



Crystal structure of Kuzel's salt $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\frac{1}{2}\text{CaSO}_4\cdot\frac{1}{2}\text{CaCl}_2\cdot 11\text{H}_2\text{O}$ determined by synchrotron powder diffraction

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ABSTRACT

The crystal structure of Kuzel's salt has been successfully determined by synchrotron powder diffraction. It crystallizes in the rhombohedral $R\bar{3}$ 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 $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ and negatively charged interlayer $[\text{Cl}_{0.50}\cdot(\text{SO}_4)_{0.25}\cdot 2.5\text{H}_2\text{O}]^-$. 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 $[\text{Cl}\cdot 2\text{H}_2\text{O}]^-$ and $[(\text{SO}_4)_{0.5}\cdot 3\text{H}_2\text{O}]^-$. 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.

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1. Introduction

Calcium sulfoaluminate (CSA) cements may have a good potential to stabilize hazardous wastes such as heavy metals [1–8], ion exchange resins [9], aluminum-containing wastes [10] or radioactive streams containing high amounts of borate and sulfate ions [11]. Their outstanding confining properties are attributed to the structural flexibility of the two main hydrates formed, namely calcium monosulfoaluminate hydrate (an AFm phase [12]) and ettringite (an AFt phase [13]), which can accommodate many substitutions, both by cations and anions [14–18]. In this article, the focus is placed on chloride ions, which can be present as ³⁶Cl in many nuclear waste streams. AFm phases exhibit good capacities to bind chloride anions contrarily to AFt phases [15,19,20]. AFm phases belong to the lamellar double hydroxide (LDH) large family. The

crystal structure of AFm phases is composed of positively charged main layers $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ and negatively charged interlayers $[\text{X}\cdot n\text{H}_2\text{O}]^-$ where X is one monovalent anion or half a divalent anion. The following general formulae $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaX}_2\cdot n\text{H}_2\text{O}$ for a monovalent anion, or $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaX}\cdot n\text{H}_2\text{O}$ for a divalent anion, are generally used in cement chemistry. Several crystallographic studies have been performed on AFm compounds incorporating one type of anion only in the interlayer: SO_4^{2-} [12], Cl^- [21–23], CO_3^{2-} [24,25], NO_3^- [26,27], I^- [28,29] and Br^- [28,29]. Few crystallographic studies were devoted to bi anionic-AFm compounds formed by Cl^- – Br^- [29], CO_3^{2-} – OH^- [30] or CO_3^{2-} – Cl^- permutation [31–33].

The present study first aimed at providing a complete crystallographic description of the SO_4^{2-} – Cl^- bi anionic-AFm compounds – Kuzel's salt of composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\frac{1}{2}\text{CaCl}_2\cdot\frac{1}{2}\text{CaSO}_4\cdot 11\text{H}_2\text{O}$ (which differs from Kuzelite, the mineral name of monosulfoaluminate of composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$ [12]) – by powder X-ray diffraction data. H. J. Kuzel proposed a description of Kuzel's salt in 1966 [34,35], involving ordering of chloride and sulfate anions which fill alternatively successive interlayer regions. However, accurate crystallographic data are still missing. The second objective was to investigate the chloride to sulfate permutation in the chloro-sulfate AFm system in order to explain the absence of any extended solid solution, as previously noticed by several authors [20].

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