

Project ID: **60296**

Project Title: **Research Program to Investigate the Fundamental Chemistry of Technetium**

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Research Objective

Technetium (^{99}Tc , half-life = 2.13×10^5 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, 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 aerobic environments. These two factors present challenges for the safe, long term immobilization of technetium in waste forms.

Because of the stability of pertechnetate, technetium has been assumed to exist as pertechnetate in the aqueous phase of nuclear waste tanks. However, recent studies indicate that a significant fraction of the technetium is in a different chemical form. This program addresses the fundamental solution chemistry of technetium in the waste tank environment, and in a second part, the stability of technetium in various waste forms. The chemistry of this element will be studied in aqueous solutions at high pH, with various added salts such as nitrate, nitrite, and organic complexants, and as a function of radiation dose, to determine whether radiolysis effects can reduce TcO_4^- . A separate facet of this research is the search for chemical forms of technetium that may be thermodynamically and/or kinetically stable and may be incorporated in various waste forms for long term storage. This phase of the program will address the problem of the possible oxidation of lower valent technetium species in various waste form matrices and the subsequent leaching of the highly soluble TcO_4^- .

Research Progress and Implications

Aqueous Chemistry of Technetium. As of June, 1999, our efforts have focused on preparing and characterizing complexes of technetium with a variety of complexants related to those present in the waste tanks (e.g. EDTA, citrate, phosphate). These solutions have been prepared in two ways: either by generation of Tc(IV) *in situ* by reduction of pertechnetate with a variety of nitrogen-based reductants in the presence of complexants, or by generation and isolation of discrete technetium (IV) salts, and subsequent metathesis reactions with complexants. Nitrogen-based reductants such as hydrazine and hydroxylamine are commonly used to generate Tc(IV) *in situ* for stability studies, so characterization of the complexes formed in these reductions is important. The need for characterization is particularly evident in light of literature reports that these reductants can, under certain conditions, generate metal nitride species. The technetium nitride moiety is quite robust under a range of conditions. We have verified the presence of nitride species by isolating a Tc(V) nitride complex produced by reducing pertechnetate with hydrazine in the presence of dithiocarbamate as a complexing ligand. Analogous reduction reactions with hydrazine in the presence of other ligands have led to water-soluble products. We are examining a variety of methods, such as chromatography, ion exchange, etc., in order to isolate and characterize the technetium products. In addition, we have begun to examine the reduction of pertechnetate by hydroxylamine in the presence of complexants; these reductions appear to be significantly slower than those of hydrazine under comparable conditions.

Difficulties have been encountered in the generation of coordination complexes using the metathesis approach. The use of the chloride starting material, K_2TcCl_6 , in aqueous media generally results in hydrolysis rather than substitution when the reactions are conducted under neutral or basic pH conditions. Under acidic pH conditions, no reaction of K_2TcCl_6 with the complexants is observed. These reactions have also been examined in alcohols, in the hopes of avoiding the hydrolysis pathways, but the reagent does not appear to demonstrate any reactivity in neutral or acidified methanol or ethanol. Studies are now underway to investigate the reactivity of the bromo and fluoro analogs. The bromide salt, K_2TcBr_6 , is reported to be more soluble (and reactive) in methanol. The fluoride salt, K_2TcF_6 has been reported to be less sensitive to hydrolysis pathways under aqueous reaction conditions.

Technetium in Waste Forms. As of June 1999, our efforts have been in two areas, the speciation of technetium in cement waste forms and identifying new means of stabilizing technetium in "immobilized forms". The new materials for immobilizing technetium are polystyrene polymers modified to contain isocyanate groups that react with and bind heptavalent metal complexes containing oxo groups (e.g. MeMO_3 , $\text{Me}_3\text{SiOMO}_3$). The solid-support linkage is stable to large excesses of chlorotrimethyl silane and even aqueous solutions with high hydrogen peroxide concentrations. However, based on color changes incurred in this latter reaction, the polymer-bound complex appears to undergo a chemical transformation, presumably oxidation of a reduced metal complex bound to the support. EXAFS studies have been conducted on support-bound rhenium species, including a sample treated with hydrogen peroxide solution. The EXAFS results suggest varying oxidation states and coordination environments for the Re center, depending on the Re starting material used.

Our studies of technetium speciation in cements examined the effects of anions present in nuclear waste upon the speciation of technetium. In the cement, the pertechnetate is initially reduced by added sodium sulfide, which produces clusters of technetium sulfide. When high concentrations of nitrate and nitrite are present in the waste solutions, X-ray absorption studies on simulated cement waste forms show that technetium in these cements is oxidized to pertechnetate over the course of several months to one year. When these nitrate and nitrite anions are absent, the technetium remains reduced over the same time period. These data are illustrated in Figure 1. These observations suggest that technetium will not remain reduced in cements that contain high concentrations of nitrate and nitrite. Consequently, the soluble pertechnetate formed has a much greater likelihood of leaching from the waste when compared to the reduced forms of technetium. Our observation of oxidation of technetium in cements in the presence of nitrate helps to explain why previous studies have shown that pertechnetate leaches rapidly from grout prepared from double shell slurry feed (DSSF) but leaches more slowly from cladding removal wastes (CRW) and phosphate sulfate liquid waste (PSW).¹ The sum of the nitrate and nitrite concentrations in g L^{-1} for DSSF, CRW, and PSW are 177, 3 and 1, respectively.¹

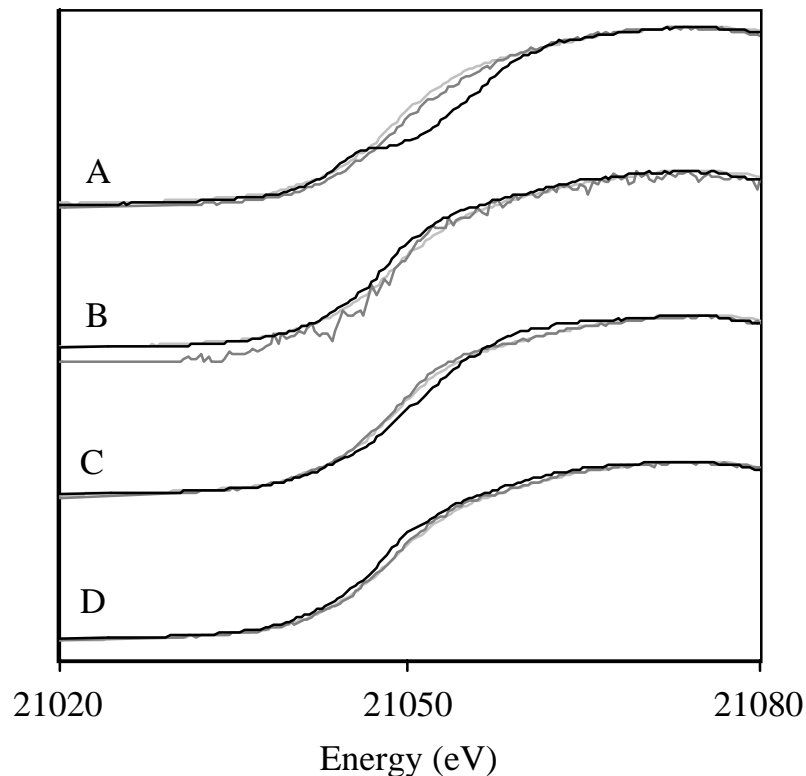


Figure 1. Technetium K-shell x-ray absorption edges for technetium in simulated cement waste forms. Oxidation is represented by edge shifts to higher energy. A and C contain nitrite and nitrate; B and D contain no nitrite or nitrate. Light gray line: immediately after synthesis; dark gray line: four months later; black line: one year later

Future Work. We will continue to investigate the solution chemistry of technetium using K_2TcBr_6 and K_2TcF_6 as starting materials. In addition, we will investigate the effect of radiation upon solutions of pertechnetate containing nitrate, nitrite, and organic species. The goal of the radiolysis experiments is to determine whether the combination of high concentrations of organic complexants and the radiation field present in the waste tanks could reduce pertechnetate in the presence of large concentrations of nitrate and nitrite. We will also reexamine simulated cement waste forms to verify our previous results and to determine whether nitrite or nitrate or both are responsible for oxidizing technetium to pertechnetate.

1) Seme, R. J.; Lokken, R. O.; Criscenti, L. J. *Waste Manag.* 1992, 12, 271.