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Solid solution between Al-ettringite and Fe-ettringite ($Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3\cdot 26H_2O$)

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ABSTRACT

The solid solution between Al- and Fe-ettringite $Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3\cdot 26H_2O$ was investigated. Ettringite phases were synthesized at different Al/(Al + Fe)-ratios ($=X_{Al,total}$), so that X_{Al} increased from 0.0 to 1.0 in 0.1 unit steps. After 8 months of equilibration, the solid phases were analyzed by X-ray diffraction (XRD) and thermogravimetric analysis (TGA), while the aqueous solutions were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). XRD analyses of the solid phases indicated the existence of a miscibility gap between $X_{Al,total}=0.3$–0.6. Some of the XRD reflections showed two overlapping peaks at these molar ratios. The composition of the aqueous solutions, however, would have been in agreement with both, the existence of a miscibility gap or a continuous solid solution between Al- and Fe-ettringite, based on thermodynamic modeling, simulating the experimental conditions.

1. Introduction

Ettringite occurs in natural alkaline environments (like Ca-rich igneous rocks, contact metamorphosed Ca-rich sediments or bioclastic sediments cemented by gypsum) with different chemical compositions, e.g. $Ca_6(Al)_2(SO_4)_3(OH)_{12}\cdot 25H_2O$ [1], $Ca_6(Si,Al,B)_3(SO_4)_2(O,OH)_{12}(OH)_4\cdot 26H_2O$ [2] and $Ca_6(Al,Si)_2(SO_4)_2(B(OH)_4)(OH)_{12}\cdot 26H_2O$ [3]. Iron containing analogues $Ca_6(Fe(III)_{1.5}Al_{0.3}Mn(II)_{0.2})_2(SO_4)_{2.3}(B(OH)_4)_{1.2}(OH)_{12}\cdot 25H_2O$ [4] and $Ca_6(Si,Al,Fe)_2(SO_4)_3(Cl,OH)_x\cdot xH_2O$ [5] have been reported. The structure of these minerals has been well investigated (e.g. [6–10]). Ettringite and it analogues form hexagonal, prismatic crystals. In pure aluminum containing ettringite columns of $[Al(OH)_6]^{3-}$ octahedra are linked together by calcium ions. The (OH) groups are shared between Al-octahedra and Ca-polyhedra and each of the latter contains four water molecules, which are located on the outer surface of the columns. Al(III) can be substituted by Fe(III) as well as by e.g. Cd(II) and Cr(III) [11–14]. The sulfate tetrahedra can be partially or entirely replaced by e.g. SeO_4^{2-} and CrO_4^{2-} [15–17].

Ettringite occurs not only in natural environments, but is also formed during hydration of Portland cement and super-sulfated blast furnace slag cements [18]. It forms from the cement clinker phases aluminate (idealized $Ca_3Al_2O_5$) and ferrate (idealized $Ca_2(Al_xFe_{1-x})_2O_5$), gypsum/anhydrite ($CaSO_4\cdot 2H_2O/CaSO_4$) and water. The Fe(III) present in ferrite can either partly replace Al(III) in ettringite or in other hydrates form during cement hydration such as monosulfate ($Ca_4[Al_{1-x}Fe_x(OH)_6]_2(SO_4)\cdot 6H_2O$) or hydrogarnet ($Ca_6[Al_{1-x}Fe_x(OH)_4]_2(OH)_4$), or it can precipitate as $Fe(OH)_3$, or as Ca–Al–Fe-gel [19–26]. The differentiation between iron free and iron containing phases in the hydrated cement samples is very difficult by the methods commonly used in cement chemistry (i.e. X-ray diffraction (XRD), thermogravimetric analysis (TGA), environmental scanning electron microscopy (ESEM), Raman spectroscopy), since the structural modification of the crystals is small and therefore difficult to detect. Pure iron containing ettringites ($Ca_6[Fe(OH)_6]_2(SO_4)_3\cdot 26H_2O$) have been synthesized and their solubility has been determined [12,27–29]. Buhlert and Kuzel [11] investigated the solid solution series between Al- and Fe-ettringite. They suggested a possible miscibility gap between 20 and 30 mol% Al ($X_{Al}=0.2$–0.3), but the results were ambiguous, since the detected peak broadening was weak. Neubauer et al. [30] stated that ettringite phases immediately formed after the mixing of cement with water show a high substitution of aluminum by iron and of sulfate by carbonate. They performed in-situ X-ray diffraction and evaluated their data with Rietveld refinement. Neubauer et al. [30] found that the *c* lattice parameter of ettringite is highest at the very early hydration period of the cement. During the induction period they observed a decrease of the *c* parameter. From that they concluded that probably the ettringite crystals ripe, incorporating aluminum and sulfate.

The goal of this study was to examine the formation of solid solutions of the system $Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3\cdot 26H_2O$ and to determine the solubilities of the solid phases. The different solids were

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synthesized and a thermodynamic model was established and compared to the experimental results of the solid and the liquid phases.

2. Methods

2.1. Synthesis of the solid solution series

A solid solution series $Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3\cdot 26H_2O$ was synthesized by adding freshly prepared CaO, $Fe_2(SO_4)_3\cdot 5.3H_2O$ and/or $Al_2(SO_4)_3\cdot 16.2H_2O$ to 0.032 M KOH-solution. The amounts of the reactants were varied in that way that $X_{Al,total}$ increased from $X_{Al,total}=0.0$ to $X_{Al,total}=1.0$ in 0.1 unit steps; the liquid/solid ratio was constant ($l/s=10$) in all experiments. $X_{Al,total}$ is defined as the molar ratio of Al added to the system: $X_{Al,total}=\frac{x_{Al}}{x_{Al}+x_{Fe}}$, where x_{Al} are the moles of Al and x_{Fe} are the moles of Fe added to the system.

The mixtures were stored in sealed PE bottles and shaken at 20 °C for eight months. In contrast to Al-ettringite, where equilibrium is reached after a couple of days [31], for Fe-ettringite equilibrium is reached only after approximately 6 months [29]. Therefore the different mixtures of the solid solution series were equilibrated for 8 months.

After equilibration, the solid and the liquid phases were separated by vacuum filtration through 0.45 µm nylon filters. Both the mixing and the filtration were done in a N_2-filled glove box (N_2 was continuously bubbled through KOH-solution) to minimize CO_2 contamination. Afterwards the solid and the liquid phases were analyzed to characterize the precipitates and the dissolved concentrations of the different elements.

2.2. Characterization of the solid phases

After separating the liquid and solid phases, the solid precipitates were dried for three weeks in N_2-filled desiccators over saturated $CaCl_2$ solution; relative humidity was approximately 30%. The dry solid phases (masses of the solid phases amounted to 3.7 g–4.8 g for each sample) were ground by hand with an agate mortar in a N_2-filled glove box to <63 µm and analyzed by X-ray diffraction (XRD) and thermogravimetric analysis (TGA). For environmental scanning electron microscopy (ESEM) studies, a part of the dry solid phases was not ground but freshly fractured.

The XRD analyses were performed on a PANalytical X'Pert PRO system using CuK_α radiation (generator: 40 kV and 40 mA). The samples were transferred by backloading into specimen holders of 16 mm diameter. The measurement was carried out between 5 and 80° 2θ with a measuring speed of approximately 0.1°/s. For evaluation of the data the software X'Pert HighScore Plus V. 2.0a was used. To determine the lattice parameters of the different synthesized phases the following evaluation steps were carried out: first the background was set manually, and then a peak search was performed followed by a profile fitting. The indexing of the reflections was done using the Treor method. Approximately 45 reflections up to 75° 2θ were used for indexing. The cell parameters were then refined by least square algorithm. These cell parameters served as input for a Rietveld refinement of the lattice parameters using the ettringite structure published by Goetz-Neunhoeffer and Neubauer [38]. The refined parameters were background (5th order polynom), specimen displacement, scale factor, lattice parameter, profile parameters *U*, *V*, *W* (Pseudo Voigt profile), and preferred orientation in (100).

For TGA (Mettler Toledo TGA/SDTA851^e) about 8–12 mg of the ground sample was heated under N_2 over a temperature range of 30 to 980 °C at a rate of 20 °C/min.

The weight loss measured by TGA was used to calculate the amount of ettringite formed assuming that up to 300 °C only water evaporated ($Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3\cdot 26H_2O - 32H_2O \leftrightarrows 3CaO\cdot[Al_{1-x}Fe_xO_{1.5}]_2\cdot 3CaSO_4$).

ESEM studies were performed on Philips ESEM FEG XL 30 using low vacuum mode (at approximately 1 Torr H_2O).

2.3. Characterization of the liquid phase

One part of the liquid phases of each sample was instantly diluted (1:10 for inductively coupled plasma optical emission spectroscopy (ICP-OES) and 1:100 for inductively coupled plasma mass spectrometry (ICP-MS)) with nitric acid (diluted 1:10 from Merck HNO_3 suprapur quality, 65%, with high-purity water (18.2 MΩ/cm), prepared by a MilliQ-Gradient A10 System (Millipore)) in order to stabilize metals in solution and prevent the adsorption of the dissolved ions into the PE vials used. Another part of each sample was left untreated to measure the pH-value. This was done without any delay to minimize CO_2-contamination. Prior to the measurements the pH-meter (Knick pH-Meter 766 with a Knick SE 100 pH/Pt 1000 electrode) was calibrated with 0.001 to 1.0 M KOH-solutions.

The concentrations of calcium, sulfur and potassium were measured by ICP-OES (Varian, VISTA Pro) and the concentration of aluminum and iron by ICP-MS (Finnigan MAT, ELEMENT2).

2.4. Thermodynamic modeling

Thermodynamic modeling was carried out using the geochemical code GEMS [32]. GEMS is a broad-purpose geochemical modeling code, which computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. Chemical interactions involving solids, solid solutions, gas mixture and aqueous electrolyte are considered simultaneously. The default database of GEMS code was used, which is based on the PSI chemical thermodynamic database [33].

The Gibbs free energy of formation at 25 °C of the ettringite phases was adjusted to 20 °C using following equation:

$$\begin{aligned}\Delta_a G^0_T &= \Delta_f G^0_{T_0} - S^0_{T_0}(T-T_0) - \int_{T_0}^{T}\int_{T_0}^{T}\frac{C^0_p}{T}\,\mathrm{d}T\mathrm{d}T \\ &= \Delta_f G^0_{T_0} - S^0_{T_0}(T-T_0) - a_0\left(T\ln\frac{T}{T_0} - T + T_0\right) \\ &\quad - 0.5a_1(T-T_0)^2 - a_2\frac{(T-T_0)^2}{2T\cdot T_0^2} - a_3\frac{2\left(\sqrt{T}-\sqrt{T_0}\right)^2}{\sqrt{T_0}}\end{aligned} \tag{1}$$

Where $\Delta_a G^0$ is the apparent Gibbs free energy of formation at any given temperature, which refers to the Gibbs free energy of the elements at 25 °C, $T=$ the given temperature (293.15 K in this study), $T_0=298.15$ K, S^0 is the entropy, C^0_p is the heat capacity and a_0, a_1, a_2 and a_3 are empirical coefficients (see Eq. (2)).

$$C^0_p = a_0 + a_1T + a_2T^{-2} + a_3T^{-0.5}. \tag{2}$$

A more detailed description of the temperature correction used in GEMS is given in [34–35].

Activity coefficients of aqueous species γ_i were computed with the built-in expanded extended Debye–Hückel equation in Truesdell–Jones form with individual parameters a_i and common third parameter b_γ [33]:

$$log\gamma_i = \frac{-A_\gamma z_i^2\sqrt{I}}{1+B_\gamma a_i\sqrt{I}} + b_\gamma I \tag{3}$$

where z_i denotes the charge of species *i*, *I* the effective molal ionic strength, $b_\gamma=0.064$, and A_γ and B_γ are *P,T*-dependent coefficients. This activity correction is thought to be applicable up to 1–2 m ionic strength [32,36].