



Engineered Barrier System hydrothermal experiments for a Grimsel Granodiorite host rock: Mineralogical evolution at repository pressures and temperatures.

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The U.S. Spent Fuel and Waste Storage and Transport (SFWST) Campaign is studying generic geologic repository options for disposal of used fuel. The focus of our experimental work is to characterize Engineered Barrier Systems (EBS) conditions in high temperature repositories. Mineral alteration in bentonite EBS materials is one of the concerns regarding the repository stability during heating and cooling stages.

Hydrothermal experiments on EBS materials were conducted to characterize high temperature interactions of bentonite clay and Grimsel granodiorite with candidate waste container steels (304SS, 316SS, low-C steel) for deep geological disposition of nuclear spent fuel. The hydrothermal experiments were performed using Dickson reaction cells at temperatures and pressure of up to 250°C and 15 – 16 MPa for six to eight weeks. Wyoming bentonite was saturated with a synthetic Grimsel granodiorite groundwater solution (1:9 ratio) in combination with stainless and low-C steel coupons. Fluid samples were collected periodically throughout the experiment duration and analyzed for major cations and anions. The solid-reaction products and steel coupons were characterized post experiment via XRD, XRF, SEM, and EMP.

Preliminary mineralogic phase transformations for the experiments are as follows: Smectite clays did not transition to illite, however muscovite was identified (by XRD) as a major reaction product. Clinoptilolite, appears to have formed from the remnant glass which was present in the original bentonite. The Si/Al ratios for the clinoptilolite are dominantly between 4 and 6. The Na/(Na+Ca) values range from 0.55 to 0.75. Calcite and gypsum were also observed as minor reaction products. Aqueous SiO₂ remains saturated with respect to quartz throughout the experiments.

In these experiments containing Grimsel granodiorite and Wyoming bentonite, spherical, calcium aluminum silicate hydrate (CASH) phases formed within the fine-grained clay matrix. Based on the composition of this mineral, the C(A)SH phases are likely a hydrated calcium silicate, such as Al-tobermorite (Ca_{4.3}Si_{5.5}Al_{0.5}O₁₆(OH)₂4(H₂O)). The formation of CASH minerals contrasts with the products of previous experiments with Wyoming Bentonite ± Opalinus Clay host rock. In those experiments, zeolites (analcime–wairakite solid solution) formed that have similar morphologies and textural contexts. However, the EMP analyses of the spherical minerals formed in the Grimsel host experiments had significantly lower SiO₂ and Al₂O₃ content and very high CaO. Very Ca-rich hydrous minerals, such as Al-tobermorite, have been observed in experiments involving bentonite and cement with highly alkaline bulk chemistries and pH > ~10 (Savage et al., 2007). In comparison, the solution pH over the course of the Grimsel experiments did not exceed ~7 and the experiments did not involve cement. The pH of the solution in each experiment started at ~8.5 and decreased to 6.5 by the end of the experiment. Future investigations will focus on why CASH minerals formed instead of analcime–wairakite in the experiments with Grimsel granodiorite and Wyoming bentonite.