

THE EFFECT OF SATURATION ON THE MIGRATION OF MULTIVALENT RADIONUCLIDES IN NON-WELDED TUFF

T. T. Vandergraaf, D. J. Drew, C. J. Hamon
Engineered Barriers and Analysis Branch, Waste Technology Unit
Whiteshell Laboratories, AECL, Pinawa, MB R0E 1L0, Canada

W. A. Seddon
AECL Technologies Inc.
U.S. Department of Energy, Office of Repository Development
1551 Hillshire Drive, Las Vegas, NV, 89134-6321, USA

ABSTRACT

Laboratory radionuclide migration experiments have been performed under unsaturated and saturated conditions at a scale of 1 m in blocks of non-welded tuff from the Calico Hills formation underlying the Topopah Spring formation which has been selected as the host rock for the US spent fuel repository in Yucca Mountain. With the exception of microbiological scoping investigations, the experiments were performed under full QA protocol. The duration of the experiments was approximately 600 days. Na-fluorescein, ^{22}Na , ^{60}Co , $^{95\text{m}}\text{Tc}$ and/or ^{99}Tc (as the pertechnetate anion), ^{137}Cs , and ^{237}Np were used as tracers in both experiments and were injected continuously at a flow rate of 10 mL/hr, corresponding to an infiltration rate of about 17 cm/a. Tritiated water (^3HOH) was used as the truly conservative reference tracer. The tracer concentrations in the saturated block were obtained by taking aqueous samples along the flow field in real time, while the spatial distribution of the radionuclides in the unsaturated block was obtained by extracting core samples at the completion of the migration experiment. The results showed that, under unsaturated conditions, transport of Tc was similar to that of ^3H . A peak in the ^{237}Np concentration as a function of depth in the unsaturated block may be due to a mineral heterogeneity of the tuff or to changes in the redox conditions in the block. Under saturated conditions, the chemical conditions became highly reducing, leading to significant retardation of the ^{99}Tc along the flow field. Microbial activity in the saturated block was implicated in the formation of these chemically reducing conditions. If these conditions can be demonstrated to exist in the saturated zone downstream from the proposed repository, the geological formations underlying the proposed repository horizon can potentially act as a geological barrier to the transport of some multivalent radionuclides. However, if, over time, the chemical conditions would become oxidizing, the Tc and Np, retained along the flow field could, potentially, be released in elevated concentrations. The environmental impact of changing oxidation states over time may have to be investigated.

INTRODUCTION

The host rock selected for the US spent fuel repository is the Topopah Spring tuff formation in Yucca Mountain. This formation is underlain by the non-welded Calico Hills formation (1). Transport of any radionuclides leached from the emplaced wastes is expected to be vertically downward from the Topopah Spring formation through the unsaturated zone in the Calico Hills formation. Radionuclides reaching the water table will be transported horizontally in the saturated zone to a discharge area. An understanding of the transport behavior of radionuclides through the geological formations underlying the repository horizon under unsaturated and saturated zones is essential to assess the environmental impact of the disposal of high-level nuclear wastes. Although field migration experiments have been performed under unsaturated conditions in non-welded tuff at the Busted Butte Test Facility (BBTF) at the Nevada Test Site, only chemical analogs of radionuclides could be used in these experiments (1). The transport

behavior of radionuclides under these conditions must therefore be inferred from results obtained in these field experiments and a comparison between the sorptive behavior of chemical analogs and radionuclides and from laboratory studies performed on relatively small scales in various national laboratories. The availability of suitable laboratory facilities and supporting infrastructure at the Atomic Energy of Canada's Whiteshell Laboratories in Pinawa, Manitoba presented a unique opportunity to study the migration of selected radionuclides in tuff from the geological formations of interest to the US DOE nuclear waste disposal program.

EXPERIMENTAL

Geological Material

Tuff blocks with nominal dimensions of 120 x 120 x 100 cm were excavated from Vitric Zone 1 of the Topopah Spring Tuff formation (Tptpv1) and from the Calico Hills formation (Tac) in the BBTF in the autumn of 1999. Busted Butte itself is a small (2.5 km x 1 km), north-trending mountain block primarily made up of thick ignimbrite deposits of the Paintbrush Group and is located to the southeast of Yucca Mountain, on the western part of the Nevada Test Site [1]. The tuff blocks were excavated from the rear wall of the main adit of the BBTF and transported to the Whiteshell Laboratories. Details of the excavation of the tuff blocks and their transport to the Whiteshell Laboratories have been presented previously [2]

Transport Solution

Synthetic Busted Butte pore water was used as the transport solution in all migration experiments. The target chemical composition [2] is shown in Table I.

Table I Chemical Composition of Synthetic Busted Butte Pore Water

Constituent	Conc. (mg/L)
Ca	26
Mg	3.8
Na	21
K	3.2
Si	338
Cl	18
NO ₃	233
F	1.7
HCO ₃	51

Migration Experiments

The schematic of the experimental arrangement used in the migration experiments under unsaturated conditions has been reported previously [2]. For the experiment under unsaturated conditions, a porous polyethylene sheet with 35 μm pores was attached to the bottom of the block to ensure that unsaturated conditions would be maintained in the block for the duration of the experiment. A collection system was installed underneath this membrane with 36 collection ports in a square array. An acrylic plenum was attached to the top of the plywood enclosures and a dynamic partial vacuum applied to the collection system to impose a slight pressure differential across the polyethylene membrane to maintain a vertical unsaturated flow through the blocks.

Addition of the synthetic Busted Butte pore water at a rate of 10 mL/h at each of two locations on the upper surface of the large block was started in October 2000 to establish a stable, unsaturated flow through the block. This flow rate corresponds to an infiltration rate of about 17 cm/a. The first indication of water exiting at the block at the bottom was observed in March 2001. By April 2001, the flow through the block had stabilized sufficiently to start the addition of synthetic pore water containing $^3\text{H}_2\text{O}$, ^{22}Na , ^{60}Co , $^{95\text{m}}\text{Tc}$, ^{99}Tc , ^{137}Cs and ^{237}Np to the top of the block for the duration of the migration experiment. The migration experiment was terminated in November 2002. The duration of the migration phase of this experiment was 589 days. Water samples were collected from the 36 sampling ports for the duration of the experiment and analyzed spectrophotometrically for Na-fluorescein and by liquid scintillation counting for ^3H and ^{99}Tc . Selected samples were analyzed by gamma spectrometry.

For the experiment under saturated conditions, the second large block was encased in a stainless steel shroud to avoid potential leaks. Two 38-mm diameter boreholes were drilled vertically in opposite corners of the block to a depth of 50 cm to serve as injection and withdrawal boreholes and to give a flow path of ~100 cm. Five 20-mm diameter vertical boreholes were drilled between the injection and withdrawal boreholes to a depth of 75 cm and equipped with Teflon™ inserts, each with five sampling ports at 10 cm intervals. Four additional vertical boreholes with a diameter of 2.5 cm were drilled in each of the four corners of the block to flood the block slowly with synthetic Busted Butte pore water. After the block had been saturated, an acrylic cover was fitted to the top of the block. The schematic for this experiment has also been reported previously [2].

For the experiment under saturated conditions, a flow of 10 mL/h of synthetic Busted Butte pore water was established in March 2001 between the injection and withdrawal boreholes of the block. The injection of the suite of radionuclide tracers, identical to that used in the large unsaturated block, was also started in March 2001 and terminated in November 2002. A Pt electrode was installed in the line leading from the withdrawal port to monitor the redox conditions in the water exiting the block. Samples of the eluted water were analyzed spectrophotometrically for Na-fluorescein, by liquid scintillation counting for ^3H and ^{99}Tc , and by gamma spectrometry for the other radionuclides. To obtain information on the spatial distribution of the tracers in the saturated block during the migration experiment, small volumes of water were extracted along the flow field in the block through the sampling ports in the five vertical boreholes located between the injection and withdrawal boreholes.

Post Migration Experiment Analysis

At the termination of the migration experiment in the unsaturated block, samples of tuff were removed by coring into the block from the upper surface using a 38-mm diameter diamond-tipped coring bit. The samples were weighed and analyzed by gamma spectroscopy and then dried to constant weight to obtain an indication of the degree of saturation of the rock matrix and to allow the radionuclide concentrations to be expressed in Bq/gram dry weight.

Supporting Experiments

Static batch sorption experiments were performed in support of the radionuclide migration experiments using the method by Weaver [3]. The results have been reported elsewhere [4].

To determine the presence and viability of microbes, samples of the tuff block that was used in the migration experiment under saturated conditions were obtained using a sterile drill. These, and samples of unconsolidated tuff from the Calico Hills and Topopah Spring formations and samples of synthetic Busted Butte pore water were analyzed for the presence of microbes using a suite of microbial procedures [5]. Since no QA microbial procedures were available, these investigations are considered to be of a

scoping nature. In addition, a series of static experiments was performed in combinations of slurries of synthetic Busted Butte pore water (sterilized or non-sterilized), Na-fluorescein (sterilized and non-sterilized), and unconsolidated non-welded tuff (sterilized and non-sterilized) in 250-mL Erlenmeyer flasks. The synthetic Busted Butte pore water, with and without Na-fluorescein, was filter-sterilized through a 0.2- μm filter. The unconsolidated tuff was sterilized by autoclaving at 121 $^{\circ}\text{C}$ for one hour, incubating for 24 hours and re-autoclaving at 121 $^{\circ}\text{C}$ for another hour. Pt or Au electrodes were inserted into the flasks, and the flasks sealed tightly with silicone rubber. After about 60 days, the flasks were opened in an anaerobic chamber and the contents analyzed microbiologically for sulphate-reducing bacteria (SRB) and nitrate-reducing bacteria (NRB). A quantitative determination of aerobes and anaerobes (viable bacteria) was performed with a pour plating technique using an R2A medium. Colonies were picked from some of the aerobic plates tested for Gram, oxidase and catalase reactions and identified using BIOLOGTM, a bacterial identification system (BIOLOGTM Hayward, CA).

RESULTS AND DISCUSSION

Migration Experiments

The distribution of the water collected in the 36 sampling ports in the large block used in the migration experiment under unsaturated conditions fluctuated considerably over the duration of the experiment. This may simply have been due to unstable flow at this scale. A representative elution profile from one of the sampling ports is shown in Figure 1 and shows that the elution profiles of the Na-fluorescein, $^3\text{H}_2\text{O}$ and ^{99}Tc were very similar and that no evidence of accelerated transport of the anionic species is observed, in contrast to an earlier, trial, migration experiment performed at a scale of 30 cm under unsaturated conditions [4]. The average residence time of the non-sorbing tracer in the block was ~ 600 d. This corresponds to a linear flow velocity of the transport solution of ~ 1.7 mm/d. As expected from the results obtained in the trial migration experiment and the measured sorption coefficients, no evidence of the other tracers was observed in the transport solution eluted from this block.

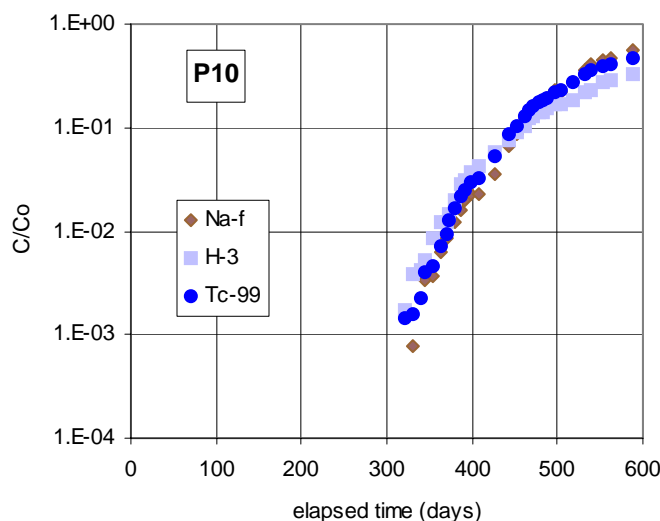


Fig. 1 Elution profiles for Na-fluorescein, $^3\text{H}_2\text{O}$ and ^{99}Tc for water collected from sampling port 10.

The elution profile obtained in the migration experiment performed under saturated conditions showed a much different behavior for ^{99}Tc (Figure 2). The peak observed at ~ 50 days was most likely due to a

short-circuit of the flow field which resulted in the flow of the solution being directed over the top of the block instead of through the block. A similar peak was observed for the two conservative tracers ~150 days after the start of the migration experiment. However, the ^{99}Tc concentration decreased after a few months and fell below the detection limit after ~12 months. Samples obtained along the flow field also showed this decrease with time and distance from the injection point and indicate that the ^{99}Tc was removed from solution early on in its transport through the block.

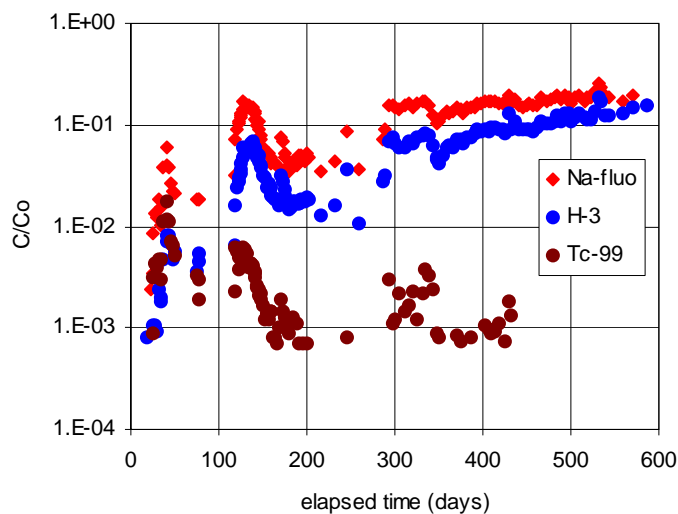


Fig. 2. Elution profiles for Na-fluorescein, $^3\text{H}_2\text{O}$ and ^{99}Tc for water collected from the withdrawal borehole in the saturated block.

The most likely explanation for this behavior is that the injected Tc(VII) is reduced to a sparingly soluble lower oxidation species with, possibly, a higher affinity for the geological material [6,7]. This is consistent with very low measured Eh values (-500 mV, uncorrected) obtained with the in-line Pt electrode.

The first arrival of ^{237}Np at sampling points 25 cm from the injection borehole was detected ~400 days after tracer injection was initiated. This is much later than would be expected from the experimentally obtained sorption coefficient for ^{237}Np [2] and may also be the result of chemically reducing conditions in the block.

Post-Experiment Analysis of the Flow Field

The concentration profiles of the gamma-emitting radionuclides used in the migration experiment under unsaturated conditions are shown in Figure 3. The spike in the concentration of all four radionuclides located at a depth of ~30 cm is due to contamination by tuff debris from a higher elevation in the block.

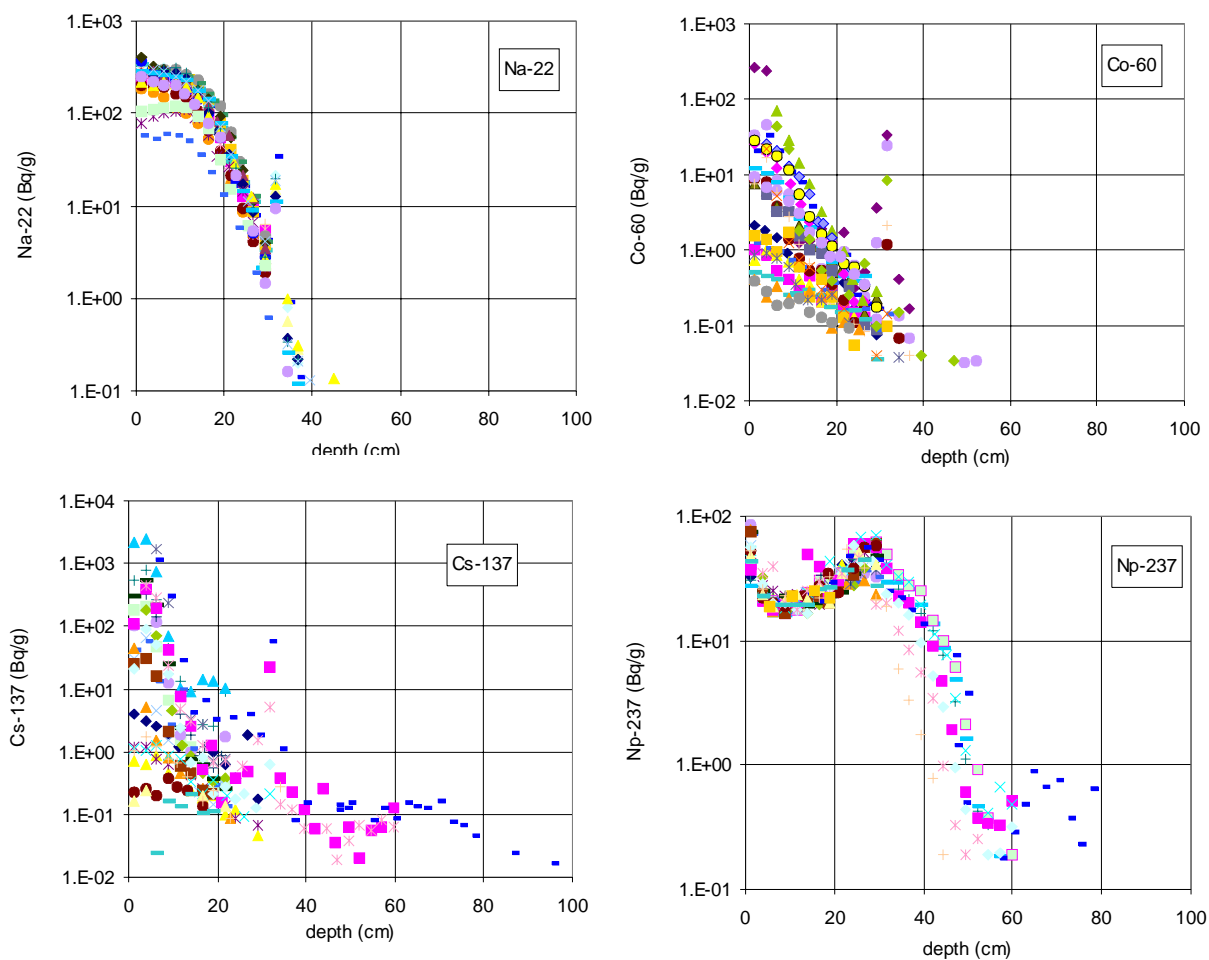


Fig. 3 Radionuclide concentration profiles in unsaturated block at the termination of the migration experiment.

It should be noted that the tuff samples were obtained by drilling downward into the block from the upper surface, i.e., from a zone of higher radionuclide concentrations to lower concentrations. This, coupled with the direction in which the holes were drilled allowed some of the most highly contaminated tuff to fall into the borehole. The drilling was performed in two stages, down to a depth of 30 cm, and from 30 cm to a depth of 60 cm and, in one location, to the bottom of the block.

The concentration of the ^{22}Na , ^{60}Co , and ^{137}Cs decreased with increasing depth, as would be expected. The scatter in the ^{60}Co and ^{137}Cs concentrations is somewhat greater than that of ^{22}Na and may also be due to cross contamination. The concentration profile for ^{237}Np shows, after an initial decrease, an increase starting at a depth of 10 cm. The ^{237}Np increased gradually and reached a maximum at a depth of ~30 cm. This anomalous behavior can be attributed to a vertical mineralogical heterogeneity in the tuff block reflecting the bedding of the tuff layers. The tuff samples retrieved from the block at a depth of 20 to 30 cm appeared to contain more fine-grained material. Since sorption takes place on the surfaces of the mineral grains, the increase in ^{237}Np concentration may reflect a higher sorption capacity. The reason why this increased sorptive capacity was not reflected in the transport behavior of ^{22}Na , ^{60}Co , or ^{137}Cs may be that these radionuclides had not been transported in sufficient concentrations to this depth in the block. However, it is also possible that, over the duration of the migration experiment the conditions in

the unsaturated block became chemically reducing and that the Np was reduced from Np(V) to a sparingly soluble Np(IV) species. Scoping calculations using the chemical speciation code PHREEQC [8] and the database phreeqc_noorg-ymp_25.dat [9] showed that, as the conditions change from oxidizing to reducing, Np is reduced before Tc (Figure 4, going from left to right). This would explain why the injected Tc was transported under unsaturated conditions without retardation (Figure 1).

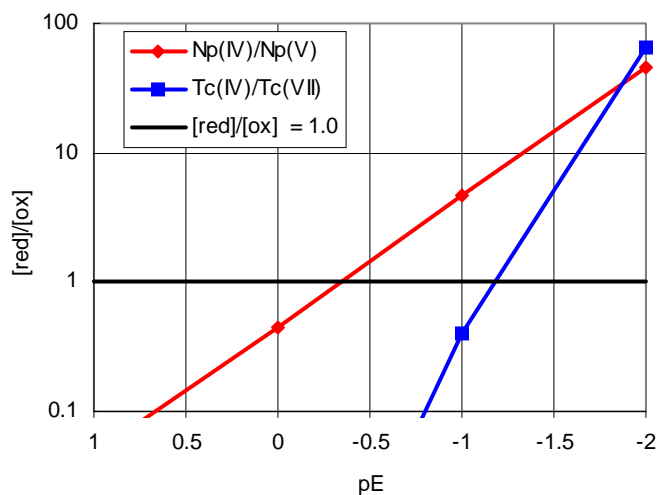


Fig. 4 Calculated ratios of chemically reduced and chemically oxidized Tc and Np states as a function of pE. (pE = Eh/0.059V [10]).

Supporting Microbial Investigations

Microbes were found to be ubiquitous in both the geological material and in the synthetic pore water used in these migration experiments. Both aerobic and anaerobic heterotrophs were identified in the geological material removed from the tuff blocks using a sterile drill. However, the aerobic heterotrophs exceeded the anaerobic heterotrophs by orders of magnitude. No SRB were detected in either the tuff or the synthetic pore water.

The initial numbers of bacteria in the tuff and in the pore water were relatively low. The numbers of bacteria greatly increased when pore water and the tuff material were combined. A wide range of species of bacteria was detected with BIOLOG. Most bacteria were gram negative, oxidase positive. This indicates that they were non-enteric bacteria (bacteria requiring lower temperatures). The presence of bacteria appeared to affect the redox process of tuff under saturated conditions. Depending on the conditions of the individual static experiments, different bacteria or combinations of bacteria may have prevailed and produced the wide range of results. For example, the chemical conditions in one static experiment, in which neither the tuff nor the pore water was sterilized, did not become chemically reducing, while the conditions in another experiment, which differed only by the addition of non-sterilized Na-fluorescein, did become chemically reducing. This result is puzzling and seems to indicate that the Na-fluorescein may have had some effect on the bacteria. This effect was not observed in the experiments where either the pore water or the tuff was sterile

In the experiments where both tuff and pore water were sterilized it was found that *Ralstonia pickettii* (a bacterium which can pass through a 0.2- μ m filter) was the only bacterium present. In spite of the fact that

the conditions were not completely sterile, no chemical reduction occurred, leading to the conclusion that *Ralstonia pickettii* was not responsible for chemical reduction. This same pore water was used in another experiment which had sterilized pore water and nonsterilized tuff. Conditions in that case became chemically reducing, indicating that the tuff contained bacteria that are capable of creating reducing conditions. All experiments that had non-sterilized tuff or non-sterilized pore water (or Na-fluorescein) produced chemically reducing conditions except one experiment which had both non-sterilized tuff and non sterilized pore water and nonetheless remained oxidizing. This experiment did not have any apparently different results for microbial numbers than the rest of the tests and it is puzzling why this experiment behaved the same as those with sterile components.

Fluorescein anions did not appear to have influenced the numbers of bacteria, except possibly in one of the batch experiments. The other bacterium that was positively identified was *Sinorhizobium meliloti*, a common soil bacterium.

CONCLUSION

The results from these large-scale migration experiments have shown that, under unsaturated conditions, transport of Tc is not retarded by the geological formations underlying the proposed repository horizon. The transport behavior of ^{22}Na , ^{60}Co , and ^{137}Cs agreed qualitatively with that predicted on the basis of experimentally determined sorption coefficients. The anomalous transport behavior of ^{237}Np can be explained by the heterogeneous mineral composition along the flow path in the tuff.

Under saturated conditions, however, a marked decrease in the measured redox conditions in water collected from the block and a concomitant loss of Tc from solution were observed. The transport of ^{237}Np is also slower than predicted from its sorption coefficient and is thought also to be due to the chemically reducing conditions that existed in the block.

Supporting microbial investigations have shown that microbial activity may have led to the formation of chemically reducing conditions. Indigenous bacteria in the formation underlying the repository horizon or anthropogenic bacteria that may be introduced inadvertently in the tuff during the emplacement of the wastes can be expected to generate chemically reducing conditions in the far field.

The results suggest that any Tc released from the waste repository in Yucca Mountain may initially migrate vertically downward through the unsaturated zone with little or no retardation as long as chemically oxidizing conditions prevail and Tc is present as Tc(VII). However, if chemically reducing conditions exist in the saturated zone, the bulk of the Tc is expected to be reduced to a lower oxidation state and precipitate or sorb onto the geological material. The Tc concentration in the groundwater will then be solubility controlled, resulting in a very low flux of this radioelement. The retardation of the Np along the flow field would be enhanced if chemically reducing conditions were to prevail in the saturated zone.

Any ^{99}Tc and ^{237}Np that could be leached from the waste form in the repository would concentrate at a redox boundary and, as long as the conditions remained chemically reducing, would be contained by the geosphere. However, if the conditions were to become oxidizing at some future time, the sorbed or precipitated Tc or Np could be mobilized. The subsequent migration of the Np would be controlled by its sorption behavior, but the Tc would be oxidized to Tc(VII) and be transported through the geosphere without retardation. The environmental impact of changing oxidation states would have to be investigated.

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