PYROCHEMICAL SEPARATIONS TECHNOLOGIES ENVSIONED FOR THE U.S. ACCELERATOR TRANSMUTATION OF WASTE SYSTEM*

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Pyrochemical Separations Technologies Envisioned for the U.S. Accelerator Transmutation of Waste 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 baseline process selected combines aqueous and pyrochemical processes to enable the efficient separation of uranium, technetium, iodine, and the transuranic elements from LWR spent fuel. The diversity of processing methods was chosen for both technical and economic factors. A six-year technology evaluation and development program is foreseen, by the end of which an informed decision can be made on proceeding with demonstration of the ATW system.

Introduction

Commercial nuclear power stations in the United States will have generated nearly 87,000 tonnes (heavy metal) of spent fuel by 2015, even if there are no new plants built and no extensions of the operating licenses of existing plants. A system for fissioning the transuranics present in this fuel and transmuting certain selected long-lived fission products is being evaluated in a six-year study that began in October 1999. The design concepts for this system, known in the U.S. as the Accelerator Transmutation of Waste (ATW) System, are evolving. It is likely that the system will comprise an accelerator-driven subcritical assembly for accomplishing the desired transmutations while generating electric power, the revenues from which will serve to offset, in part, the costs of the system. An operating lifetime of 60 years has been chosen for initial systems studies.

An aqueous solvent extraction process has been selected as the baseline process for treatment of the LWR spent fuel. This selection was based on the need to process about 1,450 tonnes of spent fuel per year with high extraction efficiency for all of the actinide elements and with high decontamination of the uranium present in the spent fuel. The fuel to be processed will have cooled for at least 25 years from the date of reactor discharge. Owing to proliferation concerns commonly associated with conventional

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solvent extraction processes such as PUREX, a pyrochemical process is being evaluated as an alternative to PUREX. The alternative process must facilitate the recovery of 99.9% of the uranium and transuranic elements present in the fuel, and it must produce a separated uranium stream so that there is no carryover of fertile uranium into the transmutation cycle. In addition, it is required that the extracted uranium be of sufficient purity that it is disposable as low-level waste or qualified for surface storage in non-shielded containers.

The remaining fuel treatment processes in the ATW System are envisioned to be pyrochemical. The nitrate solution resulting from the first extraction cycle of the PUREX process is to be reduced to solid oxide and thence to metal. The metal product, containing all of the transuranic elements, some of the rare earth fission products, and all of the noble metal fission products, is then electrorefined to separate the transuranics. The TRU product is fabricated into metallic fuel subassemblies, which are inserted in the accelerator-driven transmuter array. These subassemblies are operated to burnups on the order of 33% and then discharged for processing to recycle the unburned transuranics and extract the newly-generated long-lived fission products. A second pyrochemical process is utilized to perform these extractions. The key step in this second process is a chloride volatility separation. These pyrochemical processes will be described in detail in the following sections.

Factors Driving Process Selection

The U.S. Accelerator Transmutation of Waste program is motivated by the need to provide assurances that the high-level wastes from civilian nuclear power generation can be disposed of without significant risk to the public and to future generations. It also addresses the concern that nuclear fuel buried in a deep underground repository presents a potential source of weapons materials for future proliferators. It is constrained by the U.S. policy regarding civilian use of plutonium: this policy presently avers that the U.S. will not engage in reprocessing of spent fuel for the purpose of recovering plutonium for civil use. Excess weapons plutonium will be burned in selected reactors in the form of mixed oxide (MOX) fuel, but plutonium recycle is proscribed and the U.S. nuclear utilities have been obliged to operate with the once-through fuel cycle. The current low price of uranium makes the once-through cycle economically favorable, but the prospects for timely emplacement of commercial spent nuclear fuel in a mined geologic repository are not particularly good.

An intensive study[1] of the performance of the proposed repository at the Yucca Mountain site in the state of Nevada concluded that the major contributors to the dose to the general population living 20 km from the repository thousands of years from now would be neptunium-237, iodine-129, and technetium-99, if the current policy of direct disposal is followed. This is attributed to the relatively high groundwater mobility of these species in the geologic structures in the vicinity of the repository. The source of ^{237}Np is the alpha-decay of ^{241}Am. Actinides other than neptunium were not significant factors in the offsite dose rate, due to their very limited solubility in water. However, a recent finding[2] that highly soluble Pu(VI) oxide may form readily in contact with water could have a remarkable effect on the predicted performance of the repository and make imperative the elimination of transuranics in general from material intended for repository disposal.

Approximately one year ago, the U.S. Department of Energy initiated a study intended to set forth a course of action that could lead to implementation of an ATW system that would be capable of dealing with the inventory of commercial spent nuclear fuel accumulated by 2015, without consideration of spent

fuel that might be produced by new plants constructed in the interim. The exercise was completed in late 1999 and duly reported[3] to the Congress of the United States, which had mandated the study. The baseline system for partitioning and transmutation recommended in this "roadmap" document is illustrated in Figure 1, where it is contrasted with the French version of the "Double Strata" fuel cycle[4]. The essential difference between these two approaches is the manner of dealing with the transuranic elements. In the Double Strata scheme, plutonium is multi-recycled, initially in light water reactors in the form of MOX fuel, and later in fast reactors. Because the PUREX process[5] separates pure uranium and pure plutonium but leaves the other transuranics, or minor actinides, in the stream with fission products, primarily the lanthanides, an additional aqueous separation process is required for the extraction of neptunium, americium and curium, which are directed to an accelerator-driven system for destruction. It may not be possible to complete this destruction without recycling the fuel fed to the ADS; a pyrochemical process has been postulated in Figure 1 for accomplishing this recycle step.

The ATW system is predicated on the policy position of the United States regarding civil plutonium utilization. It is possible, however, within the constraints of this policy, to realize the energy potential residing in the transuranic elements present in the LWR spent fuel. This can be done by fissioning these elements in the fast neutron energy spectrum of an accelerator-driven subcritical assembly and generating electricity by utilization of the thermal energy released. Therefore, all of the transuranic elements present in the LWR spent fuel are recovered and sent directly to the accelerator-driven system. A solvent extraction process was chosen for the head-end treatment of the LWR spent fuel, because it is desired to remove the bulk of the material present in the spent fuel (the uranium). Uranium removal is important for two reasons: it eliminates a fertile constituent that could breed more transuranics if fed to the transmuter, and it reduces the ultimate volume of the high-level waste produced by the overall process. The use of a solvent extraction process enables extraction of uranium at a purity level that would make it disposable as a Class C low-level waste or suitable for surface storage in an unshielded facility. Because the solvent extraction process envisioned is limited to uranium extraction only, it has been termed the "*UREX*" process. The head-end operations also include the extraction of iodine and technetium, which are intended for transmutation, probably to reside in the outermost regions of the subcritical assembly, similar to the radial blanket region in a fast reactor. A schematic flowsheet for the ATW treatment of LWR oxide spent fuel is shown in Figure 2.

Removal of the uranium from the system greatly reduces the mass of material that must be carried through subsequent processing steps, from 1,450 tonnes heavy metal per year to 35 tonnes heavy metal per year. This makes the utilization of pyrochemical processing very appealing, to capitalize on the compactness of the pyrochemical systems. Other features of pyrochemical processes are compelling as well, including the fact that the process proposed does not separate plutonium from the other transuranics. This tends to enhance the nonproliferation characteristics of the system, as part of a close-coupled system for the destruction of weapons-usable materials. Furthermore, the pyrochemical process recommended does not present the complication of a carryover of lanthanide fission products with the extracted transuranics, so no supplementary extraction processes are required. The very low volume of liquid wastes generated in the hybrid UREX/PYRO process was also a consideration in baseline process selection.

ATW System "PYRO-A" Process

The head-end partitioning process presently envisioned for the ATW system calls for initial partitioning by means of a conventional aqueous solvent extraction process that is truncated at the first uranium extraction stage. That is, the uranium present in the LWR oxide spent fuel feed is removed quantitatively ($\geq$99.9% recovery) and the transuranic elements and fission products (other than xenon, krypton, tritium, iodine and technetium) are left in the raffinate solution. As shown in the schematic flowsheet in Figure 2, the raffinate is directed to an oxide conversion step where the nitrates are converted to solid oxides. The oxides are then reduced with metallic lithium and the metallic product is electrorefined to separate the transuranic elements from the fission products. That portion of the overall flowsheet that involves the conversion to oxide, reduction of the oxide to metal, and electrometallurgical separation of the transuranics, has been termed the "*PYRO-A*" process.

A preliminary schematic process flowsheet for the PYRO-A process is shown in Figure 3. The UREX raffinate could be treated by a conventional oxalate precipitation/filtration/calcination step to produce the oxides of the transuranics and fission products, but this method would produce an additional waste stream that would have to be dealt with and may not facilitate the 99.9% overall recovery target set for the transuranic elements. Alternatives to this process are therefore being considered. Whatever the method chosen, the resultant oxide product would then be reacted with lithium metal in a lithium chloride carrier salt at a temperature of 650°C to reduce the oxides to the metallic state. Metallic lithium for use in the oxide reduction process is regenerated by electrowinning from the Li_2O-bearing LiCl carrier salt. The Group IA and IIA fission product elements, as well as some of the rare earth fission products, are not reduced and remain in the carrier salt; subsequently, these fission products are removed in the ceramic waste stream as described below. The remaining fission products and the transuranic elements are reduced to the metallic state and are transferred to an electrorefining vessel operating at 500°C with a LiCl-KCl electrolyte, where they are placed in the anode baskets. A more complete description of the reduction step is provided elsewhere.[6]

In the electrorefiner, the transuranic elements are electrotransported to a solid cathode. The elements that will form stable chlorides (e.g., Nd, Ce) will be dissolved in the electrolyte as chlorides, while those that are more noble (e.g., Ru, Mo, Zr) will remain behind in the anode basket as metals. Periodically, the electrolyte salt and the LiCl carrier salt are passed through a zeolite-packed column, where the fission products are extracted into the zeolite. The effluent salt is recycled, and the zeolite is mixed with glass frit and sintered to form the ceramic high-level waste form. The residue in the anode baskets is melted with suitable alloy additions to form the metal waste form (also a high-level waste). The cathode deposit of transuranic elements is removed from the electrorefiner, treated to remove the entrained electrolyte salt, and consolidated into ingots as feed for the fabrication of transmuter fuel assemblies.

ATW System "PYRO-B" Process

The combination of metallic fuel with very high zirconium content and rather limited annual throughput requirements (~35 tonnes heavy metal per year) led to the selection of a pyrochemical process, referred to as "*PYRO-B*," for the treatment of the irradiated transmuter blanket fuel assemblies. The PYRO-B flowsheet is designed to extract the TRU elements (for recycle into fresh transmuter blanket fuel) and technetium and iodine fission products (for incorporation in transmutation assemblies) from spent transmuter blanket fuel and to provide waste streams that are compatible with either the ceramic

(i.e., glass-bonded sodalite), or metallic (i.e., zirconium-iron alloy) waste form. The selection of pyrochemical processes for the treatment of the transmuter blanket fuel was based on their robust and compact nature, compatibility with the desired waste forms, and probable cost effectiveness. In contrast to the LWR fuel processing, high material throughput is not required for the treatment of spent transmuter blanket fuel, but the fuel will not likely have cooling times exceeding 6-12 months. Therefore, radiation levels and decay heat levels will be high; this does not pose a problem for pyrochemical processes, because the reagents used are stable and the equipment is designed for high-temperature application in the first place.

Two pyrochemical process options are being considered for treating irradiated transmuter blanket fuel: a chloride volatility process and an electrometallurgical process. The difference between the two options is the method by which the zirconium, the major component of the fuel, is removed from the transuranics and fission products. The baseline option for irradiated transmuter blanket fuel processing, as depicted in Figure 4, is based on a chloride volatility process (similar to the Kroll process) for zirconium extraction, coupled to an electrowinning process for TRU and fission product separation. Chloride volatility was chosen as the mechanism for TRU and zirconium separation because of the high zirconium content in the fuel and the existing industrial experience in zirconium metal production.

With the chloride volatility process, irradiated transmuter blanket fuel is removed from the transmutation system and allowed to cool for a reasonably short time; the fuel pins are separated from the fuel assembly hardware, and the pins are chopped. The chopped fuel is chlorinated, and the matrix zirconium from the fuel alloy, iron from the cladding, and the transition metal fission products (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 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 non-volatile metal chlorides (e.g., TRU, rare earths, Cs, Sr) are transferred from the volatility system to a molten salt (LiCl-KCl) bath in which the transuranics are electrowon from the solution and recycled to fuel fabrication. Periodically, the fission products are removed from the molten salt and converted to a stable ceramic waste form as described above. Iodine is removed from the molten salt, fabricated into targets and placed in transmutation assemblies. The technetium produced by the fission of transuranic elements in the transmuter blanket fuel remains in the zirconium stream and is recycled, without separation from the zirconium and the other noble metal fission products, into the transmuter system as part of the fresh blanket fuel.

The backup electrometallurgical option involves the electrotransport of zirconium from an anode basket containing chopped ATW transmuter blanket fuel and deposition of the zirconium on a solid cathode. The transuranic elements partition to the molten salt electrolyte together with Group IA and IIA fission products and lanthanides. Technetium remains in the anode basket as a residue along with the other noble metal fission products. This anode heel is removed from the cell and incorporated in the fabrication of suitable transmutation target subassemblies. Iodine partitions to the molten salt as soluble metal iodides, which must somehow be collected and directed into the transmutation cycle. The transuranic elements are removed from the salt by electrowinning and deposited at a solid cathode that is periodically harvested. The extracted metallic TRU elements are cleaned of any adhering electrolyte salt

and sent to transmuter fuel fabrication. The depleted electrolyte salt is then periodically treated to remove the rare earth and active metal fission products for immobilization in the ceramic waste form.

ATW System Waste Form Production

It was the intention during development of the conceptual baseline process flowsheet to avoid the generation of liquid wastes to the greatest extent possible. A significant volume of metallic waste, comprising the cladding hulls and other constituents of the LWR spent fuel assemblies, will be generated during the UREX operations preceding the solvent extraction steps. It is anticipated that these materials will be sent directly to the metal waste form preparation process. Subsidiary treatment of the cladding hulls will probably be required, for the purpose of maintaining the target actinide recovery level of 99.9%; a separate hull leaching treatment will create additional waste streams that must be accommodated.

While technically not a waste stream, the uranyl nitrate product of the UREX process will require further processing for its proper disposition. The solution will be treated by the same means developed for the corresponding solution of TRU elements and converted to a suitable oxide form (probably U_3O_8 if the option for disposal as a low-level waste is selected, and UO_3 if the material is to be stored for future use). Residual liquids from the uranium and TRU extraction steps are to be evaporated to dryness and any radioactive residue sent to the ceramic or metal waste streams.

The PYRO-A process waste streams lead to two high-level waste forms, one ceramic and one metallic, as seen in Figure 3. The fission products that do not tend to form stable chlorides (e.g., Ru, Re, Pd, Nb, Mo) will remain in the electrorefiner anode baskets, retained by the fine-mesh screens lining these baskets. The basket liners are held at temperature to allow salt to drain off, and are then combined with the cladding hulls (and, possibly, other fuel assembly constituents), melted, and cast into ingots. In the early stages of metal waste form development, a composition of Zircaloy-8 wt. % stainless steel (Zr-8SS) was selected for use with Zircaloy-clad fuel. The SS-15Zr composition selected for use with stainless steel clad fuel is now a well-characterized waste form material with well-understood properties[7]; it is being prepared in the course of the demonstration of the electrometallurgical treatment process demonstration with sodium-bonded fuel and blanket assemblies discharged from the EBR-II reactor in Idaho. Development of the Zr-8SS waste form has not proceeded beyond the initial studies, which showed Zr-8SS properties and behavior are quite favorable for application as a waste form for the ATW system. However, development work is still needed to bring Zr-8SS technology to an appropriate level of maturity. The microstructure of this alloy composition, shown in Figure 5, appears to be reasonably stable. With the large excess of zirconium, the comparatively small concentration of noble metal fission products tends to be localized in the primary α-zirconium phase and not at phase boundaries. Limited corrosion studies with this composition, using representative concentrations of (non-radioactive) fission product elements, suggest that the alloy will possess excellent corrosion resistance in a typical repository environment.

Again referring to Figure 3, salt-borne fission products in the PYRO-A process derive from the oxide reduction step and from the electrorefining process. The salt stream from the oxide reduction step must be combined with sufficient KCl to make the salt compatible with the electrorefiner salt stream and the subsequent processing steps. The two salt streams are then combined and passed through a zeolite column, where the fission products in the salt are extracted into the zeolite structure. The salt-loaded zeolite is removed from the column when the limiting heat loading (due to decay heating by the sorbed

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radionuclides) is reached. The salt-loaded zeolite is crushed, mixed with glass frit, and the mixture heated above the softening point of the glass (i.e., to 850°C) to produce a solid monolith. During this heating process, the zeolite transforms to sodalite. Much of the salt and its solutes remain within the sodalite lattice, but the rare earth fission products and any trace actinide elements will tend to form stable secondary phases, generally oxides or oxychlorides. The resultant glass-sodalite composite ceramic waste form has been shown[8] to have good corrosion and leach resistance. There is more experience with the environmental behavior of this waste form than with the metal waste form, so recent development work has focused on reducing waste volume and minimizing fabrication costs. Figure 6 shows a large section of the ceramic waste form; such sections have been prepared by ambient-pressure sintering of zeolite containing non-radioactive fission product elements at concentrations up to 5 wt. % and with 25% glass binder. It appears that the fraction of glass can be reduced further.

The pyrochemical processes that make up the PYRO-B flowsheet (Figure 4) are characterized by low amounts of secondary waste generation. This is a key advantage of this family of process options. Figure 4 does not show the detail of waste form production, but the process involves the same two waste streams and method of production encountered with the PYRO-A process. If an electrorefining alternative were to be used instead of the chloride volatility step, it is possible that a mixed chloride/fluoride electrolyte might be required. This would change substantially the production of the ceramic waste form, because the zeolite system for immobilization of fission products is not compatible with fluoride ions. Prior research on the processing of other fuel types (e.g., molten fluoride salt fuels) led to the development of a fluorapatite waste form with excellent properties; it is not certain, however, that the waste volume minimization objectives could be met with this process variation.

Recycle of the zirconium extracted in the course of transmuter blanket fuel processing could significantly reduce the volume of the metal waste form produced. Using conservative estimates for fission product loading of the waste forms, the processing of 1,450 tonnes (heavy metal content) of LWR spent oxide fuel per year for transmutation would produce nearly 400 cubic meters of high-level waste annually, assuming no recycle of zirconium. This amounts to about 0.28 cubic meters per tonne of fuel processed, which is comparable to the best results achieved to date at contemporary PUREX reprocessing plants. It is quite likely that this value could be reduced to 0.1 m^3/t after a modest experimental effort at process optimization. For purposes of comparison, the unpackaged volume of 1,450 tonnes of LWR spent fuel is about 600 cubic meters, or approximately 0.4 m^3/t. High-level waste volume is considered to be a significant metric, because a volumetric reduction in waste volume is directly reflected in avoidance of the cost of fabricating, loading, handling and emplacing repository disposal containers.

Acknowledgment

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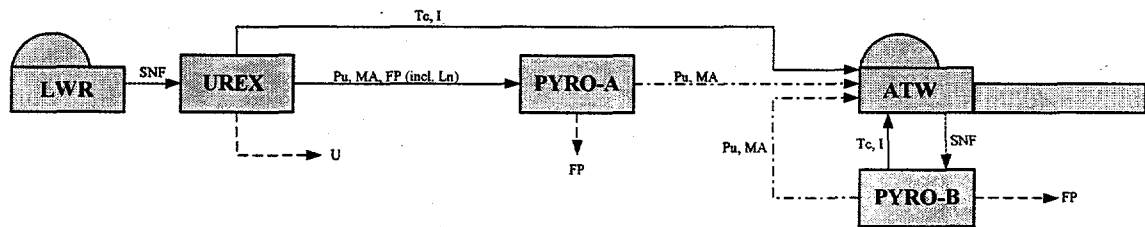
Double-Strata System
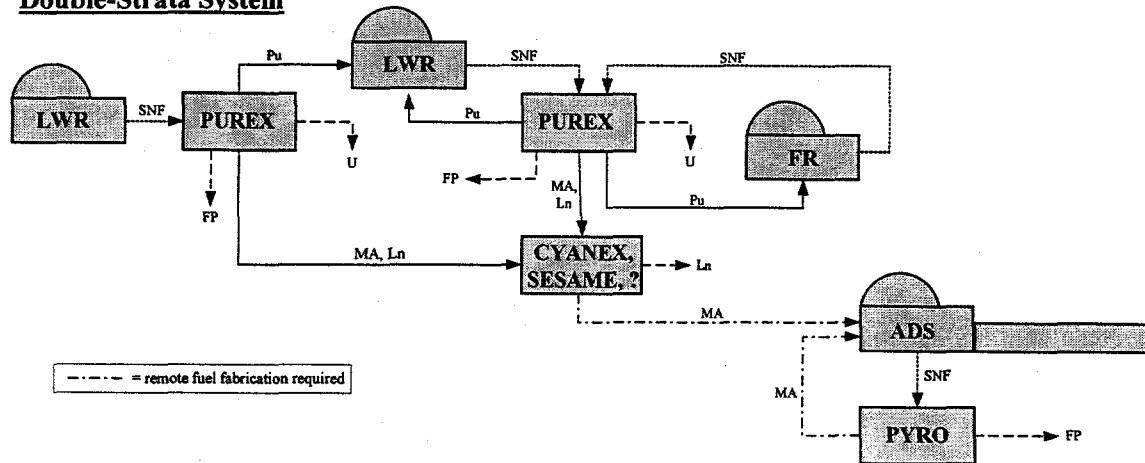
ATW System

Figure 1. Comparison of French double-strata system to U.S. ATW system. SNF: spent nuclear fuel; LWR: light water reactor; ADS: accelerator-driven system; ATW: accelerator transmutation of waste; MA: minor actinides (Np, Am, Cm,...); FP: fission products; Ln: lanthanides. Dashed lines represent material sent to high-level waste form production.
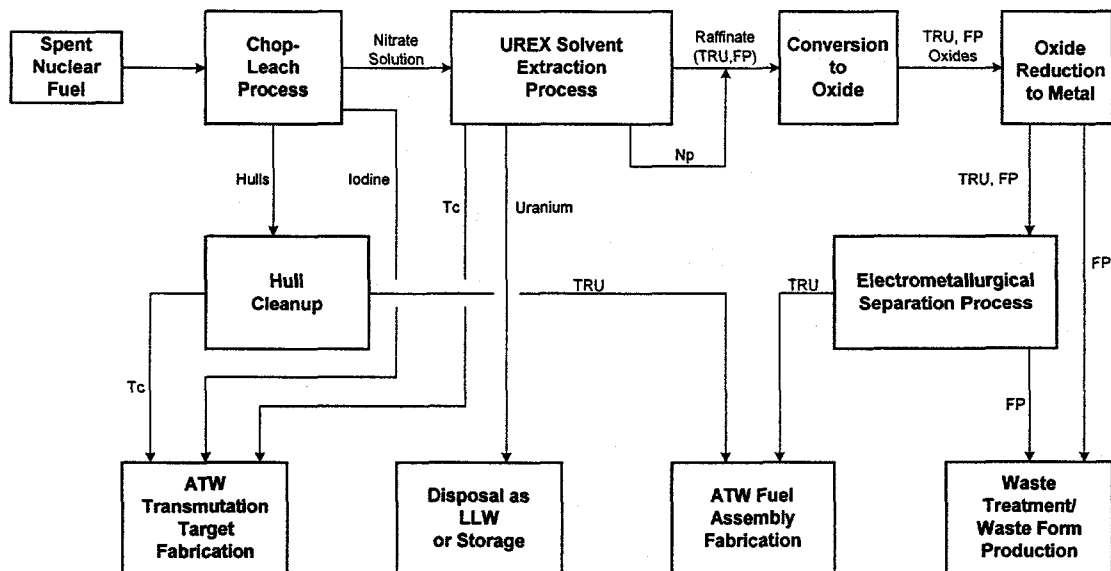

Figure 2. Current reference flowsheet for the treatment of LWR oxide spent fuel for the Accelerator Transmutation of Waste (ATW) system.
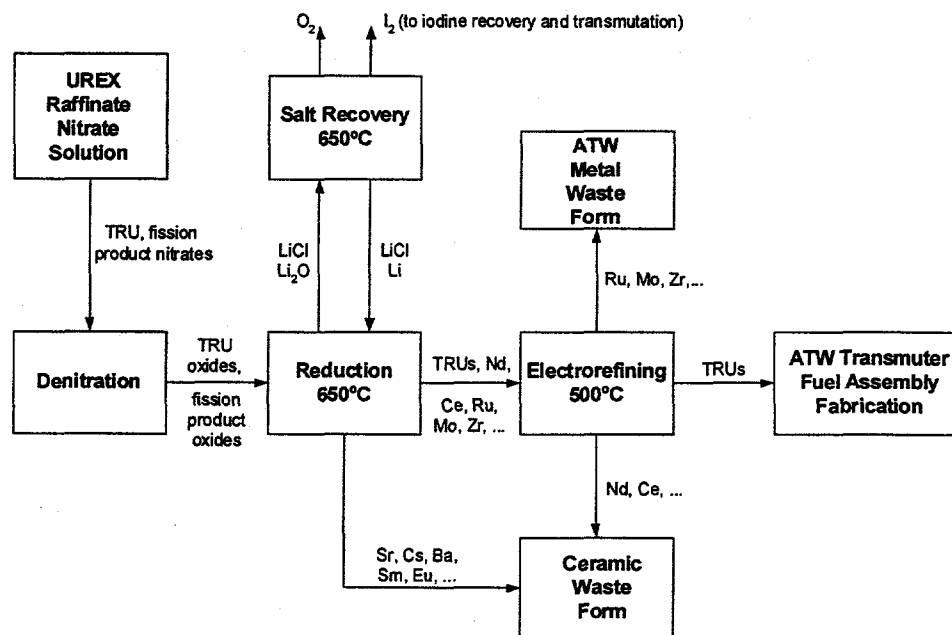
Figure 3. Flowsheet for the ATW PYRO-A process for the treatment of UREX raffinate.
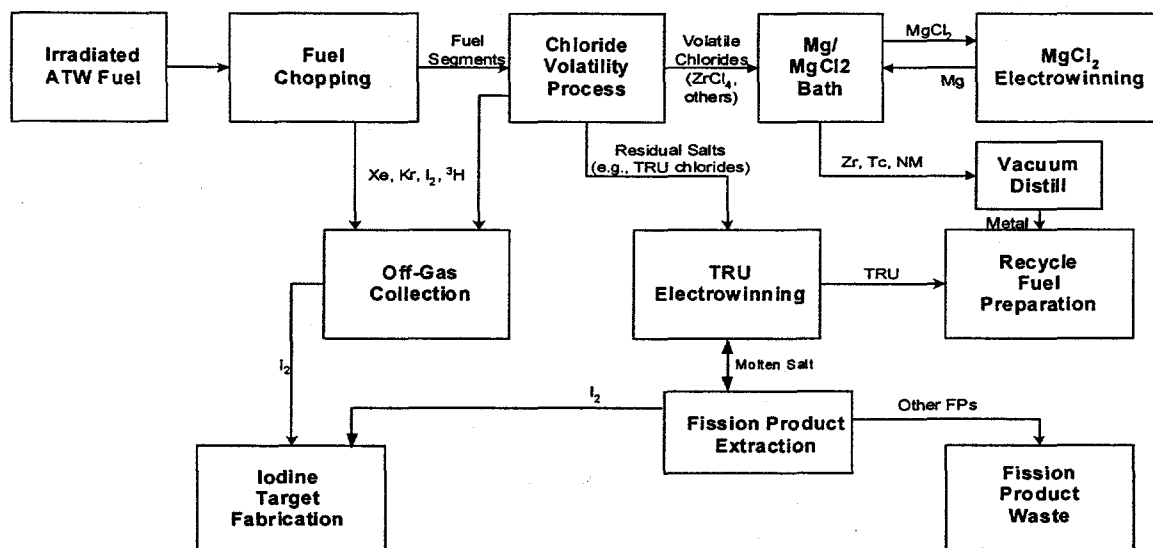

Figure 4. Flowsheet for the PYRO-B process for the treatment of irradiated ATW transmuter blanket fuel.
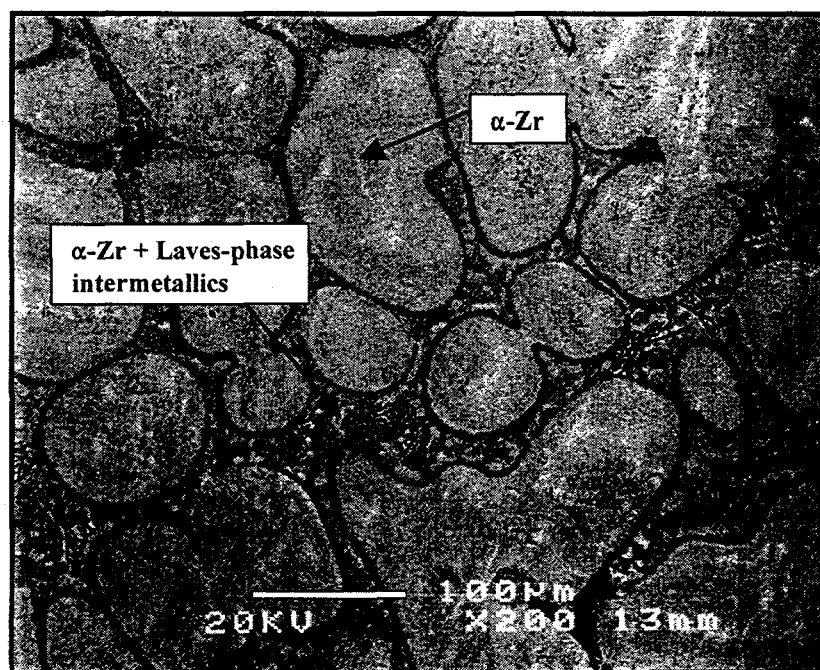
Figure 5. Backscattered electron image of Zr-8SS alloy. The noble metal fission products tend to reside in the primary α-zirconium phase.
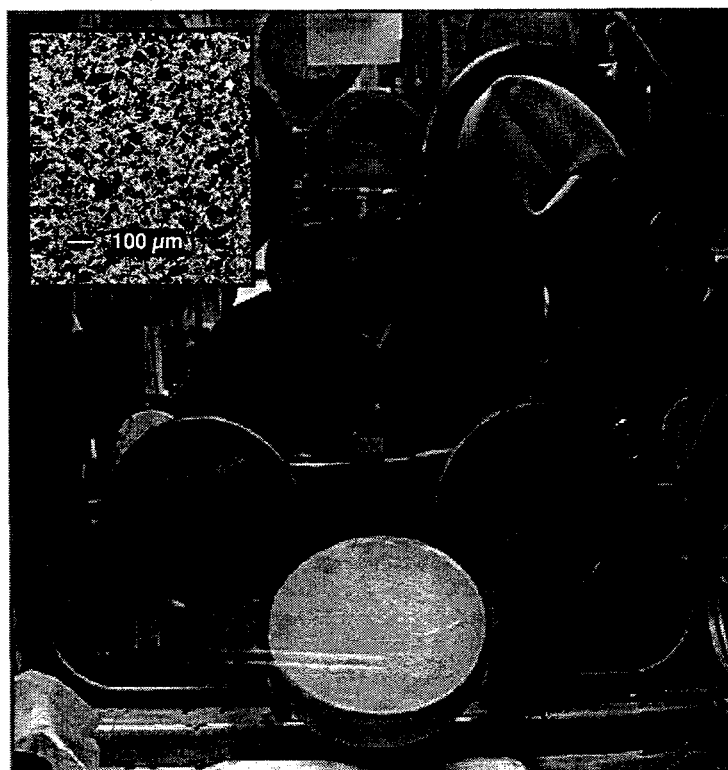

Figure 6. Sample of simulated ceramic waste form prepared by sintering at ambient pressure at 850°C. Inset shows microstructure of glass-sodalite composite.