

Thermodynamic consistency, geochemical codes, and predictions

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Geochemical modeling has become a popular and useful tool for a wide range of applications from research on fundamental water-rock interactions to regulatory requirements for hazardous wastes. Unfortunately, these applications often do not reflect an understanding of the science behind the calculations, or the limitations of the modeling for the specific context. Models are based on assumptions that are not always acknowledged or understood.

Most geochemical codes must utilize thermodynamic data on aqueous speciation and mineral solubilities. But how well do we understand mineral solubilities under natural or engineered conditions? How reliable are the thermodynamic or kinetic data? How well do we need to know this basic data before we can feel confident that wastes are safe for human and environmental health? When modeling a repository or hazardous waste site, how reliable are our assumptions of speciation, solubility, or redox chemistry? These questions vex those who attempt to evaluate geochemical models.

At one mine-waste site, litigation ensued between the regulators and industry about whether arsenic sorption or scorodite solubility would limit mobility. The thermodynamic data on arsenic was inadequate to resolve this controversy.

Thermodynamic databases and compilations abound and far outnumber critical evaluations. Calorimetric data are not always consistent with measured solubility data and new measurements are needed. For years the solubility data on barite and celestine did not agree with the calorimetric data. This discrepancy was resolved in 2002 by making new calorimetric measurements. More examples include solubility of schwertmannite, the K_1 for aqueous Al-SO₄ complexing, organic-Al complexing, and supersaturation of calcite, barite, fluorite, and Fe(OH)₃ for surface or ground waters.

Thermodynamic consistency has been only rarely a priority for evaluating data on an international basis and needs more support. Discussions should include the serial-network (NBS) method *versus* the simultaneous-fit method. Geochemical evaluations must consider mixed electrolyte solutions, comparisons between measured and calculated speciation, and the equilibrium assumption.

Predictions based on modeling should be considered "logical" not "temporal," i.e. modeling does not predict the future as much as constrain the possibilities. Model solutions often are not unique. "Validation" of models has no scientific basis and should be removed from the nuclear waste lexicon.

Waste isolation strategies for heavy metals and radionuclides in the subsurface

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The safe geologic disposal and isolation of heavy metals and radionuclides requires that their releases to the environment be predictable and sufficiently minimized to satisfy regulatory criteria. Releases of specific contaminants may be acceptably limited or controlled when: (1) they are at or near chemical equilibrium with respect to pure solids or solid solutions of low solubility; (2) their dissolution or desorption rates are acceptably low; and/or (3) the geologic media that surround or incorporate the contaminants or lie in the direction of groundwater flow (e.g. mill tailings, clay backfills, clay barriers, porous reactive barriers), limit contaminant release rates to diffusion rates, and/or dilution and dispersion during advective flow reduces contaminant concentrations to acceptable levels. The environmental conditions at a waste site may be engineered or naturally occurring. Whether resultant contaminant releases are acceptable or not must be determined by considering them within a total system performance analysis.

We will discuss several examples of natural and engineered geologic systems that can effectively limit the release of waste contaminants to the environment. Situations include:

- Insolubility of spent nuclear fuel in low-Eh granitic groundwaters that are already at equilibrium with natural UO₂;
- Retention of U leached from spent fuel and in mine waters under oxidizing conditions by precipitation in secondary silicate and phosphate minerals;
- Immobilization of Np from spent fuel by its precipitation in solid solutions or its adsorption and reduction at the surface of ferrous iron minerals;
- Immobilization of As and Ni in secondary minerals and adsorbed within buried mill tailings below the water table; and
- Precipitation and removal of heavy metals as sulfides in low-Eh systems.