

Research Program to Investigate the Fundamental Chemistry of Technetium

Lead PI: David K. Shuh, 70A-1150, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Co-investigators: Ian L. Pegg, Vitreous State Laboratory, The Catholic University of America, 400 Hannan Hall, 620 Michigan Avenue, NE, Washington, DC 20064

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 Tc 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 Tc in oxidizing environments. These factors present challenges for the separation and immobilization of Tc. The objective of this research project is to provide new knowledge about the chemical behavior of Tc so that the factors underlying its speciation in nuclear waste and in waste forms can be understood and the problems can be addressed. In particular, the behavior of Tc and Re in glass will be examined since Re is often used as a non-radioactive surrogate to predict the behavior of Tc.(1) In this project, glasses containing both Re and Tc will be prepared, so that the behavior of both metals can be compared under identical conditions

Research Progress and Implications

In the past year, glasses containing both Re and Tc have been prepared under different redox conditions using either mixtures of N_2 and O_2 or CO_2 and CO . The technetium and rhenium speciation was determined using X-ray absorption near edge spectroscopy (XANES). The glasses were prepared using waste surrogates and glass additives for Hanford Waste tanks AN-107 and AN-105. The primary intent of these experiments was to compare the speciation of Re and Tc in glasses prepared under identical conditions (the glass samples contain both elements) to determine whether Tc and Re behave analogously during vitrification.

Figure 1 shows the Tc and Re XANES spectra for a series of glasses prepared under different redox conditions. The spectra were fit using the XANES spectra of known species as standards. The results are given in Table 1. There is a very striking difference in the behavior of Tc and Re in this system. Although Tc(IV) can be formed during vitrification and can even be the most abundant Tc species present, Re(IV) appears to be unstable with respect to disproportionation under vitrification conditions. Under most conditions, the only Re species formed is Re(VII) , and under very reducing conditions, Re(0) and Re(VII) are present, but Re(IV) is absent. In addition, XANES spectra of other glasses containing Re show only Re(VII) in all cases.

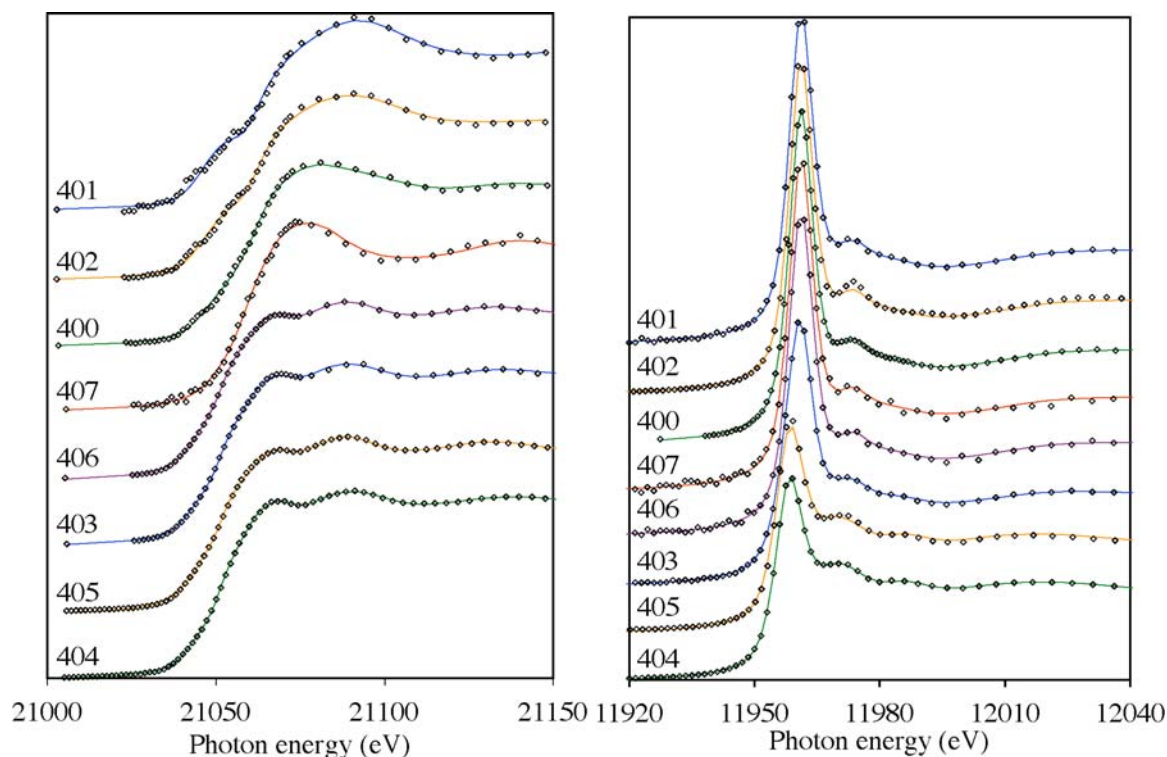


Figure 1: Tc (left) and Re(right) XANES spectra for glass samples prepared under different redox conditions, listed from most oxidizing (top) to most reducing (bottom). Sample number is given next to spectra trace. Data are indicated by diamonds, the fit is indicated by the solid line.

Table 1: Tc and Re speciation in glasses prepared under different redox conditions

Sample	Type	Gas	Tc(VII) ^a	Tc(IV) ^a	Tc(0) ^a	Re(VII) ^a	Re(VI/IV) ^{a,b}	Re(0) ^a
401	AN-105	Air	90	3	7	99	0	1
402	AN-105	N ₂	70	19	11	100	0	0
400	AN-107	Air	45	55	0	100	0	0
407	AN-105	100 ppm O ₂	0	100	0	100	0	0
406	AN-107	100 ppm O ₂	1	1	98	95	1	4
403	AN-107	N ₂	3	2	95	60	0	40
405	AN-107	CO/CO ₂	0	0	100	0	6	94
404	AN-105	CO/CO ₂	0	0	100	0	0	100

a) Speciation is given in %.

b) Re(IV) and Re(VI) fractions are summed together

These results very strongly suggest that Re(IV) is unstable towards disproportionation during vitrification while Tc(IV) is stable towards disproportionation under these conditions. Since the conditions present in the melt are sodium rich, the actual disproportionation reaction is $2 \text{Na}_2\text{SiO}_3 + 7 \text{MO}_2 = 3 \text{M} + 2 \text{SiO}_2 + 4 \text{NaMO}_4$ (M=Tc or Re). However, thermodynamic parameters are not available for the sodium system, so the potassium system is examined instead. In addition, the heat capacities of TcO₂ and ReO₂ are estimated using the heat capacities (Shomate equation) of MoO₂ and WO₂, respectively.(2,3) Figure 2 shows the Gibbs free energy of the reaction $2 \text{K}_2\text{SiO}_3 + 7 \text{MO}_2 = 3 \text{M} + 2 \text{SiO}_2 + 4 \text{KMO}_4$ (M=Tc or Re). Bearing in mind the noted estimates of some of the

thermodynamic parameters, figure 2 clearly supports the postulate that Re(IV) is unstable towards disproportionation in the glass melt and that Tc(IV) is stable except possibly at the very highest temperature.

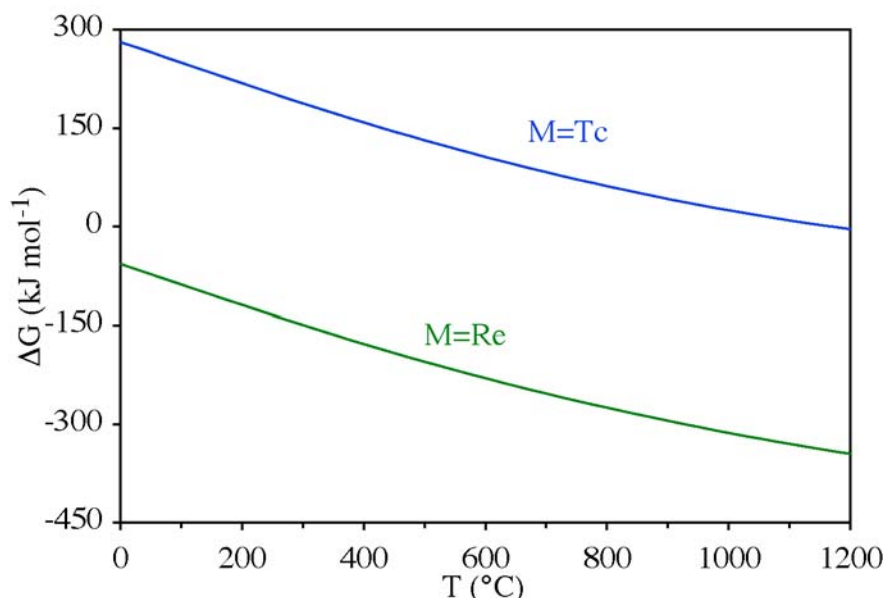


Figure 2: Gibbs free energy for the reaction $2 \text{K}_2\text{SiO}_3 + 7 \text{MO}_2 = 3 \text{M} + 2 \text{SiO}_2 + 4 \text{KMO}_4$ (M=Tc or Re) as a function of temperature. Heat capacity was estimated using Shomate equation parameters where available.

The observation that Re(IV) is unstable towards disproportionation has implications for the use of Re as a surrogate for Tc in melter tests.^(1,4,5) Since the species responsible for technetium volatilization is most likely MTcO_4 , especially CsTcO_4 ,^(1,6) reduction of Tc(VII) to Tc(IV) in the glass melt would decrease the volatility of the technetium during vitrification as has been previously observed. However, Re(IV) is not accessible during vitrification. Consequently, the volatility of Re should not be greatly affected by changing redox conditions during vitrification (the very reducing conditions that result in Re(0) are available during vitrification of actual or simulated waste), and Re is probably not a useful surrogate for studying Tc volatilization. However, Re should be a conservative surrogate for Tc volatilization in that the volatilization of Re will always be greater than or equal to that of Tc.

Future Work

The relative rate of leaching of Tc and Re from glasses containing both elements will be studied. Strategies for reducing Tc volatilization by incorporating Tc in titanium or iron oxides prior to vitrification will be examined (Tc(IV) has a very similar ionic radius to Ti(IV) and Fe(III), both of which are significant components of waste glasses).

References

- (1) Darab, J. G.; Smith, P. A. Chemistry of technetium and rhenium species during low-level radioactive waste vitrification. *Chem. Mater.* **1996**, 8, 1004-1021.
- (2) Chase, M. W., Jr. NIST-JANAF Thermochemical tables, fourth edition. *J. Phys. Chem. Ref. Data, Monograph 9* **1998**.
- (3) Rard, J. A.; Rand, M. H.; Anderegg, G.; Wanner, H. *Chemical Thermodynamics of Technetium*; Elsevier Science: Amsterdam, 1999.
- (4) McGrail, B. P.; Pierce, E. M.; Schaef, H. T.; Rodriguez, E. A.; Steele, J. L.; Owen, A. T.; Wellman, D. M. Laboratory testing of bulk vitrified and steam reformed low-activity waste forms to support a preliminary risk assessment for an integrated disposal facility. PNNL-14414, Pacific Northwest National Laboratory, Richland, WA, 2003.
- (5) Kim, D. S.; Vienna, J. D.; Hama, P. R.; Schweiger, M. J.; Matyas, J.; Crum, J. V.; Smith, D. E.; Seigny, G. J.; Buchmiller, W. C.; J.S. Tixier, J.; Yeager, J. D.; Belew, K. B. Development and testing of ICV glasses for Hanford LAW. PNNL-14351, Pacific Northwest National Laboratory, Richland, WA, 2003.
- (6) Migge, H. Simultaneous evaporation of Cs and Tc during vitrification- a thermochemical approach. *Mat. Res. Soc. Symp. Proc.* **1990**, 176, 411-417.