Project 90163
Research Program to Investigate the Fundamental Chemistry of Technetium

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Research Progress and Implications

Tc and Re glasses were prepared using waste surrogates and glass additives for the Low Activity Waste (LAW) fractions from the Hanford Waste tanks AN-107 and AN-105. The AN 107 waste has a higher organic content than the AN-105 waste and should, therefore, provide more reducing environments during glass synthesis. Tc K-edge and Re LII-edge XANES spectra were measured for this series of glasses that were each prepared under slightly different conditions.

Technetium is typically found in two different valences: Tc4+ and the highly mobile Tc7+. Tc K-edge features for Tc4+ are distinctly different from those for Tc7+. As a result, the proportions of Tc4+ and Tc7+ in each glass could be obtained to an uncertainty of near + 5% by fitting the Tc XANES spectrum for each glass with the sum of two weighted standards spectra: one for Tc4+ and the other for Tc7+. For one AN-105 glass, fitting determined that Tc is mostly oxidized with 90% Tc7+ and 10% Tc4+. The fitting results of four AN-107 glasses show a wide variation. Three of the four glasses indicate mostly oxidized Tc, where speciation ranges from 95% Tc7+ and 5% Tc4+ to 73% Tc7+ and 27% Tc4+. The fourth AN-105 glass was not heated to as high of a temperature as the others and the resulting fit indicates a more reduced Tc distribution: 23% Tc7+ and 77% Tc4+. Therefore, the Tc-speciation results for the glasses do not closely follow the natural expectation that the AN-107 glasses might be more reduced than the AN-105 glasses.

Fitting the Re LII-edge XANES spectra for the glasses was not as straight-forward due to some complicating factors. Re can be typically found in one of three valences: 4+, 6+, and 7+; correspondingly, XANES spectra were collected for three crystalline standards: Re4+O2, Re6+O3, and NH4Re7+O4. Unfortunately, absorption edge features are similar among all three standards, where valence increase corresponds to slightly higher edge energies. Another problem is the poor signal-to-noise levels of the Re-edge data for some of the glasses investigated. XANES fitting could be done for three of the five glasses using the spectra for Re4+O2 and NH4Re7+O4, where the results have uncertainties as small as + 10%. Fitting results were not as good using other combinations of standard XANES data. Fitting for one AN-105 glass resulted in 92% Re7+ and 8% Re4+. Fitting for two AN-107 glasses indicated more reduced Re species distributions ranging from 80% Re7+ and 20% Re4+ to 85% Re7+ and 15% Re4+. This trend makes sense with respect to the higher organic content in the AN-107 formulations.

These initial results indicate that the speciation of Tc and Re do not behave identically in waste glass.

Future Work

Additional glass samples will be prepared for leach testing, as well as to further test the above results. Glasses containing higher Re concentrations will also be produced to improve signal-to-noise levels in and fitting result uncertainties for the Re LII-edge XANES spectra. Glass samples containing both Re and Tc will be prepared as a function of oxygen fugacity to examine the effect of the different reduction potentials on Re and Tc speciation in waste glasses.

DELIVERABLES: None to date but several are likely over the coming year.