

Oxidation State of Multivalent Elements in High-Level Nuclear Waste Glass

J.G. Reynolds
Washington Group International
1779 Terminal Drive, Richland, WA 99354, USA

ABSTRACT

Nuclear waste contains many different elements that have more than one oxidation state. When the nuclear waste is treated by vitrification, the behavior of the element in the melter and resulting glass product depends on the stable oxidation state. The stable oxidation state in any medium can be calculated from the standard potential in that medium. Consequently, the standard potential of multi-valent elements has been measured in many silicate-melts, including ones relevant to nuclear waste treatment. In this study, the relationship between the standard potential in molten nuclear waste glass and the standard potential in water will be quantified so that the standard potential of elements that have not been measured in glass can be estimated. The regression equation was found to have an R^2 statistic of 0.96 or 0.83 depending on the number of electrons transferred in the reaction. The Nernst equation was then used to calculate the oxidation state of other relevant multi-valent elements in nuclear waste glass from these standard potentials and the measured ferrous to ferric iron ratio. The calculated oxidation states were consistent with all oxidation state measurements available. The calculated oxidation states were used to rationalize the behavior of many of the multi-valent elements. For instance, chromium increases glass crystallization because it is in the trivalent-state, iodine volatilizes from the melter because it is in the volatile zero-valent state, and the leaching behavior of arsenic is driven by its oxidation state. Thus, these thermodynamic calculations explain the behavior of many trace elements during the vitrification process.

INTRODUCTION

The behavior of multi-valent elements in High-Level waste glass melters depends on the stable oxidation state. There is a lot of measured data on the oxidation states of the multivalent ions in nuclear waste glass under melter conditions. Also, Jain and Barnes [1] reported a ferrous to ferric iron ratio of 0.036 in a high-level waste glass quenched from the melter. However, the iron oxidation state varies somewhat, and it is desirable to be able to determine the oxidation state of other multi-valent elements from the more commonly measured iron reduction/oxidation (Redox) ratio for iron. In theory, one can use the Nernst equation to calculate the oxidation state of all of the other species in the glass from their standard potentials when the Redox ratio of iron is known [2]. In the Nernst equation (Equation 1), the ratio of the oxidized to reduced oxidation state for an element is calculated from the Redox potential of the melt (E) and the Standard Potential of the Redox couple (E°).

$$\ln\left(\frac{\text{reduced}}{\text{oxidized}}\right) = -(E - E^\circ)nF / (RT) \quad (\text{Eq 1})$$

This ratio is a function of temperature (T) in Kelvin, and the number of electrons transferred during the reaction (n), and includes the Universal Gas Constant (R), which equals 8.314 J/mol*Kelvin) and Faradays Constant (F), which equals 96,485 coulombs). Most of these parameters are known for a given Redox couple, and the Redox potential can be calculated from the measured Redox ratio of any species in the melt. Unfortunately, however, the standard potential is unknown for most Redox couples in nuclear waste glass. Fortunately, Schreiber and Coolbaugh [3] have noted that there is a strong correlation between the standard potentials of multivalent metals in nuclear waste glass with their standard potentials in aqueous solution. A number of other authors have noted a correlation between standard potentials in aqueous solution and standard potentials in commercial glasses [4, 5, 6]. It has been suggested that this strong correlation is a result of the similarities between the solvation of the ions in the melt and in water. In both systems solvation of the ion is to oxygen in the solvent network. Nobody has quantified this relationship, so that it can be easily used to predict oxidation states of other elements in the melt if their solvated structure is similar to iron. In this paper, the oxidation state of other multivalent species in glass will be calculated using a regression equation assuming that they are in equilibrium with iron at a Fe(II) to Fe(III) Redox ratio of 0.036.

STANDARD POTENTIALS FOR MULTIVALENT ELEMENTS IN GLASS AND AQUEOUS SOLUTION

Schreiber and Coolbaugh [3] calculated from experimental data the Standard Potential for multivalent elements in Savannah River Laboratory (SRL)-131 Frit. They also compiled the standard potentials of those same multivalent elements in aqueous solution. Tables I and II contain these standard potentials measured and compiled by Schreiber and Coolbaugh [3]. They noted that there is a strong correlation between the standard potential in SRL-Frit 131 and the standard potentials in aqueous solution. They did not quantify this correlation, however by developing an equation to predict the correlation. Here, this correlation will be quantified by regressing the data in Table I. The results of this regression are shown in Figure 1 and 2 as well as Equation 2 and 3. Table II contains other standard potentials measured by Schreiber and Coolbaugh [3] but excluded from the regression. Schreiber and Coolbaugh [3] noted that all of these Redox couples except the Se(0)-Se(II) couple reduce more easily in the melt than in water and thus don't fit the correlation. The Se(0)-Se(II) Redox couple was excluded because Se(0) is a solid at ambient temperatures but is a gas at melt temperatures [7, 8]. Thus, the standard potential of Se(0) in aqueous solution cannot be proportional to the standard potential at melt temperature because the Se(0) oxidation state does not form equivalent phases at these two temperatures.

Table I. Standard Potentials in SRL-131 Frit and Water, Used in Regression

Redox Couple	Standard Potential (Volts) in Aqueous Solution[3]	Number of Electrons Transferred	Standard Potential (Volts) in SRL-131 Frit [3]
Au(3)-Au(0)	1.42	3	3
Pd(2)-Pd(0)	0.92	2	2.3

Redox Couple	Standard Potential (Volts) in Aqueous Solution[3]	Number of Electrons Transferred	Standard Potential (Volts) in SRL-131 Frit [3]
Ni(3)-Ni(0)	1.75	3	1.7
Rh(3)-Rh(0)	0.76	3	1.4
Se(6)-Se(4)	0.88	2	0.2
Cr(6)-Cr(3)	1.22	3	-0.3
Sb(5)-Sb(3)	0.68	2	-0.3
As(5)-As(3)	0.58	2	-1.7
Ni(2)-Ni(0)	-0.24	2	-5.3
Sn(4)-Sn(2)	0.14	2	-5.5
Co(2)-Co(0)	-0.28	2	-6
Fe(2)-Fe(0)	-0.41	2	-6.3
Co(3)-Co(2)	1.83	2	1.4
Ce(4)-Ce(3)	1.44	1	-0.1
Fe(3)-Fe(2)	0.77	1	-1.7
V(5)-V(4)	1	1	-1.9
U(5)-U(4)	0.61	1	-2.2
Cu(1)-Cu(0)	0.52	1	-3.3
Mo(6)-Mo(5)	0.48	1	-3.8
V(4)-V(3)	0.34	1	-4
Ti(4)-Ti(3)	0.03	1	-5
Mn(3)-Mn(2)	1.51	1	0.8

Table II. Standard Potentials in SRL-131 Frit and Water, Excluded from Regression

Redox Couple	Standard Potential (Volts) Aqueous Solution [3]	Number of Electrons Transferred	Standard Potential (Volts) SRL-131 Frit [3]
Se(0)-Se(2-)	-0.92	2	-5.7
U(6)-U(5)	0.06	1	-1.5
Cr(3)-Cr(2)	-0.41	1	-3.4
Cu(2)-Cu(1)	0.16	1	-0.8
Ag(1)-Ag(0)	0.8	1	0.5
Eu(3)-Eu(2)	-0.35	1	-4.3

$$E_{gl}^{\circ} = 3.6275E_{aq}^{\circ} - 5.0742 \quad (\text{Eq. 2})$$

$$E_{gl}^{\circ} = 4.5636E_{aq}^{\circ} - 4.2218 \quad (\text{Eq. 3})$$

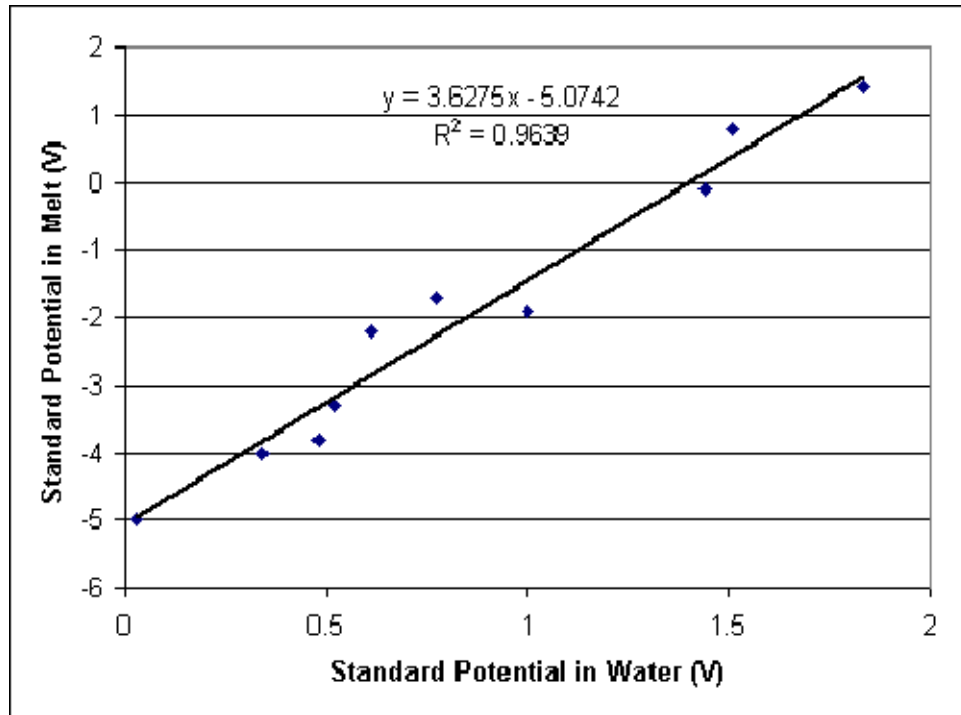


Fig. 1. Correlation Between the Standard Potential in Water and in Melt When $n = 1$.

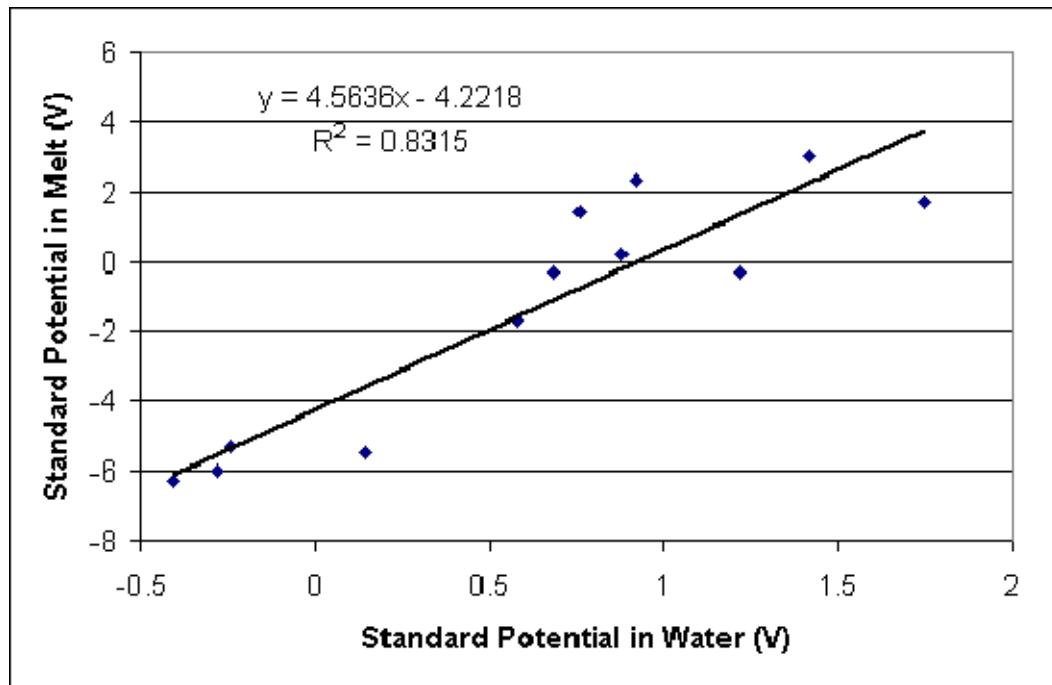


Fig. 2. Correlation Between the Standard Potential in Water and in Melt when $n > 1$

Two different regression equations were developed. The first, Equation 2 above, is to be used for Redox couples where only one electron is transferred ($n=1$ in Equation 1) when converting from one oxidation state to the other. The R^2 statistic for the regression was 0.96. The second equation (Equation 3) is to be used when n in Equation 1 is two or greater. The R^2 for this regression was 0.83. The reason that two regression equations were used is because a better R^2 was obtained than when all the data was combined together.

Equations 2 and 3 above provide the regression equation for standard potential (E_{gl}°) for molten DWPF frit 131 from the tabulated standard potentials in aqueous solution (E_{aq}°). Using Equations 2 and 3 as well as the standard potentials in aqueous solution from a standard reference [9], the standard potential of unmeasured Redox couples of interest in glass were calculated and are reported in Table III at a melt temperature of 1150 °C (1423 K).

Table III. Estimated Standard Potentials for Elements in Molten Glass

Redox Couple	E° Aqueous Solution [9]	n (Equation 1)	E° Glass
Tl(3)-Tl(1)	1.25	2	1.483
Se(6)-Se(4)	1.15	2	1.026
Sn(2)-Sn(0)	-0.136	2	-4.844
Tc(7)-Tc(4)	0.738	3	-0.854
Re(7)-Re(4)	0.51	3	-1.894
I(0)-I(1-)	0.535	1	-2.843
I(7)-I(0)	1.195	7	1.232
Cl(0)-Cl(1-)	1.358	1	-0.147
Cl(7)-Cl(0)	1.34	7	1.893
F(0)-F(1-)	2.87	1	5.337
F(1)-F(1-)	2.1	1	2.544

CALCULATION OF OXIDATION STATES

In the previous section, a regression was fit to the data of Reference 3 generating a mathematical relationship between standard potential in aqueous solution and standard potential in waste glass was determined. In this section, an example of the calculation of the oxidation states of the multivalent elements is performed for High-level waste glass using the standard potentials measured in Tables I, and II, and calculated in Table III for SRL-131 Frit. The oxidation states can be calculated for each Redox couple using Equation 1 if the E for the glass at the melt temperature is known. Jain and Barnes [1] reported that the Fe(II) to Fe(III) Redox ratio in molten high-level waste glass from West Valley ranged from 0.036 to 0.045. These Redox ratios are not significantly different from the Redox ratio observed in Hanford Waste Treatment Plant pilot melter tests. With a Redox ratio of 0.036 and an E° in the glass of -1.7, the E of the molten glass was calculated to be -1.29 volts when the Fe(II) to Fe(III) Redox ratio was used in Equation 1 at a melt temperature of 1150 °C (1423 K).

The Redox ratio for each multivalent element of interest was calculated at the melt temperature using the standard potentials in Tables I, II, and III and the E of -1.29 volts. The measured

values of the E° were used from Tables I, and II when available. The calculated values for E° reported in Table III, where used for the unmeasured values. The results of these calculations are shown in Table IV. The oxidation state assignments are shown in Table V.

Table IV. Ratio of Reduced to Oxidized Species in Each Redox Couple

Couple	Reduced to Oxidized Ratio	Couple	Reduced to Oxidized Ratio
Ag(I)-Ag(0)	$2.15 \times 10^{+06}$	Re(VII)-Re(IV)	4.0×10^{-07}
As(V)-As(III)	1.30×10^{-03}	Ni(III)-Ni(II)	$3.74 \times 10^{+10}$
Au(III)-Au(0)	3.13×10^{-46}	Ni(II)-Ni(0)	4.62×10^{-29}
Ce(IV)-Ce(III)	$1.63 \times 10^{+04}$	Pd(II)-Pd(0)	$2.44 \times 10^{+25}$
Cl(0)-Cl(-I)	$1.11 \times 10^{+04}$	Rh(III)-Rh(0)	$3.46 \times 10^{+28}$
Co(3)-Co(2)	$1.77 \times 10^{+04}$	Se(VI)-Se(IV)	$2.42 \times 10^{+16}$
Cr(VI)-Cr(III)	$3.26 \times 10^{+10}$	Sb(V)-Sb(III)	1.02×10^{-07}
Eu(III)-Eu(II)	2.33×10^{-11}	Sn(IV)-Sn(II)	1.78×10^{-30}
F(0)-F(-I)	$2.67 \times 10^{+23}$	Tc(VII)-Tc(IV)	$4.37 \times 10^{+04}$
Fe(III)-Fe(II)	3.60×10^{-02}	Ti(IV)-Ti(III)	7.81×10^{-14}
Fe(II)-Fe(0)	3.95×10^{-36}	Tl(I)-Tl(0)	$4.08 \times 10^{+19}$
I(VII)-I(0)	$2.67 \times 10^{+62}$	U(VI)-U(V)	1.83×10^{-01}
I(0)-I(-I)	3.09×10^{-07}	U(V)-U(IV)	6.15×10^{-04}
Mn(III)-Mn(II)	$2.47 \times 10^{+07}$	V(IV)-V(III)	2.67×10^{-10}
Mo(VI)-Mo(V)	1.36×10^{-09}	V(V)-V(IV)	7.07×10^{-03}

Table V. Summary of Oxidation State Assignments

Element	Oxidation State Assignment	Element	Oxidation State Assignment
Ag	0	Ni	2
As	5	Pd	0
Au	3	Rh	0
Ce	3	Sb	3
Cl	-1	Se	4
Cr	3	Sn	4
Eu	3	Tc	4
F	-1	Ti	4
Fe	3	Tl	1
I	0	U	6
Mn	2	V	5
Mo	6	Re	7

DISCUSSION

The oxidation state of several elements has been measured in waste glasses made in pilot melter or crucibles under atmospheric conditions. The assignments in Table V are consistent with these studies. The oxidation states of vanadium were found to be +5, and manganese to be +2 [10, 11] in glasses generated at a pilot melter, consistent with the assignments calculated in Table IV and V. Both uranium and molybdenum were found to be in the +6 oxidation state in crucible scale glasses melted under atmospheric conditions [12, 13, 14], also consistent with the assignments in Table V. Given that these results were not used as inputs to the calculation of the oxidation state assignments, the correct result of the calculations provides some assurance that the equation 1 is providing the correct oxidation state assignments for other elements where known oxidation state measurements are available.

The oxidation state of four noble metals, Ag, Au, Pd, and Rh, were calculated. All but Au was calculated to be predominantly in the zero-valent state (Table IV). These results are consistent with the observation that most noble metals have very limited solubility in waste glass [14, 15] and precipitate out as zero-valent metals in the melter.

Even though the anions of Cl, F, and I don't solvate in the melt like the cations, oxidation states of these were estimated using Equation 2 or 3. Chlorine and fluorine were calculated to be predominantly in the -1 oxidation state in the melt. In contrast, iodine was found to be the zero valent state (I_2 gas). This is consistent with the observation that iodine is considerably more volatile in the melter than is chlorine or fluorine [16].

Selenium is another component that is known to be volatile in commercial glass melter [8]. The Redox calculations performed here indicate that Se(IV) is more stable than Se(VI). A lower oxidation state such as zero or -2 may be more stable than Se(IV) but this could not be determined from the present analysis. This is because the standard potential of the Se(IV)-Se(0) Redox couple would have had to be used from aqueous solution in the absence of one measured for waste glass. Zero-valent selenium is a solid at ambient temperatures but is a gas at melter temperatures [7, 8]. The gas and solid phase will not have the same thermodynamic stability, so the zero-valent selenium E° for aqueous solution cannot be comparable to the melt E° . Consequently, the present analysis can only support that the oxidation state of selenium in the melter is lower than +6. If Se(0) or Se(-2) are the stable form of selenium at the melter temperature, then selenium would be volatile in the melter than if it were in the +4 oxidation state because zero-valent selenium is a gas, and because Se(-2) can volatilize from the melter as H_2Se [7].

These results explain the leaching behavior observed for As during the Toxicity Characterization Leach Procedure (TCLP), a durability test for HLW glass [17]. Both As and Fe leaching are found to be highly retarded during the TCLP test, with the Fe forming Fe(hydro)oxide minerals at the glass surface [17, 18]. At pH = 4.9, As(V) is readily immobilized by reacting with

Fe(hydr)oxides at pH = 4.9, but As(III) is not [19]. Arsenic (III) is highly soluble at pH = 4.9. The thermodynamic calculations indicate that As(V) is the stable phase in glass, and the As leaching behavior is consistent with an As(V) species. Thus, the oxidation state calculations performed here explain the retarded leaching of As under TCLP conditions.

Chromium was found to be predominantly in the trivalent state. Chromium is well known to increase the crystallization of spinel crystals (Cr, Fe, Ni, Zn, and Mn tetraoxide) in waste glass [20]. The enhancement of spinel crystallization is expected to be from Cr(III) rather than from Cr(VI) which won't fit in a spinel structure [21, 22]. Hence, the oxidation state calculations are consistent with the behavior of chromium in the waste glass. The oxidation state of chromium [23] as well as all Redox couples [4] are known to change with glass composition. Therefore, the oxidation states calculated here, while representative of high-level waste glass, are not necessarily identical to all high-level waste glass. Per Equation 1, the +6 oxidation state is increasingly favored as the temperature decreases. This is consistent with the observation of Hrma et al. [23] that chromium solubility increases below a threshold temperature because the concentration of Cr(III) decreases with decreasing temperature and the concentration of Cr(VI) increases with decreasing temperature.

Rhenium and technetium have similar chemistry and rhenium has frequently been used as a non-radioactive analogue for technetium [24]. The calculations for this glass at 1150 °C indicate that rhenium is in the +7 oxidation state whereas technetium is in the +4 oxidation state. Freude et al. [25] also noted that technetium(VII) is considerably easier to reduce than rhenium(VII) in molten glass. The higher oxidation state (+7) of both technetium and rhenium are more volatile than the lower oxidation state [24]. Thus, use of rhenium as a tracer for technetium is likely to over estimate the volatility of technetium from the melt. However, much of the volatilization likely occurs in the melter cold cap where the temperature is lower. At cold cap temperatures, both rhenium and technetium are in the +7 oxidation state. Thus, the oxidation states calculated in this study are not representative of the cold cap, and the elements may have different oxidation states in different portions of the melter that govern their behavior [24].

CONCLUSION

This paper uses a regression analysis based of the measured relationship between the standard potential of Redox couples in aqueous solution with the standard potential in high-level waste glass. Two separate regression equations were needed one (Equation 2) is used when there is one electron transferred during the Redox reaction, the second (Equation 3) is used when two or more electrons are transferred. The R^2 for these regressions was 0.96 and 0.83, respectively. These regression equations were then used to calculate the Redox ratio of multivalent elements in an example high-level waste glass. The Redox ratio calculations are consistent with experimental observations available. The oxidation states of these elements explain their behavior during vitrification and leaching scenarios. For instance, iodine is more volatile than other halides because iodine is in the more volatile zero valent oxidation state whereas the other halides are in the less volatile -1 oxidation state. Arsenic exhibits limited leaching because it is in the +5 oxidation state and chromium increases glass crystallization because it is in the +3 oxidation state.

ACKNOWLEDGEMENT

This work was performed for the United States Department of Energy under contract DE-AC27-01RV14136, to support the Hanford Waste Treatment Plant Project. The author is grateful to Rod Gimpel, John Vienna, Ned Bibler, and Karen Reynolds for review of the draft manuscript.

REFERENCES

1. V. Jain, and S. M. Barnes. The Effect of Redox Ratio on the Crystallization Behavior in the Canistered Product at the West Valley Demonstration Project. *Ceramic Transactions* 23: 251-257. (1991).
2. R. A. Alberty, and R. J. Silbey, *Physical Chemistry*. John Wiley & Sons, Inc. New York, NY. (1993).
3. H.D. Shreiber, and M. T. Coolbaugh. Solvation of Redox Ions in Glass-Forming Silicate Melts. *J. Non-Crystalline Solids* 181: 225-230. (1995).
4. F. G. K., Baucke, and J. A. Duffy. Oxidation States of Metal Ions in Glass Melts. *Phys. Chem. Glasses* 35: 17-21. (1994).
5. O. Cloubin, and C. Russel. Thermodynamics of Various Polyvalent Main Group Elements in a Borosilicate Glass Melt. *J. Non-Crystalline Solids* 209: 292-298. (1997).
6. G., Von Der Gonna, and C. Russel. Thermodynamics of Various Polyvalent Elements in a $15\text{Na}_2\text{O}\cdot 85\text{SiO}_2$ Glass Melt. *J. Non-Crystalline Solids*. 262: 236-243. (2000).
7. D. M. Chizhikov, and V. P. Shchastlivyi. *Selenium and Selenides*. Collet's LTD, London, U.K. (1968).
8. G. B. Hares, Selenium in Glass, in *Selenium*, Editors. R.A. Zingaro and W. C. Cooper, Van Nostrand Reinhold Company, New York, N.Y. (1974).
9. R.C. Weast. *Handbook of Chemistry and Physics*. 56th Ed., pp. D-141-D-143, CRC Press, Cleveland, OH (1975).
10. D. A. Mckeown, I. S. Muller, K. S. Matlack, and I. Pegg. X-Ray Absorption Studies of Vanadium Valence and Local Environment in Borosilicate Waste Glasses Using Vanadium Sulfide, Silicate, and Oxide Standards. *J. Non-Crystalline Solids* 298: 160-175. (2002).
11. D. A. Mckeown, W. K. Kot, H. Gan, and I. Pegg. X-Ray Absorption Studies of Manganese Valence and Local Environment in Borosilicate Waste Glasses. *J. Non-Crystalline Solids* 328: 71-89. (2003).
12. B. Biwer, L. Soderholm, R. B. Gregor, and F. W. Lytle. Uranium Speciation in Glass Corrosion Layers: An EXAFS Study. *Mat. Res. Soc. Symp. Ser.* 465: 229-236 (1997).
13. G., Calas, M. Le Grand, L. Galois, and D. Gheleb. Structural Role of Molybdenum in Nuclear Glasses: an EXAFS Study. *J. Nuclear Materials*. 322: 15-20 (2003).
14. L. Galois, J. M. Delave, D. Gheleb, G. Calas, M. Le Grand, G. Morin, A. Ramos, and F. Pacaud. Local Structure of Simplified Waste Glass: Complementarity of XAS and MD Calculations. *Mat. Res. Soc. Symp. Proc.* 506: 133-139 (1998).
15. M. Yamashita, J. Nishii, T. Akai, and H. Yamanaka. Redox Behavior of Palladium Ion in Oxide Glasses. *Mat. Res. Soc. Symp. Ser.* 412: 157-162 (1996).

16. M.H. Langowski. The Incorporation of P, S, Cr, F, Cl, I, Mn, Ti, U and Bi into Simulated Nuclear Waste Glasses: Literature Study. PNNL-10980. Pacific Northwest National Laboratory, Richland, Washington. (1996).
17. H. Gan, and I. L. Pegg. Effect of Glass Composition on the Leaching Behavior of HLW Glass Under TCLP Conditions. *Ceramic Transactions* 132: 335-344 (2001).
18. H. Gan, and I. L. Pegg. Leaching Mechanism of Borosilicate Glasses under TCLP Conditions. *Ceramic Transactions* 143: 215-223. (2002).
19. S. Dixet, and J. G. Hering. Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility. *Env. Sci. Technol.* 37: 4182-4189 (2003).
20. J. D. Viena, P. Hrma, J. V. Crum, and M. Mika. Liquidus Temperature-Composition Model for Multi-component Glasses in the Fe, Cr, Ni, and Mn Spinel Primary Phase Field. *J. Non-Crystalline Solids* 292: 1-24 (2001).
21. P. Hrma, P. Izak, J.D. Vienna, M.L. Thomas, and G.M. Irwin. Partial Molar Liquidus Temperatures of Multivalent Elements in Multi-Component Borosilicate Glass. *Phys. Chem. Glasses* 43: 119-127 (2002).
22. J. G., Reynolds. Spinel Structure and Liquidus Temperature Relationships in Nuclear Waste Glass. *J. Materials Sci.* 40: 3987-3991. (2005).
23. P. Hrma, J. D. Vienna, B. K. Wilson, T. J. Plaisted, S. M. Heald. Chromium Phase Behavior in a Multi-Component Borosilicate Melt. *J. Non-Crystalline Solids* 352: 2114-2124 (2006).
24. J. C. Darab, and P. A. Smith. Chemistry of Technetium and Rhenium Species during Low-Level Radioactive Waste Vitrification. *Chem. Mater.* 8: 1004-1021 (1996).
25. E. Freude, W. Lutze, C. Russel, and H. A. Schaffer. Investigation of the REDOX Behavior of Technetium in Borosilicate Glass Melts by Voltammetry. *Mat. Res. Soc. Symp. Proc.* 127: 199-204 (1989).