Colloids

Carriers of actinides into the environment

Nearly all natural waters contain suspended colloids, submicrometer-sized particles whose concentrations depend on the physicochemical properties of the aquifer. These natural colloids are formed as a result of the weathering of rocks, plants, and soils. They are of concern as a transport mechanism at Yucca Mountain because radionuclides that sorb strongly to the mountain's volcanic tuff could also sorb strongly to suspended tuff colloids, forming radionuclide-bearing "pseudocolloids" that could move through the aquifer. Actinides with high tendencies for sorption or complexation, such as Pu(IV) and Am(III), are strong candidates to form such pseudocolloids. In addition, colloids could also form from the weathering of high-level-waste glass and spent fuel (waste-form colloids) or from the aggregation of hydrolyzed actinide hydroxides, such as those formed with Pu(IV) (intrinsic colloids). Thus, a number of possibilities exist for colloids to carry actinides away from an underground waste repository, a process known as colloid-facilitated transport.

Evidence from the Nevada Test Site confirms that some of these possibilities are also realities. The first evidence for colloid-facilitated radionuclide transport came in 1976, 11 years after the Cheshire nuclear test. Radionuclide pseudocolloids were detected in a well 300 meters to the southwest of the detonation site. In 1996, plutonium concentrations of up to 0.63 picocurie/liter were detected at the Test Site's ER-20-5 well complex. Almost all the plutonium was associated with colloids composed of silica, zeolites, and clays. The ratio of plutonium-239 to plutonium-240 indicated that the plutonium originated from the Benham nuclear test, which was conducted in December 1968 approximately 1.3 kilometers from the ER-20-5 well complex. Thus, the plutonium traveled more than a kilometer in less than 30 years.

In both cases, however, nuclear detonations fractured saturated rock formations near the test, and the actinides were integrated into a zone of melted rock that was in direct contact with the aquifers. Further, within seconds after the detonations, actinides may have been forcefully injected through the fractures into the rock formations, although it is unlikely that such "prompt injection" is solely responsible for the migration of plutonium away from the Benham cavity. Consequently, colloid-facilitated radionuclide transport mechanisms at the Test Site may differ significantly from those at a nuclear waste repository, where the radionuclides would be isolated, at least initially, from the hydrogeologic environment.

We have conducted experiments at Los Alamos to study the formation of actinide pseudocolloids under conditions representative of those at Yucca Mountain, where nuclear spent fuel will potentially be stored in the unsaturated zone and where release scenarios involve the infiltration of groundwater. Measurements of plutonium-239 and americium-241 sorption onto hematite, smectite, and silica colloids indicate that sorption of Pu(IV) and Am(III) is completed within hours or days and is much faster than the desorption process, which occurs over months. In addition, the sorption of Pu(V) is lower than for Pu(IV) but increases with time, probably as a result of redox reactions of the Pu(V) in solution or on colloid

surfaces. The latter observation emphasizes the important connection between solution speciation and surface complexation in determining the sorption behavior of actinides onto colloids.

We also conducted field tests to investigate filtration and resuspension rates for colloids in the saturated zone at Yucca Mountain. Two sets of experiments were conducted at the C-Wells complex, which lies 2.4 kilometers east of the potential repository. In these tests, we injected tracers into the saturated zone at one well and pumped water out of a nearby well to establish flow between the wells. Polystyrene microspheres of varying sizes (280, 360, and 640 nanometers in diameter) were injected simultaneously with solute tracers into two rock formations (Bullfrog Tuff and Prow Pass Tuff) that also underlie the repository. The microspheres were selected to have sizes and surface charges that mimicked as closely as possible those of the expected pseudocolloids.

All microspheres proved mobile, but their mass recoveries at the second well were lower than those of the noncolloid tracers that were injected simultaneously. Bimodal breakthrough curves for all tracers in the Bullfrog Tuff test indicated multiple transport pathways (see Figure 17 in the preceding article). The two tests suggested that colloid transport in the two aquifers was affected by rock properties, groundwater chemistry, and colloid size. The microsphere data have enabled us to estimate rates of colloid attachment and detachment to the fractured tuff surfaces. Further field and laboratory tests are ongoing to understand colloid transport in other types of saturated media that occur at Yucca Mountain, including unfractured tuff and alluvium.

The most recent laboratory experiments have focused on measuring sorption/desorption rates and magnitudes for strongly sorbing, long-lived radionuclides onto several colloids that may be present either near the stored waste (iron oxides that result from degradation of waste canisters) or far from it (silica and montmorillonite clay) at the mountain. These experiments show that plutonium sorbs very strongly and rapidly onto iron oxides and montmorillonite clay, while its sorption onto silica is slower and weaker. The experiments also show that the presence of other ions, such as calcium, tends to slightly suppress the sorption of plutonium.

Armed with such data from both field and laboratory experiments, modelers are using the Finite Element Heat and Mass (FEHM) transport code to simulate colloid-facilitated radionuclide transport at Yucca Mountain. Key variables are the nature and concentration of the simulated colloid, actinide sorption/desorption mechanisms and kinetics, fluid saturation, and properties of the surrounding rock matrix. In these simulations, the concentration of colloids varies with the release scenario, time, and distance from the waste packages. Accurate modeling requires information about the waste (glass or spent fuel) dissolution rates, water chemistry, and actinide distribution between solid and aqueous phases. Given the wide range of uncertainty in estimates for many of these variables, results to date are largely qualitative.

Our preliminary calculations indicate that colloid-facilitated transport is indeed possible for actinides in the III and IV oxidation states and would be associated primarily with fracture flow at Yucca Mountain. Because of the low concentration of natural colloids and the large amount of immobile rock surface area available to compete for the sorption of actinides, waste-form colloids pose the greatest risk to repository performance. Actinides are expected to be nearly irreversibly sorbed to or embedded in these colloids. However, waste-form colloids would have to travel through the unsaturated zone before reaching the saturated zone. In the unsaturated zone, filtration at air/water and rock/water interfaces should impede such transport. In the saturated zone, the high velocity of groundwater in fractures reduces the attachment of waste-form colloids to fracture surfaces. Of the natural colloids in this zone, clay colloids will facilitate radionuclide transport more than silica colloids. However, more data are needed to accurately assess whether colloid-facilitated radionuclide transport could adversely affect the performance of a nuclear waste repository at Yucca Mountain. A quantitative evaluation of this transport mechanism awaits more knowledge about the site-specific behavior of the colloids, fundamental sorption/desorption mechanisms and kinetics, fracture-related filtration effects, and evolution of the local environment around the stored waste. ■