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Synthesis and crystal structure solution of potassium dawsonite: An intermediate compound in the alkaline hydrolysis of calcium aluminate cements

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Abstract

Potassium dawsonite is formed as an intermediate compound during the alkaline hydrolysis (AH) in calcium aluminate cements (CACs). A synthesis method of potassium dawsonite has been developed. The crystal structure of potassium dawsonite $KAl(CO_3)(OH)_2$ has been solved by direct methods from X-ray powder diffraction data and refined with the Rietveld method. It crystallises in the orthorhombic *Cmcm* space group with unit cells parameters $a = 6.3021(3)$ Å, $b = 11.9626(5)$ Å, $c = 5.6456(3)$ Å and $Z = 4$. The structure consists of carboaluminate chains, formed by the basic unit $[Al_2(OH)_4(CO_3)_2]^{2-}$ arranged along the c axis. The carbonate groups are placed in an alternate manner at both sides of the carboaluminate chains. The carboaluminate chains are also held together by the K^+ cations that are located in the middle of three such chains. Finally, the chemical reactions explaining the AH process in CACs are postulated.

Keywords: Calcium aluminate cements; Cement carbonation; Alkaline hydrolysis; Potassium dawsonite; Crystal structure

1. Introduction

The main special properties of calcium aluminate cements (CACs) are their rapid strength development, good resistance to sulphates and, when used with refractory aggregates, their effectiveness for making refractory concrete [1]. Due to the rapid hydration, they are useful for low-temperature applications. CACs were originally developed to provide improved durability in sulphate environments [2]; later studies, however, showed that this cement, like the Portland cement (PC), can react with external chemical compounds. The effect of CO_2 on hydrated CAC compounds has been extensively investigated [3]. In general, the carbonation process improves the mechanical strength [4], but also favours the framework corrosion [5].

Alkaline hydrolysis (AH) takes place when hardened CAC concrete is exposed to an alkaline environment. The alkalis, when present in the fine fractions of the aggregates, may release sodium or potassium ions; the AH phenomenon occurs when these alkalis participate in the carbonation process [1]. In Spain, all AH tests performed on real samples showed rather high concentrations of potassium. Consequently, due to its practical significance, the effect of this alkali on the hydration and carbonation processes was investigated. A detailed study of CAC specimen pastes [6,7] allowed identifying two differentiated zones: an inner one with normal cohesion and homogeneity, and an approximately 50-µm-thick outer one displaying some heterogeneity and containing a hydrated potassium carboaluminate: $KAlCO_3(OH)_2$ or K-dawsonite. This compound was firstly detected by infrared (IR) spectroscopy, because most peaks of its X-ray diffraction (XRD) powder pattern overlap with those of the compounds normally present in CAC cements: monocalcium aluminate and calcium carbonate. This carboaluminate evolves towards the formation of potassium bicarbonate and aluminium hydroxide [7].

In this paper, the synthesis, the characterisation and crystal structure solution from X-ray powder diffraction data of this new carboaluminate are described; the probable

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chemical reactions controlling the AH process in presence of potassium is also formulated.

2. Experimental

The synthesis of the hydrated potassium carboaluminate was carried out by adding metal aluminium powder to a 2 M potassium carbonate solution. The reactive solution was maintained at 80 °C and stirred until a white precipitate was formed. The solid was filtered with distilled water until the filtered liquid reached neutral pH. The synthesis was verified by IR spectroscopy: an ATI Matson spectrometer with a Michelson interferometer was used; the pellet was prepared by adding 2.0 mg of the synthesised sample to 300 mg of BrK and the spectrum resolution was 1 cm^{-1}. The chemical analysis of the compound, expressed as weight percentages of potassium and aluminium oxides are K_2O: 20.45, Al_2O_3: 15.6, which is slightly different to that given by the JCPDS no. 35-0545 [8], i.e., K_2O: 28.24, Al_2O_3: 30.26, H_2O: 13.02, CO_2: 26.38. The IR spectrum of the synthesised sample is reproduced in Fig. 1. Table 1 gives the assignment of the vibration frequencies to the absorption bands.

The XRD pattern used for the structure solution was collected on a BRUKER D5000 powder diffractometer (Bragg–Brentano geometry) equipped with a secondary graphite monochromator ($CuK\alpha_{12}$ radiation, flat sample). Angular range: 13–83° (2θ); step size: 0.02° (2θ); counting time: 1 s. The X-ray powder diffraction data are given in Table 2. Comparison with an additional pattern measured on an INEL X-ray PSD diffractometer with the sample in a glass capillary confirmed the presence of slight preferred orientation in the flat sample. With this information, its effect could be corrected in the Rietveld refinement.

Table 1
Vibration frequencies of the IR spectrum of K-dawsonite (cm^{-1})

OH	3445
Al–OH tension	1000
	1072
Al–O group	510
	470
CO_3^{2-}	
ν_1	1105
ν_2	870
	760
ν_3	1540
	1405
ν_4	660

3. Results and discussion

3.1. K-dawsonite synthesis

Some K-dawsonite synthesis methods [8], already present in the bibliography, have used different temperatures of synthesis and raw materials; these also differs from the optimised method developed in this research. The synthesised K-dawsonite has a high-purity and -crystalline degree; both qualities were necessary for the structure determination and refinement.

It is worth mentioning that to optimise the synthesis conditions of K-dawsonite, several syntheses at different temperatures and KOH solution concentrations were necessary. In these preliminary syntheses, another compound of similar composition but crystallising in the orthorhombic *Pmna* space group with unit cell parameters $a = 8.3312(6)$

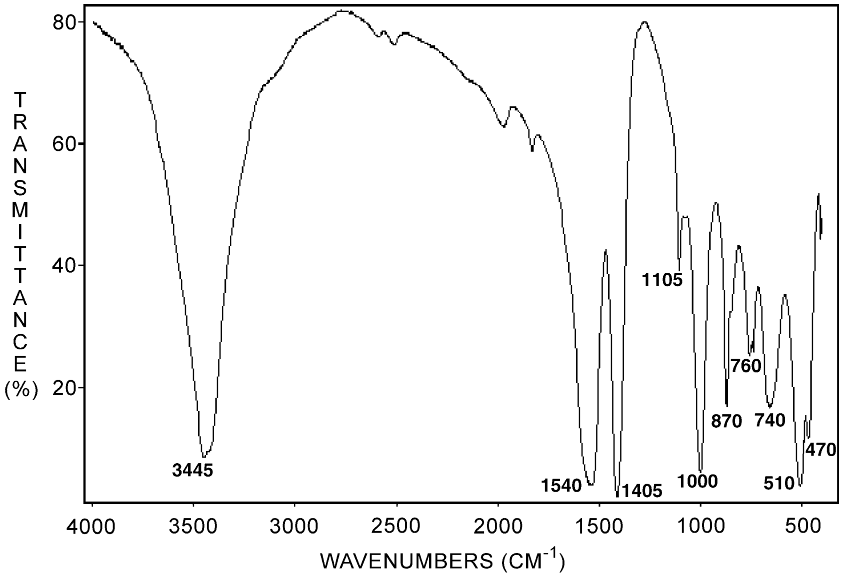

Fig. 1. Infrared spectrum of potassium dawsonite.

Table 2
XRD powder data for K-dawsonite (Cu Kα_1 data, after mathematically stripping the Kα_2 contribution)

h k l	$2\theta_{obs}$ (°)	$2\theta_{calc}$ (°)	d_{obs} (Å)	rel. I_{obs} (%)
0 2 0	14.822	14.799	5.972	7
1 1 0	15.881	15.882	5.576	91
0 2 1	21.639	21.628	4.104	32
1 1 1	–	22.393	–	< 1
1 3 0	26.439	26.429	3.368	67
2 0 0	28.311	28.299	3.150	100
0 4 0	–	29.852	–	2
1 3 1	30.897	30.879	2.892	10
0 0 2	31.706	31.672	2.820	24
2 2 0	32.089	32.080	2.787	39
0 4 1	33.911	33.893	2.641	19
0 2 2	35.137	35.125	2.552	7
1 1 2	35.637	35.620	2.517	48
2 2 1	35.904	35.896	2.499	38
1 5 0	40.294	40.288	2.236	6
2 4 0	41.679	41.600	2.165	29
+ 1 3 2		41.707		
2 0 2	–	42.983	–	< 1
1 5 1	43.497	43.484	2.079	3
3 1 0	43.704	43.715	2.069	2
0 4 2	–	44.079	–	< 1
2 4 1	44.707	44.719	2.023	4
0 6 0	45.451	45.456	1.994	54
2 2 2	45.704	45.703	1.984	35
3 1 1	–	46.720	–	< 1
0 6 1	48.381	48.377	1.880	3
3 3 0	–	48.970	–	< 1

Å, $b=5.6606(4)$ Å and $c=11.2682(8)$ Å was also formed. The crystal structure of this second compound is still unknown. Although it has not been still identified in CAC pastes or mortars, it could be possible to find it in samples with high alkali content.

3.2. Structure determination and refinement

The indexing of the title compound was performed with program TREOR90 [9]. The unit cell is orthorhombic with parameters $a=6.3021(3)$ Å, $b=11.9626(5)$ Å and $c=5.6456(3)$ Å. The only centrosymmetrical space group compatible with the observed systematic absences is *Cmcm*. Due to the analogy with the crystal data of NH_4-dawsonite ($a=6.618$ Å, $b=11.944$ Å and $c=5.724$ Å, *Cmcm*) [10], it is very probable that the crystal structures of NH_4-dawsonite and of the title compound, hereafter called K-dawsonite, are closely related. The crystal structure of K-dawsonite was solved with the direct-methods sum function tangent formula (S-TF) [11] as implemented in the program XLENS [12]. The model derived from the electron-density map (Fig. 2) was refined with the Rietveld program LSP7 [13]. The individual line profiles were described with a Pearson-VII function. The 2θ interval used in the refinement was 13–80°. Geometrical restraints were applied to the cation–anion distances: (for the octahedra) d_{Al-O}: 1.91(8) Å; (for the carbonate groups) d_{C-O}: 1.29(2) Å and d_{O-O}: 2.234(40) Å; (for the H bonds) d_{H-O1}: 1.10(15) Å and d_{H-O2}: 1.6(2) Å. The refinement converged to the following conventional residuals [13] $R_{wp}=7.8\%$, $R_p=6.1\%$, $R_B=6.3\%$ and $\chi^2=3.9$. The observed and calculated powder patterns are depicted in Fig. 3. Table 3 reproduces the final atomic coordinates for $KAl(CO_3)(OH)_2$. By comparing the final atomic positions of NH_4 and K-dawsonite, it follows that both are isostructural, but only if the nonhydrogen atoms are considered.

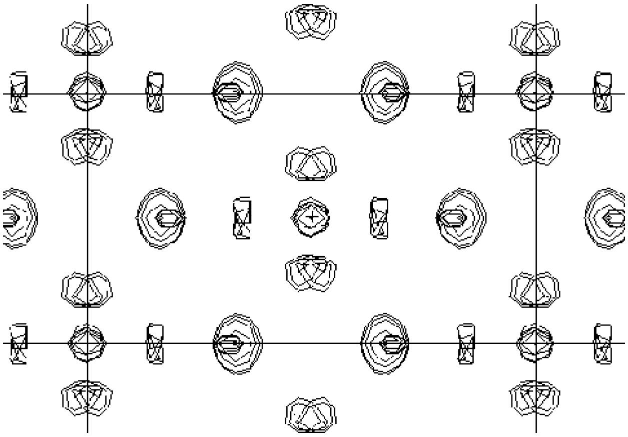

Fig. 2. Electron-density map along [001] obtained by applying the S-TF to the intensities extracted from the XRD powder pattern.

3.3. Description of the crystal structure

The structure can be best described in terms of carboaluminate chains propagating along *c*, formed by the basic unit $[Al_2(OH)_4(CO_3)_2]^{2-}$. The skeleton of one chain consists of a column of edge-sharing octahedra $AlO_2(OH)_4$ [$<d(Al–O)>=1.91(1)$ Å], with the apical O(2) atoms of two consecutive octahedra belonging to

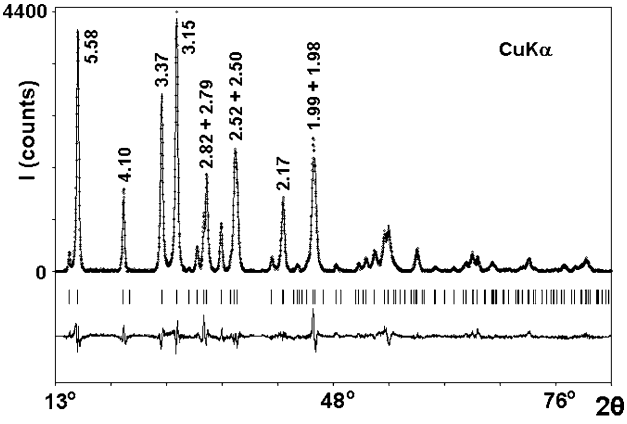

Fig. 3. Observed and calculated XRD powder patterns (crosses and solid lines, respectively). Vertical marks show positions of Bragg reflections. The lower trace is the difference profile between observed and calculated patterns.

Table 3
Final atomic coordinates for $KAl(CO_3)(OH)_2$, with e.s.d.'s in parentheses

Atom	No. sites and Wyckoff n.	x/a	y/b	z/c
Al	4a	0	0	0
K	4c	0	0.3407(2)	3/4
O(1)	8g	0.2005(5)	− 0.0128(3)	1/4
O(2)	8f	0	0.1590(2)	0.0495(8)
O(3)	4c	0	0.3221(5)	1/4
C	4c	0	0.2132(6)	1/4
H	8g	− 0.277(7)	− 0.100(3)	1/4

Table 4
Individual bond distances and angles with e.s.d.'s in parentheses for the coordination polyhedron of K^+

Distances (Å)		Angles (°)	
$K–O_1$	2.792(3) (2 ×)	$O_1–K–O_1'$	85.05(8)
$K–O_2$	2.754(3) (2 ×)	$O_1–K–O_2$	125.57(9) (4 ×)
$K–O_3$	2.832(4) (2 ×)	$O_1–K–O_3$	93.3(1) (4 ×)
		$O_2–K–O_2'$	75.7(1)
		$O_2–K–O_3$	123.3(1) (2 ×)
		$O_2'–K–O_3$	47.5(1) (2 ×)
		$O_3–K–O_3'$	170.9(1)

the same carbonate group. The carbonate groups are placed in an alternate manner at both sides of the carboaluminate chains, thus stabilising it. The carboaluminate chains in the crystal are held together by hydrogen bridges between atom O(1)–H of one chain and atom O(3) of the neighbouring one. The carboaluminate chains are also held together by the K^+ cations that are located in the middle of three such chains as shown in Fig. 4. The resulting K^+ coordination is an irregular polyhedron with the following average bond length: $<d(K–O)>=$ 2.79(4) Å. The individual bond distances and angles of the polyhedron are listed in Table 4. Notice that in K-dawsonite, each K^+ interacts with the three symmetry independent O atoms [O(1), O(2) and (O3)] present in the structure, in clear contrast to the situation found in Na-dawsonite. In this compound, the octahedrally coordinated Na^+ cations are located between two carboaluminate chains but with atom O(2) showing no relevant interaction with Na^+ [14]. The sum of bond valences for K-dawsonite estimated according to Allmann [15] is reproduced in Table 5. The resulting balance clearly shows the correctness of the refined structure.

3.4. Identification of K-dawsonite in CAC pastes by XRD

In practice, one important point is the identification of K-dawsonite in cement samples. As can be seen in Table 2, the five strongest diffraction peaks of K-dawsonite correspond in decreasing order of *d* values to 5.58, 3.37, 3.15, 2.52 and 1.99 Å. It has been found that the diffraction peak at 5.58 Å (rel. I = 91%) is the most useful for identification purposes in real samples, because, besides being very strong, it shows no overlap with the peaks of the compounds normally found in pastes and mortars of carbonated CAC. In cement samples, this peak is often somewhat broadened and slightly shifted towards 5.53 [7]. The third strongest peak at 3.37 Å (rel. I = 67%) appears close to the highest peak of aragonite, while the diffraction line at 1.99 Å (rel. I = 54%) is close to reflection 221 of aragonite (*d* value = 1.98 Å). Therefore, both peaks will be of little value for identifying K-dawsonite when this calcium carbonate polymorph is present in the cement. Unfortunately, the strongest peak in synthetic samples of K-dawsonite at 3.15 Å appears in cement samples as a

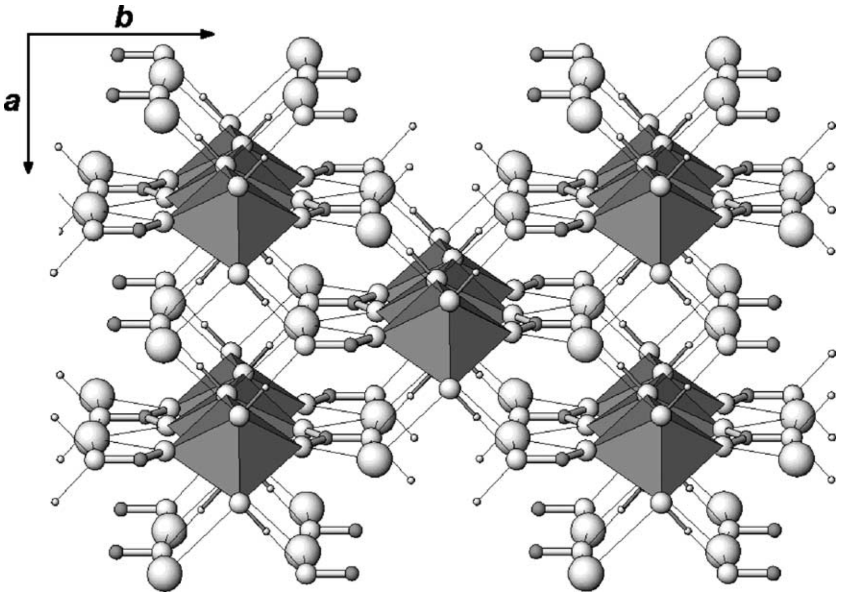

Fig. 4. Structure of $KAl(CO_3)(OH)_2$ as viewed along the *c* axis.

broad maximum [7]. An added difficulty with this peak is encountered when using feldspar sands, because some diffraction peaks can overlap it. Finally, the large peak at 2.52 (rel. I = 48%) coincides with the third strongest line of monocalcium aluminate. Hence, if the cement mortar has an important amount of anhydrate CAC, which happens when the water/cement ratio of 0.4 is used, assignment of this diffraction line to K-dawsonite would be very difficult. For illustrative purposes, Fig. 5 shows the diffraction pattern of a CAC sample hydrated in presence of alkalis (K^+) and carbonated during 2 months [7]. The somewhat broadened peak at 5.53 Å (marked with an asterisk) clearly indicates the presence of a certain amount of K-dawsonite.

3.5. Description of AH process

The AH process has been extensively investigated for a long time due to the several collapses produced on CAC buildings which caused this cement to be banished for uses in special applications only. The presence of intermediate compounds would have allowed concluding that the carbonation process would occur in the presence of alkalis. However, studies on real and also laboratory samples showed no evidences on the formation of intermediate compounds, so that serious doubts arose in the research community about the real existence of this process. This is why the chemical reactions taking place during the AH were traditionally written as [16]:

$$2Na^+(aq) + CO_3^{2-}(aq) + CaOAl_2O_3 \cdot 10H_2O(s)$$
$$\rightarrow CaCO_3(s) + 2Na^+(aq) + 2Al(OH)_4^-(aq) + 8H_2O$$

$$2Na^+ + 2Al(OH)_4^- + CO_2 + 3H_2O$$
$$\rightarrow 2Na^+(aq) + CO_3^{2-} + 2Al(OH)_3(s)$$

According to the studies on the potassium influence on the CAC pastes [6,7] that confirmed the formation of an alkali-carbonated compound, and from its structural formula $KAl(CO_3)(OH)_2$ obtained from the corresponding Rietveld refinement, the chemical reactions involved in the AH chemical process of CAC can be postulated now as follows:

$$C_xAH_y + 2KOH + (x+2)CO_2 \xrightarrow{\text{humidity}} xCaCO_3$$
$$+ 2KAl(CO_3)(OH)_2 + (y-1)H_2O$$

$$2KAl(CO_3)(OH)_2 + 2H_2O \rightarrow AH_3 + 2KHCO_3$$

or, shortly,

$$C_xAH_y + 2KOH + (x+2)CO_2 + 2H_2O$$
$$\rightarrow xCaCO_3 + AH_3 + 2KHCO_3 + (y-1)H_2O$$

Table 5
Cation–oxygen bond lengths L [Å] and bond valences v

Atom	Al	K	C	H	Σ
O(1)	1.901(2) 4 ×	2.792(3) 2 ×		1.15(3)	
	0.51 2 ×	0.17		0.80	1.99
O(2)	1.924(3) 2 ×	2.754(3) 2 ×	1.304(6) 2 ×		
	0.48	0.18	1.33		1.99
O(3)		2.832(4) 2 ×	1.303(6)	1.68(3)	
		0.15 2 ×	1.34	0.20 2 ×	2.04
$\Sigma_A v^{[e]}$	3.00	1.00	4.00	1.00	
$L(1)_{corr}$	1.64	1.94	1.38		

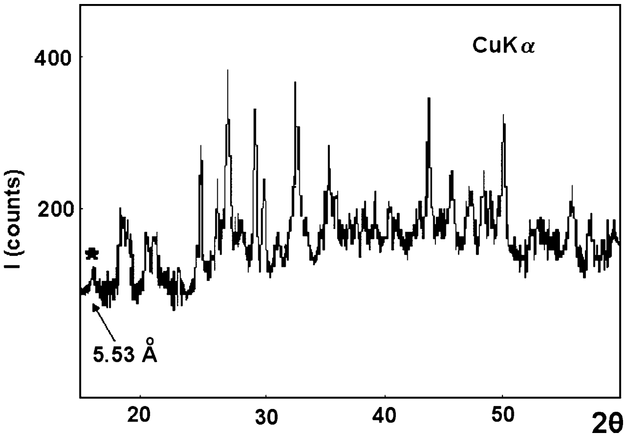

Fig. 5. XRD pattern of alkali-hydrated CAC after 2 months carbonation.

Consequently, the AH process consists on the alkaline carbonation of calcium aluminate hydrates to form calcium carbonate with K-dawsonite, $KAl(CO_3)(OH)_2$, playing the role of intermediate relevant phase. Posterior decomposition of K-dawsonite gives $Al(OH)_3$ and potassium bicarbonate. Comparison of the crystal structures of the calcium aluminate hydrate CAH_{10} [17] and K-dawsonite shows that both structures contain chains of AlO_6 octahedra which would justify the role of CAH_{10} as one probable precursor in the formation of K-dawsonite.

4. Conclusions

A synthesis method of potassium dawsonite has been optimised; with the new method, the synthesised compound has a high-purity and -crystalline degree. The crystal structure of potassium dawsonite has been solved by direct methods from X-ray powder diffraction data and was refined with the Rietveld method.

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