
Glass Composition and Solution Speciation Effects on Stage III Dissolution

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ABSTRACT:

Vitrified nuclear waste forms are currently accepted as the most chemically stable medium for disposal of the radioactive high-level waste (HLW) material generated by nuclear technology. These glasses are expected to be durable over long timescales against the typical ground-waters and run-off of most repository sites based on extensive research by an international consortium of scientists. This group has developed a phenomenological understanding and agreement about the initial stages of the corrosion process and the altered layers that form and lower the dissolution rate of the glass during so-called ‘Stage II’, where the residual (lowest) rate is observed. However, much less is known about the chemical and/or physical mechanisms that can trigger the recently observed long-term behavior of the glass and its altered surface layer; i.e., so-called ‘Stage III’ where a resumption of the high initial rate of glass dissolution has been observed to occur with samples that have otherwise exhibited dissolution at the residual rate for a long time (Stage II). Although the onset of Stage III is known to occur concurrently with the precipitation of particular alteration products, the root cause of the transition is still unknown. There are currently two hypotheses regarding the mechanistic coupling that results in Stage III alteration: (1) the chemical affinity concept suggests that as the solution nears saturation with respect to certain zeolytic phases, the precipitation of these phases alters the solution saturation state or the interfacial activity of water and a chemical gradient is formed across the altered layer through which high rate dissolution is resumed; and, (2) a transport-based hypothesis postulates that the precipitation of these saturated phases alters the existing gel layer sufficiently to break down a transport barrier and initiate Stage III dissolution.

We propose an investigation of the chemical and structural triggers of Stage III behavior through a series of studies covering a range of glass compositional space which transcends two extreme waste glass compositions (AFCI and SON68) which have been observed by many workers to exhibit very different behavior with respect to Stage III alteration. The primary chemical and structural features of these glass compositions that will be varied and characterized in detail include the Al/Si ratio, the relative concentrations of non-bridging oxygen (NBO) and charge neutralized aluminate and borate tetrahedra, and the presence and concentration of Li and Al. The uniqueness of our approach will be the control and quantitative characterization of the leachate (ie, the glass environment) and direct correlation with evolution of the altered surface and its chemical affinity. This will be achieved through the use of glass fiber samples AND near-equilibrium alkaline corrosion environments. It is our general hypothesis that solution speciation effects at high pH and near equilibrium conditions reach a tipping point that triggers Stage III. The use of glass fiber samples offers several advantages over glass powder and monoliths while the synthesis and thermodynamic modeling of ‘saturated glass solutions’ will provide control and understanding of the corrosion environment. Although our primary goal is improved understanding of the long-term residual rate and the onset of Stage III alteration, another possible outcome of this study could be new options for environmental control of the glass dissolution rate. We also aim to create an extended atlas of data for predictive modeling of glass corrosion behavior *near saturation* and thereby to model solution speciation local to the gel/glass interface. This knowledge, coupled to short-term laboratory experiments, could itself lead to screening tests for evaluation and prediction of Stage III dissolution in candidate glass waste-form compositions as a function of temperature, waste-loading and burial environment. We will also deliver graduates who have been exposed to interdisciplinary education and research that is relevant to the nuclear industry, theses and publications with multidisciplinary advisors and authors. We have a history of productive collaboration with PNNL scientists, with an established suite of unique methods and preliminary data, which will facilitate a successful program.