SAMMS SOAK UP TOXIC ACTINIDES TO BENEFIT THE ENVIRONMENT

S AMMS (short for self-assembled monolayers on mesoporous supports) are high-efficiency, high-capacity sorbent materials that can be used to sequester toxic materials from the environment, a key component of environmental remediation. The SAMMS technique, which is easy to use, less expensive, much faster, and much more effective than traditional sorption methods, has been developed by researchers from the Pacific Northwest National Laboratory (PNNL) for the sequestration of mercury and other heavy metals (Fig. 1). This research effort was later extended to include anions, cesium, radioiodine, and other toxic metallic species; and is now the basis for their latest work: the sequestration of actinides. The SAMMS technique is an important aspect in reducing the volume of radioactive waste (which includes actinides)that must undergo the waste vitrification process as a part of the U.S. Department of Energy's (DOE's) environmental cleanup efforts.
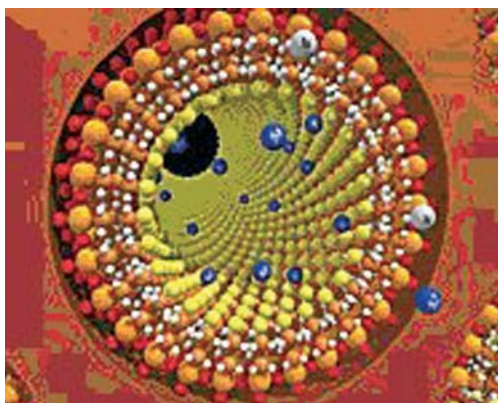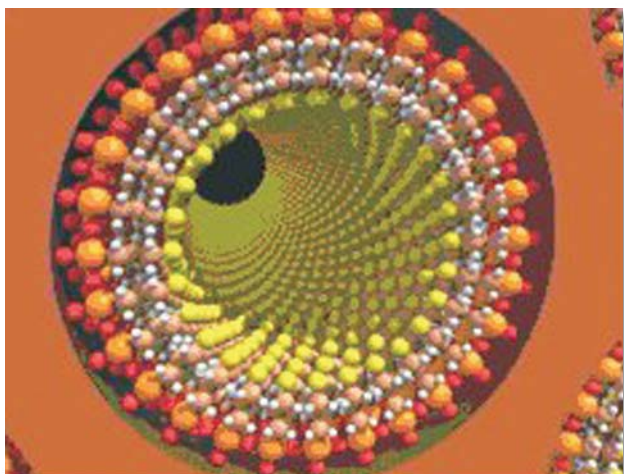

Fig. 1. SAMMS (top) without heavy metals and (bottom) with heavy metals (in this case, mercury [Hg]). Molecular self-assembly allows for the construction of highly organized arrays of binding sites available to bind heavy metals inside of a nanoporous ceramic matrix. This combination makes for a very effective, and very fast, method for removing heavy metals and radionuclides.

SAMMS materials, which were originally synthesized by PNNL scientists, bring together a nanoporous ceramic (silica-based) substrate and a technique for attaching a functional monolayer onto the pore surfaces throughout the porous substrate. Each "flavor" of SAMMS is specifically designed to sequester large amounts of a specific target contaminant (such as arsenic, cadmium, chromium, lead, mercury, or radionuclides) in a very small volume of sorbent material. In this study, the SAMMS were tailored specifically to bind actinides.

Actinide-selective SAMMS were developed by the collaborators in such a way that a variety of chemically different monolayer interfaces could be easily installed onto various substrates, allowing subtle differences in chemical selectivity to be exploited for different separation needs. In this particular study, a number of different actinide-selective ligands were employed, including glycinyl-urea (Gly-UR), salicylamide (Sal), and a couple of related phosphonate-based ligands (Phos).

Gly-UR-SAMMS were prepared by combining an isocyanate-terminated silane and a triethylamine-buffered solution of glycine, which results in the amino acid joining with the silane through a urea linkage. The resulting Gly-UR-SAMMS covered a surface area of about 4.0 silanes per square nanometer (silanes/nm^2). Sal-SAMMS were prepared by combining the carboxylic acid, carbonyl diimidazole, and 3-aminopropyltrimethoxysilane, which results in the salicylate ligand joining with aminopropylsiloxane through an amide linkage. In this case, Sal-SAMMS were attached to the surface at a population of about 1.1 silanes/nm^2. Phos-SAMMS were prepared by displacing trifluoroethanol by 3-aminopropyltrimethoxysilane from the corresponding ester, with the resulting material covering the surface at a level from 2.0 to 2.2 silanes/nm^2.

To test the effectiveness of the resulting SAMMS, the actinide (isotopic) target materials of ^{241}Am(III) (americium), ^{237}Np(V) (neptunium), ^{239}Pu(IV) (plutonium), ^{230}Th(IV) (thorium), and ^{233}U(VI) (uranium) were used. Because these actinide materials normally produce insoluble polymeric oxides or hydroxides in an alkaline environment, the collaborators performed binding studies in a pH range from 1.0 to 6.5. The actinide binding affinity of these SAMMS was found to be pH-dependent. In general, Sal-SAMMS were found to be only moderately effective. The affinity of the Gly-UR-

SAMMS was found to be highly effective at higher pH values, but rapidly decreased below a pH of 2. In addition, the Gly-UR-SAMMS were determined to bind easily with all of the actinides except Np(V) and to bind over a broader range of pH values (well below a pH of 4) than the other two SAMMS. The acetamide phosphonate (Ac-Phos) SAMMS ester was found to be effective at separating actinides that were in both aqueous and nonaqueous waste streams, while the affinity of the propionamidephosphonate (Prop-Phos) SAMMS ester was more selective over the tested actinides, especially at low pH values. Am(III) and Pu(IV) were easily and almost totally separated by a single treatment with the Prop-Phos-SAMMS ester. Overall, the phosphonic acid SAMMS were found to be excellent materials for actinide separations.

In order to better understand the structure and stability of the metal-laden SAMMS, the researchers subjected certain representative adducts to extended x-ray absorption fine structure characterization at the MR-CAT beamline 10-ID at the APS. These studies provided valuable insight into the geometry and structure of the macromolecular chelation these metal ions experience at the monolayer interface.

The SAMMS study demonstrates the superior ability of SAMMS to sequester actinides from complex toxic mixtures, even when competing ions or complexants are present. According to the collaborators, directing the SAMMS technology toward actinides could significantly reduce the volume of high-level waste that must be run through the vitrification process. As a result, these actinide SAMMS offer potentially substantial cost savings for DOE's remediation efforts.

— *William Arthur Atkins*

See: Glen E. Fryxell[1], Yuehe Lin[1], Sandy Fiskum[1], Jerome C. Birnbaum[1], Hong Wu[1], Ken Kemner[2], and Shelley Kelly[2], "Actinide Sequestration Using Self-Assembled Monolayers on Mesoporous Supports," Enviro. Sci. Tech. **39** (5), 1324 (2005). (See also Environ. Sci. Tech. **39**, 1332 [2005], which outlines the chemistry developed to effectively bind Np.)

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