

The Role of Multicomponent Cation Exchange and Dedolomitisation in Argillaceous Rock at Conditions of High-pH

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Several countries plan the geological disposal of radioactive waste in cemented repositories constructed in argillaceous host rock of low permeability and high sorption capacity. Degradation of cement and concrete used as construction and backfill material is known to produce hyper-alkaline conditions (pH above 12), which will induce mineralogical changes in the surrounding rock affecting its hydraulic and retardation properties (Adler et al., 1999).

A laboratory core infiltration experiment was performed at repository relevant conditions using a rock sample with *in-situ* moisture content at temperatures of 30°C. Effluent solute concentrations and mineralogical changes have been simulated with a one-dimensional transport model coupling advective/diffusive/dispersive transport and ion exchange and mineral equilibria in order to identify relevant processes.

Methods

The experiment was conducted on cylindrical rock samples of Opalinus Clay (middle Jurassic, Mont Terri, Northern Switzerland), which consists of up to 70% clay minerals, calcite, quartz and minor K feldspar, albite, siderite, dolomite, pyrite and gypsum (possibly associated with pyrite oxidation). The porosity calculated from water content (105°C) amounts to 15% and CEC is 10 meq/100 g.

The core sample was placed into an externally heated autoclave (30°C, 60 bars confining pressure) and infiltrated by hyper-alkaline K-Na-Ca-OH solution (pH 13.2) at constant pressure (30 bars) and He atmosphere. Chemical composition of effluent solutions was continuously monitored, and secondary minerals were analysed by SEM/EDS and XRD after termination of the injection phase.

A one-dimensional transport model (PHREEQC2; Parkhurst and Appelo, 1999) coupling advective/diffusive/dispersive transport and ion exchange and mineral equilibria was used to simulate the experiment. Values for dispersivity were calculated from the breakthrough of Cl⁻, and exchange coefficients and mineral equilibrium constants were taken from the database wateq4f.dat.

Results and Discussion

The early effluent solutions in the experiment show a recognisable pore water signature with pH values around 8.2 and high

salinities (9000 mg/l Cl⁻). The *in-situ* porewater is progressively displaced by the injected high-pH solution resulting in declining Cl⁻ contents and increasing pH values. However, pH does not exceed 10 after 4 pore volumes of infiltration and remains far below the value of the injected solution. SO₄²⁻ concentrations are controlled by equilibrium with gypsum during the first 1.5 pore volumes and then decrease. Effluent concentrations of the major cations (K⁺, Na⁺ and to a lesser extent Ca²⁺, Mg²⁺) are controlled by equilibrium with the rock's ion exchange properties resulting in a chromatographic displacement sequence. Mg²⁺ is the first cation to be displaced from the exchange population.

Reaction products that were detected include large amounts of calcite, minor hydrotalcite (Mg₆Al₂CO₃(OH)₁₆.4H₂O) and a possible clay mineral of smectitic composition. Dedolomitisation driven by gypsum dissolution is identified as relevant process for abundant calcite precipitation in the experiment. Dissolution of gypsum promotes the precipitation of calcite by addition of Ca²⁺ into solution. Hence, all carbonate supplied by dissolution of dolomite is removed from solution via calcite precipitation preventing dolomite from saturation and sustaining further dissolution of dolomite and gypsum. As the process of gypsum-driven dedolomitisation produces no hydrogen ions, calcite precipitation does not account for the effective pH buffering in the experiment. The governing pH-buffering process is precipitation of Mg-hydroxide contained in hydrotalcite and smectitic clay minerals. Mg²⁺ is mainly derived from displacement of Mg²⁺ from the rock's exchange population, and contribution from dolomite dissolution is only subordinate. pH buffering in the experiment will therefore persist until all Mg²⁺ is removed from the exchanger sites.

There is good agreement between results of the experiment and the transport model including ion exchange equilibria and mineral equilibria with calcite, dolomite, gypsum and Mg-hydroxide. The evolution towards increasing pH is generally overestimated by the model, what might be attributed to additional hydrogen-producing processes such as dissolution of aluminosilicates and proton exchange.

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Parkhurst DL & Appelo CAJ, *U. S. Geol. Survey Water-Resources Investigations Report*, **99-4259**, (1999).