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Volatility Literature of Chlorine, Iodine, Cesium, Strontium, Technetium, and Rhenium; Technetium and Rhenium Volatility Testing

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ABSTRACT

This report reviews the volatility literature relevant to iodine, strontium, cesium and chlorine as might be expected from the vitrification of low-level wastes at Hanford. In addition, the report contains a review of the aqueous chemistry and volatilization behavior of technetium and a proposed surrogate, rhenium. Some preliminary tests of technetium and rhenium volatility have been performed and are reported.

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LIST OF ACRONYMS

CC	Complexant Concentrate
CMS	Vortec Combustion and Melting System
CST	Crystalline Silico-Titanates
DF	Decontamination Factor
DSSF	Double-Shell Slurry Feed
DST	Double Shell Tank
DWPF	Defense Waste Processing Facility Melter
GED	Glass Envelope Definition
HLW	High Level Waste
HTM	High Temperature Melter
IDMS	Integrated DWPF Melter System
KfK	Kernforschungszentrum Karlsruhe
LFCM	Liquid Fed Ceramic Melter
LLW	Low Level Waste
NCAW	Neutralized Current Acid Waste
PFP	Plutonium Finishing Plant
PNL	Pacific Northwest Laboratory
PSCM	Pilot-Scale Ceramic Melter
PVTD	PNL Vitrification Technology Development
RLFCM	Radioactive Liquid Fed Ceramic Melter
SGM	Scale Glass Melter
SRL	Savannah River Laboratory
SST	Single Shell Tank
TRAC	Tracks Radioactive Components

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1.0 INTRODUCTION

Recently, the Tri-Party Agreement (TPA) among the State of Washington Department of Ecology (Ecology), Department of Energy (DOE), and the United States Environmental Protection Agency (EPA) for the clean up of the Hanford Site was renegotiated. The revised agreement specifies vitrification as the encapsulation technology for the low-level waste (LLW). Implementation of this technology requires the development of a durable glass composition for the vitrification of low-level Hanford waste.

Hanford Site single-shell tank (SST) and double-shell tank (DST) wastes are planned to be separated into low-level and high-level fractions and vitrified for long-term storage. The low-level fraction of the wastes represents the major volume (~90%) of the total wastes and is characterized by high sodium content. The estimated amount of Na_2O in the LLW is ~80 wt% on a calcined solids basis. For some types of Hanford tank wastes, minor components (i.e., Cs, Sr, I, Tc and Cl) may also affect LLW vitrification.

Volatility is an important issue for LLW management as it can affect glass properties, reduce melter/offgas system lifetime through corrosion of metal parts, or increase the risk for a release of radionuclides during processing, shipping, and storage. The loss of components during vitrification can affect viscosity and crystallinity (increase or decrease depending on the composition of the lost species), decrease glass homogeneity and decrease glass durability. Vessel vent lifetimes may also be decreased due to excessive corrosion and/or deposition/accumulation of condensed species. Accident scenarios range from uncontrolled release from melter offgas systems during vitrification to fire at the disposal site or during shipping. Unforeseen storage/shipping accident scenarios involving the simultaneous loss of integrity of waste containers and fire may also be of concern, as reheating the glass to temperatures > 800°C may result in the loss of radionuclides from the waste form.

Some components that are known to volatilize from HLW borosilicate waste glass melts include select compounds of B, Na, Cs, Mo, Tc, Cl, F, I, P, S, Se, Te, and Ru. In addition, other species contained in the waste glass may be present in the offgas due to particle entrainment (e.g. Sr and Tc compounds). Not all of these species are present in significant quantities in LLW (e.g., Se, Te, and Ru). The radionuclides Cs, Sr, Tc, and I are of particular concern since their presence in the offgas is undesirable should an uncontrolled environmental release occur. In this report the volatility literature of Cs, Sr, Tc, Re and I will be examined along with chlorine. Chlorine has been reported to enhance the volatility of cesium so the literature will also be reviewed for this component. Rhenium was included in the literature review and experimental sections since it is being considered as a non-radioactive surrogate for technetium.

This work is conducted in accordance with the Pacific Northwest Laboratory (PNL) Vitrification Technology Development (PVTD) Project Work Plan (PWP). The information obtained during this work will be used in support of the LLW program. Issuance of this report will complete milestone # PVTD-C95-02.03G.

2.0 SUMMARY

A literature review pertaining to the volatilization of Sr, Cs, Tc (and its surrogate Re), Cl, I and other related species during the vitrification of Hanford Low Level Waste (LLW) streams has been performed and the relevant information summarized. For many of these species, the chemistry which occurs in solution prior to the waste stream entering the melter is important in dictating their loss at higher temperatures. In addition, the interactive effects between the species being lost was found to be important. A review of the chemistries of Tc and Re was also performed. It was suggested that Re would indeed act as an excellent surrogate for Tc in non-radiactive materials testing. Experimental results on Tc and Re loss from sodium aluminoborosilicate melts of temperatures ranging from 900-1350°C performed at PNL are reported and confirm that Re behaves in a nearly identical manner to that of technetium.

3.0 LITERATURE REVIEW

3.1 Background

Loss of species during LLW vitrification can occur through several mechanisms. By far the greatest amount of literature available is on volatilization—loss of species through solid-to-vapor and liquid-to-vapor phase transformations. Volatilization will be the major subject of discussion in this review. Another mechanism through which loss of species can occur is entrainment. For example, certain offgas products that form during vitrification of LLW can carry or entrain with them other species at rates greater than that expected through volatilization alone. Alternatively, the formation of aerosols during vitrification can lead to loss of species through entrainment in the submicron solid particles or liquid droplets that condense in the cooler portions of the melter offgas system.

Determining the relationship between glass composition, processing conditions (e.g., temperature) and volatility is important. Modification of glass composition may reduce volatility by making diffusion more difficult. The volatilization rate may also be increased by the presence of certain species in the glass. Processing conditions such as time, melt turbulence, temperature, surface area, viscosity and offgas flow rate can also affect volatility. The relationships should be known to reduce the volatilization of troublesome components. Volatility problems can be addressed in at least three ways. These are 1) glass composition modification, 2) modification of processing conditions in the melter, 3) offgas scrubbing systems with possible recycle of products back to melter. In reality, a combination of these three will likely be implemented.

It is outside the scope of this report to discuss offgas scrubbing systems. Processing conditions also will be discussed only in general terms and as presented in the literature. The focus of this report will be the review of volatility literature and the effect of glass composition.

Volatility data from PNL and other melter runs is expressed using elemental decontamination factors (DF's). The DF and percent loss are calculated according to the following equations:

1) DF = Mass of Element Entering Melter/Mass of Element Leaving Melter as Offgas
2) % loss = 100/DF

If accumulation has occurred in the melter plenum, the DF would not be indicative because the calculation uses only the quantity measured in the offgas leaving the melter. The actual amount lost from the glass/cold cap may therefore be higher than shown by the DF. Though the DF calculation uses amount of element, this does not mean that the species was in the elemental form. In most cases, the elemental form is not the most thermodynamically favorable for volatility (e.g., Cs, Sr, Cl, and Tc). In this report, the chemical symbol for each element X is used to mean "the loss of species containing element X" where X = Cs, Sr, or I etc.

Because the operation of the melter is a continuous process, the loss of radioactive/corrosive components does not have to be high in order to generate significant amounts in the scrubber and offgas systems. The cumulative effect or amount over a period of time may be large though the actual loss small. Continuous buildup of radioactive/corrosive components downstream from the melter may cause problems with equipment maintanence as well as a radiological contamination problem. For example, during a 120-hr LFCM2 test, minimum, DF's for Si, Cl, Fe, and Na were 630, 9, 330 and 290, respectively. A 5.9 kg plug formed in a horizontal section of the offgas line which was analyzed to be 31wt% SiO_2, 10 wt% Cl, 20.3 wt% Fe_2O_3 (some of this Fe was corrosion product from the pipe), and 16.9 wt% Na_2O (the remainder consists of 16 other compounds each less than 5 wt%). Even though the DF's indicated that the amounts of Si and Na loss were small, the accumulation was sufficient to plug a pipe.

A species can leave the melter either as a gas or as part of an aerosol. **Table 3.1.1** categorizes each species as a gas, particulate, or what is termed a semi-volatile. A semi-volatile leaves the melter as part of an aerosol. The potential exists for a semi-volatile to later condense as a submicron particulate or as droplets in cooler parts of the offgas system and cause corrosion of the offgas piping. All compounds can be entrained as particulates. Particulates from the melter feed can be swept up into the offgas system as it is fed into the melter or during process upsets. See the Sr section (3.4) for more about particle entrainment.

Table 3.1.1. Types of offgas emissions (Scott et al., 1985).

Gases	Semi-volatile	Particulates
H_2, O_2, CO, CO_2, NO, NO_2, SO_2, H_2O, halogens (e.g., I_2)	Some compounds of Na, Li, K, Cs, Hg, Cd, Mo, Ru, Sb, Se, Tc, Te, B, and halogens	Fe, Al, Sr, rare earths, and all other feed components

The estimated oxide-equivalent composition of Double Shell Slurry Feed (DSSF) waste is shown in **Table 3.1.2.** The glass composition LD10M6-5412 has a DSSF waste loading of 27 wt% (20wt% Na_2O) and is a typical LLW glass formulation (Table 3.1.2). LD10M6-5412 was used for scoping studies to test glass properties of a high Na_2O containing glass and is not necessarily the glass composition that will be vitrified using actual LLW. Volatile components in the glass include Cs, I, Cl, F, S, Mo (surrogate for Tc), Na, K, and B. Other glass components may become entrained as particles and end up in the offgas (e.g., Sr).

Vitrification of LLW-glass former slurries will inevitably involve three general processes that, depending on the process flow diagram and melter, may overlap. These include 1) drying of the slurry to remove water, 2) calcining the dried product to form oxides, and 3) melting the calcine to form the glass. Although much of the kinetics literature is concerned with species loss during melting, for some of LLW components one needs to be concerned about loss during the calcination (e.g. Tc and Cs) and slurry drying (e.g. Tc) processes as well.

For example, at low pH, technetium in the form of $HTcO_4$ is volatilized via evaporation from aqueous solutions (Colton) (see section 3.5.3). Volatility of $HTcO_4$ increases with increasing solution temperature. The volatilization of ruthenium, via a Ru(NO) complex, from a heated nuclear waste simulant solution also occurs by evaporation of the complexes at about 130°C (Cains et. al.).

Table 3.1.2. Oxide-equivalent composition of the LD10M6-5412 glass and the DSSF waste and glass precursor additive components.

Oxide	Base glass (wt%)	Component	
		DSSF (wt%)	Additives (wt%)
SiO_2	55.63		76.09
Na_2O	20.00	74.39	
B_2O_3	4.98		6.81
CaO	3.98	0.01	5.44
Al_2O_3	11.96	12.74	11.66
Others*	3.44	12.86	
Total	100.00	100.00	100.00
*Others			
Cl	0.44	1.64	
Cr_2O_3	0.04	0.17	
F	0.43	1.59	
I	0.15	0.56	
MoO_3	0.15	0.57	
Fe_2O_3	0.005	0.02	
K_2O	1.46	5.42	
MnO	0.001	0.00	
MgO	0.005	0.02	
P_2O_5	0.24	0.88	
SO_3	0.24	0.88	
SrO	0.12	0.43	
Cs_2O	0.17	0.63	
Total	3.45	12.86	

The formation of liquid aerosols containing LLW components is an important issue when dealing with slurry fed melters. As the LLW-glass former slurry is sprayed onto the hot melt or calcine surface, atomization of the solution into an aerosol can occur, increasing the loss of some species by increasing the volatilization from the high surface area droplets as well as by entrainment as condensed submicron particles that become part of the off-gas (Baumgartner et. al.). Dried LLW-glass former slurries and calcines can emit dust-like aerosols from their hot surfaces, again increasing the loss of certain species by entrainment in particles (Baumgartner et. al.).

Entrainment of LLW component species in the NO_x off-gas during calcining has significantly increased the loss of ruthenium (Baumgartner et. al.; Cains et. al.; Igarashi et. al.) as well as technetium, strontium and selenium (Igarashi et. al.). Cains et. al. also report significant loss of cesium (0.4% of the amount fed to the melter) at temperatures below which $CsNO_3$ and $CsNO_2$ decompose to Cs_2O (<450°C), perhaps suggesting that the NO_x entrainment mechanism is involved here as well. These researchers also showed a significant increase in ruthenium loss (2% absolute) when the simulant slurry was dried at 90°C as opposed to 120°C. The effect was attributed to a decrease in the amount of nitrates present after drying at 120°C, hence, a corresponding decrease in the amount of NO_x available for entrainment.

At elevated calcining/melting temperatures, i.e., about 600-1000°C, where the melting of certain compounds occurs but where the relatively high surface area calcine/frit particles have not yet consolidated into a melt, loss of LLW components can be extremely high. In this temperature regime, a liquid film forms and wets the calcine/frit particles, which generally do not consolidate completely until about 1200°C, and provide a high surface area vehicle though which the loss of many species is highest (Vida). The predominant mechanism involved at this stage is most likely diffusion of species through the liquid along the interior pore surfaces to exterior surfaces where volatilization or aerosol formation occurs (Brinker and Scherer). Igarashi et. al. have shown a large increase (23-34% absolute) in technetium and selenium loss (presumably as entrainment in aerosol particles) by 800°C as well as a slight increase (2-4%) in the loss of ruthenium and strontium. Baumgartner et. al. have shown that after 10 hours at 900°C, simulated nuclear waste calcines containing a variety of species yielded crystalline aerosol particles containing Tc and Cs (presumably $CsTcO_4$) with a mean particle diameter of 2-4 microns that collected in the cooler parts of the melter. At 1100°C, similar calcines yielded amorphous aerosol particles containing Tc and Cs with mean particle diameters of 2-4 microns after 10 hours and 0.2 microns after 22 hours. The rate of Tc and Cs loss (and Rb via $RbTcO_4$) correspondingly increased (and paralleled each other, suggesting the formation of $MTcO_4$ compounds) at these temperatures as well (Baumgartner et. al.; Cains et. al.; Igarashi et. al.; Vida). These temperatures correlated well with the presence of liquid $CsTcO_4$ (melting point 595°C) and $RbTcO_4$ (melting point 581°C) which, as stated above, coat the high surface area frit particles making Tc and Rb loss highest in this temperature region (Vida). Minimizing the time spent in this region of high Cs-Rb-Tc volatility (i.e., accelerating the melting process) will certainly be an important aspect to the LLW vitrification flow diagram and melter design.

Once the glass has fully consolidated, volatilization of species from glass melts is a more complex process involving many variables such as temperature, glass composition, time, melt turbulence, and offgas flow. Three simultaneous subprocesses occur during volatilization from a melt. These are 1) diffusion of the component through the melt to the surface, 2) transport through the melt/vapor interface, and 3) transport in the atmosphere. Of the three subprocesses, diffusion through the melt is considered to be rate controlling (Cable and Chaundry) for static melt conditions. Neglecting convective flow, the total loss in weight (M) per unit surface area would then be generally given by

$$M = (4/\pi)^{1/2} C_0 (Dt)^{1/2} \qquad (3.1.1)$$

where C_0 is the uniform initial concentration of volatile material in the melt, D is the effective diffusion coefficient of the species through the melt and t is time (Cable et. al.). Improvements on this model have been summarized by Cable et. al. and involve modifying the above equation to include flux of volatiles from the melt surface to the vapor. However, as stated above, this model as well as its improvements generally only consider static conditions.

Increasing the temperature of the melt will decrease the viscosity and increase the diffusion coefficent. Thus, at relatively short times (<20 hours) at melt temperature, transport of volatile species through the melt is generally enhanced at higher temperatures and may contribute to the higher volatilities of various species such as borates and metaborates (Oldfield and Wright). However, at longer times, volatile species are removed from the surface of the glass melt and crystallization may occur in the depleted region. Thus, diffusivity through this crystallized layer may hinder the transport of volatile species to the surface and hence decrease the rate of volatilization from the melt (Oldfield and Wright). Volatilization may also be enhanced in relation to the above model due to melt convective flow flow.

3.2 Chlorine and Iodine

This section discusses the volatility of chlorine and iodine present as sodium salts in glass. For additional information about the volatility of other chlorides, fluorides, and iodides salts (not necessarily in glass, but in solution), see the Cs, Tc, Re, and Mo sections of this report. It was not always clear from the literature what species of Cl or I is volatilizing. In many cases no attempt was made to determine the species. In the case of Cl, Na or Cs were often present in corrosion products or collected particles along with Cl. Cl can volatilize as NaCl, CsCl, Cl_2, HCl. Iodine was reported to volatilize as gaseous I_2 (Spalding, Button et. al., Volf, Scott et. al.).

Chlorine and iodine have a limited solubility in borosilicate glasses. In a commercial glass, such as Pyrex, Cl usually does not exceed 0.1 wt% . For a soda-lime-silica glass of composition, 75 wt% SiO_2, 9.2 wt% CaO, and 15.8 wt% Na_2O at 1400°C approximately 1.4 wt% Cl was soluble (Volf). Solubility limits for Cl and I are dependent upon several factors including glass composition and temperature. Unlike F, which significantly substitutes for O in a SiO_4^{4-} tetrahedra, Cl and I do so only in a very limited quantity. Volf attributes this to the similarity in effective radius between F^-, OH^- and O^{2-}. It is likely then the volatility of $F < Cl < I$ if ionic radius is the only factor considered. The data from PSCM-23 supports that volatility of $F < Cl$

(DF's=> 6.6 Cl, 9.2 F). However, data on I volatility was not available as I was not present in the melter feed.

Chlorine volatilizes in significant quantities and can also increase the volatility of other components such as F (Volf) and Cs (Spalding). Chlorine has been reported to form a molten salt layer with sulfate over silicate melts. Cesium and strontium radionuclides have been reported to concentrate in this layer. The phase decomposition of the sulfate/chloride layer leads to the volatilization of Cs and Sr (Stefanovskii and Lifanov). Thus, Cl can enhance the volatility of radionuclides. Chlorine in the offgas stream also increases the corrosion of piping and other metal parts. Severe corrosion of offgas metal parts occurred during LFCM2 due to Cl and S containing compounds (Goles and Sevigny). Furthermore, the potential for a steam explosion from the presence of molten salts in liquid-fed melters has also been reported by Goles and Sevigny.

NaCl is added (< 2wt%) to commercial glass batch to decrease the melt surface tension and promote melting through better wettability of batch particles. NaCl combines with Na_2CO_3 to give a eutectic mixture with a melting point of 838°C, 213°C below the melting temperature of soda. The fluid eutectic reacts faster with SiO_2 causing intensified melting. NaCl and KCl have been used as refining agents in commercial glass melting. The refining effect occurs intensely between 1100 to 1200°C and liberates gaseous HCl by the following reaction (Volf):

$$2NaCl + H_2O + SiO_2 \Rightarrow Na_2SiO_3 + 2HCl \qquad (3.2.1)$$

Above 804°C, volatilization of NaCl occurs (Volf). However, as shown by Spalding (1994), significant amounts of Cl can volatilize in the 800 to 1000°C temperature range. In commercial melting, NaCl additions have also been used to reduce the thickness of the batch blanket (cold cap).

It has been suggested that photochromic glasses might provide important clues for increasing the amount of chlorine or iodine in glass as chloride. Increasing the solubility of Cl in glass may help reduce Cl volatility by reducing the thermodynamic favorabilty of Cl diffusion to the melt surface. Since Cl volatilization occurs during melting and is a function of the melt and vapor properties, it is unlikely that the crystallization of silver halides as in commercial photochromic glasses (which occurs later during cooling the glass) will reduce Cl volatility during melting. Araujo et. al states that silver halide precipitation from many glasses is not possible and that it is largely a function of having high solubility in the glass at high temperature, but low solubility of silver halides at low temperature. The presence of small evenly dispersed halide crystallites would be necessary in the melter at melting temperature to reduce volatility. Typically, photochromic glasses use a mixture of halides to produce small silver halide crystallites which are precipitated from a homogeneous glassy matrix (Paul). The amount of Cl is approximately < 2 wt%, the average being less than 1 wt%. The average crystallite size is about 100 Å. Ag is usually less than 0.7wt%. Activated by u.v. radiation, silver separates from the halogen, inducing a darkening color change. After the source of light is removed, silver recombines with the halogens and the glass is again transparent. Br, F, and I can be used as well Cl to form the metal halide compound. Polyvalent oxides of As, Sb, Sn, Pb, Cu, and Cd can increase the sensitivity and photochromic absorbance. The total halogens does not usually exceed 5 wt%. Thus, the amount of Cl in photochromic glasses is not much more than what is typically present as an impurity in glasses (i.e. <1 wt%).

A potential problem also exists with the use of Ag. Silver ion readily reduces to silver metal leading to increased risk for the settling of Ag metal into a conductive sludge on the bottom of the melter. Shreiber reports that at 1150°C for a borosilicate glass SRL-131, about 80% of the Ag is present as metal and 20% as Ag(+1 oxidation state). The factors which should be considered are electrical conductivity increase from the addition of Ag, the amount of AgI or Ag metal crystallinity that could be tolerated by the melter (i.e., primarily the amount of settling in melter which would not inhibit processing), durability, viscosity increases from the precipitation of crystallites, liquidus temperature, volatility, and environmental concerns.

One method suggested for reducing chlorine volatility is opacification. Chlorine causes opacification when added in amounts of > 2 wt% KCl. Alternatively, chlorine can react with Ca and P to produce apatite. There are two types of opal glasses: spontaneous and heat-treated. Most commercial opal glasses are heat treated to grow the crystallites which cause opalescence. Spontaneous opals form crystals upon cooling. In the case of LLW vitrification, chlorine volatilization occurs during melting and is a function of the melt and vapor properties. It is unlikely that opacifying the glass will reduce Cl volatility during melting since opacification of the commercial glasses occurs later during cooling or reheating. Again, the presence of small evenly dispersed halide crystallites would be necessary in the melter at melting temperature to reduce volatility. In addition, the factors which should be considered are: the amount of apatite crystallinity that could be tolerated by the melter (i.e., primarily the amount of settling in melter which would not inhibit processing if apatite were crystallized in the melter), thermal expansion mismatches which might cause cracking during cooling, durability, viscosity increases from the precipitation of crystallites, liquidus temperature, volatility, and environmental concerns. Furthermore, the addition of Ca and P to produce apatite may cause the formation of a Ca rare earth phosphate scum layer which was reported during the PSCM-19 melter run (Perez).

Some evidence exists that B may increase the solubility of Cl. Button et. al. observed that Cl could substitute for O in lithium borate glasses. Up to 14 wt% Cl was soluble in lithium borate glasses (12.7 mol% $(LiCl)_2$-23.4 mol% Li_2O-63.6 mol% B_2O_3) melted at 940°C. Cl due to its valency of -1 is non-bridging when it binds to B. The oxygen-to-boron ratio was decreased as Cl was added to the glass. However, the reduction in Cl vaporization losses was attributed by Button to lower melting temperatures and shorter soak times in the lithium borate system when compared to silicate glasses. Araujo et. al. theorized that nickel chloride complexes could form in potassium aluminoborosilicate glasses based on color changes observed when Ni was present in the glass; possibly affecting Cl solubility. However, the glasses investigated had a starting amount of 1 wt% Cl and the amount of NiO was 0.25 wt% so the effect may be for small concentrations. It was not clear from the paper if the presence of NiO actually increased Cl solubility; color changes were observed and attributed to chloride complexes of Ni.

Chlorine DF's from PNL joule-heated melters—runs PSCM-1 thru 8, PSCM-23, LFCM 4, 6, 8 and SSHTM (LLW)[1]—ranged from 1.5 to 6.6 and are listed in **Table 3.2.1.** The DF's show that Cl is very volatile and losses from the melter were high. About 83% of submicron particulate compositions from PSCM-4 consisted of NaCl. Offgas line deposits formed during melter idling periods contained 20-90% NaCl and up to 30% S. The melter runs were performed under a variety of conditions (e.g., feed rate, plenum temperature, offgas flowrate, pH, etc.) with feeds of different composition. This may account for the variability of the DF's. Offgas deposits containing alkali borates, chlorides, fluorides, chromates and sulfates have also been reported by Jantzen (1991) during the operation of the Scale Glass Melter (SGM). Jantzen (1992) investigated the presence of compounds in a DWPF canister filled during Campaign 10 of the SGM. Sodium and potassium chlorides, sulfates and borates were found on the interior canister walls, (neck and shoulder above the melt line). Thus, these compounds appear to be volatilizing during the pouring of the glass from the melter as well as during vitrification.

Iodine DF's have not been measured in most PNL melter runs because the melter feeds did not contain I or was at such a low concentration that I was not detected in the offgas (NCAW waste target was 4.5×10^{-6} wt% I^- or 1.25×10^{-6} wt% I^- in glass). Perez and Nakaoka reported an iodine DF of 1.3 for vitrification in PSCM (run number not specified). The "as batched" concentration of iodine was 0.01wt% in glass, but based on the reported DF very little iodine ended up in the glass. For the LFCM-8 run, the DF for I based on offgas measurements was

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[1] Perez, Shafer, Buchmiller, 1994

Table 3.2.1. Average chlorine decontamination factors (DF) from PNL melter runs.

Run name	Chlorine DF
PSCM-1	3.1
PSCM-2	3
PSCM-3	4
PSCM-4	5
PSCM-5	1.5
PSCM-6	2.9
PSCM-7	6.4
PSCM-8	4.7
PSCM-19	-
PSCM-23	6.6
LFCM-4	2.2
LFCM-6	2.7
LFCM-7	-
LFCM-8	4
SSHTM (LLW)	5 (estimated)

determined to be ~1.0 [1]. For the HWVP design specification for I, Goles and Nakaoka recommend a DF of 1. Scott et. al. report that nearly all volatile iodine out-gasses in reprocessing steps that occur prior to calcination or vitrification; thus, there is not an abundance of literature on the volatility of iodine from glass. Iodine is released primarily as I_2 gas. However, Scott et. al. state that Hg has volatilized as Hg_2X_2 compounds, where X is a halogen. Additional data on iodine is available from some PNL reports which were not focused on vitrification. Scott presented a discussion of I^- recovery methods (using scrubbers) from the offgas based on the reviews of Holladay (1979) and Burger et. al. (1983). Knox and Farnsworth studied the volatility of I-131 from spray calcined feed. About 31 wt% of I-131 volatilized at 800°C.

3.3 Cesium

Cesium volatility during the vitrification of Hanford nuclear waste is a concern because Cs is present in the waste mainly as the radionuclides Cs-137 and Cs-134. Minimization of the amount of radioactive cesium in the offgas stream reduces the risk of an uncontrolled environmental

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[1] Perez, Whitney, Buchmiller, Daume, Whyatt, 1994

release. For additional information about the volatility of other cesium salts (not necessarily in glass, but in solution), see the Tc and Re section (3.5) of this report.

3.3.1 Cesium Speciation in Vapors

The volatility of cesium from the waste glass has been summarized in several references: Spalding (1989, 1992, and 1994), Kamizono et.al. (1986, 1989), Vance et.al., Terai and Kosaka, Asano and Yasue (1985), Asano et al. (1984), Gray, Scott et.al., Goles and Nakaoka (1990), Goles and Sevigny (1983), Perez et.al. (1985), Perez and Nakaoka (1986), Albrethsen, Wilds, Kelley. Cesium is an alkali metal and is extremely reactive with air and water (explosively so with water, as H_2 gas is formed as a by-product) (Cotton and Wilkinson). It is more reactive than all the other alkali metals (Li, Na, K, Rb) except for Fr (Brown and Lemay). It is thermodynamically unlikely that Cs metal would form under the oxygen partial pressure and temperature conditions in melter or offgas (Bonnell). Wilds has reported Cs (g) was detected by Knudsen cell spectrometer but details and discussion were not given to support this conclusion. Asano et. al, (1984) stated that when neutral vapors are impacted with electrons of energy below 70eV, the mass spectra contain peaks of ions formed from many ionization processes. This processes include simple ionization, dissociative ionization, ion-pair formation and secondary ion formation. The mass spectrometer thus can split Cs compounds into smaller units such as Cs^+, $CsBO^+$, $CsBO_2^+$, $Cs_2BO_2^+$, Cs^{2+}, CsO^+, $NaCsBO_2^+$. It is not a simple task to determine specific parent vapors.

Experiments performed by Asano et al. (1984, 1985) using a Knudsen cell mass spectrometer were unable to confirm the presence of Cs (g) or CsO (g) among the volatile species over a sodium cesium borosilicate glass. The glass had a composition of Na_2O-B_2O_3-$3SiO_2$-$0.15Cs_2O$. The vapors of $Cs_2(BO_2)_2$(g), $NaCs(BO_2)_2$(g), Na(g), $NaBO_2$(g), $Na_2(BO_2)_2$(g) and $CsBO_2$(g) were reported to volatilize from the glass which was heated to 1200°C from batch materials for 1.5 hrs at a background pressure $< 2 \times 10^{-5}$ Pa. Asano et. al.(1984 to 1988) have also studied the vapors from sodium borosilicate glasses and sodium borosilicate glasses with tellurium. Knudsen cells are typically under vacuum while samples are heated and measurements made. Since melters are typically operated in air with water present, it is possible that the gaseous species as determined by Knudsen cell experiments may be different in the melter.

Other authors (Goles, 1983; Burkholder, 1987; Jantzen 1991 and 1992) have found Cs in offgas or canister deposits with borates, chlorides, sulfates, and fluorides. Based on this evidence, Cs may volatilize as chlorides, sulfates, or fluorides as well as borates. Baumgartner et.al. and Vance et.al also report that Cs may volatilize as pertechnate or molybdate, respectively.

3.3.2 Volatility from Calcines and Glass

Spalding (1989, 1992, and 1994) studied the volatility of Cs from soil and soil limestone mixtures from the White Oak Creek floodplain. The compositions are listed in **Table 3.3.2.1.** Samples were counted before and after heat treatments using gamma-ray spectroscopy to determine the initial and final amounts of Cs-137. Selected results of the Spalding study are summarized in **Table 3.3.2.2.** Cs volatility was increased by the presence of chlorine. NaCl was particularly effectively and resulted in >99% of the Cs being lost after repeated amendments of 5% NaCl were made to samples which were then heat treated at 1000°C. A variety of other substances were tested including NaF, CaF_2,$CaCl_2$, HCl, PVC, $NaNO_3$, Na_2SO_3, Na3PO$_4$, Cs_2CO_3, K_2CO_3, Na_2CO_3, Li_2CO_3, $Na_2B_4O_7$, graphite, polystyrene, 304-L stainless steel, 316-L stainless steel, ZnO, Sb_2O_3, Mo, and Fe. Of these, $CaCl_2$ and HCl were nearly effective as NaCl. PVC resulted in about 30% of Cs-137 volatilization. **Figure 3.3.2.1** shows the retention of Cs-137 with one-time additions of NaCl, HCl, $CaCl_2$ and PVC. Sodium borate caused a significant amount of cesium volatility after heating to 1200°C. Molybdenum metal slightly increased Cs-137 retention. Cs_2CO_3 and K_2CO_3 slightly improved the retention of Cs-137 but the mechanism was not determined. All other components did not affect cesium volatility significantly. Though the Cs species were not specifically measured, Cs likely volatilized as CsCl, $Cs_2(BO_2)_2$ or $CsBO_2$ (see

Table 3.3.2.1. Composition (mol %) of soils and limestones used to study thermal effects on the volatilization of Cs-137.

Species	^{137}Cs Soil	1987 Soil	1991 Soil	1987 Limestone	1992 Limestone
SiO_2	55.8	57.34	56.47	4.28	8.16
TiO_2	ND	0.81	0.80	0.08	0.03
Al_2O_3	14.1	18.35	17.20	1.59	1.57
Fe_2O_3	5.7	6.23	6.38	0.72	0.61
MnO	0.1	0.09	0.13	0.03	0.04
MgO	1.3	1.83	2.38	3.13	17.69
CaO	2.5	2.53	3.87	45.67	29.28
Na_2O	0.4	1.03	0.18	0.06	0.00
K_2O	ND	3.76	3.55	1.04	0.88
P_2O_5	ND	0.24	0.12	0.06	0.01
loss on ignition	7.3	5.53	9.57	40.47	41.78
total	87.2	98.36	100.65	95.61	100.50
Cl (ppm)	ND	58	85	245	340

ND = not determined

Table 3.3.2.2. Results of Spalding study of Cs-137 volatility.

Variable	Heating Rate (°C/min)	Temperature (°C)	Hold time (h)	^{137}Cs retained (%)
Sample initial bulk density varied from 0.9 to 2.3 g/cm^3 (calcined @ 850°C for 4 h prior to treatment)	11	1500	4	No effect
Heating rate (calcined @ 850°C for 4 h prior to heat treatment)	1	1500	2	81
	23	1500	2	102
Limestone (calcined @ 850°C for 4 h prior to treatment)	23	1500	24	50-65% for 0.45 fraction of limestone in melt, 100% for 0 fraction of limestone.
Heat treatment temperature (calcined @ 850°C for 2 h prior to treatment)	1	850	8	100.5
	1	950	8	100
	1	1050	8	100.3
	1	1150	8	95
	1	1250	8	92
	1	1350	8	95.5
	1	1450	8	95.3
Sequential heating of 7:3 soil:limestone mixture with 4-10% NaCl (calcined @ 700°C for 2 h prior to treatment)	1	800	2	100
	1	900	2	45-55
	1	1000	2	12-12
	1	1100	2	6-10
Sequential heating soil with 6-20% NaCl (calcined @ 700°C for 2 h prior to treatment)	1	700	2	100
	1	800	2	90-99
	1	900	2	68-94
	1	1000	2	36-92
	1	1100	2	28-92
	1	1400	2	28-85
Repeated additions of 5% NaCl to 7:3 soil:limestone mixture (calcined @ 850°C or 950°C)	10	900	0.5	<1% after ten additions of NaCl and ten heat treatments
	1	1000	2	

previous section for the discussion of Cs vapor species).

The effects of surface area, bulk density, and limestone were also studied by Spalding. Surface area effects were investigated by some simple melting tests. Examination of samples prepared from raw (batch) materials showed that volatilization of Cs-137 was not observed after a melt was

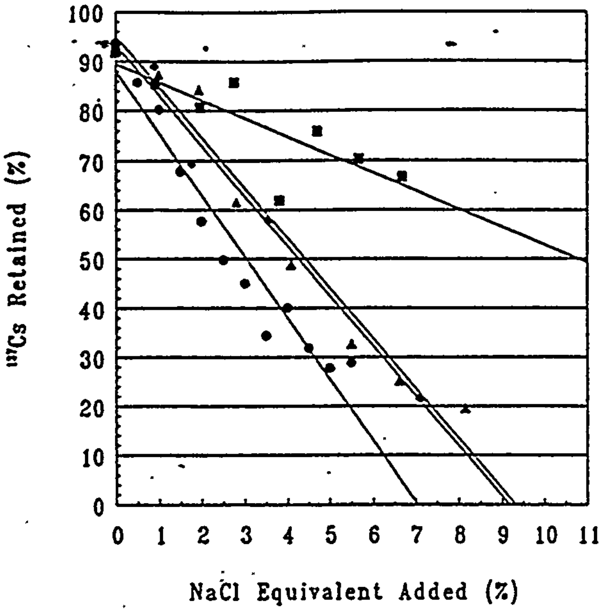

Figure 3.3.2.1. Affect of HCl, NaCl, PVC, and CaCl2 on the retention of ^{137}Cs (Spalding, 1994).

achieved. However, if previously melted samples were crushed and reheated, Cs-137 volatilized. Starting bulk density of samples was found to have little effect on Cs volatility. Limestone did not affect the temperature of Cs-137 volatility but did increase the amount. Limestone supplies an increased amount of CaO, making the mixture more refractory, which may delay melting. Since melting resulted in the reduction of surface area, a delay would allow more time for Cs-137 to escape, resulting in an increase in the overall amount of Cs-137 volatilized.

A 7:3 soil:limestone mixture without NaCl amendment produced the maximum amount of Cs-137 volatilization between 1150 to 1250°C. Cs-volatility for NaCl amended samples was found to significantly increase in the range of 800°C to 1000°C. NaCl not only increased the volatility of Cs-137 but also lowered the temperature range of maximum volatility. **Figures 3.3.2.2 and 3.3.2.3** show the retention of Cs-137 as a function of temperature for samples with and without NaCl amendments. The heat treatment time below melting also increased the volatility of Cs. More information about the White Oak Creek testing can be obtained in other reports (Spalding et. al., 1989 and Spalding et.al, 1992).

Gray studied the volatility of cesium from calcines and glasses. The compositions of these materials are shown in **Table 3.3.2.3.** The first two materials, 72-68 and 76-183, are glasses.

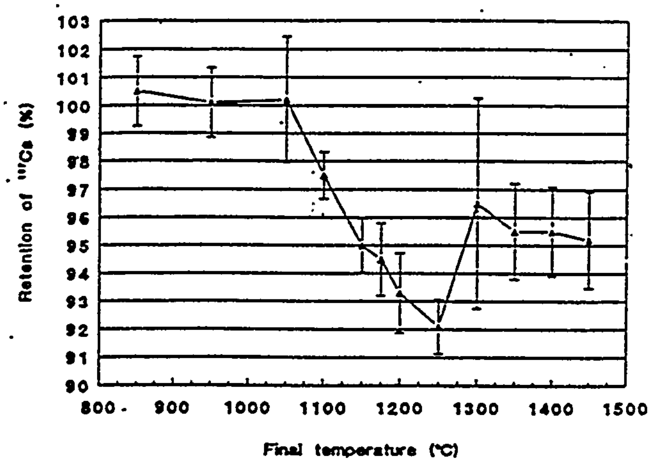

Figure 3.3.2.2. Retention of ^{137}Cs by 7:3 soil:limestone mixtures when heated to different temperatures and held for 8 h. Error bars indicate ±1 standard deviation for each group of samples (Spalding (1994).

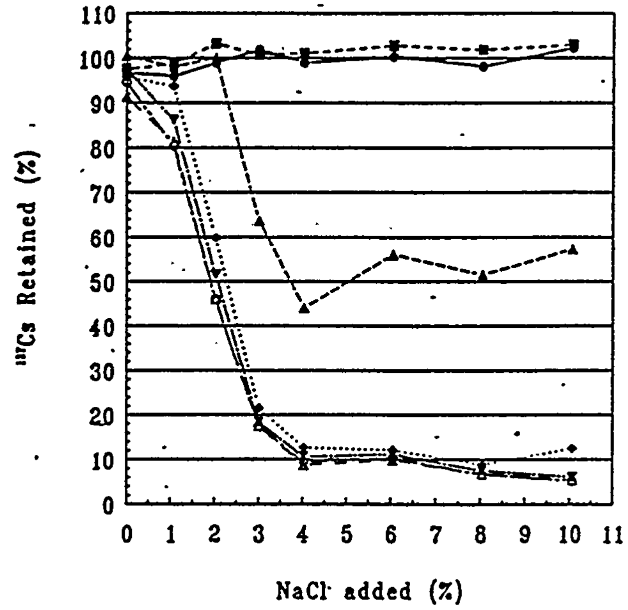

Figure 3.3.2.3. Retention of ^{137}Cs by 7:3 soil:limestone during sequential heating to various final temperatures and additions of NaCl (Spalding, 1994).

Table 3.3.2.3. Composition of glasses, waste caline, and supercalcines for the volatility study of high-level radioactive waste forms (gray, 1980).

Species	Glass 72-68	Glass 76-183	Waste calcine PW-4b	Supercalcine SPC-2	Supercaline SPC-4
B_2O_3	11.30	9.50	-	-	-
Na_2O	4.12	11.64	-	0.18	0.19
MgO	1.50	-	-	-	-
Al_2O_3	-	1.00	-	4.43	4.53
SiO_2	27.71	35.50	-	19.00	17.64
P_2O_5	0.44	3.36	1.75	4.16	4.26
K_2O	4.12	2.00	-	-	-
CaO	1.50	2.00	-	4.93	2.09
TiO_2	-	6.00	-	-	-
Cr_2O_3	0.23	0.19	0.92	0.54	0.55
MnO_2	-	-	-	-	-
Fe_2O_3	1.00	1.60	3.98	4.68	4.79
Co_2O_3	-	0.16	-	-	-
NiO	0.09	0.56	0.36	0.22	0.22
CuO	-	3.00	-	-	-
ZnO	21.64	-	-	-	-
Rb_2O	0.23	0.19	0.92	0.55	0.56
SrO	2.20	0.56	2.79	2.86	4.23
ZrO_2	3.28	2.62	13.06	7.66	7.84
MoO_3	4.29	3.38	17.08	8.02	8.21
RuO_2	1.97	1.57	7.85	0.47	0.48
Rh_2O_3	0.32	-	1.27	-	-
PdO	0.98	-	3.98	-	-
Ag_2O	0.06	0.05	0.24	-	0.14
CdO	0.06	0.05	0.24	0.15	0.15
TeO_2	0.48	0.39	1.91	-	-
Cs_2O	1.91	1.53	7.64	4.46	4.57
BaO	2.54	0.83	4.14	2.43	2.48
RE_2O_3	8.03	12.34	31.98	35.26	37.07
Total	100.00	100.00	100.00	100.00	100.00

PW-4b is a simulated waste (calcine). SPC-2 and SPC-4 are calcines which have chemicals added to crystallize and tie up hazardous fission products. Cesium amounts varied from 1.5 wt% to 7.6 wt%. Three other glasses were also studied: 72-68 with 10wt% Al_2O_3, 76-183 with no TiO_2, and 76-183 with 12wt% TiO_2. Gray observed that the total volatility increased with an increase in moisture in the air as shown in **Figure 3.3.2.4.** The weight loss was made of contributions from Te, Cs, Ru, K, Rb, Mo, Na, and B. At 1073K and 1273K, the weight loss increased as the water content of the air increased form 0 to 15 wt%. As the temperature increased, the effect on weight loss appeared to decrease. At 1473K, a plateau or saturation condition was reached. However, Cs volatility slightly decreased in 72-68 with a 7.1 wt % addition of water (**Figure 3.3.2.5**) at higher temperatures and slightly increased at lower temperatures when compared to 72-68 in dry air. The loss of Cs after 4 h in dry air except where noted is also shown in the figure as a function of temperature for several glasses and calcines. The volatility of Cs increased with temperature. At 1473K, all the glasses fit a square-root-time ($t^{1/2}$) relationship after an hour. A nearly linear relationship was observed at lower temperatures. Diffusion limited vaporization is implied by the $t^{1/2}$ dependence. A linear relationship with time suggests that a surface reaction is the limiting mechanism (Terai and Kosaka). The volatility was significant above 1000K which is a temperature that might only be encountered during vitrification or an accident involving a fire.

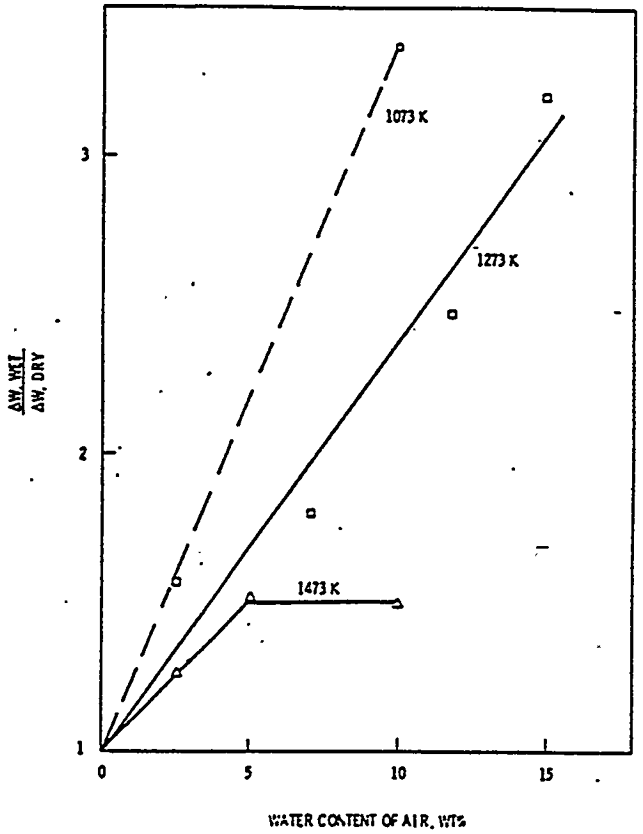

Figure 3.3.2.4. Effect of moisture on weight loss from 72-68 glass in 4 hours.

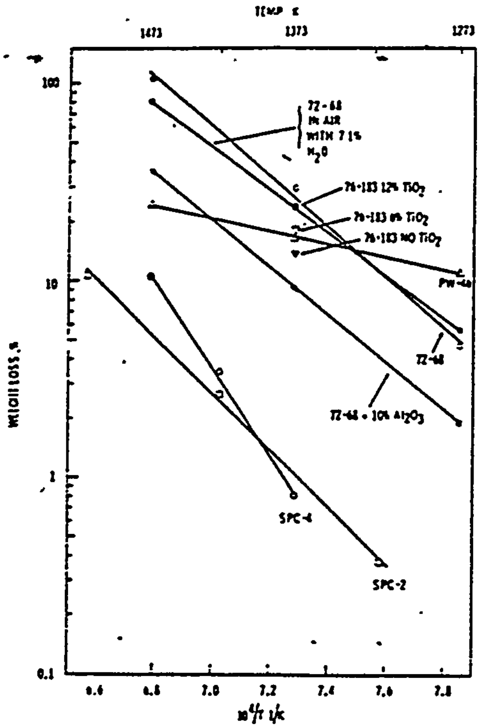

Figure 3.3.2.5. Loss of cesium in 4 hours in dry air except as noted (Gray, 1980).

The volatility was different for the glasses and the calcines which shows the importance of glass composition on Cs volatility. The addition of 10 wt% Al_2O_3 to glass 72-68 reduced Cs volatility by 17 %. For glass 76-183 with different amounts of TiO_2, the volatility of Cs increased with wt% TiO_2 in the glass. Kelly (1975) and Wilds (1978) have reported that TiO_2 affected the volatility of Cs from glasses prepared from zeolites. In these studies, Cs in the glass was typically 0.1 wt% or less. In Kelly's study, for a 10 wt% TiO_2 addition, the volatility increased 0.53 to 1.18 wt % absolute of Cs_2O in glass. In Wilds study, a 0.02 mg/cm^2 increase in Cs volatility was reported for a 10wt% increase in TiO_2. However, a 0.06 change was reported in duplicate tests so that 0.02 appears to be well within the standard deviation for the volatility study. The evidence is therefore not conclusive.

Figure 3.3.2.6 shows weight loss for several species as a function of TiO_2 (Gray, 1980). The change is most severe for Cs and Te. About 11% more Cs and 30% more Te were lost when the 12wt% TiO_2 was added to 76-183. Gray reported that viscosity may have played a role in volatilization from the glass. TiO_2 is reported to decrease the viscosity of glass (Volf). The effect is stronger at higher temperatures than at lower temperatures. This may account for the observed

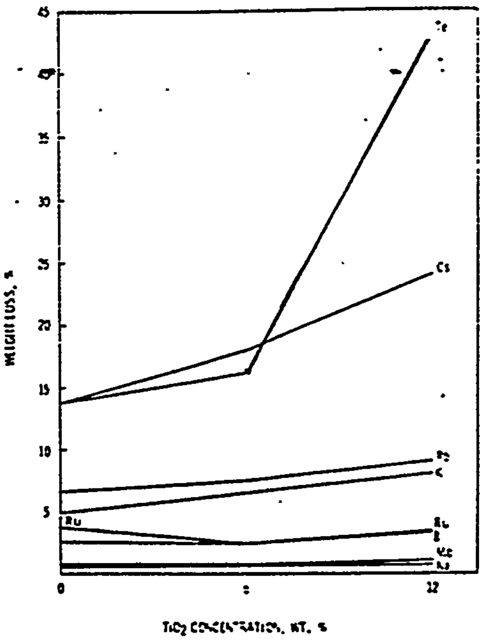

Figure 3.3.2.6. Effect of TiO_2 concentration on loss of elements from 76-183 glass in 4 hours in dry air at 1373K (Gray, 1980).

increase in Cs loss with increase in TiO_2. Similarly, Al_2O_3 increases viscosity and this may account for the reduction of volatility observed for the 10 wt% Al_2O_3 glass 72-68.

Baumgartner et. al. studied the vaporization from salt cake material, with simulated highly radioactive waste (HAW), during heating to 1100°C. Approximately 18% of the Cs volatilized. Crystals and glassy spheres containing both Cs and Tc were found in aerosols and were thought to be $CsTcO_4$. Thus, Cs may volatilize as $CsTcO_4$.

3.3.3 Volatility from PNL and Vendor Melter Runs

The average Cs DF's from PNL joule-heated melters (runs PSCM-1 thru 8; LFCM 4, 6, 7; Radioactive Liquid Fed Ceramic Melter -7 (RLFCM); Kernforschungszentrum Karlsruhe (KfK)); and the Integrated Defense Waste Processing Facility (DWPF) Melter System (IDMS) runs ranged from 2.2 to 140. **Table 3.3.3.1** summarizes the DF's for some of the PNL melter runs. All DF data is reported as elemental Cs; the form measured by ICP. It is thermodynamically unlikely that Cs metal was formed either in the melter or offgas (Bonnell). The melter runs were performed under a variety of conditions (e.g., feed rate, plenum temperature, offgas flowrate, pH, cold cap coverage, etc.) with feeds of different composition which may account for the variability of the DF's. Cesium was present in the offgas in concentrations higher than could be accounted for by

Table 3.3.3.1. Average Cesium decontamination factors (DFs) from PNL and other melter runs.

Run	Feed type	Cs DF
PSCM-1	alkaline	51
PSCM-2	alkaline	3
PSCM-3	acidic	3.8
PSCM-4	acidic	16
PSCM-5	acidic	9.5
PSCM-6	acidic	14
PSCM-7	acidic	13
PSCM-8	acidic	130
PSCM-9	NA	14
PSCM-15	NA	62
PSCM-16	NA	59
PSCM-19	acidic w/sugar added	97
PSCM-20	NA	140
PSCM-21	NA	33
PSCM-22	NA	14
PSCM-23	acidic	83
LFCM-4	alkaline	57
LFCM-6	alkaline	10
LFCM-7	acidic	12
RLFCM-7 (normal)	NA	10
RLFCM-7 (spiked)	NA	28
KfK	NA	20-60
IDMS	NA	132

NA = not available

particle entrainment. The majority of the cesium found in the off-gas consisted of submicron particles. This lead to the conclusion that the primary mechanism for cesium leaving the melter was volatilization/condensation rather then particle entrainment. The volatile Cs compound was not identified. However, chlorine was present as an effluent and correlated with Cs effluent. When chlorine increased, Cs increased, suggesting that Cs might be volatilizing as CsCl. However, a precise mass balance for Cl and possible cations was not available nor was the presence of crystalline CsCl reported. The data was limited and more than a general trend based on the effluents was not presented (Burkholder and Allen).

Though a difference in DF's was reported between formic acid feeds (average Cs DF = 28) and alkaline feeds (average Cs DF = 30) it is not conclusive that this difference is significant for Cs. For the range of Cs DF's reported and variability observed among acidified and alkaline feeds, the difference in feed chemistry effects appears small and within the standard deviation of the experiments. As stated previously, it is not thermodynamically likely that Cs redox is affected at the partial pressures of oxygen and under the other conditions in the melter or in the melter feed. H_2 is released from formated feeds with a large amount of NOx; so, that it is uncertain whether the melter atmosphere would be reducing enough to form Cs metal. Because the solution/slurry chemistry is very complex, a chemical reaction resulting in the precipitation of a Cs compound could affect the volatility of Cs in the melter (See Tc section). For example, had the acid used been HCl instead of HCOOH it is possible that Cs volatility would have been increased based on the results of Spalding. Slurry/melter feed chemistry may therefore affect volatility but it is not clear that during PSCM and LFCM tests reported in Table 3.3.3.1 that the addition of HCOOH affected the volatility of Cs. This is not to say that there was no observed effect on volatility from the addition of HCOOH. The volatility of the redox sensitive Ru was clearly affected by the addition of HCOOH (Goles et. al., 1983). Ru metal and RuO_2 are much less volatile than RuO_4 and were not detected in the offgas stream of acidified melts. Other species which are more likely to be sensitive to formic acid/hydrogen generation and may have the volatility affected by acidification are S, Te, Tc, Mo, and Se. Nodules containing Ni, Ru, Te, Se, and S have been found at the bottom of PSCM for acidified feeds in tests PSCM-4 through PSCM-8.

The RLFCM runs vitrified simulated wastes containing very high amounts of radioactive Cs-137 and Sr-90. The radioactive glass in canisters was prepared for Germany to test their repository. Cs_2O content in glass varied from 2.08 wt% to 5.74 wt%. SrO in glass varied from 1.65 wt% to 2.67 wt% (Holton Jr. et. al.). Over 10 MCi of Cs-137 and Sr-90 were processed in RLFCM. The DF for Cs was about 10 during the normal feeding of the melter. Volatility of Cs decreased during spiked feed additions to a DF of 28 (Burkholder and Brouns). High particle entrainment was observed during spiked feeding. Both volatile and normally nonvolatile species were observed to have DF's near 30 which was the mass DF during spiked additions. Some feed was basically being swept out onto the offgas. Cs volatility appeared to be suppressed by these events possibly because the offgas was saturated. A plug that formed in the off-gas line during the operation of RLFCM was found to consist mainly of Cs, Na, and B. Based on the ratio of B:Na:Cs of 2:1:1 the volatile species was theorized to be alkali metaborates or $CsBO_2$ and $NaBO_2$. However, the analysis was limited.

The KfK melter runs were performed in Germany from 1990 to 1993. Cs volatility was found to be sensitive to the amount of cold cap coverage. The low value of 19.8 resulted when only 50 to 60% of the melt surface was covered by the cold cap. The low coverage was caused by a low melter fed rate of 25 l/h. The use of sparging air also disturbed the cold cap and increased the volatility of Cs. The melter DF's for Cs under standard processing conditions were much higher (36-60). Cs_2O in the glass was < 1 wt%.[1] The Cs DF for the Integrated Defense Waste Processing Facility (DWPF) Melter System (IDMS) was 132 (Zamecnik).

3.3.4 Volatility from Crystalline Material

Carpenter et. al. investigated Cs vaporization from Synroc mineral, barium-cesium hollandite ($Ba_{0.9}Cs_{0.1}Al_2Ti_6O_{16}TiO_2$). The transpiration method was used to obtain equilibrium vapor pressures of Cs at 1075°C in a Ar- 5%H_2 reducing atmosphere. In this method a carrier gas is flowed over the surface of heated sample to capture any volatile species. The species then condenses out in a cooler part of the apparatus and is collected for measurement. The volatile species was assumed to be Cs(g). A heat of vaporization of 217±15 kJ/mol was determined. When a wet atmosphere was used the volatility of Cs increased to about 3.5 times higher than the dry runs. The authors believed this to be the result of Cs forming CsOH and $Cs_2(OH)_2$ which are more volatile than Cs(g). The heat of vaporization for Cs metal is 66 kJ/mol (CRC).

In addition to Carpenter, the volatility of cesium aluminosilicates and titanosilicates was investigated. Odoj et. al. used a Knudsen cell and mass spectrometer to measure the volatility from $CsAlSiO_4$, $CsAlSi_2O_6$ (pollucite mineral), and $CsAlSi_5O_{12}$. The enthalpies were determined to be 84 kcal (352 kJ) at 1400K, 100 kcal (418 kJ) at 1550K, and 122 kcal (511 kJ) at 1650K for $CsAlSiO_4$, $CsAlSi_2O_6$ (pollucite mineral), and $CsAlSi_5O_{12}$, respectively. Vance et. al. studied the volatile loss of cesium and molybdenum titanosilicate glass melts (which are used to form sphene, $CaTiSiO_5$, glass-ceramics) at temperatures between 1300 to 1400°C and sodium borosilicate glass melts at temperatures between 1150 to 1250°C. Titanosilicate melts doped with 2.1 wt% Cs_2O showed no significant increase in weight loss or Cs volatilization over that of the undoped melt at 1400°C for times of up to 24 hours. Titanosilicate melts doped with 1.0 wt% MoO_3, however, exhibited a much greater weight loss than that of the base glass. The total gravimetric loss of the Mo doped samples exceeded that which was calculated on the bases of Mo volatilization alone, indicating that some other species from the glass melt is accompanying the Mo during volatilization (i.e., $NaMoO_4$). When the glass melt was doped with 2.0 wt% Cs_2MoO_4, Cs volatility increased over that of the Cs_2O-only doped melt, but the volatility of Mo was still

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[1] Personal communication with ML Elliot, Oct 13, 1994.

much greater than that of Cs, indicating again that there is a combination of $CsMoO_4$ and $NaMoO_4$ volatilization.

For the sodium borosilicate melts doped with Cs and Mo studied by Vance et. al., the relative volatility of Cs was higher than that for the equivalently doped titanosilicate glasses, whereas the Mo volatilization was lower. Vance et. al. discuss the possibility that the volatilization of both Cs and Na in sodium borosilicate glasses occurs through $CsBO_2$ and $NaBO_2$ volatile species. Hence, the Mo volatility is decreased at the expense of increased Cs volatilization.

3.3.5 Volatility of Glass From Heated Canisters

Kamizono et. al. (1986) studied the volatility of Cs-134 from simulated radioactive borosilicate waste glass in an almost closed stainless steel canister. The glass composition is shown in Table 3.3.5.1. This was done to explore the scenario of a fire occurring in the storage facility causing

Table 3.3.5.1. Radioactive simulated waste glass compositions used to study the volatility of ^{134}Cs from a stainless steel canister (Kamizono et al., 1986).

Species	wt%	Species	wt%
SiO_2	45.20	Cs_2O	0.98
B_2O_3	13.90	BaO	0.62
Al_2O_3	4.90	La_2O_3	0.51
CaO	4.00	CeO_2	1.91
Na_2O	10.80	Pr_6O_{11}	0.49
ZnO	2.50	Nd_2O_3	1.65
Li_2O	2.00	Sm_2O_3	0.33
Rb_2O	0.12	Eu_2O_3	0.06
SrO	0.34	Gd_2O_3	0.04
Y_2O_3	0.20	SeO_2	0.02
ZrO_2	2.64	RuO_2	0.80
MoO_3	1.73	Ru	0.12
MnO_2	0.26	Rh	0.15
Ag_2O	0.03	Pd	0.43
CdO	0.03	Fe_2O_3	2.90
SnO_2	0.02	NiO	0.40
Sb_2O_3	0.01	Cr_2O_3	0.50
TeO_2	0.23	P_2O_5	0.30

heating of the canister and a possible release of Cs from the waste glass. About 0.98 wt% Cs_2O was present in the glass initially studied by Kamizono et. al. Radioactive Cs-134 was added to the glass in the amount of 1.89 x 10^{10} Bq of Cs-134. The glass was melted at 1200°C for 2 hours and then poured into a canister. The canister was kept at 600°C for 2 hours and allowed to cool at a rate of < 40°C/min. A gamma scanning method was used to determine the distribution of Cs-134. The distribution was found to be homogeneous in the glass within a ±0.2 cm resolution. About 14% of Cs-134 was found to have either volatilized during vitrification or left in the melter. After the waste glass was placed in the canister and cooled, the canister was reheated five times to various temperatures between 400°C and 1000°C. The air above the glass in the canister was sampled for Cs-134. Cs-134 was found to volatilize and remain suspended in the air above the glass even after the canister was cooled to 25°C. The authors theorized that Cs-134 vapor condensed into fine particles similar to fumes described by Aitcin et. al. which easily remain suspended inside the canister at temperatures < 500°C. About 23 Bq/cm^3 was present in the air at temperatures < 500°C. A heat of vaporization of 140 kJ/mol was calculated for the first reheating cycle to 1000°C. Subsequent reheating during the second (T=900°C), third (T=900°C), and fourth (T=700°C) cycles found a much lower heat of vaporization of 53 kJ/mol. The lower heat of vaporization was due to Cs-134 vaporizing from the canister wall where it had condensed after the first heating cycle. The amount of radioactivity present in the air was considered to be a significant amount. It was estimated that 4 x 10^7 Bq (1.1 mCi) air contamination would result in the canister if the glass contained 3 x 10^{13} Bq (811 Ci) initially. This amount is considered reasonable for a waste glass to contain initially.

In a continuation of Kamizono et. al. (1986) work, Banba et. al. and Kamizono et. al. (1989) performed a similar set of experiments for volatility of actual waste glass in a stainless steel canister using Cs-137 and Ru-106. The glass composition is shown in **Table 3.3.5.2.** A heat of vaporization of 140 kJ/mol was calculated for both Cs-137 and Ru-106 which agrees with that for Cs-134 reported by Kamizono. The volatility of ^{106}Ru was about one-fifth of ^{137}Cs at 600°C and 800°C. The amount of radioactivity present in the air was considered significant. It was estimated that 1.8 x 10^2 Bq/cm^3 ^{137}Cs and 20 Bq/cm^3 ^{106}Ru air contamination would result in the canister if the glass contained 7.4 x 10^{13} Bq/cm^3 of ^{137}Cs and 3.1 x 10^{10} Bq/cm^3 of ^{106}Ru initially. These amounts are considered reasonable for a waste glass to contain initially.

3.4 Strontium

SrO is fairly refractory. It has a melting point of 2430°C. This is much higher than Cs_2O which decomposes at 400°C. It is not surprising that Strontium-90 is much less volatile than Cs-137. In addition, Sr-90 is an alkaline earth which has very different properties than an alkali metal (stable

Table 3.3.5.2. Composition of simulated high-level waste glass mixed with actual waste compositions used to study the volatility of ^{134}Cs from a stainless steel canister (Kamizono et al., 1986).

Species	wt% *	Species	wt% *
SiO_2	41.22	Cs_2O	0.84
B_2O_3	14.02	BaO	0.53
Al_2O_3	3.81	La_2O_3	0.44
CaO	7.10	CeO_2	2.88
Na_2O	9.19	Pr_6O_{11}	0.42
MgO	1.60	Nd_2O_3	1.42
K_2O	1.23	Sm_2O_3	0.28
Rb_2O	0.10	Eu_2O_3	0.05
SrO	0.29	Gd_2O_3	0.03
Y_2O_3	0.17	SeO_2	0.02
ZrO_2	1.41	RuO_2	0.69
MoO_3	1.49	Ru	0.10
MnO_2	0.29	Rh	0.13
Ag_2O	0.03	Pd	0.37
CdO	0.03	Fe_2O_3	4.06
SnO_2	0.02	NiO	0.28
Sb_2O_3	0.01	Cr_2O_3	0.35
TeO_2	0.20	P_2O_5	1.17
TiO_2	0.07		

* The sum of this composition is 96.3 wt%. An additional 3.7 wt% of oxide is expected to come from the actual HLW solution. The glass composition is called J-10 and has been developed by the Japan Atomic Energy Research Institute.

valence of 2, higher melting point, etc.). Strontium DF's from the vitrification of simulated waste glasses in PNL joule-heated melters (runs PSCM-1 thru 8; LFCM 4, 6, 7; RLFCM-7; and KfK) ranged from 41 to 7400. **Table 3.4.1** summarizes the Sr DF's for some of the PNL melter runs. All DF data is reported as elemental Sr; the form measured by ICP. It is thermodynamically unlikely that Sr metal was formed either in the melter or offgas. The melter runs were performed under a variety of conditions (e.g., feed rate, plenum temperature, offgas flowrate, pH, etc.) with feeds of different composition. This accounts for much of the variability of the DF's as seen in the table.

Table 3.4.1. Average Strontium decontamination factors (DFs) from PNL and other melter runs.

Run	Feed type	Sr DF
PSCM-1	alkaline	7400
PSCM-2	alkaline	640
PSCM-3	acidic	640
PSCM-4	acidic	250
PSCM-6	acidic	1800
PSCM-7	acidic	4200
PSCM-8	acidic	550
PSCM-19	acidic w/sugar added	430
PSCM-23	acidic	840
LFCM-4	alkaline	204
LFCM-6	alkaline	290
LFCM-7	acidic	55
RLFCM-7 (normal)	NA	130
RLFCM-7 (spiked)	NA	50
KfK	NA	41-230

NA = not available

Strontium, present in the offgas system, was believed to be mainly due to particle entrainment. This conclusion was based on the fact that the ratio of strontium in the offgas to other constituents in the offgas was the approximately the same as the ratio of strontium in the melter feed. The relatively large particle size (77.6% of particles were > 16 µm) of Sr containing particles in the cyclonic sampling system also supported the particle entrainment conclusion (Goles and Sevigny). Sr in the offgas became high only when particle entrainment was high (Burkholder and Allen; Goles and Sevigny). LFCM-7, which has the highest Sr DF of 55, had the highest particle entrainment losses with few exceptions of all the melter runs (Goles and Sevigny). The high particle entrainment losses were caused in part by high melter in-leakages of 90-100 scfm (Burkholder and Allen). The in-leakage during LFCM-7 (average Sr of DF = 55) was 4.5 times higher than PSCM-3 which had a much higher Sr DF of 640.

In general, conditions that increased particle entrainment increased the loss of Sr from PNL melters. These conditions include high in-leakage, feeding rate, and process up-sets that caused the cold cap to collapse resulting in direct contact of the incoming slurry with the molten pool of glass. The resulting surge in offgas increases the particle entrainment significantly. Overfeeding, foaming, glass reboil, feed rate variations/interruptions and cold cap bridging are other process upsets that can cause the cold cap to collapse, increase particle entrainment, and cause the release of Sr.

Though a difference was reported between formic acid acidified feeds (average Sr DF = 1200) and alkaline feeds (average SrO DF = 2100) it is not conclusive that this difference is significant. The Sr DF for LFCM-7 was averaged in with the acidified feeds even though it was an order of magnitude less than any other Sr DF. This reduced the average acid DF for Sr significantly (DF 1488 without LFCM-7). PSCM-1 had a much higher DF than any of the other alkaline feeds of 7400. This increased the alkaline DF average (DF 378 without PSCM-1). The trend is thus reversed when two data points are removed. This should not be taken to mean that Sr volatility is always insensitive to changes in the melter feed. The chemistry of the melter feed is complex due to the presence of many compounds and it is possible that Sr species may be altered through chemical reaction resulting in a volatility change.

As stated previously in the Cs section, the RLFCM runs vitrified simulated wastes containing very high amounts of radioactive Cs-137 and Sr-90. Cs_2O content in glass varied from 2.08 wt% to 5.74 wt%. SrO in glass varied from 1.65 wt% to 2.67 wt% (Holton Jr. et. al.). The DF for Sr was about 130 during normal processing of the melter. Volatility of Sr increased during spiked feed additions to the melter to a DF of 50 (Burkholder and Brouns). High particle entrainment was observed during spiked feeding and thought to be the cause of the increase in Sr volatility.

During the operation of KfK melter, Sr volatility was found to be sensitive to the amount of cold cap coverage. The low value of 41 resulted during the use of sparging air which disturbed the cold cap and increased the volatility of Sr. The Sr DF was also lower (about 65) when only 50 to 60% of the melt surface was covered by the cold cap. The low coverage was caused by a low melter fed rate of 25 l/h. The melter DF's for Sr under standard processing conditions were much higher (about 200). SrO in the glass was < 1 wt%.[1]

Baumgartner et. al. studied the vaporization from salt cake material, which simulated highly radioactive waste (HAW), during heating to 1100°C. Approximately 0.001% of the Sr volatilized.

Cotton and Wilkonson report $SrCl_2$ is volatile. It is therefore possible that volatility of Sr could be increased if $SrCl_2$ forms during melting. In the literature data reviewed to date, the volatility of Sr

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[1] Personal communication with ML Elliot, Oct 13, 1994.

had been much lower that Cs and the volatilite species $SrCl_2$ has not been mentioned. It may be worthwhile to look at the volatility of Sr from a glass melt when $SrCl_2$ is present.

3.5 Technetium and Rhenium

3.5.1 General Chemistry

It is evident from the results obtained from Tc and Re volatility testing on Hanford LLW base glass compositions (section section 4.0) that even for melt temperatures as low as 900°C, DFs of only 1.25 were obtained. To better understand the volatility of Tc compounds and their Re surrogates a review of the lower temperature LLW processing steps, including the solution chemistry, is necessary.

Technetium has a $[Kr]4d^5 5s^2$ electronic configuration which allows valence states between 0 and +7. Species of oxidation state -1 have also been identified. The most stable oxidation state of technetium is +7 followed by +4 (Vida, pp. 5-9). Technetium species with oxidation states less than +4 are rapidly oxidized to Tc^{4+} and ultimately to Tc^{7+} and those with oxidation states between +4 and +7 usually disproportionate to corresponding mixtures of Tc^{4+} and Tc^{7+}.

The general chemistry of rhenium is similar to that of technetium, the +7 and +4 oxidation states being the most stable. Since we need to be concerned about the use of rhenium as a surrogate for technetium in much of the simulant work, whenever possible in this review, the data and/or behavior for a given technetium compound with be given along with that of the analogous rhenium compound.

3.5.2 Aqueous Solution Chemistry at Ambient Temperature

3.5.2.1 *Formation of Oxoacids and Oxosalts*

The highly hygroscopic Tc_2O_7 (see below) forms a strong pertechnetic acid, $HTcO_4$, on contact with water (Vida, pp. 5-9). Pertechnetic acid is easily ionized to form H^+ and the pertechnetate anion, TcO_4^-, and is about as strong an acid as HBr (Rard, pp. 24-67; Rulfs et. al.). Pourbaix diagrams indicate that the pK_a of $HTcO_4$ is -0.12 (Pourbaix, 1976). Pertechnetic acid can be neutralized with almost any cation (e.g., Li^+, K^+, Tl^+, NH_4+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cs^+, Na^+, and Rb^+) to form solid pertechnetate salts (Vida, pp. 5-9; Rard, pp. 3-24).

Rhenium heptoxide, Re_2O_7 is also highly hygroscopic, readily forming the perrhenic acid, $HReO_4$, in the presence of water (Colton). Like its pertechnetate counterpart, perrhenic acid also forms solid perrhenates in the presence of appropriate cations.

Table 3.5.2.1.1. Aqueous solubilities of selected pertechnetates and perrhenates.

Cation			TcO_4^-		
Na^+	11.299	11.299			
Sr^{2+}					
NH_4^+	0.594				
Ba^{2+}				0.165	
K^+	0.1057	0.1057	0.106		
Rb^+		0.0470	0.04700	0.04699	
Ag^+			0.0209	0.0208	0.0346
Cs^+		0.0163	0.0140	0.0139	0.0205
Tl^+			0.0020	0.0020	0.00319
Units	mol/kg	mol/L	mol/L	mol/L	mol/L
Temp. (°C)	25	NK	20	20	30
Ref.	Rard	Vida	Schwochau	Rard	Rard
Cation			ReO_4^-		
Na^+			3.66	3.50	5.32
Sr^{2+}					1.87
NH_4^+			0.233	0.227	0.325
Ba^{2+}					0.128
K^+			0.0370[b]	0.034	0.0508
Rb^+				0.031	0.0468
Ag^+					0.0388
Cs^+			0.020[a]		0.0287
Tl^+			0.0035		0.00656
Units			mol/L	mol/L	mol/kg[c]
Temp. (°C)			20	20	30
Ref.			Lebedev	Peacock	Colton

[a] Value measured at 19°C.

[b] Value measured at 21.5°C.

[c] Concentration units are in moles of salt per kg of water.

NK = not known.

The solubilities of some of these pertechnetates and perrhenates in aqueous environments are given in **Table 3.5.2.1.1.** In general, the pertechnetates are more soluble in water than the corresponding perrhenates (Colton).

3.5.2.2. *Redox and Hydrolysis Behavior*

The Eh vs pH behavior of technetium species in aqueous environments has been summarized in **Figure 3.5.2.2.1** (Vida, pp. 5-9). The data used to construct the diagram was based on experimentally determined standard potentials (Pourbaix, 1966) and hydrolysis constants (Gorski and Koch). The species which predominates over the entire pH range of 0-14 for oxidizing Eh

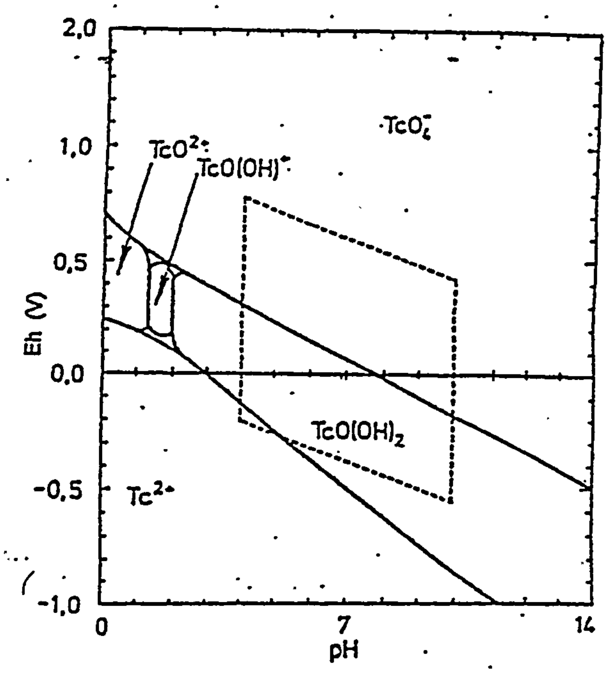

Figure 3.5.2.2.1. The Eh vs pH behavior of technetium species in non-complexing aqueous environments (Vida, pp. 5-9).

values (Eh > 0) is the pertechnetate anion, TcO_4^-, which corresponds to the stable +7 oxidation state.

Under more reducing conditions, most studies indicate that TcO_4^- in aqueous solution undergoes a $3e^-$ or $2e^-$ reduction to form Tc^{4+} or Tc^{5+} species respectively. In some cases, a $1e^-$ reduction of TcO_4^- occurs to form a Tc^{6+} species (Rard, pp. 24-67). Rulfs et. al. have suggested that $HTcO_4$ can even be reduced to H_2TcO_4 (a Tc^{6+} species) by H_2O. As stated above, in general, the Tc^{5+} and Tc^{6+} species are unstable and disproportionate into the more stable Tc^{4+} and Tc^{7+} species.

Further reduction of TcO_4^- solutions yields Tc^{4+} species (Vida, pp. 5-9; Rard, pp. 24-67). Owūnwanne et. al. discuss the formation of a hydrolyzed Tc^{4+} species with an overall charge of +2, most likely TcO^{2+} (Rard, pp. 24-67), by reduction of TcO_4^- with Sn^{2+} in perchlorate solutions of pH between 1.1 and 2.0. Further hydrolysis of TcO^{2+} to $TcO(OH)^+$ and $TcO(OH)_2^0$ is possible at a pH between 1.3 and 2.2. Dimerization of the $TcO(OH)_2^0$ species to $[TcO(OH)_2^0]_2$ is reported to occur by a pH of 2.7 (Rard, pp. 24-67). The equilibrium constants for the hydrolysis and dimerization of various Tc^{4+} species are summarized by Vida (pp. 5-9).

Still under reducing conditions, amorphous hydrated TcO_2, i.e., $TcO_2 \cdot 2H_2O$ (Rard, pp. 24-67; Pourbaix, 1976) or $TcO(OH)_2$ (Vida, pp. 5-9), precipitates to form a brown-black solid at pH values above 3 or 4 (Owunwanne et. al.; Spitayn et. al.). Furthermore, $TcO_2 \cdot 2H_2O$ has also been directly precipitated by coulometric reduction of TcO_4^- solutions above pH 3 (Rard, pp. 24-67; Mazzocchin et. al.).

Rard (pp. 24-67) has summarized the stability ranges of hydrolyzed Tc^{4+} species under reducing conditions: pH < 1.5, TcO^{2+}; 1.5 < pH < 2.2, $TcO(OH)^+$ and $TcO(OH)_2{}^0$; pH > 2.2, $TcO(OH)_2{}^0$ and $[TcO(OH)_2{}^0]_2$; pH > 3, precipitation of $TcO_2 \cdot 2H_2O$. Vida (pp. 5-9) summarizes that precipitates of $TcO(OH)_2$, i.e., $TcO_2 \cdot 2H_2O$, form above a pH of 2 under reducing conditions. Rard, however, cautions the interpretation of electrochemical data for technetium species for a variety of reasons: e.g., the thermodynamic irreversibility of many of the involved redox couples, the ambiguous nature of many of the oxidized or reduced species, and the interference of catalytically discharged hydrogen.

3.5.2.3 *Formation and Stability of Halo and Oxyhalo Species*

Reduction of TcO_4^- by aqueous HCl occurs at all HCl concentrations. Reduction is extensive and fast at HCl concentrations above approximately 5 mol/l, whereas below this value, reduction rate drops rapidly with decreasing HCl concentration (Rard, pp. 24-67). Increasing the temperature also increases the rate of TcO_4^- reduction. It should be noted for reference that HBr reduces TcO_4^- more rapidly than HCl and that small amounts of Br^- added to HCl solutions also tends to increase the reduction rate (Rard, pp. 24-67).

Initially, TcO_4^- is reduced by HCl (and HBr) to the Tc^{5+} oxyhalo anions, $TcOCl_4^-$ and $TcOCl_5^{2-}$, followed by a slower reduction to the Tc^{4+} halo anion $TcCl_6^{2-}$. This later reduction has been reported to require up to two-years to produce chromatographically pure $TcCl_6^{2-}$ (Rard, pp. 24-67).

In contrast, HI reduces TcO_4^- directly to TcI_6^{2-} under most conditions. However, ion exchange reactions between I^- and $TcOCl_4^-$ and $TcOBr_4^-$ are known to occur yielding $TcOI_4^-$. Also, adding I^- to HCl solutions causes instantaneous reduction of TcO_4^- to the Tc^{4+} specie $Tc(OH)Cl_5^{2-}$.

Solid salts of technetium halo anions have been reported to exist (Rard, pp. 3-24; Schwochau), in particular K^+, Rb^+, Cs^+, and NH_4^+ salts of TcF_6^{2-} and $TcCl_6^{2-}$. In general, these salts have low solubilities (10^{-2}-10^{-4} mol/kg) in solutions of their corresponding hydrohalic acids (Rard, pp. 3-24).

$MTcF_6$ (Tc^{5+}), K_2TcI_6 (Tc^{4+}), and K_2TcI_3 (Tc^{+}) compounds have also been reported to exist, none of which were stable in aqueous solutions (Rard, pp. 3-24). Various technetium oxyhalo salts have also been prepared. Again, most of these compounds were unstable in aqueous environments, disproportionating into $TcO_2{\cdot}2H_2O$ and TcO_4^- (Rard, pp. 3-24). The solid oxyhalides, TcO_3F and $TcOF_4$, have been prepared by the reduction of TcO_4^- by anhydrous HF (Peacock, 1973). Technetium (and rhenium) oxyhalides in general, readily hydrolyze in basic aqueous environments to give pertechnetic acid and hydrohalic acid (Peacock, 1966).

Additional information relevant to the chemistry of a large variety of other halo and oxyhalo technetium compounds in general are summarized by Rard. Although their existence in LLW solutions can not be completely ruled out, the relevance of all of these species is questionable due to the oxidizing aqueous solution environments encountered (see below).

3.5.3 Aqueous Solution Chemistry at Elevated Temperatures

In saturated aqueous pertechnetic acid solutions, $HTcO_4$ is described as being easily volatilized, the vapor pressure being about 4 torr at 50°C (323K) and about 60 torr at 100°C (373K) (Vida, pp. 5-9). Colton summarized the vapor pressure, p in torr, of a saturated solution of pertechnetic acid as a function of absolute temperature with the equation

$$\log(p)\ [\text{torr}] = [-2375/T] + 8.201 \qquad (3.5.3.1).$$

This equation gives a vapor pressure of 7 and 68 torr at 323 and 373K, respectively, and is in good agreement with those values reported above. However, in waste stream simulants containing, among other things, lower concentrations of technetium (2.2×10^{-2} mol/l), Cains et al. did not observe (or was beyond the limit of detection) volatilization of technetium (or cesium) species at temperatures of 116-121°C (389-394K).

Red crystals of $Tc_2O_7{\cdot}H_2O$, also referred to as anhydrous $HTcO_4$, ultimately form by concentrating aqueous $HTcO_4$ solutions over concentrated H_2SO_4 (Rard, pp. 3-24; Boyd et. al., 1952). Additionally, as discussed in section 3.5.2.1, pertechnetic acid can be neutralized by most cations to form pertechnetate salts with various solubilities in aqueous environments. Concentrating solutions containing the pertechnetate anion and appropriate cations is expected to cause precipitation of those pertechnetate salts with the lowest solubility products, e.g., $RbTcO_4$ and $CsTcO_4$. Based on similarities in solubility, analogous behavior is expected for perrhenate species.

Precipitation of Tc^{4+} species will occur under conditions were oxidation to Tc^{7+} species can be prevented. For aqueous solutions containing only technetium species, the various hydrolyzed forms of Tc^{4+}, i.e., TcO^{2+}, $TcO(OH)^+$ $TcO(OH)_2{}^0$ and $[TcO(OH)_2{}^0]_2$, are expected to hydrolyze further during solution heating, eventually leading to the precipitation of $TcO_2{\cdot}2H_2O$.

From the discussion in section 3.5.2.3 it follows that under sufficiently reducing conditions in hydrohalic acid (i.e., HCl, HF, HI) solutions, various solid technetium (and rhenium) halide and oxyhalides as well as halo and oxyhalo salts can form during solution concentration. The stability of these precipitated species in excess LLW solution, however, is questionable. The Tc^{5+} and Tc^{3+} salts as well as K_2TcI_6 will most likely not be stable in the oxidizing, low concentration hydrohalic acid aqueous environments present in typical LLW streams. Furthermore. the halides and oxyhalides as well as the oxyhalo technetium salts hydrolyze in aqueous environments. Although similar in nature to the salts discussed above, it is not evident what the stability of the M_2TcF_6 and M_2TcCl_6 salts (Tc^{4+} species) would be under similar conditions.

3.5.4 Solid-State and Melt Chemistry

3.5.4.1 *Technetium heptoxide, Tc_2O_7*

With a melting point of approximately 119°C (392K) and a boiling point of 311°C (584K), bright yellow crystalline Tc_2O_7 is easily volatilized. Providing technetium with its most stable valence state, +7, Tc_2O_7 is expected to be the end oxidation product of many technetium compounds. **Table 3.5.4.1.1** summarizes the melting and boiling temperatures as well as the volatility data available for this compound and its rhenium analog, Re_2O_7. The available thermodynamic data of these compounds are summarized in **Table 3.5.4.1.2.**

Table 3.5.4.1.1. Available melting point (T_m), boiling point (T_b), and volatility data for Tc_2O_7 and Re_2O_7. The estimated vapor pressure, p (torr), fitted to the available data is given by $\log p = [-A/T] + B$.

Compound	State	Reference	T_m (°C)	T_b (°C)	A	B
Tc_2O_7	solid	Colton	119.5	-	7205	18.28
	liquid	Colton	-	310.6	3571	8.999
	-	Rard	119.5	310.8	NA	NA
	-	Vida	118.4	310.6	NA	NA
Re_2O_7	solid	Ogawa	297	-	7218	14.84
	liquid	Ogawa	-	363	3920	9.047
	solid	Smith	300.3	-	7320	15.01
	liquid	Smith	-	360.3	3868	8.98

NA = not available
- = not applicable.

Table 3.5.4.1.2. Thermodynamic properties of Tc_2O_7 and Re_2O_7.

Property	Tc_2O_7		Re_2O_7	
	Value	Reference	Value	Reference
ΔG_f (kJ/mol)	-935.6 (s) -888.5 (g)	Rard Rard	-1067 (s)	Colton
ΔH_f (kJ/mol)	-1110 (s) -1120 (s) -987.4 (g)	Colton Rard Rard	-1241 (s)	Boyd
ΔS (J/mol-K)	166.0 (s) 449.4 (g)	Rard Rard	207.3 (s) 439.3 (g)	Busey Busey
ΔG_{sub} (kJ/mol)	48.1	Rard	NA	-
ΔH_{sub} (kJ/mol)	132.6	Rard	138.3 140	Ogawa Smith
ΔS_{sub} (J/mol-K)	283.4	Rard	244	Smith
ΔH_{fus} (kJ/mol)	NA	-	61.13 66.1	Ogawa Smith
ΔS_{fus} (J/mol-K)	NA	-	115	Smith
ΔH_{vap} (kJ/mol)	NA	-	75.10 74.1	Ogawa Smith
ΔS_{vap} (J/mol-K)	NA	-	117	Smith

NA = not available
- = not applicable.

3.5.4.2 *Pertechnetates, $M^{(x)}[TcO_4]_x$*

Pertechnetates and perrhenates include a broad range of compounds involving the pertechnetate or perrhenate anion bound to a cation, and have previously been discussed in section 3.5.2.1. The thermodynamic properties available for some of the pertechnetates and perrhenates are summarized in **Table 3.5.4.2.1** (Vida, pp. 26-50).

Volatility data for the pure alkali metal pertechnetates listed in Table 3.5.4.2.1 are not available. Vida (pp. 26-50), however, discusses the decomposition of $2CsTcO_4$ (liquid) to Cs_2O (gas) and Tc_2O_7 (gas). The volatility of Tc_2O_7 has been discussed above in section 3.5.4.1, and may ultimately limit the volatility of $CsTcO_4$. Vida as well as Cains et al. discuss the highly volatile nature of Cs_2O - nearly three orders of magnitude higher than other alkali metal oxides under similar conditions. Hence, although $CsTcO_4$ has the highest melting point of the pertechnetates listed in Table 3.5.4.2.1, its highly volatile decomposition products makes this particular pertechnetate highly volatile in general. Vida (pp. 26-50) reports that for a range of pertechnetates added to borosilicate glass frits, volatilization of technetium from the glass melt was highest for $CsTcO_4$.

Table 3.5.4.2.1. Available melting point (T_m), boiling point (T_b), and thermodynamic properties of pertechnetates and perrhenates.

Cation	Anion						
	TcO_4^-			ReO_4^-			
	T_m (°C)	ΔH_m (kJ/mol)	ΔS_m (J/mol)	T_m (°C)	T_b (°C)	T_m (°C)	ΔH_m (kJ/mol)
Na^+	378	21	32.3	≈300	NA	420	33
Li^+	401	23	34.1				
Fe^{3+}				NA	705[a]		
K^+	532	31	38.5	550	1095[b]	555	36
Rb^+	581	31	36.3				
Cs^+	595	35	40.3			620	34
Ca^{2+}				≈1040	NA		
Ref.	Vida			Lebedev		Lukas	

[a] Value extrapolated from vapor pressure data given by Lebedev.

[b] Boiling point extrapolated from vapor pressure data given by Lebedev is 1092°C. The text indicates a boiling point of 1370°C which is most likely a typographical or translational error. It was assumed that the reported boiling point should be 1370K (1097°C). The value indicated in Table 6 is an average of the two values.

NA = not available.

Solid pertechnetic acid, $HTcO_4$, has also been reported to decompose to H_2O and Tc_2O_7 (Colton). The vapor pressure of (presumably) H_2O over the solid pertechnetic acid as a function of absolute temperature has been determined to follow the relation

$$\log(p)\ [\text{torr}] = [-2395/T] + 8.207 \qquad (3.5.4.2.1).$$

3.5.4.3 *Hydrated and Anhydrous Technetium Dioxide, TcO_2.*

As stated above, under reducing conditions, Tc^{4+} species can hydrolyze, causing precipitation of amorphous hydrated TcO_2, i.e., $TcO_2 \cdot 2H_2O$. The free energy of formation of this compound has been determined to be -836.3kJ/mol (Rard, pp. 3-24). It has been reported that crystalline anhydrous TcO_2 can be prepared by thermal decomposition of the ammonium pertechnetate, NH_4TcO_4, in an inert atmosphere (Rard, pp. 3-24). $TcO_2 \cdot 2H_2O$ can be dehydrated to yield TcO_2 under similar conditions. The analogous reactions occur in the rhenium system (Colton).

Both TcO_2 and ReO_2 are very stable compounds. The only thermodynamic data available is for the heat of sublimation of the rhenium: 274.6kJ/mol (Colton). The vapor pressure of ReO_2 as a function of absolute temperature has been determined to follow the relation (Colton):

$$\log(p)\ [\text{torr}] = [-14{,}437/T] + 11.65 \qquad (3.5.4.3.1).$$

3.5.4.4 *Technetium Halides, $Tc^{(z)}X_z$ and Oxyhalides, $Tc^{(z)}O_yX_{z-2y}$ and Their Corresponding Salts*

The available volatility data for various technetium and rhenium fluorides and oxyfluorides are summarized in **Table 3.5.4.4.1.** In general, technetium (and rhenium) fluorides and oxyfluorides are extremely volatile and certainly may provide a vehicle for technetium volatility.

Not much information has been published on the analogous chlorides, oxychlorides, iodides, and oxyiodides. The limited information and comments on the chloride and oxychloride systems are summarized in **Table 3.5.4.4.2.**

3.5.5.5 *Technetium Volatility from Melts*

Vida reviewed the technetium volatility data obtained for various melt processes and sources of technetium. Although the details are unclear, Tc volatilization ranged from 6-75% for melt temperatures between 1000-1200°C. Baumgartner reports a Tc volatility of about 65% from a borosilicate-based glass melt at 1100°C. Decontamination factors (DFs) for technetium ranged from

Table 3.5.4.4.1. Available melting point (T_m), boiling point (T_b), and volatility data for technetium and rhenium fluorides and oxyfluorides. The estimated vapor pressure, p (torr), fitted to the available data is given by $\log p = [-A/T] + B - C\log T$.

Compound	State	T_m(°C)	T_b(°C)	A	B	C
ReF_7	solid	48.3	-	2206	13.04	1.470
	liquid	-	73.7	244.3	-21.6	-9.91
TcF_6	solid	37.4	-	3565	41.13	18.28
	liquid	-	55.3	2405	24.81	5.804
ReF_6	solid	18.7	-	1765	9.123	0.179
	liquid	-	33.8	1957	18.21	3.599
TcF_5	-	50	NA	NA	NA	NA
ReF_5	solid	48	-	NA	NA	NA
	liquid	-	221.3	3037	9.024	0.000
$ReOF_5$	solid[a]	35	-	1959	8.620	0.000
	liquid	-	55	1679	7.727	0.000
ReO_2F_3	solid	95	-	NA	NA	NA
	liquid	-	126	3437	10.36	0.000
$TcOF_4$	-	133	165	NA	NA	NA
$ReOF_4$	solid	108	-	3888	11.88	0.000
	liquid	-	171	3206	10.09	0.000
TcO_3F	solid	18.3	-	3239	12.45	0.000
	liquid	-	100	2065	8.471	0.000
ReO_3F	-	147	164	NA	NA	NA

[a] There is a solid-solid transformation at 30°C. This data is for the solid that exists between 30°C and 41°C.

Table 3.5.4.4.2. Available information for selected technetium and rhenium chlorides and oxychlorides.

Compound	State[a]	Comments
$TcCl_6$	solid	Melts at 25°C. Quite volatile.
$ReCl_6$	solid	Melts at 25°C. Volatile.
$ReCl_5$	solid	Melts at 220°C.
$TcCl_4$	solid	-
$ReCl_4$	solid	Readily hydrolyzed by moisture.
$ReCl_3$	solid	Nonvolatile.
$TcOCl_3$	solid	Nonvolatile.
$TcOCl_4$	solid	-
$ReOCl_4$	solid	Melts at 29-34°C, boils 223-225°C. Hygroscopic.
TcO_3Cl	liquid	-
ReO_3Cl	liquid	Boils at 128-131°C. Hygroscopic.

[a] Stable state at room temperature.

about 1.5 to 17 for both of these references. In general, adding a reductant (e.g. Si, C, sugar, etc.) to the waste solution and/or to the melt decreased the volatility of technetium significantly. This is certainly reasonable considering the literature that was just reviewed above: keeping the technetium in a lower oxidation state generally lowers its volatility (e.g., TcO_2 vs Tc_2O_7).

4.0 TECHNETIUM AND RHENIUM VOLATILITY TESTING

4.1 Procedure

4.1.1. Batched Oxide/Carbonate Studies

The base glass used for these studies was L6-5412, the theoretical final composition of which is summarized in **Table 3.1.2.** Technetium or rhenium was added to the batched glass as NH_4TcO_4 or NH_4ReO_4 in appropriate amounts to yield 0.01 or 0.001 wt% Tc/Re. The batched glass additives were placed in a platinum crucible with the lid partially covering the crucible. The crucible and glass batch were placed in a furnace at room temperature and heated in air to temperature at a rate of 10°C/min. Once at temperature the melt was either quenched immediately or allowed to dwell at the temperature for 30 minutes before quenching. The resulting cooled glasses were then analyzed for Tc or Re using ICP-AES.

4.1.2. DSSF-Glass Precursor Slurry Studies

The desired final base-glass composition for this work was that of L6-5412. To achieve this to a first approximation, the glass composition given in **Table 3.1.2** was divided into two sets of components: those that are expected for the nominal LLW stream and those from the glass precursor additives (Table 3.1.2). A LLW loading of 27 wt% in the final glass was targetted, which corresponded to a mixture of 10.0 mL DSSF 10N Na simulant per 10.28 grams of glass forming additives. When required, NH_4ReO_4 was spiked directly into the DSSF simulant to yield a 0.01wt% Re (a technetium surrogate) loading in the final glass.

The DSSF-glass former slurry was placed in a Coors CN180 cylindrical alumina crucible and dried at temperatures ranging from 90 to 120°C for 24 hours. The dried slurries were then heated at 1000°C for 30 minutes.

Work was performed on the Re spiked samples to study the drying, calcining, and foaming behavior of the system without the worry of radiaoctive contamination.

4.2 Results and Discussion

4.2.1. Batched Oxide/Carbonate Studies

The results of the technetium and rhenium volatility studies from batched oxide/carbonate melts are summarized in **Table 4.2.1.1.** Technetium and rhenium volatilities, based on the difference between the starting and ending concentrations, are extremely high (>95%) for samples held at temperatures for 30 minutes. Volatilization of technetium was slightly lower when the samples were immediately quenched upon reaching the target temperature. Regardless, the lowest volatility of Tc (80%) was obtained at 900°C with no dwell time.

Table 4.2.1.1. Experimentally determined volatility data (including decontamination factors, DFs) for Tc and Re in L6-5412 based glas melt systems.

Melt temperature (°C)	Time at melt temperature (mins)	% Tc Volatilized	% Re Volatilized
900	0	79.8±3.2 (DF=1.25)	NP
900	30	98.3±0.3 (DF=1.02)	97.9±0.3 (DF=1.02)
1150	30	99.0±0.2 (DF=1.01)	98.6±0.2 (DF=1.01)
1350	0	89.8±1.6 (DF=1.11)	NP
1350	30	99.3±0.1 (DF=1.01)	99.2±0.1 (DF=1.01)

NP = experiment not performed

4.2.2. DSSF-Glass Former Slurry Studies and Implications

In contrast to the oxide/carbonate (dry-batched) feed, where ≈98±1% of the Re was lost during melting at 900°C, using a dried simulated DSSF/glass precursor feed, which most closely resembles the actual Hanford LLW material, the amount of Re lost during melting at 1000°C was only 40±6%. There are obvious differences between these two feeds which must ultimately be effecting the volatility of the rhenium during vitrification. Although these differences demonstrate the need for the careful designing of tests, they also reflect on possible means of preventing rhenium (and technetium) volatilization during vitrification:

First, the dry-batched feed contains NH_4ReO_4, whose Re_2O_7 oxidative-decomposition product becomes highly volatile above ≈300°C (i.e., above its melting point). The DSSF-based feed initially contains $CsReO_4$ (see above), which doesn't become significantly volatile until it melts at ≈600°C.

Secondly, $NaNO_3$ melts at 320°C and would form the bulk of the liquid phase at low temperatures during vitrification of the DSSF-based feed. In the dry-batched feed, however, the Na_2CO_3 wouldn't melt until 850°C. Although lower temperature eutectics can form between Na_2CO_3 and a host of other components in the batch, significant liquid phase formation will generally occur at higher temperatures for the dry-batched feed compared to that for the DSSF-based feed. Thus, the densification of the feed from a collection of glass precursor particles having open porosity to a more consolidated viscous melt containing closed pores (i.e., bubbles) will occur at lower temperatures for the DSSF-based feed compared to that of the dry-batched feed. In general, for a given base-glass feed, increasing the point of high volatility (e.g., melting point) of the technetium/rhenium source and lowering the consolidation temperature of the melt will shorten the time during which there exists both a high vapor pressure of technetium/rhenium-containing species and an unconsolidated glass precursor material consisting of open, high surface area pores through which volatilized and/or entrained species can readily escape.

Lastly, the DSSF-based feed contains organics—specifically, EDTA. The presence of organics during calcination and melting will have a significant effect on the redox properties of the system and will ultimately influence Re and Tc volatility.

4.3 Conclusions

It is clear from the batched oxide/carbonate results that Tc volatilization is extreme, even for temperatures as low as 900°C. This supports the evidence presented in the above literature review that the chemistry occuring at low temperatures (below about 600°C) dictates the volatility at higher temperatures. Also, Re appears to parallel the volatility behavior of Tc well under these conditions.

Through a review of the literature and of our own experimental data, we have concluded that the use of rhenium as a surrogate for technetium is well substantiated. Due to their similarity in chemistry, homologous rhenium compounds should occur in dried Hanford LLW simulants ($CsReO_4$) and in the liquid ($CsReO_4$, $KReO_4$, and $NaReO_4$) and vapor (Re_2O_7 and $ReO_3(OH)$) phases during vitrification. The thermal stabilities and volatilities of the technetium and analogous rhenium compounds were found to be very similar.

The methods employed to test the volatility of technetium and rhenium during LLW and LLW simulant vitrification were found to be important as well. Test feeds that did not chemically model the actual melter feed produced volatility results that were very different than those obtained from actual vitrification runs. Feeds that contained precursors to highly volatile technetium and rhenium compounds (i.e., NH_4TcO_4 and NH_4ReO_4) yielded glasses after vitrification that contained less than 3% of the original technetium and rhenium. Properly simulated feeds containing $CsReO_4$, $NaNO_3$, KNO_3, C, etc. after drying were vitrified into glasses containing at least 64% of the original rhenium.

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