Experiment *vs* modelling: Diffusive and advective interaction of high-pH solution in argillaceous rock at 30°C

M. Adler
U. Mäder
N. Waber

Water-Rock Interaction Group, Institute of Geology and Institute of Mineralogy and Petrology, University of Bern, Baltzerstrasse 1, CH-3012 Bern, Switzerland

Disposal strategies for high-level radioactive waste in several countries envisage cementiceous repositories in argillaceous rock (e.g. Opalinus Clay in Switzerland). Current knowledge predicts degradation of concrete and an emanating high-pH plume that induces alteration to the geologic near-field with resultant modification of the retardation properties for subsequent migration of radionuclides compared to unaltered host rock.

Experimental data on high-pH alteration of argillaceous material are available from batch experiments at elevated temperature (75–200°C, e.g. Chermak, 1992, 1993) and from flow-through column experiments at 70°C (Bateman *et al.*, 1997), all on ground material. Experiments carried out for this study were performed on solid rock samples at low temperature and aim at bridging the gap to evidence from powdered rock samples, and are intended to be used as a test case for alternate hypotheses and techniques underpinning modeling approaches using coupled reactive transport algorithms (e.g. Steefel and Lichtner, 1994; Bateman *et al.*, 1997).

Experimental

Diffusion experiments and flow-through experiments were performed with solid rock Opalinus Clay (middle Jurassic, Mont Terri, Northern Switzerland) and K-Na-Ca-hydroxide solution with an initial pH of 13.2. The mineral composition of Opalinus Clay is approximately 25% kaolinite, 20% illite, 15% calcite, 15% quartz, 10% chlorite, 10% mixed layer illite/smectite and minor K-feldspar, albite, siderite, ankerite, pyrite, with a porosity of 14%. Diffusion experiments were arranged to have one fresh rock surface exposed to the high-pH solution with all other surfaces sealed by epoxy, i.e. to confine fluid infiltration to one direction. In the flow-through experiments two parallel faces of the rock sample were unprotected, one exposed to the high-pH solution, the other open to atmosphere in order to enhance fluid transport by evaporation and capillary forces. All experiments were run at a low temperature of 30°C. Diffusion experiments were conducted under controlled N_2 atmospheric conditions and the high-pH solution in the flow-through experiments was isolated from air. Measured specific fluxes in the flow-through experiments range from $4-10 \times 10^{-6}$ kg/s/m^2 (two pore volumes per month).

Analyses on reacted rock samples were carried out after 3, 6 and 12 months for the diffusion experiments and after 8 months for the flow-through experiments. Reaction products were characterised by scanning electron microscopy (SEM) combined with energy dispersive spectrometry (EDS) and X-ray diffraction (XRD).

Results of diffusion experiments

Reacted Opalinus Clay showed rusty spots and stripes on the infiltration surface of all samples due to pyrite alteration. Reaction fronts extending 1.0 mm into the rock matrix have been observed after 6 and 12 months. At 6 months, these zones are characterised by a rusty discoloration of the rock-matrix probably due to pyrite and siderite alteration, whereas at 12 months the matrix shows a leached, light gray color. XRD analyses on these zones reveal a reduction in kaolinite, quartz and calcite contents compared to unaltered rock.

Reaction products after 3 months are Ca-Al-Si gels with minor potassium that formed on the infiltration surface of the samples. After 6 months, prismatic crystals of a possible Ca-zeolite were found on bedding planes adjacent to the infiltration surface. They are partly overgrown with Ca-Si-hydroxide phases (CSH). An unequivocal identification of these secondary phases is not possible due to their very small size (<10 μm) and volume fraction. Phillipsite, a K-Ca-zeolite, could be identified by means of XRD, but as several morphologically different phases have been observed in SEM, there is likely more than one zeolite phase present. The newly formed crystals are very small and grow on bedding planes, that functioned as major pathways for the high-pH solution. They are locally intimately intergrown to form very thin coatings sealing up micro-cracks.

Flow-through experiments

SEM analyses on samples that were reacted with high-pH solution for 8 months show a chromatographic succession of different secondary mineral phases with increasing distance from the infiltration surface. The zone adjacent to the infiltration plane is characterised by extensive formation of a fibrous Ca-Al-Si-hydrate (CASH) phase, accompanied by minor portlandite. XRD analyses on the CASH failed indicating a poorly crystalline phase.

A flaky K-Fe-Mg-Al-silicate, most probably a clay mineral forms between 3–5 cm above the infiltration surface. These phases form on bedding planes that acted as pathways for the high-pH solution and are locally intergrown with secondary gypsum. This zone additionally contains secondary calcite and dolomite.

In the uppermost part of the profile adjacent to the evaporative surface secondary sulphates formed ranging in composition from syngenite-type to glauberite-type. Generally, secondary precipitates grow along discrete planar features of enhanced permeability such as bedding planes, interfaces of shell debris and micro-cracks.

Modelling approach

The objective of modelling is to build confidence into the numerical description of rock–water interaction, and to evaluate the relative importance of simplifying initial and boundary conditions, as well as the relevance of alternate processes and geometries that can be simulated by different reactive transport models.

The overall alteration pattern in the flow-through experiments is the result of an interplay of a saturated advective zone adjacent to the infiltration plane, and an unsaturated zone extending from the evaporative surface that also allows for gaseous counterdiffusion. Morphological evidence of alteration products suggests that fluid/gas transport occurs preferentially along discrete planar features at the micrometre scale, but that the overall chromatographic sequence is fairly evenly developed at the centimetre-scale. It is thus possible to model portions of the system with a variety of approaches ranging from fully coupled multi-dimensional multi-phase models to relatively simple one-dimensional box models or reaction-path models, or from fracture/dual-porosity models to homogeneous porous medium models.

The diffusion experiments provide for better constrained initial and boundary conditions. The distribution of alteration products also indicates the importance of discrete planar features that form zones of enhanced diffusive transport.

Preliminary modeling results of the saturated zone with a batch model, a reactive transport model, and a 1-D finite difference model require relatively fast reaction rates compared to literature values, and suggest a significant sensitivity to the thermodynamic properties of the poorly characterized C(A)SH phases. Further modeling work is in progress.

Discussion

The purpose of our controlled experiments under near-natural conditions and those expected to occur in a repository scenario was to demonstrate the feasibility of both laboratory and in-situ experiments. It is demonstrated that alteration products form within 3-12 months at 30-35°C under a variety of conditions for the infiltration of a high-pH solution. The identification of reaction products and their spatial distribution is difficult and requires careful sample preparation and analysis by SEM-EDS and XRD methods, but further work is required.

The results of the experiments form a valuable test case for alternate modelling approaches as well as to address the issues of thermodynamic properties for poorly characterized phases and highly uncertain reaction rates at low temperature and highly alkaline conditions. Such experiments form a viable avenue for building confidence into predictive modeling of reactive transport.

References

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