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RADIONUCLIDE MIGRATION IN TUFF UNDER UNSATURATED CONDITIONS

T.T. Vandergraaf, D.J. Drew, K.V. Ticknor, and W.A. Seddon
Waste Technology Business Unit
Atomic Energy of Canada, Ltd
Whiteshell Laboratories
Pinawa, MB, R0E 1L0 Canada

Introduction

An understanding of the transport of radionuclides through unsaturated and saturated tuffaceous material is essential in assessing the safety of the proposed high-level waste repository at Yucca Mountain. Migration experiments with conservative and chemically reactive non-radioactive tracers have been performed at the Busted Butte Unsaturated Zone underground facility, SE of Yucca Mountain, and with radionuclides in columns of crushed tuff at the Los Alamos National Laboratory. In this paper, complementary radionuclide migration experiments, performed under unsaturated conditions in a small block of tuff excavated from Busted Butte, are described.

Work Description

A ~ 40 x ~ 40 x ~ 30 cm trial block of tuff was excavated from the non-welded, vitric Calico Hills Formation in the Busted Butte Unsaturated Zone test facility[1] and shipped to the Whiteshell Laboratories for the migration experiments. The location of the block straddled a thin layer of ash, "white ash bed 2." Figure 1 shows the partially excavated pillar from which the block was cut. Prior to removal of the block the excavated pillar was shrink-wrapped and encased in two-part epoxy (Wolcott Park RE2038/HD3404) and plywood.

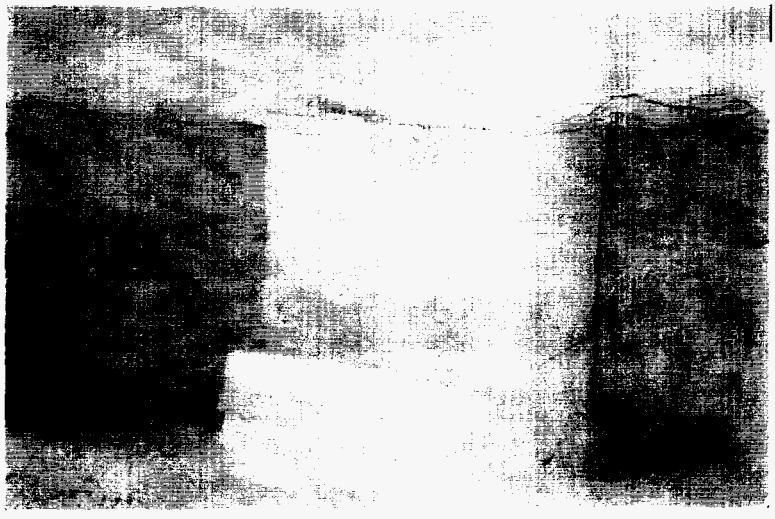

Figure 1: Partially Excavated Trial Block from the Calico Hills Formation at Busted Butte

A schematic representation of the experiment is shown in Figure 2. A porous polyethylene membrane with 70 μm pores was located between the bottom of the block and an aluminum grid plate containing a 3 x 3 matrix of collection ports. Acrylic plena

were located above and below the block and served as chambers to allow a pressure differential of ~5 cm of Hg to be imposed vertically across the block to facilitate transport of water through the polyethylene membrane and to prevent the block from saturating near the bottom. Three horizontal holes were drilled through the block and equipped with perforated 3/8" OD Teflon™ tubing containing lengths of cotton rope to sample moisture and radionuclides during the migration experiment.

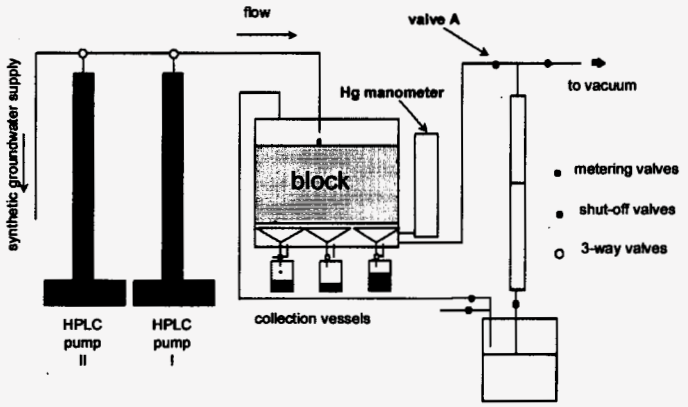

Figure 2: Schematic of Unsaturated Migration Experiment

A flow of synthetic Busted Butte pore water was added to the top of the block at a rate of 20 mL/hr, equivalent to a rate of precipitation of ~125 cm/a, approximately one order of magnitude greater than the current annual precipitation. After flow stabilization had been achieved, an 800-mL volume of synthetic Busted Butte pore water containing $^{3}H_2O$, $^{22}Na^{+}$, $^{60}Co^{++}$, $^{95m+99}TcO_4^{-}$, $^{137}Cs^{+}$, $^{237}NpO_2^{+}$, and a fluorescent dye, Na-fluorescein, was added to the top of the block at the same flow rate. This addition was followed with synthetic Busted Butte pore water for a period of ~87 days, again at the same flow rate. The eluted pore water was collected and analyzed spectrophotometrically and radiometrically.

A series of supporting static batch sorption experiments was performed in triplicate on disaggregated representative samples of tuff from the same formation at solid:solution ratios of ~1:5 and ~1:20. Sorption studies were performed using the technique described by Weaver[2] with each tracer individually and as a mixture of all six tracers.

Results

Stabilizing the friable tuffaceous material *in situ* by encapsulating the excavated pillar in epoxy and plywood prior to removal of the block prevented the material from disaggregating during further excavation and subsequent shipment. The plastic shrink-wrap provided an adequate barrier to the ingress of the epoxy into the rock matrix.

The supporting static batch sorption experiments with individual tracers gave slightly negative R_d values for Na-fluorescein (-0.13 ± 0.26 mL/g) and for $^{95m+99}Tc$ (-0.06 ± 0.20

mL/g). The R_d values obtained for the other tracers were 0.73 ± 0.34 mL/g for ^{237}Np, 6.35 ± 0.33 mL/g for ^{22}Na, 1360 ± 220 mL/g for ^{137}Cs and 2040 ± 600 mL/g for ^{60}Co. Some of the uncertainty in these measurements is thought to be a result of sample heterogeneity.

The R_d values for the tracers in the mixed radionuclide contact solution were significantly lower for the species that sorbed appreciably, typically by a factor of three to five, suggesting competition for the available sorption sites. The R_d value for ^{237}Np from the mixed radionuclide solution was 3.7 ± 6.2 mL/g, with the larger error of measurement reflecting interference by other radionuclides in the gamma spectra. The effect of different solid:solution ratios on sorption was negligible.

Approximately 11 L of synthetic Busted Butte pore water was added to the block before the first indication of water exiting the block was observed. No evidence of ponding on the surface of the block was observed during the migration experiment, suggesting that unsaturated conditions were maintained in the block. The unsaturated conditions were subsequently confirmed by determining the degree of saturation of the cotton sampling ropes; this ranged from 16 to 80%. The combined flow rate measured at the sampling ports remained slightly lower than the injection rate, indicating that the block became progressively more saturated as the migration experiment progressed. Over the duration of the experiment, 79 L of synthetic Busted Butte pore water was injected and 55 L collected. At the termination of the migration experiment, a faint trace of the Na-fluorescein was observed at the top of the block toward the periphery of the block, indicating lateral transport of the tracer toward zones of low saturation.

Initially, flow of the synthetic pore water from the block was unevenly distributed over the nine collection ports, and some variation in this distribution as a function of time was observed. This variation is most likely due to very small differences in the hydraulic conductivity between the location of the injection point and the nine sampling ports. However, once the flow had stabilized, the flow distribution proved to be reasonably stable.

The elution profiles for Na-fluorescein, ^{95m}Tc, and $^{3}H_2O$, combined for the nine sampling ports, are shown in Figure 3. Compared to the elution of the truly conservative tracer $^{3}H_2O$, both the Na-fluorescein and the ^{95m}Tc were eluted slightly earlier. This is consistent with the sorption coefficients obtained on the same geological material and can be explained by the anion exclusion effect. Both the fluorescein anion and the $^{95m+99}TcO_4^-$ are negatively charged ionic species and are repelled by the negatively charged mineral surfaces. This repulsion prevents the anions from diffusing into the pores of the tuff to the same extent as the uncharged $^{3}H_2O$ molecules.

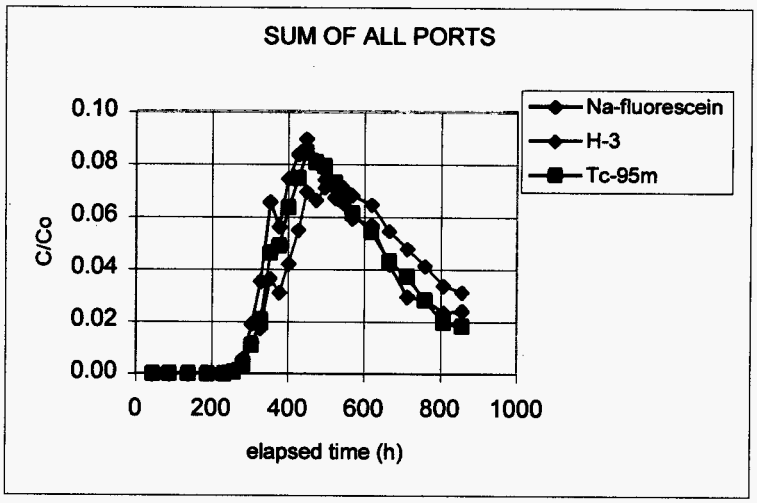

Figure 3: Combined Elution Profiles for $^{3}H_2O$, ^{95m}Tc, and Na-fluorescein

Toward the termination of the migration experiment, small amounts of ^{237}Np were observed in the eluent, but none of the other radionuclides were detected. This, again, is consistent with the experimentally obtained sorption coefficients that predict that, of the cationic tracers, $^{237}NpO_2^+$ would be the first one to be eluted. Comparing the location of the ^{237}Np elution peak with that of the $^{3}H_2O$, a retardation factor of ~3.6 was obtained. Using the standard retardation equation,

$$R = 1 + \frac{\rho(1-\varepsilon)}{\varepsilon} R_d$$

where ρ = bulk density (2.6 for felsic rock)
ε = porosity (0.5 for Calico Hills tuff)
R_d = sorption coefficient (0.73 ± 0.34 for ^{237}Np)

A retardation value of 2.9 ± 0.9 is obtained. This agrees well with the retardation observed in the migration experiment and supports the observations by Triay et al. using columns of crushed tuff[3].

Conclusions and Discussion

Sorption increased in the order: Na-fluorescein=TcO_4^-<Np<Na<<Cs<<Co. Sorption of $^{60}Co^{++}$, and $^{137}Cs^+$ was markedly lower from mixed radionuclide solutions than from solutions containing a single radionuclide. Sorption of $^{22}Na^+$ was slightly lower from mixed radionuclide solutions. These results suggest that, in performance assessment calculations, saturation of sorption sites must be take into consideration.

Under the conditions of this experiment, anionic species, including TcO_4^- and the fluorescein ion, are transported slightly faster than the transport solution. The retardation of Np, added as NpO_2^+, is low and agrees with the low observed sorption coefficient. This is not to say that retardation of Np through the entire geosphere associated with the disposal scenario in Yucca Mountain will be low: under chemically reducing conditions, NpO_2^+ is reduced to a sparingly soluble and highly sorbing species. Some ^{22}Na, ^{95m}Tc and ^{3}H was observed in the water associated with the cotton sampling

ropes suggesting that ^{22}Na is also reasonably mobile. However, no ^{137}Cs or ^{60}Co was observed either in the eluted water or in the sampling ropes; this is consistent with the high sorption values obtained for these radionuclides.

Post-migration experiment analysis of the tuff is in progress, using a variety of techniques to determine the spatial distribution of the radionuclides remaining in the block. Radionuclide transport experiments, under unsaturated and saturated conditions, are planned in larger, ~1 m^3 blocks of tuff excavated from the same site.

Acknowledgements

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