



## Review

## Volatile species of technetium and rhenium during waste vitrification

Dongsang Kim<sup>a,\*</sup>, Albert A. Kruger<sup>b</sup><sup>a</sup> Pacific Northwest National Laboratory, Richland, WA 99352, United States<sup>b</sup> U.S. Department of Energy, Office of River Protection, Richland, WA 99352, United States

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## ABSTRACT

Volatile loss of technetium (Tc) during vitrification of low-activity wastes is a technical challenge for treating and immobilizing the large volumes of radioactive and hazardous wastes stored at the U.S. Department of Energy's Hanford Site. Various research efforts are being pursued to develop technologies that can be implemented for cost effective management of Tc, including studies to understand the behavior of Tc during vitrification, with the goal of eventually increasing Tc retention in glass. One of these studies has focused on identifying the form or species of Tc and Re (surrogate for Tc) that evolve during the waste-to-glass conversion process. This information is important for understanding the mechanism of Tc volatilization. In this paper, available information collected from the literature is critically evaluated to clarify the volatile species of Tc and Re and, more specifically, whether they volatilize as alkali pertechnetate and perrhenate or as technetium and rhenium oxides after decomposition of alkali pertechnetate and perrhenate. The evaluated data ranged from mass spectrometric identification of species volatilized from pure and binary alkali pertechnetate and perrhenate salts to structural and chemical analyses of volatilized materials during crucible melting and scaled melter processing of simulated wastes.

## 1. Introduction

Large volumes of radioactive and hazardous wastes generated during > 45 years of plutonium production are stored in underground tanks at the U.S. Department of Energy's (DOE) Hanford Site in Washington State. Treatment of these legacy wastes involves separation into high-volume, low-activity waste (LAW) and low-volume, high-level waste (HLW) fractions. Both waste fractions will then be vitrified into separate borosilicate glass waste forms at the Hanford Waste Treatment and Immobilization Plant (WTP) that currently is under construction [1–3]. The immobilized HLW will be transported to a deep geologic repository when such a location becomes available while the immobilized LAW will be stored at the onsite in the Hanford Integrated Disposal Facility (IDF) [1–3].

Hanford LAWs are aqueous solutions that vary in composition from tank to tank. The solutions consist of Na<sup>+</sup> and K<sup>+</sup> as the major cations; various anions including NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, OH<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, Al(OH)<sub>4</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>; organics, and other minor ionic species (see references [4,5] for various simulated LAW compositions). The major radionuclides that are of concern are water soluble and, therefore, primarily partition to LAW are Cs-137, I-129, and Tc-99. However, Cs-137 will be removed from aqueous solution via ion exchange as a part of the pretreatment process and sent to the HLW stream [6]. The

liquid LAW will be mixed with specifically designed additives consisting of silica sand and boric acid as the main ingredients and other chemicals and minerals (e.g., lithium carbonate, hematite, kyanite, wollastonite, zincite, and zircon) [7]. The slurry mixture, referred to as “melter feed,” “glass feed,” or in short “feed,” then will be processed in the Joule-heated ceramic melter into a glass waste form.

Both Tc and I are semi-volatile, and a large fraction of each evaporates during vitrification in the melter, which operates at a nominal temperature of 1150 °C [5,8,9]. Small-scale melter tests with simulated Hanford LAW glass feeds have shown that the fraction retained in glass (referred to as “retention”) varied from 18% to 66% for Tc (tested with Tc-99m, a short-lived isotope as a surrogate for Tc-99) and from 1% to 56% for I (tested with nonradioactive I) depending on the feed composition [10–13]. A large fraction of volatilized I is expected to pass through the primary WTP off-gas treatment system (i.e., submerged bed scrubber and wet electrostatic precipitator) [5]. This I fraction will be captured downstream in other off-gas treatment system components (e.g., carbon beds) and sent to the IDF [14]. On the other hand, almost all (> 98%) of the Tc that leaves the melter is expected to be captured by the primary off-gas system.

The environmental concern with Tc-99 is its high mobility in subsurface soils and long half-life (2.1 × 10<sup>5</sup> y). The highly soluble TcO<sub>4</sub><sup>-</sup> does not adsorb well onto the surface of minerals [15–18] and, thus,

\* Corresponding author.

E-mail address: [dongsang.kim@pnnl.gov](mailto:dongsang.kim@pnnl.gov) (D. Kim).

migrates nearly at the same velocity as groundwater [19]. Previous studies [20–22] have shown that Tc-99 is a major dose contributor to the IDF Performance Assessment. However, once immobilized in the glass waste form, the estimated Tc concentration in groundwater is predicted to be a few orders of magnitude lower than the benchmark concentration [14]. Therefore, the baseline WTP plan has been to recycle the off-gas stream that contains volatilized Tc back to the melter through a pretreatment facility to maximize the final retention of Tc in glass product. A negative impact of this off-gas recycle strategy is that the off-gas stream also sends other volatile components such as S and Cl back to the melter. These components are known to limit the loading of waste in the glass [3,23–25] and, thus, decrease the fraction of waste from the tank farm in the glass product and increase the glass volume [26]. Therefore, a strategy or technology to immobilize Tc in the glass waste form without recycling the off-gas stream can be important for optimizing the waste treatment and disposal mission at DOE's Hanford site.

There have been a number of scaled melter tests to determine the effect of LAW feed compositions and melter processing parameters on the retention of Tc and Re (nonradioactive surrogate for Tc) in glass as a part of process enhancements for WTP [5,11,12,27]. In addition to scaled melter tests, various concepts and potential technologies are being explored to help develop strategies that can be used to manage Tc without recycling the off-gas stream from the WTP primary off-gas system. There are two main research areas being pursued: 1) separating and treating Tc from LAW or the off-gas scrub solution and 2) increasing Tc retention in glass. Research activities on Tc separations explore various materials that can selectively remove Tc from LAW or the off-gas scrub solution [28–39]. Depending on the Tc sources, i.e., LAW or the off-gas scrub solution, and on the properties of the Tc-capture materials, there are different potential routes in handling the Tc that has been removed [37]. Research activities to increase Tc retention in glass involve a series of studies that are being performed to understand the mechanism of Re/Tc escape from, or incorporation into, the glass melt during melting of Hanford LAW glass feeds [11,12,40–44]. These efforts build on experimental tests undertaken to investigate the solubility of Re and Tc in a typical LAW glass [45,46] and formation of Re and Tc salts [47–49]. This contribution is a part of this series of studies with the goal of eventually developing methods that can increase the Tc single-pass retention in glass.

One of the main questions important for understanding the Tc and Re volatilization mechanism is the form or species of Tc and Re that volatilize during melting of LAW glass feeds. Volatile species of Tc and Re also were discussed in a previous review on chemistry of all relevant Tc and Re species by Darab and Smith [50], however, the data available at the time were mostly from thermodynamic and mass spectroscopic studies of Tc- or Re-containing oxides and salts and some data from vitrification studies of European high-activity wastes (HAW). This article analyzes data available in the literature, including data reviewed by Darab and Smith [50], and more recent data from crucible melting and scaled melter tests relevant to vitrification of Hanford LAWs. The goal of the present review is to clarify the likely volatile Tc and Re species that evolve upon heating of Hanford LAW glass feeds to help understand the mechanism of Tc volatilization during vitrification.

## 2. Re surrogate for Tc

Rhenium has been the preferred surrogate for Tc [50–52] because of the similarities in chemistry, ionic size, speciation in glass, and volatility compared to other candidates such as Mn, W, Cr, Mo, or Ru. However, differences in reduction potentials between  $\text{Re}^{7+}$  and  $\text{Tc}^{7+}$  have been measured in glass melts [53] and in aqueous solutions [54–56], and therefore, different behaviors have been observed for Re and Tc under certain reducing conditions [51,57–59]. From crucible melting tests of simulated LAW glass feeds melted under prototypic oxidizing conditions, Kim et al. [51] and Luksic et al. [37] showed that

Tc and Re follow the same trends for partitioning into salt phases and final retention in glass. When the feeds were modified to provide highly reducing conditions, Tc and Re showed different partitioning characteristics and resulted in higher retention of Tc in glass than Re [51].

Lukens et al. [58] showed that Re is a good surrogate for Tc as long as relatively oxidizing condition is used, defined as a measured  $\text{Fe(II)/Fe(total)}$  ratio in the final glass less than approximately 0.1. In the study by Kim et al. [51] discussed earlier, the highly reducing feeds that resulted in different partitioning characteristics and glass retention between Tc and Re had a  $\text{Fe(II)/Fe(total)}$  ratio  $> 0.5$  in the samples heated from room temperature to 800 and 1200 °C at a 5 °C/min rate. In summary, if typical operating conditions for the WTP with air bubbling are considered, the redox condition is expected to be relatively oxidizing (i.e., in general exhibiting a  $\text{Fe(II)/Fe(total)}$  ratio  $< 0.1$ ); therefore, the behavior of Tc and Re in regard to partitioning characteristics and glass retention would be expected to be similar.

## 3. Volatile Tc and Re species

The primary chemical form of Tc found in Hanford LAW is the pertechnetate anion  $[\text{Tc(VII)O}_4^-]$ , although a significant but unknown (2% to 25%) fraction of Tc is present as soluble non-pertechnetate species such as Tc(I) carbonyl compounds [60,61]. It is possible that non-pertechnetate Tc species will become oxidized during the early stage of vitrification although this hypothesis needs to be experimentally confirmed. All crucible and small-scale melter tests with simulated LAW glass feeds to date have been performed with pertechnetate and/or perrhenate. Therefore, this review focuses only on volatilization of Tc(VII) and Re(VII), which narrows the potential volatile species as alkali pertechnetates/perrhenates and  $\text{Tc}_2\text{O}_7/\text{Re}_2\text{O}_7$  as described further below.

Similar to what Vida [62] discussed for his study of Tc volatilization from pertechnetate melt in contact with glass frit particles, which simulate the vitrification process of liquid HAW in the Joule-heated melter, two Tc species are theorized to volatilize during melting of Hanford LAW feeds. One possibility is the evaporation of alkali pertechnetate either from pure molten pertechnetate according to Reaction (1) or more likely from mixed salt (nitrates, sulfates, etc.) containing pertechnetate.



The other is volatilization of  $\text{Tc}_2\text{O}_7$  either from decomposition of pertechnetate melt (pure pertechnetate or mixed in salt) according to Reaction (2) or from reaction of pertechnetate melt (pure pertechnetate or mixed in salt) with other waste or additive components that are present in the LAW glass feed.



The same discussion is applicable to Re in terms of  $\text{MReO}_4$  and  $\text{Re}_2\text{O}_7$  where M represents alkali metals, Na, K, and Cs that are of interest for Hanford LAW vitrification.

The boiling points of liquid  $\text{Tc}_2\text{O}_7$  and  $\text{Re}_2\text{O}_7$  are 311 °C and 363 °C (50), respectively, while that of alkali pertechnetate/perrhenate is known only for  $\text{KTcO}_4$  at ~1000 °C [63] and  $\text{KReO}_4$  at 1095 °C [50,64]. The  $\text{Tc}_2\text{O}_7$  and  $\text{Re}_2\text{O}_7$  would rapidly boil off once formed from mixed salt at temperatures below 600 to 800 °C, which according to Jin et al. [41] is a temperature range of primary interest for Re incorporation into glass-forming melt during melting of Hanford LAW glass feeds. Therefore, the question narrows to whether the formation of  $\text{Tc}_2\text{O}_7$  or  $\text{Re}_2\text{O}_7$ , that is, decomposition of  $\text{MTcO}_4$  or  $\text{MReO}_4$ , occurs or not during early stage of feed melting processes. The observation by Jin et al. [41] that there was no noticeable Re loss below 600 °C suggests that decomposition of  $\text{MReO}_4$  did not occur below that temperature although that does not exclude its potential decomposition above 600 °C.

#### 4. Volatilization from molten salt

Almost all Hanford LAW components that were solubilized in aqueous solution become molten salt as temperature increases during vitrification (with the exception of aluminate). Once any low-melting major component such as sodium nitrate (melting point of 308 °C) become molten, it can dissolve (or form a eutectic melt with) other waste and some additive components that have higher melting points such as sulfates, carbonates, perhenates, and pertechnetates. This mixed salt reacts with other additive chemicals (boric acid) and minerals (quartz, kyanite) to form early glass-forming melts during feed-to-glass conversion process. It is likely that initial volatilization of Tc or Re would occur from molten salt phase before glass-forming melt incorporate Tc or Re as discussed by Jin et al. [41]. Therefore, information on the volatile species identified from volatilization studies of pure or simple mixed salts can be helpful.

##### 4.1. Tc and Re volatilization from single and binary pertechnetate or perhenate salt

According to Rouschias [65], the alkali (for Na, K, Rb, and Cs) perhenates melt and boil without decomposition. In agreement with this statement, analysis using high-temperature mass spectrometry combined with a Knudsen effusion cell identified monomers  $M\text{ReO}_4$  and to a lesser degree dimers  $(M\text{ReO}_4)_2$  as the main gas species [66–69]. Mixed dimers  $MM'(\text{ReO}_4)_2$  were observed from binary perhenates in addition to monomers and simple dimers [70–72]. A negligible dissociation was observed only for lithium perhenate, but with the vapor pressure of  $\text{Re}_2\text{O}_7$  and  $\text{Li}_2\text{O}$  at  $\sim 900\text{ K}$   $10^3$  times smaller than that of  $\text{LiReO}_4$  [68]. Knudsen-cell mass spectrometry also was used for K and Cs pertechnetates by Gibson [73] who identified  $\text{KTcO}_4$ ,  $(\text{KTcO}_4)_2$ , and  $\text{CsTcO}_4$  as major vapor constituents. The dimer  $(\text{CsTcO}_4)_2$  also was believed to be a significant vapor component although it could not be directly identified due to experimental limitations [73]. In short, there is experimental evidence that pure or binary alkali perhenates  $M\text{ReO}_4$  ( $M = \text{Li}$  through  $\text{Cs}$ ) and alkali pertechnetates  $\text{MTcO}_4$  ( $M = \text{K}$  and  $\text{Cs}$ ) evaporate according to Reaction (1).

##### 4.2. Tc volatilization from single pertechnetate salt mixed with glass frit

Vida [62] studied volatilization of Tc from heating of various Tc sources including alkali pertechnetates mixed in glass or glass ceramic frit. Among three alkali pertechnetates tested,  $\text{CsTcO}_4$  exhibited higher volatilization compared to  $\text{NaTcO}_4$  and  $\text{KTcO}_4$ . It was hypothesized that the higher volatility of  $\text{CsTcO}_4$  over that of  $\text{NaTcO}_4$  and  $\text{KTcO}_4$  may be understood by analogy to other alkali salts; that is, the volatilization of  $\text{CsNO}_3$  is higher than other nitrates due to the high volatility of  $\text{Cs}_2\text{O}$  formed by decomposition. It was further argued that because the boiling point of  $\text{Tc}_2\text{O}_7$  is 311 °C, Cs and Tc should volatilize simultaneously during thermal decomposition of a  $\text{CsTcO}_4$  melt according to Reaction (2). However, it should be noted here that this argument was made without any experimental evidence or published data that supports the occurrence of  $\text{CsTcO}_4$  thermal decomposition.

The experimental method used by Vida [62] involved heating a relatively small mass of sample (50 to 450 mg) by introducing the mixture to a furnace pre-heated to 1200 °C and holding at this temperature for 2 h. As mentioned by Vida [62], once the Tc salt melts and wets the glass particles, the large surface area formed facilitates rapid volatilization of Tc, but the volatilization becomes very slow (a diffusion-controlled process) after the glass particles become sintered and fully encapsulate the Tc salt. In this setup, Tc volatilization is likely to occur the same way from the pure molten salts discussed above, dependent on the melting point and vapor pressure of each salt. The melting point of each salt determines the starting temperature at which the salt wets the glass frit and thus the temperature range for volatilization. Considering that  $\text{CsTcO}_4$  has the highest melting point among

the three alkali pertechnetates (i.e., the narrowest temperature range), its higher volatility is likely attributed to a higher vapor pressure of  $\text{CsTcO}_4$  than  $\text{NaTcO}_4$  and  $\text{KTcO}_4$  within the temperature range up to that glass frit becomes fully sintered.

##### 4.3. Re volatilization from simple mixed salt on molten glass surface in a closed system

A series of experiments was performed to measure the solubility of Re and Tc in a typical Hanford LAW glass using a vacuum-sealed fused silica crucible [45,46]. A separate experiment was performed to establish the Re mass balance within the closed system [47]. Pre-melted glass powder was mixed with  $\text{KReO}_4$  in an amount to yield a target Re concentration of 6500 ppm mass (metal basis) if 100% were retained. The frit and  $\text{KReO}_4$  mixture was placed into a fused quartz tube and vacuum sealed. The sealed tube (ampoule) containing the sample was heated to 1000 °C and maintained at that temperature for 2 h. Because the amount of Re added is higher than the thermodynamic solubility in this glass ( $\sim 3000$  ppm) at 1000 °C [45], the undissolved perhenate salt is transported to the melt surface by bubbles that formed from the open pores between glass particles. This approach is similar to the method used by Vida [62] in that the mixture of glass frit and perhenate/pertechnetate is heated to a pre-determined temperature but, unlike Vida [62], uses a closed system (i.e., there is no volatile loss to outside the ampoule).

The pure  $\text{KReO}_4$  salt becomes a mixed salt of  $(\text{Na,K})\text{ReO}_4$  and  $(\text{Na,K})_2\text{SO}_4$  via ion exchange with Na and  $\text{SO}_4$  in the glass during bubble transport and at the interface between the molten glass and salt. The mixed salt partially volatilizes to the ampoule head space, reaching equilibrium between the liquid salt phase on the glass surface and the gas phase. At the completion of heating for 2 h at 1000 °C, the ampoule was removed from the furnace, air quenched, and then separated into two parts after natural breakage at the glass melt meniscus. Each part was separately washed with room-temperature deionized water to dissolve the soluble salt phase. The salt solution and remaining solid samples were analyzed (see Table 2 in reference [47]). Because the upper part of the thin ampoule wall cools much faster than the lower part of bulky molten glass (see Fig. 2 in [47]), the vapor species in the head space primarily deposit on the crucible wall. As a result, analyzing the crucible wall deposit can provide a rough indication of the composition of volatile components in the head space at 1000 °C.

The mass of each of the four elements detected in the wall wash and glass wash samples given in Kim and Schweiger [47] was used to calculate the moles of elements (see Table 1). Table 1 also includes the total cation ( $\text{K} + \text{Na}$ ) and anion ( $\text{Re} + 2\text{S}$ ) charges, cation to anion charge ratio ( $\text{C}/\text{A}$ ), and  $\text{K}/\text{Na}$  and  $\text{Re}/\text{S}$  ratios, where K, Na, Re, and S represent the number of moles of each element. The total cation to anion charge ratio of 1.12; that is, 12% excess cation charge could be from dissolution of glass components (potentially alkali metal oxides) into mixed salt during heat treatment or could be within the experimental error. Given the sampling and analytical uncertainties involved in the method used by Kim and Schweiger [47], the following

**Table 1**  
Moles of each element analyzed in wall and glass wash solution samples out of total 61.72 g of collected materials (calculated from the mass of the element in each sample given in Table 2 of Kim and Schweiger [47]).

Component	K	Na	Re	S	K + Na	Re + 2S	C/A <sup>a</sup>	K/Na	Re/S
Wall wash, $\mu\text{mol}$	36.8	97.9	97.7	4.49	135	107	1.26	0.38	21.8
Glass wash, $\mu\text{mol}$	56.0	539	449	49.0	595	547	1.09	0.10	9.2
Total	92.8	637	547	53.5	730	654	1.12	0.15	10.2

<sup>a</sup> Cation to anion charge ratio given as  $(\text{K} + \text{Na})/(\text{Re} + 2\text{S})$  where K, Na, Re, and S represent the number of moles of each element.

discussion is based only on relative comparison:

- The larger C/A ratio in the wall wash than in the glass wash likely excludes the potential that alkali perhenates decompose and volatilize as  $\text{Re}_2\text{O}_7$ , leaving alkali oxides ( $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ ); that is, if  $\text{Re}_2\text{O}_7$  was the dominant volatile species, the C/A ratio would be much smaller in the wall wash than in the glass wash.
- The larger K/Na and Re/S ratios in the wall wash than in the glass wash suggest that Re volatilizes preferentially with K presumably as  $\text{KReO}_4$ .

The vapor pressure of a volatile component at a constant temperature can be expressed as

$$p_i = \gamma_i x_i p_i^0 \quad (3)$$

where  $p_i$ ,  $\gamma_i$ , and  $x_i$  are the vapor pressure, activity coefficient, and mole fraction of the  $i$ th component in a mixed salt and  $p_i^0$  is the vapor pressure of the pure  $i$ th component. As a crude approximation, we assumed that the glass wash represents the salt composition in equilibrium with the gas phases given as wall wash composition, the excess total cations are primarily Na, and the sulfate primarily volatilizes as  $\text{Na}_2\text{SO}_4$ ; that is, the amount of  $\text{K}_2\text{SO}_4$  is negligible. This approximation leads the decreased moles of Na from 539 to 491  $\mu\text{mol}$  for glass wash and from 97.9 to 69.9  $\mu\text{mol}$  for wall wash after accounting for excess Na, resulting in the  $\text{NaReO}_4$  moles of 393 for glass wash and 60.9 for wall wash after accounting for Na associated with  $\text{Na}_2\text{SO}_4$ . Then, the  $\text{KReO}_4$  to  $\text{NaReO}_4$  ratios for the mole fraction and vapor pressure are calculated as  $x_{\text{KReO}_4}/x_{\text{NaReO}_4} = 56.0/393 = 0.14$  from the glass wash and  $p_{\text{KReO}_4}/p_{\text{NaReO}_4} = 36.8/60.9 = 0.60$  from the wall wash, which gives  $\gamma_{\text{KReO}_4} p_{\text{KReO}_4}^0 / \gamma_{\text{NaReO}_4} p_{\text{NaReO}_4}^0 = 4.2$ . This result signifies that, at the same molar concentrations, the vapor pressure of  $\text{KReO}_4$  is roughly four times larger than that of  $\text{NaReO}_4$ ; that is, at 1000 °C, Re volatilizes preferentially with K as  $\text{KReO}_4$  from this salt mix.

## 5. Tc volatilization during melting of simulated high-activity waste

Because Tc also is one of the main radioactive components of concern in European HAWs, significant research effort has focused on the chemistry of Tc for the vitrification of HAWs [62,63,74–77]. Information on Tc behavior from these studies is helpful, although there are major differences in composition between the European HAWs and Hanford LAWs, especially, Tc concentrations in European HAWs are orders of magnitude higher than in Hanford LAWs. In addition, pre-melted glass frit is used in the vitrification of European HAWs, whereas additive minerals and chemicals are used for Hanford LAWs.

Lammertz et al. [63] performed crucible melting of simulated HAW and a glass frit mixture with a 1:9 mass ratio of simulated waste oxides to glass frit, which corresponds to waste oxide loading of 10 wt%. The simulated liquid waste of 3 M  $\text{HNO}_3$  was chemically pre-denitrated with formaldehyde, mixed with glass frit, and then dried. Tc was supplied in the form of  $\text{NH}_4\text{TcO}_4$ . The dried powder was heated to 1050 °C at a rate of  $\sim 10$  °C/min, and the volatile losses of Cs and Tc were determined at the end of heat treatment using Cs-137 and Tc-99m as tracers. The target concentration of Cs in the glass was constant at 4460 ppm mass (0.47 wt%  $\text{Cs}_2\text{O}$ ), while the target concentration of Tc varied from 0 to 1930 ppm, which corresponds to a Tc/Cs molar ratio of 0 to 0.58. The volatile loss of Cs after heat treatment was between 8 and 12% independent of target the Tc concentration from 0 to 1930 ppm. Considering that the loss of Tc ranged from 75% to 60%, the constant Cs loss suggests that noticeable volatilization of Cs and Tc as  $\text{CsTcO}_4$  did not occur under the heating conditions applied to the waste with a target Tc/Cs molar ratio of 0.58 or less.

Baumgärtner et al. [74,75] reported the volatility of Tc, Cs, and Rb from dried simulated HAW solution. The target concentrations of Cs

and Rb in the dried simulated HAW were 4.4 and 0.55 wt%, respectively. The effect of Tc addition was tested using the dried simulated HAW spiked with 1.4 wt% Tc, corresponding to a target Tc/Cs molar ratio of 0.43. The simulated liquid waste was dried and heat treated for 26 h at 1100 °C. The off-gas aerosols collected in the 0.2  $\mu\text{m}$  membrane filter were chemically (Cs and Rb) and radiologically (Tc) analyzed to determine total volatile loss. Compared to the test without Tc, addition of Tc increased the volatile loss of Cs from 4% to  $\sim 20\%$  and that of Rb from 1.6% to  $\sim 5\%$ . The Tc loss was about 50%. Using the same experimental setup, the kinetic properties of volatilization also was studied. The dried simulated waste was heated from 200 to 1100 °C at 100 °C intervals while maintaining each temperature step for 24 h. The filter was changed every hour and was analyzed to determine the volatilization rate. It was found that the volatile loss of Tc started to be measurable at 700 °C and paralleled that of Cs and Rb from 800 to 1100 °C. In addition, analysis of filtered aerosol particles found  $\text{CsTcO}_4$ ; that is, Tc was found with Cs in crystals deposited in the aerosol filters. Based on these observations, it was concluded that Cs volatilization increases in the presence of Tc, likely through the formation and volatilization as  $\text{CsTcO}_4$ . This conclusion apparently contradicts the finding by Lammertz et al. [63] discussed above.

Cains et al. [76,77] reported the volatility of Cs and Tc during crucible calcination and vitrification of simulated wastes with and without Tc. The target Tc/Cs molar ratio was 0.41 in the simulated waste with Tc. The 10 mL simulated liquid waste was evaporated to dryness under an infrared lamp and then was calcined by heating to  $\sim 600$  °C at a rate of 10 °C/min and then holding at 600 °C for 3 h (calcination). The resulting calcined material was mixed with glass frit and melted by heating to 1050 °C at a rate of 10 °C/min and then holding at 1050 °C for 8 h (vitrification). The calcine-to-glass mass ratio was 1:3, which corresponded to a waste oxide loading of 25 wt%. Both calcination and vitrification were performed in a tube furnace with an Ar purge. All off-gas components were washed and analyzed radiologically for Cs-134 (tracer) and Tc. Four to seven repeated measurements under the same test conditions showed that the addition of Tc increased the Cs volatility from  $0.38 \pm 0.26\%$  to 0.7–18.7% during

**Table 2**  
Compositions of HAW Solutions (in mg/L) Used in Tc Volatilization Studies. Minor waste components with < 100 mg/L in all three wastes were excluded.

Element	Lammertz et al. [63]	Baumgärtner et al. [74,75]	Cains et al. [76,77]
Ba	278	360	3708
Ce	576	650	6726
Cs	544	650	7177
La	254	315	3473
Mo	690	865	9212
Nd	780	1028	10,962
Pd	260	345	NA
Pr	240	343	3241
Rb	70	82	940
Ru	347	550	5357
Sm	160	217	1804
Sr	180	220	2366
Tc	234	209	2156
Te	113	145	1404
Y	94	115	1334
Zr	730	915	9761
Al	0	0	21,774
Cr	0	0	2184
Fe	1880	0	14,631
Li	0	0	7705
Mg	0	0	27,222
Na	1610	0	0
Ni	0	0	1585
Total	9040	7104	144,720
$\text{NO}_3^-$	3 M	NA	12.5 M

NA: not available, that is, information not given in the reference.

calcination at 600 °C for 3 h and from  $1.3 \pm 1.1\%$  to 7–20% during vitrification at 1050 °C for 8 h. In addition, the Cs volatility was approximately proportional to the Tc volatility, which was 0.9 to 40.3% during calcination and 17 to 29% during vitrification. The measured Tc-to-Cs molar ratio in off-gas samples was near 1 for calcination and between 1 and 2 for vitrification. The authors suggested that Cs volatilization increased in the presence of Tc, likely through formation and volatilization of CsTcO<sub>4</sub>, which agrees with the conclusion of Baumgärtner and coworkers [74,75] but contradicts the finding of Lammertz et al. [63].

The apparently contradicting results discussed above can be explained on the bases of differences in test materials and conditions. Table 2 shows the composition of simulated HAWs used in each study in milligrams of element per liter of simulated waste solution. All three wastes had approximately similar proportions of fission product components (i.e., waste components Ba through Zr in Table 2), although the absolute concentrations were different. However, the components that are added to simulate additional process chemicals and corrosion products (Al through Ni in Table 2) were very different. For alkali metals, which are of interest as sources to form volatile alkali pertechnetates, Na was used by Lammertz et al. [63] and Li by Cains and coworkers [76,77], whereas no process chemicals and corrosion products were used by Baumgärtner and coworkers [74,75]. It is noted that none of the wastes contained K. Table 3 summarizes the concentrations of the components of interest in simulated waste, test materials and conditions, and key results from the three set of studies described above.

As summarized in Table 3, unlike other studies, Baumgärtner et al. [74,75] did not add glass frit, and used 100% dried simulated waste that had Cs and Rb as the only alkali metals and, therefore, the only volatile components at the 1100 °C test temperature. All other waste components become refractory oxides with high melting points after decomposition of nitrates. Based on the volatile Cs and Rb losses of ~20% and ~5%, respectively, when Tc was added to the simulated waste as discussed earlier, the volatilized Cs and Rb correspond to ~0.98 and ~0.05 mmol/L, respectively. Assuming that the volatilized moles of Cs and Rb are proportional to the vapor pressure of their pertechnetates as an average during the test period leads to  $p_{\text{CsTcO}_4}/p_{\text{RbTcO}_4} \sim 20$ . Note that this is a very simplified assumption for the purpose of qualitative evaluation because volatilization occurs under non-equilibrium conditions and both the composition of salt (HAW) and concentration of volatile components change during the test period. From Cs/Rb molar ratio of 5 in the simulated waste (see Table 3),  $x_{\text{CsTcO}_4}/x_{\text{RbTcO}_4} = 5$ , then from Eq. (3)  $\gamma_{\text{CsTcO}_4}p_{\text{CsTcO}_4}^0/\gamma_{\text{RbTcO}_4}p_{\text{RbTcO}_4}^0 \sim 4$ . This result suggests that, at the same molar concentrations, the vapor pressure of CsTcO<sub>4</sub> is roughly 4 times larger than that of RbTcO<sub>4</sub> at 1100 °C. In short, CsTcO<sub>4</sub> is a dominant volatile species of Tc from this simulated waste at 1100 °C because of both higher  $\gamma p_i^0$  value for CsTcO<sub>4</sub> and higher Cs concentration than Rb.

Based on results reported by Lammertz et al. [63], it can be

reasoned that the lack of the effect of Tc on Cs volatilization is likely because NaTcO<sub>4</sub> is a dominant volatile species rather than CsTcO<sub>4</sub> in this specific system within the applicable temperature range. Based on a Na/Cs molar ratio of 17 (see Table 3) in the simulated waste, it can be assumed that  $x_{\text{NaTcO}_4}/x_{\text{CsTcO}_4} = 17$  disregarding the minor effect of Rb for simplification. If the difference in  $\gamma p_i^0$  values between NaTcO<sub>4</sub> and CsTcO<sub>4</sub> is relatively small, e.g., if  $\gamma_{\text{CsTcO}_4}p_{\text{CsTcO}_4}^0/\gamma_{\text{NaTcO}_4}p_{\text{NaTcO}_4}^0 < 2$ , then from Eq. (3),  $p_{\text{NaTcO}_4}/p_{\text{CsTcO}_4} > 8.5$ , in other words, the vapor pressure of NaTcO<sub>4</sub> would be more than eight times larger than that of CsTcO<sub>4</sub>. Although there are currently no thermodynamic data to support this example, it would explain the observation that the volatile loss of Cs was not affected by Tc concentration within the experimental error. The Na/Cs molar ratio of 17 does not include Na from glass frit because it is unlikely that a significant amount of Na from glass would dissolve into the salt to affect the Na/Cs molar ratio in the waste. Note that the experiment by Lammertz et al. [63], which is similar to that of Vida [62], involves heating the waste and glass frit mix at a rate of 10 °C/min to 1050 °C without holding at this temperature. Therefore Tc volatilization would become negligible once the glass frit becomes fully sintered.

A similar argument based on Eq. (3) also is applicable to the experimental findings by Cains et al. [76,77] who reported that Cs volatilization increased in the presence of Tc during both calcination and vitrification even at a high Li-to-Cs molar ratio of 21 (see Table 3). The results that Li had no effect, similarly to Na, can be justified if the  $\gamma p_i^0$  value for LiTcO<sub>4</sub> is very small compared to CsTcO<sub>4</sub>, i.e.,  $\gamma_{\text{CsTcO}_4}p_{\text{CsTcO}_4}^0/\gamma_{\text{LiTcO}_4}p_{\text{LiTcO}_4}^0 \gg 1$ .

The  $\gamma_i$  value in a general form of Eq. (3) depends on the concentration of  $i^{\text{th}}$  volatile species ( $x_i$ ), the composition of salt mix, and the temperature while,  $p_i^0$  depends only on temperature. Because the  $\gamma_i$  and  $p_i^0$  values are not available for alkali pertechnetates and perhenates (e.g., in any of the systems given in Table 3, except for  $p_i^0$  value for KReO<sub>4</sub>(l) [50,78]), the above discussions based on Eq. (3) required various hypotheses. Nonetheless, the evaluation of Tc volatility data from the three different systems discussed above provides reasonable support that Tc in mixed salts of simulated waste volatilizes as alkali pertechnetates according to Reaction (1).

The simultaneous evaporation of Tc and Cs as CsTcO<sub>4</sub> also was supported by thermodynamic calculations by Migge [79]. In that publication, it was argued that the lack of effect of Tc concentration on Cs loss by Lammertz et al. [63] contradicts experimental results by Baumgärtner et al. [74,75] and Migge's own thermodynamic study results [79]. However, as discussed in this section, all the experimental results, including those obtained later by Cains and coworkers [76,77], can be explained based on Eq. (3) for the materials with different compositions, i.e., there is no contradiction. It is noted that the implication of contradicting results mentioned by Migge [79] likely originated from the incorrect information that, as stated by Migge [79],

**Table 3**  
Summary of test conditions and key results from volatilization studies during heating of HAW solutions.

Reference		Lammertz et al. [63]	Baumgärtner et al. [74,75]	Cains et al. [76,77]
Concentration in simulated waste solution, mmol/L	Tc	0–2.4 (max)	0 or 2.1	0 or 22
	Cs	4.1	4.9	54
	Rb	0.8	1.0	11
	Na	70.0	0	0
	Li	0	0	1110
Tc/Cs mole ratio		0 to 0.58	0 or 0.43	0 or 0.41
Test materials (wt% in oxides basis)		10% dried simulated waste + 90% glass frit	100% dried simulated waste	100% dried simulated waste + 25% calcined simulated waste + 75% glass frit
Heating condition		10 °C/min to 1050 °C	26 h at 1100 °C; 200 to 1100 °C at 100 °C interval	calcination: 10 °C/min to 600 °C and 3 h at 600 °C vitrification: 10 °C/min to 1050 °C and 8 h at 1050 °C
Key results		Tc had no effect on Cs loss.	Tc increased Cs and Rb losses.	Tc increased Cs loss; Cs loss was roughly proportional to Tc loss.
Notes		Presumably Tc volatilized primarily as NaTcO <sub>4</sub> .	Tc volatilized primarily as CsTcO <sub>4</sub> .	Tc volatilized primarily as CsTcO <sub>4</sub> .

NA: not available (i.e., information not found in the literature).

Lammertz et al. [63], and Baumgärtner et al. [74,75] used “...the same glass and HAW solution...”

## 6. Volatilization during melting of simulated Hanford LAW glass feed

This section presents data obtained from analyzing the off-gas materials collected during crucible melting and melter processing of the simulated Hanford LAW and HLW glass feeds.

### 6.1. Tc and Re volatilization during crucible melting of simulated LAW glass feed

Kim and coworkers [51] performed crucible melting tests of simulated LAW glass feeds formulated for one of the Hanford tank wastes (S-109) for the Demonstration Bulk Vitrification System [80,81] project to investigate the effect of feed modifications on the volatilization of Tc and Re. Equivalent moles of Tc and Re were spiked in each feed to achieve target concentrations of 4.3 ppm mass Tc and 8.1 ppm mass Re in glass if 100% were retained. This Tc concentration represents a typical value expected in Hanford LAW glasses. Dried feed to make 200 g glass was heated at 5 °C/min to 1000 °C or 1200 °C and air quenched. A water cooled Inconel® tube placed inside a Pt crucible with a tight lid (but not sealed) was used to trap and collect volatile deposit materials for structural and chemical analyses.

X-ray diffraction (XRD) analyses of condensate deposit samples identified NaCl as a primary phase in the samples from all feeds, with the results being in good agreement with the chemical analyses results. A potassium pertechnetate/perrhenate phase was identified in the samples from three out of four different feeds tested. This phase was not found in one feed that showed the least volatility of Tc and Re, likely because amount was below detection limit. XRD patterns for  $\text{KTcO}_4$  [82] and  $\text{KReO}_4$  [83] are virtually indistinguishable because both compounds have the same crystal structure with very similar cell dimensions and, therefore, are likely to occur as a solid solution,  $\text{K(Tc,Re)O}_4$ . Identification of  $\text{K(Tc,Re)O}_4$  in the off-gas deposit materials supports the volatilization of Tc and Re according to Reaction (1) even from the simulated Hanford LAW glass feeds with low concentrations of Tc and Re. XRD patterns for  $\text{NaTcO}_4$  [82] and  $\text{NaReO}_4$  [84] are almost identical, but are different from those for  $\text{KTcO}_4$  [82] and  $\text{KReO}_4$  [83], which have the same crystal structure but different cell dimensions. This implies that the off-gas deposit was definitely  $\text{K(Tc,Re)O}_4$  not  $\text{Na(Tc,Re)O}_4$ , although the potential presence of  $\text{Na(Tc,Re)O}_4$  below detection limit of XRD cannot be ruled out considering the low target concentrations of Tc and Re. Nonetheless, the XRD results suggest that Tc and Re preferentially volatilize as  $\text{K(Tc,Re)O}_4$  over  $\text{Na(Tc,Re)O}_4$ .

The target Na/K molar ratio in simulated S-109 waste is 400 and in glass is 20. The majority of K in glass originates from additive soil that contained 2.2 wt%  $\text{K}_2\text{O}$ , resulting in a target  $\text{K}_2\text{O}$  of 1.5 wt% in glass. Unlike the feeds tested by Lammertz et al. [63], which would stop losing Tc once the glass frit becomes fully sintered (likely below 800 °C), the bulk vitrification feeds released Tc and Re even during heating from 1000 to 1200 °C. This is because the bulk vitrification glass is formulated for a nominal processing temperature of 1350 °C and does not use glass frit that sinters to form closed pores. Therefore, it is likely that a certain fraction of K is supplied from dissolution or reaction of soil, which would release K into the molten salt from which Tc/Re would volatilize, therefore resulting in a Na/K molar ratio somewhere in between 20 and 400. Then, the dominant volatility of  $\text{K(Tc,Re)O}_4$  over  $\text{Na(Tc,Re)O}_4$  implies that the  $\gamma_i p_i^0$  value for  $\text{K(Tc,Re)O}_4$  is > 20 times larger than that for  $\text{Na(Tc,Re)O}_4$  in this system.

### 6.2. Re volatilization during scaled melter processing of simulated LAW glass feed

Extensive scaled melter tests have been performed by the Vitreous

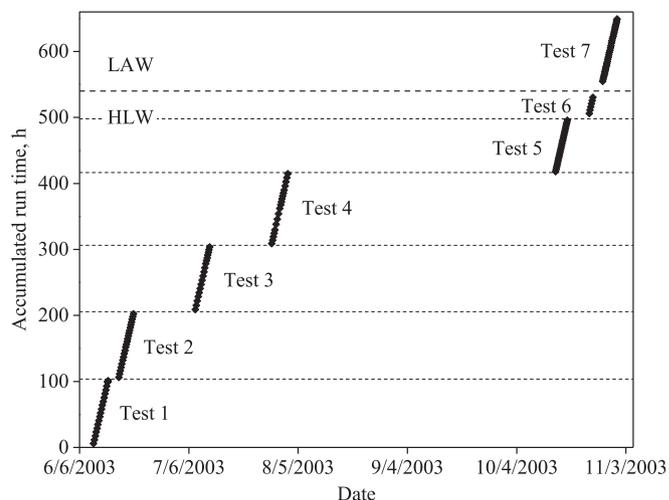


Fig. 1. Accumulated run time versus sampling time during seven melter tests by Matlack et al. [85].

State Laboratory (VSL) at Catholic University of America in support of WTP to operate the vitrification plant at Hanford. Most melter tests involved collecting and analyzing off-gas samples for various purposes, including identifying and quantifying the volatility of volatile and semi-volatile components. Matlack et al. [85] provides data that help identify the volatile Re species during melting of the simulated LAW glass feeds formulated for the WTP melter operating at a nominal processing temperature of 1150 °C. The small-scale melter used by Matlack et al. [85] (called DM-100) has a melt pool surface area of 0.108 m<sup>2</sup> (compared to 10 m<sup>2</sup> for the WTP LAW melter) with a nominal molten glass mass of ~120 kg. A 0.3 μm particulate filter and NaOH impinger were used for off-gas sampling. The particulate filter was kept at 120 °C ± 14 °C to collect all solid particles and some gaseous species. The volatile constituents that pass through the particulate filter are captured by the NaOH impinger solution.

A total of seven tests were performed over approximately six months with 2 to 73 days of idling period between each Test. Six tests (Tests 1 through 6) were conducted using simulated HLW (AZ-102) feeds and one test (Test 7) used simulated LAW (AN-105) feeds. Tests 1 through 6 lasted about 100 h while Test 5 lasted 80 h and Test 6 lasted 34 h. Fig. 1 shows the actual time of each test versus accumulated melter run time that was used to plot the off-gas data. Each test consisted of two to six test segments except for Test 5, which was performed without Tc or Cs to remove spiking components from the glass melt pool before Test 6. The target concentrations of  $\text{ReO}_2$  and  $\text{Cs}_2\text{O}$  in glass are summarized in Table 4 and plotted in Fig. 2 as a function of accumulated run time with vertical dotted lines between each Test. Off-gas sampling typically was done for 1 h two or three times per test segment toward the end of each test segment.

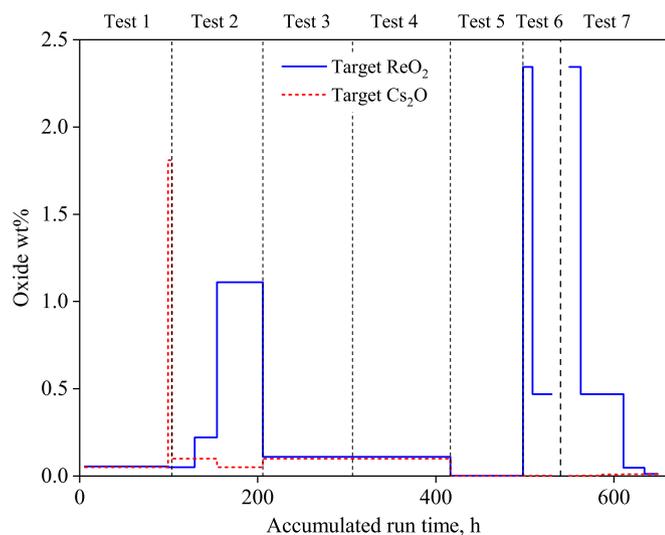
The primary interest in analyzing the melter emission data from Matlack et al. [85] was to evaluate the effect of Re concentration on Cs emission and vice versa. However, because of frequent and/or simultaneous changes of  $\text{ReO}_2$  and  $\text{Cs}_2\text{O}$  target concentrations as summarized in and as shown in Fig. 2, it was not possible to draw definite conclusions. Therefore, attention was expanded to the emission of other alkali metals and, as a reference, boron. Fig. 3 shows the emissions of K, Na, and B as a function of accumulated run time during all seven test periods. The elemental emission was defined as the emitted or volatilized fraction of total element added to the feed, which was calculated from the emission rate and input rate of each element reported in Matlack et al. [85]. The target concentration of  $\text{ReO}_2$  in wt% also is plotted in Fig. 3. In general, K showed a higher emission rate than B and Na, which exhibited similar emission rates that likely were within the analytical error.

**Table 4**  
Target concentrations of ReO<sub>2</sub> and Cs<sub>2</sub>O in melter feeds tested by Matlack et al. [85] (in wt% if 100% retained).

Feed	Test number	Test segment <sup>a</sup>	Target ReO <sub>2</sub> wt%	Target Cs <sub>2</sub> O wt%
HLW	1	A	0.055	0.05
		B	0.05	1.81
	2	A	0.05	0.1
		B	0.221	0.1
		C	1.11	0.05
	3	A, B, C, D	0.11	0.1
4	A, B, C, D	0.11	0.1	
5	NA	0	0	
LAW	6	A	2.3437	0.0002
		B	2.3437	0.0005
	C	0.4687	0.0011	
	7	A	2.3437	0.0002
		B	2.3437	0.0005
		C	0.4687	0.0011
D		0.4687	0.0093	
E	0.0469	0.0106		
F	0.0117	0.0106		

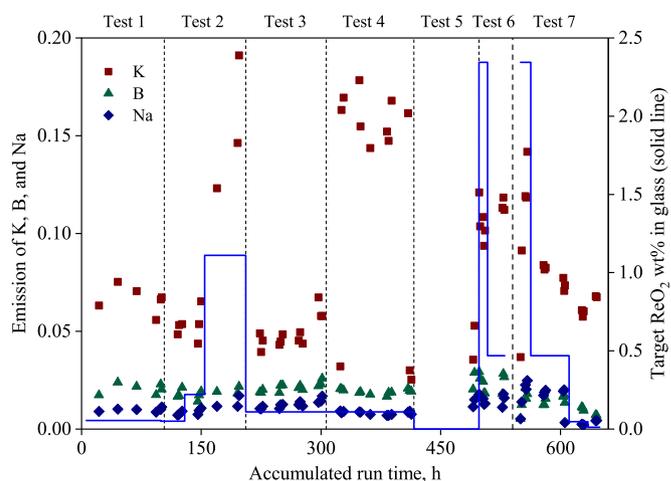
NA: not applicable.

<sup>a</sup> Each test consisted of two to six test segments except for Test 5. Each test segment was labeled in alphabetical order.



**Fig. 2.** Target concentrations of ReO<sub>2</sub> and Cs<sub>2</sub>O during seven tests by Matlack et al. [85]. There were idle times (see Fig. 1) between tests that were separated by vertical dotted lines.

In Fig. 3, three occasions that involved large increases of target ReO<sub>2</sub> concentrations in glass from 0.22 wt% or lower to 1.1 or 2.3 wt%—the last segment of Test 2 (C), and first two segments of Tests 6 (A and B) and Test 7 (A and B). During these times, the K emission increased whenever ReO<sub>2</sub> target concentration increased. As expected, within data scatter, emissions of Na and B seem to be unaffected by the ReO<sub>2</sub> target concentration. It is believed that the increased K emission was caused by preferential volatilization of Re as KReO<sub>4</sub>. The target concentration of K<sub>2</sub>O was constant at 0.03 wt% in HLW glass and 0.44 wt% in LAW glass, resulting in target Re-to-K molar ratios of 8 (Test 2) and 17 (Test 6) for HLW feeds and 1.1 (Test 7) for an LAW feed as summarized in Table 5. This implies that the Re concentration was high enough to influence the emission of K. As mentioned previously, evaluating the change of Cs emissions in response to the large Re addition was not possible because the target concentration of Cs varied from previous test periods and also within each test. It is likely that a certain fraction of Re also volatilized as NaReO<sub>4</sub>, but its impact on Na emissions cannot be detected because of high concentration of Na in



**Fig. 3.** Emission of K, B, and Na (solid symbols for left y axis) during melter tests and target concentration of ReO<sub>2</sub> (solid blue line for right y axis) (by Matlack et al. [85]). Elemental emission is the emitted fraction of total element added to the feed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

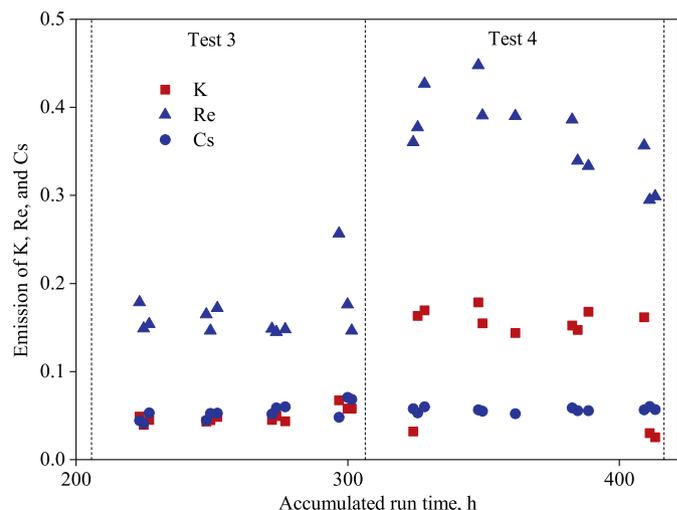
**Table 5**  
Target molar ratios in the HLW and LAW feeds in selected tests by Matlack et al. [85].

Test	Re/Cs	Re/K	Re/Na
HLW Test 2C	14	8.0	0.01
HLW Test 6A	7567	17	0.03
HLW Test 6B	3027	17	0.03
LAW Test 7A	7567	1.1	0.02
LAW Test 7B	3027	1.1	0.02
HLW Tests 3 and 4	0.7	0.8	0.001

these feeds and, therefore, low Re/Na molar ratios of 0.01 to 0.03 as shown in Table 5.

Another interesting observation from Fig. 3 is that Test 4 resulted in a major increase of K emissions without Re increase. Fig. 4 shows K emissions along with Re and Cs emissions for Tests 3 and 4 that used fixed target concentrations of 0.11 wt% ReO<sub>2</sub> and 0.1 wt% Cs<sub>2</sub>O (Table 4). For Test 3, Cl was added to the feeds to have target Cl concentrations in glass of 0.05, 0.1, 0.15, and 0.2 wt% during four test segments compared to no Cl in the baseline feed.

As shown in Fig. 4, there were no noticeable changes in Re, Cs, and K emissions as Cl additions gradually increased. The feeds for Test 4



**Fig. 4.** Emissions of K, Re, and Cs during tests 3 and 4 by Matlack et al. [85]. Elemental emission is the emitted fraction of total element added to the feed.

were added with sugar from zero in the baseline feed to four different levels that were estimated to achieve the iron redox, Fe(II)/Fe(total), of 7 (measured was 7.6), 15 (11), 22 (15), and 30 (27) in the final glass. Fig. 4 shows that emissions of K and Re in Test 4 increased over those from Test 3 whereas there was no change in Cs emission between Tests 3 and 4, suggesting that Re dominantly volatilized as  $\text{KReO}_4$  over  $\text{CsReO}_4$ . As shown in Table 5, the Re/K and Re/Cs molar ratios are comparable to each other at 0.8 and 0.9, respectively, suggesting that higher volatility of  $\text{KReO}_4$  was caused by its much higher  $\gamma_i p_i^0$  value; that is,  $\gamma_{\text{KReO}_4} p_{\text{KReO}_4}^0 / \gamma_{\text{CsReO}_4} p_{\text{CsReO}_4}^0 \gg 1$ . It also is possible that a certain fraction of Re volatilized as  $\text{NaReO}_4$ , but a high concentration of Na in these feeds and, therefore, a low Re/Na molar ratio of 0.001 (Table 5) precludes detecting any potential impact.

## 7. Summary and conclusions

From studies using high-temperature mass spectrometry combined with a Knudsen effusion cell, it was evident that pure or binary alkali perhenates and alkali pertechnetates volatilize according to Reaction (1) (Section 4.1). We argued that the higher volatility of  $\text{CsTcO}_4$  than  $\text{NaTcO}_4$  and  $\text{KTcO}_4$  observed during crucible melting of alkali pertechnetates mixed with glass frit can be attributed to the higher vapor pressure of  $\text{CsTcO}_4$ , not because of the decomposition of  $\text{CsTcO}_4$  (Section 4.2). Based on the results of the analyses of crucible deposit materials that are assumed to be approximately in equilibrium with mixed salt on the glass melt surface, we proposed that Re volatilizes preferentially as  $\text{KReO}_4$  because the  $\gamma_i p_i^0$  value of Eq. (3) for  $\text{KReO}_4$  is roughly four times larger than that for  $\text{NaReO}_4$  (Section 4.3).

We also used Eq. (3) to explain the experimental results of Tc, Cs, and Rb volatility during melting of simulated European HAW only or mixed with glass frit. We suggested that the  $\gamma_i p_i^0$  value for  $\text{CsTcO}_4$  is approximately four times larger than that for  $\text{RbTcO}_4$  although it may be only slightly larger than that for  $\text{NaTcO}_4$ , likely less than two times. We also proposed that the indication of no Tc volatilization as  $\text{LiTcO}_4$  in the presence of high concentration of Li might be attributed to an extremely small  $\gamma_i p_i^0$  value for  $\text{LiTcO}_4$  (Section 5).

For the results of structural and chemical analyses of off-gas materials collected during crucible melting of simulated Hanford LAW glass feeds, it was proposed that Tc and Re preferentially volatilize as  $\text{K(Tc,Re)O}_4$  over  $\text{Na(Tc,Re)O}_4$ , which can be also justified if the  $\gamma_i p_i^0$  value for  $\text{K(Tc,Re)O}_4$  is approximately > 20 times larger than that for  $\text{Na(Tc,Re)O}_4$  in this system (Section 6.1). Evaluation of volatility results from small-scale melter tests with simulated Hanford LAW glass feeds revealed that the addition of Re increased K emissions and the addition of reducing agent increased both K and Re emissions but did not affect Cs emissions. From these results, we proposed that Re preferentially volatilizes as  $\text{KReO}_4$  over  $\text{CsReO}_4$ , which can be explained if the  $\gamma_i p_i^0$  value for  $\text{KReO}_4$  is significantly larger than that for  $\text{CsReO}_4$  (Section 6.2). In summary the  $\gamma_i p_i^0$  values of  $\text{M(Tc,Re)O}_4$  for alkali metals of interest at Hanford are estimated to be in the order of  $\text{K} > \text{Cs} \approx \text{Na} \gg \text{Li}$  for the systems evaluated in this article although the rank and relative differences likely change for the systems with different composition.

Two previously published reports suggested the potential for decomposition of  $\text{CsTcO}_4$ . The hypothesis by Vida [62] that the decomposition of  $\text{CsTcO}_4$  is likely responsible for its higher volatility relative to other alkali pertechnetates was based on an analogy to other alkali salts without any experimental or published data on  $\text{CsTcO}_4$ . The absence of an increased Cs loss when Tc is added, an observation by Lammertz et al. [63], which was regarded as a contradiction to simultaneous evaporation of Tc and Cs as  $\text{CsTcO}_4$  [79], can be explained if Tc preferentially volatilized as  $\text{NaTcO}_4$  from the waste with a high concentration of Na. That is, as far as authors of this paper know, there is no direct evidence that decomposition of  $\text{CsTcO}_4$  occurs. As summarized above, there is direct evidence that pure or binary alkali perhenates and alkali pertechnetates evaporate according to Reaction (1),

and all experimental data on Re and Tc volatility from mixed salts and simulated wastes could be justified based on the effects of the concentration and thermodynamic properties of volatile species on their vapor pressure as represented by Eq. (3). We believe that these results provide convincing, although somewhat indirect, evidence that Tc and Re volatilize as alkali perhenates and alkali pertechnetates during vitrification of Hanford LAW according to Reaction (1) instead of decomposition into alkali oxides and  $\text{Tc}_2\text{O}_7$  or  $\text{Re}_2\text{O}_7$ .

Additional information that can be derived from the present study is that the potential concern discussed in Matlack et al. [85] regarding the possible effect of Tc on increased volatilization of Cs is not relevant to LAW and HLW at Hanford because of the low concentrations of Cs and Tc compared to the concentrations of K and Na.

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