Chloride and carbonate immobilisation by monosulfoaluminate: study of the solid solutions in the \([\text{CO}_3]^{2-} - \text{Cl}^- - \text{SO}_4^{2-}\) AFm systems.

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Abstract
Cementitious matrices are being used worldwide as a containment medium for radioactive and non-radioactive waste to retard the mobility of contaminants. AFm phases are hydrates precipitated during the hydration process of Portland and CSA cements. The most important AFm phase is the monosulfoaluminate (i.e. the sulphate AFm phase). These phases, to retard the mobility of contaminants. AFm phases are hydrates precipitated during the hydration process of Portland cement. The aim of the present study was to focus on the possibility to trap these three anions (sulfate, carbonate and chloride) by considering the existence of solid solutions and definite compounds. The crystallographic structures of two AFm mixed compounds were fully characterised: the chloro-carboaluminate compound \([\text{Ca}_2\text{Al(OH)}_6]\cdot[\text{Cl}_{1/2}\cdot(\text{CO}_3)_{1/2}\cdot2.25\text{H}_2\text{O}]\) from single crystal data and the chloro-sulfoaluminate compound, called Kuzel’s salt \([\text{Ca}_2\text{Al(OH)}_6]\cdot[\text{Cl}_{1/2}\cdot(\text{SO}_4)_{1/2}\cdot2.5\text{H}_2\text{O}]\), from synchrotron powder data. The synthesised \([\text{Ca}_2\text{Al(OH)}_6]\cdot[\text{Cl}_{1/2}(\text{CO}_3)_{1/2}]\) samples have shown the existence of two polymorphs for chloro-carboaluminate (monoclinic and rhombohedral) at 25°C and only the rhombohedral polymorph at 85°C. In the cases of the two other poles \(\text{Cl}-\text{SO}_4\) and \(\text{CO}_3\cdot\text{SO}_4\) only definite compounds were detected, with a new carbo-sulfoaluminate compound observed by powder X-ray diffraction and Raman spectroscopy.

Originality
Chemistry of AFm phases and anion exchange has already been studied, namely for carbonate, chloride and sulfate anions. Nevertheless the understanding of the ionic immobilisation mechanisms in AFm phases need close studies in order to quantify the nature of the binding mechanisms which are very species sensitive. For this purpose, it is of great importance to characterise in detail the crystallographic structure of mixed compounds (containing two anionic species). The present paper presents the first resolved structures of bi-anionic AFm compounds: the chloro-carboaluminate (related to hydroaluminate) and the chloro-sulfoaluminate (Kuzel’s salt). Long-range order characterisations, combined with local environment characterisation brought by spectroscopic analyses (Raman and NMR), has been efficiently used to locate chloride and carbonate into the structure, and understands the anion exchange mechanisms. X-ray powder diffraction analysis on chloro-sulfoaluminate AFm phase has evidenced, for the first time, the existence of a second-stage AFm phase. This crystallographic study explains the absence of large solid solution domains for the chloride-sulphate system.

Chief contributions
The crystallographic characterisations, namely based on X-ray single crystal analyses, of AFm phases performed the last decade (on carboaluminate, Friedel’s salt structure transition, binitroaluminate, and the Br or I related Friedel’s salt halides) allow to improve knowledge on AFm crystal-chemistry. We investigate now the crystallographic description of more complicated systems; i.e. bi-anionic AFm phases. Such detailed structure description are needed to predict the long-term behaviour of binding hydrates from cementitious matrix, and the potential impact of the immobilised waste on the environment. This is particularly true when considering the immobilisation of radio-nuclides in concrete. The aim of our project is the chemical understanding and thermodynamic modelling of the process responsible for the retention of contaminant species in cimentitious systems.

Keywords: AFm phases, chloride, sulfate, carbonate, X-ray diffraction.

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1. Introduction

Calcium sulfoaluminate (CSA) cements may have a good potential to stabilize hazardous wastes such as heavy metals ion exchange resins, aluminum-containing wastes or radioactive streams containing high amounts of borate and sulfate ions (Cau Dit Coumes et al. 2009). The hydration of CSA leads to the formation of two principal hydrates: monosulfoaluminate (AFm phase) and ettringite (AFt phase). These two phases present interesting structural flexibility; their crystallographic structure admits many substitutions for both cations and anions (Chrysochoou et al. 2006, Glasser et al. 1999, Gougar et al. 1996). This paper focus on the chloride and carbonate, which can be present as 36Cl and 14C in many nuclear waste streams, insertion into the monosulfoaluminat AFm structure. AFm phases belong to the lamellar double hydroxide (LDH) large family. The crystal structure of AFm phases is composed of positively charged main layers [Ca2Al(OH)6] 3+ and negatively charged interlayers [X·nH2O] where X is one monovalent anion or half a divalent anion. The following general formulae 3CaO·Al2O3·CaX·nH2O for a monovalent anion, or 3CaO·Al2O3·CaX·nH2O 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: SO42- (Allmann, 1977), Cl- (Terzis, 1987, Rapin et al., 2002, Renaudin et al., 1999a), CO32- (Francois et al., 1998, Renaudin et al., 1999b), NO3- (Renaudin et al. 1999c, 2000), I- and Br- (Rapin et al., 1999, Renaudin et al., 2004). Few crystallographic studies were devoted to bi anionic-AFM compounds: the CO32-·OH- system (Fischer., 1982), the Cl-·Br system (Renaudin et al., 2004), and more recently two new structures of mixed AFm phases, corresponding to the Cl-·CO32- permutation (Sacerdoti and Passaglia, 1988, Mesbah et al., 2010a and 2010b) and the Cl-·SO42- permutation (Kuzel, 1966, Mesbah et al., 2010c). The aim of this work was the investigation of the existence of mixed AFm compounds containing sulfate, chloride and carbonate anions. This crystallographic study is the first step to evaluate the real capacity of CSA cements to trap nuclear wastes in real conditions. The formation of solid solution, and of definite compounds, has been investigated at two temperatures: 25°C and 85°C.

2. Experimental section

Mixed AFm powdered samples were synthesised in aqueous solution by mixture of CaA (3CaO·Al2O3) with the desired anions from CaCl2·2H2O, CaCO3 or CaSO4·2H2O in demineralised and decarbonised pure water to reach a final water to solid mass ratio of 50. The prepared suspensions were introduced in closed polypropylene bottles under nitrogen atmosphere and stirred during one month at 25°C. The same experience was realised at 85°C during 21 days in Teflon reactors. After that, the suspensions were centrifuged twice with demineralised water and a third centrifugation with isopropanol. Obtained powders were dried in desiccators under N2 at ambient temperature and 31 r.h. controlled by saturated potassium acetate. X-ray powder diffraction (XRPD) patterns were recorded on the X-pert pro diffractometer in Bragg Brentano configuration using Cu Kα radiation (λ = 1.54184 Å). Powder patterns were recorded at room temperature in the interval 3° < 2θ < 120°, with a step size Δ2θ = 0.0167° and a total counting time of 3 hours. Silicon was used as standard to extract the instrumental resolution function and Rietveld refinements were realised using FullProf program to describe the long-range ordering. Micro Raman and 27Al were used to investigate the local order in the interlayer region.

3. The chloro-carboaluminate system: [Ca2Al(OH)6]·[Cl1-x·(CO3)x·0.5·nH2O]

The chloro-carboaluminate sytem corresponds to this of hydrocalumite, a natural mineral described in 1988 (Sacerdoti and Passaglia, 1988). Our results on this chloro-carboaluminate AFm system study have indicated the formation of a large solid solution domain (Mesbah et al., 2010a and 2010b), and the crystal structure of the AFm phase related to hydrocalumite [Ca3Al(OH)6]·[Cl0.5·(CO3)0.5·2H2O] has been described. The corresponding X-ray powder patterns from the chloro-carboaluminate samples synthesized at 25°C and 85°C are presented in Figure 1. Depending on the temperature and the chloride to carbonate substitution level used for syntheses, samples were respectively designated as AFm-[Cl1-x·(CO3)x·0.5]-25°C and AFm-[Cl1-x·(CO3)x·0.5]-85°C.
3.1. Mineralogical composition of the 25°C-series

X-ray powder patterns shows the presence of three AFm phases: 1/ monocarboaluminate (Ca$_4$Al$_2$(OH)$_{12}$CO$_3$·5H$_2$O, triclinic $P1$ symmetry) was observed at high $x$ values ($x > 0.80$), 2/ the two polymorphs of chloro-carboaluminate occurred for large $x$ domains (one with rhombohedral symmetry appears for $0.25 \leq x \leq 0.95$, and the other with monoclinic symmetry appears for $0.50 \leq x \leq 0.95$). Monocarboaluminate predominated for $x \geq 0.95$, while chloro-carboaluminate was the main species for lower $x$ values.

All the samples from the AFm-[$\text{Cl}_{1-x}$(CO$_3$)$_{x/2}$]-25°C series with $0.50 \leq x \leq 0.95$ could therefore be roughly described by a two-phase mixture composed of the rhombohedral chloro-carboaluminate polymorph mixed either with monoclinic chloro-carboaluminate polymorph or with monocarboaluminate. Monocarboaluminate is replaced by the monoclinic chloro-carboaluminate polymorph when the $x$ nominal value decreases from 1.00 to 0.80 (Figure 2). The weight amount of the rhombohedral chloro-carboaluminate polymorph fluctuated around 55 wt % for $0.50 \leq x \leq 0.90$, and reached 100 % for $x = 0.25$. The other 45 wt % for $0.50 \leq x \leq 0.95$ were composed of monocarboaluminate at high $x$ values ($x \geq 0.90$) or of monoclinic chloro-carboaluminate polymorph at lower $x$ values ($x \leq 0.85$). The monocarboaluminate weight amount decreased deeply when chloride was introduced: (66 wt % for $x = 0.95$, 40 wt % for $x = 0.90$, and 5 wt % only for $x = 0.85$), which was compensated by the formation of monoclinic chloro-carboaluminate (4 wt % for $x = 0.95$, 8 wt % for $x = 0.90$, and 35 wt % only for $x = 0.85$). The existence of the two polymorphs for chloro-carboaluminate samples, monoclinic and rhombohedral, returns to the known structure transition of Friedel’s salt. The carbonate-dependence of $T_s$ in the AFm-[$\text{Cl}_{1-x}$(CO$_3$)$_{x/2}$]-25°C series has been described (Mesbah et al.; 2010a) and indicated that AFm-[$\text{Cl}_{1-x}$(CO$_3$)$_{x/2}$] compounds should be consider as carbonated Chloride AFm phases; i.e. carbonated Friedel’s salt.
3.2. Mineralogical composition of the 85°C-series

The samples synthesized at 85°C were single phased (Figure 1). The rhombohedral polymorph only (and not the monoclinic one) of chloro-carboaluminate has been observed \((x = 0.25, 0.50 \text{ and } 0.75)\). Sample AFm-\([\text{CO}_3]_{0.50}\)-85°C contained the triclinic monocarboaluminate phase only. The increase in the temperature of synthesis led to the stabilization of the rhombohedral polymorph: which exhibited the same symmetry than the Friedel’s salt HT-structure. The single phase feature of samples with \(x = 0.25, 0.50 \text{ and } 0.75\) agrees with the existence of an AFm-\([\text{Cl},\text{CO}_3^2]\) solid solution. Calculated chemical composition (from SEM analyses) and refined chemical composition (from Rietveld treatments) agreed fairly well with the targeted nominal composition. Observation made from the 25°C- and the 85°C-series agreed with the metastability feature of the monoclinic chloro-carboaluminate polymorph; namely its disappearance in the 85°C-series.

4. The chloro-sulfoaluminate system: \([\text{Ca}_2\text{Al}(\text{OH})_6]\cdot[\text{Cl}_{1-x} \cdot (\text{SO}_4)_{x/2} \cdot n\text{H}_2\text{O}]\)

The crystal structure of Kuzel’s salt \([\text{Ca}_2\text{Al}(\text{OH})_6]\cdot[\text{Cl}_{0.5} \cdot (\text{SO}_4)_{0.25} \cdot 2.5\text{H}_2\text{O}]\) has been determined (Mesbah et al., 2010c). It corresponds to a second-stage layered compound with two successive kinds of interlayers: one contains chloride anions only and the other contains sulfate anions with water molecules. The possibility to exchange chloride by sulfate or sulfate by chloride in the different kinds of interlayer was investigated. Samples with \(x = 0.25, x = 0.50 \text{ and } x = 0.75\) (on both side of the Kuzel’s salt stoichiometry) have been synthesized at 25°C and 85°C. X-ray powder patterns corresponding to the six samples are presented in Figure 3.

4.1. Mineralogical composition of the 25°C-series

Qualitative analyses of the X-ray powder patterns showed multi-phased powders, with the presence of four different hydrates: monosulfoaluminate, Kuzel’s salt, Friedel’s salt (the two LT- and HT-polymorphs were present simultaneously), and ettringite (the only AFt phase). The stabilization of the two polymorphs of Friedel’s salt was probably due to a weak carbonate contamination (as explained above). The major phase in the AFm-\([\text{Cl}_{3\alpha} \cdot (\text{SO}_4^2)_{\alpha/2}]\)-25°C sample was Friedel’s salt (the two polymorphs HT + LT were present). Kuzel’s salt and ettringite were present as minor phases, whereas monosulfoaluminate was not observed. The AFm-\([\text{Cl}_{3\beta} \cdot (\text{SO}_4^2)_{3\beta/2}]\)-25°C sample contained the four hydrates. Ettringite and Kuzel’s salt predominated over monosulfoaluminate. Kuzel’s salt is the main phase for the \(x = 0.50\) samples only, indicating the absence of large solid solution domain.
4.2. Mineralogical composition of the 85°C series

The sulfate-rich AFm-[Cl\textsubscript{1/4}(SO\textsubscript{4}\textsuperscript{2-})\textsubscript{3/8}]-85°C sample synthesized at 85°C was mostly composed of monosulfoaluminate, with small amounts of Kuzel’s salt. Ettringite, the stability domain of which is decreased at 85°C, was no longer observed. The AFm-[Cl\textsubscript{3/4}(SO\textsubscript{4}\textsuperscript{2-})\textsubscript{1/8}]-85°C sample contained the two chloride-containing AFm phases: Kuzel’s salt and Friedel’s salt (mixture of the two LT- and HT-polymorphs). The AFm-[Cl\textsubscript{1/2}(SO\textsubscript{4}\textsuperscript{2-})\textsubscript{1/4}]-85°C sample was mostly composed of the Kuzel’s salt, with traces of monosulfoaluminate.

These results, in agreement with previous study (Balonis et al., 2010), clearly show that the extended anionic permutation into the two kinds of interlayer regions is not allowed in the Kuzel’s salt structure. The staging feature of Kuzel’s salt explains the difficulties to substitute chloride and sulfate: the modification in one kind of interlayer involves a modification in the other kind of interlayer in order to preserve the electroneutrality of the compound. The second-stage feature of Kuzel’s salt implies that each interlayer should stay mono-anionic.

5. The carbo-sulfoaluminate system: [Ca\textsubscript{2}Al(OH)\textsubscript{6}]·[(SO\textsubscript{4}\textsuperscript{2-})\textsubscript{1/2-x}·(CO\textsubscript{3}\textsuperscript{x/2})\textsubscript{n}H\textsubscript{2}O]

Six samples of AFm phases containing both carbonate and sulfate anions were synthesized: the three compositions with x = 0.25, 0.50 and 0.75 at 25°C and 85°C. The corresponding X-ray patterns are presented in Figure 4.

5.1. Mineralogical composition of the 25°C-series

The qualitative analysis of the three powder patterns corresponding to samples obtained at 25°C showed the presence of three hydrates, ettringite, monocarboaluminate and a third phase. This third phase corresponds to a new mixed AFm phase containing both carbonate and sulfate anions into the interlayer space. The absence of displacement of the diffraction peaks indicates the existence of definite compounds without formation of extended solid solution.

5.2. Mineralogical composition of the 85°C series

Figure 4 shows the three syntheses realised at 85°C. Like the 25°C-series, samples are not single-phase. Nevertheless ettringite do not occur and is replaced by monosulfoaluminate. Monocarboaluminate and the third AFm phases are always observed. The new AFm phase is formed only in the presence of both carbonate and sulfate. The layer spacing of this carbo-sulfoaluminate AFm phase is closed to this of hemicarboaluminate. Nevertheless its stability above 40°C indicates it can not consist of hemicarboaluminate (Matschei et al., 2007). Raman spectra realised on an isolated crystal from sample AFm-[((CO\textsubscript{3})\textsubscript{1/4}(SO\textsubscript{4}\textsuperscript{2-})\textsubscript{1/4}]-85°C is presented in figure 5. Vibrations characteristic to carbonate (1087 cm\textsuperscript{-1}) and sulfate (1006 cm\textsuperscript{-1}) indicate: 1/ carbonate anions are weakly bonded in the centre of interlayer region (as observed in chloro-carboaluminate AFm, and not as monocarboaluminate), and 2/ sulfate anions are not equivalent to those in monosulfoaluminate (which present a sulfate vibration at 982 cm\textsuperscript{-1}). The crystallographic study is in progress to solve the
structure and confirms the existence of a new mixed AFm phase with the permutation of carbonate and sulfate.

Figure 4: PXRD patterns of the six powdered AFm-[(CO$_3$)$_{1/2-x}$(SO$_4$)$_x$] samples: left (the 25°C-series) and right (the 85°C-series). E, Ms, and Mc, respectively refer to ettringite, monosulfoaluminate, monocarboauminate. AFm-CO$_3$-SO$_4$ corresponds to a new mixed carbonate-sulfate AFm phase.

Figure 5: Raman spectra from the AFm-[(CO$_3$)$_{1/4}$(SO$_4$)$_{3/4}$] compound.

6. Conclusions
This study investigates the potential of monosulfoaluminate (AFm hydrate largely formed in CSA, and also Portland, cement pastes) to stabilize chloride and carbonate anions: containment medium for radioactive and non-radioactive waste. The simultaneous presence of the three Cl$^-$, CO$_3^{2-}$ and SO$_4^{2-}$ anions, with different geometric feature involves the formation of mixed AFm compounds. The trapping of chloride and carbonate could be possible in the presence of sulfate by their incorporation in the AFm phases. The formation of extended solid solution (chloro-carboaluminate case) or definite compounds (chloro-sulfoaluminate and carbo-sulfoaluminate cases) has been demonstrated. Crystal structures of mixed AFm phase explain the formation or not of extended solid solutions.

7. References
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