Crystal Structure Solution of Hydrated High-Alumina Cement from X-ray Powder Diffraction Data**

Francesc Guirado,* Salvador Galí, Servando Chinchón, and Jordi Rius

The use of high-alumina cement (HAC; a quickly binding cement with a high aluminum oxide content) in concrete, precast, prestressed elements became highly controversial after the roofs of three educational buildings collapsed in the United Kingdom in 1973 and 1974. There were further incidents in other countries, and in 1990 an apartment building fell down in Barcelona, Spain. The relevant technical characteristics of HAC are better resistance to sulfates than Portland cements, good refractory properties, and above all a rapid gain in concrete strength which allows quick manufacture. However, a subsequent, complex evolution of this material—which is still not well understood—leads to the collapses.

The main phase present in HAC is $CaAl_2O_4$; additional components are Ca_2FeAlO_5, $Ca_{12}Al_{14}O_{33}$, and minor amounts of Ca_2AlSiO_7 and Ca_2SiO_4. After binding the cement with water (hydraulic reaction), $CaAl_2O_4$ gives raise to a metastable hexagonal phase currently but erroneously labeled as $CaAl_2O_4 \cdot 10\,H_2O$ (or CAH_{10}). Furthermore, some $Ca_2Al_2O_5 \cdot 8\,H_2O$ and an amorphous phase are present. The dominant crystalline phase in the paste (which determines the valuable cementitious properties), CAH_{10} slowly transforms into a new cubic phase with the hydrogarnet structure plus gibbsite and water. This unavoidable conversion is completed within several years; the rate depends on the humidity and the temperature. The effect of this rather slow conversion is an increase in concrete porosity and loss of strength. Chemical reactions facilitated by the porosity probably cause the continuous loss of strength, even after full conversion. Since 1990 a great deal of work has been undertaken in Catalonia to throw light on the extent of HAC pathology in buildings. It became apparent that the phase CAH_{10} was poorly characterized, and that the solution of its crystal structure would be of much practical importance in understanding the behavior of this phase in concrete.

The hydration of $CaAl_2O_4$ below 20 °C yields an undetachable mixture of an amorphous and a crystalline phase with an overall composition of $CaAl_2O_4 \cdot n\,H_2O$ ($n \approx 5-8$). All attempts to isolate the crystalline phase were unsuccessful, and the relative proportions of the phases in the mixture as well as their individual compositions and water content remained unknown. These uncertainties could not be cleared up until the structure was refined. The poor quality of the crystalline material was an additional drawback and accounted for the fact that the crystal structure remained unsolved since Assarsson reported the existence of this phase in 1933.[1]

Nevertheless, several works have given partial information on the structure by using different techniques (^{27}Al NMR, IR, thermogravimetry (TG), and X-ray diffraction (XRD)).[2–5] According to the NMR data, the coordination at aluminum should be a slightly distorted octahedron of OH^- groups, and, by mimetism with gibbsite, the structure was believed to include rings of edge-sharing $Al(OH)_6$ octahedra. IR spectra of CAH_{10} revealed the presence of both H_2O and OH^- groups in the structure. Accurate kinetic analyses of the loss of water with increasing temperature, based on thermogravimetric and thermodiffractometric measurements, showed that a small amount of crystalline water is lost at about 94 °C without appreciable changes in the structure. This water was thought to be interlaminar. A subsequent, more important loss at about 126 °C produces the collapse of the crystalline portion.[6]

Since the unit-cell parameters of CAH_{10} were already known,[4] the integrated intensities could be extracted from the X-ray powder pattern with a modified LeBail method[7] using the whole-profile fitting program AJUST.[8] Inspection of the list of integrated intensities showed that reflections of type ($00l$) with $l = 2n+1$ were systematically absent, and reflections of type ($h-hl$) and ($h-2hl$) with $l = 2n+1$ were present. Accordingly, the allowed space groups are $P6_322$ (182), $P6_3/m$ (176), and $P6_3$ (173). Whereas space group $P6_322$ has Laue symmetry $6/mmm$, $P6_3$/m and $P6_3$ belong to the Laue group $6/m$. This means that reflections of type (hkl) and (khl) systematically overlap in $P6_3/m$ and $P6_3$. A first attempt to solve the structure in $P6_322$ was unsuccessful. Consequently, the structure was solved assuming $P6_3$ symmetry. The whole-profile fitting procedure with use of $6/m$ Laue symmetry yielded 30 resolved integrated intensities from a total of 158 reflections ($2\theta_{max} = 51.3°$, $d_{min} = 1.78$ Å). For the systematically overlapped reflections, equipartioned intensities were assumed.[9]

The structure was solved with the SUMF tangent formula (SUMF-TF)[10] implemented in the program XLENS.[11] The electron-density map with the best figures of merit is shown in Figure 1; inspection of this map revealed the positions of Ca^{2+} and OH^- ions as well as the water molecule bound to Ca^{2+}. Surprisingly, Al^{3+} did not appear in this map, so its position was deduced from crystallochemical considerations. The fact that the electron-density map obtained assuming $P6_3$ symmetry possesses a center of symmetry indicated that the true space group is $P6_3/m$.

The model derived from the electron-density map was introduced as the starting structure for the Rietveld refinement with the program FULLPROF.[12] A Pearson-VII function was selected to describe individual line profiles,

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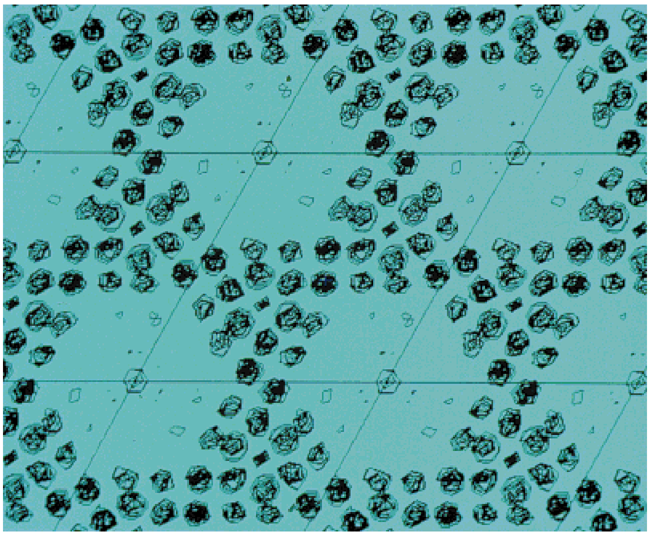

Figure 1. Electron-density map along [001] obtained by applying the SUMF-TF to the equipartioned intensities, which were extracted from the X-ray powder diffraction pattern with a resolution of up to 1.78 Å. One striking feature of this structure is the large channel parallel to the *c* axis, which can be seen clearly in this image. The graphic was produced with the FAN program.[20]

and possible angular variation of the mixing parameter was allowed. Peaks below 30° (2θ) were corrected for asymmetry following the model proposed by Berar and Baldinozzi.[13] The reflections with the 2θ intervals 5–9° and 70–100° were excluded from the refinement. Owing to the shortage of intensity data and the large number of atoms involved, geometrical restraints were applied to the cation–anion distances: $d_{Ca-O} = 2.468(7)$ Å (average distance for the coordination number eight) and $d_{Al-O} = 1.91(6)$ Å (average distance for coordination number six). The refinement converged to the conventional Rietveld residuals[14] $R_p = 16.7$, $R_{wp} = 18.0$, $R_B = 8.6$, and $\chi^2 = 3.5$. The result is shown in Figure 2. Table 1 gives the final atomic coordinates for CAH_{10}, which is better reformulated as $[CaAl_2(OH)_8(H_2O)_2] \cdot 1.84\,H_2O$. The occupation parameters of the two "free" water molecules were refined after different isotropic temperature factors for groups of atoms were included in the refinement

Table 1. Refined atomic coordinates and isotropic temperature factors [Å^2] for $CaAl_2(OH)_8(H_2O)_2 \cdot 1.84\,H_2O$.

Atom	Wyckoff site	x	y	z	B_i	Occupation
Ca	6*h*	0.5185(7)	0.2791(8)	0.25	2.9(4)	1
Al	12*i*	0.5795(8)	0.4969(7)	0.068(1)	1.5(2)	1
O(1)	12*i*	0.623(1)	0.410(1)	0.072(2)	3.3(3)	1
O(2)	12*i*	0.403(1)	0.235(1)	0.039(2)	4.0(8)	1
O(3)	12*i*	0.521(1)	0.574(1)	0.072(2)	3.3(3)	1
O(4)	12*i*	0.330(1)	0.436(1)	0.090(2)	3.3(3)	1
O(5)	6*h*	0.663(1)	0.565(2)	0.25	3.3(3)	1
O(6)	6*h*	0.505(2)	0.428(2)	0.25	3.3(3)	1
O(7)	12*i*	0.000(3)	0.249(4)	0.921(3)	25(1)	0.71(7)
O(8)	6*h*	0.316(5)	0.567(3)	0.25	25(1)	0.42(4)

The structure is based on ring-shaped units of three edge-sharing $Ca(OH)_6(H_2O)_2$ polyhedra at $z = 0.25$ which are laterally linked to the next units at $z = 0.75$ and $z = -0.25$ through two $Al(OH)_6$ octahedra. Each octahedron shares one edge with two Ca-containing polyhedra and one edge with two adjacent octahedra (Figure 3) to produce zig-zag chains of Al octahedra along the *c* axis. This peculiar atom connectivity gives rise to an extremely open structure with a large channel along *c* that is centered by the 6_3 screw axis. The balance of electrostatic valences for the oxygen centers of $CaAl_2(OH)_8(H_2O)_2$ estimated according to Allmann[15] is reproduced in Table 2. It allows recognition of the chemical role played by each oxygen atom. It can be seen that all oxygen atoms in the rigid part of the structure are in the form of hydroxy groups except for O(2), which belongs to a water molecule that is tightly bound to Ca^{2+}. The remaining water molecule in the structure is at partially occupied positions on the Ca units (O(8)) or inside the channel (O(7); see Table 1). The presence of water on the Ca units explains the slight shortening of the *c* axis by about 2% at 94 °C. The partial occupation as well as the abnormally high temperature factor of the water molecule in the channel suggest the possible existence of more disordered water molecules in the channel.

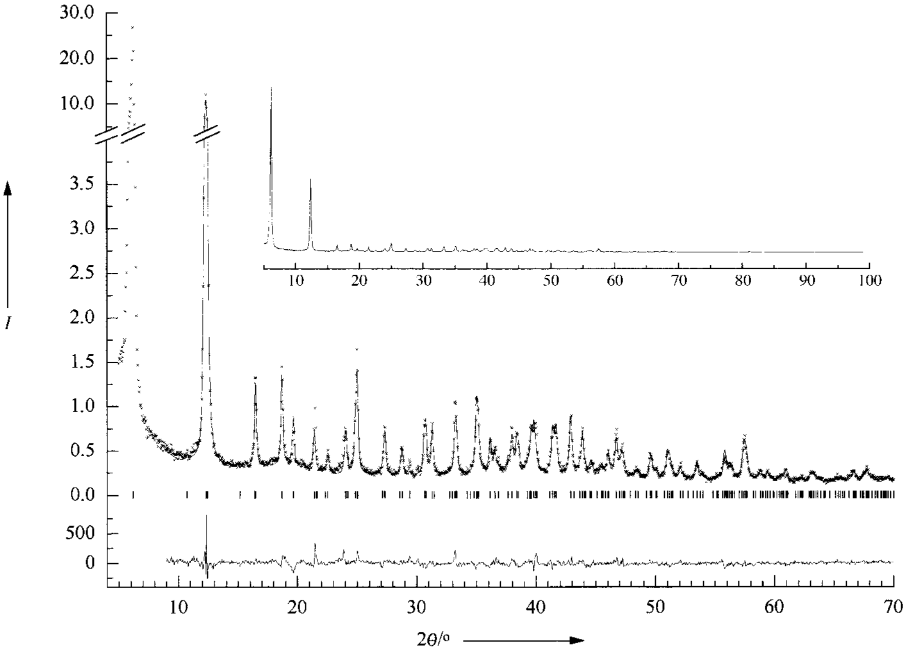

Figure 2. Calculated (inset) and experimentally observed (crosses) X-ray powder diffraction patterns of $[CaAl_2(OH)_8(H_2O)_2] \cdot 1.84\,H_2O$ as well as the difference profile (bottom). Intensity *I* is given in units of 10^{-3}. Measurement conditions: angle range 5–100° (2θ), step size 0.05° (2θ), counting time 15 s. An illumination correction was applied for reflections below 24° (2θ); the first diffraction line at very low angle could not be properly corrected and was excluded from the refinement. Reflections above 70° (2θ) were excluded as well. The short tick marks below the pattern give the positions of the Bragg reflections.

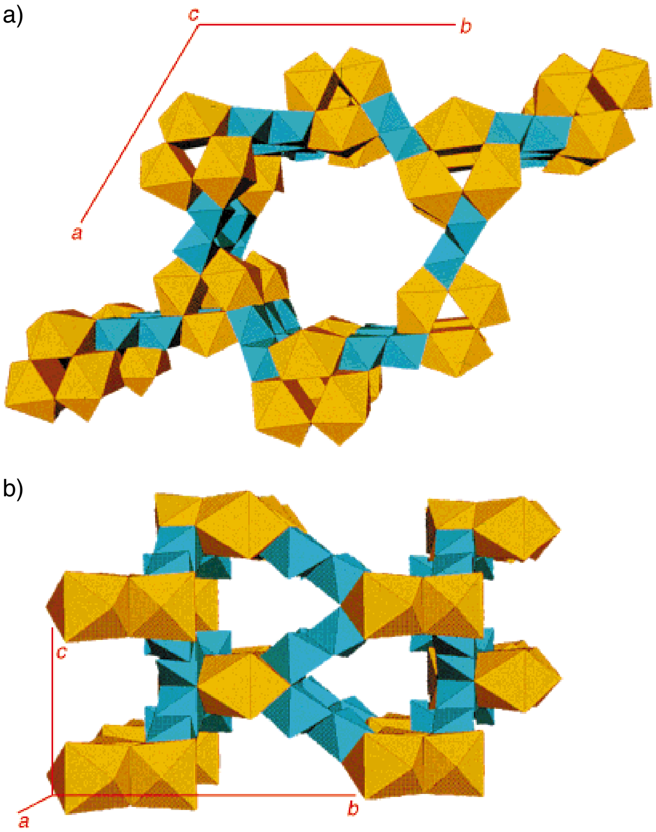

Figure 3. Structure of $[CaAl_2(OH)_8(H_2O)_2] \cdot 1.84\,H_2O$ as viewed a) along the *c* axis and b) along the *a* axis. Three-membered, ring-shaped units of polyhedra (yellow) with central Ca atoms are mutually connected to chains of octahedra (blue) with central Al atoms that run parallel to the *c* axis. The (free) water molecule not involved in the formation of the structure, which shows very high temperature factors, is located in three types of cavities. The most important is a tunnel parallel to the *c* axis, whose axis coincides with the symmetry axis 6_3 containing the O(7) water molecule (see Table 1). In b) the chains of Al-containing octahedra that are parallel to the *c* axis and the cavities parallel to the *a* axis can be observed. There are threefold intersecting tunnels at levels $z = 0.25$ and $z = 0.75$ (but rotated by 60°). The O(8) water molecule is inside these cavities.

The $Ca(OH)_6(H_2O)_2$ polyhedron is similar to the $Ca(OH)_8$ unit in hydrogarnet ($Ca_3Al_2(OH)_6$)[16, 17] and ettringite ($(Ca_6(Al(OH)_6)_2(SO_4)_3 \cdot 26\,H_2O)$).[18] The structure of the former is more compact, since each $Ca(OH)_8$ polyhedron shares four edges with four different $Ca(OH)_8$ and four more edges with four $Al(OH)_6$ polyhedra. These are in turn surrounded by six $Ca(OH)_8$ polyhedra. The slow conversion of the hexagonal phase into hydrogarnet and gibbsite (plus water) takes place with conservation of the first coordination shell—that is, without completely destroying the original structure. However, CAH_{10} is highly unstable in the presence of circulating water under atmospheric conditions, and quickly transforms into calcite and aluminum hydroxide.

The structural formula obtained from the refinement and given above can be converted into a conventional formula, namely $CaAl_2O_4 \cdot 7.8\,H_2O$. This composition is very similar to the overall composition of the hydrated product (with crystalline and amorphous parts). Hence, the amorphous and crystalline portions have very similar compositions, a result that was not apparent when this work was initiated.

Table 2. Metal–oxygen bond lengths L [Å] and bond valences v (italics) of the oxygen atoms estimated according to Allmann;[15] $L(v) = L(1) - 2k \lg v$. The $L(1)$ and $2k$ values for Ca and Al are 1.896, 0.95 and 1.644, 0.88, respectively. The exchange of charge in the hydrogen bridges (Δe) is based on hydrogen-bond strengths according to Zachariasen.[18] The type of group that the oxygen atom belongs to is given in the last column. The coordination numbers for Al and Ca are 6 and 8, respectively.

Atom	Ca^{2+}	Al^{3+}	$\Sigma_c v$[a]	Δe	$\Sigma_c v_{corr}$	Type
O(1)	2.46[c], 2.44[c]	1.89	–	–	–	OH^-
		0.53	*1.05*	–	*1.05*	
	0.25, 0.27					
O(2)	2.41[c]	–	–	–	--	H_2O
	0.29	–	*0.29*	*– 0.28*	*0.01*	
O(3)	–	1.93, 1.87	–	–	–	OH^-
	–	*0.47, 0.55*	*1.02*	--	*1.02*	
O(4)	–	1.87	–	–	–	OH^-
	–	*0.55*	0.55	*+ 0.28*	*0.83*	
O(5)	2.57	1.97[d]	–	–	–	OH^-
	0.20	*0.43*	*1.06*	–	*1.06*	
O(6)	2.56	1.91[d]	–	–	–	OH^-
	0.20	*0.497*	*1.19*	–	*1.19*	
$\Sigma_A v$[e]	2.02	3.03				

[a] $\Sigma_c v$ = sum of bond valences for each anion. [b] $\Sigma_c v_{corr}$ = sum of bond valences for each anion after considering the H-bond charge exchange. [c] Two bonds per cation. [d] Two bonds per anion. [e] $\Sigma_A v$ = sum of bond valences for each cation. O(4)···O(2) 2.66(4) Å ≈ 0.28 valence units.

Experimental Section

The $CaAl_2O_4$ phase was obtained by heating an equimolar mixture of pure reactants Al_2O_3 and $CaCO_3$ at 1300°C for 200 h. The progress of the reaction was periodically controlled by XRD. The final sintered product was finely ground and sieved through a 10-μ sieve. The optimal conditions were determined to be hydration of $CaAl_2O_4$ at 5°C with excess water with periodic stirring. The final product was filtered, washed with acetone, and characterized by XRD. The X-ray powder diffraction pattern used for the structure solution and refinement was collected in reflection geometry on a high-resolution RIGAKU powder diffractometer equipped with a Cu rotating anode and a primary curved Ge(111) monochromator. Comparison with an additional pattern measured using a INEL X-ray PSD diffractometer with the sample enclosed in a glass capillary confirmed the absence of a preferred orientation in the flat sample.

To prepare a sample suitable for neutron diffraction, $CaAl_2O_4$ was hydrated with deuterated water as well. The results of neutron diffraction were very disappointing: Only few peaks emerged from an intense background, suggesting a high thermal and positional disorder of the deuterium atoms.

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$a = b = 16.387(2)$, $c = 8.279(1)$ Å, $Z = 6$, $V = 1925$ Å^3, $\rho_{calcd} = 1.548\ g\,cm^{-3}$, white powder, $\lambda = 1.5406$ Å, T ≈ 25 °C, data range 5–100° (2θ), 1900 data points, 30 independent reflections, no absorption correction, Rietveld refinement with X-ray powder data with geometrical constraints; data range used 9–70° (2θ), $R_p = 16.7$, $R_{wp} = 18.0$, $R_B = 8.6$, $\chi^2 = 3.5$, $R_p = 100\Sigma|y_{oi} - y_{ci}|/\Sigma|y_{oi}|$, $R_{wp} = 100(\Sigma w|y_{oi} - y_{ci}|^2/\Sigma w|y_{oi}|^2)^{0.5}$, $R_B = 100\Sigma|I_k - I_{ck}|/\Sigma|I_k|^2 = (R_{wp}/R_{exp})^2$. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshaften (Germany), on quoting the depository number CSD-407150.

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Self-Complementarity Achieved through Quadruple Hydrogen Bonding**

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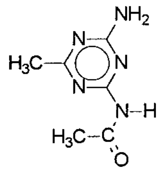
Hydrogen bonds are among the most useful interactions for encouraging molecules to self-assemble into well-defined aggregates.[1] The strength and selectivity of hydrogen bonds can be increased by introducing arrays of donor (D) and acceptor sites (A). Arrays of two and three hydrogen bonds have already been studied in detail, and their strength in $CHCl_3$ depends upon the particular arrangement of donor and acceptor sites. In triply hydrogen bonded complexes, for example, association constants vary from $K_a = 10^2 - 10^3\,M^{-1}$ for DAD–ADA pairs to $K_a = 10^5 - 10^6\,M^{-1}$ for DDD–AAA pairs.[2] Jorgensen[3] rationalized these differences as the result of secondary electrostatic interactions. Rules derived from this analysis are now widely used to design complementary host–guest systems characterized by high selectivity and recognition as well as strong binding.

However, for a number of applications ranging from container molecules[4] to supramolecular tubes,[5] self-complementarity is required. This is evidently found only in arrays with an even number of hydrogen bonds. Although examples exist of self-complementary arrays consisting of two hydrogen-bonding units,[6] arrays with four adjacent hydrogen-bonding sites are notably absent from the supramolecular literature.[7] Recently we reported the dimerization of a diacetyl diaminotriazine involving four hydrogen bonds with a dimerization constant K_{dim} of $35\,M^{-1}$.[8]

Here we show the generality of dimerization by way of the DADA sequence in readily available compounds, and present examples with unexpectedly high dimerization constants. Conceptually, the DADA arrays in compounds **1**–**6** are derived from DAD arrays in diaminotriazines or diaminopyrimidines that have been extended by an oxygen acceptor atom from a *cis* amido or ureido group. The required *cis*-amide conformation in **1**, **2**, and **5** is favored by repulsion between the amide oxygen atom and nitrogen atoms in the heterocyclic ring, whereas an intramolecular hydrogen bond preorganizes the array in ureido derivatives **3**, **4**, and **6**.



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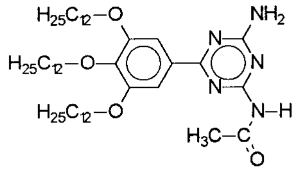

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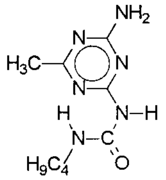

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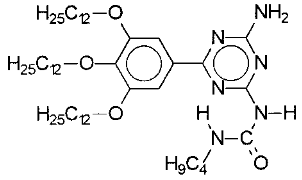

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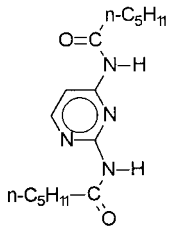

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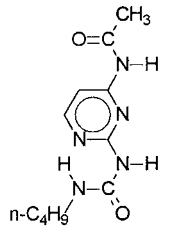

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