Project ID: 73778 6/15/2001

Research Program to Investigate the Fundamental Chemistry of Technetium

Lead PI: David K. Shuh, 70A-1150, Lawrence Berkeley National Laboratory, Berkeley, CA 97270

Co-investigators: Carol J. Burns, D453, Los Alamos National Laboratory, Los Alamos, NM 87545
Wayne W. Lukens, Jr., 70A-1150, Lawrence Berkeley National Laboratory, Berkeley, CA 97270

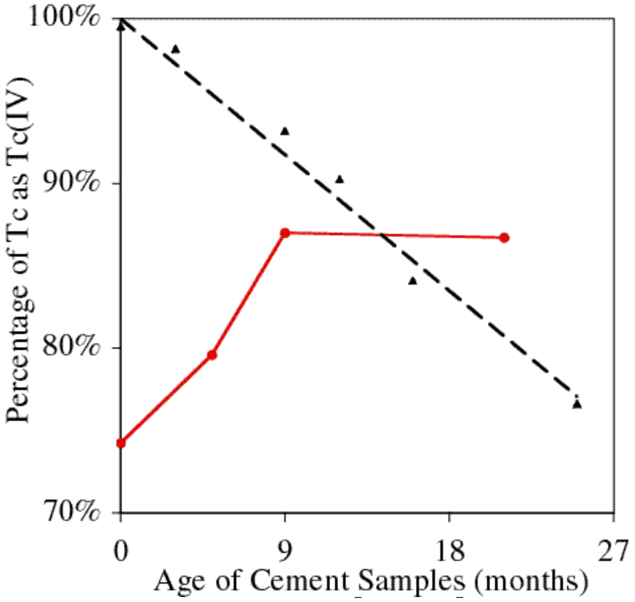
Research Objective

Technetium (^{99}Tc, half-life = 2.13x10^5 years, β-emitter) is one of the radionuclides of major concern for nuclear waste disposal. This concern is due to the long half-life of ^{99}Tc, the ease with which pertechnetate, TcO_4^-, migrates in the geosphere, difficulties in incorporating technetium into glass waste forms, and the corresponding regulatory considerations. The problem of mobility of pertechnetate in the environment is compounded by the fact that pertechnetate is the thermodynamically stable form of technetium in oxidizing environments. Because of this stability, pertechnetate was presumed to be the predominant chemical form of technetium in the aqueous phase of nuclear waste tanks. However, studies have indicated that a significant fraction of the technetium is in a different chemical form.[1,2] These factors present challenges the separation and immobilization of technetium. The objective of this project is to investigate the chemical behavior of technetium so that these problems may be understood and the challenges addressed.

Research Progress and Implications

Chemistry of technetium alkoxide complexes. Our work has identified lower valent technetium alkoxide complexes as the soluble species that are likely to be present in high-level waste environments. One of our goals is to synthesize and isolate these species, first using rhenium (to develop the chemical syntheses) and then technetium. So far, we have not been able to successfully isolate the prerequisite rhenium analogs. These anionic alkoxide complexes are either insoluble or extremely soluble in common solvents, which greatly complicates their isolation as pure compounds.

Immobilization of pertechnetate in cement. We are currently finishing work on the behavior of technetium in blast furnace slag (BFS) based cement. The speciation of technetium as a function of the presence of nitrite, nitrate, and/or oxygen has been examined. The results are presented in Figure 1, which shows the evolution of the oxidation state of technetium in two sets of cement samples. One set is sealed with respect to atmosphere whereas the other set is open to atmosphere. Both sets of samples contain members that contain or do not contain nitrate and nitrite. Within the two sets, no appreciable difference in the speciation of technetium is attributed to the presence of nitrate or nitrite. The results strongly suggest that oxygen will oxidize the reduced technetium in BFS based cement but nitrate and nitrite are unreactive with the reduced technetium species.



(dashed line) and isolated from the atmosphere (solid line).

The implications of this work are twofold. First, the technetium in these BFS cements is air sensitive and will be slowly oxidized to pertechnetate upon exposure to air. Second, in the absence of air, the technetium will remain reduced and will not be oxidized by nitrate or nitrite. The results suggest that in a given BFS cement waste form, the bulk of the technetium will remain reduced since the potentially reactive components of the waste matrix, nitrate and nitrite, do not oxidize the reduced technetium species. However, the technetium at the surface of the waste form will be oxidized by atmospheric oxygen as it diffuses through the pore system. The complex reaction-diffusion mechanism of the oxidation technetium species in this manner has previously been addressed, and our results are consistent with the reported model.[3]

In addition to the BFS cement research, we are readying a furnace for preparing technetium containing ceramic and glass materials. The evolution of the speciation of technetium in these matrices will be studied by X-ray absorption fine structure (XAFS) spectroscopy. We are also preparing and evaluating potential solid state “getters” for pertechnetate.

Future Work

Chemistry of Tc(IV) alkoxide complexes. Since the isolation of the Tc(IV) alkoxide species identified in our previous work will require a much greater amount of time than anticipated, we will examine instead the chemistry of two known Tc(IV) alkoxide species: Tc(eg)$_2^{2-}$ and Tc(THMT)$_2^{2-}$ where eg is ethylene glycolate and THMT is [tris(hydroxymethyl)methyl]trimethylammonium.[4,5] The chemistry of these alkoxides is expected to be very similar to that of the Tc(IV) alkoxide complexes produced by radiolysis. Consequently, studying the chemical behavior of Tc(eg)$_2^{2-}$ and Tc(THMT)$_2^{2-}$ should provide information that is directly applicable to the behavior of other Tc(IV) alkoxide complexes.

Two general areas of chemistry will be explored using these complexes: separation and oxidation. Since Tc(IV) and Tc(V) form stable complexes with sulfur containing ligands, exchange resins containing thiol groups will be examined to determine their ability to remove these technetium species from highly alkaline solution. The reaction of the Tc(IV) alkoxide complexes with various oxidizers will be studied in alkaline solution both with and without the easily oxidized components of high-level waste, nitrite and various organic compounds.

Immobilization of technetium. We will prepare and study technetium-containing titanium and iron based ceramics to determine the evolution of the technetium speciation in these materials. In addition, we will examine technetium-containing glass samples either prepared by BNFL or prepared at LBNL using BNFL glass formulations. We will continue to study pertechnetate sorbents that work by either ion exchange or covalent immobilization.

References

1) Schroeder, N. C.; Radzinski, S.; Ashley, K. R.; Cobb, S. L.; Cutrell, B.; Whitener, G. *Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Waste (101-SY and 103-SY)* LA-UR-95-4440, Los Alamos National Laboratory: Los Alamos, NM, 1995.

2) Blanchard Jr., D. L.; Brown, G. N.; Conradson, S. D.; Fadeff, S. K.; Golcar, G. R.; Hess, N. J.; Klinger, G. S.; Kurath, D. E. *Technetium in Alkaline, High-Salt, Radioactive Tank Waste Supernate: Preliminary Characterization and Removal* PNNL-11386, Pacific Northwest National Laboratory: Richland, WA, 1995.

3) Smith, R. W.; Walton, R. C. *Mat. Res. Soc. Symp. Proc.* **1993**,*294*, 247.

4) Alberto, R.; Anderegg, G.; May, K. *Polyhedron* **1986**, *5*, 2107.

5) Alberto, R; Albinati, A.; Anderegg, G.; Huber, G. *Inorg. Chem.* **1991**, *30*, 3568.