Research Program to Investigate the Fundamental Chemistry of Technetium

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Research Objectives

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, 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. 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. In particular, the behavior of technetium and rhenium in glass will be examined since rhenium is often used as a non-radioactive surrogate to predict the behavior of technetium. In this project, glasses containing both rhenium and technetium will be prepared, so that the behavior of both metals can be compared under identical conditions

Research Progress and Implications

Glasses containing only Re, only Tc, and both Re and Tc have been prepared and examined using X-ray absorption near edge spectroscopy. The glasses that contained only Re had contained ReO_4^- as the sole rhenium species as determined by comparison with a pure ReO_4^- standard and by analysis of their Re L_2 EXAFS spectra (see Figures 1 and 2). The glasses that contained only Tc and both Tc and Re were prepared using waste surrogates and glass additives for Hanford Waste tanks AN-107 and AN-105. In all cases, substantial foaming and volatilization of Tc was observed. The XANES spectra of a series of glasses prepared under slight different conditions have been measured, and the speciation of Tc and Re is currently being determined on these glasses.

Figure 1: Re L_2 EXAFS of the rhenium species in waste form glasses prepared under reducing conditions. In all cases, the only rhenium species present is ReO_4^- .

Figure 2: Re L_2 EXAFS of the rhenium species in waste form glasses prepared under oxidizing conditions. In all cases, the only rhenium species present is ReO_4^- .

Future Work

More glass samples will be prepared and sent to VSL for leach testing. Glass samples containing both Re and Tc will be prepared as a function of oxygen fugacity to examine the effect of the different reduction potentials of Re and Tc upon their speciation in wasteform glasses.