Crystal structure of Kuzel’s salt 3CaO·Al₂O₃·1/2CaSO₄·1/2CaCl₂·11H₂O determined by synchrotron powder diffraction

Adel Mesbah a, Michel François b, Céline Cau-dit-Coumes a, Fabien Frizon a, Yarooslav Flinkchuk c, Fabrice Leroux d, Johann Ravaux e, Guillaume Renaudin f,g,⁎

a Commissariat à l’Energie Atomique et aux Énergies Alternatives, CEA DEN/DTEC/SPDE, F-30207 Bagnols sur Céze, France
b Institut Jean Lamour, UMR 7198, Université Henri Poincaré, Nancy Université, F-54506 Vandoeuvre les Nancy, France
c Swiss-Norwegian Beam Lines at ESRF, 6 rue Jules Horowitz, BP 220, F-38043 Grenoble, France
d Institut de Chimie Séparative de Marcoule, UMR 5257 CEA/CNRS/UM2/ENSCM, BP 17171, CEA Marcoule, F-30207 Bagnols-sur-Cèze, France
e Clermont Université, ENSCF, Laboratoire des Matériaux Inorganiques, BP 10448, F-63000 Clermont-Ferrand, France
f CNRS, UMR 6002, LMR, F-63177 Aubière, France

corresponding author at: Clermont Université, ENSCF, Laboratoire des Matériaux Inorganiques, BP 10448, F-63000 Clermont-Ferrand, France. Tel.: +33 4 73 40 73 36;
E-mail address: guillaume.renaudin@ensccf.fr (G. Renaudin).

The crystal structure of Kuzel’s salt has been successfully determined by synchrotron powder diffraction. It crystallizes in the rhombohedral R3 symmetry with a = 5.7508 (2) Å, c = 50.418 (3) Å, V = 1444.04 (11) Å3. Joint Rietveld refinement was realized using three X-ray powder patterns recorded with a unique wavelength and three different sample-to-detector distances. Kuzel’s salt is the chloro-sulfoaluminate AFm phase and belongs to the layered double hydroxide (LDH) large family. Its structure is composed of positively charged main layer [Ca₂Al(OH)₆]⁺ and negatively charged interlayer [Cl₀.₅·(SO₄)₀.₂₅·2.₅H₂O]⁻. Chloride and sulfate anions are ordered into two independent crystallographic sites and fill successive interlayer leading to the formation of a second-stage compound. The two kinds of interlayer have the compositions [Cl·2H₂O]⁻ and [(SO₄)₀.₅·3H₂O]⁻. The crystal structure explains why chloride and sulfate anions are not substituted and why the formation of extended solid solution in the chloro-sulfate AFm system does not occur.

© 2011 Elsevier Ltd. All rights reserved.
2. Experimental section

2.1. Synthesis

Powder samples with nominal compositions \([\text{Ca}_2\text{Al(OH)}_6\cdot\text{Cl}_x\cdot\text{SO}_4\cdot\text{H}_2\text{O}]\) were synthesized in aqueous solution. The starting powders \(\text{Ca}_2\text{Cl}_2\cdot\text{H}_2\text{O}\) (Aldrich, \(\geq 99\%\)) and \(\text{CaSO}_4\cdot\text{H}_2\text{O}\) (Aldrich, \(\geq 99\%\)) were mixed in pure boiled water (decarbonated) to reach a water/solid mass ratio of 50.

Two series of syntheses were prepared, each of them with \(x = 0.25, 0.50\) and 0.75. The first one was performed at room temperature for one month in closed polypolyene bottles, and the second one at 85 °C for three weeks in closed Teflon reactors. The six suspensions were stored under nitrogen and continuous stirring. At the end of the experiments, the products were centrifuged twice in demineralised and decarbonated water before performing a third centrifugation with isopropanol. The obtained precipitates were filtered with an holographic Notch detector by using a monochromatic wavelength \((\lambda = 0.70093 \, \text{Å})\). The calculated absorption coefficient \(\mu - R\) (\(\mu = \text{linear absorption coefficient}, R = \text{radius of the capillary}\)) was estimated at 0.338. Repetitive measurements showed the non-destructive nature of the X-ray dose. Three sample-to-detector distances were used (150, 250 and 400 mm) in order to combine the advantages of high structural and angular resolutions. The detector parameters and the wavelength were calibrated with NIST LaB\(_6\) (660b). An instrumental resolution function was determined from the LaB\(_6\) data for each sample-to-detector distance.

2.2. SEM analysis (EDS)

Scanning electron microscopy (SEM) analyses were performed with a field emission gun electron microscope (FEI QUANTA 200 ESEM FEG model) coupled with a Bruker SDD 5010 energy dispersive spectrometer (EDS). As the compounds to be analyzed may be damaged under the electron beam, the beam current was lowered by using a 30 µm aperture, whereas the acceleration voltage was maintained at 15 kV and the acquisition time limited to 30 s.

Kuzel’s salt sample synthesized at room temperature was analyzed to check its chemical composition. It was prepared by dispersion in ethanol, deposited on a carbon holder, and fully coated with carbon. The particle sizes ranged between 0.5 and 20 µm. Fifty measurements were performed on one sample, and each analysis was recorded on different crystals. A statistical treatment of the chemical analyses allowed rejecting outliers.

2.3. Thermogravimetry analyses (TGA)

Thermogravimetric analyses (TGA) were performed with a Netzsch STA 409 PC instrument between 20 °C and 1200 °C under nitrogen atmosphere using a heating rate of 2 °C/min. TGA were used to determine the amount of water contained in the interlayer region and to check the anionic stoichiometry.

2.4. Raman spectroscopy

Micro-Raman spectra were recorded at room temperature in the back scattering geometry using a Jobin-Yvon T64000 device. The spectral resolution, about 1 cm\(^{-1}\), was obtained with an excitation source at 514.5 nm (argon ion laser line, Spectra Physics 2017). The Raman detector was a charge coupled device (CCD) multichannel detector cooled down at 140 K by liquid nitrogen. The laser beam was focussed onto the sample through an Olympus confocal microscope with \(\times 100\) magnification. The laser spot was about 1 µm. The measured power at the sample level was kept low (<15 mW) in order to avoid any damage of the material. The Raman scattered light was collected with a microscope objective at 360° from the excitation and filtered with an holographic Notch filter before being dispersed by a single grating (1800 grooves per mm).

2.5. X-ray diffraction

2.5.1. Laboratory powder diffraction

Powder X-ray diffraction (PXRD) patterns were recorded using Cu Kα radiation \((\lambda = 1.54184 \, \text{Å})\) on an X’Pert Pro PANalytical diffractometer, with θ-2θ geometry, equipped with a X’Celerator solid detector and a Ni filter. PXRD patterns were recorded at room temperature in the interval 2°<2θ<120°, with a step size \(\Delta 2\theta = 0.0167°\) and a total counting time of about 3 h.

2.5.2. Synchrotron powder diffraction

Synchrotron powder diffraction data were recorded at the Swiss–Norwegian Beam Lines at ESRF (Grenoble, France) for the Kuzel’s salt sample synthesized at 25 °C i.e. \(\text{AfM-[Cl}_1/2\text{(SO}_4^{1/2}\text{)}_1/4\text{-}2\text{5}°\text{C}}\). White powder was introduced into a Lindemann capillary (0.5 mm by diameter). Data collection was performed at 295 K with a MAR345 Image Plate detector by using a monochromatic wavelength \((\lambda = 0.60093 \, \text{Å})\). The calculated absorption coefficient \(\mu - R\) (\(\mu = \text{linear absorption coefficient}, R = \text{radius of the capillary}\)) was estimated at 0.338. Repetitive measurements showed the non-destructive nature of the X-ray dose. Three sample-to-detector distances were used (150, 250 and 400 mm) in order to combine the advantages of high structural and angular resolutions. The detector parameters and the wavelength were calibrated with NIST LaB\(_6\) (660b). An instrumental resolution function was determined from the LaB\(_6\) data for each sample-to-detector distance.

2.5.3. Indexation and Le-Bail procedure

Indexing was made for the pattern recorded with a sample-to-detector distance of 400 mm (high angular resolution). Standard peak search method was used to locate the diffraction peak maxima with the Reflex program from Material Studio system software (Accelrys). The X-Cell indexing program allowing space group determination was used [36] and solution was found in rhombohedral R3 space group. The three proposed lattice parameters were \(a = 5.758\,\text{Å}\), and \(c = 50.4313\,\text{Å}\) (figure of merit FOM = 1700 for the 18 first reflections). A Le-Bail fitting was made using Fullprof [37]. The peak shape was described with the Thomson–Cox–Hastings function [38]. The profile matching refinement using the first pattern recorded with a sample-to-detector distance of 150 mm (large angular range) led to the following good agreement factors: \(R_p = 1.27\%\) and \(R_w = 1.53\%\) with \(a = 5.7508(1)\,\text{Å}\), \(c = 50.4184(7)\,\text{Å}\) and \(V = 1444.02(2)\,\text{Å}^3\). No superstructure peaks were observed, and the previously proposed hexagonal axis \(c = 100.6\,\text{Å}\) by H. J. Kuzel [34,35] was not considered at this stage of the study.

2.5.4. Structure solution and refinement strategy

The structure was solved by using the direct methods from the EXPO 2004 program [39] working on the extracted intensities from Le-Bail procedure. The centrosymmetric R3 space group symmetry was confirmed, and not R3. The absence of the c glide mirror could be explained by the ordering of the anions: chlorides, and sulfur atoms from sulfate groups were located on the 3a and 3b Wyckoff sites respectively. The structure was refined with Fullprof program [37] using joint refinement from the three patterns. The model contained 11 atomic sites. Ow were water molecules (Ow1, Ow2: linked molecules), Ow3: weakly bonded molecules), O1 and O2 were the apical and basal oxygen atoms of the sulfate groups respectively. The refinement of 61 parameters (36 intensity dependent parameters, 25 profile parameters) including: 1 zero shift, 1 scale factor, 2 lattice parameters, 13 atomic coordinates, 9 temperature factors, led to the final agreement factors \(R_{F} = 1.23(3) = 7.01, 6.78, 6.47, \) and \(R_{I} = 1.23(3) = 7.87, 6.98, 5.69\) for the sample-to-detector distances of 150, 250 and 400 mm respectively. Refinement parameters are collected in Table 1.

The four following constraints on occupancy factors were used: \(\text{occ} (S) = 0.5, \text{occ} (O1) = \text{occ} (O2) = 0.25, \text{occ} (\text{Ow3}) = 0.1667\). It
allowed fixing the composition to $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CaSO}_4 \cdot 1/2\text{CaCl}_2 \cdot 11\text{H}_2\text{O}$, in agreement with TGA and EDS results.

The four following soft restraints on interatomic distances were also applied: $d_{\text{CaO}-\text{O}_1}=d_{\text{CaO}-\text{O}_2}=1.45(5)$ Å, $d_{\text{CaO}-\text{Ow}_1}=d_{\text{CaO}-\text{Ow}_2}=2.50(5)$ Å.

Constraints and restraints were used to take into account the complex nature of the two kinds of interlayer regions, as well as the presence of disorder in the interlayer due to statistical distribution between one sulfate group and two water molecules on the Ow3 site, and to the orientational disorder of the sulfate tetrahedra.

## 3. Results and discussion

### 3.1. Kuzel’s salt characterization

The Kuzel’s salt sample synthesized at room temperature, AFm-[Cl$_{1/2}$(SO$_4^{2-}$)$_{1/4}$]-25 °C ($x=0.5$), was the only single phase material (Fig. 1, top). This powder was used for the X-ray synchrotron powder diffraction measurement. The AFm-[Cl$_{1/2}$(SO$_4^{2-}$)$_{1/4}$]-85 °C sample contained small amount of calcium monosulfoaluminate hydrate (Fig. 1, bottom). The $x=0.25$ samples (AFm-[Cl$_{1/2}$(SO$_4^{2-}$)$_{1/4}$]-25 °C and AFm-[Cl$_{1/2}$(SO$_4^{2-}$)$_{1/4}$]-85 °C) mainly contained Kuzel’s salt and Friedel’s salt. Finally, the $x=0.75$ samples (AFm-[Cl$_{1/2}$(SO$_4^{2-}$)$_{1/4}$]-25 °C and AFm-[Cl$_{1/2}$(SO$_4^{2-}$)$_{1/4}$]-85 °C) comprised a mixture of Kuzel’s salt and a sulfate-rich phase (mainly ettringite for the synthesis at room temperature, and monosulfoaluminate for the synthesis at 85 °C; see Fig. 1).

#### 3.1.1. Kuzel’s salt chemical composition

The chemical composition of Kuzel’s salt was determined by combining SEM-EDS analyses and TGA. The simultaneous presence of the two anions was clearly evidenced, with a calculated anionic Cl$^-$/SO$_4^{2-}$ molar ratio of 1.8 for the Kuzel’s salt synthesized at room temperature. The Ca/Al/Cl/S atomic ratios were measured as 2.00/1.80/0.50/0.26, which agreed fairly well with the electroneutrality of the compound.

The first weight loss recorded by TGA (see Fig. 2) between 25 and 300 °C corresponded to the departure of the eleven water molecules per formula unit 3CaO·Al$_2$O$_3$·1/2CaSO$_4$·1/2CaCl$_2$·11H$_2$O (calc = 33.90%, exp = 34.08%). Dehydration and dehydroxylation were mostly combined at 300 °C. The second weight loss between 450 °C and 900 °C completed at 300 °C. The second weight loss between 450 °C and 900 °C corresponded to the departure of carbonate (calc = 6.07%, exp = 7.53%), and the last weight loss between 1000 °C and 1200 °C was attributed to the decomposition of sulfate (calc = 6.36% for departure of SO$_3^-$).

### Table 1

Crystal and structure refinement data of Kuzel’s salt. Standard deviations are indicated in bracket.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Kuzel’s salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>3CaO·Al$_2$O$_3$·0.5CaSO$_4$·0.5CaCl$_2$·11H$_2$O</td>
</tr>
<tr>
<td>Structural formula</td>
<td>[Ca$_3$(Cl$_2$O$_6$)$_2$(0.25SO$_4$·0.5Cl)·2.5H$_2$O]$^{-}$</td>
</tr>
<tr>
<td>Calculated formula weight (g·mol$^{-1}$)</td>
<td>583.919</td>
</tr>
<tr>
<td>T(K)</td>
<td>293 K</td>
</tr>
<tr>
<td>System</td>
<td>Rhombohedral</td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.7508(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>50.4185(29)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>14440.04(11)</td>
</tr>
<tr>
<td>Z/Dx (g·cm$^{-2}$)</td>
<td>3.2014</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.70993</td>
</tr>
<tr>
<td>Angular range 2θ (°)</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>Nx, Ny, Nz</td>
<td>1473, 1443, 1338</td>
</tr>
<tr>
<td>R$<em>{p}$, R$</em>{wp}$, R$_{f}$</td>
<td>2.01, 2.58, 2.41</td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>7.01, 6.78, 6.47</td>
</tr>
<tr>
<td>N of profile parameters</td>
<td>52</td>
</tr>
<tr>
<td>N intensity dependent parameters</td>
<td>25</td>
</tr>
</tbody>
</table>

exp = 6.94% by referring to the temperature of decomposition of anhydrite CaSO$_4$. The residual powder, obtained after calcinations at 1200 °C, was analyzed by PXRD. It was composed of a mixture of lime (CaO) and mayenite (Ca$_{12}$Al$_{14}$O$_{33}$) – PDF files 43–1001 and 48–1882 respectively – in agreement with SEM results and TGA interpretations.

The apparent minor underestimation of the chloride content could be explained by the carbonate contamination of our powders. This observation was confirmed by Raman spectroscopy with vibration at 1086 cm$^{-1}$ (Fig. 3) which is characteristic of weakly bonded carbonate anion in the center of the interlayer region [31,32]. The carbonate contamination explained also the simultaneous presence of the low temperature (LT–) and the high temperature (HT–) polymorphs of Friedel’s salt in both AFm-[Cl$_{3/4}$(SO$_4^{2-}$)$_{3/8}$]$_{3/8}$ samples, as indicated by the LT + HT notations in Fig. 1. It has been shown that
carbonate to chloride substitution is easily realized in Friedel’s salt and lead to a decrease of the temperature of transition [31,32]; this weak carbonate contamination explains the simultaneous presence of both polymorphs.

3.1.2. Crystal structure description of Kuzel’s salt

Joint Rietveld refinement (Fig. 4 shows the Rietveld plot obtained for one pattern) led to complete description of the Kuzel’s salt structure. Refined atomic parameters are given in Table 2. A general representation of the Kuzel’s salt structure is presented in Fig. 5 along the [100] direction. The layered feature of this bi-anionic AFm compound was clearly maintained, likewise the previously described chloro-carboaluminate AFm compound [32]. Main layer in Kuzel’s salt structure was typical of the AFm family: the oxygen coordination for one pattern) led to complete description of the Kuzel’s salt structure transition. Unlike observed in Friedel’s salt, the chloride-down to 100 K (not shown here) to check the presence of an eventual structure transition. Unlike observed in Friedel’s salt, the chloride-

Table 2

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq (Å²)</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>6c</td>
<td>2/3</td>
<td>1/3</td>
<td>0.0784(1)</td>
<td>7.8(14)</td>
<td>1.0</td>
</tr>
<tr>
<td>Ca1</td>
<td>6c</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0901(1)</td>
<td>15.0(13)</td>
<td>1.0</td>
</tr>
<tr>
<td>Ca2</td>
<td>6c</td>
<td>0.0</td>
<td>0.0</td>
<td>0.4000(1)</td>
<td>26.0(17)</td>
<td>1.0</td>
</tr>
<tr>
<td>Oh1</td>
<td>18f</td>
<td>0.4180(10)</td>
<td>0.3868(15)</td>
<td>0.0993(1)</td>
<td>6(3)</td>
<td>1.0</td>
</tr>
<tr>
<td>Oh2</td>
<td>18f</td>
<td>0.0126(10)</td>
<td>0.2708(13)</td>
<td>0.0581(1)</td>
<td>5(2)</td>
<td>1.0</td>
</tr>
<tr>
<td>Ow1</td>
<td>6c</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1397(1)</td>
<td>50.5(5)</td>
<td>1.0</td>
</tr>
<tr>
<td>Ow2</td>
<td>6c</td>
<td>0.0</td>
<td>0.0</td>
<td>0.3504(1)</td>
<td>49.5(5)</td>
<td>1.0</td>
</tr>
<tr>
<td>Cl</td>
<td>3a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>112(4)</td>
<td>1.0</td>
</tr>
<tr>
<td>S</td>
<td>3b</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>48(5)</td>
<td>0.5(–)</td>
</tr>
<tr>
<td>O1</td>
<td>6c</td>
<td>0.0</td>
<td>0.0</td>
<td>0.4712(1)</td>
<td>1–Ueq(S)</td>
<td>0.25(–)</td>
</tr>
<tr>
<td>O2</td>
<td>18f</td>
<td>0.2689(13)</td>
<td>0.185(3)</td>
<td>0.5004(3)</td>
<td>1–Ueq(S)</td>
<td>0.25(–)</td>
</tr>
<tr>
<td>Ow3</td>
<td>18f</td>
<td>x(O2)</td>
<td>y(O2)</td>
<td>z(O2)</td>
<td>=Ueq(S)</td>
<td>0.166(–)</td>
</tr>
</tbody>
</table>

The sulfate-containing interlayer in Kuzel’s salt, as well as in monosulfoaluminate structure, presents similar types of disorders: 1/ a statistical disorder between one sulfate anion and two water molecules (O2 and Ow3 positions located on the same general position), and 2/ an orientational disorder of tetrahedral sulfate anions (up and down). Raman spectrum from Kuzel’s salt (Fig. 3) presents the sulfate modes of vibration in perfect accordance with band positions previously observed for monosulfoaluminate [41]: ν1 mode at 581 cm⁻¹ (compared to 982 cm⁻¹ for monosulfoaluminate), ν2 mode at 453 cm⁻¹ (compared to 453 cm⁻¹), v3 modes at 1095 and 1150 cm⁻¹ (compared to 1095 and 1154 cm⁻¹) and ν4 mode at 616 cm⁻¹ (compared to 615 cm⁻¹). This correlation evidences the equivalent sulfate-containing interlayer in both Kuzel’s salt and monosulfoaluminate structures.

The sulfate-containing interlayer in Kuzel’s salt, as well as in monosulfoaluminate structure, presents similar types of disorders: 1/ a statistical disorder between one sulfate anion and two water molecules (O2 and Ow3 positions located on the same general position), and 2/ an orientational disorder of tetrahedral sulfate anions (up and down). Raman spectrum from Kuzel’s salt (Fig. 3) presents the sulfate modes of vibration in perfect accordance with band positions previously observed for monosulfoaluminate [41]: ν1 mode at 581 cm⁻¹ (compared to 982 cm⁻¹ for monosulfoaluminate), ν2 mode at 453 cm⁻¹ (compared to 453 cm⁻¹), v3 modes at 1095 and 1150 cm⁻¹ (compared to 1095 and 1154 cm⁻¹) and ν4 mode at 616 cm⁻¹ (compared to 615 cm⁻¹). This correlation evidences the equivalent sulfate-containing interlayer in both Kuzel’s salt and monosulfoaluminate structures.

The sulfate-containing interlayer in Kuzel’s salt, as well as in monosulfoaluminate structure, presents similar types of disorders: 1/ a statistical disorder between one sulfate anion and two water molecules (O2 and Ow3 positions located on the same general position), and 2/ an orientational disorder of tetrahedral sulfate anions (up and down). Raman spectrum from Kuzel’s salt (Fig. 3) presents the sulfate modes of vibration in perfect accordance with band positions previously observed for monosulfoaluminate [41]: ν1 mode at 581 cm⁻¹ (compared to 982 cm⁻¹ for monosulfoaluminate), ν2 mode at 453 cm⁻¹ (compared to 453 cm⁻¹), v3 modes at 1095 and 1150 cm⁻¹ (compared to 1095 and 1154 cm⁻¹) and ν4 mode at 616 cm⁻¹ (compared to 615 cm⁻¹). This correlation evidences the equivalent sulfate-containing interlayer in both Kuzel’s salt and monosulfoaluminate structures.

The sulfate-containing interlayer in Kuzel’s salt, as well as in monosulfoaluminate structure, presents similar types of disorders: 1/ a statistical disorder between one sulfate anion and two water molecules (O2 and Ow3 positions located on the same general position), and 2/ an orientational disorder of tetrahedral sulfate anions (up and down). Raman spectrum from Kuzel’s salt (Fig. 3) presents the sulfate modes of vibration in perfect accordance with band positions previously observed for monosulfoaluminate [41]: ν1 mode at 581 cm⁻¹ (compared to 982 cm⁻¹ for monosulfoaluminate), ν2 mode at 453 cm⁻¹ (compared to 453 cm⁻¹), v3 modes at 1095 and 1150 cm⁻¹ (compared to 1095 and 1154 cm⁻¹) and ν4 mode at 616 cm⁻¹ (compared to 615 cm⁻¹). This correlation evidences the equivalent sulfate-containing interlayer in both Kuzel’s salt and monosulfoaluminate structures.

The sulfate-containing interlayer in Kuzel’s salt, as well as in monosulfoaluminate structure, presents similar types of disorders: 1/ a statistical disorder between one sulfate anion and two water molecules (O2 and Ow3 positions located on the same general position), and 2/ an orientational disorder of tetrahedral sulfate anions (up and down). Raman spectrum from Kuzel’s salt (Fig. 3) presents the sulfate modes of vibration in perfect accordance with band positions previously observed for monosulfoaluminate [41]: ν1 mode at 581 cm⁻¹ (compared to 982 cm⁻¹ for monosulfoaluminate), ν2 mode at 453 cm⁻¹ (compared to 453 cm⁻¹), v3 modes at 1095 and 1150 cm⁻¹ (compared to 1095 and 1154 cm⁻¹) and ν4 mode at 616 cm⁻¹ (compared to 615 cm⁻¹). This correlation evidences the equivalent sulfate-containing interlayer in both Kuzel’s salt and monosulfoaluminate structures.

The sulfate-containing interlayer in Kuzel’s salt, as well as in monosulfoaluminate structure, presents similar types of disorders: 1/ a statistical disorder between one sulfate anion and two water molecules (O2 and Ow3 positions located on the same general position), and 2/ an orientational disorder of tetrahedral sulfate anions (up and down). Raman spectrum from Kuzel’s salt (Fig. 3) presents the sulfate modes of vibration in perfect accordance with band positions previously observed for monosulfoaluminate [41]: ν1 mode at 581 cm⁻¹ (compared to 982 cm⁻¹ for monosulfoaluminate), ν2 mode at 453 cm⁻¹ (compared to 453 cm⁻¹), v3 modes at 1095 and 1150 cm⁻¹ (compared to 1095 and 1154 cm⁻¹) and ν4 mode at 616 cm⁻¹ (compared to 615 cm⁻¹). This correlation evidences the equivalent sulfate-containing interlayer in both Kuzel’s salt and monosulfoaluminate structures.

The sulfate-containing interlayer in Kuzel’s salt, as well as in monosulfoaluminate structure, presents similar types of disorders: 1/ a statistical disorder between one sulfate anion and two water molecules (O2 and Ow3 positions located on the same general position), and 2/ an orientational disorder of tetrahedral sulfate anions (up and down). Raman spectrum from Kuzel’s salt (Fig. 3) presents the sulfate modes of vibration in perfect accordance with band positions previously observed for monosulfoaluminate [41]: ν1 mode at 581 cm⁻¹ (compared to 982 cm⁻¹ for monosulfoaluminate), ν2 mode at 453 cm⁻¹ (compared to 453 cm⁻¹), v3 modes at 1095 and 1150 cm⁻¹ (compared to 1095 and 1154 cm⁻¹) and ν4 mode at 616 cm⁻¹ (compared to 615 cm⁻¹). This correlation evidences the equivalent sulfate-containing interlayer in both Kuzel’s salt and monosulfoaluminate structures.
3.2.2. Mineralogical composition of the 85 °C series

Monosulfoaluminate. The four hydrates. Ettringite and Kuzel’s salt predominated over temperature and 85 °C. Laboratory X-ray powder patterns corresponding x=0.75 (on both side of the Kuzel’s salt stoichiometry) at room temperature were investigated by the syntheses with x=0.25 and -1/2(SO4(2-))3/8]-85 °C sample was mostly composed of monosulfoaluminate, with smaller amount of Kuzel’s salt. Ettringite was no longer observed. The AFm-[Cl6×Ow2 3.432(1)]-85 °C was not observed. The AFm-[Cl6×Ow2 3.432(1)]-85 °C was solved and refined by synchrotron powder diffraction method. This was the first AFm structure determined ab initio from X-ray powder diffraction data using direct method with a full crystal structure description achieved by Rietveld refinement. Kuzel’s salt is a two-stage layered compound with two distinct interlayers, which are alternatively filled by chloride anions only (for one kind of interlayer) and by sulfate anions and water molecules (for the other kind of interlayer). Kuzel’s salt structure is composed of the perfect intercalation of the Friedel’s salt structure and the monosulfoaluminate structure (the two end-members of the studied bi-anionic AFm compound). The structural properties of Kuzel’s salt explain the absence of extended chloride to sulfate or sulfate to chloride substitution.

4. Conclusion

The crystal structure of the Kuzel’s salt with general formula 3CaO·Al2O3·1/2CaSO4·1/2CaCl2·11H2O was solved and refined by synchrotron powder diffraction method. This was the first AFm structure determined ab initio from X-ray powder diffraction data using direct method with a full crystal structure description achieved by Rietveld refinement. Kuzel’s salt is a two-stage layered compound with two distinct interlayers, which are alternatively filled by chloride anions only (for one kind of interlayer) and by sulfate anions and water molecules (for the other kind of interlayer). Kuzel’s salt structure is composed of the perfect intercalation of the Friedel’s salt structure and the monosulfoaluminate structure (the two end-members of the studied bi-anionic AFm compound). The structural properties of Kuzel’s salt explain the absence of extended chloride to sulfate or sulfate to chloride substitution.

Acknowledgments

Laurent Petit, from Electricité de France, is deeply acknowledged for his support of the project. The authors also thank SNBL for the in-house beam time allocation.

References
