The role of zeolite phase transformations in nuclear repository engineered barrier systems

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The U.S. Used Fuel Disposition Campaign is studying generic 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 is one of the concerns regarding bentonite stability during heating and cooling stages.

Experiments were performed at 160 bar and either sequentially stepped from 125 ºC to 300 ºC or continuously at 300 ºC over a period of ~6 weeks. An unprocessed bentonite from Colony, Wyoming and K-Ca-Na-Cl-rich brine (Stripa groundwater) was used at a 9:1 water:rock ratio. The baseline experiment contained brine + clay, while other experiments also contained metals replicating canisters (304SS, 316SS, low carbon steel). Experiments were buffered at low oxygen fugacity.

Potassium was mobilized and exchanged with interlayer Na, transitioning the clay from Na-montmorillonite to K-smectite. Illitization was bound by the overall bulk composition of the experiment. Clinoptilolite (and remnant glass) present in the starting bentonite mixture are unstable above 150 ºC. Hence, the zeolite and glass broke down at high temperatures but crystallized as analcime. Precursor clinoptilolite underwent recrystallization at 300°C producing, a Si-rich analcime in addition to authigenic silica phases. The reaction is:

clinoptilolite + 0.92 Na^+ + 0.02 Ca^{2+} → 8 **analcime** + 0.14 K^+ + 0.20 Mg^{2+} + 11.62 **SiO_2** + 12.64 H_2O + 0.03 Fe^{2+} + 0.40 H^+)

This zeolite alteration could provide a ~2% volume loss in total bentonite volume along with increased silica cementation. Overall, it would appear that silica levels are controlled by the zeolite reactions and smectite partial dissolution. When clinoptilolite alters during the high temperature thermal pulse of a repository, analcime will form and exist as radionuclide sorbing phase.