The crystallisation of colloidal As-S phases: an *in situ* X-ray diffraction study

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The precipitation of sparingly soluble As^{III} sulphides occurs in many natural environments and their formation controls a large part of the global arsenic cycle. However, the formation mechanisms of arsenic sulphide minerals are poorly understood due to the lack of thermodynamic and kinetic data pertaining to their nucleation and growth. The main crystalline As-S phases in aqueous solutions below 300˚C are orpiment, As_2S_3, and realgar, AsS and these phases form under very specific chemical and physical conditions (pH, redox, temperature) and are therefore, very accurate geochemical indicators. Below 100˚C a mixture of aqueous As^{III} and H_2S instantly precipitates a poorly ordered colloidal As-S suspension (of As_2S_3 composition) but the transformation of this colloid into crystalline orpiment or realgar requires either a structural ordering or a change in sulphur and arsenic oxidation states. The crystallisation of the amorphous precursor occurs in nature below 100˚C, yet this process has only been achieved in the lab at high temperatures from the melt. The kinetics and activation energies for this process at hydrothermal temperatures and in aqueous solutions are not known.

In this study, the chemical and physical conditions controlling the nucleation and growth of crystalline orpiment from the amorphous colloidal As_2S_3 precursor were evaluated experimentally using *in situ* synchrotron-based energy dispersive X-ray diffraction (ED-XDR). The experiments were carried out *in situ*, in reducing hydrosulphide solutions and at temperatures between 75 and 260˚C. The time dependent changes in Bragg peak areas and intensities were used to derive information about the nucleation and growth kinetics of crystalline orpiment. In addition, the real time data were used to determine the reaction mechanisms and the activation energy for the formation of orpiment from reduced, aqueous sulphide solutions at hydrothermal conditions.

Dissolution kinetics of smectite under acidic conditions

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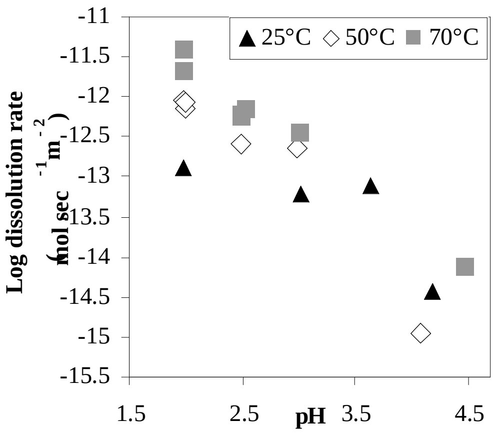
Smectite was selected as a potential sealant in the multibarrier systems designated for storage of radioactive waste. A major concern, which directly affects the protective properties of the barrier, is the dissolution and precipitation of smectite. Interpretation and modelling of the environmental processes strongly depend on our understanding of the environmental parameters that control the rate of dissolution and precipitation. For this reason, flow-through experiments were carried out to study the effect of pH and temperature on the dissolution rate of smectite.

Smectite dissolution rate (Fig.1) varies as a function of temperature and fluid composition from $1.88\cdot10^{-15}$ mol m^{-2} s^{-1} (at 50°C and pH 4) to $3.64\cdot10^{-12}$ mol m^{-2} s^{-1} (at 70°C and pH 2). Dissolution rate increases with temperature and decreases with increasing pH. Apparent activation energies were calculated from the slope of log rate vs. the temperature reciprocal. As the pH decreases the apparent activation energy increases from 8 kcal/mol at pH 3 to 14 kcal/mol at pH 2. Although the observations may be described reasonably well by a single proton promoted mechanism as is evident by the steady increase in rate with decreasing pH (Fig. 1), detailed examination of the data shows that between pH 3 and 2.5 the dissolution rate remains relatively constant. The change in slope and the pH dependence of the apparent activation energy may indicate that more than one reaction mechanism controls the rate, as was suggested for kaolinite dissolution by Cama et al. (2002).

Fig.1: The effect of pH and on smectite dissolution rate



Reference:

Cama J., Metz V., and Ganor J. (2002), *Geochim. Cosmochim. Acta*, submitted.