



Reactions during melting of low-activity waste glasses and their effects on the retention of rhenium as a surrogate for technetium-99



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ABSTRACT

Volatile loss of radioactive technetium-99 (⁹⁹Tc) to off-gas is a major challenge when vitrifying low-activity waste (LAW) at the U.S. Department of Energy's Hanford Site in Washington State. We investigated the partitioning and incorporation of rhenium (Re) (a nonradioactive surrogate for ⁹⁹Tc) into the glass melt during crucible melting of two simulated LAW feeds that have exhibited a large difference in ^{99m}Tc/Re retention in glass from small-scale melter tests. Each feed was prepared from a simulated liquid LAW and additives (boric acid, silica sand, etc.). The as-mixed slurry feeds were dried at 105 °C and heated to 600–1100 °C at 5 K/min. The dried feeds and heat-treated samples were leached with deionized water for 10 min at room temperature followed by 24-h leaching at 80 °C. Chemical compositions of the resulting solutions and insoluble solids were analyzed. Volume expansion measurements and X-ray diffraction (XRD) analyses were performed on dried feeds and heat-treated samples to characterize the progress of feed-to-glass conversion reactions. We found that incorporation of Re into the glass melt was virtually completed during the major feed-to-glass conversion reactions that occurred at ≤700 °C. The results of our study suggest that the different compositions of the salt phases formed during early stages of melting at ≤700 °C are responsible for the large difference in Re incorporation into the glass melt in these two feeds.

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1. Introduction

Approximately 210,000 m³ of radioactive and chemically hazardous wastes, which are byproducts of approximately 45 years of plutonium production, is currently stored in underground tanks at the U.S. Department of Energy's Hanford Site in Washington State. The current cleanup plan is to separate the tank wastes into high-volume, low-activity waste (LAW) and low-volume, high-level waste (HLW) fractions that will then be vitrified into separate glass waste forms for long-term storage [1–3]. The LAW, a processed aqueous solution from tanks, primarily consists of sodium nitrates and nitrites with other salts/hydroxides and organics that vary from tank to tank (see an example composition given in Schonewill et al. [4]). Vitrifying the large amount of the LAW is one of the primary missions of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) that currently is under construction. To immobilize the hazardous waste into a stable glass waste form, the LAW will be mixed with specifically designed glass-forming and modifying additives consisting of silica, boric acid, and other chemicals/minerals, and the mixture then will be vitrified.

One of the main radionuclides of concern in Hanford LAW is technetium-99 (⁹⁹Tc) [5–7]. The environmental concern with ⁹⁹Tc is

its high mobility in subsurface soils and long half-life (2.1×10^5 year). The highly soluble TcO_4^- does not adsorb well onto the surface of minerals [8–10] and, thus, migrates nearly at the same velocity as groundwater [11]. More importantly, the primary concern with processing the ⁹⁹Tc-containing waste into a glass is its extreme volatility, which results in low concentrations of Tc retained in the final product relative to target concentrations [12–16]. Recent small-scale melter tests with seven representative Hanford LAW glass feeds (simulated waste plus additives) for the WTP showed that the fraction of technetium retained in glass (referred to as retention) varied from 18% to 66% depending on the feed composition [12–14]. Although the volatilized ⁹⁹Tc can be captured in the off-gas treatment system and recycled to the melter to increase the retention, the recycle stream also contains other volatile components such as sulfur (S), chlorine (Cl), and fluorine (F) that decrease the loading of waste in the glass [17] and, thus, increase the glass volume. Maximizing the incorporation of ⁹⁹Tc into glass is desirable also to minimize the fraction that needs to be treated as a secondary waste and disposed in non-glassy waste forms [18,19].

Rhenium (Re) has been the preferred nonradioactive ⁹⁹Tc surrogate because of the similarities of Re to ⁹⁹Tc in chemistry, ionic size, speciation in glass, and volatility in glass [20]. It is known that Re and ⁹⁹Tc behave differently when redox reactions are involved because of the differences in reduction potentials of Re^{7+} and Tc^{7+} [21–24], yet the chemistry of the two elements is similar when in the same oxidation

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state. Kim et al. [21] investigated the behavior of ^{99}Tc and Re during crucible melting of simulated Hanford LAW glass feeds designed for bulk vitrification technology demonstration. For the two feed compositions treated without reducing agents, ^{99}Tc and Re showed the same trends for partitioning into salt phase, volatilization during melting, and retention in glass. However, for the two feeds modified to provide reducing conditions, ^{99}Tc and Re showed different reaction characteristics resulting in higher retention of ^{99}Tc in glass than Re, which confirmed that Re is not a suitable surrogate for ^{99}Tc when redox reactions are involved. The small-scale, Joule-heated melter tests by Matlack and coworkers [12–14] showed a similar trend for the retention of $^{99\text{m}}\text{Tc}$ (a short-lived technetium isotope as a surrogate of ^{99}Tc) and Re in the seven representative Hanford LAW glasses they processed.

Previous studies [25,26] employed a vacuum-sealed fused silica ampoule setup to measure the solubility of Re and ^{99}Tc in a representative LAW glass. The measured solubility was 3000 ppm mass for Re (used as surrogate for Tc) [25] and 2000–2800 ppm mass for ^{99}Tc [26] (both on metal basis) at 1000 °C. Given the projected concentration of ^{99}Tc in LAW glass at Hanford is ~3 ppm mass on average [26]; the solubility of ^{99}Tc is not a factor in its retention in LAW glass. In addition, the structural role of Re and Tc in glass network was discussed in Goel et al. 2013 [27] and Gassman et al. 2014 [28].

A series of studies is being performed to understand the mechanism of Re/Tc escape from, or incorporation into, the glass melt during melting of Hanford LAW glass feeds. The goal is to eventually develop methods that will increase ^{99}Tc retention. Two simulated melter feeds (AN-102 and AZ-102) that showed a large difference in Re and $^{99\text{m}}\text{Tc}$ retention in glass from the small-scale melter tests [12–14] were selected for the initial studies. The AN-102 feed showed a $^{99\text{m}}\text{Tc}$ retention of 19% and a Re retention of 27%, while the AZ-102 feed showed a $^{99\text{m}}\text{Tc}$ retention of 66% and a Re retention of 57%. The objective of this study is to identify the major factors that differentiate Re/Tc retention between these two feeds.

Our study focuses on the details of Re (used as a surrogate for ^{99}Tc) behavior during crucible melting of the melter feeds under oxidizing conditions (i.e., without addition of reducing agents) so that Re can be reasonably used as a surrogate for ^{99}Tc . The two selected LAW glass feeds were heat treated in an open crucible to investigate the partitioning and distribution of Re as a function of temperature. A three-step leaching of heat-treated samples was performed to separate the water soluble phases from the unreacted mineral and glass-forming phases (insoluble). Information on the Re partitioning into different phases and Re retention in glass was obtained by chemical analyses of leach solutions and remaining insoluble solids. To evaluate the effect of feed melting reactions on the Re partitioning or distribution, the two selected feeds also were characterized for mass change, volume change, and crystalline phase evolution as a function of temperature using the techniques previously applied for feed melting studies [29–34].

2. Materials and methods

2.1. Composition of simulated waste glass feeds

The compositions of simulated waste and additives for the AN-102 and AZ-102 glass feeds are shown in Table 1. These compositions were obtained by modifying melter feeds used in the small-scale melter tests by Matlack et al. [13,14] based on the purity and composition of the chemicals and minerals used in this study. AN-102 is a high-nitrate, medium-sulfate waste, and AZ-102 is a low-nitrate, high-sulfate waste. The LAW glasses designed to immobilize the wastes were correspondingly named as AN-102 glass (designated as LAWE7H by Matlack et al. [13,14]) and AZ-102 glass (LAWE10H) for convenience. The target Re concentration in both glasses is 8.1 ppm (mass fraction, as Re metal), a molar equivalent to 4.3 ppm ^{99}Tc , which was used in a previous study [21] as a typical ^{99}Tc concentration in Hanford LAW glasses.

Table 1
Compositions of AN-102 and AZ-102 melter feeds for 1 L of simulated waste [14].

Component	AN-102	AZ-102
<i>Simulated LAW (g/L)</i>		
Al(NO ₃) ₃ ·9H ₂ O	87.97	1.75
H ₃ BO ₃	0.10	-
Ca(NO ₃) ₂ ·4H ₂ O	1.46	-
Na ₂ CrO ₄ ·4H ₂ O	2.76	3.46
KOH	7.38	9.21
NaOH	52.88	3.16
NiO	0.09	0.11
PbO	0.09	0.11
SiO ₂	0.10	0.37
NaCl	3.72	4.65
NaF	1.97	2.46
Na ₃ PO ₄ ·12H ₂ O	7.56	9.39
Na ₂ SO ₄	12.07	20.32
NaNO ₂	64.80	35.51
NaNO ₃	94.65	9.68
Na ₂ CO ₃	49.21	40.97
Sodium formate (NaHCO ₂)	24.90	-
Sodium oxalate (Na ₂ C ₂ O ₄)	1.44	-
Glycolate (C ₂ H ₄ O ₃)	30.60	-
Citric acid (C ₆ H ₈ O ₇)	8.98	-
Oxalic acid (C ₂ H ₂ O ₄ ·2H ₂ O)	-	3.21
Re ₂ O ₇	0.0121	0.0151
Water (estimated)	792.96	975.01
<i>Additives (g/L simulated waste)^a</i>		
Kyanite (Al ₂ SiO ₅)	98.73	149.71
H ₃ BO ₃	200.58	252.97
Wollastonite (CaSiO ₃)	155.51	215.41
Hematite (Fe ₂ O ₃)	59.46	71.71
Li ₂ CO ₃	89.87	150.93
Olivine (Mg ₂ SiO ₄)	35.54	87.65
Na ₂ CO ₃	-	34.02
Quartz (SiO ₂)	362.31	472.28
Rutile (TiO ₂)	15.22	18.82
Zincite (ZnO)	39.63	49.81
Zircon (ZrSiO ₄)	50.83	64.17
Total dry feed mass ^b (g)	1560.4	1711.9
Target glass mass (g)	1145.3	1431.4
Calculated mass loss ^c	26.6%	16.4%

"-" indicates zero value.

^a These values represent the amounts of additives mixed into 1 L of as-prepared simulated waste (i.e., the feed volume increases after adding the additives).

^b Sum of all simulated waste chemicals plus additives excluding estimated water.

^c A difference between the total dry mass of feed components and target glass mass divided by the total dry mass of feed components.

For the simulated waste, each chemical was added to deionized (DI) water in a predetermined order and was allowed to dissolve completely before the next chemical was added to ensure that all components are fully dissolved. A mix of additive chemicals/minerals was added to the simulated waste to prepare the slurry feeds (also referred to as "melter feed" or "glass feed;" equivalent to "glass batch" in commercial glass production). The slurry feed then was thoroughly mixed and dried at 105 °C for 12 h to obtain the "dried feed" used in various tests described below.

2.2. Pellet test

Dried feed was prepared as cylindrical pellets to monitor the volume change during heating according to the methods developed for the feed melting studies by Hirma and others [29,30]. Pellets were made by uni-axial pressing 1.5 g of dried feed at 7 MPa. Each pellet was 13 mm in diameter and ~6 mm high. Pellets placed on an alumina plate were heated at 5 K/min and photographed through a window in the furnace at a 10–50 °C interval depending on the temperature range. The images were evaluated in Photoshop® to obtain the area profiles of samples as a function of temperature.

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