# Exploration and Modeling of Structural Changes in Waste Glass Under Corrosion

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**ABSTRACT**

Vitrification is currently the world-wide treatment of choice for the disposition of high-level nuclear wastes. In glasses, radionuclides are atomistically bonded into the solid, resulting in a highly durable product, with borosilicate glasses exhibiting particularly excellent durability in water. Considering that waste glass is designed to retain the radionuclides within the waste form for long periods, it is important to understand the long-term stability of these materials when they react in the environment, especially in the presence of water. Based on a number of previous studies, there is general consensus regarding the mechanisms controlling the initial rate of nuclear waste glass dissolution. Agreement regarding the cause of the observed decrease in dissolution rate at extended times, however, has been elusive. Two general models have been proposed to explain this behavior, and it has been concluded that both concepts are valid and must be taken into account when considering the decrease in dissolution rate. Furthermore, other processes such as water diffusion, ion exchange, and precipitation of mineral phases onto the glass surface may occur in parallel with dissolution of the glass and can influence long-term performance. Our proposed research will address these issues through a combination of aqueous-phase dissolution/reaction experiments and probing of the resulting surface layers with state-of-the-art analytical methods. These methods include solid-state nuclear magnetic resonance (SSNMR) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). The resulting datasets will then be coupled with computational chemistry and reaction-rate modeling to address the most persistent uncertainties in the understanding of glass corrosion, which indeed have limited the performance of the best corrosion models to date. With an improved understanding of corrosion mechanisms, models can be developed and improved that, while still conservative, take advantage of the inherent durability of the waste form to enable secure repositories to be engineered with a much higher density of waste disposition.

We propose the synthesis, corrosion, and characterization of two sets of glass samples— containing approximately 8 single-component oxides each—as models for corrosion studies of more complicated glass systems (which can contain in excess of 25 single-component ingredients). Powdered samples and millimeter-sized coupons of these simpler glasses will be corroded in solutions that begin at circumneutral pH, but are known to increase in alkalinity as corrosion proceeds and saturation in silica species is approached. Through carefully selected isotopic substitutions with nuclides that are readily detected with SSNMR and TOF-SIMS methods, we will be able to follow the diffusion of atoms into and out of the reacted surface layers of these glasses and provide new data for testing with existing reaction models. The models can then be further extended or updated to take our new data into account, allowing the existing long-term glass corrosion models to more accurately reflect the extraordinary durability of these systems. With improved models, a significant opportunity exists to better utilize the storage volume of any geologic repository.