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Review

Volatile species of technetium and rhenium during waste vitrification

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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⁺ and K⁺ as the major cations; various anions including NO₃⁻, NO₂⁻, OH⁻, Cl⁻, F⁻, CO₃²⁻, SO₄²⁻, CrO₄²⁻, Al(OH)₄⁻, and PO₄³⁻; 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 × 10⁵ y). The highly soluble TcO₄⁻ does not adsorb well onto the surface of minerals [15–18] and, thus,

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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 Re^{7+} and 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 $\text{Fe(II)}/\text{Fe(total)}$ 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 $\text{Fe(II)}/\text{Fe(total)}$ 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 $\text{Fe(II)}/\text{Fe(total)}$ ratio < 0.1); therefore, the behavior of Tc and Re in regard to partitioning characteristics and glass retention would be expected to be similar.

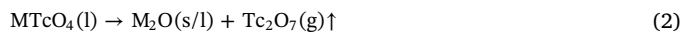
3. Volatile Tc and Re species

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 Tc_2O_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 MReO_4 and Re_2O_7 where M represents alkali metals, Na, K, and Cs that are of interest for Hanford LAW vitrification.

The boiling points of liquid Tc_2O_7 and Re_2O_7 are 311 °C and 363 °C (50), respectively, while that of alkali pertechnetate/perrhenate is known only for KTcO_4 at ~1000 °C [63] and KReO_4 at 1095 °C [50,64]. The Tc_2O_7 and Re_2O_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 Tc_2O_7 or Re_2O_7 , that is, decomposition of MTcO_4 or 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 MReO_4 did not occur below that temperature although that does not exclude its potential decomposition above 600 °C.

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