

THE EFFICIENT SEPARATIONS AND PROCESSING  
INTEGRATED PROGRAM

W. L. Kuhn  
J. M. Gephart

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Pacific Northwest Laboratory  
Richland, Washington 99352

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# THE EFFICIENT SEPARATIONS AND PROCESSING INTEGRATED PROGRAM

William L. Kuhn  
Pacific Northwest Laboratory  
P.O. Box 999  
Richland, Washington 99352  
(509)372-4553

## ABSTRACT

The Efficient Separations and Processing Integrated Program (ESPIP) was created in 1991 to identify, develop, and perfect separations technologies and processes to treat wastes and address environmental problems throughout the U.S. Department of Energy (DOE) complex. The ESPIP funds several multi-year tasks that address high-priority waste remediation problems involving high-level, low-level, transuranic, hazardous, and mixed (radioactive and hazardous) wastes. The ESPIP supports applied R&D leading to demonstration or use of these separations technologies by other organizations within DOE's Office of Environmental Restoration and Waste Management. Examples of current ESPIP-funded separations technologies are described here.

## I. INTRODUCTION

A wide range of wastes and environmental problems exist at more than 100 contaminated installations in 36 states and territories as a result of half a century of nuclear processing activities by DOE and its predecessors. The cost of cleaning up this legacy is estimated to be on the order of hundreds of billions of dollars. The ESPIP was begun because billions of dollars could be saved if new separations technologies and processes could produce even a marginal reduction in cost. Treating essentially all DOE defense wastes requires separation methods that concentrate the contaminants and/or purify waste streams for release to the environment or for downgrading to a waste form less difficult and expensive to dispose of.

Initially, ESPIP R&D efforts focused on treatment of high-level waste (HLW) from underground storage tanks because of the potential for large reductions in disposal costs and hazards. As further separations needs emerge and as waste management and environmental restoration priorities change, the program has evolved to encompass the breadth of waste management and environmental remediation problems.

## II. MISSION AND SCOPE

The mission of the ESPIP is to

- Provide separations technologies to process, concentrate, and immobilize a wide spectrum of radioactive and hazardous defense wastes at DOE sites.
- Coordinate separations technologies R&D within DOE's Office of Environmental Management (EM).
- Foster future expertise in separations technologies by encouraging university participation.
- Transfer separations technologies developed by DOE to the U.S. industrial sector to facilitate competitiveness of U.S. technology and industry in the world market.

The ESPIP provides the following categories of separations technologies:

- radionuclide removal
- toxic materials removal
- conditioning and chemical treatment of wastes to enhance separations
- solid/liquid separation
- organic destruction.

Areas of separations development investigated by ESPIP are described here.

#### A. Chemical Reactions

The ESPIP sponsors development of improved chemical processes, such as destruction processes for organics or nitrates when needed. The ESPIP also pursues research on chemical reactions that enhance chemical separations or eliminate a separations step by destroying a contaminant. However, where such technologies are already being pursued within EM, ESPIP coordinates activities.

#### B. Waste Storage and Waste Forms

When radionuclides are separated from low-level waste (LLW) or mixed waste, they can be routed to form smaller, specialized waste streams. Wastes that emit penetrating radiation, generate significant decay heat, or represent the greatest radiological risk can be separated into interim waste forms, in volumes small enough to make specialized on-site storage economically practical. The waste forms would need to be suitable for long-term disposal as well so they could be moved to permanent off-site storage when and if it becomes available.

#### C. Process Development Supporting Chemical Separations

Most separations technologies pertinent to EM waste remediation problems involve transfer of a contaminant from a liquid phase to a solid or some other liquid phase. In some cases the contaminant may originate in a solid phase, in which case some process (either leaching or dissolving) is needed to put the contaminant into a liquid as an intermediate step...Also, dissolved organic compounds can sequester contaminants and impede desired separations, in which case some process is needed to destroy the organic species. Accordingly, the ESPIP sponsors research on processes such as organic destruction and leaching and dissolution of tank waste sludges to enable liquid-based separation technologies.

### III. CURRENT ESPIP-SPONSORED RESEARCH

#### A. Sludge Dissolution Leaching

The objective of this program is to perform experimental and modeling R&D on Melton Valley Storage Tank (MVST) sludge at Oak Ridge National Laboratory (ORNL) to test possible sludge washing and treatment strategies and to provide a description of sludge chemistry. In these studies, actual MVST waste is being treated in a hot cell. In addition, surrogate waste material is being used in tests designed to provide an understanding of MVST material that would be difficult or prohibitively expensive to obtain from studies of actual waste. A modeling effort is in place to help direct the experimental studies to aid in understanding the results of the experimental tests and to ensure that the processing of the waste is done with techniques that make sense from a chemical standpoint. A comparative assessment of Hanford Site waste and modeling needs is included in the sludge washing program.

#### B. Removal and Recovery of Metal Ions from Aqueous Streams Using Polymer Pendant Ligands

Under this task, ESPIP researchers are investigating the use of polymer-supported pendant ligand technology in the removal of toxic metal ions from DOE waste streams. Polymer pendant ligands are

organic ligands with metal-ion removal capabilities attached to the modified surfaces of 3%, 10% or 20% cross-linked divinylbenzene-polystyrene beads. The metal-ion removal step usually occurs through an ion exchange or binding phenomena, and consequently regeneration and reuse of the beads is achievable.

The research objectives of this project are to prepare the polymer supported ligands, evaluate the ligands for selectivity with respect to the metal ions of interest, study rates of removal of metal ions to determine residence times necessary for demonstration experiments, and define regeneration and reuse procedures. Work is initially focusing on the waters in the Berkeley Pit, and the metal ions targeted for removal from the pH ~2.6 solution are Cu, Zn, Mg, Mn, Al, Fe, Cd, Ni and Ca. The first six of these metals are of economic importance and represent ~\$720 million of projected recovery value.

### C. Distillation Separation of Chloride Salts from Plutonium

ESPIP researchers are looking for ways to treat the large number of residue and waste salts throughout the DOE complex that have resulted from past pyrochemical processing of Pu. These salts contain large amounts of Pu and require treatment for disposal. This problem is especially acute at Rocky Flats where the ~20 metric tons of salt contain the largest fraction of the Pu inventory.

The best treatment technology would provide a clean separation between the salt and the actinides with minimum amounts of secondary waste generation. Distillation separation of the salt matrix may constitute such a technology. This process has the potential to produce chloride salts that may be discarded as low-level waste and a concentrated actinide oxide powder that would be stored as special nuclear material. Distillation separation is based on the large difference in vapor pressures between most chloride salts that constitute pyrochemical residues and the actinide oxides and oxychlorides. However, the Pu content in these salts is usually in the form of plutonium trichloride.

Vapor pressure differences between alkali and alkaline earth chlorides and plutonium trichloride are too small to effect a good separation, therefore  $\text{PuCl}_3$  must be converted to an oxide or oxychloride through an oxidation process. An oxygen sparge process developed at Los Alamos has proven very effective in accomplishing this and can be ultimately combined with a distillation separation process.

Initial experiments performed with Pu salts thus far have shown distillation is viable: the Pu content has been reduced from the tens of percent to tens of ppm range. Essentially complete and clean separation of the salt from plutonium oxide powder has been achieved. We expect that as improved equipment and processing is developed the Pu content of the distilled salt will be lowered below the target level of 1 ppm  $^{239}\text{Pu}$ , thus allowing disposal of the salt as low-level waste. The theoretically achievable level is many orders of magnitude below 1 ppm.

### D. Separation of Tritium from Water Using Composite Membranes

In this task, ESPIP researchers are developing composite membranes to separate tritium (via HTO) from contaminated groundwater. Membrane systems are inherently energy efficient. Polymeric membranes can be configured into spiral-wound modules for efficiency; several modules can be grouped in a "cascade" for solute removal depending on waste stream concentration. Large separation factors can often be obtained using membranes even for liquids with close boiling points. The physical properties of light and heavy water are sufficiently different to suggest useful separation factors; these properties include diffusion coefficients, vapor pressures, and surface tensions.

Scientists have performed proof-of-principle laboratory tests indicating that significant separations can be achieved for HTO from water using membrane technology. The tests used Hanford Site well water containing 10,800 pCi/L HTO. A synthesized polar membrane was used that is stable during radiation exposure as well as exposure to harsh acids and bases.

Currently, the task is focusing on membrane materials development that includes 1) improvement of

the polymeric membrane formulation, 2) establishment of the corresponding composite support material, and 3) evaluation of the improved membranes.

#### E. Development and Testing of Sorbents

ESPIP is developing high-capacity, selective solid extractants for cesium, strontium, chromium, silver, technetium and noble metals from nuclear wastes. To achieve this goal, we are taking a broad-based approach that entails identification and testing of potential candidates for new solid-based sequestering agents as well as development and application of existing materials. Collaborative efforts are under way with Allied Signal and Texas A&M University and 3M/IBC Advanced Technologies (IBC).

This project is designed to test the capacity, selectivity, and stability of selected sequestering agents and substrates in representative physical, chemical, and radiation environments. Emphasis has been placed on developing and demonstrating extractants with potential applications in nuclear waste management that would result in major cost reductions and environmental benefits. Although contributions from this task should be useful in addressing a variety of problems in the DOE complex, specific applications at the Hanford Site have been initially targeted. A major goal for both 3M/IBC and Allied Signal/Texas A&M for FY 1994 is to continue to obtain necessary scientific and engineering information required to remove cesium and strontium from highly alkaline waste at the Hanford Site.

1. 3M/IBC Membrane Technology Development. A major emphasis of this subtask is to provide improved sequestering agents, and to implement their use as ion exchangers in the form of webs or filter structures. Novel agents have been selected for screening tests. The capacities, distribution ratios as a function of waste composition, physical properties, and chemical and radiolytic stability of materials with demonstrated potential for application in separations are being determined.

Empore™ membrane technology provides a state-of-the art method for enmeshing surface-active particles in a net-like matrix of polytetrafluoroethylene (PTFE) fibrils to form a membrane that has good integrity and handling strength and an extremely high particle surface availability. The membranes can be configured into convenient formats. Empore membranes can achieve equal or better performance than columns with less particle mass because the technology allows the use of smaller (10 µm) particles. The particle loading is dense (90%) and highly uniform throughout the membrane.

Thus, a membrane containing Superlig™ 601 was evaluated and compared with "packed column" performance. Its fast flow characteristics exceeded packed column performance (400-fold increase in flow rates) while its separation efficiency was similar to packed column results. In addition, four ligands have been synthesized that are specific for Cs and Sr under acidic and basic conditions. Parts per billion Cs and Sr have been isolated from large excesses of Na and K.

A polymer membrane that is more radiolytically stable (up to 2000 megarad) than PTFE has been combined with active particles. Samples were tested using a Co-60 source. In addition, Empore™ membranes have been made with both titania and zirconia instead of silica particles for use in highly alkaline environments.

Two reduced-scale filter housings have been obtained and prototype cartridges have been fabricated to demonstrate an operating system that will minimize the required volume of test solutions. A small-scale, solution processing system has been identified and ordered to test the cartridge loading and elution concept.

2. Allied Signal/Texas A&M Exchanger Development. Texas A&M and Allied Signal researchers have screened and developed three classes of exchangers: sodium titanates, zirconium arylphosphonate phosphates, and modified layered minerals.

The preferred strontium selective exchanger is a unique phase of sodium titanate  $\text{Na}_4\text{Ti}_9\text{O}_{20}$ , which has

a layer spacing of 10 Å and exhibits a  $K_d$  of 21,000 mL/g for Sr from a feed containing 80 ppm Sr, 0.1 M sodium hydroxide and 5 M sodium nitrate. The material was pelletized to a useful size range, and tested in a column mode under several sets of conditions. Scale-up to the 1-kg size was accomplished for testing.

A propylamine-intercalated sodium biotite mica was developed which has a layer spacing of 12.3 Å when dry and up to 15.4 Å when wet. This material exhibits a  $K_d$  of 660 mL/g for Cs from a feed containing 19 ppm Cs, 1 M sodium hydroxide, and 5 M sodium nitrate. This material has been pelletized to a useful size range and tested in a column mode. Scale-up to 300 g was accomplished for testing.

### 3. Material and Systems Testing

In conjunction with the two contracts (AS and 3M), other areas of research are directed toward the same goals. These include development of molecular models of crown ether macrocycles and the metal complexes; interaction with industry, academia, and the national laboratories in the study and understanding of binders and alternative web systems; testing and interaction with 3M and AS as they prepare new materials for testing; evaluation of other ion exchange materials being tested with simulated and actual Hanford wastes; and the initial evaluation for testing engineered systems with actual wastes from West Valley, ORNL and Hanford.

PNL has developed the first quantitative structure-stability relationship model for metal ion complexation by crown ether macrocycles, a class of ligands with known Sr and Cs specificity. These models are being applied to determine relationships between ligand structure and complex stability that are required for the rational design of ligands with improved selectivity characteristics.

Samples of 3M/IBC webs; AS sodium titanates and biotites; Sandia National Laboratories crystalline silicotitanates; Westinghouse Savannah River Company resorcinol-formaldehyde; and CS-100 resins were tested for comparison as a function of pH. Concerns for binder and web radiation and chemical stability were identified.

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