

SEPARATIONS TECHNOLOGIES SUPPORTING THE DEVELOPMENT OF A  
DEPLOYABLE ATW SYSTEM\*

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# **Separations Technologies Supporting the Development of a Deployable ATW System**

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## **ABSTRACT**

A program has been initiated for the purpose of developing the chemical separations technologies necessary to support a large Accelerator Transmutation of Waste (ATW) system capable of dealing with the projected inventory of spent fuel from the commercial nuclear power stations in the United States. The first several years of the program will be directed toward an elucidation of related technical issues and to the establishment, by means of comprehensive trade studies, of an optimum configuration of the elements of the chemical processing infrastructure required for support of the total ATW system. By adopting this sort of disciplined systems engineering approach, it is expected that development and demonstration costs can be minimized and that it will be possible to deploy an ATW system that is an environmentally sound and economically viable venture.

## **INTRODUCTION**

The elimination of certain radionuclides from commercial spent nuclear fuel intended for disposal in a mined geologic repository can have a significant positive effect on the overall performance of the repository, as measured by long-term dose effects to the human population in the vicinity of the repository. The identity of the elements to be transmuted and the efficiency with which they are to be extracted from the high-level waste product(s) dictate the chemical processes that must be employed to effect such extraction. The Yucca Mountain Project repository Total Systems Performance Assessment (TSPA) in its most recent form (1), as done for the repository Viability Assessment (VA), demonstrated that significant dose reductions can be gained by fissioning of the transuranic elements (Np, Pu, Am, Cm) and by extraction and transmutation of the fission products technetium and iodine.

Consideration of the TSPA-VA modeling results led to a set of working criteria for the chemical processing of commercial light water reactor (LWR) spent nuclear fuel for partitioning and transmutation within the framework of the Accelerator Transmutation of Waste (ATW) system. A roadmap for the development of the ATW technology has recently been published (2). Because of the importance of the transuranic (TRU) elements to nonproliferation objectives and to repository performance, a recovery target of better than 99.9% TRU was adopted for the roadmap report. The recovery target for technetium and iodine was set at greater than 95%. It was further assumed that the removal of uranium from the commercial spent fuel should be done in such a way that the

uranium could be either disposed as a non-TRU, Class C low-level waste or stored in a low-cost surface facility for future utilization. In either case, this would remove nearly 95% of the mass of the spent fuel from subsequent, possibly more complex, extraction steps and permit disposal of the uranium at a cost significantly lower than that for high-level waste disposal.

In the course of preparation of the ATW technology development roadmap, a group of experts in separations technologies carefully considered the technology options available and identified a baseline process flowsheet for the focus of developmental funding. The baseline process combines aqueous and pyrochemical processes to permit the efficient separation of the uranium, technetium, iodine and transuranic elements from the LWR fuel in the head-end step. For the internal ATW fuel cycle, the baseline process specifies another pyrochemical process to extract the TRUs, technetium and iodine from the transmuted-irradiated fuel. The diversity of processing methods was chosen for both technical and economic factors; aqueous methods are deemed to be better suited to large tonnages of commercial oxide spent fuel, while it is considered that pyrochemical methods can be exploited effectively in smaller-scale applications, particularly with metallic fuels. Those process options are described in the following report sections.

## **TREATMENT OF LWR SPENT FUEL**

Spent fuel discharged from commercial light water reactors (LWRs) is a reasonably homogeneous collection of oxide fuel in zirconium alloy cladding. If the current plants operate to the end of their license periods, the inventory of commercial spent fuel in the United States will amount to about 87,000 metric tons (heavy metal content). Conventional aqueous reprocessing of such fuels has been carried out for several years in France and the United Kingdom, using updated versions of the PUREX process developed initially in the U.S. for production of defense materials. Operating commercial reprocessing plants in Europe have capacities in the range of 800 metric tons per year, and a plant of similar size is under construction in Japan. At COGEMA's LaHague site on the Normandy coast, shown in Figure 1, two large PUREX plants (UP3 and UP2-800) are in operation. The operation of similar plants for ATW purposes is clearly technically feasible.

The PUREX process is a solvent extraction process normally using tributyl phosphate as the organic solvent. It produces an excellent separation of plutonium and uranium, with decontamination factors as high as  $10^7$  and recovery efficiencies for uranium and plutonium on the order of 99.9%. Fission products and the minor transuranic elements (Np, Am, and Cm) are not recovered, being directed in the aqueous raffinate stream to high-level waste immobilization processes such as vitrification.

In the ATW roadmapping activity, a hybrid process for LWR spent fuel treatment was adopted as an initial reference process. The chop-leach step at the front end of the process involves the dissolution of the LWR spent fuel with nitric acid. During the dissolution step, more than 95% of the iodine present in the fuel can be removed from the



Figure 1. Aerial view of the COGEMA LaHague reprocessing site in France.  
Photograph courtesy of COGEMA Inc., Bethesda, Maryland.

aqueous solution by sparging with air and NO. As depicted in Figure 2, the process employs a truncated solvent extraction process that co-extracts uranium, neptunium and technetium and leaves the other fission products and transuranics (Pu, Am, and Cm) in the aqueous raffinate stream. The neptunium and technetium are then separated; the neptunium is recombined with the other transuranic elements and the technetium is sent to blanket transmutation assembly fabrication. The uranium will be sufficiently pure

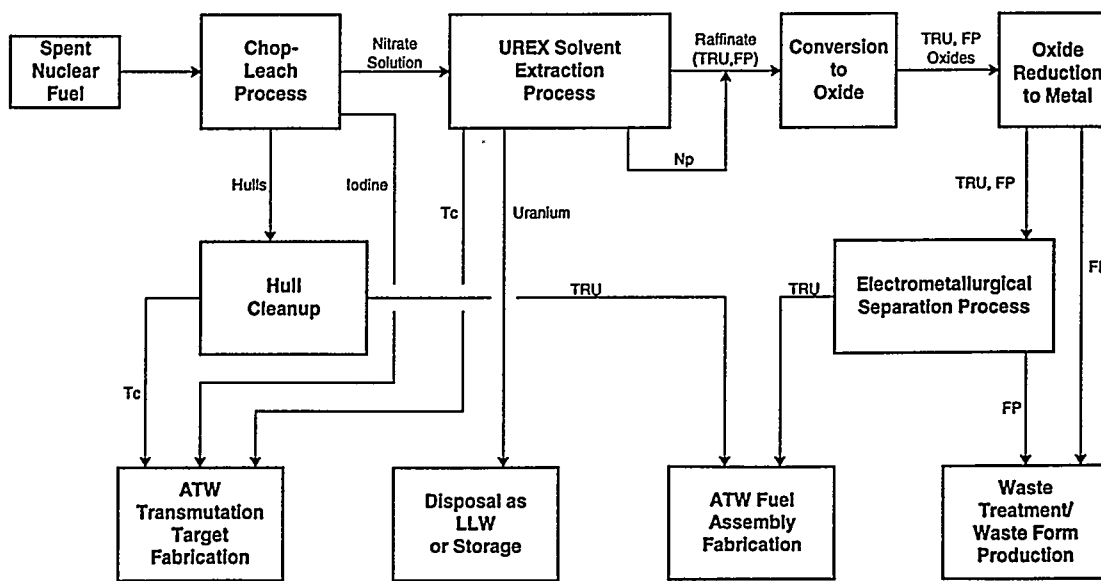


Figure 2. Flowsheet for the treatment of LWR oxide spent fuel for the Accelerator Transmutation of Waste (ATW) system.

after this process that it can be stored in an unshielded surface storage facility for future use; alternatively, it can be converted to a stable oxide and would qualify for disposal as a low-level waste provided the regulation (3) controlling its definition is revised. Because in this application the solvent extraction process does not separate plutonium, it has been referred to as the "UREX" process. Liquid wastes produced in the UREX process are not expected to contain more than trace amounts of radionuclides, and plans are to simply evaporate the wastes to dryness and collect the trace radionuclides for disposal with other process waste streams.

In the next step of the LWR fuel treatment process, known as "PYRO-A," the nitrate solution of fission products and transuranics is treated to convert the constituents to solid oxide form. These oxides are then reacted with metallic lithium in a molten lithium chloride bath; the transuranic oxides are efficiently reduced to the metallic state, as are the noble metal fission products and some of the rare earths. The other fission products remain in the salt. The transuranics are then separated from the fission products by an electrorefining step in which the TRU elements are deposited at the cathode of the electrorefining cell. The fact that the transuranics are not separated at this point confers an added degree of proliferation resistance to the process. The transuranics are then fabricated into fuel assemblies for fissioning in the ATW transmuter system. The complete PYRO-A process has been demonstrated at the 20 kg batch scale. The key electrorefining step has been carried out at production scale (175-350 kilograms per day) using an electrorefiner of the size shown in Figure 3.

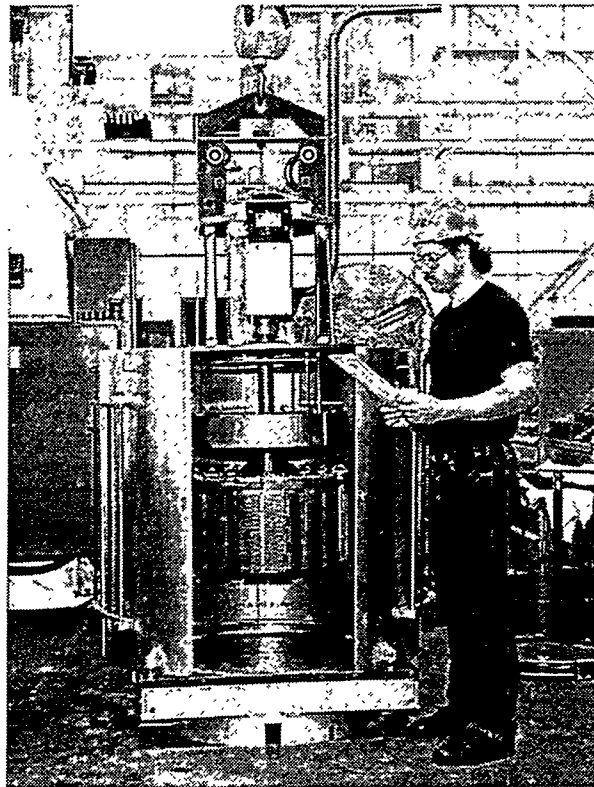


Figure 3. Prototype production-scale electrorefiner, with cathode tubes removed to show anode baskets. Argonne National Laboratory photograph.

## TREATMENT OF ATW TRANSMUTER IRRADIATED FUEL

The initial concept for the ATW transmuter blanket fuel is a dispersion of TRU elements in a zirconium matrix. The target discharge burnup for this fuel is about 33%, meaning that all of the transuranics in the fuel are fissioned in three passes through the accelerator-driven system. This necessitates a fuel treatment system for the discharged blanket fuel, to recover the unburned transuranics for recycle and to extract the newly-formed fission products for subsequent transmutation of technetium and iodine. Because the ATW blanket fuel is metallic, it is ideally suited to a pyrochemical treatment process. The large concentration of zirconium in the fuel, however, complicates process selection somewhat and necessitates inclusion of a step to remove the zirconium. The overall process has been termed "PYRO-B." As shown in the PYRO-B flowsheet in Figure 4, the chopped fuel is chlorinated, and the zirconium along with other transition metals (e.g., Tc, Ru, Mo) are vapor transported from the crucible containing the chlorides to a magnesium bath where the metal chlorides are reduced. The limited solubility of

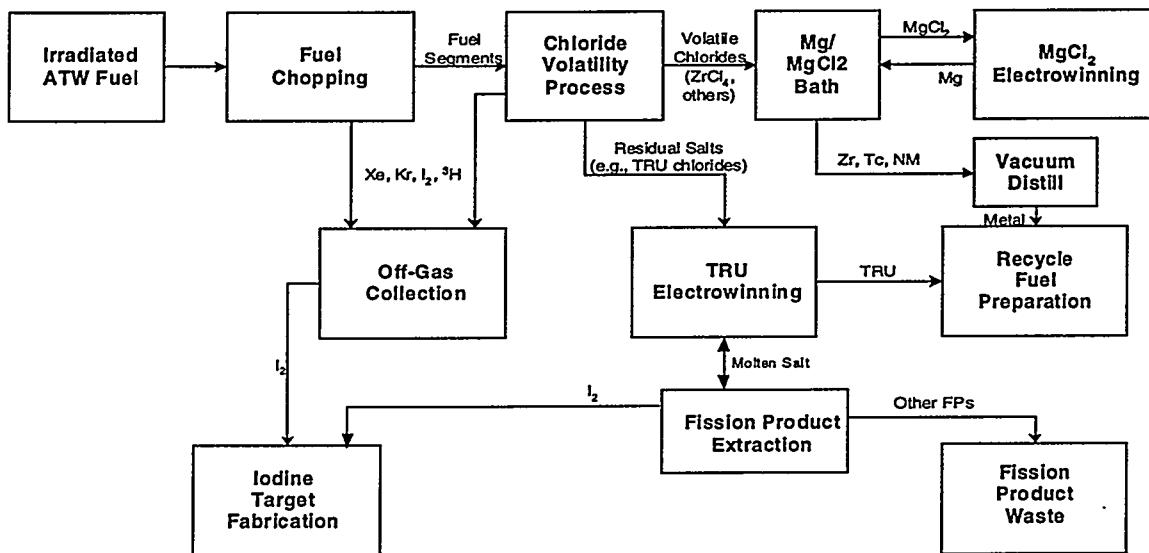


Figure 4. Flowsheet for the PYRO-B process for treatment of ATW-irradiated fuel.

zirconium and the other transported metals in the magnesium allows for their separation from the magnesium / magnesium chloride mixture. The zirconium-based metal product is removed from the volatility processing system and any residual magnesium chloride left on the surface of the product is removed by vacuum distillation prior to sending the metal to the fuel fabrication process. Magnesium and chlorine are reclaimed by electrochemically decomposing the magnesium chloride produced during the reduction process. The remaining metal chlorides (e.g., TRU, rare earths, Cs, Sr) are transferred from the volatility system to a molten salt bath in which the TRUs are recovered from the



solution by electrowinning and recycled to fuel fabrication. Periodically, the fission products are removed from the molten salt and converted to a stable waste form.

## WASTE FORM PRODUCTION

The baseline pyrochemical processes for the front- and back-end treatment operations will result in two types of high-level waste forms. The waste streams include salt-borne and metallic materials that are to be immobilized for disposal in glass-bonded sodalite and a metal waste form alloy, respectively. The development of these waste form materials is already proceeding; they are presently being qualified for the repository disposal of fission products and actinides from the treatment of the Experimental Breeder Reactor-II (EBR-II) spent nuclear fuel. Since ATW systems will destroy TRU actinides and the most significant long-lived fission products, ATW waste forms will not contain these long-lived isotopes. The demonstrated behavior of the ceramic and metal waste forms indicates that they will be more than adequate for application in the ATW concept.

The ceramic waste form is designed to immobilize halides as well as alkali, alkaline earth, and rare earth elements (e.g., Cs, Sr, Ba, Ce, and Nd) retained as ionic solutes in the molten salt. Trace amounts of actinides can also be accommodated quite readily in this waste form. The salt-borne fission products and trace actinides are immobilized along with the electrolyte salt by sorbing them into anhydrous Zeolite A. The salt-loaded zeolite is mixed with glass frit and consolidated into a monolithic body at a temperature near the melting point of the glass. During this consolidation process, the zeolite transforms to sodalite. Figure 5 shows a typical slab section of the consolidated

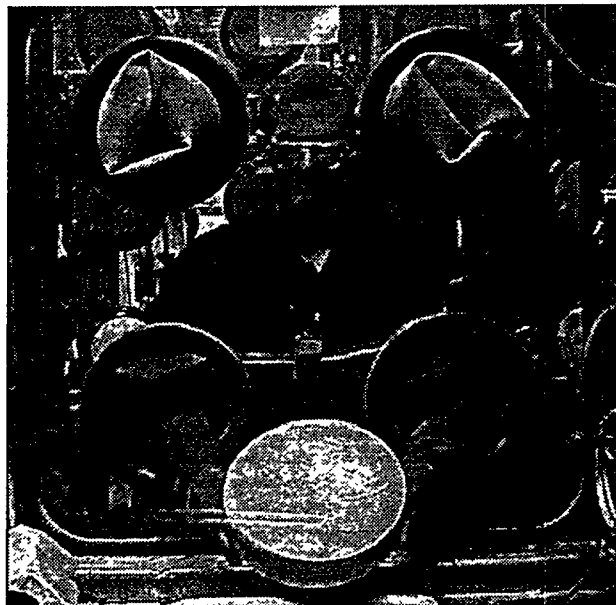


Figure 5. Glass/Sodalite composite ceramic waste form. This sample of simulated ceramic wasteform is a section 25 cm (10 inches) in diameter, prepared by sintering at ambient pressure. Argonne National Laboratory photograph.

waste form; it has a density of over 99.9% of theoretical and a loading capacity of (in this case, nonradioactive) fission product elements on the order of 5 weight percent. The fission product content is constrained by the centerline temperature of the waste form in a disposal canister, which has been conservatively limited to 650°C. Higher loadings may prove to be possible in the future as long-term characterization test data become available.

Much of the salt and its solutes remain within the sodalite lattice, but the rare earth fission products and actinides form stable secondary phases. The ceramic waste form has been demonstrated to have good corrosion and leach resistance and exhibits adequate mechanical properties for a high-level waste form; it has also been shown to be effective for the containment of iodine. For ATW, the expected salt-borne wastes will contain short-lived fission products (e.g., Cs, Sr, Ba, and the rare earths), but actinides will not be a waste disposal issue due to their very low concentration in this waste form.

The metal waste form comprises remnant metallic constituents that are electrochemically noble (inert) in the electrorefining process; these metals are melted and cast into alloy waste forms. The metallic waste includes cladding hulls from the spent fuel assemblies (typically Zircaloy-4), noble metal fission products (e.g., Ru, Re, Pd, Nb, Mo, and Tc), zirconium metal from the ATW fuel matrix, and trace residual amounts of uranium metal. Because cladding hulls represent 85 to 99 wt % of the metal waste stream, the stainless steel-zirconium (SS-Zr) alloy system was selected for development to minimize alloying additions. This efficiently incorporates the cladding hulls from the front-end process. Figure 6 shows the microstructure of a Zr-rich SS-Zr alloy containing

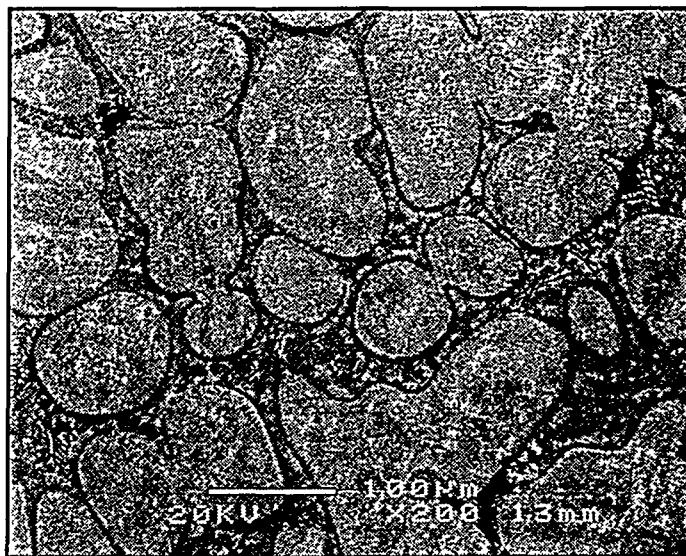


Figure 6. Backscattered electron image of Zr-8SS alloy. The primary phase (bright) is  $\alpha$ -Zr and the matrix phases comprise secondary  $\alpha$ -Zr plus Laves-phase intermetallics. The noble metal fission product elements tend to reside in the primary  $\alpha$ -Zr phase. Photo courtesy of D. P. Abraham, Argonne National Laboratory.

noble metal fission products. The nominal composition of this alloy, Zr-8SS, is slightly hypoeutectic as a compromise between fission product solubility, accommodation of the large amount of zirconium to be disposed, and melting temperature. Corrosion tests have shown this alloy to be an excellent high-level waste form and ideally suited to the ATW application.

## **FUTURE PROGRAM**

The next five years of this program will be devoted to a series of trade studies and limited experiments focusing on key technical issues. This science-based approach is intended to facilitate an informed decision in 2006 or 2007 on implementation of the ATW system. This avoids a commitment to costly demonstration facilities until there is reasonable assurance that the ATW system can be operated successfully at a cost commensurate with the benefits of long-lived radionuclide transmutation.

## **ACKNOWLEDGEMENTS**

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