

Effects of temperature on hydrothermal alteration of low-pH cement

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In underground spent fuel repository designs, cements play an integral part of the structure and barrier systems in place to prevent radionuclide migration. Traditional cements have highly alkaline porewater driven by equilibration with portlandite ($\text{Ca}(\text{OH})_2$) in the cement structure. However, highly alkaline ($\text{pH}>11$) solutions may have deleterious effects on other critical components of the barrier system, such as by affecting the swelling and exchange properties of smectite minerals in bentonite buffers. Cement formulations that replace traditional cement components with siliceous materials resulting in reduced portlandite abundance (“low-pH” cements) are therefore becoming increasingly standard in underground repository designs. At elevated temperatures, such as may be caused by localized heating from the spent fuel, low-pH cement alteration rates are comparatively under-studied. Defining kinetic rate parameters for hydrothermal alteration of low-pH cements will then place useful constraints on evaluating their long-term stability in underground repositories.

To characterize rates of low-pH cement alteration during a heating event under repository conditions, we conducted a series of hydrothermal experiments at elevated temperatures. Low-pH shotcrete liner similar to that used in underground tests of repository barrier materials was immersed in a solution approximating the chemistry of groundwater equilibrated with a crystalline host. The reactants (shotcrete and groundwater solution) were combined in a Dickson-type gold-cell rocking autoclave maintained at varying temperatures and elevated pressure (100-200 °C, 15 MPa) for several weeks. The reactant solution was sampled periodically during the experiment to characterize changes to solution chemistry and monitor rates of cement alteration. Fluid chemistry samples collected over the duration of the experiments were analyzed for changes resulting from water-rock interaction and evaluated with respect to thermodynamic stability of secondary minerals of interest. Post-mortem XRD and SEM analysis of solid reactants focus on alteration in the reaction rim at the cement-solution interface to characterize the depth of alteration and reaction products specific to low-pH cement. The alteration rates and reaction products are compared to results from previous hydrothermal experiments with ordinary Portland cement at elevated temperatures.