



MATERIALS
RESEARCH
SOCIETY

SYMPOSIUM PROCEEDINGS

Volume 824

Scientific Basis for Nuclear Waste Management XXVIII

EDITORS

John M. Hanchar
Simcha Stroes-Gascoyne
Lauren Browning

Field-Scale Migration of ^{99}Tc and ^{129}I at the Nevada Test Site

Qinhong Hu and David K. Smith

Chemical Biology and Nuclear Science Division, Lawrence Livermore National Laboratory
7000 East Avenue, MS L-231, Livermore, CA 94550, U.S.A.

ABSTRACT

The groundwater at the Nevada Test Site (NTS) contains many long-lived radionuclides, including ^{99}Tc (technetium) and ^{129}I (iodine), as a result of 828 underground nuclear weapons tests conducted between 1951 and 1992. We synthesized a body of data collected on the distribution of ^{99}Tc and ^{129}I in groundwater to assess their migration at NTS, at field scales over distances of hundreds of meters and for durations up to forty years and under hydrogeologic conditions very similar to the proposed geological repository at Yucca Mountain. The results of our study show that Tc does not necessarily exist as a mobile and conservative species TcO_4^- , as has been commonly assumed. This conclusion is corroborated by recent in situ redox potential measurements, which show that groundwaters at multiple locations of the NTS are not oxidizing, and mobility of reduced Tc species ($\text{TcO}_2 \cdot n\text{H}_2\text{O}$) is greatly decreased. Speciation of iodine and its associated reactivity is also complex in the groundwater at the NTS, and its effect on the mobility of iodine should be the subject of future studies.

INTRODUCTION

The current performance assessment model for the proposed Yucca Mountain high-level nuclear waste repository assumes that ^{99}Tc and ^{129}I move at the same rate as water in the subsurface. However, it is probably over-conservative to apply a retardation factor of one for these redox-sensitive radionuclides. At the NTS, a large number of radionuclides (tritium, fission products, activation products, and actinides) are present at various concentrations as a result of underground nuclear weapons tests. Using the body of information that has been gathered since 1973 regarding the distribution of these radionuclides in groundwater, we are continuing to gain insight into radionuclide migration at the NTS. Because Yucca Mountain is located on the western edge of NTS, this insight can be used to assess the performance of a nuclear waste repository in the absence of engineered barriers [1] (Figure 1).

DATA ANALYSES

A database was set up to compile dissolved radionuclide concentration data, available at Lawrence Livermore National Laboratory, from 18 monitoring wells for 14 nuclear tests at the NTS, with a total of 206 sampling events. In this study, we focused on the measured activity for ^3H (tritium), ^{99}Tc , and ^{129}I , as available. These activities were decay-corrected to September 23, 1992, the date of the last underground nuclear test at NTS, permitting us to directly compare the measured activity with residual radionuclide inventory from all nuclear tests at NTS [2]. This radionuclide inventory (available to the general public) sums the radionuclide totals for individual tests into five principal geographic test areas.

radiologic source ratio) helps us understand the migration behavior of radionuclides; a ratio of one suggests the radionuclide migrates conservatively as tritium does.

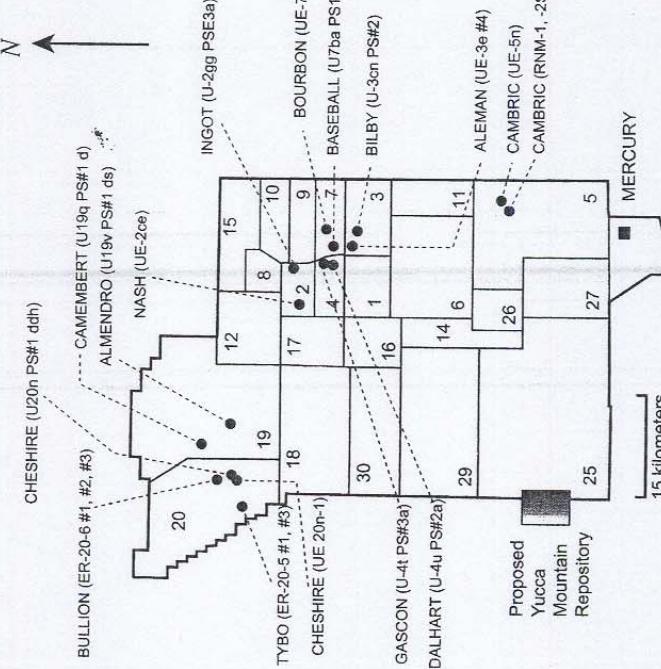


Figure 1. Map of the proposed Yucca Mountain repository and the near-field sampling locations at Nevada Test Site. Both test name and affiliated near-field well (in parentheses) are provided. Because tritium is probably the best tracer for tracking water flow and radionuclide transport, we used a ratio approach with tritium as the reference nuclide (i.e., $^{90}\text{Tc}/\text{H}$ and $^{14}\text{H}_2/\text{H}$) to assess the migration of other radionuclides. Depending on the location of the monitoring well, we obtained either a distribution ratio or migration ratio in the groundwater sample collected (Figure 2). This ratio was further normalized by dividing it with the radiologic source ratio of the source-term inventory for the principal geographic test center wherein the nuclear test was located. This normalization provides us with an estimate of the radionuclide distribution and migration behavior, compared to tritium. In other words, if a radionuclide behaves as tritium, the normalized concentration ratio will be one. Using samples gathered from the near-field wells in the cavity-chimney region, we obtained the normalized ratio value of radionuclides (distribution ratio divided by the radiologic source ratio) to determine their distribution in the aqueous phase; a ratio significantly lower than one indicates that this radionuclide is predominantly nonsoluble. Some monitoring wells are satellite wells located a certain distance (up to several hundred meters) away from the cavity-chimney region, so the resultant normalized ratio (migration ratio divided by the

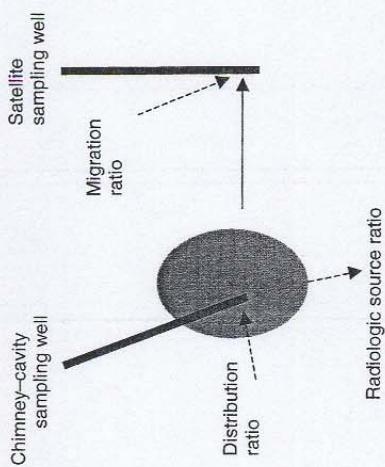


Figure 2. Illustration of hypothetical cross-section for nuclear test chimney-cavity and satellite sampling wells.

DISCUSSION

Technetium-99

^{99}Tc is a long-lived ($t_{1/2} = 2.13 \times 10^5$ years), abundant (6% yield) fission product of ^{235}U and ^{239}Pu . Depending upon the redox conditions, Tc primarily exists in two stable oxidation states. It forms a reduced species (predominantly $\text{Tc}(\text{IV})$) at redox potential (Eh) values below about 220 mV in neutral pH conditions. At higher Eh, it occurs as $\text{Tc}(\text{VII})\text{O}_4^-$. Due to its weak interaction with mineral surfaces, TcO_4^- is considered one of the most mobile radionuclides in the environment. In contrast, transport of $\text{Tc}(\text{IV})$ species are expected to be strongly retarded from their interactions with minerals and/or precipitation because of their low solubility. From experiments conducted with five sediments and groundwaters in Germany, a different sorption coefficient was obtained for Tc under aerobic and anaerobic conditions [3]. In relation to the redox potential, a drastic drop in the K_f (sorption distribution) value for Tc was observed for about three orders of magnitude within a small range of Eh (at 170 ± 60 mV for a pH of 7 ± 0.5).

At the NTS CHERSHIRE site, ^{99}Tc appears to occur predominantly as TcO_4^- because it showed very constant concentration ratios to tritium in the cavity, formation, and satellite measurements [4]. However, the $^{99}\text{Tc}/\text{H}$ ratios at three other available satellite wells are about two orders of magnitude lower than the cavity-chimney values (Figure 3). This indicates that field-scale migration of ^{99}Tc at the NTS does not behave as tritium and has an apparent retardation factor of about 100. A very similar pattern is observed for the $^{99}\text{Tc}/\text{H}$ data not normalized to the geographic source-term inventories. Furthermore, the normalized ratio about 0.1 for cavity-

chimney samples indicates that 10% of ^{99}Tc (compared to 98% for ^3H) [5] produced from nuclear tests is present in the aqueous phase. To understand the nonconservative transport of ^{99}Tc , we need to consider the redox chemistry of local groundwater at NTS.

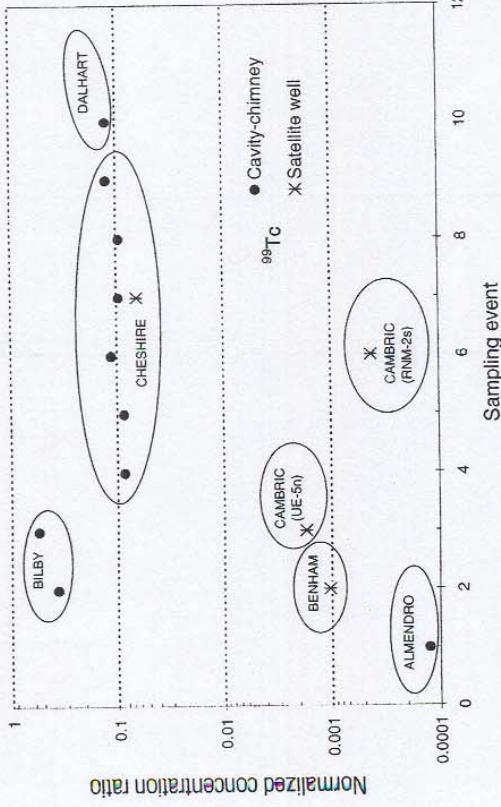


Figure 3. Normalized concentration ratio for ^{99}Tc in the hot wells.

It has often been assumed that deep aquifers (>250 m) are of reducing condition since they are isolated from the atmosphere. Although the water table at the NTS ranges from 400 to 700 m deep, the groundwater is considered oxygenated. Nevertheless, this assumption is based on limited information. Since 2000, several geochemical parameters (temperature, pH, specific conductivity, dissolved oxygen, and Eh) have been measured in situ in uncontaminated wells at the NTS, and a wide range of Eh values were observed from a total of 19 wells [6]. The measured Eh indicates that water in seven wells is mildly oxidizing (Eh ranges from about 200 to 400 mV), water in six wells is mildly reducing (about -100 to 200 mV), and water in six wells is strongly reducing (from -300 to -100 mV). These data suggest that Tc will not always exist as TcO_4^- and act as a mobile radionuclide in the groundwater of the NTS, as shown in Figure 3.

Iodine-129

Similar to ^{99}Tc , ^{129}I has a long half-life ($t_{1/2} = 1.57 \times 10^7$ years) as well as a unique and complex chemistry in the environment. The fate and transport of ^{129}I in groundwater are dictated by its chemical speciation. In normal environments, aqueous iodine usually occurs as the highly mobile iodide anion (I^-). Under more oxidizing conditions, iodine may be present as the more reactive iodate anion (IO_3^-), so its interaction with clays and organic matter leads to its retarded transport [7]. Coexistence of several iodine species has been reported in various aqueous systems. Although a substantial fraction of the ^{129}I migrated from the RNM-1 cavity well to the RNM-

2s satellite well at the CAMBRIC site, some of the ^{129}I is immobile or its migration is retarded [8]; the author postulates that reactive HIO is the predominant species and that it may interact with matrix materials. Measurements from other contaminated wells exhibit no difference between cavity and satellite well samples (Figure 4). The CHESHIRE site is the only location for which both cavity and satellite well samples are available, and its results show nearly the same normalized ratios among these samples. The normalized $^{129}\text{I}/\text{H}$ ratio value is abnormally large for the BOURBON (ratio 28.3) and NASH (ratio 8.32) tests, which may be related to using the nonspecific radiological source term for calculations. Based on limited data, it is likely that ^{129}I is migrating conservatively at the NTS.

Even if this is so, it would not be surprising if the iodine migration were retarded because a portion of the NTS groundwater is strongly oxidizing, and the presence of high-valence-state iodine species leads to their interactions with geological media. In a leachate of a tuff sample collected from an underground nuclear explosion in hole U7ais, at least three iodine species exist: IO_4^- , IO_3^- , and I^- with proportions of 10, 40, and 50%, respectively [9]. This leachate was further used for batch sorption-desorption studies in alluvium samples at the CAMBRIC site, resulting in a high sorption value of $640 \pm 300 \text{ mL/g}$ [9].

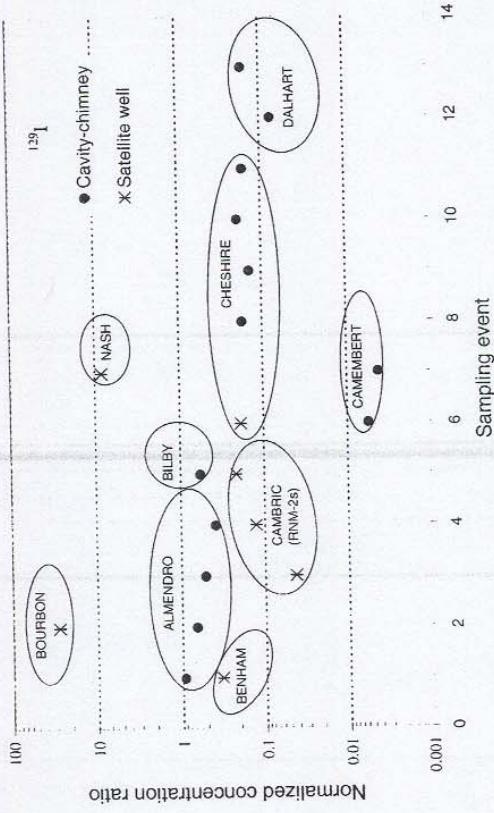


Figure 4. Normalized concentration ratio for ^{129}I in the hot wells.

CONCLUSIONS

It is very important to gain more knowledge of the speciation and reactions of presumably mobile radionuclides, such as long-lived redox-sensitive ^{99}Tc and ^{129}I , so that we can understand their transport behavior at the NTS, as well as their potential performance of the proposed Yucca Mountain repository for high-level nuclear waste. Tc does not necessarily exist as the mobile and conservative species TcO_4^- , as commonly assumed. This is not unexpected because the speciation

and migration behavior of ^{99}Tc will be significantly controlled by the geochemical conditions of surrounding groundwater. Recent in situ redox potential measurements have indicated that groundwaters at the NTS are not uniformly oxidizing, and the mobility of Tc is greatly reduced in a nonoxidizing environment. Furthermore, as with Tc, the speciation and migration behavior of iodine is complex and depends on the redox conditions, and different species have different reactivities and mobilities. Because of the comparable hydrogeologic settings, understanding radionuclides (especially ^{99}Tc) will provide a better evaluation of how the geological repository will perform.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. The work is funded through the Science and Technology Program of the Office of Civilian Radioactive Waste Management of the U.S. Department of Energy. The authors thank Timothy Rose, Annie Kersring, Jean Moran, and Karen Rath for stimulating discussions and helpful comments.

REFERENCES

- D. K. Smith, A. B. Kersting, J. L. Thompson, and D. L. Finnegan, *Scientific Basis for Nuclear Waste Management XXIV*, Materials Research Society, **63**, 1023–1032 (2001).
- D. K. Smith, D. L. Finnegan, and S. M. Bowen, *J. Environ. Radioactivity*, **67**, 35 (2003).
- K. H. Lieser, and C. H. Bauscher, *Radiochim. Acta*, **42**, 205 (1987).
- R. W. Buddemeier, R. C. Finkel, K. V. Marsh, M. R. Ruggieri, J. H. Rego, and R. J. Silva, *Radiochim. Acta*, **52/53**, 275 (1991).
- International Atomic Energy Agency (IAEA). *The radiological situation at the atolls of Marurua and Fangataufa: Inventory of radionuclides underground at the atolls*, Technical Report, Vol. 3, Vienna (1998).
- D. L. Finnegan, and J. L. Thompson, *Laboratory and field studies related to radionuclide migration at the Nevada Test Site in support of the Underground Test Area Program and Hydrologic Resources Management Project*, Los Alamos National Laboratory, Los Alamos, NM, LA-14042-MS (2003).
- M. Sheppard, and D. H. Thibault, *Appl. Geochem.*, **7**, 265 (1992).
- E. A. Bryant, *The CAMBRIC migration experiment—A summary report*, Los Alamos National Laboratory, Los Alamos, NM, LA-12335-MS (1992).
- K. Wolfsberg, Sorption–desorption studies of Nevada Test Site alluvium and leaching studies of nuclear explosion debris, Los Alamos National Laboratory, Los Alamos, NM, LA-7216-MS (1978).

Using Linear Free Energy Relationship to Predict the Stability Constants of Aqueous Complexes of Metal-Organic Ligands

Huifang Xu* and Yifeng Wang***

* Department of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, New Mexico 87131, hfx@unm.edu

**Sandia National Laboratories, Albuquerque, NM 87185, ywang@sandia.gov

ABSTRACT

The Sverjensky-Mölling linear free energy relationship was originally developed to correlate the Gibbs free energies of formation of an isostructural family of solid phases to the thermodynamic properties of aqueous cations. In this paper, we demonstrate that the similar relationship also exists between metal complexes and simple metal cations in aqueous solutions. We extend the Sverjensky-Mölling relationship to predict the Gibbs free energies of formation or dissociation constants for a family of metal complexes with a given complexing ligand. The discrepancies between the predicted and experimental data are generally less than 1.5 kcal/mol (or one log unit for stability constants). The use of this linear free energy correlation can significantly enhance our ability to predict the speciation, mobility, and toxicity of heavy metals in natural environments. According to the obtained results, Gibbs free energies of formation of cations ($\Delta G_f^\circ, \text{M}^+$) can be used as an indicator for the hardness/softness of a metal cation (acid). The higher negative value of a metal cation, the harder acid it will be. It is logical to postulate that the coefficient a_{SL} characterizes the softness of a complexing ligand (base).

INTRODUCTION

Metal complexation with various inorganic or organic ligands in aqueous solutions directly controls the solubility, sorption, and toxicity of toxic metals including radionuclides in natural environments [1–4]. The quantitative calculations of metal complexation thus have been routinely used in predicting the fate and impact of heavy metals in natural environments [2, 5]. The effectiveness of these calculations heavily depends on the completeness and quality of the thermodynamic databases on which the calculations are based. Unfortunately, the thermodynamic data for many metal complexes, especially those with radionuclides, are currently either unknown or poorly constrained. Therefore, there is a need for (1) developing a method to predict the unknown thermodynamic data based on a limited number of the existing measurements and (2) using this method to check the internal consistency of the thermodynamic databases that are used in the calculations. It is essential to have reliable data for metal organic complexes in order to evaluate impacts of pollutants on water and soils.

Empirical linear free energy relationships have been proven useful for correlating thermodynamic properties and predicting unknown thermodynamic data [6–9]. The Hammett linear free energy relationship is a classic example that has been widely used for substituted aqueous organic reactions [6–8]. Directly analog to the Hammett relationship and explicitly accounting for Born solvation energy, Sverjensky and Mölling have developed a linear free energy relationship that can correlate the Gibbs free energies of formation of an isostructural family of solid phases to the thermodynamic properties of aqueous metal cations [9]. The Sverjensky-Mölling relationship has been successfully applied to a series of minerals containing divalent cations, and it has been extended to the minerals containing tetravalent cations (M^{4+}) [10] and trivalent cations for mineral surface complexes for trace metal incorporation [26]. In this report, we demonstrate that the similar relationship also exists between metal complexes and simple metal cations in aqueous solutions. We extend the Sverjensky-Mölling relationship to predict the Gibbs free energies of formation or dissociation constants for a family of metal complexes with a given complexing ligand. We believe that the use of this extended linear free energy correlation can significantly enhance our ability to predict the speciation, mobility, and toxicity of heavy metals in natural environments.

LINEAR FREE ENERGY RELATIONSHIP

The Sverjensky-Mölling linear free energy relationship was originally developed for an isostructural family of solid phases containing different metal cations. Considering that the local environment of a cation in