Solubility of Fe-ettringite and its Solid Solution with Al-ettringite

G. Moeschner[1,2], B. Lothenbach[1], F. Winnefeld[1], A. Ulrich[1], R. Figi[1],
R. Kretzschmar[2]
[1]*Empa, Duebendorf, Switzerland;* [2]*ETH Zurich, Zuerich, Switzerland*

The hydration products of ferrite in Portland cement are expected to be similar to the hydration products of the pure aluminate phase. The solubility of Fe-ettringite was studied within the pH range 11-14. It turned out that the formation of pure Fe-ettringite has a slow kinetic, so that equilibrium was not reached before 180 days. After analyzing the liquid (ICP-OES, ICP-MS) and the solid phase (XRD, TGA) a solubility constant of log K_{S0} = -44.0 for Fe-ettringite was calculated at pH between 11 and13. At higher pH values Fe-monosulfate and Fe-monocarbonate became stable in the synthesized mixtures. In a second step the possible solid solution formation between Fe- and Al-ettringite was investigated by mixing reagents with different Al/Fe-ratios in KOH-solution at pH 12.5. XRD analyses of the solid phases indicated that there is a continuous solid solution between the two endmembers Al-ettringite and Fe-ettringite, since the main diffraction peak of the ettringite phases did not show a broadening and the determined c-axis decreased gradual, when more aluminium entered the solid phase.

1. Introduction

The ferrite phases ($Ca_2(Al_xFe_{1-x})O_5$) present in Portland cement show slow hydration kinetics in contrast to C_3A. The formed hydration products of ferrite are expected to be similar to the hydration products of aluminate [1-3], e.g. Fe-ettringite, Fe-monosulfate or Al/Fe solid solutions like Al/Fe-ettringite, Al/Fe-monosulfate. In addition the formation of amorphous iron hydroxide is possible.

Both the pure iron containing hydrates and the aluminum and iron mixed phases have been synthesized previously and investigated in terms of their structure [4-6]. Up to now no experimental data of their solubility are available.

Babushkin et al [7] estimated the thermodynamic data of Fe-ettringite on the basis of the thermodynamic data of Al-ettringite. Hence the solubility product of Fe-ettringite can be calculated (K_{S0} = -49.8). Lothenbach and Winnefeld [8] calculated a solubility product K_{S0} = -49.4 for Fe-ettringite for the reaction $Ca_6[Fe(OH)_6]_2(SO_4)_3 \cdot 26H_2O$ D $6Ca^{2+} + 2Fe(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O$.

The solubility of Fe-ettrinigite provides information about the stability of Fe-ettringite compared to Al-ettringite and if there is a possibility for the formation of a solid solution of the composition $Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3\cdot 26H_2O$.

The purpose of this study is to determine the solubility product of Fe-ettringite and to investigate experimentally, if a solid solution between Fe- and Al-ettringite exists.

2. Method

Fe-ettringite was synthesized by adding stoichiometrical amounts of freshly burnt CaO and $Fe_2(SO_4)_3\cdot 5.3H_2O$ to KOH solutions at different concentrations (*c*(KOH) = 0.001 – 1.0 mol/l). The solubility product was determined from both precipitation experiments and dissolution experiments (modified after [9]). For the precipitation experiment 0.64 g CaO, 0.97 g $Fe_2(SO_4)_3\cdot 6H_2O$ and 50 g of the respective KOH solution were mixed. The samples were shaken for 180 days in sealed PE bottles at 20 °C until equilibrium was reached. For the dissolution experiments half of the chemicals used in the precipitation experiments were mixed. After 180 days 25 g of the respective KOH solution were added and the samples were shaken for further 180 days.

To confirm the point of time of the achievement of equilibrium a kinetical experiment was carried out establishing the same conditions as in the precipitation experiment but keeping the used KOH solution at a constant concentration (*c*(KOH) = 0.016 mol/l).

The different mixtures of the solid solution of $Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3\cdot 26H_2O$ were synthesized by adding stoichiometrical amounts of CaO, $Fe_2(SO_4)_3\cdot 5.3H_2O$ and/or $Al_2(SO_4)_3\cdot 16.2H_2O$ to KOH solution (*c*(KOH) = 0.032 mol/l). The amounts of the chemicals were varied in the way that x increases from x = 0.0 to x = 1.0 in 0.1 unit steps. The samples were equilibrated for 260 days.

The solid and the liquid phases of the samples were separated by pipetting the supernatant and filtering it through a 0.45 µm nylon filter.

One part of the solutions was immediately acidified with supra-pure nitric acid to measure calcium and sulphur by ICP-OES and iron and aluminum by ICP-MS. Before some of the untreated solutions were used to measure the pH values, the pH meter was calibrated with fresh KOH solutions (*c*(KOH) = 0.001 – 1.0 mol/l) to minimize the alkali error. Therefore the obtained voltage was correlated to the target pH value of the respective KOH solution considering ionic strength as well as the measured temperature of the solution.

The solid phases were dried in a desiccator above saturated $CaCl_2$ solution at a relative humidity of approximately 30 %. The dried solid phases were then grinded and analyzed by XRD and TGA. Mixing, separating and grinding of the samples was done in a N_2 filled glove box (the atmosphere was continuously bubbled through KOH solution) to prevent carbonation of the samples

The water loss measured by TGA was used to calculate the amount of Fe-ettringite ($Ca_6[Fe(OH)_6]_2(SO_4)_3 \cdot 26H_2O - 32H_2O$ D $3CaO \cdot Fe_2O_3 \cdot 3CaSO_4$), portlandite ($Ca(OH)_2 - H_2O$ D CaO) and AFm phases - Fe-monosulfate and Fe-monocarbonate - ($Ca_4[Fe(OH)_6]_2(SO_4) \cdot 6H_2O - 12H_2O$ D $3CaO \cdot Fe_2O_3 \cdot CaSO_4$ and $Ca_4[Fe(OH)_6]_2(CO_3) \cdot 6H_2O - 12H_2O$ D $3CaO \cdot Fe_2O_3 \cdot CaCO_3$) formed. Since the separation of Fe-monosulfate and Fe-monocarbonate by TGA was not possible these two phases are summarized as AFm phases.

For the examination of the solid solution series the XRD data were used to determine the lattice parameters for the different mixed phases. Peak search and profile fitting were carried out on the raw data. The indexing of reflections was done by the Treor method. At last the cell parameters were refined (least error square minimization).

3. Results

3.1 Kinetics

As presented in Fig. 1 the kinetical experiment showed that after 180 days at a pH of 12.2 chemical equilibrium was reached, since Fe-ettringite was the only stable phase identified. After 7, 24, 45 and 90 days gypsum still could be detected as a second stable phase.

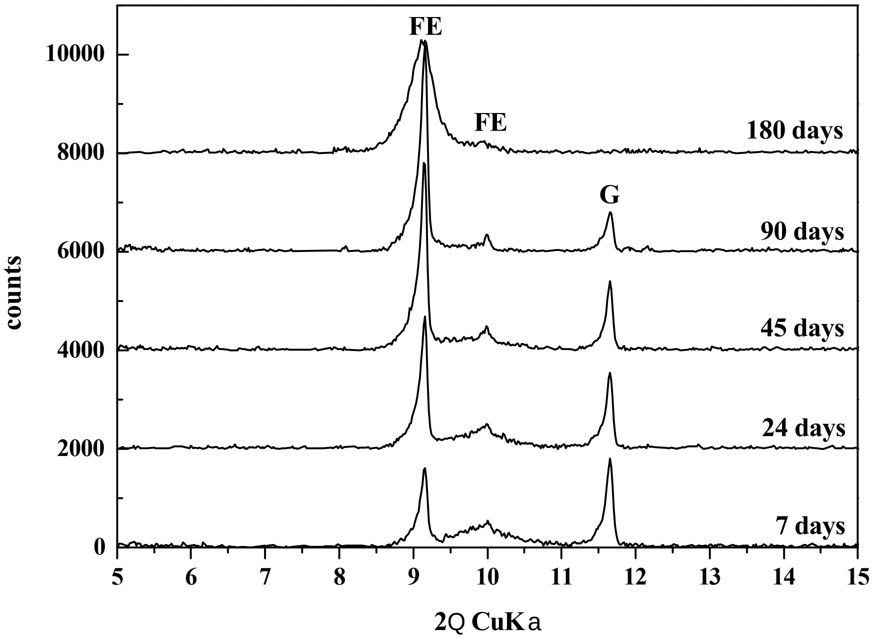

Fig.1: X-ray diffraction spectra for synthesized Fe-ettringite after different time periods of ageing.
FE: Fe-ettringite, G: Gypsum

3.2 Precipitation and Dissolution Experiments

The measured calcium and sulfate concentrations for the determination of the solubility of Fe-ettringite are presented in Fig. 4.

The analysis of the solid phases of the precipitation experiment by TGA and XRD (Fig. 2A) revealed that Fe-ettringite was stable up to pH 13. At higher pH values Fe-ettringite became instable and Fe-monosulfate and Fe-monocarbonate were formed. The presence of Fe-monocarbonate showed that, even it was paid special attention to minimize carbonation, some CO_2 had entered into the solid phase, either during preparation, equilibration or measurements.

In the dissolution experiments Fe-monosulfate was formed at pH ≥ 12.8. Also Fe-monocarbonate was formed earlier than in the precipitation experiments, namely at pH ≥ 13.6 (Fig. 2B).

Both the precipitation and the dissolution experiments indicated correspondingly that in KOH solution above a pH of approximately 13 Fe-monosulfate became more stable than Fe-ettringite.

The water content of Fe-ettringite was determined by TGA and was equivalent to 32 H_2O, which approved the assumed composition of $Ca_6[Fe(OH)_6]_2(SO_4)_3 \cdot 26H_2O$.

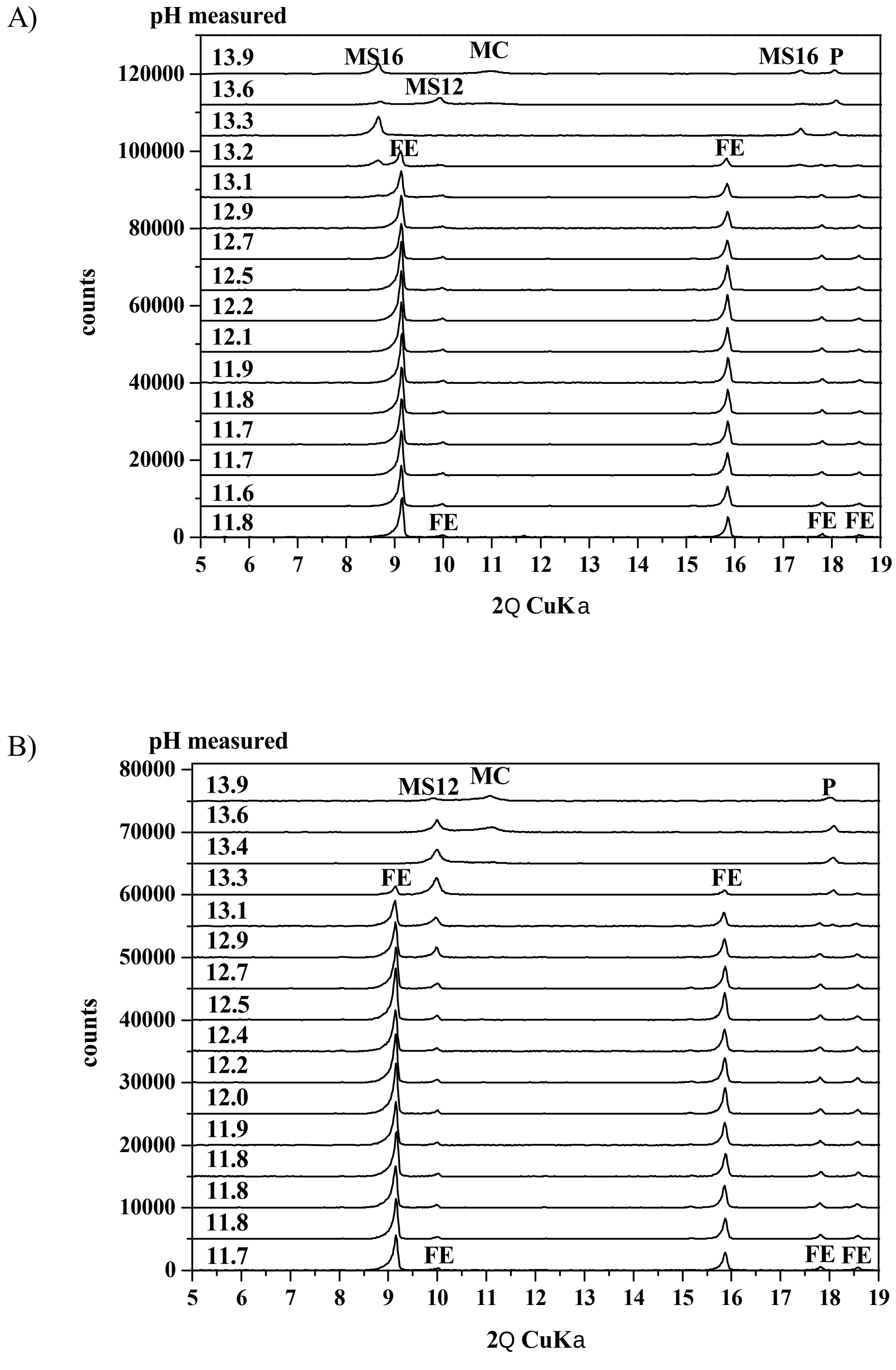

Fig. 2: X-ray diffraction spectra for A) precipitation and B) dissolution experiments. FE : $Ca_6[Fe(OH)_6]_2(SO_4)_3 \cdot 26H_2O$, MS12 : $Ca_4[Fe(OH)_6]_2(SO_4) \cdot 6H_2O$, MS16 : $Ca_4[Fe(OH)_6]_2(SO_4) \cdot 10H_2O$, MC : $Ca_4[Fe(OH)_6]_2(CO_3) \cdot 6H_2O$; P : Portlandite; 2Θ value cf. [10]

3.3 Solid Solution Experiment

The measured concentrations for calcium and sulfate for the solid solution experiments $Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3{\cdot}26H_2O$ are shown in Fig. 6.

The modification of the unit cell in direction of the c-axis at different Al/Fe ratios ($X_{Al,total}$ = mol(Al)/(mol(Al)+mol(Fe))) added to the system) is presented in Fig. 3. The lattice constant c got smaller the more aluminum entered the solid phase. The modification of the c-axis suggested a continuous solid solution.

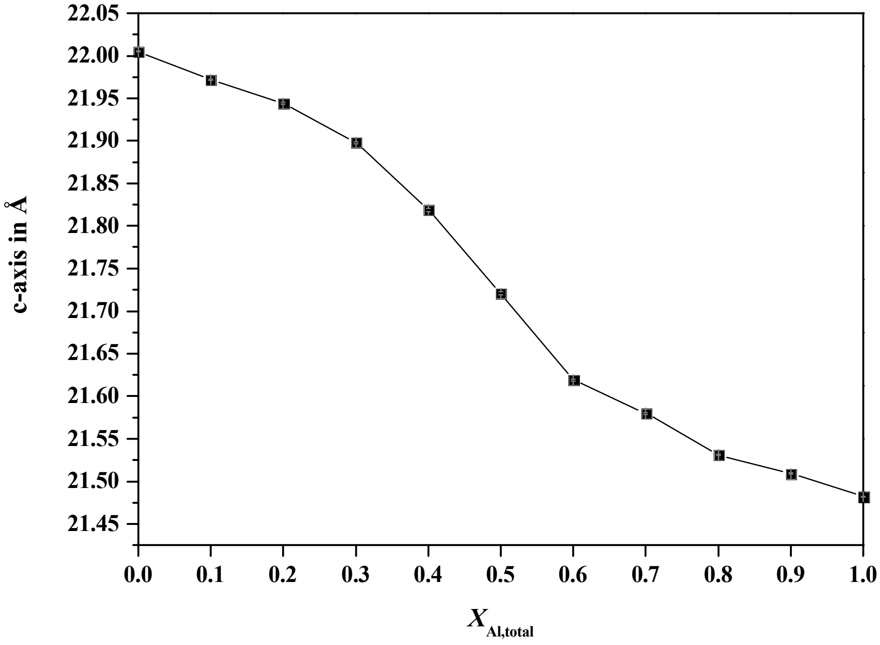

Fig. 3: Modification of the c-axis of $Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3{\cdot}26H_2O$ at different Al/Fe ratios (**$X_{Al,total}$**) in direction of the c-axis.

4. Modeling

The thermodynamic modeling was performed with the geochemical modeling program GEMS (Geochemical Equilibrium Modeling by Gibbs Energy Minimization) [11]. The thermodynamic data for the aqueous species and for portlandite, gypsum and iron hydroxide stem from the PSI-GEMS database [12].

On the basis of the measured ion concentrations the solubility products of Fe-ettringite, Fe-monosulfate and Fe-monocarbonate can be determined.

The solubility product K_{S0} of Fe-ettringite was calculated accordingly to:
$K_{S0} = \{Ca^{2+}\}^{6} \cdot \{Fe(OH)_4^{-}\}^{2} \cdot \{SO_4^{2-}\}^{3} \cdot \{OH^{-}\}^{4} \cdot \{H_2O\}^{26} = 10^{-44.0\pm0.7}$
For Fe-monosulfate
$K_{S0} = \{Ca^{2+}\}^{4} \cdot \{Fe(OH)_4^{-}\}^{2} \cdot \{SO_4^{2-}\} \cdot \{OH^{-}\}^{4} \cdot \{H_2O\}^{6} = 10^{-33.1\pm0.5}$
For Fe-monocarbonate
$K_{S0} = \{Ca^{2+}\}^{4} \cdot \{Fe(OH)_4^{-}\}^{2} \cdot \{CO_3^{2-}\} \cdot \{OH^{-}\}^{4} \cdot \{H_2O\}^{6} = 10^{-35.4\pm0.3}$
where {} denotes the activity.

These solubility products were then added to the GEMS database [12] and the experiments were modeled and compared with the experimental data.

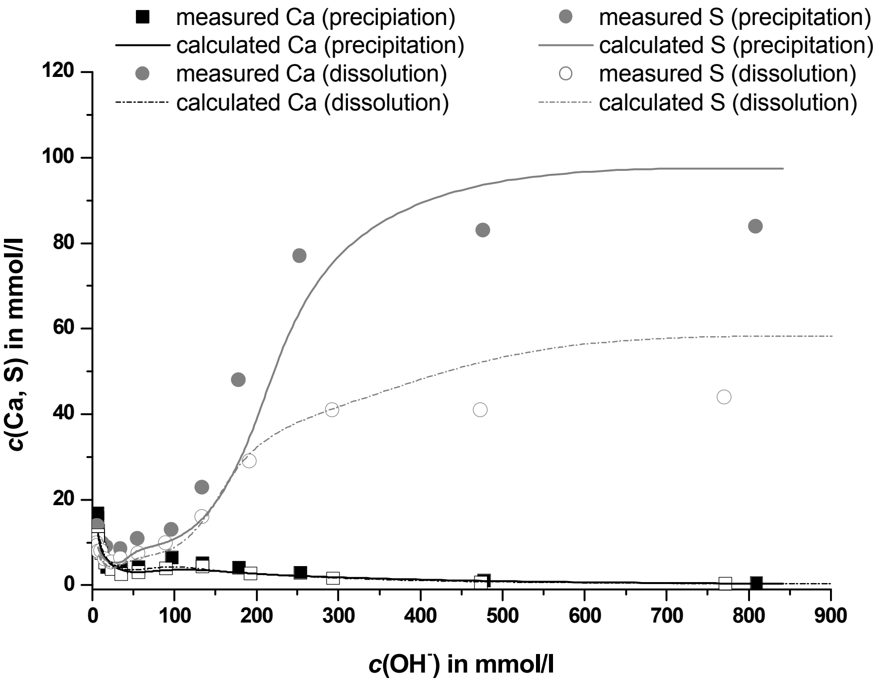

Fig. 4: Measured and calculated concentration of calcium (Ca) and sulfur (S) in the aqueous solution of both precipitation and dissolution experiments (at 20 °C).

As shown in the Fig. 4 the calculated calcium und sulfate concentrations were concordant with the measured concentrations. Also for potassium and iron a good agreement was obtained.

The good correspondence between experimental and calculated concentrations in both experiments indicated that (i) thermodynamic equilibrium had been reached and that (ii) in fact, Fe-ettringite, Fe-monosulfate and Fe-monocarbonate were the dominant solid phases in the K-Fe(III)-SO_4-(CO_2)-H_2O mixtures investigated.

Further it should be noted that even though Fe-ettringite was found to be unstable above a pH value of ~13 under the experimental conditions used, Fe-ettringite could be stable at pH >13 under different conditions (e.g. in the presence of high sulfate concentrations in fresh cement pastes at higher pH values).

The composition of the solid phases of the precipitation and dissolution experiments obtained from the mass losses during TGA measurements as well as the modeled composition are shown in Fig. 5.

The precipitation experiments were prepared so that maximal 2.5 g Fe-ettringite could precipitate. Three samples of this experiment showed a clearly higher mass. That and the formation of Fe-monosulfate containing 16 H_2O (see Fig. 2A) indicated that these three samples had not completely dried. Furthermore according to thermodynamic calculations traces of iron hydroxide ought to precipitate at OH^- concentrations ≤ 19 mmol/l. This could not be proved by TGA and XRD measurements, as the detection limit of TGA is too high and as amorphous iron hydroxide is undetectable by XRD. Since separation of Fe-monosulfate and Fe-monocarbonate by TGA was not possible, they were summarized as AFm-phases.

In the dissolution experiments maximal 1.25 g Fe-ettringite could precipitate. This value was not exceeded in any sample and only Fe-monosulfate containing 12 H_2O (MS12) was present (Fig. 2B). Again Fe-monosulfate and Fe-monocarbonate were summarized as AFm phases and iron hydroxide should precipitate at OH^- concentrations ≤ 18 mmol/l.

In agreement with the experimental results Fe-monosulfate and Fe-monocarbonate were calculated to become stable at somewhat higher pH values in the precipitation experiments than in the dissolution experiments.

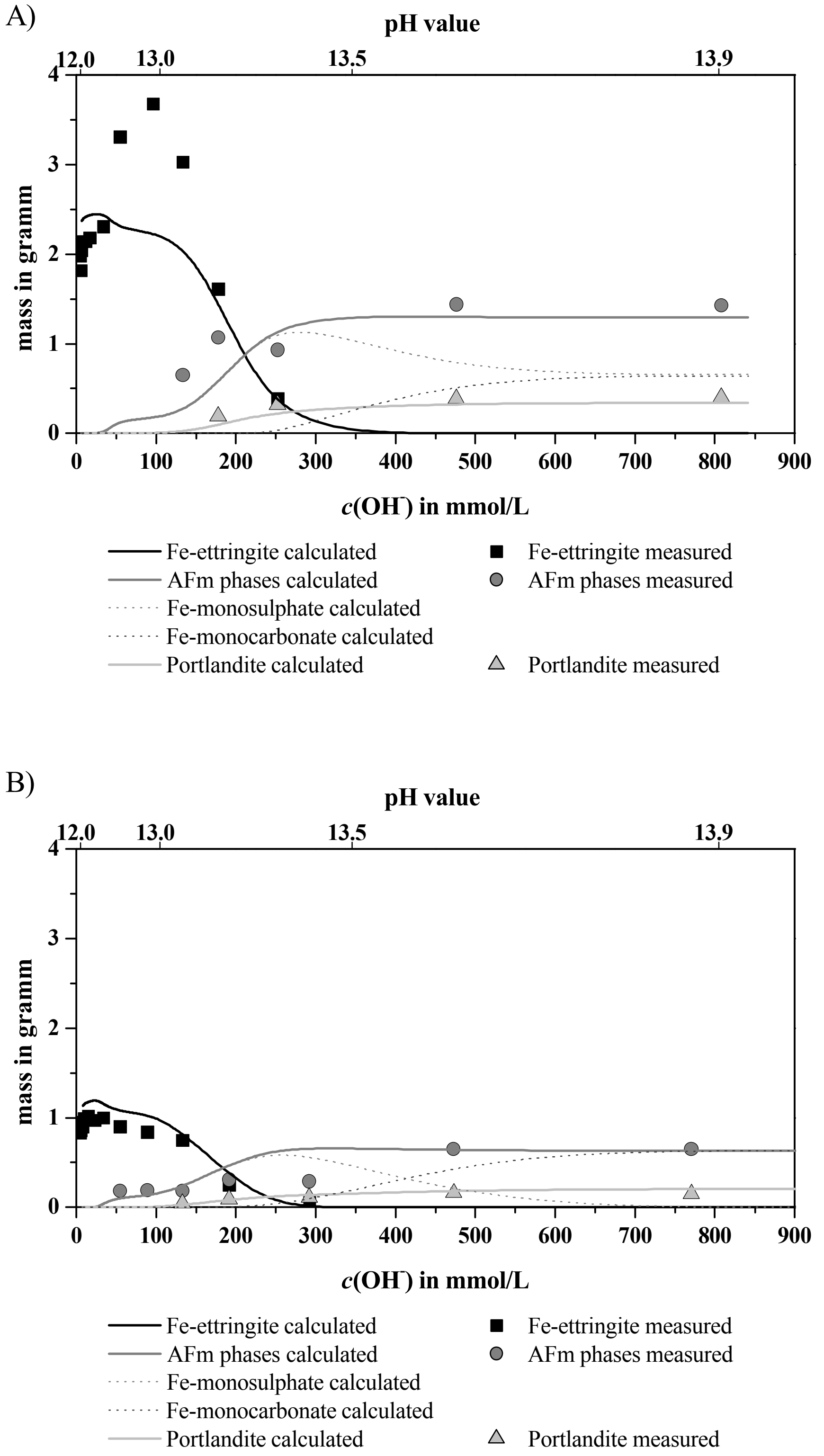

Fig. 5: Measured and calculated distribution and mass of the solid phases of A) precipitation and B) dissolution experiments (at 20 °C).

Also for the solid solution series the experiment was modeled assuming a continuous solid solution between Al- and Fe-ettringite (Fig. 6). The modeled and experimental data agreed well. Therefore the results of XRD analysis and the assumption of a continuous solid solution were confirmed.

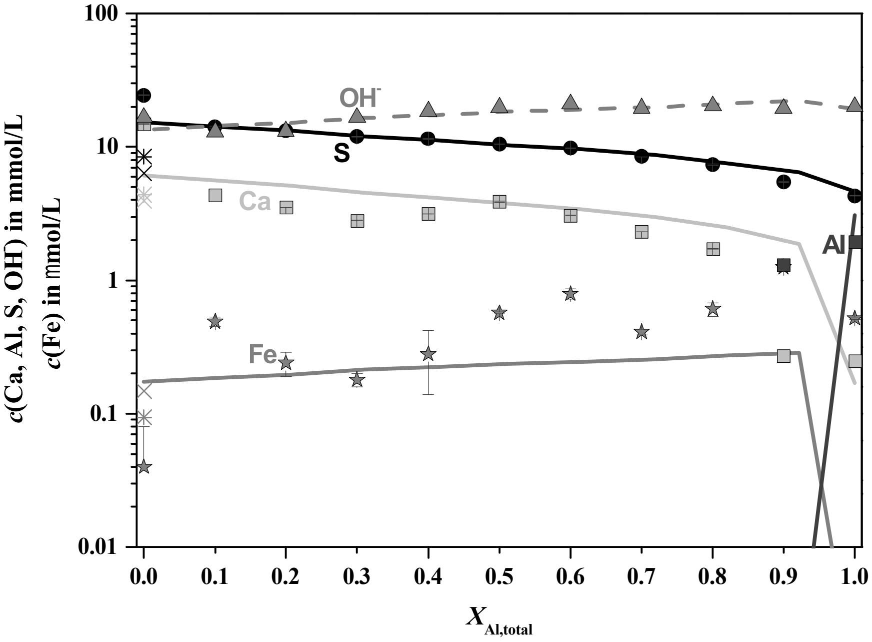

Fig. 6: Measured and calculated ion concentrations within the aqueous solutions of the solid solution experiment (at 20 °C). Ca: calcium, Fe: iron, S: sulfur, Al: aluminum. *: measured concentration of the precipitation experiment of Fe-ettringite, x: measured concentration of the dissolution experiment of Fe-ettringite.

5. Conclusions

In comparison to the estimated solubility products of Fe-ettringite (log K_{S0} = -49.8 respectively log K_{S0} = -49.4 [7, 8]) the solubility product calculated in this study was with a solubility constant of log K_{S0} = -44.0 clearly higher. The outcome of this is that Fe-ettringite is more soluble and thus it is less stable as hitherto assumed.

Fe-monosulfate (log K_{S0} = -33.1) and Fe-monocarbonate (log K_{S0} = -35.4) showed a slight lesser solubility as assumed by Lothenbach & Winnefeld 2006 [8] and Babushkin 1985 [7] (log K_{S0}(Fe-monosulfate) = -32.0; log K_{S0}(Fe-monocarbonate) = -27.2). This means both phases are more stable as expected.

Furthermore it was observed that Fe-ettringite was stable under the experimental conditions used at pH ≤ 13 and that above pH =13 Fe-monosulfate and Fe-monocarbonate became stable.

Also a continuous solid solution between Al and Fe containing ettringite could be obtained.

But it has to be pointed out that the direct assignment to the cement system is not possible due to the fact that the conditions are very different, e.g. the high sulfate content or the much higher content of aluminum in contrast to the iron content.

References

[1] M. Collepardi, S. Monosi, G. Moriconi, Tetracalcium aluminoferrite hydration in the presence of lime and gypsum, Cem Concr Res 9 (1979) 431-437

[2] H. F. W. Taylor, Cement chemistry, ed., Thomas Telford Publishing, London 1997

[3] A. Emanuelson, S. Hansen, Distribution of iron among ferrite hydrates, Cem Concr Res 27 (1997) 1167-1177

[4] L. A. Galimova, V. P. Danilov, I. N. Lepeshkov, B. E. Yudovich, N. A. Shebanov, A study of the formation and decomposition of the calcium iron(III) double hydroxide sulphate $Ca_6Fe_2(OH)_{12}(SO_4)_3 \cdot 26H_2O$ in the $3Ca(OH)_2 + Fe_2(SO_4)_3$ --> $3CaSO_4 + 2Fe(OH)_3$-H_2O system at 20 °C, Russ J Inorg Chem 33 (1988) 445-448

[5] H.-E. Schwiete, T. Iwai, Ueber die ferritische Phase im Zement und ihr Verhalten bei der Hydratation, ed., Westdeutscher Verlag, Köln und Opladen 1965

[6] S. J. Barnett, in: X-ray Powder Diffraction Studies of Ettringite and Related Systems, Staffordshire University, Staffordshire, 1998, p. 159

[7] V. I. Babushkin, G. M. Matveyev, and O. P. Mchedlov-Petrossyan, Thermodynamics of Silicates, Springer-Verlag, Berlin 1985

[8] B. Lothenbach, F. Winnefeld, Thermodynamic modelling of the hydration of Portland cement, Cem Concr Res 36 (2006) 209-226

[9] C. J. Warren, E. J. Reardon, The solubility of ettringite at 25°C, Cem Concr Res 24 (1994) 1515-1524

[10] J. L. Gallias, in: Second International Conference on the Interfacial Transition Zone in Cementitious Composites. RILEM proceedings, 1998 pp. 171-178

[11] D. A. Kulik, PSI Villigen, Switzerland, 2002, available at http://les.web.psi.ch/Software/GEMS-PSI/

[12] W. Hummel, U. Berner, E. Curti, F. J. Pearson, T. Thoenen, Nagra/PSI Chemical Thermodyanmic Data Base 01/01, Universal Publishers/uPublish.com, Parkland, Florida 2002