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Research Program to Investigate the Fundamental Chemistry of Technetium

Dr. Norman M. Edelstein
Lawrence Berkeley National Laboratory
MS 70A-1150
1 Cyclotron Road
Berkeley, California 94720
Phone: 510-486-5624
E-mail: nedel@lbl.gov

Dr. David K. Shuh
Lawrence Berkeley National Laboratory
MS 70A-1150
1 Cyclotron Road
Berkeley, California 94720
Phone: 510-486-6937
E-mail: dkshuh@lbl.gov

Carol J. Burns
Los Alamos National Laboratory
MS J514
P.O. Box 1663
Los Alamos, New Mexico 87545
Phone: 505-665-1765
E-mail: cjb@lanl.gov

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Dr. Norman M. Edelstein, Lawrence Berkeley National Laboratory

Dr. David K. Shuh, Lawrence Berkeley National Laboratory
Carol J. Burns, Los Alamos National Laboratory

Research Objective

Technetium (^{99}Tc, β emitter, half-life 2.1 x 10^5 years, spA= 1.7 x10^{-2} Ci/g) is one of the radionuclides of major concern because of regulatory considerations for radioactive waste disposal. The propensity of Tc as pertechnetate, TcO_4^-, to migrate in the geosphere necessitates its safe, long-term immobilization. Technetium is found in the nuclear waste storage tanks at the Hanford and at the Savannah River sites in highly alkaline environments along with multi-molar concentrations of nitrate, nitrite, and Na ions and lesser amounts of organic complexants, phosphate, sulfate chloride, fluoride, and carbonate. It has been assumed that technetium is present in the waste tanks as the pertechnetate ion but a recent study has suggested that at least in part, technetium is present in another form. There is a lack of information on Tc chemistry in oxidation states III-V with simple inorganic (OH^-, CO_3^{2-}, PO_4^{3-}, SiO_4^{4-}) and common organic ligands (EDTA, citrate, oxalate) under alkaline conditions. This is essential information needed for pretreatment schemes, processing, and the assessment of stability of Tc in waste form materials. Further complicating the Tc waste tank chemistry is the added effect of an intense radiation field originating from ^{137}Cs and ^{90}Sr. The interactions of the ionizing radiation with water, nitrate, nitrite, and other minor components create highly reactive species that can strongly perturb the oxidation-reduction conditions.

The stability of Tc in waste form materials is of paramount importance for long term storage concerns and the solid state chemical properties of many candidate Tc compounds are unknown. There have been few systematic studies of Tc stability in lower valent solids with the exception of TcO_2. Thus, it is not possible at present to assess the long term stability of many Tc compounds relevant to proposed waste form materials.

This experimental research program addresses the characterization of the chemistry of technetium pertinent to the waste tank environment and to various waste forms. The solution and solid state chemistry of this element will be studied in aqueous solutions as a function of pH with the various salts added such as nitrate and nitrite, and as a function of radiation dose. The second part of this program is a search for stable, lower valent Tc materials which may prove useful for waste storage.

Research Progress and Implications

This report summarizes the results after nine months of a three year project.

To determine the stability of reduced Tc species in solution we are testing the stability of a number of Tc^{4+} complexes with various complexing ligands as a function of pH. Samples of TcO_4^- in solution have been reduced with hydrazine and with H_3PO_2. These solutions have been treated with complexing ligands such as EDTA, citric acid, PO_4^{3-} and with varying concentrations of Cl^- with pH between 1 - 5. The above samples were examined by X-ray absorption spectroscopy (XAS) and preliminary data analysis indicates all samples contained Tc^{4+}. These samples are to serve as standards for subsequent work where the pH of the solutions will be changed to more basic values. These solutions will be subjected to gamma irradiation.

Earlier studies of Tc encapsulated in cements have shown that although the Tc was originally in the tetravalent state, it was slowly oxidized to TcO_4^- on a time scale of months to years. To determine if nitrate and/or nitrite play a role in the oxidation process, TcO_4^- was introduced in two synthetic salt solutions and then encapsulated in cement. One salt solution contained both nitrate and nitrite as usual, but these anions were absent in the second salt solution. Two sets of Tc doped cements were prepared and in one set phosphate ion was added as a complexing agent for the reduced Tc species. XAS studies and preliminary data analysis show technetium present only as the Tc^{4+} in these cements.

Another facet of this investigation is the synthesis and characterization of reduced Tc and Re compounds. Although Re is not a good Tc surrogate in certain situations, it is useful in the development of synthetic routes. Initial investigations have centered around optimization of procedures for the generation of redox-pure oxohalides of technetium and rhenium in a variety of oxidation states. These complexes are suitable as precursors for complexation and precipitation studies. While known aqueous routes for the preparation of reduced forms of technetium can result in products of unreliable purity, non-aqueous preparations utilizing halogenating agents such as phosphorus pentachloride or chlorotrimethylsilane give very high yields of halogenated complexes such as $[MO_3Cl_2]^-$ (M = Tc, Re) and $[cis\text{-}ReO_2Cl_4]^-$. Further reaction time can give reduced products (such as in the direct isolation of $[TcOCl_4]^-$), while in other cases mild reducing agents can be employed to generate d^1- and d^2-oxohalide complexes. Structural determination of several members of this series (PPN[cis-ReO_2Cl_4], $PCl_4[ReOCl_5]$) have been undertaken to provide data for comparison with other oxohalide structures. Extension of these procedures to the generation of bromide and iodide analogs is possible through the use of trimethylsilylbromide or -iodide, respectively. The use of different halide precursors can yield different products from metathesis reactions.

Planned Activities

One of the major efforts of this program is to follow the reactions of TcO_4^- in alkaline aqueous solutions. This will be done with and without nitrate and/or nitrite present as a function of pH and of ionizing radiation dosage. We have considered using ^{60}Co as the method of irradiating the solutions. However, ^{60}Co has high energy gamma rays (~1.2 MeV) and the ionization in a small amount of solution will be limited. As an alternative we are exploring the use of ^{241}Am which has a 60 keV gamma ray that will be much more efficiently stopped by aqueous salt solutions. If one considers 1.5 g of ^{241}Am as a point source the amount of radiation from this source is about 20,000 R/hr. However, encapsulating this source will reduce the amount of radiation available. The fabrication of the containment vessel is underway as well as and the necessary permits to utilize a source of this magnitude are in process.

Tc solutions as described above will be prepared at more alkaline pH values. These solutions will be measured by XAS before and after gamma irradiation to characterize the Tc species. The original solutions used as standards will also be remeasured to determine the stability of the reduced species. All the Tc cements prepared in this project will be remeasured by XAS at three to six month intervals to determine if the reduced Tc species is being oxidized.

Based upon the premise that insolubility of precipitated products encapsulated in solid matrices may result in resistance to reoxidation and leaching of TcO_4^-, synthetic approaches are also being formulated for the generation of solubility-limited technetium complexes by either sol-gel condensation or precipitation routes. In particular, we have devised routes for the synthesis of alkoxide complexes (which may be useful in protonation reactions designed to generate precipitated products), and will examine the base-induced condensation of technetium and rhenium complexes of the formula $MO_3(OSiMe_3)$ to generate the dimeric heptoxides $M_2O_7L_2$ (L = Lewis base).