The effect of LMW organic ligands on Plutonium and Uranium solubility under hyperalkaline conditions

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The chemical degradation of organic materials present in low/medium activity nuclear waste leads to the formation of LMW organic ligands that may contribute to the mobilisation of radionuclides. Among the expected ligands, isosaccharinic acid (ISA), acetate, phthalate and adipate have been identified as the most relevant compounds resulting from the degradation of polyurethane, cellulose and plastics materials. This work aims at assessing the effect of these organic ligands on the possible mobilization of Uranium and Plutonium under the hyperalkaline conditions defined by a cementitious environment.

The first step has consisted of the preparation of a complete and consistent database including complexes of U and Pu with ISA, acetate, phthalate and adipate. The sensitivity study has focused on the solubility of U and Pu under alkaline conditions and has taken into account the following parameters: a) a concentration range of organic compounds; b) a concentration range of calcium and c) a redox conditions range (from reducing to oxidant conditions).

Under the studied conditions, acetate, phthalate and adipate show almost no effect on U and Pu solubility, given both, the low affinity of these ligands toward U and Pu and the high affitnity of Ca present in the system towards the studied ligands. Indeed, the presence of Ca in the system reduces the amount of available free organic ligand to radionuclide complexation showing a minor influence of organics ligands on Plutonium and Uranium solubility. Nevertheless, ISA has been shown to significantly increase the solubility of U and Pu, even when Ca is present in the system.

Using reactive transport models and chronosequence data to elucidate differences between laboratory and field mineral dissolution rates

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Silicate mineral weathering rates in soils have implications for processes including ecosystem nutrient cycling, soil formation, and groundwater quality. The orders of magnitude difference between laboratory and field dissolution rates results from factors including hydrology, proximity to chemical equilibrium, inhibition of aqueous species (e.g., aluminum), and reactive surface area. An ideal approach to quantifying the effects of such factors on differences between laboratory and field rates is to use a reactive transport code to model dissolution.

The Merced chronosequence is an ideal system for applying the reactive transport model FLOTRAN because of the large dataset collected for soils ranging in age from 40 to 3000 ka. Measured values were used for the mineral volume, porewater chemistry, flow rates, and BET surface area (SA). If the measured values were used with laboratory values for the rate constants and pH-dependence, model dissolution proceeded too quickly. The only way to achieve model results that matched the field data was to reduce the product of the rate constant and reactive SA. Laboratory rate constants were assumed to be intrinsic rates (whereas field rates can be thought of as “apparent” rates). Thus reducing the reactive SA of the parent material by 3 orders of magnitude compared to the BET SA gave results that matched field data well. Alternatively, a good model fit was achieved with a non-TST (non-linear) rate law by decreasing the reactive SA by 2 orders of magnitude. Model results did not match field data well when increased clay solubility, decreased clay precipitation, or inhibition of plagioclase dissolution by aqueous species were used as primary fitting parameters.

Mineral dissolution, including plagioclase dissolution, across the Merced chronosequence was successfully modeled by reducing the parent material reactive SA. Chronosequence data provided constraints that increased the uniqueness of model fits. For example, greater clay solubility reduced plagioclase dissolution in younger chronosequence soils, but resulted in too little K-feldspar dissolution in the oldest soil. These model results point to the usefulness of reactive transport models for understanding field weathering and corroborate other studies that point to the importance of developing techniques to measure reactive SA.