Nanoporous Transition Metal Phosphate Materials for Sequestration of Redox Sensitive Contaminants

D. M. WELLMAN¹, S.V. MATTIGOD¹, G.E. FRYXELL¹, L.N. CLAYTON¹, J. N. GLOVACK¹, AND K.E. PARKER¹

¹ PACIFIC NORTHWEST NATIONAL LABORATORY, 902 Battelle Blvd., P.O. Box 999, MS K6-81, Richland, WA, USA, 99354 ; dawn.wellman@pnl.gov

Nanoporous materials offer an efficient way of selectively concentrating many types of metal wastes in a very small volume. Silica-based sorbent materials have demonstrated extremely high binding affinities for numerous metals and precluded subsequent leaching from the laden material. However, silica-based materials require surface activation and are unstable under alkaline (pH >9) conditions. Nanoporous transition metal phosphates offer a new class of compounds with inherently high ion sequestration characteristics.

We synthesized a number of thermally stable, nanoporous transition metal phosphate materials (NP-TMPO), including tin, iron, vanadium, indium, niobium, and palladium, using cationic surfactants such as, hexa/octadecyltrimethylammonium halides metal salts, and phosphoric acid. The resulting nanoporous phosphates were characterized by using X-ray diffraction (XRD), highresolution transmission electron microscopy (HR-TEM), Xray absorption near edge spectroscopy (XANES), and extended absorption fine structure spectroscopy (EXAFS).

Adsorption studies of these materials were conducted to assess their effectivness in sequestering radionuclides, technetium(VII), neptunium(V), thorium(IV), and a toxic metal, chromium(VI). Equilibrium was achieved rapidly (<1 hour) at solution to solid ratio of 100. Therefore, a batch contact time of 2 hours was used to ensure that these values represent true equilibrium conditions. The data demonstrate the nanoporous, calcined tin (II) phosphate effectively removed > 95% of all target elements from solution.

Data obtained via X-Ray Absorption Near Edge Spectra/Extended X-Ray Absorption Fine Structure (XANES/EXAFS) illustrate the sequestration of Tc(VII), Np(V), and Cr(VI) with nanoporous tin phosphate materials occurs through redox-coupled reactions with the target metals being reduced to their least soluble valence states, namely, Tc(IV), Np(IV), and Cr (III).

Development of reduced Lewis metal nanoporous phosphate materials is a novel approach with added functionality. This enhances the inherent capability of these materials for sequestration of redox-sensitive contaminats, based on two possible mechanisms: 1) sorption to nanoporous ligand sites and 2) reduction of the oxidized contaminant to less-soluble valence states by coupled reaction of nanoporous metal oxidation.