A potential steel passivating layer: fe-saponite and chlorite growth on steel in high P,T engineered barrier experiments

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Experimental work for the US Used Fuel Disposition campaign has started to characterize the stability and alteration of a bentonite-based Engineered Barrier Systems (EBS) with different waste container materials in brine at higher heat loads and pressures.

Experiments were run at ~150 bar 300° C for 6 weeks. Unprocessed bentonite from Colony, Wyoming was used as the clay buffer. Redox conditions were buffered at magnetite-iron oxygen fugacity. A K-Na-Ca-Cl-based brine replicated deep groundwater compositions. The experimental mixtures were brine–clay-various steels with a liquid/clay ratio of ~9. Reaction mineralogy and aqueous geochemistry of each experiment was evaluated.

No smectite illitization was observed in these reactions. It would appear that illitization was retarded due to a limitation of K^+ in the closed-system. However, notable clay mineral reactions occurred at the steel surfaces. Authigenic chlorite and Fe-saponite grew with their basal planes perpendicular to the steel plate, forming a 10 – 100 μm thick 'corrosion' layer. The steel plates act as a substrate for chlorite/Fe-saponite growth. XRD and microprobe analyses of the silicate mantling on the low-carbon steel indicates the phase is a Fe saponite with a composition of $(Na_{0.09}Ca_{0.03})$ $(Fe_{2.20}Mg_{0.12}Al_{0.86})$ $(Al_{0.58}$ $Si_{3.42})O_{10}(OH)_2$. Stainless steel (304) is mantled by a chlorite/Fe saponite mixture. This phyllosilicate mix is high in Fe (33.99 wt% FeO), Cr (1.35 wt % Cr_2O_3) and Ni (1.34 wt % NiO).

Mineral growth on the waste containers was influenced by the container, clay buffer, and fluid compositions, in addition to pressure and temperature conditions Results show that the waste container may act as a substrate for chlorite /saponite growth in response to corrosion and the chlorite /saponite can act as a passivating agent.

Biotite and phlogopite dissolution: Topographic observation by VSI

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The dissolution kinetics of two micas (biotite and phlogopite) was investigated by vertical scanning interferometry (VSI). Topographical data at the basal surface during dissolution at pH 1 and 2 (25 -100 ºC) of nitric and oxalic acid solutions were used to determine the micas' dissolution mechanisms.

Single biotite and phlogopite fragments of approximately 100 mm^2 were reacted in 250 mL of acidic solution up to 44 days. The cleavage surfaces were examined by VSI before and after the reaction.

On the one hand, the biotite dissolution in nitric acid was dominated by step-edge retreat together with a phenomenon of layer peeling at the step edges [1]. At longer reaction times dissolution channels developed, leaving mineral islands. In the presence of oxalic acid, biotite step-edge retreat was also observed. In addition, formation of rounded etch pits of different size and density, depending on the experimental conditions, took place by covering the surface rather uniformly. Moreover, some peculiar dissolution microstructures were found at the mineral-solution interface.

On the other hand, VSI images of phlogopite surface showed step-edge retreat and formation of triangular crystallographically controlled etch pits [2,3] of different size, being non-homogeneously distributed over the basal surface. In the presence of oxalic acid, the phlogopite dissolution features were similar to those observed in nitric acid, but higher etch pit density and etch pit alignment were observed.

Hence, as the mechanisms that control the dissolution of the different mica minerals depend on the presence/absence of oxalic acid, it is necessary to study the effects of the compositional factor and the presence of inorganic ligands on the dissolution kinetics of micas.

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