

Environmental Management Science Program ANNUAL PROGRESS REPORT

U.S. Department of Energy

Combined Extraction of Cesium, Strontium, and Actinides from Alkaline Media : An Extension of the Caustic-Side Solvent Extraction (CSSX) Process Technology

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Research Objective

This fundamental research on combined cesium, strontium, and actinide separation from alkaline media by solvent extraction addresses the EM need for more efficient processes for the combined separation of these elements.

The goal of this research is to obtain fundamental information for the development of more efficient processes for the combined separation of cesium, strontium, and transuranic elements from high level waste within the U.S. DOE complex. These improved processes are targeted primarily for treating the wastes present at the U.S. DOE's Hanford and Savannah River sites. Combined separation of the radionuclides from these wastes would permit disposal of the treated waste as low-level waste, significantly reducing the volume of high level waste. Solvent extraction using the calixarene-based CSSX process has been shown to be a very effective separation method for cesium removal from High Level Waste (HLW) present at the U.S. Department of Energy's (U.S. DOE's) Savannah River Site

The wastes present at these sites are highly alkaline and accordingly most of the actinides are in the sludge phase. However, enough actinide materials still remain in the supernatant liquid requiring separation followed by disposal in a geological repository. The current technologies being considered at Hanford for cesium removal (resins) and at Savannah River for strontium and actinides (monosodium titanate) are not proving to be entirely satisfactory, either in their performance or due to potential complications. Alternatives need to be presented and developed. The principal goal of this work is to extend the solvent extraction technology chosen in October 2001 by U.S. DOE to remove cesium from the SRS high level waste. It would include removal of strontium and actinides, therefore addressing the need to develop an alternative to MST that would achieve the separation of all radionuclides, possibly in one stage by combining selective ligands in the solvent. The benefits would involve a reduction in the number of operations, in the amount of secondary wastes, and in the footprint of the process. The combined extraction of cesium, strontium, and actinides is more appealing, though if cesium and strontium are removed from the high-level waste, and if uranium and transuranium elements are present in large enough quantities that the raffinate would still meet the regulatory definition of transuranic waste (TRU). If the actinides were removed along with cesium and strontium, only one stream of HLW would then be generated, and the raffinate could be disposed as LLW. To remove the actinides and strontium present in the waste, new classes of ligands will be developed and used. Extremely strong chelators capable of binding actinides in alkaline media have been developed in Berkeley based on the demonstrated complexing properties of siderophores. Synthetic analogs of catecholamides or hydroxamic acids showed to be powerful and highly specific actinide(IV) sequestering agents – the 2,3-dihydroxyterephthalamides (TAMs) and the hydroxypyridinones (HOPOs). These ligands bind to actinides with high stability constants that manifest themselves in two important ways: 1) these ligands prevent metal hydrolysis and precipitation at high pH, and, 2) they are capable of sequestering metals that are present in low concentrations. Amido derivatives of calix[8]arenes are known to be good and selective for strontium under acidic or neutral conditions. Their synthesis and tests under alkaline conditions is also one of the objectives of these studies. Ultimately, the solvent system developed for the removal of cesium, strontium, and actinides will be tested on actual waste.

Research Progress and Implications

This report summarizes work performed during the first 9 months of a three-year project. A complete set-up in a new laboratory was achieved, allowing us to perform extraction experiments using alpha emitters. Analytical methods (alpha scintillation counting and ICP-MS) were developed to measure with precision the quantity of actinides in caustic media. Measurement controls in acidic media were implemented to confirm the results and detect immediately any precipitation of the actinides from the caustic solutions. The recipe of actinide-bearing waste simulant used at SRS was obtained and reproduced. The composition of the simulant was checked over several weeks. It was found that a slow precipitation of uranium and plutonium occurred, while the concentration of neptunium remained the same. It is strongly suspected that the precipitation is due to the preparation method that departed slightly from that used at SRS, but could not be followed at ORNL because of the type of stock solutions available. Four actinide extractants were received from Berkeley. Solubility studies showed that chloroform was one of the best diluents. Solvent extraction tests were run in that system. However, during the solvent extraction contacts with the caustic waste simulant, a small amount of CCl_2 was generated and degraded the ligands. Replacing chloroform by an aliphatic alcohol should resolve this issue. Solubility of the ligands in 1-octanol is sufficient for 3 of the 4 compounds to be used in solvent extraction experiments scheduled at the end of June. A lot of attention is also given to strontium extraction for which the synthesis of strontium-selective calixarenes is to begin soon.

Planned Activities

In the next year, more solvent extraction studies will be performed with the current ligands for actinides, probably with a couple of different diluents. The feedback on the extraction properties will allow the group in Berkeley to modify the structure of the compounds accordingly. Actinide stripping from the solvent using mild acidic solution will also be investigated. A method will be devised to prepare a waste simulant where uranium and plutonium do not fall out of the caustic solution over time. Preparation and use of stock solutions in high concentrations of sodium carbonate will be tested. Strontium extraction will be tested with the new alkoxycalix[8]arene octaamide. Collaborators at SRS tentatively identified and obtained the agreement to store 500 mL of actual tank waste supernate. This supernate will be used in next year's solvent extraction batch tests.

Information Access

The project being in its first year, no publication is available at this time. In the future, a list of publications or presentations relevant to this project will be posted on the www home page of the ORNL Chemical Separations Group: <http://www.ornl.gov/csg>.