Title: “Early anaerobic corrosion of potential canister material in compacted bentonite”

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In the context of the multi-barrier system for deep geological repositories for the disposal of high-level nuclear waste, the stability of potential canister and geotechnical barrier materials is of key importance for long-term safety. It is expected that the canister near-field conditions will change over time due to groundwater saturation, temperature decrease and oxygen consumption. Consequently, the geochemical environment undergoes a transition from oxic – warm – unsaturated to anoxic – cool – saturated. At the current status of the German site selection act, the geochemical environment as well as the electrolyte in contact with the canister and surrounding buffer material are not defined yet. Nevertheless, the transient environment is assumed to affect the material behavior over time, potentially leading to corrosion of the canister material and subsequent changes in the properties of both the canister and the buffer material.

Here we present a study on the effect of corrosion of potential canister materials on alteration of compacted Wyoming bentonite in a synthetic ground water with composition close to electrolyte compositions within crystalline host rocks. The salt concentrations of the synthetic pore water from crystalline rocks in Germany were calculated based on given ionic compositions of Stober et al. [1]. All metal coupons (cast iron type EN-GJS-400-15 and oxygen-free phosphorous copper) were ground with 600/800/1200-grit SiC paper and subsequently cleaned with acetone to guarantee a defined surface state before exposure experiments. Metallographic pre-characterization of the coupons was performed by light optical (LOM) and scanning electron microscopy (SEM). Exposure experiments were undertaken for 1 and 3 months in compacted bentonite in tailor made corrosion cells under anoxic conditions at 60 °C. Granulated bentonite was uniaxially compacted to a dry density of 1.50 g/cm^3. To ensure anaerobic conditions, the corrosion cells were assembled and dismantled within a glovebox system. At the end of the exposure experiments subsequent analysis of the physico-chemical changes at the metal/bentonite interface was performed by (µ)-X-ray diffraction (XRD), µ-X-ray-fluorescence analysis (µXRF), SEM, LOM and Raman spectroscopy.

The exposure of cast iron for one month at 60 °C in compacted bentonite revealed changes on the metal coupon and at the interface in the bentonite. With Raman spectroscopy, the formation of mackinawite (FeS) and magnetite (Fe_3O_4) was observed. The same results were confirmed by supplementary SEM-EDX analysis. The interface in the bentonite shows brownish to black discoloring and a 1 mm brownish halo extending into the bentonite. µ-XRD analysis revealed the formation of magnetite.

Additionally, metal/bentonite interfaces after exposure for 4.5 and 7 years in the MaCoTe experiment at Grimsel Test Site were studied by µXRF, XRD and SEM for comparison. The impact of the observed bentonite alteration for the long term safety will be discussed.

[1] Bucher, K., Stober, I. (2000). The Composition of Groundwater in the Continental Crystalline Crust. In: Stober, I., Bucher, K. (eds) Hydrogeology of Crystalline Rocks. Water Science and Technology Library, vol 34. Springer, Dordrecht.