.1		
O4—Al—O2'	94.5		
O5—Al—O2'	176.2		

2.9 (1) to 3.0 (1), *i.e.* well within the error limits. The reliability factors are still not brilliant, but acceptable when considering the poor peak-to-background ratio and the good agreement between the observed and calculated diffraction patterns (see Fig. 6).

The crystal structure described by the coordinates given in the supplementary material is quite similar to the structure shown in Fig. 5. The framework structure is twisted slightly and the water molecules, in particular the H_2O^7 and H_2O^8 molecules, have moved apart (see Table 5). Fig. 6(a) shows the neutron diffraction pattern obtained for the hydrogenated sample *E3*. Fig. 6(b) shows the difference pattern between the observed and calculated diffraction patterns using the atom positions and occupancies given in the supplementary material. Fig. 6(c) shows the corresponding difference pattern obtained using the atom positions and occupancies given in the supplementary material.

5. Summary and discussion

The previously published structure of calcium aluminate decahydrate was based on a crystal structure analysis of powder X-ray diffraction, where the first and most dominant peak in the pattern was excluded (Guirado *et al.*, 1998). Fig. 2 of Guirado's paper displays the diffraction pattern in the 2θ range 5–100° with the section from 5 to 70° shown on an enlarged scale. An illumination correction was applied to the peaks below $2\theta = 24^\circ$. The difference plot is displayed only in the 2θ range 9–70°. The first and very intense diffraction peak at $\sim 6.3^\circ$ could not be properly corrected and was excluded from the refinement (Guirado *et al.*, 1998). The meaning of an illumination correction is unclear and the exclusion of a reflection which could not be reproduced with a proper intensity by the model is an error. With the first reflection included in the pattern, the difference plot in Fig. 2 of Guirado *et al.* (1998) would have shown a discrepancy similar to that displayed in Figs. 1(c) and 2(c) of the present work.

The structure of Guirado *et al.* (1998) has a framework of CaO_8 and AlO_6 coordination polyhedra, and wide channels where water molecules could be located. The present inves-

tigation uses neutron diffraction patterns as well as Cu $K\alpha_1$ and synchrotron X-ray powder diffraction patterns, and the first strong reflection of the X-ray patterns has naturally been included in the analysis. The structure building program *FOX* (Fávre-Nicolin & Cerny, 2004) was used and confirmed the framework part of the structure, but could not confirm the published positions of the O atoms associated with the water molecules in the channels. The positions of the hydroxide ions and water molecules were located by means of the *FOX* program using neutron powder diffraction data. Finally, the coordinates of all the atoms and the occupancies of the water molecules in the channels were refined by a full-profile crystal structure analysis of the neutron diffraction data using the *FULLPROF* program (Rodríguez-Carvajal, 1993). Illustrative drawings of the crystal structure by means of the program *ATOMS* are shown in Figs. 5 and 7.

Two types of diffraction data (X-rays and neutrons) and three types of sample preparations [nominal $\text{CaAl}_2\text{O}_4 \cdot 10\text{D}_2\text{O}$, $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ and $\text{CaAl}_2\text{O}_4 \cdot 10(\text{H}_2\text{O})_{0.64}(\text{D}_2\text{O})_{0.36}$] were used in these investigations. Each of these data sets plays an important role in achieving the final result. The X-ray diffraction data showed that the present diffraction data were similar to the data used by Guirado *et al.* (1998). The zero-matrix sample $\text{CaAl}_2\text{O}_4 \cdot 10(\text{H}_2\text{O})_{0.64}(\text{D}_2\text{O})_{0.36}$, which has zero neutron-scattering contribution from the H atoms, shows

beyond doubt that the previously published positions of the O atoms of the water molecules were incorrect. Finally, the $\text{CaAl}_2\text{O}_4 \cdot 10\text{D}_2\text{O}$ and $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ neutron diffraction patterns were essential for the determination of the hydrogen positions.

The use of neutron diffraction data implies the synthesis of deuterated samples. The reaction between CaAl_2O_4 and D_2O must take place in the temperature range 273–288 K and goes possibly through an amorphous stage. The samples used in this investigation were prepared during a long period of time and the quantity of crystalline material in the samples of CAD_{10} or CAH_{10} is larger than in samples where only CA has reacted with water for a few days. This may explain why Guirado *et al.* (1998) obtained the CAD_{10} sample which could not be used for a powder neutron diffraction crystal structure analysis because only a few peaks emerged on an intense background.

Our powder neutron diffraction patterns at 1.6 and 79 K of the deuterated sample had surprisingly high backgrounds. This may be ascribed to the content of amorphous material in the sample and to a disorder of the water molecules in the wide channels of the structure. The high background of the patterns made the model calculations with *FULLPROF* (Rodríguez-Carvajal, 1993) difficult, but a satisfactory background was achieved through an iterative process. Attempts to refine the displacement parameters individually showed a high degree of

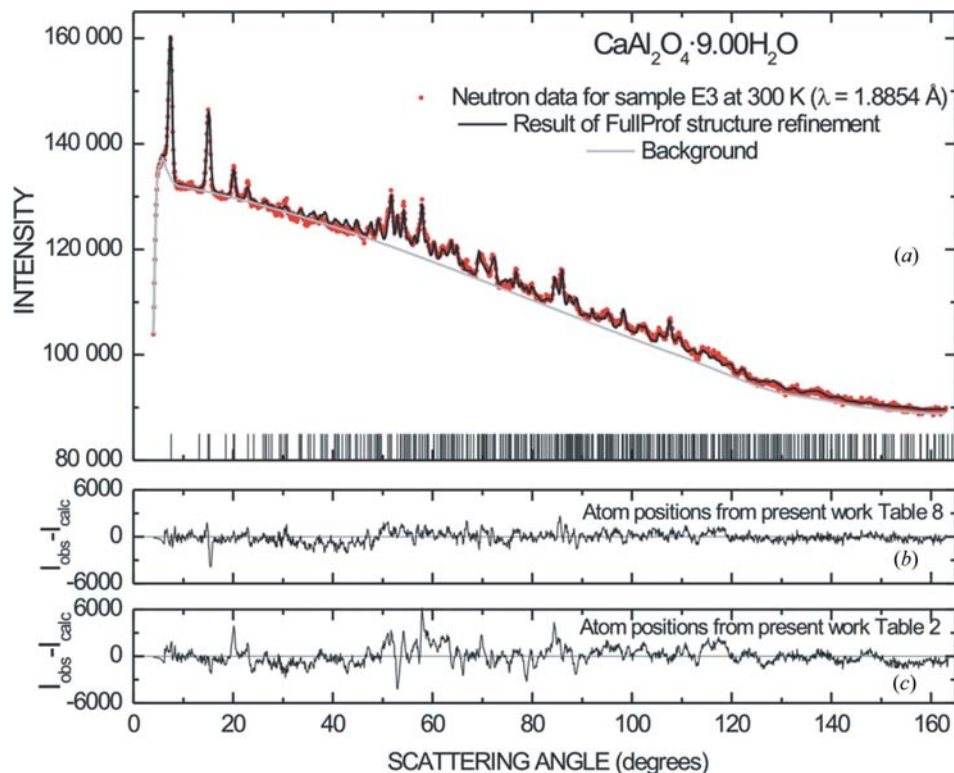


Figure 6

Neutron diffraction pattern for sample *E3* obtained at the HRPT neutron powder diffractometer at SINQ/PSI in Switzerland using 1.8854 Å neutrons. The positions of the Bragg reflections are shown as vertical bars below the diffraction pattern in Fig. 6. The difference between the measured diffraction data and the patterns calculated using the atom positions and occupancies given in the supplementary material and two are shown in (b) and (c), respectively.

correlation to the background and the occupancies of the water molecules in the channels. Therefore, the displacement parameters were fixed at what is considered to be realistic values at low temperatures ($B = 1 \text{ \AA}^2$ for Ca, Al and O atoms and $B = 2 \text{ \AA}^2$ for D and H atoms). These values were also used to refine the 300 K neutron data from the hydrogenated sample, since the poor peak-to-background ratio did not allow a meaningful estimate of the displacement parameters.

Despite these difficulties, it was possible to locate OD ions on the framework polyhedra and the water molecules in the channels which most likely have zeolitic nature. The occupation of the water molecules as determined by *FULLPROF* seem to vary with the sample investigated, as illustrated by the results for *C1*, *C2* and *C3* in Table 2. Presumably, this is an artefact which does not reflect an actual difference in the water content of the three samples taken from the same preparation. A more likely explanation is that the different occupancies are caused by the different types of diffraction data used in the

FULLPROF analysis. Hence, for the neutron data from sample *C3* the scattering contribution from the water molecules is considerably more significant than the scattering contribution from the water molecules in the X-ray diffraction data from samples *C1* and *C2*. The results of the *FULLPROF* refinement of the diffraction data are summarized in Tables 3 for the deuterated sample *C3* and in Tables 5 and 6 for the hydrogenated sample *E3*.

The distances between the O atoms of the water molecules in the channels and the water molecules bonded to the Ca atoms are 2.736 (2.585) Å for O6–O9 and 2.620 (2.430) Å for O8–O9 for the deuterated and hydrogenated samples, respectively, and thus it is concluded that the water molecules D_2O^6 and D_2O^8 , and H_2O^6 and H_2O^8 are hydrogen bonded to the framework structure.

Two of the three partly occupied water molecules in the channels have the O7 and O8 atoms in general positions with a very close O7–O8 distance of only 2.373 Å in the deuterated sample. Hence, the occupancies of these two water molecules were restrained so that their sum did not exceed 12. This gave a total of 2.42 water molecules in the channels or the total composition $CaAl_2O_4 \cdot 8.42D_2O$, which is in good agreement with the composition found in the thermogravimetric analysis ($CaAl_2O_4 \cdot 8.28D_2O$). The same restraint was applied for the refinement of the hydrogenated sample and resulted in the composition $CaAl_2O_4 \cdot 9.00H_2O$, i.e. a total of 3.00 water molecules in the channels. This value is somewhat lower, but, within experimental error, comparable to the composition ($CaAl_2O_4 \cdot 9.43H_2O$) found in the thermogravimetric analysis. The O7–O8 distance of 2.649 Å is somewhat larger than in the deuterated sample, which might indicate that the restraint on the total occupancies of H_2O^7 and H_2O^8 could be removed. A test refinement without restraint on the total occupancies of H_2O^7 and H_2O^8 resulted in slightly better *R* factors and the composition $CaAl_2O_4 \cdot 9.37H_2O$, which is in excellent agreement with the thermogravimetric analysis. However, the corresponding structure has unrealistically large H–O–H angles of ~ 121 and $\sim 130^\circ$ for H_2O^6 and H_2O^9 , respectively. Therefore, this test refinement is inconclusive with regard to the correct composition of the hydrogenated sample.

The agreement between observed and calculated neutron diffraction powder patterns from the deuterated sample *C3* (Fig. 4) is reasonable, but there are rather large fluctuations in the difference pattern (Fig. 4*b*). Although the discrepancy is most pronounced in the region of the background hump, a change of the background in this region does not diminish the fluctuations. A search for additional water molecules in the channels was made by a careful inspection of the difference-Fourier maps calculated by *FULLPROF*. However, this search did not indicate additional scattering density. The agreement between observed and calculated neutron diffraction patterns of the hydrogenated sample *E3* (Fig. 6) is remarkably good in view of the poor peak-to-background ratio. This probably reflects the fact that the background of the hydrogenated sample is much easier to model than that of the deuterated sample. The atom positions for the two samples differ only slightly, but although the diffraction data from the hydro-

genated sample may be modelled reasonably well (see Fig. 6*c*) with the atom positions of the deuterated sample (see supplementary material) the opposite is not the case.

In conclusion, the crystal structure of $CaAl_2O_4 \cdot 8.42D_2O$ may be compared with the crystal structures of related compounds. The hydrogen bonds in the crystal structures of gibbsite [$Al(OH)_3$] and bayerite [$Al(OH)_3$] between hydroxyl groups were in the ranges 2.834–3.245 and 2.915–3.237 Å, respectively (Giese, 1976). In the crystal structure of bayerite the O–D distances in the OD groups are in the range 0.939–1.025 Å, the Al–O distances are in the range 1.855–1.943 Å and the O–O distances within the AlO_6 octahedra in the range 2.411–2.822 Å (Zigan *et al.*, 1978). In the crystal structure of $CaAl_2O_4 \cdot 8.42D_2O$ the hydrogen bonds were found to be in the range 2.620–2.736 Å, the O–D distances in the ions of the structure in the range 0.979–1.076 Å and in the water molecules in the range 1.028–1.121 Å. The Al–O distances were found to be in the range 1.855–2.024 Å and the O–O distances in the AlO polyhedron in the range 2.379–3.011 Å. These findings imply that the atom distances found in the present investigation of calcium aluminate decahydrate are in the ranges to be expected for this type of compound.

APPENDIX A

Details of the *FULLPROF* refinement of the occupancy of the 'loose' water molecules in sample *C3* and some results

Initially only the scale factors and the occupancies of the three free water molecules (D_2O^6 , D_2O^7 and D_2O^8) were allowed to vary. This refinement quickly converged, but the difference pattern showed that the background determined by *FULLPROF* in the profile-matching mode (see §3.1) was inadequate.

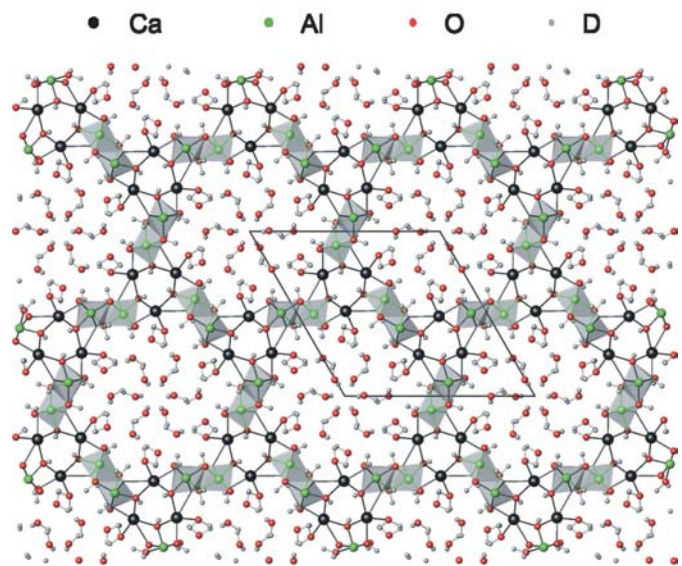


Figure 7
Basal plane projection of several unit cells of $CaAl_2O_4 \cdot 8.42D_2O$, showing the nano-sized water-filled channels of the structure. The Ca, Al, O and D atoms are shown as spheres of decreasing size.

The reason for this is most likely that *FULLPROF* introduces peaks at all the possible Bragg positions of the $P6_3/m$ space group in the profile-matching mode and not only at the Bragg positions with non-negligible structure factors. Therefore, the following iterative process was used. First the background parameters were refined together with the scale factors and the occupancies in a *FULLPROF* structure refinement followed by refinement of the instrument and lattice parameters by *FULLPROF* in the profile matching mode. This double refinement converged after a few repetitions, but was also repeated a few times during the subsequent refinement of the atom coordinates.

A1. Unconstrained D_2O^7 and D_2O^8

Once the refinement of the background and the occupancies of the water molecules had converged, the coordinates of the D atoms of the water molecule were included one by one and refined until convergence was reached. Afterwards the D atoms of the OD groups were successively included, resulting in a steady reduction of the R factors and χ^2 . Then the positions of the O atoms of the water molecules and the OD groups were successively included and refined until finally the Ca and Al atom coordinates could also be included as refineable parameters. The resulting reliability values for sample C3 at 1.6 (and 79 K), respectively: $R_p^S = 0.146$ (0.143), $R_B^S = 0.067$ (0.066), $R_F^S = 0.041$ (0.040) and $\chi^2 = 0.164$ (0.155), where R_p^S is the conventional Rietveld R factor.

A2. Constrained D_2O^7 and D_2O^8

In the above refinement the occupancies of the three 'loose' water molecules were allowed to vary independently. However, this resulted in a structure where the positions of the two water molecules in general sites [12(*i*) sites] were too close and had a total occupancy larger than 12. Also some of the H/D atoms of these molecules were too close. Therefore, an additional constraint on the sum of the occupancies of these two water molecules (D_2O^7 and D_2O^8) was introduced in the final refinement of the neutron diffraction pattern of sample C3, giving reliability values for sample C3 at 1.6 (and 79 K), respectively: $R_p^S = 0.161$ (0.157), $R_B^S = 0.082$ (0.082), $R_F^S = 0.050$ (0.049) and $\chi^2 = 0.189$ (0.178), where R_p^S is the conventional Rietveld R factor.

This work is partly based on experiments performed at the Swiss spallation neutron source SINQ and the Swiss light

source SLS, Paul Scherrer Institute, Villigen, Switzerland. We also acknowledge the beamtime allocation at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, USA. We acknowledge Bo B. Iversen and Henrik Birkedal at the Department of Chemistry at the University of Aarhus, Denmark, for cooperation in collecting the Stoe Stadi powder diffraction data. Aziz Daoud-Aladine at ISIS, Didcot, UK, is gratefully acknowledged for valuable help and advice with the *FULLPROF* Rietveld analysis. We express our thanks to Vincent Fávre-Nicolin for his patient and speedy response to our many questions on the use of *FOX*. We acknowledge Jens Wenzel Andreassen at Risø National Laboratory, Denmark, for his advice on the interpretation of the Fourier maps and Rita G. Hazell at the Department of Chemistry at the University of Aarhus, Denmark, for her help with the preparation of the CIF file. The research was supported by the European Commission under the 6th Framework Program through the key action: Strengthening the European Research Area, Research Infrastructures, Contract No. RII3-CT-2003-505925 and the Danish Natural Science Research Council through the Danish Neutron Scattering Centre DANSCATT. The research carried out at NSLS x7a was financed through contract No. DE-AC02-98CH10886 with the US Department of Energy (Division of Chemical Sciences).

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