
Understanding fundamental science governing the development and performance of nuclear waste glasses

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ABSTRACT:

The Hanford site in Washington State houses ~56 million gallons of radioactive wastes stored in 177 underground tanks, generated as a result of 45 years of plutonium production in support of the nation's defense programs. This waste must be immobilized and permanently stored, and the plan is to separate the tank wastes into low activity waste (LAW) and high level waste (HLW) streams. The U.S. Department of Energy (DOE) is building a Waste Treatment and Immobilization Plant (WTP) at Hanford site to separately vitrify these two waste streams in borosilicate glass using Joule-heated ceramic melters (JHCM). Although the process of nuclear waste immobilization *via* vitrification seems simple, in practicality, it is faced with complex problems starting from the design of glass compositions (owing to the compositional complexity of waste), to processing in melters and long term performance of the final vitrified waste forms. This Integrated Research Program aims to combine the strengths of experimental and computational materials science to address following four key challenges and knowledge gaps.

i. Formulating crystal tolerant HLW glasses with enhanced waste loadings. It is desirable to maximize waste loading in glass to decrease the overall volume and cost without posing unacceptable risk to melter operation. A major factor limiting waste loading in HLW glasses is the crystallization and accumulation of spinel crystals (comprising Fe, Ni, Cr, and Mn with general formula AB_2O_4) in the glass discharge riser of the melter during idling. Once formed, spinels are stable to temperatures much higher than the typical JHCM operating temperatures (~1150°C), and therefore do not dissolve, potentially resulting in clogging of the discharge channel and interference with the flow of glass from the melter.

In this project, we will focus on understanding the fundamental science governing nucleation and crystallization of spinels in the melter as a function of glass chemistry and melt environment. Crystal accumulation rate as a function of idling time, temperature, and viscosity of glass melt will be assessed. The obtained data, combined with that from previous and ongoing efforts, will be used to support the development of a predictive model for crystal accumulation as a function of glass composition.

ii. Understanding the fundamental science governing the chemical durability of HLW glasses. Once the HLW glass melt is poured into steel canisters, it will be transported to a deep geologic repository. During the ultimate geological disposal, the intrusion of groundwater into a repository is the most likely mechanism by which radionuclides may be removed from the HLW glass once the steel canister degrades (~1000 years). Radionuclides may be carried to the biosphere unless the glasses are stable in the presence of water over geological time scales. In general, the dissolution of silicate/borosilicate glass is known to proceed *via* three kinetic regimes: *Stage I* – the initial rate, *Stage II* – the residual rate, and in some cases *Stage III* – a resumption of relatively rapid alteration. While there exists agreement on initial dissolution rate (*Stage I*) being governed by hydrolysis of silicon-oxygen-metal bonds, the debate is open regarding the mechanisms limiting *Stage II*, which is considered most important in geological disposal scenarios.

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In this project, we will focus on performing hybrid (Monte Carlo and Molecular Dynamic) computational techniques along with experimental observations of the reactions occurring during *Stage II* and *III* corrosion in aluminoborosilicate glasses with chemistry similar to HLW glasses. The major emphasis of the work is to provide the molecular level understanding of the re-polymerization that occurs in *Stage II* that creates a protective alteration layer and slows dissolution of the glass.

iii. Understanding the thermochemistry controlling the incorporation, solubility, and retention of anionic species in LAW borosilicate glasses. During processing of Hanford LAW in glass melter, as well as in other nuclear wastes, a molten alkali sulfate salt (known as “yellow phase”) may be formed on the melt pool surface. This salt layer can cause many problems, including corrosion of melter components in contact with the salt, a low resistance path to short out the JHCM, and concentration of radioactive components (Tc-99, I-129, etc.) in a water-soluble phase on cooling. Despite the attempt by current WTP constraints to address this problem and maximize waste loading without salt formation, most of the knowledge is empirical in nature. However, it is likely that some structural features of borosilicate glasses at atomistic levels control the total solubility of anions in the melt and partitioning to salt.

In this project, we will focus on understanding the fundamental drivers that control the solubility of various anions and oxyanions in LAW borosilicate glasses. The emphasis will be on understanding the science governing partitioning of particular elements into a salt phase on the surface of glass melt, and the mechanisms of incorporation of these anions in a realistic melting scenario starting from nitrate-rich feeds. Both experimental and computational approaches will be used to understand glass-salt interaction.

iv. Understanding the fundamental science controlling technetium incorporation into LAW borosilicate glass. Hanford waste contains an estimated $\sim 9 \times 10^2$ TBq (~ 1500 kg) of ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$ yr). According to current estimates, $>90\%$ of this inventory will be immobilized in LAW glass. However, due to its high volatility at temperatures >900 °C, it is difficult to incorporate technetium in borosilicate glasses *via* traditional glass melting, thus resulting in low retention of Tc in the final waste form. Additionally, the pertechnetate oxyanion is highly mobile in groundwater, so immobilization in glass is critical for long-term environmental safeguarding.

In this project, we will develop understanding of the chemical structure of Tc in the volatile state and in glass, focusing on improving Tc retention in the glass and understanding potential glass dissolution mechanisms causing its release. Structures of possible volatile species will be simulated and then synthesized to compare to volatile species captured in simulated melter tests. Additionally, alternative Tc management strategies will be explored, including magnetic separation and reintroduction of sorbed Tc nanoparticles into the glass melter to increase Tc retention.

The goal of this IRP is to supply actionable information to DOE to reduce costs and risks associated with nuclear waste vitrification. Primary information will be compositional dependence and glass chemistry effects on undesirable processing outcomes such as low waste loading, crystal formation, technetium volatility, and salt formation. We anticipate the training of excellent students to help fill the pipeline of next-generation researchers focused on nuclear waste immobilization issues.

The proposed work is a collaborative effort between premier academic and research organizations in the US. The team comprises a talented and experienced mix of experimental and computational scientists encompassing expertise in various aspects of nuclear waste glasses: synthesis, processing, and crystallization (Goel – Rutgers, Matyas – PNNL, McCloy – WSU), molecular and atomistic structure (McCloy – WSU, Du – UNT, Dixon – PNNL), glass chemical durability (Ryan – PNNL, Goel – Rutgers, Garofalini – Rutgers), and technetium chemistry in glasses (Soderquist – PNNL, McCloy – WSU).