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Uptake of chloride and carbonate ions by calcium monosulfoaluminate hydrate

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ABSTRACT

Decommissioning of old nuclear reactors may produce waste streams containing chlorides and carbonates, including radioactive $^{36}Cl^-$ and $^{14}CO_3^{2-}$. Their insolubilization by calcium monosulfoaluminate hydrate was investigated. Carbonates were readily depleted from the solution, giving at thermodynamic equilibrium monocarboaluminate, monocarboaluminate + calcite, or calcite only, depending on the initial ratio between the anion and calcium monosulfoaluminate hydrate. Chloride ions reacted more slowly and were precipitated as Kuzel's salt, Kuzel's and Friedel's salts, or Friedel's salt only. Rietveld refinement of X-Ray powder diffraction patterns was successfully used to quantify the phase distributions, which were compared to thermodynamic calculations. Moreover, analysing the lattice parameters of Kuzel's salt as a function of its chloride content showed the occurrence of a restricted solid solution towards the sulfate side with general formula $3CaO\cdot Al_2O_3\cdot xCaCl_2\cdot(1-x)CaSO_4\cdot(12-2x)\cdot H_2O$ $(0.36\le x\le 0.50)$.

1. Introduction

Calcium sulfoaluminate (CSA) cements may have a good potential to stabilize hazardous wastes such as heavy metals [1–7], ion exchange resins [8], aluminum-containing wastes [9] or radioactive streams containing high amounts of borate and sulfate ions [10]. Unlike Portland cement, hydration of CSA cement leads to the formation of two principal hydrates: calcium monosulfoaluminate hydrate [11] and ettringite [12] with general formula $3CaO\cdot Al_2O_3\cdot CaSO_4\cdot 12H_2O$ and $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$, respectively. Their contents are very sensitive to the amount of added sulfate: the former dominates in a gypsum-deficient environment, whereas the latter tends to increase in a gypsum-rich system [13]. Both ettringite and calcium monosulfoaluminate hydrate have a flexible structure and can admit various substitutions on their cationic or anionic positions [14–18].

In this study, the focus is placed on chloride and carbonate anions, which may contain long-lived radioactive isotopes ^{36}Cl and ^{14}C, in waste streams produced during the decommissioning of old nuclear reactors (UNGG-type, graphite moderated, cooled by carbon dioxide, and fuelled with natural uranium metal). In the literature, AFm phases are considered as good candidates to bind chloride anions contrarily to AFt phases [15,19,20]. Two Cl-containing AFm phases are involved: Kuzel's salt $3CaO\cdot Al_2O_3\cdot 1/2CaSO_4\cdot 1/2CaCl_2\cdot 11H_2O$, a crystallized compound containing ordered chloride and sulfate anions, and Friedel's salt $3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$, a phase containing chloride anions only. Moreover, it is well known that cement-based materials can be easily carbonated, leading to the formation of calcium hemicarboaluminate hydrate $3.5CaO\cdot Al_2O_3\cdot 1/2CaCO_3\cdot 12H_2O$, calcium monocarboaluminate hydrate $3CaO\cdot Al_2O_3\cdot CaCO_3\cdot 11H_2O$ and/or calcite [21–26]. The AFm phases belong to the lamellar double hydroxide (LDH) large family. Their structure is composed of positively charged main layers $[Ca_2Al(OH)_6]^+$ and negatively charged interlayers $[X\cdot nH_2O]^-$, where X is one monovalent anion or half a divalent anion. The following general formulae $3CaO\cdot Al_2O_3\cdot CaX_2\cdot nH_2O$ for a monovalent anion, or $3CaO\cdot Al_2O_3\cdot CaX\cdot nH_2O$ for a divalent anion, are generally used in cement chemistry. Several structural studies have been performed on AFm compounds incorporating one type of anion only in the interlayer: SO_4^{2-} [11], Cl^- [27–29], CO_3^{2-} [30,31], NO_3^- [32,33], I^- [34,35] and Br^- [34,35]. Others studies were devoted to bi anionic-AFm compounds formed by $Cl^- - Br^-$ [35], $CO_3^{2-} - OH^-$ [36], $CO_3^{2-} - Cl^-$ [37–39] or $SO_4^{2-} - Cl^-$ permutation [40].

The present study was undertaken within a project aiming at assessing the binding capacities of chloride and carbonate anions by hydrated CSA cements. The first step was to investigate the uptake of Cl^- and CO_3^{2-} by calcium monosulfoaluminate hydrate.

2. Experimental section

2.1. Samples preparation

Calcium monosulfoaluminate hydrate with general formula $3CaO\cdot Al_2O_3\cdot CaSO_4\cdot 12H_2O$ was synthesized in aqueous solution. The

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starting reagents, tricalcium aluminate ($Ca_3Al_2O_6$) and gypsum ($CaSO_4{\cdot}2H_2O$), were mixed in decarbonated water (boiled during 1 h and cooled under nitrogen atmosphere) to reach a final water/solid mass ratio of 50. The suspension was introduced in a Teflon reactor and stirred continuously at 80 °C during three weeks. The temperature was chosen to avoid the formation of ettringite, which is unstable over ~70 °C under these conditions [41]. Then, the suspension was filtered twice using pure water and finally rinsed with isopropanol. The precipitates were subsequently dried in a desiccator over potassium acetate (≈20% r.h.) at room temperature.

Sorption tests were carried out by adding 0.5 g (8.03×10^{-4} mole) of calcium monosulfoaluminate hydrate to 10 mL of sodium chloride (NaCl) or sodium carbonate (Na_2CO_3) solutions. The suspensions were kept under stirring at 20 °C. Two series of sorption tests were performed, firstly to study the exchange rate between sulfate and chloride or carbonate, and secondly to investigate the influence of the initial concentration of chloride or carbonate on this exchange.

In the first series of experiments, the Cl^-/monosulfoaluminate and CO_3^{2-}/monosulfoaluminate molar ratios were fixed to 2 and 1 respectively, and the stirring time varied from 1 to 28 days. The second series of experiments lasted for 28 days. The Cl^-/monosulfoaluminate molar ratios were fixed to n = 0.2, 0.5, 1, 1.5, 2, 5 and the CO_3^{2-}/monosulfoaluminate ratios to 0.25, 0.75, 1, 2, 3.5 and 5. At the end of an experiment, the suspension was filtered at 0.45 μm. The solid fraction was analyzed by X-ray powder diffraction and thermogravimetry. The anion concentrations in the solution were determined by ion chromatography and total inorganic carbon analysis.

2.2. Solid characterization

Thermogravimetric analyses were carried out under nitrogen on 50 ± 2 mg of sample using a TGA/DSC Netzsch STA409 PC instrument at 10 °C/min up to 1000 °C.

X-ray powder diffraction (XRPD) patterns were recorded on a Bruker D8 diffractometer, equipped with a “Lynx eye” detector, using Cu Kα radiation ($\lambda = 1.54184$ Å). XRPD patterns were recorded at room temperature within the interval $4° < 2\theta < 120°$, with a step size $\Delta 2\theta = 0.011°$ and a total counting time of 8 h for each sample. The measurements were carried out with the Debye Scherrer geometry (capillary) to reduce the preferred orientation effect. Quantitative phase analysis was performed using Rietveld method with the FullProf_Suite program [42]. All refinements used the Thomson–Cox–Hastings Pseudo Voigt convoluted with an axial divergence asymmetry function [43]. The instrumental function was extracted from pure silicon measured under the same conditions.

Rietveld refinement were performed considering the structural models described by Allmann for monosulfoaluminate [11], Rapin et al. for Friedel's salt [28], Mesbah et al. for Kuzel's salt [40], Goetz-Neunhoeffer and Neubauer for ettringite [44], François et al. for monocarboaluminate [30] and for calcite [45]. Rietveld treatments were used to characterize the mineralogical composition of the samples after contact with chloride and carbonate solutions (quantitative analyses), and to characterize the restricted Kuzel's salt solid solution (lattice parameters and anionic contents in the interlayer regions). Concerning the refinements involving the restricted Kuzel's salt solid solution, the following three constraints were applied: 1) full occupancy of the anionic 3*a* and 3*b* sites by considering the presence of water molecule with $X_{Cl} + X_{Ow} = 1$ in chloride interlayer and $X_S + X_{Ow} = 1$ in sulfate interlayer (X is an occupancy parameter, the corresponding atom being given in subscript), 2) $X_{Cl} + 2\ X_S = 1$ to respect electroneutrality of the crystal, and 3) $X_{Os1} = X_S$ and $X_{Os2} = 3\ X_S$ to respect the sulfate geometry (Os1 and Os2 are the apical and basal oxygen atoms of the sulfate anion, respectively). For more details, see the complete structural description of Kuzel's salt recently reported [40].

2.3. Solution analysis

Chloride and sulfate anions were analyzed using ionic chromatography (Dionex DX 500 equipped with AS9 HC analytical column and AG9 HC guard column, injection volume = 100 μL, eluent = Na_2CO_3 9 mmol/L, flow rate = 1 mL/min, detection = suppressed conductivity (ASRS 300 suppressor in the autosuppression recycle mode)). Carbonates were analyzed using a total organic carbon analyzer from Shimadzu (TOC V-VPN). The quantification limits were 0.5 mg/L for chloride, 1 mg/L for sulfate, and 0.1 mg/L for carbonates. Concentrations were measured with ±5% accuracy.

2.4. Thermodynamic modelling

Thermodynamic calculations were carried out using the CHESS software [46]. The solubility constants of the selected cement phases were taken from the CEMDATA 07 database [47], and from [20] for Kuzel's salt.

3. The $CaO-Al_2O_3-CaSO_4-CaCl_2-H_2O$ system

Details of the X-ray powder patterns corresponding to the chloride sorption tests are presented in Fig. 1.

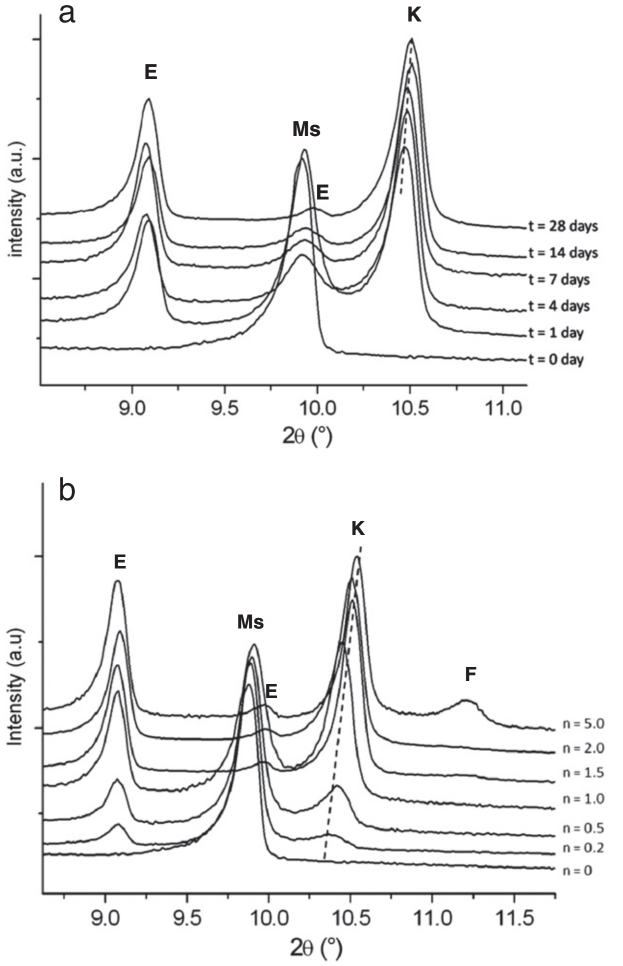

Fig. 1. XRPD patterns recorded after sorption tests with chloride anions (zoom on (00l) reflexions). Influence of the reaction time (a) and of the initial chloride concentration (b) on the phase assemblage. Hydrates are labelled: Ms (calcium monosulfoaluminate hydrate), K (Kuzel's salt), E (ettringite) and F (Friedel's salt). n indicates the initial chloride/monosulfoaluminate molar ratio. The time series was performed at n = 2.