

Project 90163

Research Program to Investigate the Fundamental Chemistry of Technetium

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Research Progress and Implications Portions of two Tc glasses, LBNL-118 (Hanford AP-101 tank formulation) and LBNL-121 (higher organic content Hanford AN-107 tank formulation), were placed in vapor hydration test (VHT) stainless steel pressure vessels and exposed to a hydrous atmosphere at 238oC for 24.9 days. After being removed from the vessels, complete sample alteration is clearly visible for both samples. X-ray absorption spectra were then collected on these samples to characterize the Tc speciation within the alteration layers. The X-ray fluorescence signal was significantly improved for both VHT samples compared with that collected for the corresponding unaltered glasses, so much so that X ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data could be collected for each VHT sample. This signal improvement for the VHT samples indicates that a significant amount of the Tc in the original glasses has migrated closer to the VHT sample surface; this surface enrichment results in a stronger Tc X ray signal than is the case for the more homogeneously distributed Tc in the original glasses. Significant Tc enrichment toward the VHT sample surface and Tc depletion at the VHT sample center was also observed by scanning electron microscopy coupled with wavelength dispersive x-ray spectroscopy (SEM WDS) for both samples. SEM-WDS analyses indicate that little to no Tc has been incorporated into any of the crystalline phases on or in the VHT samples, and that Tc enrichment appears to take place within an amorphous gel-like layer under a crystalline surface layer. Technetium XANES data for both VHT samples are similar to those for amorphous $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ (a- $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$) and indicate 100% Tc^{4+} . The LBNL-121 VHT sample XANES is slightly shifted to lower energy and shows no evidence of the 21,045 eV pertechnetate (TcO_4^-) peak compared with the XANES for LBNL-121 glass that indicates 80% Tc^{4+} + 20% Tc^{7+} . X-ray absorption data for unaltered LBNL 118 glass have not been collected yet; however, Raman spectra show significant amounts of pertechnetate in this glass that is not evident at all in the LBNL-118 VHT sample XANES. These changes indicate that any pertechnetate originally present in the LBNL-118 and LBNL-121 glasses was completely reduced to Tc^{4+} during VHT treatment. Technetium EXAFS indicate significant structural differences among the two VHT samples and a- $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$. The partial radial distribution function (RDF) for the LBNL-118 VHT sample has a nearest-neighbor Tc-O peak near 1.70 Å and a Tc Tc peak near 2.4 Å, similar to that for a- $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ [1]. The EXAFS fitting results for both VHT samples are consistent with local environments typically found for Tc^{4+} , which complement the XANES findings. The best fitting results for a- $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ indicate: 2.01 Å Tc-O distances for four nearest-neighbor oxygens, 2.49 Å Tc-O distances for two other oxygens (each may be associated with H_2O), and two Tc second-nearest neighbors at 2.57 Å. These results are consistent with findings from an earlier study on a $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ [1] that determined Tc to be in a distorted octahedral $\text{TcO}_4 \cdot 2\text{H}_2\text{O}$ environment that formed chains of these units, where each unit shares two oxygens with a neighboring $\text{TcO}_4 \cdot 2\text{H}_2\text{O}$. The LBNL-118 VHT sample fitting indicate an average nearest-neighbor Tc-O distance of 2.00 Å with a coordination near six, another Tc-O component at 2.45 Å with a coordination near one, and a Tc-Tc distance of 2.56 Å with a coordination near one. The partial RDF for the LBNL-121 VHT sample only has a Tc-O peak near 1.7 Å, where fitting indicates six-coordinated Tc with an average Tc-O distance of 2.00 Å. Technetium in the LBNL-118 VHT sample may be within Tc_2O_{10} dimers, where two TcO_6 units share two oxygen atoms; whereas, Tc in the LBNL-121 VHT sample appears to be within isolated TcO_6 units. Technetium in the LBNL-118 VHT sample may be found in two amorphous phases: borosilicate glass, and a- $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ (evidence from the 2.45 Å Tc-O

component). In this case, most of the Tc would be within the TcO₆ units in borosilicate glass, while minor amounts may be within a-TcO₂·2H₂O.

Two rhenium-rich LAW-based melter glasses, WVT-G-126B (0.83 wt.% Re₂O₇) and WVT-G-128B (0.65 wt.% Re₂O₇), were placed in VHT vessels for 24.9 days at 238°C. Both melter glasses were synthesized under oxidizing conditions, where the Re LII XANES and EXAFS data indicate 100% Re⁷⁺ within perrhenate (ReO₄⁻) environments in the unaltered glasses. After VHT treatment, both samples show extensive alteration. XANES data of both VHT samples indicate minor differences with respect to the perrhenate XANES features for the corresponding unaltered glasses and that Re remains fully oxidized Re⁷⁺ as perrhenate after glass alteration.

The VHT results indicate that Tc and Re behave quite differently when VHT alteration takes place in these waste glasses. During glass VHT alteration, Tc is reduced, becoming 100% Tc⁴⁺, while apparently also migrating closer to the sample surface. Tc clustering within Tc₂O₁₀ units may take place within the altered sample if significant amounts of Tc⁷⁺ are present in the original glass. If a majority of the Tc is present as Tc⁴⁺ in the original glass, then Tc appears to exist within isolated TcO₆ units in the altered sample. In contrast, Re is found within perrhenate environments before and after VHT treatment.

Product consistency tests (PCT) have been carried out on eight AN-107 and AP 101 type waste glasses, four containing Re and the other four containing both Tc and Re. Analysis of the results is in progress. Initial results for the four Re-glasses indicate normalized Re leaching that is slower than B or Na. Significant fractional releases of technetium was observed for all of the glasses.

Future Work

Further characterization of the above VHT samples will be carried out using scanning electron microscopy and X-ray diffraction techniques. VHT samples have been and will be produced that contain both Tc and Re and will be characterized using XANES and EXAFS. One set of VHT experiments will include a recent series of identical composition glasses produced under a variety of redox conditions controlled by bubbling various CO/CO₂ gas mixtures through the melt. Analysis of the PCT results will be completed. Additional tests and analyses will be performed to further elucidate the similarities and differences between technetium and rhenium in waste glasses and the leached (PCT or VHT) counterparts.

References

[1] W.W. Lukens, J.J. Bucher, N.M. Edelstein, D.K. Shuh, Environ. Sci. Technol., 36 (2002) 1124.

DELIVERABLES: None submitted but three papers in preparation. Expect these to be submitted in the next few months.