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Bentonite evolution at elevated pressures and temperatures: An experimental study for generic nuclear repository designs

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Abstract

Geologic disposal of spent nuclear fuel in high-capacity metal canisters may reduce the repository footprint, but it may yield high-thermal loads (up to 300 °C). The focus of this experimental work is to expand our understanding of the hydrothermal stability of bentonite clay barriers interacting with metallic phases under different geochemical, mineralogical, and engineering conditions. The hydrothermal experiments were performed using flexible Au/Ti Dickson reaction cells mounted in an externally heated pressure vessel at 150–160 bars and temperatures up to 300 °C for five to six weeks. Unprocessed Wyoming bentonite, containing primarily montmorillonite with minor amount of clinoptilolite, was saturated with a K-Ca-Na-Cl-bearing water (~1900 mg/L total dissolved solids) at a 9:1 water:rock mass ratio. The bentonite and solution combination contained either steel plates or Cu-foils and were buffered to low Eh using magnetite and metallic iron. During reactions, pH, K^+, and Ca^{2+} concentrations decreased, whereas $SiO_{2(aq)}$, Na^+, and SO_4^{2-} concentrations increased throughout the experiments. Pyrite decomposition was first observed at ~210 °C, generating $H_2S_{(aq,g)}$ that interacted with metal plates or evolves as a gas. The aqueous concentrations of alkali and alkaline earth cations appear to be buffered via montmorillonite and clinoptilolite exchange reactions. Illite or illite/smectite mixed-layer formation was significantly retarded in the closed system due to a limited K^+ supply along with high Na^+ and $SiO_{2(aq)}$ concentrations. Precursor clinoptilolite underwent extensive recrystallization during the six weeks, 300 °C experiments producing a Si-rich analcime in addition to authigenic silica phases (i.e., opal, cristobalite). Analcime and feldspar formation partially sequester aqueous Al^{3+}, thereby potentially inhibiting illitization. Associated with the zeolite alteration is a ~17% volume decrease (quartz formation) that translates into ~2% volume loss in the bulk bentonite. These results provide chemical information that can be utilized in extending the bentonite barriers' lifetime and thermal stability. Zeolite alteration mineralogy and illitization retardation under these experimental conditions is important for the evaluation of clay barrier long-term stability in a spent nuclear fuel repository.

Keywords: Analcime, bentonite, clinoptilolite, electron microscopy, hydrothermal, illite/smectite, montmorillonite, nuclear repository, X-ray powder diffraction