

Technetium Incorporation in Glass for the Hanford Tank Waste Treatment and Immobilization Plant – 15066

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ABSTRACT

A priority of the United States Department of Energy (U.S. DOE) is to dispose of nuclear wastes accumulated in 177 underground tanks at the Hanford Nuclear Reservation in eastern Washington State. These nuclear wastes date from the Manhattan Project of World War II and from plutonium production during the Cold War. The DOE plans to separate high-level radioactive wastes from low activity wastes and to treat each of the waste streams by vitrification (immobilization of the nuclides in glass) for disposal. The immobilized low-activity waste will be disposed of here at Hanford and the immobilized high-level waste at the national geologic repository. Included in the inventory of highly radioactive wastes is large volumes of ^{99}Tc ($\sim 9 \times 10^2$ TBq or $\sim 2.5 \times 10^4$ Ci or ~ 1500 kg).

A problem facing safe disposal of Tc-bearing wastes is the processing of waste feed into in a chemically durable waste form. Technetium incorporates poorly into silicate glass in traditional glass melting. It readily evaporates during melting of glass feeds and out of the molten glass, leading to a spectrum of high-to-low retention (ca. 20 to 80%) in the cooled glass product. DOE-ORP currently has a program at Pacific Northwest National Laboratory (PNNL), in the Department of Materials Science and Engineering at Rutgers University and in the School of Mechanical and Materials Engineering at Washington State University that seeks to understand aspects of Tc retention by means of studying Tc partitioning, molten salt formation, volatilization pathways, and cold cap chemistry.

Another problem involves the stability of Tc in glass in both the national geologic repository and on-site disposal after it has been immobilized. The major environmental concern with ^{99}Tc is its high mobility in addition to a long half-life (2.1×10^5 yrs). The pertechnetate ion (TcO_4^-) is highly soluble in water and does not adsorb well onto the surface of minerals and so migrates nearly at the same velocity as groundwater. Long-term corrosion of glass waste forms is an area of current interest to the DOE, but attention to the release of Tc from glass has been little explored. It is expected that the release of Tc from glass should be highly dependent on the local glass structure as well as the chemistry of the surrounding environment, including groundwater pH. Though the speciation of Tc in glass has been previously studied, and the Tc species present in waste glass have been previously reported, environmental Tc release mechanisms are poorly understood.

The recent advances in Tc chemistry that have given rise to an understanding of incorporation in the glass giving rise to significantly higher single-pass retention during vitrification are presented. Additionally, possible changes to the baseline flowsheet that allow for relatively minor volumes of Tc reporting to secondary waste treatment will be discussed.

INTRODUCTION

Roughly $200,000 \text{ m}^3$ of high-level waste is currently stored in 177 underground tanks at the Hanford site near Richland, Washington. This waste was generated by the reprocessing of roughly 100,000 t of spent uranium fuel to recover materials for defense purposes. The initial part of reprocessing comprised of chemical de-cladding of the fuel (primarily aluminum clad fuel was processed, but also some zirconium clad and steel clad fuels) using three primary processes: (i) bismuth phosphate carrier precipitation, (ii)

REDOX solvent extraction, and (iii) PUREX solvent extraction. In each case, the fuels were chemically degraded leading to the generation of radioactive wastes. Further, the generated wastes were primarily neutralized with NaOH and stored in carbon steel tanks. Once in the tanks, some wastes were further processed to remove water, uranium, cesium, and strontium. The combination of these processes generated a highly complex waste stream that is not found anywhere else in the world.

The cornerstone of Hanford tank waste management strategy is the Hanford tank Waste Treatment and Immobilization Plant (WTP), which is currently under construction and is expected to begin operation within this decade. The WTP will receive the waste from tanks and separate it into high-level waste (HLW) and low-activity waste (LAW) fractions by the following series of processes currently in the baseline operational strategy: (i) the HLW solids will be filtered and washed to remove excess supernatant, (ii) aluminum and chromium will be removed by caustic and oxidative leaching (respectively), (iii) the cesium will be removed from the liquid fraction by ion exchange, and finally (iv) excess water will be removed from the LAW fraction by evaporation. The resulting LAW fraction that contains <5% of the activity and >90% of the mass and volume will be treated separately from the HLW fraction.

Volatile loss of radioactive ^{99}Tc to offgas and hence the possibility of low retention in glass is a concern during vitrification of low-activity waste (LAW) stored at the US Department of Energy's Hanford site [1-8]. Studies are underway to understand the mechanism of ^{99}Tc retention in or escape from glass melt during early stage of glass batch melting and eventually to help develop the strategy for the ^{99}Tc management during LAW vitrification.

DISCUSSION

Technetium (from Greek τεχνητός, meaning artificial) is a fission product of uranium [9] and therefore is present in nuclear waste including Hanford tank waste. Technetium is known to be predominantly in the pertechnetate form in most of the Hanford tank waste and is expected to partition to the LAW fraction when processed through WTP as described above. ^{99}Tc is a radioactive isotope of particular concern due to its very high mobility in ground water (as pertechnetate ion, TcO_4^-) and long half-life (2.1×10^5 years). The primary concern in processing the waste containing ^{99}Tc is its volatility and hence low retention in a glass waste form processed by melting [10]. Volatility is not problematic in evaporation and drying processes but does create trouble in high temperature molten glass processing from either liquid or dried feed [10]. Other sources of ^{99}Tc loss could include entrainment with volatilized solvent, formation of aerosols, dust particles in scrubber systems, and other similar sources, which can be partially mitigated by engineering systems and recycling [1]. Some recent work has looked at the relative importance of volatility with and without the cold cap [11]. Partitioning to the molten salt phase has also been suggested as a mechanism for low retention of Re (^{99}Tc) in glass [12]. Volatilization can occur from the salt layer more readily than from the glass, especially if sulfate is present [13].

Rhenium has been used as a surrogate material for ^{99}Tc for laboratory testing, as its chemistry, ionic size, and other chemical aspects are very similar, more so than other candidates such as Mn, W, or Ru [1]. Rhenium commonly occurs in the 7+ oxidation state as Re_2O_7 or ReO_4^- (perrhenate ion), but also in the 4+ state in ReO_2 and the 6+ state in ReO_3 (unlike ^{99}Tc) [1, 14, 15]. Studies of Re diffusion heated in air (oxidizing conditions) have shown that Re^{7+} in a glass melt is reduced to Re^{6+} near the surface of the melt to oxidize Fe^{2+} to Fe^{3+} in a coupled redox reaction, with Re^{6+} species diffusing faster than Re^{7+} species [14]. In hydrothermal fluids, Re is predicted to be present with Cl in a Re^{4+} oxidation state [14]. In silicate melts of the diopside-anorthite eutectic (Si-Al-Ca-Mg-O), Re is present as Re^{6+} and Re^{4+} with no evidence for Re^{7+} even at high oxygen fugacities (fO₂) [16]. Rhenium compounds should be similar to those expected

for technetium in LAW simulants (KReO₄), and in liquid (CsReO₄, NaReO₄, and KReO₄) and vapor (Re₂O₇ and ReO₃(OH)) phases during vitrification [1]. Prior to the undertaking of the work partially described herein, assessments focused on the performance of the WTP included a secondary LAW treatment only as a simple “black-box” with infinite capacity for “excess” LAW and infinite capacity to stabilize the LAW offgas inventory. The set of assumptions that were valid at the time gave rise to a simplified process diagram as presented in Figure 1.

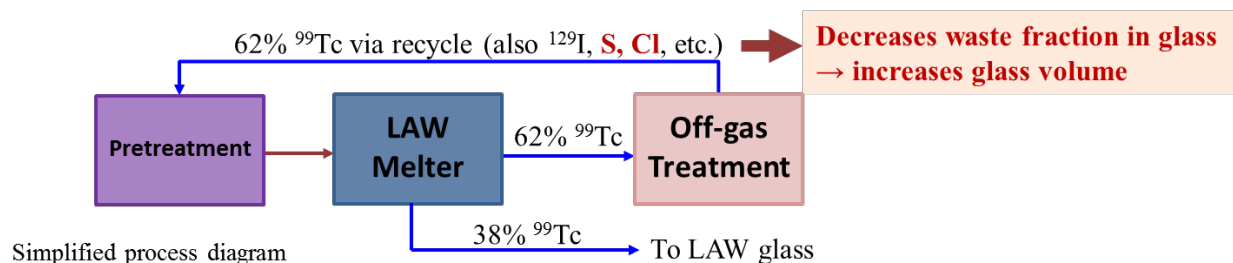


Figure 1. Simplified Process Flow Diagram from Recent System Planning

Some significant differences in behavior between Re and ⁹⁹Tc in glass are important to consider. A key difference between ⁹⁹Tc and Re is that Tc⁷⁺ is more easily reduced to Tc⁴⁺ than is Re⁷⁺ to Re⁴⁺ [1,17]. In experiments with glasses of varying redox conditions comparing ⁹⁹Tc to Re, only Re⁰ and Re⁷⁺ but no Re⁴⁺ or Re⁶⁺ were observed, even though in comparable ⁹⁹Tc glasses Tc⁰, Tc⁴⁺, and Tc⁷⁺ were observed [18]. Thus, it has been suggested that, at least in borosilicate LAW glasses, Re may not be a representative substitute for ⁹⁹Tc under reducing conditions [18]. Additionally, in vapor hydration tests (VHTs [19]), ⁹⁹Tc was always reduced to Tc⁴⁺ regardless of the starting distributions of ⁹⁹Tc valence, whereas Re⁷⁺ species were always dominant in the comparable Re glasses [17, 20]. While ⁹⁹Tc is enriched at the outer corroded gel layer of amorphous silicate and almost absent at the center, Re concentrations are low near the surface of comparable samples and approach that of unreacted glass near the center. This result highlights the different mobility of Re and ⁹⁹Tc in hydrothermal environments. However, it should be noted that the corrosion mechanism in VHT tests is not representative of that expected for waste glass in a disposal environment, particularly with regard to temperature [21]. Additionally, a series of recent melter tests suggest that the retention of Re is approximately 8% higher than ⁹⁹Tc for similar glasses [12].

CONCLUSIONS

The current effort at ORP advances a modified process diagram that incorporates the bases for pursuing the demonstration of higher single-pass retentions of ⁹⁹Tc in LAW treatment and modifications to the presumed path of recycle of the offgas overheads back through the LAW Facility. Challenges to the assumptions that allowed for the simplified process flow diagram, shown above, since resulted in pursuit of the full spectrum of inputs to be included in a new process flow. The priority of the ORP glass program has been to offer fundamentally simple chemical solutions that would be transparent to the WTP as designed. Our strategy began with establishing that its solubility in the borosilicate melt was not limiting retention [3, 22]. It has subsequently included determining the mechanisms for retention in LAW melts and HLW melts. We have since initiated investigation of the role of the effect of feed composition (e.g., AN-102: medium sulfur, high nitrates vs. AZ-102: high sulfur, low nitrates). The interest being generated by single pass retentions of ⁹⁹Tc being ca. 30% vs. 65% [23]. Additionally, this effort is yielding the fruits to allow for identical chemistries pursued for retention of ⁹⁹Tc for incorporation in glass but also should readily open disposal paths secondary waste forms with significantly enhanced performance characteristics. The details of these efforts are the subject of our other presentations. Alas, having been unsuccessful to rigorously establish chemical surrogacy between Tc and Re has resulted in the inconvenience of a

significantly greater number of ^{99}Tc -bearing feeds requiring testing. This conclusion was drawn based upon our consistent observations from the effect of various reducing conditions (Re is not a good surrogate) and from effect of ^{99}Tc minerals (Re cannot be incorporated into minerals). To this end, we're currently preparing to install the Laboratory-Scale Melter, shown schematically in Figure 2, in a controlled facility and anticipate initiating our first experiments this year. The reader's attention is called to <http://www.hanford.gov/page.cfm/AdvancesinGlassChemistry> for a compilation of our published results.

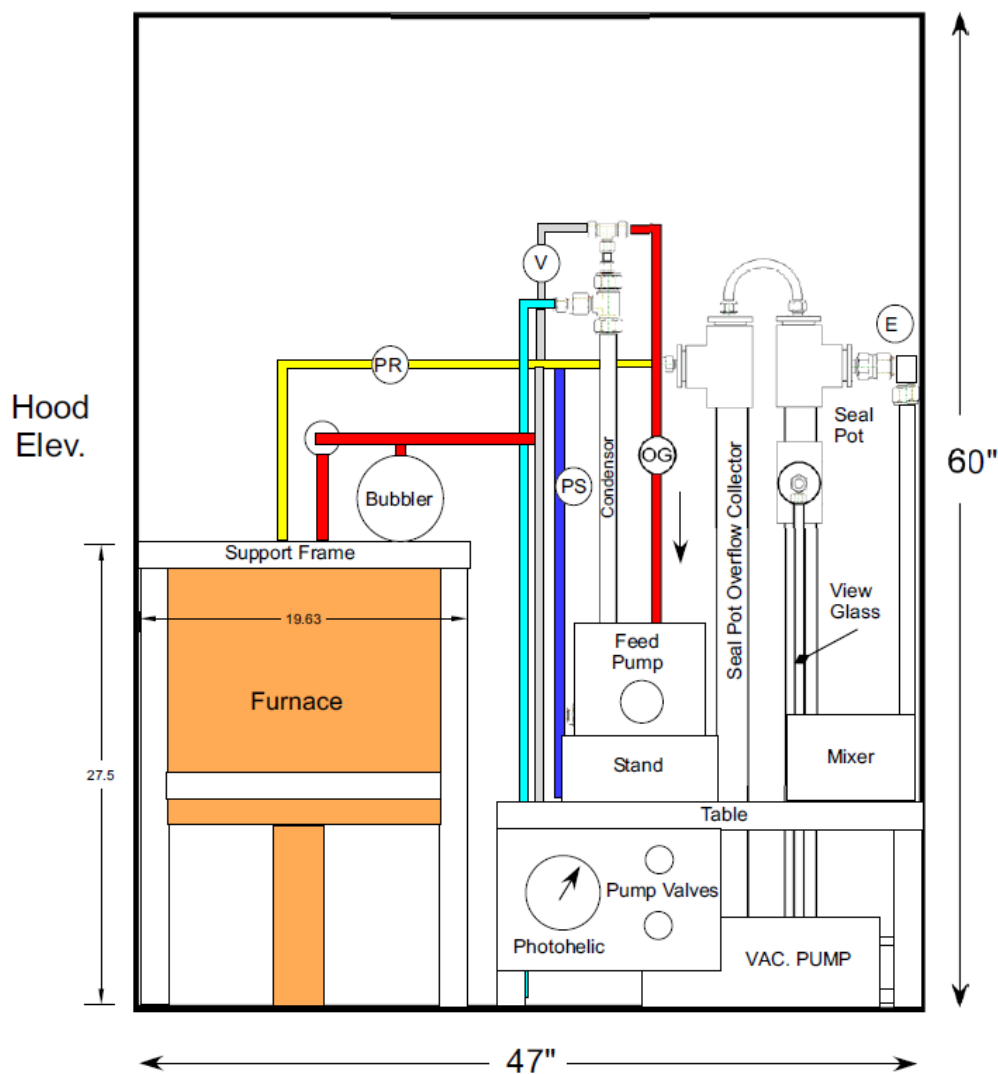


Figure 2. Laboratory-Scale Melter for ^{99}Tc Experiments with Continuous Feeding

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