Ca-Al-hydrates: Solid solutions?

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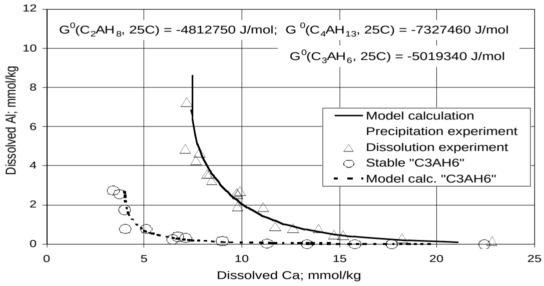
Introduction

Hydrated cements and related mixed phases are widely used as matrix materials in radioactive waste disposal. They may host a large variety of hazardous cations and anions (Pöllmann 1994). Although well characterized mineralogically, most mixed phases cannot be used in quantitative predictions due lack of thermodynamic data. Using Gibbs energy minimisation modelling, we thus aim at improving the thermodynamics of solid solutions in the $CaO\text{-}Al_2O_3\text{-}H_2O$ system.

Results

Wells et al. (1943) measured solubilities of stable and metastable Ca-Al-hydrates from under- and oversaturation and termed the metastable phases an intercrystallised mixture of $2CaO.Al_2O_3.8H_2O$ and $4CaO.Al_2O_3.13H_2O$. Using just two parameters, we achieved a consistent quantitative description of these “historical measurements” by i) assuming ideal solid solution behaviour, and by ii) introducing G_f^0-estimates for the two given end-members (Figure 1). Supporting thermodynamic data were taken from Hummel et al. (2002).

Figure 1: Ideal binary solid solution model for mixed Ca-Al-hydrates compared to C_3AH_6.



Outlook

Generally, the theory predicts decreasing solubilities of trace elements that form solid solutions with increasing amounts of suitable host phases. This situation is often met in backfill/matrix materials of radioactive repository systems. From considering solid solution formation we consequently expect not only deeper insights into the chemistry of hydrated cements, but also significant improvements in quantitative geochemical modelling related to performance assessment.

References

Pöllmann H., (1994), *Min. Processing*, 3-15.

Wells L.S., Clarke W.F. and McMurdie H.F., (1943), *J. Res. National Bureau of Standards*, **30**, 367-409.

Hummel W., Berner U., Curti E., Pearson F. J. and Thoenen T., (2002), Nagra Technical Report, Nagra, Wettingen, Switzerland, and Universal Publishers/uPublish.com, Parkland, Florida, 585p, in press.

A Mössbauer and XANES spectroscopic study of Fe oxidation states in silicate glasses

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The oxidation state ratio of Fe is a sensitive indicator of oxygen fugacity (fO_2). The Fe^{3+}/Fe^{2+} ratio of a quenched silicate melt or glass is theoretically related to the fO_2 by an exponent of 0.25 as expected from the reaction $FeO + 0.25\ O_2 = FeO_{1.5}$. In this study, Mössbauer spectroscopy was used to determine the Fe^{3+}/Fe^{2+} dependence on fO_2 for a series of glasses. Features in the Fe *K*-edge *X*-ray absorption near edge structure (XANES) spectra were then correlated with the Mössbauer determined Fe^{3+}/Fe^{2+} ratio. This provides a XANES calibration curve for the oxidation state of Fe in a silicate glass. XANES spectroscopy is capable of micron spatial resolution and is ideally suited to the analysis of melt inclusions.

Anorthite-diopside eutectic melts containing 1 wt% Fe_2O_3 (93.5 at% ^{57}Fe) were equilibrated at 1400˚C over a $\log fO_2$ range from –11 to +4. Mössbauer spectra were obtained on quenched glasses at both room temperature and 4.2 K. Fe *K*-edge XANES spectra were recorded in fluorescence mode at the Australian Nuclear Beamline Facility, Photon Factory, Japan.

Fe^{3+}/Fe^{2+} ratios were determined from Mössbauer spectra for 16 values of fO_2. The oxidation state ratio is related to the fO_2 by the expected exponent of 0.25 ± 0.01 ($\log[Fe^{3+}/Fe^{2+}] = \log(fO_2)^{0.25} + \log K$). This differs from a value of ~0.22 found previously for natural compositions (Sack *et al.*, 1980). The discrepancy is attributed to non-ideal behaviour of Fe at high concentrations.

The energies of the XANES 1s-3d pre-edge transition centroid and *K* absorption edge were found to correlate linearly with the oxidation state. Correlations also exist with the area of peaks in the derivative spectrum corresponding to 1s-4s and 1s-4p type transitions. These smooth trends suggest the prospect of using XANES spectra to determine Fe^{3+}/Fe^{2+} ratios accurately. However, variations in Fe coordination affect both the energy and intensity of spectral features and may limit the general applicability of XANES calibrations. To obtain accurate Fe^{3+}/Fe^{2+} and fO_2 values it may be necessary to reference the spectrum of an unknown to those obtained from a series of synthetic analogues.

Sack R.O., Carmichael I.S.E., Rivers M. and Ghiorso M.S., (1980), *Contirb. Mineral. Petrol.* **75**, 369-376.