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Research Program to Investigate the Fundamental Chemistry of Technetium

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Research Objectives

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 for the separation and immobilization of technetium. The objective of this research project is to provide new knowledge about the chemical behavior of technetium so that the factors underlying technetium speciation in nuclear waste and in waste forms can be understood and the problems can be addressed.

Research Progress and Implications

Chemistry of technetium alkoxide complexes. Our previous work has identified lower valent technetium alkoxide complexes as the soluble species that are likely to be present in high-level waste environments.[3] In the waste tanks, the ligand that would form the most hydrolytically stable Tc(IV) complex is gluconate,[4] which has been reported to be present in concentrations up to 0.3M in the complexant concentrate or Envelope C tanks.[5] We have prepared both Tc(IV) and Tc(V) gluconate complexes by reduction of pertechnetate in the presence of 0.1M gluconate and 1M sodium hydroxide. We obtained the XANES (and EXAFS) spectra of both complexes. However, the XANES spectra of the technetium species in waste tanks AN-107, SY-101 and SY-103 do not agree with the spectra of the Tc gluconate complexes.[2] Therefore, the soluble, nonpertechnetate species cannot be a Tc(IV) or Tc(V) gluconate complex.

Immobilization of pertechnetate in cement. We have completed a study of the behavior of technetium in blast furnace slag (BFS) based grout. The speciation of technetium as a function of the presence of nitrite, nitrate, and/or oxygen was examined. The results are presented in Figure 1, which shows the evolution of the oxidation state of technetium in

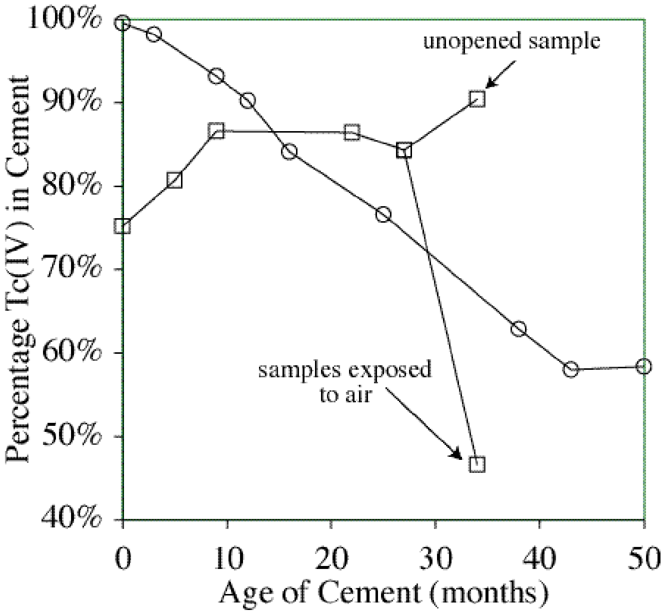

Figure 1: The evolution of the technetium oxidation state in unsealed samples (circles) and isolated from the atmosphere (squares), the arrows indicate whether the initially sealed samples were opened.

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 with and without 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 towards the reduced technetium species. To confirm that oxygen is responsible for the oxidation, two of the sealed samples were opened and exposed to air. After 3 months, the fraction of Tc(IV) in these samples decreased by 30%, while the amount of Tc(IV) was unchanged in the sample that remained sealed as shown in Figure 1.

The implications of these results 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 TcS_2 and $TcO_2 \cdot xH_2O$. However, the technetium near the surface of the waste form will be oxidized by atmospheric oxygen as it diffuses through the pore system of the grout. 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.[6]

Technetium in glass. We have set up a furnace for safely preparing technetium containing glass samples. A series of glass samples has been prepared by melting either glass frit, from Isabelle Muller at the Vitreous State Laboratory, or glass precursors mixed with sodium pertechnetate or sodium pertechnetate in a double shell slurry feed analog. We have obtained the EXAFS and/or XANES spectra of these samples and have used the data to determine the speciation of technetium in these samples.

In glasses with very simple formulations (only Na, Si, Al, Ca, and B oxides) and simple feed components (only $NaAlO_2$ and NaOH), the volatilization of technetium during vitrification is quite low regardless of the oxidation state of technetium in the glass as determined qualitatively by the intensity of the technetium X-ray fluorescence peak observed during EXAFS experiments. However in these glasses, Tc(IV) is present in the glass as TcO_2 inclusions rather than uniformly distributed through the matrix. A technetium K-edge EXAFS spectrum (and fit) from one of these glass samples is given in Figure 2. In more complex glasses typical of real glass and feed compositions, technetium retention is lower, but the Tc(IV) is more uniformly distributed through the glass matrix and is not present as TcO_2. Since the technetium X-ray fluorescence yields from these samples is only a qualitative measurement of the technetium concentration, the quantitative technetium retention in the glass will be accurately determined by other methods.

Figure 2. EXAFS spectrum (left) and its Fourier Transform (right) of a simple borosilicate glass containing Tc(IV) as inclusions of TcO_2. Data are indicated by dots, and the fit is given by the solid line.

Other technetium waste forms. An insoluble technetium material that resists oxidation could form the basis of a durable technetium waste form. One such material is the black residue formed during storage of ammonium pertechnetate. This insoluble black material is not oxidized by prolonged exposure to alkaline hydrogen peroxide. Analysis of the EXAFS spectrum of this material is consistent with TcN, which has been reported to be resistant to oxidation by hydrogen peroxide.[7] The sample has not perceptibly oxidized after 3 months in air. Under the same conditions, $TcO_2 \cdot xH_2O$ is completely oxidized after one week.

Future Work

Chemistry soluble technetium complexes. Since the nonpertechnetate species in Hanford waste is not a Tc(IV) or Tc(V) gluconate complex, we are examining other possible lower valent species to determine whether their XANES spectra are consistent with the XANES spectrum of technetium in Hanford waste.

Immobilization of technetium. We are currently working with the technetium containing glass samples. Part of each sample will be dissolved and counted to determine the technetium concentration, so that the volatilization of the technetium during vitrification can be compared to the feed chemistry and the final oxidation state of the technetium. The technetium leach rates for the glasses will also be determined so that the role of glass composition and the technetium oxidation state in the glass can be evaluated.

Alternative synthetic routes to technetium nitride will be investigated to determine whether simpler syntheses can be developed (the reported technetium nitride synthesis involves heating ammonium pertechnetate to >300° C under flowing ammonia).[7] The solubility and leach rate of TcN under different conditions will be determined.

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