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Impacts of Reducing Conditions in the Saturated Zone at Yucca Mountain

Bill W. Arnold[1], Arend Meijer[2], Elena Kalinina[3], Bruce Robinson[4], Sharad Kelkar[4], Carlos Jove-Colon[1], Stephanie Kuzio[1], Scott James[1], Ming Zhu[5]

[1]*Sandia National Laboratories, PO Box 5800, Albuquerque, New Mexico, 87185-0778, USA: bwarnol@sandia.gov.*
[2]*GCX, Tucson, Arizona, USA.*
[3]*RHYM, LLC, Albuquerque, New Mexico, USA.*
[4]*Los Alamos National Laboratory, Group EES-6, MS T003, Los Alamos, New Mexico, 87545, USA.*
[5]*Bechtel/SAIC, Las Vegas, Nevada, USA.*

Abstract – *Variations in groundwater redox chemistry in the saturated zone near Yucca Mountain could have significant impacts on processes associated with the potential transport of redox-sensitive radionuclides from the proposed repository to the accessible environment. This study examines geochemical data relevant to the distribution of redox conditions in the saturated zone, the relationships between redox state and solubility and sorption coefficients for technetium and neptunium, and sensitivity in transport model simulations. Results indicate evidence for a zone of reducing conditions in the volcanic rocks of the saturated zone located to the east and south of the repository and along the inferred flow paths from the repository. A working hypothesis is that these reducing conditions are related to the presence of minor pyrite in the matrix of some volcanic units. Chemical equilibrium modeling of technetium solubility using EQ3/6 software codes is used to estimate the value of solubility limits as a function of Eh. Surface complexation modeling with the EQ3 code is used to estimate neptunium sorption coefficient values as a function of Eh. A general analytical approach, one-dimensional reactive transport modeling, and the three-dimensional saturated zone site-scale transport model using the FEHM software code are used to evaluate the impacts of solubility limits and enhanced sorption in reducing zones on the simulated transport of technetium and neptunium in the saturated zone. Results show that if precipitation occurs in response to flow through a reducing zone, then the peak concentration released to the accessible environment will be restricted to the solubility limit. Simulations also show that enhanced sorption within a reducing zone of modest width leads to significantly greater retardation of radionuclides in the saturated zone.*

1. INTRODUCTION

The saturated zone (SZ) is a potentially significant pathway by which radionuclides originating from the proposed high-level radioactive waste repository at Yucca Mountain would be transported for release to the accessible environment. The nature and spatial distribution of redox conditions in the SZ could have significant impacts on the migration of redox-sensitive radionuclides (e.g., ^{99}Tc and ^{237}Np). Chemical speciation of these redox-sensitive radionuclides results in lower solubility and enhanced sorption under reducing conditions.

Such radionuclides are consequently more mobile in groundwater at higher Eh values. If solubility limits were exceeded at locations along the flow path from the repository in the SZ, some radionuclide mass would be precipitated from the groundwater and immobilized as a solid phase. This process would delay the overall rate of release of radionuclides to the accessible environment. Similarly, geochemical conditions that enhance the sorption of radionuclides along the flow path in the saturated zone would lead to greater overall retardation of radionuclides and further delay their release.

Two previous studies are directly relevant to these potential effects in the Yucca Mountain SZ. An assessment of the potential impacts of reducing conditions in the saturated zone at Yucca Mountain on ^{99}Tc transport and overall repository performance has been conducted [1]. Their study considered the impacts of lower solubility and enhanced sorption assuming reducing conditions in the tuff and alluvial aquifers. It was concluded that simulated peak dose from ^{99}Tc at 50,000 years is reduced by three orders of magnitude when solubility limits are considered, and that enhanced sorption in the alluvium has an even greater impact on reducing simulated dose [1]. A synthesis of data on the distribution of ^{99}Tc and ^{129}I in groundwater from the

Nevada Test Site to assess their migration from underground nuclear testing was conducted and concluded that ^{99}Tc did not necessarily migrate as a conservative species and that retardation of ^{99}Tc migration could be attributed to locally reducing conditions [2].

Redox conditions and the impacts on radioelement speciation and solubility are important considerations for other geological disposal programs. Uniformly oxidizing conditions in the SZ have been conservatively assumed in transport modeling for most previous repository performance assessment calculations at Yucca Mountain. However, hydrochemical data indicate that redox conditions are not uniform in the SZ down gradient of the repository location and that reducing conditions may exist locally.

This study consists of examining the distribution of redox conditions in the SZ, the relationship between solubility and redox conditions, the relationship between sorption and redox conditions, the conceptualization of these processes, sensitivity analyses, and conclusions. These assessments are conducted for neptunium and technetium, which are representative of redox-sensitive elements in the repository and are potential key contributors to simulated dose in the individual protection analyses with the Total System Performance Assessment (TSPA) model. Both site-specific and analogue data are used to assess redox conditions in the SZ and to infer relationships between solubility and sorption. The sensitivity analyses of radionuclide transport in the SZ are conducted with a one-dimensional model that incorporates the processes of solubility limits and enhanced sorption and with a three-dimensional site-scale SZ transport model, which incorporates enhanced sorption. Uncertainties in conceptual models and in parameter values are addressed in the evaluations of data and in the sensitivity analyses. Finally, the potential impacts to performance assessment calculations are discussed.

2. ANALYSIS APPROACH

2.1 Redox Conditions in the SZ

Redox conditions in the SZ are inferred from reduction/oxidation potentials measured using an inert platinum electrode, the presence of reductants and oxidants, and the concentrations of species in redox couples (e.g., Fe^{2+}/Fe^{3+}). Uncertainties in determining redox conditions in groundwater samples are related to factors such as the potential for contamination of samples, instrumentation errors, and apparent inconsistencies due to chemical disequilibrium. Given inherent uncertainties, an approach based on a preponderance of evidence is used to identify oxidizing and reducing locations in the SZ. Groundwater samples that contain more than 1.0 mg/L of dissolved oxygen (DO) are designated as oxidizing based on the DO analyses alone. Groundwater samples with less than 1.0 mg/L or lacking DO measurements are viewed as potentially reducing and other geochemical data are used to assess the most likely redox state at those locations in the SZ.

In addition to DO concentrations of less than 1.0 mg/L, reducing waters generally have iron concentrations greater than 0.1 mg/L and measured Eh values less than 200 mV/SHE. A plot of iron concentrations against DO concentrations is shown in Figure 1. Note that total iron concentrations in groundwaters with little or no dissolved oxygen range from 0 mg/L to around 5 mg/L. The three iron concentrations in excess of 0.5 mg/L in oxidizing groundwaters probably represent borehole construction artifacts. Data on total iron concentration are of particular importance in inferring the location of reducing groundwater in the SZ.

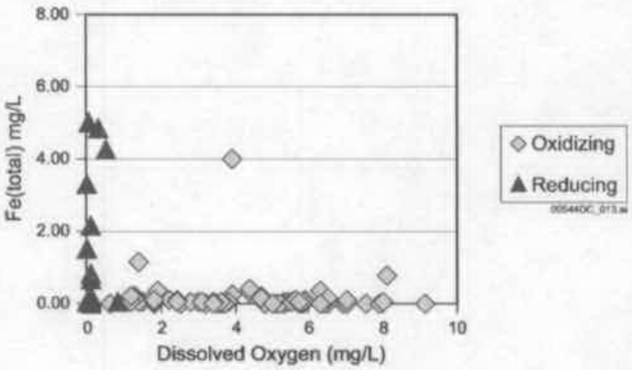

Fig.1. Measured dissolved oxygen versus measured total iron in oxidizing (DO>1.0 mg/L) and reducing (DO<1.0 mg/L) groundwaters.

2.2 Solubility Calculations

Chemical equilibrium modeling of technetium solubility was conducted to evaluate the values of solubility limits and the range of Eh over which the transition from high solubility to low solubility occurs. The EQ3 software was used to simulate technetium solubility under oxidizing and reducing conditions, as endpoints. The EQ6 software was used to simulate solubility along a reaction path, ranging from oxidizing to reducing conditions. The impacts of groundwater composition, the controlling solid phase, pH, and temperature were evaluated in the analyses.

Technetium solubility under reducing conditions is limited either by TcO_2 or $TcO_2{\cdot}xH_2O$ [3]. In one set of experimental studies the dissolution of technetium under reducing conditions was limited by $TcO_2{\cdot}1.6H_2O$ [4]. EQ3 calculations were carried out using wells J-13 and p#1 water compositions with the measured pH of 6.9 (J-13), 6.7 (p#1) and pH of 8.5 and assuming both crystalline and hydrated technetium oxide as the controlling solid.

2.3 Sorption Calculations

The sorption of neptunium onto quartz, as a function of Eh, was evaluated using a non-electrostatic surface complexation model. A dilute water composition similar to water compositions found in the SZ at Yucca Mountain was used and a quartz surface area of 0.02 m^2/g was chosen. For oxidizing conditions, the neptunium binding constant reported by [5] was used for neptunium sorption on quartz. For reducing conditions, a binding constant was derived for Np^{4+} sorption by using Th^{4+} as an analogue to Np^{4+}. A binding constant for Th^{4+} on quartz was derived using the surface complexation model available in the PHREEQC code and sorption coefficients for thorium on quartz in dilute water reported by [6]. Chemical equilibrium simulations for neptunium sorption for varying values of Eh were conducted using the EQ3 software.

2.4 Impacts on Radionuclide Transport

The potential impacts of solubility limits and enhanced sorption related to reducing conditions in the SZ were evaluated for the redox-sensitive radionuclides ^{99}Tc and ^{237}Np. Sensitivities of transport simulations to these factors were analyzed using general analytical approaches, one-dimensional reactive transport simulations, and the three-dimensional SZ site-scale transport model.

In the general analytical approach to evaluating sensitivity to solubility limits, the ^{99}Tc mass release rate required to exceed the solubility limit is calculated as a function of volumetric groundwater flow, for varying values of the solubility limit. The one-dimensional reactive transport simulations are conducted with the FEHM code using a representative groundwater flow pathway extracted from the three-dimensional SZ site scale flow model. The reactive transport model includes the processes of matrix diffusion in fractured tuff (using the generalized dual porosity model option of FEHM), sorption in the tuff matrix, and potential precipitation of ^{99}Tc in zones where the solubility limit is exceeded. A 1000 m wide reducing zone is included at a distance 5000 m down gradient of the repository.

In the general analytical approach to evaluating the sensitivity to enhanced sorption, the effective sorption coefficient for the entire SZ flow path is calculated as a function of the fraction of the flow path with reducing conditions. The SZ site-scale transport model is used to evaluate the impacts of the width of the potential reducing zone and the values of the resulting enhanced sorption coefficients on simulated radionuclide transport times.

3. RESULTS

3.1 Redox Conditions in the SZ

As shown in Figure 2, oxidizing groundwaters are quite common in the Yucca Mountain area. These groundwaters occur in volcanic units near northern Yucca Mountain, in alluvium along Fortymile Wash, and in volcanic units at various locations on and around Yucca Mountain. Note that the groundwater from a well that penetrated the Paleozoic aquifer beneath Yucca Mountain (p#1) is also oxidizing. In arid environments, oxygenated groundwater can persist over relatively long flow distances in regional flow systems. Oxidizing groundwater has been observed in the Continental Intercalaire aquifer of Algeria and Tunisia up to 300 km from the outcrop and apparent recharge area of the aquifer [7]. Low organic contents in desert soils, the thick vadose zone containing atmospheric oxygen, and rapid, highly episodic limited infiltration probably facilitate highly oxidizing recharge to the SZ in arid environments.

Reducing groundwater occurs in several wells completed in volcanic units to the south and east of the proposed repository location (Figure 2). In addition, reducing conditions are encountered in several wells in the alluvium. However, most of these locations in the alluvium are not along the inferred flow path from the repository and would thus not impact radionuclide transport to the accessible environment.

The working hypothesis for the existence of reducing groundwater in the volcanic units of the SZ is that flow through local areas of tuff containing minor disseminated pyrite consumes DO and results in low Eh. Pyrite has been identified as a primary component of the lower Tram Tuff [8] and groundwater is produced from this unit in well H-3. Other wells with reducing conditions may contain groundwater that has been in contact with the

Tram Tuff or with other volcanic strata containing minor pyrite. It is important to note that once DO is removed from groundwater by reaction with a reductant such as pyrite, the water generally remains reducing unless mixing with oxygenated groundwater as it moves down gradient.

Measurements of redox parameters in groundwaters pumped from wells located directly east of Yucca Mountain suggest the existence of a north-south zone of reducing groundwaters in volcanic units. This zone transects the transport pathways from the repository predicted by the flow model.

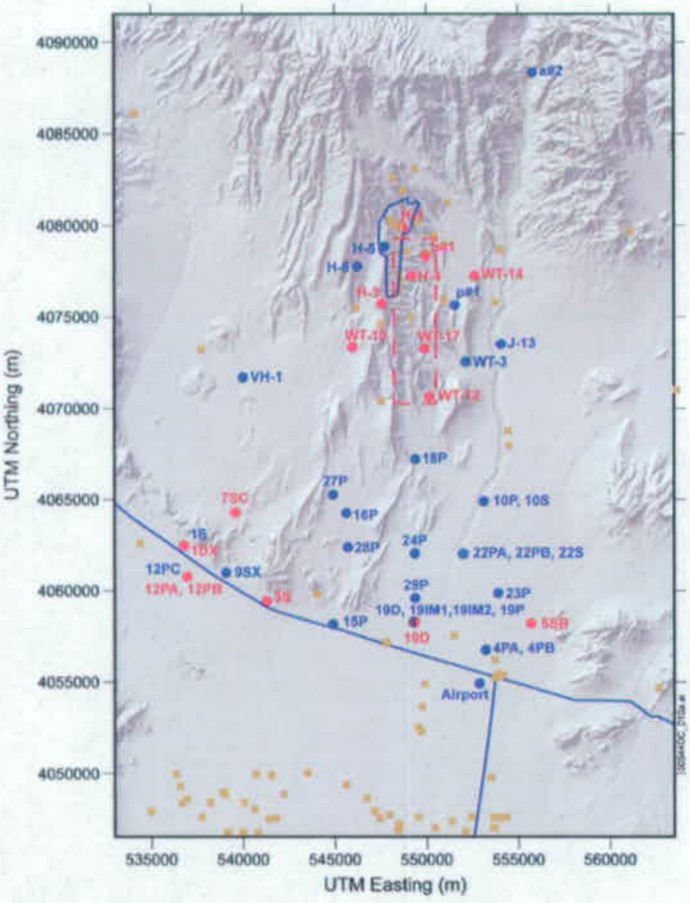

Fig. 2. Map showing locations of wells with oxidizing and reducing groundwaters. Wells with oxidizing groundwater shown with blue circles and wells with reducing groundwaters shown with red circles. Wells in which redox conditions have not been measured are shown with the brown squares.

3.2 Solubility Calculations

The results of the technetium solubility calculations indicate a solubility of 4×10^{-9} M under reducing conditions in the SZ, assuming $TcO_2 \cdot 1.6H_2O$ as the controlling solid phase (see Figure 3). This calculated value is insensitive to temperature, pH, and water composition within the parameter ranges considered. If TcO_2 is used as the controlling solid, the calculated solubility is significantly lower, at 4×10^{-13} M. Figure 3 shows that the transition from lower to higher solubility ranges from -100 mV to about +300 mV.

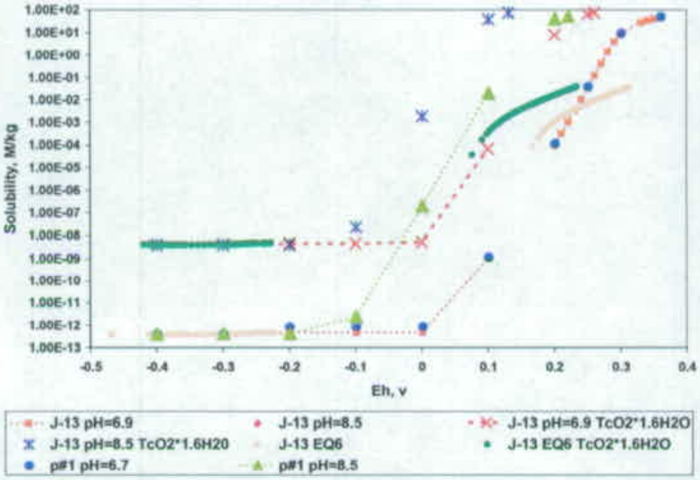

Fig. 3. Technetium solubility in J-13 and p#1 water from EQ3 and EQ6 calculations.

The results of the technetium solubility calculations shown here are in general agreement with experimental studies and with ranges of values selected for use in performance assessment analyses [1,3,4]. Based on this analysis, literature data, and uncertainty in the controlling solid phase for technetium solubility, a value of 4×10^{-9} M is used in the transport sensitivity analyses in this study.

3.3 Sorption Calculations

The results of the surface complexation modeling of neptunium sorption in the SZ as a function of Eh are shown in Figure 4. These results show a dramatic contrast in the calculated sorption coefficient, with the K_d being over three orders of magnitude higher under reducing conditions than under oxidizing conditions. The transition in sorption behavior for neptunium occurs over the range of approximately 0 mV to +300 mV Eh.

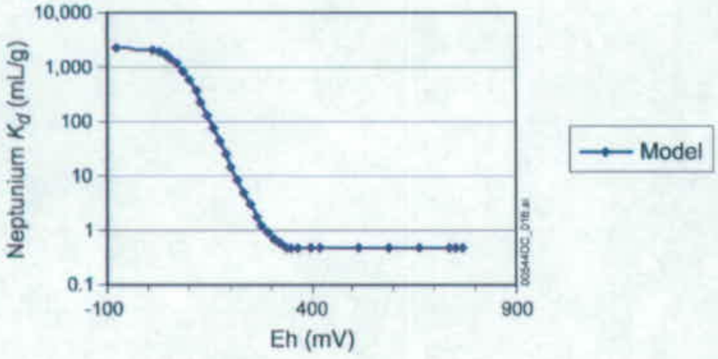

Fig. 4. Surface Complexation Modeling Results for Neptunium Sorption on Quartz in Dilute Groundwater as a Function of Eh.

Experimental studies of neptunium sorption using dilute water compositions indicate a very similar functional relationship between sorption coefficient and Eh [9] to the calculated result using the surface complexation model. These experimental results indicate a sorption coefficient on the order of 1000 mL/g, with a somewhat sharper transition in behavior in the range of +150 mV to +250 mV Eh. Similar experimental results for sediments and groundwater also from the Gorleben site in Germany for technetium sorption have been obtained [10], although the value of the sorption coefficient for technetium under oxidizing conditions is lower than for neptunium.

3.4 Impacts on Radionuclide Transport

The general analytical approach used to assess the potential impacts of technetium solubility limits on SZ transport indicates that if the 1 Ci/year of ^{99}Tc were released from the repository and the mass were contained in less than 100 acre-ft/year of groundwater flow in the SZ, then the expected solubility limit for reducing conditions of 4×10^{-9} M would be exceeded and precipitation would occur. These results suggest that conditions in which the solubility limit for technetium would be exceeded in reducing zones could occur, but would be limited to scenarios in which the release rate for technetium is high and/or releases are concentrated in a restricted flow path through the SZ.

For the one-dimensional reactive transport model a steady state flow path in the model is established in a preliminary run where the flow rates approximate those extracted from the three-dimensional SZ site-scale flow model. Transport is simulated by injecting radionuclide at the water table beneath the UZ, and recording concentration versus time at the compliance boundary.

Breakthrough curves for ^{99}Tc are presented in Figure 5 representing concentration versus time just inside the entrance to the redox zone (solid curves) and at the compliance boundary (dashed curves). A simulation with sorption (K_d = 50 mL/g) and solubility-limited reaction (solubility of 4×10^{-9} M) in the reducing zone (black curves), and a simulation with sorption in the reducing zone, but no solubility-limited reaction (red and green curves) are shown. Note the differing scales on the left and right axes of the plot shown in Figure 5 and the much lower concentrations indicated for the solubility-limited case.

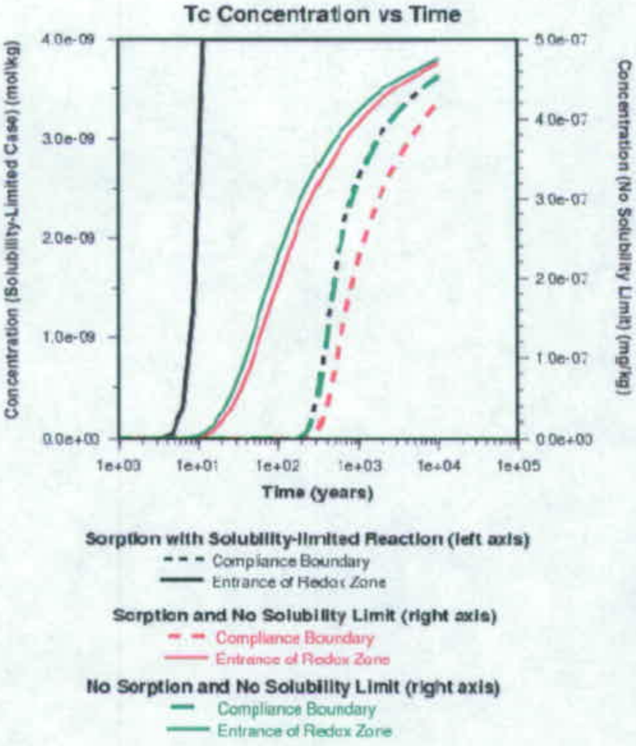

Fig. 5. ^{99}Tc Breakthrough Curves at the Compliance Boundary and at the Entrance of the Reducing Zone for the One-Dimensional Streamtube Model.

The most important difference in the simulations with and without solubility limits shown in Figure 5 is the much lower concentration at the compliance boundary (outlet concentration) for the solubility-limited case (dashed black curve). Radionuclides, upon reaching the reducing zone, precipitate into the fractures of the tuff so that the aqueous concentration downstream from that point cannot exceed the solubility limit of 4×10^{-9} M.

Simulations with the one-dimensional reactive transport model for a source with a specified duration rather than a continuous source show that precipitation does not behave as an irreversible retardation mechanism, in that the radionuclide can re-dissolve when the source of radionuclides upstream of the reducing zone is exhausted. The principle impact of solubility-limited reaction is to attenuate the maximum downstream concentration at the solubility limit, but radionuclide mass is not removed from the system (other than by radioactive decay). The mass that precipitates is delayed until it can become remobilized by dissolution.

For the SZ site-scale transport model simulations a zone of reducing conditions and enhanced sorption is defined (as shown by the dashed red line in Figure 2) to evaluate the impacts of enhanced sorption. Example resulting breakthrough curves at the accessible environment are shown in Figure 6.

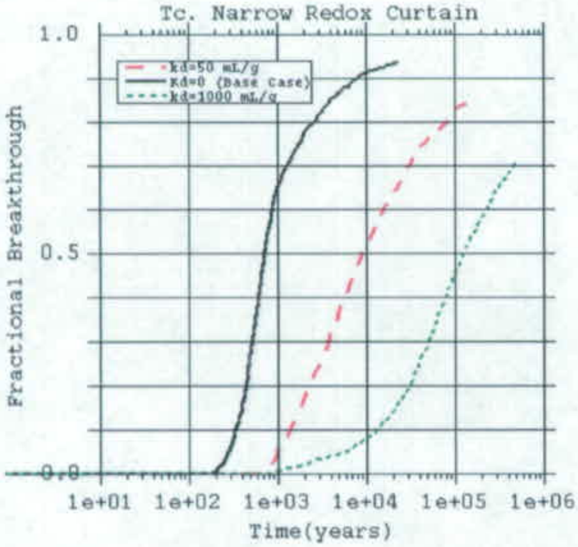

Fig. 6. Breakthrough Curves for Technetium with Narrow Redox Curtain and $K_d = 0$ (base case), $K_d = 50$, and $K_d = 1000$ mL/g.

The technetium transport simulations indicate that even for a moderate value of $K_d = 50$ mL/g, and the narrow redox zone, the 50 percent breakthrough time increases by more than an order of magnitude from a transport time of 723 years for the base case to 9,110 years under SZ groundwater flow for present-day climatic conditions. For technetium $K_d = 1,000$ mL/g, the value likely to be encountered in a fully reducing zone, the 50 percent breakthrough time increases even more dramatically to 126,500 years. For the neptunium transport simulations with a narrow redox curtain and sorption coefficient of 200 mL/g, the 50 percent breakthrough time increased by a factor of approximately 2.5, from the base value of 25,820 years to 64,900 years under present-day climatic conditions.

4. CONCLUSIONS

4.1 Conceptual Model of Redox Conditions, Solubility Limits, and Enhanced Sorption

Assessment of redox measurements in groundwater samples indicates that there are reducing conditions in the fractured volcanic aquifer to the east and south of Yucca Mountain. The most likely reductant responsible for these conditions is pyrite in the volcanic units (particularly the Tram Tuff). Although groundwater samples come from fractures in the volcanic units of the SZ, reducing conditions probably also exist in the rock matrix, given the inferred role of pyrite in controlling the redox conditions. The conceptual model of redox conditions in the SZ includes a "curtain" of reducing conditions to the east and south of Yucca Mountain extending from the water table into the older volcanic units. This curtain is located such that all or most of the flow pathways from beneath the repository in the SZ would encounter it. There is also a (strata-bound) reducing zone in the lower Tram Tuff that results from the presence of primary pyrite. Oxidizing conditions are presumed to occur elsewhere in the SZ flow system, including the shallow volcanic units elsewhere, the regional carbonate aquifer, and the alluvium along the flow paths to the accessible environment. Although, reducing conditions in alluvium have been inferred in several Nye County wells, they have not been observed in wells completed in the alluvium along the predicted SZ flow paths from beneath the repository, with the possible exception of one zone in well NC-EWDP-19D.

Where reducing conditions exist in the SZ, the transport of redox-sensitive species would be subject to potential precipitation due to lower solubility and enhanced sorption due to higher sorption coefficients under reducing conditions. It is assumed that chemical equilibrium would exist in reducing zones with regard to aqueous speciation of radionuclides, precipitation and dissolution, and sorption. Precipitation of radionuclides in fractured volcanic units could occur in the fractures and in the rock matrix. However, it is anticipated that precipitation would occur primarily in the fractures because redox-sensitive radionuclides would be transported into zones of reducing conditions via fracture flow. It is assumed that radionuclides precipitating from the aqueous phase due to lower solubility limits in the reducing zones would be immobilized (at least temporarily) by direct precipitation or co-precipitation as mineral coatings on fracture surfaces or within matrix pores. Enhanced sorption would occur in the rock matrix of volcanic units in the SZ. As with sorption under oxidizing conditions, in radionuclide transport modeling, sorption is assumed to occur only in the matrix and not on fracture surfaces. As a result, this conceptual model requires diffusion of radionuclides into the rock matrix for access to the enhanced sorption therein.

There are some potentially significant uncertainties in this conceptual model that are not implemented in the sensitivity analyses presented here. A general spatial distribution of reducing conditions in the volcanic aquifer near Yucca Mountain has been defined, but there could be greater spatial heterogeneity in redox conditions than is represented in the sensitivity analyses. Due to uncertainties in the interpretations of chemical data and to limited data resolution, the spatial structure of redox conditions could be more complex. In particular, there could be areas of local oxidizing conditions within the reducing curtain and there could be isolated zones of reducing conditions within the generally oxidizing zones of the aquifer. Another conceptual uncertainty is the nature of the precipitation process for radionuclides in reducing zones. It is assumed that the precipitate would be immobile, but precipitation as or onto colloids is a possible process that potentially could allow further migration of radionuclides.

4.2 Impacts on Radionuclide Transport

A simplified approach was presented to assess the relation between radionuclide mass input, the volumetric groundwater flow rate in the SZ, and solubility limits. This approach provides a method to determine whether the radionuclide precipitation will occur under specific volumetric groundwater flow rates and radionuclide release rates. This simplified approach provides a first-order assessment of the potential relevance of solubility limits to radionuclide transport in the SZ and concluded that precipitation of ^{99}Tc in reducing zones in the SZ could be a significant process for relatively large releases of technetium into small to moderate volumes of groundwater in the SZ.

A one-dimensional reactive transport model for the SZ was developed to explicitly simulate the coupled processes of radionuclide precipitation, matrix diffusion, and sorption. The results showed that the assumed inlet ^{99}Tc concentration of 5×10^{-7} M dropped by about two orders of magnitude to 4×10^{-9} M at the compliance boundary due to chemical precipitation in the reducing zone. Results also show that the process of precipitation is not an irreversible retardation mechanism because the radionuclides present in the system can re-dissolve when the radionuclide source is exhausted. Despite the fact that precipitation could be reversible under certain circumstances, solubility-limited behavior is potentially important to repository system performance because the dose contribution of a radionuclide is directly proportional to the concentration at the compliance boundary. A sensitivity analysis found that the influence of precipitation relies solely on the presence of a reducing zone through which radionuclides pass, rather than on the size of that zone.

An effective sorption coefficient approach was developed to examine the general sensitivity of enhanced sorption in the SZ due to locally reducing conditions. This simplified approach relates the effective sorption along the entire flow path in the SZ to the fraction of the flow path with reducing conditions and associated enhanced sorption. Results show that even for a small fraction of the flow path through reducing geochemical conditions, the effective sorption coefficient for the entire flow path can be significantly higher. The steepest rise in the effective sorption coefficient with increasing fraction of the flow path length is at the smallest flow path fractions.

In addition, explicit transport simulations were performed using the three-dimensional base-case site-scale SZ transport model to study the sensitivity of breakthrough curves to the sorption coefficients of neptunium and technetium expected to occur under reducing conditions. These simulation results indicate significantly greater retardation of ^{99}Tc and ^{237}Np in the SZ due to the potential presence of locally reducing conditions.

4.3 Implications for Performance Assessment

Overall, this analysis indicates that the impacts of solubility limits and enhanced sorption in reducing zones in the SZ could have a significant impact on the simulations of ^{99}Tc and ^{237}Np transport in TSPA calculations. The potential impacts of solubility limits for technetium in the SZ are dependant upon the concentrations of technetium entering and within the SZ.

There are not enough data to discard TcO_2 as a solubility-controlling solid in the determination of technetium solubility. The use of this controlling solid results in four orders of magnitude lower solubility limit than what was used in the one-dimensional reactive transport model sensitivity calculations. Consequently, the implications for TSPA could be even greater than estimated in this study. The results of the three-dimensional sensitivity analysis using the values of enhanced sorption coefficients within the hypothesized reducing zone showed that the transport times for ^{99}Tc and ^{237}Np ranged from one to three orders of magnitude longer than the base-case results, depending upon the width of the reducing zone and the value of the sorption coefficient.

There are uncertainties in the processes associated with redox conditions in the SZ that would require consideration in the TSPA calculations, including uncertainties associated with the conceptual model, redox measurement uncertainties, and parameter uncertainties. There is spatial variability in redox conditions in groundwater flow systems over a wide range of scales, from centimeters to kilometers. The extent of redox measurements at the Yucca Mountain site is limited, for example the WT wells were not measured for dissolved oxygen. Accurate assessment of the extent of the reducing zone is limited by the data available. There is also uncertainty associated with the sorption coefficient parameters and solubility limits.

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