

The Effect of Iron on the Stability of Montmorillonite

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Current designs for the future geological disposal of high-level radioactive wastes (HLW) envisages the use of an engineered multibarrier system. This could comprise a massive steel overpack surrounding waste canisters and isolated from the host rock by a substantial layer of bentonite (Savage, 1995). The stability of these backfill materials is of great importance to the effective isolation of HLW. Iron dissolved from steel canisters during corrosion processes may react with the montmorillonite component of the bentonite backfill.

Potential reactions include:

1. Incorporation of aqueous iron complexes into smectite interlayers, with formation of (oxy)hydroxide phases on sheet surfaces/edges. This may result in a loss of cation exchange capacity and/or swelling capacity.

2. Dissolution of smectite with crystallisation of non-swelling iron-rich phases such as chamosite.

3. Production of iron-rich smectite (such as nontronite) by diffusion / re-crystallisation.

Batch reactor experiments in conjunction with thermodynamic modelling are being used to determine the likelihood of these reactions occurring in a HLW repository. Unfortunately, reliable thermodynamic data for clays are scarce. Therefore, various techniques (Chermak and Rimstidt, 1989; Ransom and Helgeson, 1994) have been used to constrain values of Gibb's free energy and enthalpy of formation, as well as standard molal volume, entropy and heat capacity coefficients for end member smectites. Thermodynamic modelling has shown that the stability of iron rich smectite and chlorite depends on various factors, including aqueous iron activity, aqueous silica activity, pH and Log f_{O_2} .

Experiments have been conducted whereby Na-montmorillonite is reacted with degassed FeCl₂ solutions at temperatures up to 250°C ($P = P_{sat_H2O}$), under relatively anoxic conditions.

XRD analyses of batch reactor solid run products at various states of hydration were carried out using a position-sensitive detector geometry (Batchelder and Cressey, 1998). This allows XRD "snapshots" to be taken as samples dehydrate. Reduction in the basal spacings over time indicated that the run products were still smectites, although they had lost approximately five percent of their swelling capacity relative to the starting material. The experimental products also show that as dehydration occurs, there is a sudden shift in the d(001) spacing (from 18.3 to 15.8Å) which occurs within approximately 30 seconds. The final d(001) spacing at ambient humidity was 14.9Å. These basal spacing characteristics are seen for samples that have been exposed to FeCl₂ for time periods of seconds or weeks, at various temperatures. This indicates that the incorporation of iron complexes into the smectite interlayers is a rapid reaction, which is independent of temperature. ICP-AES analyses of fluids from the experiments indicates that the iron complex displaces sodium and other exchangeable cations from inter-layer sites. Further characterisation of these run products is underway using TEM and FT-IR techniques, in order to detect small scale mineralogical changes and to determine the stability of the octahedral sheet of the smectite in the presence of iron.

Further experimental mixtures include degassed FeCl₂ solutions, Na-montmorillonite, metallic iron, calcium carbonate and reducing agents. These experiments will give an indication as to whether the aforementioned reaction pathways may occur and if so, over what timescales.

Batchelder M & Cressey G, *Clays and Clay Minerals*, **46**, 183-194, (1998).

Chermak JA & Rimstidt JD, *American Mineralogist*, **74**, 1023-1031, (1989).

Ransom B & Helgeson HC, *Geochimica et Cosmochimica Acta*, **58**, 4537-4547, (1994).

Savage D, *The scientific and regulatory basis for the geological disposal of radioactive waste*. Wiley and Sons, (1995).