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The Influence of Porous Medium on Citrate Facilitated Dissolution of Uranyl-Phosphate: Connecting Batch Flow Reactors with Micromodels

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The addition of phosphate is a remediation strategy to decrease the mobility of uranium by forming a uranyl-phosphate precipitate. However, plant exudates, like citrate, can remobilize the uranium. This specific study uses batch dissolution and microfluidics experiments to examine the influence of fluid flow on citrate facilitated dissolution of uranyl-phosphate. The uranyl-phosphate was synthesized by mixing U(VI) and HPO_4^{2-} , and characterized as the mineral chernikovite ($\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$) with x-ray diffraction (XRD). The SEM images of the precipitate show well-defined homogeneous particles, approximately 2 μm , and the percent composition from the energy dispersive analysis corroborates the XRD results. Batch flow reactor and micromodel experiments were used to study the dissolution reaction at pH 4 with varying citrate concentrations, and the effluent was analyzed with inductively coupled plasma-mass spectrometry. The experiment used a micromodel with double inlet ports and a single outlet port with homogenous pore structures to study the impact of flow through a porous media. Raman spectroscopy and infrared spectroscopy were used to examine changes in the chernikovite over the course of the experiments.

The batch flow reactor experiments reveal that the citrate increases the amount of dissolved uranium by a factor greater than 25 with greater dissolution at longer residence times and higher citrate concentrations. After the addition of citrate to the system, the concentration of dissolved uranium increases rapidly followed by a slower decrease in uranium concentration which suggests a dissolution mechanism involving defect sites and/or a surface diffusion limitation from citrate saturation of the chernikovite particle surface. For the micromodel experiments, the chernikovite was formed in situ, precipitated down the center mixing line, and identified using Raman spectroscopy. Despite identical procedures, the size and morphology of the chernikovite precipitate that formed in the micromodels varied which impacts the dissolution of uranium. The dissolution in the micromodel experiments agrees with the trends observed in the batch flow reactor experiments, with the concentration of uranium in solution increasing with increasing citrate concentrations and with the initial increase of uranium in solution followed by the decrease. Although the micromodel dissolution experiments have much faster residence times, the concentration of uranium in solution is comparable to the concentration results from the batch flow reactor experiments with a maximum of 42 ppm in 10 mM citrate and 7 ppm in 0.1 mM citrate. This suggests that the dissolution reaction kinetics are sufficiently fast so that the shorter residence time in the micromodel does not impede the reaction. Changes in the UO_2^{+2} 870 cm^{-1} peak in the Raman spectra and the IR spectra peaks in the 1050-930 cm^{-1} range were observed between the chernikovite not exposed to citrate and the precipitate remaining after the dissolution experiments which possibly indicates a loss of structure during dissolution.

This study contributes to the larger project by providing kinetics data that will be used in studies examining the mobilization and uptake of uranium by plants. Because the micromodel is a controlled system, it is an ideal tool to isolate and study specific physical characteristics and chemical conditions. Therefore, the micromodel experiments provide a unique link between the chemistry observed in batch solution experiments and the release of radionuclides in column and field lysimeter experiments.