A preliminary study on Titanium-clay interactions

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Posiva and SKB are developing a horizontal disposal design alternative, termed KBS-3H (SKB/Posiva 2008). In this design alternative, modules of a Cu-waste canister surrounded by bentonite blocks is placed in a perforated steel cylinder, a so-called supercontainer (SC), before emplacement in the deposition drifts. The current design for the SC is based on carbon steel. But because corrosion will lead to high hydrogen levels and iron-clay interactions, alternative materials are also being considered. A promising alternative are Ti alloys which display high strength and are known to behave as chemically inert materials under variety of conditions (e.g. Schutz 2005).

Also for the Ti alloys, both the corrosion rate and interaction behaviour with other components in the drift needs to be known. In particular, it needs to be demonstrated that corrosion-derived Ti has no significant detrimental effects on the bentonite buffer which is one main barrier within the KBS-3H concept. Unfortunately, the benign inert behaviour of Ti makes it difficult to perform meaningful experiments. Hence, it is not surprising that so far, very little research work on this topic has been carried out and experience is very limited.

A preliminary batch-type investigation has been launched to shed more light on Ti-clay interaction processes and on the Ti species resulting from these interactions. A series of experiments including purified MX-80 bentonite or synthetic "Ti-free" montmorillonite were mixed with metallic Ti nanopowder or foil in 0.1 M NaCl solutions at different pH and temperature conditions. After several months, solid and solute samples from the first set of tests were analyzed by wet chemistry and spectroscopic methods. Ti speciation was analyzed with XAS combined with XRF as elemental mapping tool. A further series of tests will be analyzed in the near future. In addition to reacted samples, a number of reference and starting materials (e.g. MX-80, Rokle bentonite, Opalinus Clay, Illite du Puy) were characterized by XAS. Preliminary results can be summarized as:

(1) Natural clay materials contain significant but variable amounts of Ti. The standard purification procedure for bentonites to remove accessories does not or only barely removes Ti.
(2) The Ti in the natural clays materials Rokle bentonite, Opalinus Clay, Illite du Puy occurs as microcrystalline TiO_2 (presumably as anatase), as depicted in Fig. 2. On the other hand, the Ti spectra in MX-80 suggest the presence of structural Ti in the smectite, but the evidence is not conclusive so far.
(3) The exposure of purified MX-80 to titanium powder at room temperature within a period of five months did not lead to measurable additional Ti in the clay. This was even true for samples exposed to acidic or alkaline conditions where corrosion rates and solubility of Ti are known to be higher (Mattson & Olefjord 1984).

Thereof, the following preliminary conclusions can be drawn:
- The Ti content in natural bentonites is concentrated mainly in the so-called clay fraction. Ti occurs therein either as separate small TiO_2 particles (Rokle, Opalinus Clay, Illite du Puy) or as structural Ti. As indicated by the study of Karnland et al. (2006), the properties of natural bentonites are not affected by the presence of Ti. In that study, the bulk properties (swelling pressure, hydraulic conductivity) were very similar for the different bentonites containing variable Ti content, ranging from 0.1 to 4.8 weight % TiO_2 in the purified clay fractions. The transfer rates of Ti from the metallic source, even in reactive powder form, to the clay are very low and no enrichment above

background concentrations after several months could be observed. In order to obtain measurable effects, both the corrosion process must be increased and the background concentration must be reduced. Tests with Ti-free clay material at increased temperature are still ongoing and will hopefully enable identification of reacted Ti species.

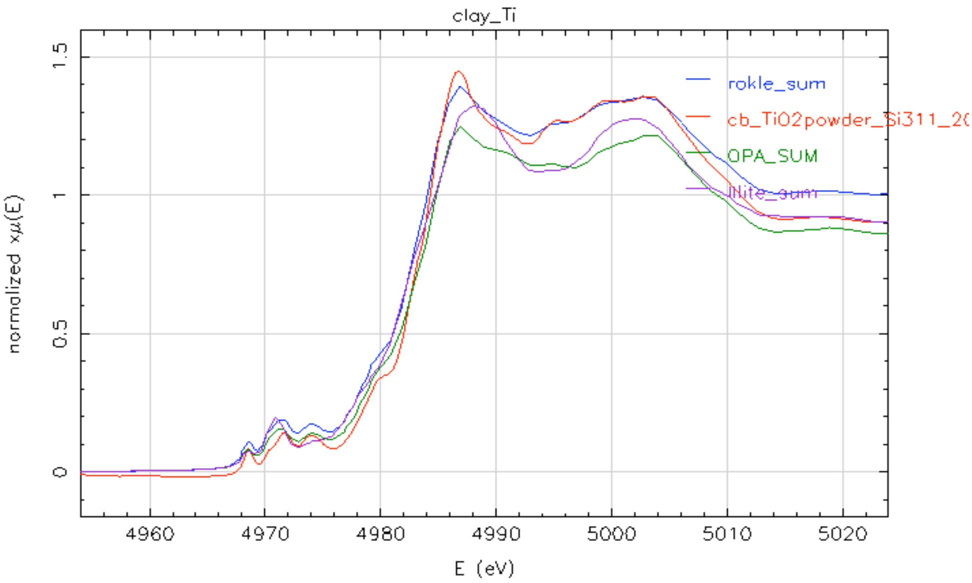

Figure 1. *EXAFS spectra displaying Ti pre-edge features for natural clays (Rokle, OPA clay, Illite du Pully) and anatase powder*

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