

Chemical Separations for the Nuclear Fuel Cycle

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September 2018



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**Prepared for the
U.S. Department of Energy**

**Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517**

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INTRODUCTION

Research into the treatment of used nuclear fuel for recycle of fissile material or waste management has been ongoing for over 70 years. The focus of the research has changed over time, but the primary technology, solvent extraction, has been the primary approach for most of this period. Extensive research into new processes and the development and synthesis of literally hundreds of new extractant molecules has been performed. This presentation will provide a brief overview of early approaches for U and Pu recovery, process development for management of legacy tank waste, and recent developments for the partitioning of trivalent minor actinides (Am, Cm) from used nuclear fuel.

Reprocessing Used Nuclear Fuel

Large-scale reprocessing had its start in the Manhattan Project. During World War II. In operation by December 1944, the T Plant was the world's first reprocessing facility. Plutonium was separated from metallic uranium fuel that had been lightly irradiated in the B Reactor.

The Hanford T Plant used a bismuth phosphate process, developed by Glenn Seaborg and the Metallurgical Laboratory at the University of Chicago, to separate plutonium from irradiated fuel. The B Plant, a second facility based on this precipitation process, also operated at Hanford before the end of the war. The bismuth phosphate process was successfully scaled from an initial separation of 20 micrograms of plutonium to kilogram quantities in the T-plant in only two years time. This represents an unprecedented scale-up factor of a billion.

Two other large reprocessing plants were also built at Hanford. Completed in 1951, the REDOX Plant was the first reprocessing plant based on countercurrent, continuous flow separation of plutonium and uranium. This process used methyl isobutyl ketone (hexone) as the solvent and was the first process used to recover both uranium and plutonium. The PUREX (Plutonium Uranium Reduction Extraction (1)) Plant went into operation in 1956, applying the technology that has since been used at industrial scale in several countries. The PUREX flowsheet was developed by

the Knolls Atomic Power Laboratory and implemented at Hanford by General Electric.

The first large PUREX reprocessing plant built by the U.S. government, called the F-Canyon, was designed and constructed in 1954 by DuPont at the Savannah River site in South Carolina. PUREX was also used in specialized plants for reprocessing highly enriched uranium fuels at Savannah River (H-Canyon) and in Idaho (Idaho Chemical Processing Plant). None of these plants were designed or operated for processing commercial fuel.

By contrast, attempts to commercialize reprocessing in the United States were unsuccessful. Of the three plants that were constructed, only one ever operated—the Nuclear Fuel Services plant at West Valley, New York. From 1966 through 1972, the West Valley plant processed fuel from several utility-owned reactors as well as some fuel from the N-Reactor in Hanford, Washington. With a nominal capacity of 300 t/y, the plant's PUREX process worked well. However, when the plant was shut down due to changing regulatory requirements, modifications were assessed to be too expensive and it never restarted.

A novel 300 t/y plant was designed and built by General Electric in Morris, Illinois in the early 1970s. The Midwest Fuel Recovery Plant was designed to use closely coupled solvent extraction and fluoride volatility processes rather than the complete PUREX flowsheet. However, non-radioactive testing revealed that the compact design had not incorporated sufficient buffer storage between processes. Realizing that the plant would not be capable of reliable operation, General Electric simply used the fuel storage facility, and never started the plant.

Between 1970 and 1975, Allied General Services built a large 1500 t/y reprocessing plant in Barnwell, South Carolina. The plant underwent startup testing with fresh uranium in 1976 while the rules on plutonium conversion and high-level waste vitrification were being resolved by the Nuclear Regulatory Commission. However, in 1977 the Carter administration cancelled the licensing proceedings and the plant had to be mothballed.

Several European reprocessing plants have been built and successfully operated, including the Eurochemic 300 t/y plant at Mol, Belgium, a 35 t/y German pilot plant, and the

modern British and French commercial reprocessing plants B205, THORP, UP2-800, and UP3. The Japanese Tokai Reprocessing Plant has operated with approximately 90 t/y capacity since 1977. In 1993, Japan Nuclear Fuel Limited (JNFL) began constructing a large reprocessing plant near Rokkasho on Japan's northern coast. The 800 t/y plant has been in startup testing since the mid-2000s (startup delayed due to issues with vitrification melter designs and later the Fukushima Daiichi accident). A reprocessing facility for power reactor fuel was completed at Mayak, Russia in 1976. Called RT-1, the plant uses a more conventional PUREX process. It was built with a capacity of 400 t/yr of used fuel. China and India have also built and operated small PUREX plants for both civilian and military purposes.

Waste Management

In the 1980s to early 2000s, the primary focus at most DOE sites and many research organizations were on separation technologies focused on management of legacy radioactive tank waste at Hanford, Savannah River, and Idaho. Numerous technologies were developed and many demonstrated with actual wastes in lab-scale pilot plants, however, the vast majority of these technologies were never implemented. A summary of processes developed and demonstrated include the Transuranic Extraction (TRUEX) process (2), the Strontium Extraction (SREX) process (3), the cobalt dicarbollide/PEG process (4), the Universal Extraction (UNEX) process (5), the Fission Product Extraction (FPEX) process (6), and numerous ion exchange materials for separation of cesium and/or strontium (Ammonium molybdochosphate ((AMP-PAN) (7), ferrocyanides (8), crystalline silicotitanate (CST)(9), resorcinal formaldehyde)(10). The one process which has been operated at production-scale is the Caustic Side Solvent Extraction (CSSX) process developed at Oak Ridge National Laboratory and implemented at Savannah River Site for the separation of cesium from tank waste (11).

Partitioning for Advanced Fuel Cycles

A review of international R&D programs over the past two decades indicates that the primary focus of separations research has been in the area of partitioning of minor actinides for advance fuel cycles and transmutation. There have been many approaches investigated, but in the past few years, the approaches seem to be converging on some common themes. It is difficult to cover this topic in a short summary, however, an excellent summary of international progress and trends in partitioning was recently published (12). Early approaches to partition trivalent minor actinides involved two sequential processes, one to separate the minor actinides and the lanthanides from transition metals (after U and Pu (and possibly Np) were removed) and a second process to separate the minor actinides from the lanthanides by exploiting the “softer” nature of the 5f elements over the

4f elements. Some examples include the TRUEX and TALSPEAK processes (13), which were studied in the US and the DIAMEX and SANEX processes studied in France (14). Recent focus has been on the combination of the two processes into a single process. This development also has seemed to converge on the use of diglycolimide extractants to extract both the trivalent minor actinides and the lanthanides, followed by the selective stripping of one from the other. Approaches developed and tested included the innovative SANEX process (15), Euro-GANEX process (16) and the ALSEP (Actinide Lanthanide Separation) process (17). Many of these processes have been tested in lab-scale countercurrent tests, but have not been implemented at industrial scale.

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