The mechanism and kinetics of citrate facilitated dissolution of uranyl-phosphate

B. FERGUSON[1*], L. MURDOCH[1], F. LIU[2], A. RAO[2], M. TRUMM[3], AND B. A. POWELL[1]

[1]Dept. of Environmental Engineering and Earth Science, Clemson University, Anderson, SC 29625 (*correspondence: bofergu@g.clemson.edu)
[2]Clemson Nanomaterials Institute and Dept. of Physics and Astronomy, Clemson University, Anderson, SC 29625
[3]Institute for Nuclear Waste Disposal, Karlsruhe Insitute of Technology, 76021 Karlsruhe, Germany

The formation of uranyl-phosphate precipitates is a remediation strategy to limit the mobility of uranium in contaminated soils. However, exposure to plant exudates, like citrate, can remobilize the uranium. The purpose of this study is to examine the kinetics and extent of citrate facilitated dissolution of the chernikovite ($UO_2HPO_4{\bullet}4H_2O$) to gain a better understanding of the fate of uranyl-phosphate precipitates in the environment. A combination of batch and flow-through experiments and solid phase characterization before and after citrate exposure provides insight into the dissolution mechanisms. Batch dissolution experiments reveal that increasing citrate concentrations increase the concentration of dissolved uranium, but at citrate concentrations greater than 10mM, citrate saturates the surface of the chernikovite hindering the dissolution. Furthermore, ^{14}C, ^{235}U, and ^{32}P exchange experiments indicate exchange between the citrate in solution and the phosphorous in the mineral on the order of hours. Raman and XRD analyses of the solid remaining after exposure to citrate show that the citrate alters the structure of the chernikovite, resulting in a downshift in the UO_2^{+2} 870 cm^{-1} peak in the Raman spectra verified by density functional theory calculations and additional peaks in the XRD pattern. Continuously stirred tank reactor (CSTR) kinetic experiments reveal that steady state dissolution of chernikovite is only achieved after the precipitate is pre-treated with citrate to achieve a more uniform chemical environment for dissolution. The dissolution of the pre-treated precipitate reaches steady state within 30 minutes and increases with increasing hydraulic residence time in the CSTR, indicating equilibrium is not achieved within 80 minutes. Together, these results suggest that the dissolution of chernikovite is a fast reaction with a complex mechanism where the citrate not only removes the uranium but also alters the crystal structure of the mineral.