
Introduction: Because equilibrium is rarely attained between solids and solution at Earth’s surface, kinetics typically control weathering and release rates of elements from the solid into solution. Over the last two decades, geologists and geochemists have used Transition State Theory (TST) as the theoretical basis for the development of kinetic rate laws that have been used to describe weathering of silicate minerals and glasses. The most eloquent proponents of this approach are Aagaard and Helgeson [1], who fashioned a rate law that takes into account temperature, solution composition, and the deviation from thermodynamic equilibrium of the system. However, a growing body of evidence demonstrates failure of this model to accurately predict alteration rates even under the most common range of environmental conditions. Yet, mass action expressions derived from TST form the basis of rate laws being used in some of today’s most sophisticated reactive-transport codes being applied for several DOE-EM site remediation problems. The demonstrable failure of the TST rate law raises considerable doubt about reliability of predictions with these models and any cleanup decisions made with them as well. At issue is whether scientists can correctly predict the long-term fate of environmentally significant elements. Some examples from dissolution experiments with Na-borosilicate waste glass are outlined below.

A. Ion-Exchange Processes in Borosilicate Glass. Exchange of alkali cations from glass with hydrogen species from the solution has been considered to be an unimportant, tertiary reaction that has little bearing on the long-term corrosion resistance of glass. Our investigations have proven, however, that in solutions that are silica-saturated (the common disposal system condition), the ion exchange (IEX) reaction is the dominant mechanism releasing sodium to solution [2]. A consequence of IEX is that when H’ from water exchanges with Na’, the hydroxyl ion thus produced silanates Si in the glass matrix. Continued silanation causes a breakup of the Si—O network. Therefore, dissolution and IEX become linked with the result that the dissolution rate is insensitive to the activity of silicic acid in solution. As such, dissolution rates are governed by “secondary” reactions that cannot be predicted using a TST-type model.

B. Effects of “Inhibitor” Species on Rates. Numerous investigators have documented the effect of rate-inhibiting species on dissolution rates of silicates. Dissolved Al and Fe in particular have been shown to decrease dissolution rates of amorphous SiO2 [3, 4] as well as more complex sodium borosilicate glass [5]. This effect persists even when the solid does not contain Al or Fe. Because these elements are not present in the solid phase, the chemical affinity term in TST is undefined with respect to these components. Attempts to incorporate the effects of these species as interfacial reaction “inhibitors” into TST models have failed: Predicted rates of dissolution can be at a maximum in cases where the solution is silica-saturated but has near-zero concentration of the inhibitor, which is clearly impossible. The examples given above clearly highlight the dilemma of applying traditional TST models to complex environmental problems. An improved kinetic rate theory must be fashioned to build credible Performance Assessments for waste disposal issues.

References: