Unsaturated-zone water/rock interaction and U-series isotope mobility at Yucca Mountain, Nevada

LEONID A. NEYMARK AND JAMES B. PACES

U.S. Geological Survey, DFC Box 25046, MS 963, Denver, CO 80225, USA (lneymark@usgs.gov, jbpaces@usgs.gov)

Yucca Mountain, a ridge of Miocene-age felsic tuffs in southern Nevada, is the site of the proposed repository for high-level radioactive waste. Water percolating through the rocks in the 500-m-thick unsaturated zone (UZ) at Yucca Mountain during the last million years has mobilized U, resulting in U-series radioactive disequilibrium in the tuffs. U and Th concentrations, as well as ^{238}U-^{234}U-^{230}Th activity ratios (AR), have been determined by thermal ionization mass spectrometry in samples of whole rock, pore water, and secondary fracture-coating minerals to determine the degree of U-series disequilibrium in the Yucca Mountain UZ.

Whole-rock samples from a vertical profile through the UZ show systematic variations in U and Th concentrations related to lithostratigraphy. In contrast, variations in $^{234}U/^{238}U$ AR (0.94 to 1.01) and $^{230}Th/^{238}U$ AR (0.93 to 1.10) do not correlate with lithostratigraphy. Instead, the degrees of disequilibrium crudely correlate with the measured water saturation in the rocks and reflect small but pervasive amounts of Pleistocene water/rock interaction in otherwise unaltered devitrified tuff. Most samples, obtained from both fracture surfaces and rock interiors, have $^{234}U/^{230}Th$ AR <1, indicating U removal.

Pore-water samples with U concentrations of ~0.1 to 30 ng/g have present-day $^{234}U/^{238}U$ AR between ~2 and 9. Concentrations of U in secondary fracture-coating minerals range from 0.001 µg/g in calcite to 500 µg/g in opal. U-series dating indicates that outer portions of these minerals are <500 ka and that water percolating through these fractures had $^{234}U/^{238}U$ AR similar to water percolating through pores in the rock matrix. The enrichment of ^{234}U in samples of pore water and fracture-coating opal with depth is complementary to the depletion of ^{234}U in whole-rock samples.

U-series disequilibrium in samples of tuffs, secondary fracture-coating minerals, and percolating water is an indication of pervasive but very slow processes of water/rock interaction in the UZ at Yucca Mountain. Further, the data indicate that water/rock interaction in both the tuff matrix and the fractures has resulted in similar degrees of U-series disequilibrium.

Chemical factors controlling U(VI) mobility in a Hanford aquifer

D.L. BOND[1], J.A. DAVIS[1] AND J.M. ZACHARA[2]

[1]US Geological Survey, Menlo Park, CA 94025, USA, (dlbond@usgs.gov, jadavis@usgs.gov)
[2]Pacific Northwest National Laboratory, Richland, WA 99352, USA (john.zachara@pnl.gov)

The 300-Area at the Hanford Reservation in Washington is listed on the Environmental Protection Agency's National Priority List with contamination resulting from Cold War Era nuclear fuel processing. Legacy disposal of uranium-contaminated waste water to cribs and retention basins has resulted in groundwater plumes with U(VI) concentrations up to 10 times above the MCL. The movement of uranium through the aquifer is of concern as the groundwater is in contact with the nearby Columbia River.

Various extraction techniques were employed to investigate the sorbed and co-precipitated fractions of U(VI) present in sediments collected from the vadose zone beneath two processing ponds. Abiotic sorption and desorption processes were studied in batch systems using synthetic groundwaters with variable chemical compositions. Kinetic solution data were collected for 2 weeks to 2 months. A surface complexation model (SCM) was developed based on laboratory data to describe U(VI) sorption equilibria at the site.

Up to 40% of the total uranium was released from the highly buffered solids during contact with artificial groundwater. U(VI) desorption was extremely sensitive to the alkalinity values of the groundwater due to aqueous carbonate complexation with U(VI). The release of U(VI) to solution followed a biphasic kinetic pattern with an initial rapid release within the first 24 hr and a slower release over several weeks. Desorption of surface species and dissolution of U(VI)-bearing mineral phases each contribute to the measured U(VI) release.

The sorption results for 19 samples were modeled using a non-electrostatic SCM containing two reactions:

$$2SOH + UO_2^{2+} = SO_2UO_2 + 2H^+$$

$$SOH + UO_2^{2+} + 2H_2CO_3 = SOUO_2(HCO_3)_2^- + 3H^+$$

This semi-empirical model may be useful in predicting temporal changes in U(VI) concentrations that occur due to a wide range of alkalinity values in vadose zone waters caused by the mixing of infiltrating Columbia River water with groundwater, as well as seasonal factors in groundwater alkalinity.