Decoding Zeolite Crystallization and Stage III in Nuclear Waste Glasses by Coupled Modeling and Experiments

PI: Mathieu Bauchy – UCLA

Collaborators: Gaurav N. Sant – UCLA
Joseph V. Ryan – PNNL

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ABSTRACT:

Under specific conditions of pH and temperature, nuclear waste immobilization borosilicate glasses may exhibit a sudden acceleration in their corrosion kinetics (stage III)—a behavior that has been associated with the formation of zeolite crystals. However, thus far, none of the available models have been able to predict the thermodynamic propensity and kinetics of zeolite precipitation as a function of the solution conditions. This is on account of: (i) a lack of fundamental knowledge regarding the nucleation & growth mechanisms of zeolitic phases, (ii) uncertainty regarding the compositions (types) of zeolite(s) that may form and the rate-limiting step in their precipitation as a function of the solution conditions, and (iii) the complexities that arise due to the vast parametric space (i.e., solution chemistry, temperature, number of secondary phases, etc.) that encompass these systems under conditions of environmental exposure.

To resolve these challenges, this project seeks to unambiguously identify the thermodynamic propensity for zeolite precipitation and the kinetics thereof as a function of the solution conditions (composition, pH, and temperature). To this end, the proposal works toward the following specific objectives: (i) to predict the thermodynamic stability of relevant secondary phases (zeolites, clays, C–S–H, etc.) as a function of the solution conditions, (ii) to reveal the rate-limiting step of zeolite precipitation and to quantify zeolite precipitation kinetics as a function of the solution conditions, and (iii) to embed this thermodynamic and kinetic data into a model that is able to predict the corrosion kinetics of borosilicate glasses that find use in nuclear waste immobilization applications.

To achieve these objectives, high-throughput reactive molecular dynamics simulations that are validated by well-controlled dissolution-and-solubility experiments will be carried out. To ensure control of the chemical environment, the dissolution/solubility studies will be carried out in glass-free solution with fixed saturation states. Zeolite seeding studies will be used to independently assess their thermodynamic stability and nucleation & growth kinetics. This data will populate a self-consistent thermodynamic database that can be used to assess the kinetics and the stability fields of zeolitic phases within a Gibbs energy minimization (GEM) framework. This framework will provide a basis to examine and test our working hypotheses and accurately identify threshold solution compositions and temperatures under which zeolites are expected to form and persist. Importantly, the thermodynamic and kinetic models developed herein will be integrated into a mechanistic model for glass corrosion in collaboration with PNNL. Via PNNL's collaboration and engagement, this project will directly support DOE's nuclear waste immobilization activities by offering a technical, science-based foundation that will: (i) facilitate predictions of the long-term corrosion rates and extents of existing nuclear waste immobilization glasses to help ensure safe and successful vitrification operations, (ii) inform the development of advanced glass formulations with enhanced durability, and (iii) enable cost-savings that result from making more decisive and hence less conservative predictions while offering higher levels of nuclear waste embedment in smaller, more compact glass volumes.