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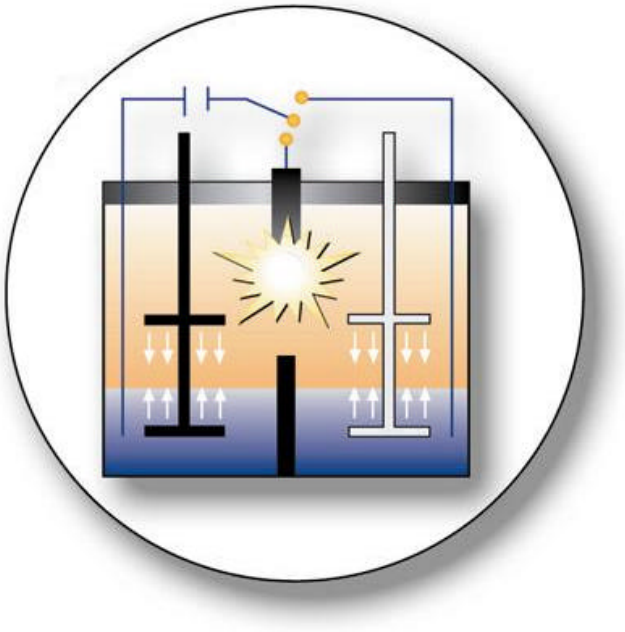

A Roadmap for Developing ATW Technology:

Separations & Waste Forms Technology

September 1999

ANL-99/15

Preparation of A Technology Development Roadmap
for the
Accelerator Transmutation of Waste (ATW) System:

Report of the ATW Separations Technologies and Waste Forms Technical Working Group

August 1999

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Abstract

In response to a Congressional mandate to prepare a roadmap for the development of Accelerator Transmutation of Waste (ATW) technology, a Technical Working Group comprised of members from various DOE laboratories was convened in March 1999 for the purpose of preparing that part of the technology development roadmap dealing with the separation of certain radionuclides for transmutation and the disposal of residual radioactive wastes from these partitioning operations. The Technical Working Group for ATW Separations Technologies and Waste Forms completed its work in June 1999, having carefully considered the technology options available.

A baseline process flowsheet and backup process were identified for initial emphasis in a future research, development and demonstration program. The baseline process combines aqueous and pyrochemical processes to permit the efficient separation of the uranium, technetium, iodine and transuranic elements from the light water reactor (LWR) fuel in the head-end step. The backup process is an all- pyrochemical system. In conjunction with the aqueous process, the baseline flowsheet includes a pyrochemical process to prepare the transuranic material for fabrication of the ATW fuel assemblies. For the internal ATW fuel cycle the baseline process specifies another pyrochemical process to extract the transuranic elements, Tc and I from the ATW fuel. Fission products not separated for transmutation and trace amounts of actinide elements would be directed to two high-level waste forms, one a zirconium-based alloy and the other a glass/sodalite composite.

Baseline cost and schedule estimates are provided for a RD&D program that would provide a full-scale demonstration of the complete separations and waste production flowsheet within 20 years.

Preparation of A Technology Development Roadmap
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August, 1999

1.0. Introduction

The elimination of certain radionuclides from commercial spent nuclear fuel intended for disposal in a mined geologic repository can have a significant positive effective 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. For technical guidance, the Separations Technologies and Waste Forms Technical Working Group (hereafter, TWG) examined the repository Total Systems Performance Assessment (TSPA) in its most recent form as done for the repository Viability Assessment (VA). That study demonstrates that significant dose reductions can be gained by extraction and transmutation of technetium and iodine. It further mandates that the transuranic elements (Np, Pu, Am, Cm) be transmuted by fissioning, which also permits the generation of electric power with the ATW system.

Consideration of the TSPA-VA modeling results prompted the TWG to specify 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 ATW system. First, the TWG concluded that the removal of uranium from the commercial spent fuel should be done in such a way that the uranium can be disposed as a non-TRU, Class C low-level waste. This will remove nearly 95% of the mass of the spent fuel from subsequent, possibly more complex extraction steps and permit disposal at a cost significantly lower than that for high-level waste disposal. A target of better than 99.9% recovery of the uranium in the spent fuel has been established. 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 has been adopted. And finally, the recovery target for technetium and iodine has been set at greater than 95%. These target values refer to overall system performance. A separate report in this compendium on the effects of partitioning and transmutation on repository performance provides a description of the factors influencing repository performance and an indication of the bases for the recovery targets chosen.

For the present purposes of preparing a technology development roadmap, the TWG has carefully considered the technology options available and identified a baseline process flowsheet and a backup flowsheet for the initial period of the RD&D program, assumed to be the period 2000-2010. Downselection to a single reference process flowsheet would take place in 2006, to facilitate preparation for the extensive demonstration period. 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. The

backup flowsheet is an all pyrochemical system. In conjunction with the aqueous process, the baseline flowsheet includes a pyrochemical process to prepare the TRU material for fabrication of the ATW fuel assemblies. For the internal ATW fuel cycle the baseline process specifies another pyrochemical process to extract the TRUs, Tc and I from the ATW fuel. Figure 1 provides the overall baseline process flowsheet. It is important to note that this process does not separate plutonium at any stage.

Considerable deliberation preceded the decision of the TWG to propose an aqueous front-end process. The decision was driven largely by two factors: (1) perceived ability to meet the purity requirements for the uranium product that would permit its disposal as a Class C low-level waste, and (2) technical maturity of the technology, providing assurance that cost minimization targets could be met. The electrometallurgical process that offers great promise for this application has not been operated at the scale required, and extensive further development is required to achieve the uranium product purity targets. The electrometallurgical process is carried as a backup technology for this purpose, with the necessary development activities to permit a reasonable evaluation of its feasibility included in the early stages of the recommended program.

The processing of irradiated ATW fuel, assumed for these planning purposes to be transuranics and various fission product elements contained in a zirconium metal matrix, leads to some of the least technically mature steps in the overall flowsheet. Because there is limited commercial experience with the processing of zirconium matrix fuels at these scales, consideration should be given to the selection of a different fuel matrix – one that not only embodies ideal nuclear characteristics, but also one that lends itself more readily to chemical processing. In order to achieve the most economical and practical ATW process, it might be necessary to compromise somewhat on the fuel design. Nevertheless, the recommended program has been set forth on the basis of the zirconium matrix fuel, for purposes of conservatism in the estimates of cost and schedule. A modified fuel would simplify processing, but could have unacceptable impacts on system performance. A trade study is clearly called for in this case and should be part of the initial phase of the program.

The overall scenario used for the ATW roadmapping study consists of the eventual deployment of eight ATW stations, preceded by an initial prototype station with approximately half the capacity of the full-sized stations. Each of the full-sized stations will comprise eight transmuter units for fissioning of transuranic elements and transmutation of iodine/technetium targets. The transmuter units are assumed to operate with metallic fuel having the approximate composition 23 wt.% TRU and 77 wt.% Zr. A chemical processing plant to support one full-sized ATW station (8x840 MWt) would have a throughput requirement of about 170 MTHM LWR spent fuel per year and 26 MT (total fuel mass) ATW-irradiated fuel per year.

This RD&D roadmap recommendation does not address the deployment scenarios for chemical processing plants, nor does it consider such issues as transportation, IAEA full-scope safeguards, and measures for materials protection, control and accountancy that would be required in a deployed plant. Because of the significant impact of deployed plant size on process scale-up issues, a tacit assumption has been made regarding siting; i.e., that each 8x840 MWt ATW station would be supported by a complete on-site chemical processing system for both LWR and ATW fuels.

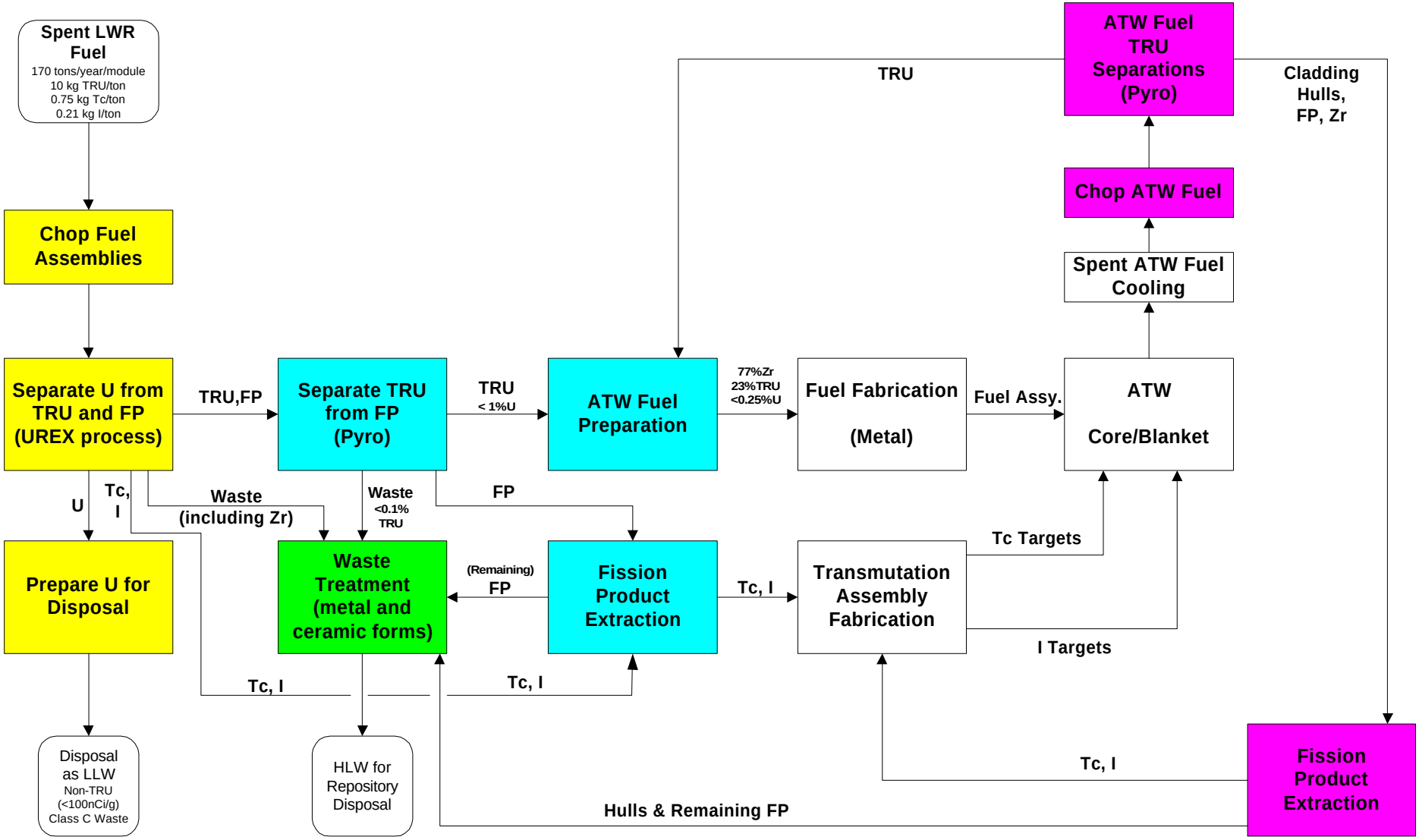


Figure 1. Baseline Process Flowsheet

The high-level waste output of the processing systems will take two forms: (1) a ceramic waste form, within the defense waste glass composition envelope, that immobilizes Cs, Sr, Ba and other active metal fission products; and (2) a metallic waste form with nominal composition Zr-8 wt.% SS (SS: stainless steel) that immobilizes residual Tc as well as other transition metal fission products such as Mo, Ru and Sb. These waste forms would be virtually identical to the wastes being produced currently as part of the demonstration of sodium-bonded metallic fuel treatment. With proper design, the baseline process will not produce a large volume of liquid waste.

A three-phase development program for processing technologies is envisioned. The first phase, consists of laboratory-scale R&D and would comprise flowsheet development and validation through small-scale testing. The second phase, involving pilot-scale testing, would include the demonstration of individual process operations. Extensive use of existing hot cells in the DOE complex would be necessary during this phase. Early in this second phase, the reference process for plant design will be selected. Pilot-scale operations with the selected processes would continue, eventually making a transition to the mission of providing fuel loadings for the early ATW demonstration units and, in the case of the pyrometallurgical process, operating with the fuel and transmutation assemblies discharged from these demonstration plants. The third phase of the program, the plant-scale demonstration phase, would consist of a full-scale demonstration of the integrated reference process. Facilities constructed during this phase are envisioned to be collocated with the prototype ATW unit (4x840 MWt).

One key technical barrier that is inherent for the separations processing and waste form production steps is the nature of the radioactivity to be handled. The transuranics include high-specific-activity alpha emitters (mostly curium-244) and neutron emitters (curium isotopes and notably, californium-252), which will be produced in larger amounts as burnups increase in ATW fuel. Thus, all process steps, including fuel fabrication, must be performed remotely in shielded facilities. This will require special equipment designs to accommodate remote operation, equipment maintenance, and equipment replacement. Such operations are currently done on a small pilot plant scale throughout the DOE complex and there is an extensive operating/maintenance/replacement experience base—but only on a small scale. Much of the U.S. experience base with large-scale remote chemical operations is disappearing as technologists age and retire. By the projected time of implementation of the ATW system, little of that experience will be available. Scale-up of these operations must therefore be considered as a major technical barrier.

2.0 LWR Fuel Processing

2.1 Summary

The LWR fuel processing part of the flowsheet is designed to extract from LWR spent fuel (1) the TRU elements (as metals) for use in the fabrication of ATW fuel, (2) the fission products Tc and I for inclusion in ATW transmutation assemblies, and (3) the uranium in a form that can be disposed of as a Class C low-level waste. Three alternatives are being considered to accomplish these tasks:

Baseline Process. The TWG recommends as the baseline separations process for development a hybrid system, consisting of an initial PUREX-based aqueous processing step that will be termed "UREX", followed by a series of pyrochemical steps collectively termed the electrometallurgical “EM” process. The UREX process would produce a pure U stream for waste, technetium and iodine streams for target fabrication, and a TRU-fission product oxide stream. The EM process would then separate the TRUs from the fission products and convert the TRUs to a metallic form suitable for fabrication of ATW fuel.

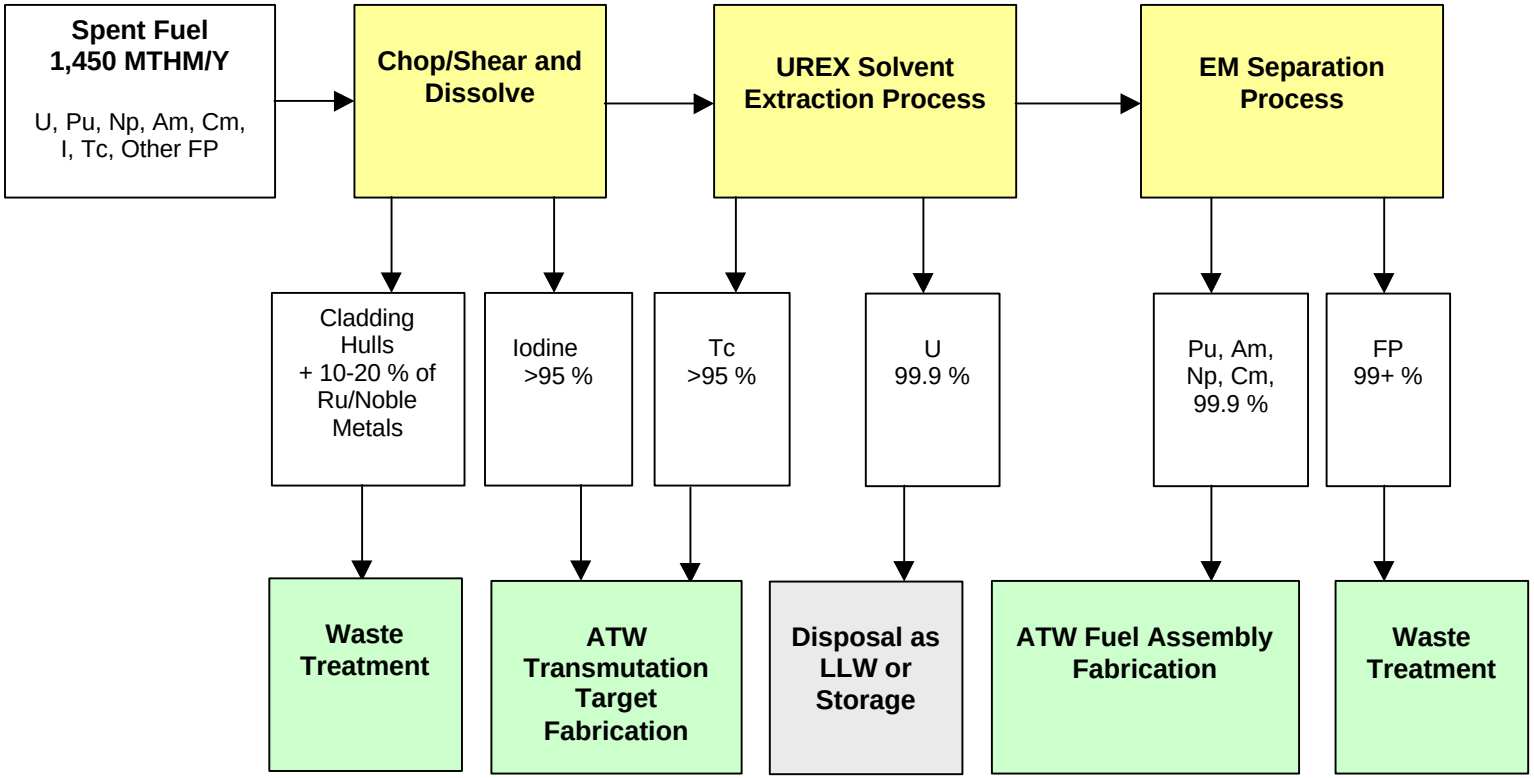
Backup Process 1. The recommended backup process is an "all pyro" option that uses a variation of the basic EM pyroprocess to perform all aspects of the required separations without any aqueous steps. An “all aqueous” process would be equally viable as a backup to the baseline process; the technology for this sort of system is well-advanced, and necessary developments to make it available as a deployment option are within the scope of the baseline program.

Backup Process 2. An alternative backup process consists of an initial UREX aqueous processing step, followed by an aqueous TRUEX-based step, and in turn followed by the EM process. The UREX process would produce a pure U stream for waste, technetium and iodine streams for target fabrication, and a TRU-fission product oxide stream for the TRUEX process. The TRUEX step would then further separate the TRUs from the fission products. The EM process would then convert the TRUs to a metallic form suitable for making ATW fuel. This backup option necessitates the inclusion of a modest amount of R&D to bring the already-developed TRUEX process to a level that would permit its inclusion in the field of candidates for the selection of the reference process.

The TWG-selected baseline process includes aqueous-based processing steps for the light-water reactor spent fuel to remove the bulk materials (zircaloy cladding and uranium). This will leave only about 4% of the original cladding/fuel mass to be processed in subsequent separations systems. The baseline process also includes isolation of the fission products iodine and technetium to enable transmutation of the long-lived ^{129}I and ^{99}Tc. Figure 2 provides a basic flowsheet of the baseline (UREX/EM) process.

The following sections describe the current state of the technology, the required state of the technology and the path required to reach the goals of the ATW process. A timeline for the associated R&D effort is presented.

Figure 2: LWR Spent Fuel Processing Overview



2.2 Current State of Technology

2.2.1 UREX Process

The UREX process is an alteration of the PUREX process, which is used worldwide for reprocessing commercial spent fuel. Large-scale plants are in operation in England, France, and Russia and the Japanese are preparing to start up another large plant. The UREX process does not recover plutonium, but partitions plutonium to the waste along with the fission products. Uranium recovery and purification are well studied, with a large amount of data available in the literature. Little additional RD&D will be required to ensure a uranium product that meets NRC Class C low level waste criteria. Partitioning of plutonium to the waste can be readily accomplished with existing technology; however, some work will be required to prove that the chosen complexants and reductants do not contribute to waste volume and do not cause problems during solvent extraction. Figures 3-5 illustrate the UREX process as presently conceived.

France and Japan have data to show that 97-98% of technetium and 99% of neptunium can be recovered with uranium and partitioned into different streams for subsequent conversion to ATW assemblies or targets. Studies exist to show that >95% of the iodine can be removed from the aqueous feed solution during dissolution by sparging with air and NO. Some RD&D will be required to identify the best technology for capturing iodine from the off-gas in a form that can be used for target fabrication.

Although the oxalate precipitation/filtration/calcination process has been used extensively on the plant scale for conversion of TRU components to oxide, the process is not normally used to convert multi-components (TRU elements and fission product elements) simultaneously to mixed oxides; thus, new development work will be required. Also, a more simple and efficient modified direct thermal denitration process has been developed and demonstrated for uranium and thus offers a variant with improved performance which should be developed and demonstrated for mixed TRU and fission product elements.

2.2.2 TRUEX Process

The TRUEX Process was developed in the 1980's to decontaminate TRU material from nuclear wastes accumulated in the US at DOE nuclear material production sites. This process would be used to separate the transuranic (TRU) elements from the uranium extraction process raffinate. The active extractant in the TRUEX process is n-octyl-phenyl-di-isobutyl-carbamoylmethyl phosphine oxide (CMPO). The TRUEX solvent extracts the TRU's and lanthanides from the uranium extraction process raffinate. The extracted TRU's and lanthanides are then stripped from the solvent resulting in a TRU/lanthanide waste stream. The separated TRU's would be converted to oxides and then a metal form for transmutation. Additionally, if the ^{99}Tc can not be separated in the uranium extraction process it would be separated in the TRUEX process. The resulting ^{99}Tc stream would be converted into Tc targets for transmutation. The raffinate from the TRUEX process would contain the fission products, such as Cs and Sr, and would be prepared for disposal in a geological repository.

Figure 3: UREX Process First Cycle

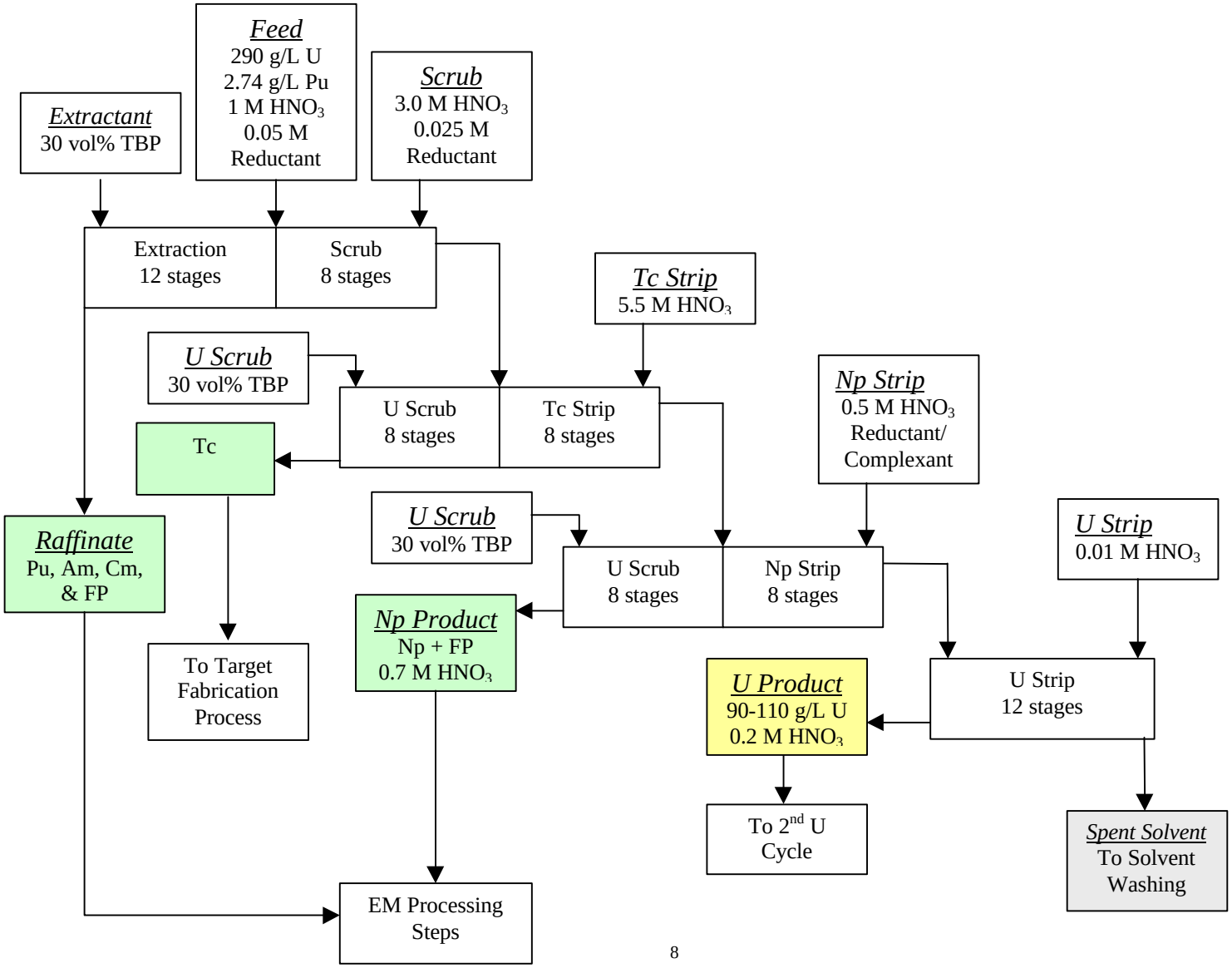


Figure 4: UREX Process: 2nd U Cycle

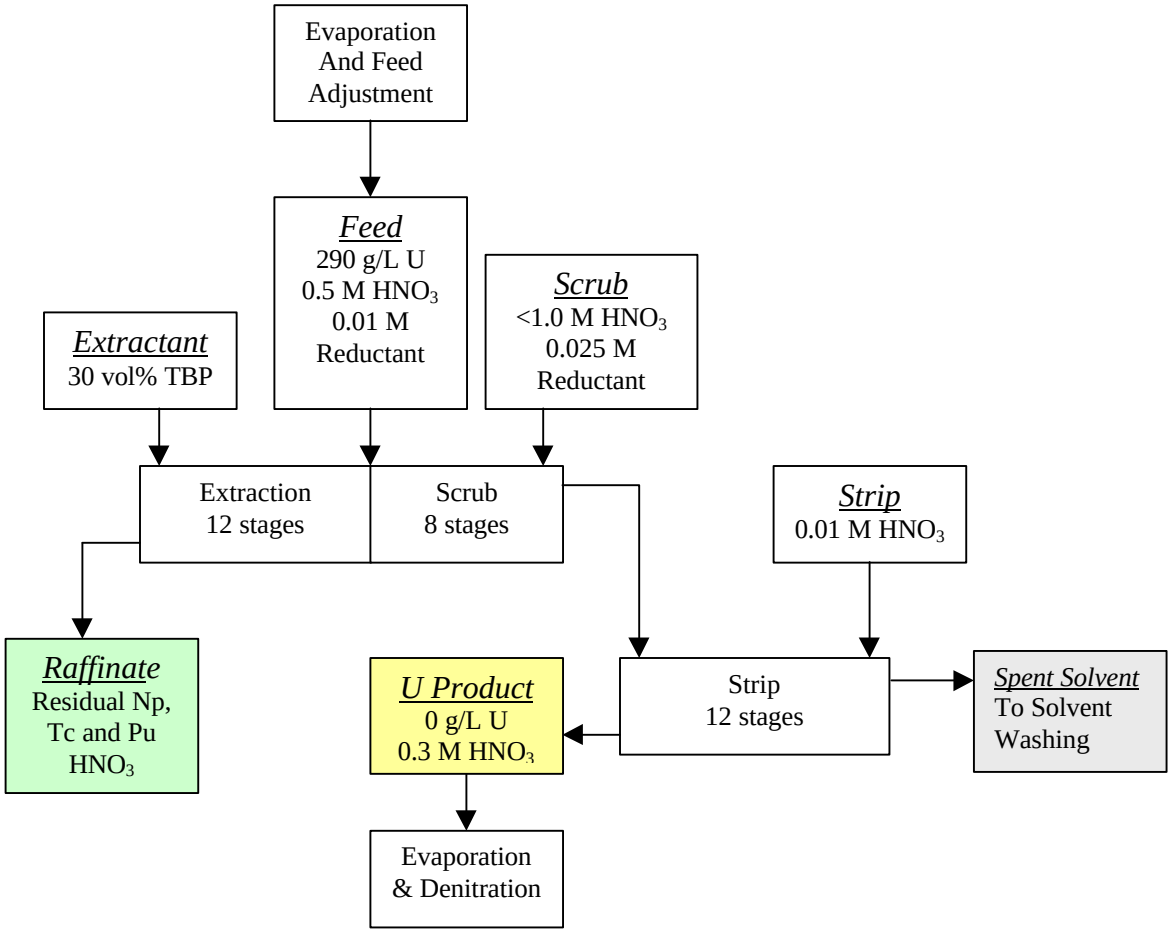
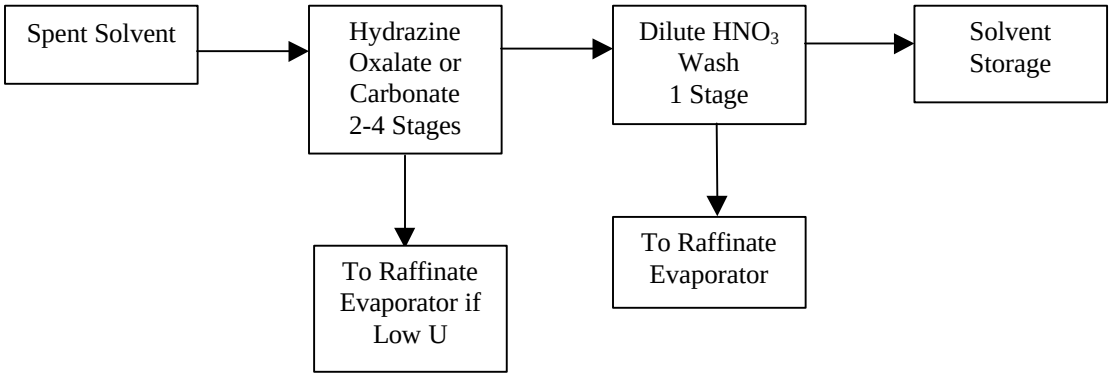


Figure 5: UREX Process: Solvent Washing



Since the initial development of TRUEX, work has continued throughout the DOE complex on site specific application of the TRUEX process. The greatest focus on TRUEX development within the DOE complex is currently underway at the INEEL. Testing and optimizing the TRUEX process for the treatment of acidic tank waste and solid HLW calcine (re-dissolved in nitric acid) is being conducted. These waste inventories were generated from past fuel reprocessing campaigns and facility decontamination. The TRUEX process has recently been successfully demonstrated with actual tank waste at the INEEL using 2-cm diameter centrifugal contactors in a shielded and remotely maintained hot cell facility (RAL). The results of these tests indicate removal efficiencies for tank waste of: (a) 99.7% for total alpha, (b) >99.9% for ^{241}Am, and (c) 99.97% for Pu. Similar tests will be conducted for redissolved HLW calcine in the next year. The process is also being studied in Japan, India, and Italy for the separation of TRUs from commercial wastes. Other potential solvent extraction processes for the separation of the TRU material from acidic waste were reviewed; for completeness these are listed in Appendix A.

2.2.3 Electrometallurgical Process

Regardless of whether an aqueous/pyrochemical or an “all pyro” option is chosen, the same two steps are involved in the EM process. The first step is a reduction step, which reduces the actinide oxides to the metallic form. The second step is an electrorefining step, which separates the TRU elements from any associated fission products. Associated with the reduction step is a salt-recovery process that allows recycling of the reduction salt. Figure 6 provides a basic flowsheet of the EM process steps.

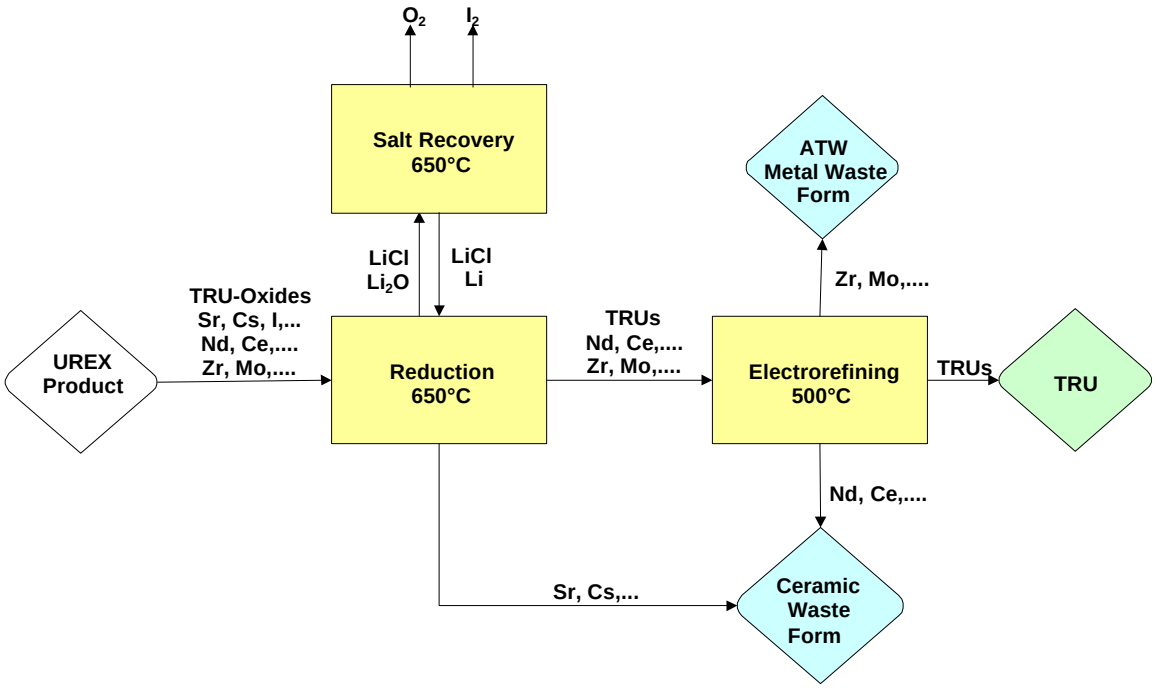
The electrorefiner technology has been well established and electrorefiners capable of holding 30-kg batches of fuel are in operation. A significant amount of work has already been accomplished to investigate various molten-salt based processes to perform the reduction of LWR fuel. The lithium/lithium chloride system was chosen due to its ability to be scaled-up to large-scale application. Development of the lithium reduction process has consisted of parallel development of the flowsheet chemistry and engineering issues associated with process scale-up. The basic chemistry of the lithium reduction process, including the salt-recovery step, has been demonstrated at the laboratory-scale (30-300 g) using simulated fuel. Engineering-scale (5-20 kg) experiments have been conducted to investigate issues associated with process and equipment scale-up. A conceptual design study for a 10 MTHM/year EM processing plant for LWR fuel has been completed. Methods for isolation of technetium from the pyro processes have not been developed.

2.3 Target State of Technology

2.3.1 UREX Process

The target state for the UREX technology is a process for spent reactor fuel with a capacity of 1,440 MTHM commercial LWR spent fuel per year that produces minimum added waste, with most reagents either recycled or converted to environmentally benign gases and exhausted through the stack. The process is to produce a uranium product that meets the criteria for NRC Class C low level waste and contains low amounts of neptunium and technetium. Further, the process is to reject plutonium to the aqueous raffinate along with americium, curium and the fission products.

Figure 6. EM Process Flowsheet



Neptunium and technetium are to be initially co-extracted with uranium and then separated. The neptunium stream will be combined with the other transuranic stream for later conversion to oxide. The technetium stream will be converted to metal for transmutation target fabrication. The raffinate is to contain < 0.1% of the uranium fed to the process. Iodine is to be removed from the aqueous solution and recovered from the offgas in a form that is compatible with target fabrication. The process is to be designed and operated so that the aqueous raffinate is easily converted for further processing to separate plutonium, americium and curium from the other fission products either by aqueous or pyrochemical processes.

2.3.2 TRUEX Process

The target state for the TRUEX technology is a process for treating the raffinate stream from the UREX process that is sized for a capacity of 1,440 MTHM per year. The TRUEX process should be optimized to produce minimum added waste via recycle or conversion to environmentally benign gases. The TRUEX Process will produce TRU material that meets the feed specification for ATW fuel fabrication. TRUEX will reject fission products such as strontium and cesium to the aqueous raffinate. If goal quantities of ^{99}Tc (>95%) have not been removed at this point, then this raffinate stream may require further processing. The raffinate is to contain < 0.1% of the TRU material. The process is to be designed and operated so that the aqueous raffinate is user friendly to waste treatment and disposal, and the product stream (TRU) is easily converted to an oxide form for feed to the fuel fabrication process.

2.3.3 Electrometallurgical Process

The target state of the EM process is for it to be mature enough to support design of the demonstration scale plant. In addition to scale-up issues, the technology must be capable of separation and isolation of I and Tc and to produce a non-TRU uranium stream. A pilot-scale EM plant that would support the “all pyro” option would have a capacity on the order of 10 MTHM LWR fuel per year. Based on the results of conceptual design studies, such a plant would require reduction vessels and electrorefiners that would hold 125 kg HM batch sizes and a salt-recovery cell (part of the reduction process) that could electrolytically decompose 1 kg of lithium oxide/hr. For the reduction and salt-recovery steps this is an order of magnitude greater than what has been demonstrated to date; for the electrorefiners it is a factor of four greater.

2.4 Key Technical Barriers

2.4.1 UREX Process

The key technical barriers in the case of the UREX process are: (1) removing iodine from the offgas stream, with low loss to the environment and in a form that is easily converted to the form needed for target fabrication; (2) achieving neptunium separation from uranium with high decontamination of the pure uranium product; (3) removing technetium from the uranium product; (4) minimizing the quantity of technetium remaining with the noble metals ruthenium and palladium; and (5) identifying plutonium reductants which do not add waste volume and do not interfere with solvent extraction.

2.4.2 TRUEX Process

The key technical barriers for TRUEX are: (1) determination of the most applicable solvent extraction technology to accomplish the TRU separation, (2) identification of the optimum combination of stripping and wash reagents in order to minimize the generation of secondary waste during the TRUEX operations, (3) identification of methods for separation of the actinides from the lanthanides if deemed necessary, (4) development of solidification processes for the TRU stream, and (5) development of a ^{99}Tc extraction process.

2.4.3 Electrometallurgical Process

Most of the technology required for the EM steps in any ATW LWR fuel processing option has been demonstrated at least at the laboratory scale. Thus, for the EM process in general the major technical challenge is scale-up of the process to support the construction of the demonstration plant. If the "all pyro" option for LWR fuel processing is chosen two additional requirements come into effect, the requirement to produce a non-TRU uranium stream and the requirement to separate Tc from the cladding hulls. The key technical barriers to achieving the target state of the EM technology are: (1) production of a non-TRU uranium stream (all-pyro option only), (2) separation of Tc from Zircaloy cladding hulls (all-pyro option only), (3) separation and isolation of I , (4) fabrication of I and Tc targets, (5) containment of Am during ATW fuel preparation (final stage of EM process), and (6) scale-up of all process steps and equipment. Items 4 and 5 are fuel/target fabrication issues and not EM process barriers.

2.5 R&D Needs

2.5.1 Laboratory-Scale R&D

There are a number of computer models for solvent extraction calculations with uranium. The best model needs to be selected which includes neptunium and fission products or can be altered to include data. Calculations need to be made to determine the optimum number of stages in each portion of the process to obtain the desired results. Essential data which are not in the literature must be generated in laboratory studies.

Literature review and laboratory studies are needed to determine the best method for removing iodine from the offgas stream. The process for capturing iodine must allow easy conversion for target fabrication. There must be evaluation of the need for removal of other components of the offgas and the best method for disposal of those components.

Laboratory studies are needed of reductants for plutonium which do not add waste volume. The most frequently used reductant is ferrous ion, but ascorbic acid or other similar reductants are advantageous because they would not add waste volume. Studies must ensure that reduction is complete at high acid and that the reductant or its oxidation products do not interfere with the solvent extraction process such as reducing decontamination factors or causing the formation of emulsions.

Laboratory studies are needed to confirm co-extraction of technetium and neptunium along with uranium and their separation into separate streams. The studies will validate computer models, which then can be used to optimize the overall process for pilot plant design. Laboratory demonstration that uranium will meet Class C criteria is mandatory. Laboratory studies are needed for the conversion of the aqueous raffinate to solid oxides. The key problem is to determine the correct conditions of temperature and airflow to minimize volatilization of fission products such as ruthenium. In addition, studies of the safety aspects of evaporation of HNO_3 solutions containing organics will be required.

Studies are needed on hull leaching to ensure removal of all the Tc and other noble metals from the hulls. Past work has shown that HNO_3-HF mixtures gave best results, but still did not remove all noble metals. It would be preferable not to use HF since that adds volume to the waste.

For the TRUEX process, laboratory-scale studies of the extraction behavior of UREX raffinate and alternative solvent extraction processes are necessary. Computer modeling must be extended to development of a flowsheet and used in determination of optimum conditions for processing. Laboratory-scale studies to improve the extraction of Tc via the TRUEX solvent and recovery of Tc in the solvent wash are recommended, as are similar studies of alternative solvent wash reagents which will minimize the amount of unwanted chemicals (e.g., Na) added to the waste streams. Also required is the development of stripping reagents which will minimize the amount of inert materials in the TRU product stream (e.g., stripping with HEDPA would add phosphate).

In the case of the EM technology, this phase will focus on demonstrating that EM is capable of performing the required separations and that it can be scaled-up to the required batch size. The end of this phase will be marked by selection of one of the three options for the LWR fuel-processing step. Included in the phase are the following activities: (1) verify flowsheet chemistry for all phases of process using simulated and irradiated fuel; (2) study scale-up issues regarding all aspects of EM process; (3) development of electrodes for salt-recovery step; (4) optimization of salt-recovery step cell configuration; (5) study methods to separate Tc from Zircaloy cladding; (6) study methods to prepare non-TRU uranium; (7) study concurrent and sequential operation of solid steel and liquid cadmium cathodes (all-pyro option only); (8) study means to isolate I and Tc and prepare targets; and (9) study behavior of TRU product with regard to Am.

2.5.2 Pilot-Scale Research, Development and Demonstration

Pilot scale demonstrations of all portions of the UREX process including chop/shear of fuel, dissolution, zircaloy hull leaching, feed clarification, solvent extraction, oxide preparation from raffinate, and offgas treatment should be conducted. Information needed for design of the full-scale plant on decontamination factors for iodine, ruthenium, zirconium/niobium, neptunium and technetium will be obtained during the testing. In addition, some equipment will be tested for operational characteristics. The pilot facilities must be capable of producing 100 kg of combined TRU isotopes for the 30 MWt demo ATW unit by 2015 and approximately 1,200 kg of combined TRU isotopes for the 420 MWt demo ATW unit by 2018. That capability requires processing about

130 MTHM commercial LWR spent fuel over a period of about 8 years, or an average of about 100 kg HM per day. This is roughly one-tenth the scale of the demonstration processing plant.

Pilot scale flowsheet development of the TRUEX (or other chosen) process in centrifugal contactors (2.0 to 5.5-cm diameter) using waste simulants should be conducted in this period, followed by demonstration with actual waste solutions. This stage will also include the pilot scale development and demonstration of solidification processes for the conversion of waste and product streams to oxide form and development of remote operations and maintenance of the TRUEX process equipment. Flowsheet computer modeling will be performed, based on experimental results, to optimize the flowsheet. Monitoring systems and instrumentation for on-line process control must also be developed and demonstrated.

This phase will focus on design, construction, and operation of pilot-scale components of the selected EM process. Included in the phase are the following activities: (1) engineering-scale (kg batch) tests of reduction step including use of irradiated fuel; (2) engineering-scale tests of salt-recovery step cell design; (3) corrosion testing of prospective construction materials for pilot and demonstration-scale plants; (4) engineering-scale tests of the electrorefiner with reduced irradiated fuel; and (5) pilot-scale plant trials with unirradiated and irradiated fuel.

2.5.3 Demonstration-Scale Activities

This phase focuses on the design, construction, and operation of the ATW demonstration plant. Operational tests of prototype full-scale equipment, including demonstration of the ability to meet functional requirements, must be done. An integrated demonstration of the process is needed to ensure that the equipment and processes will operate as needed during the lifetime of the plant. Remote operation, reliability and maintainability must be demonstrated during the tests.

2.6 R&D Linkages

The laboratory RD&D must be complete in order to design the pilot plant especially the modeling and validation of the model, raffinate conversion to solids, and offgas system definition. The target for iodine must be defined in order to develop the process for removing iodine from the offgas of spent fuel processing.

The LWR fuel processing pilot plant must be sized to give 1,300 kg of TRU for initial small ATW demonstration plants between 2009 and 2018.

The primary R&D linkages for TRUEX are (1) the characterization of the UREX raffinate stream (feed stream for TRUEX) and (2) the characterization of the TRU product stream for the fuel fabrication process.

The key linkages between the research and development effort on the electrometallurgical process and other R&D efforts include: (1) efforts to configure the EM process to isolate I and Tc and the transmutation assembly design and fabrication

efforts; (2) fuel fabrication efforts and the EM process in regard to the behavior of Am; and (3) completion of the Demonstration-Scale Facility and production of sufficient TRU material for the loading of the first ATW core.

3.0 ATW Irradiated Fuel Processing

3.1 Summary

The ATW fuel-processing portion of the flow sheet is designed to extract the TRU elements (for recycle into fresh ATW fuel) and technetium and iodine fission products (for incorporation in ATW transmutation assemblies) from spent ATW fuel and to provide waste streams that are compatible with either the ceramic (e.g., glass-bonded sodalite), or metallic (e.g., zirconium - iron alloy) waste form. The TWG selected pyrometallurgical processes for the treatment of ATW fuel because of their robust and compact nature, compatibility with the desired waste forms, and cost effectiveness. In contrast to the LWR fuel processing, high material throughput is not required for the treatment of spent ATW fuel. The projected material throughput requirement is about 100-200 kg of total fuel mass per day for likely deployment scenarios. Two options are being considered for treating irradiated ATW 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 TRU's and fission products.

The baseline option for ATW irradiated fuel processing 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. The baseline ATW fuel is a steel clad metallic fuel with a nominal fuel composition of 23 wt.% TRU – 77 wt.% Zr. The proposed electrochemical processes are similar to those used by the Integral Fast Reactor Program at ANL and for the purification of nuclear materials at LANL and LLNL. A simplified flow sheet for the chloride volatility based process is presented in Figure 7 and described below.

With the chloride volatility process, spent fuel is removed from the target / blanket system and allowed to cool, the fuel assembly hardware is removed from the pins, and the fuel pins are chopped. 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 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 electrowon from the solution and recycled to fuel fabrication. Periodically, the fission products are removed from the molten salt and converted to a stable waste form. Iodine is removed from the molten salt, fabricated into targets and placed in transmutation

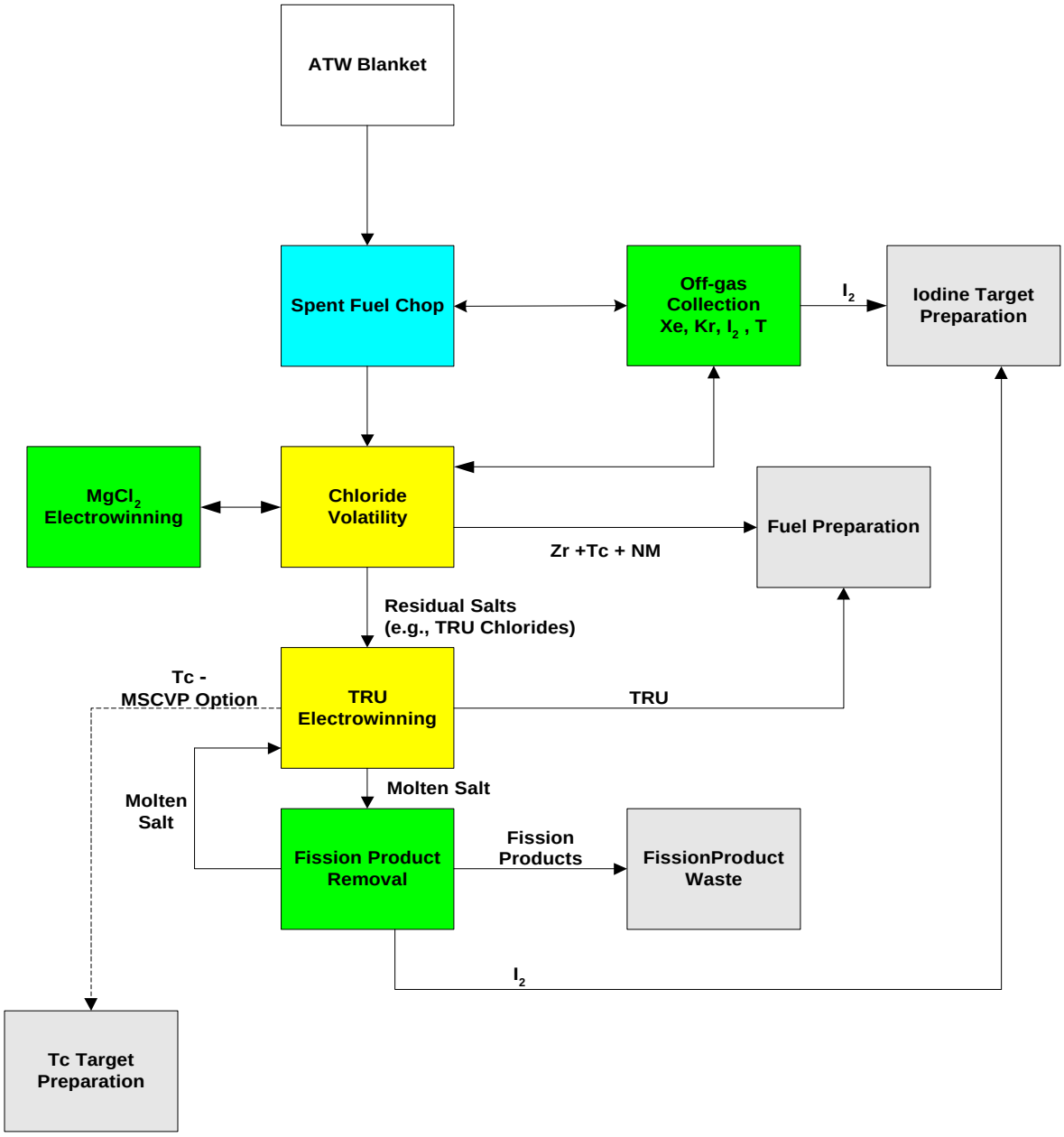


Figure 7. Baseline chloride volatility process flowsheet for ATW fuel processing.

assemblies. The technetium produced by the fission of TRUs in ATW fuel remains in the zirconium-stream and is recycled into the target / blanket system as part of the fresh fuel.

A variant of the classic chloride volatility technology should also be investigated. It is referred to as the Molten Salt Chloride Volatility Process (MSCVP). The goal of the MSCVP, namely digestion of the zirconium matrix, is the same as in the classic chloride volatility process. In the MSCVP, chlorination of the zirconium matrix occurs in a molten chloride salt phase and is mediated by a less stable metal chloride such as bismuth chloride that is soluble in the molten chloride salt. Bismuth chloride is formed by sparging chlorine gas into a pool of molten bismuth. The molten metal pool lies at the bottom of a vessel containing a molten chloride salt. The conditions used in this approach are still sufficiently oxidizing to form gaseous zirconium tetrachloride. The active metal fission products, rare earths, and transuranic components of the spent fuel are also oxidized to form non-volatile metal chlorides that are soluble in the molten chloride salt. Thermodynamic calculations indicate that the noble metals, notably technetium, rhodium, molybdenum, and ruthenium, are not oxidized in this process and will remain in the metallic state. The transuranics can then be removed from the molten salt by electrowinning in the same manner described above for the classic chloride volatility process. Zirconium metal can still be recovered from the volatile zirconium tetrachloride using the magnesium reduction approach described above.

Upon comparing classic chloride volatility and MSCVP, it becomes evident that MSCVP is merely a different way of combining the zirconium chlorination step and the TRU electrowinning step. The difference between the two approaches lies in the fate of the noble metal fission products. In the classic chloride volatility approach, technetium, rhodium, molybdenum, and ruthenium will most likely be chlorinated and distill over with the zirconium tetrachloride. They are recovered as metals along with zirconium in the magnesium reduction step. In the MSCVP, the same noble metal fission products will most likely remain as metals in the basket used to contain the spent fuel as it is suspended in the molten salt phase.

Although MSCVP does not have the technological maturity of the classic chloride volatility process, it offers the following potential advantages: (1) decreased likelihood of corrosion of process equipment by chlorine gas; (2) fewer process transfer steps, by eliminating the transfer of TRU and fission product chlorides to a molten salt electrowinning bath; (3) safer management of decay heat from active metal fission products by immediate dispersal in a molten salt; and (4) concentration of noble metal fission products (including technetium) in a separate stream as opposed to following zirconium in the process. This last point may or may not be an advantage depending on what is the best way to transmute the technetium.

The back-up option for ATW fuel processing is based on electrometallurgical processes used for the separation of zirconium, TRUs, and fission products. Two types of electrometallurgical processes are proposed for use in the treatment of spent fuel: electrorefining and electrowinning. The focus of the electrorefining process is the extraction or transport of Zr from the spent fuel. Similar to the chloride volatility

process, the electrorefining process was chosen for zirconium extraction or transport because of the existing industrial experience in zirconium metal production and purification. One of the important factors that must be considered in processing ATW fuel is the rate of zirconium extraction or transport from the fuel. Electrorefining provides a different transport pathway than the chloride volatility process. The principal advantages of the electrorefining process are that the cell current controls the Zr transport rate and no gas phase transport is required. It also facilitates the partitioning of the TRU, active metal, and rare earth fission products to the molten salt that allows for more efficient decay heat management. However, electrorefining of zirconium-based materials is usually conducted in a mixed chloride / fluoride molten salt medium. Introducing the fluoride-based molten salt medium also introduces the need for additional waste form development; perhaps apatite-based waste forms are appropriate. The aforementioned electrowinning process is used to separate the TRUs from the fission products dissolved in the molten salt medium. A simplified flow sheet for the back-up processing option is presented in Figure 8 and described below.

The head-end of the backup option consists of the same spent fuel cooling and chopping process described for the baseline option. Prior to sending the chopped fuel to the electrorefining step, it is treated by a hydride / dehydride process that breaks the zirconium-based fuel into small particles. This increases the fuel surface area and allows for more efficient dissolution and electrotransport of the zirconium. Zirconium is extracted from the fuel in the anode and transported to the cathode of the electrochemical cell while allowing the TRUs to partition to the molten salt. Subsequently, the TRUs are removed from the molten salt solution by electrowinning and recycled into fresh fuel. Zirconium is also recycled for use in fresh ATW fuel. Technetium remains at the anode heel with the other noble metals. This heel is removed from the cell and cast into ATW transmutation assemblies. Iodine partitions to the molten salt where it forms soluble metal iodides. It must be removed from the salt, collected, and fabricated into targets and placed into transmutation assemblies. Periodically, the rare earth and active metal fission products are removed from the molten salt and converted into stabilized waste forms.

3.2 State of Technology

The current state of each of the major technologies proposed for use in the treatment of ATW fuel is described below. Each paragraph gives a brief description of the scale at which the technology has been demonstrated, if it has been applied to the treatment of nuclear fuels, and whether the technology is directly applicable to the ATW system. The baseline option for ATW fuel treatment is described first. The back-up option is described in the last three paragraphs of the section. Technologies common to both options are not repeated for the back-up option.

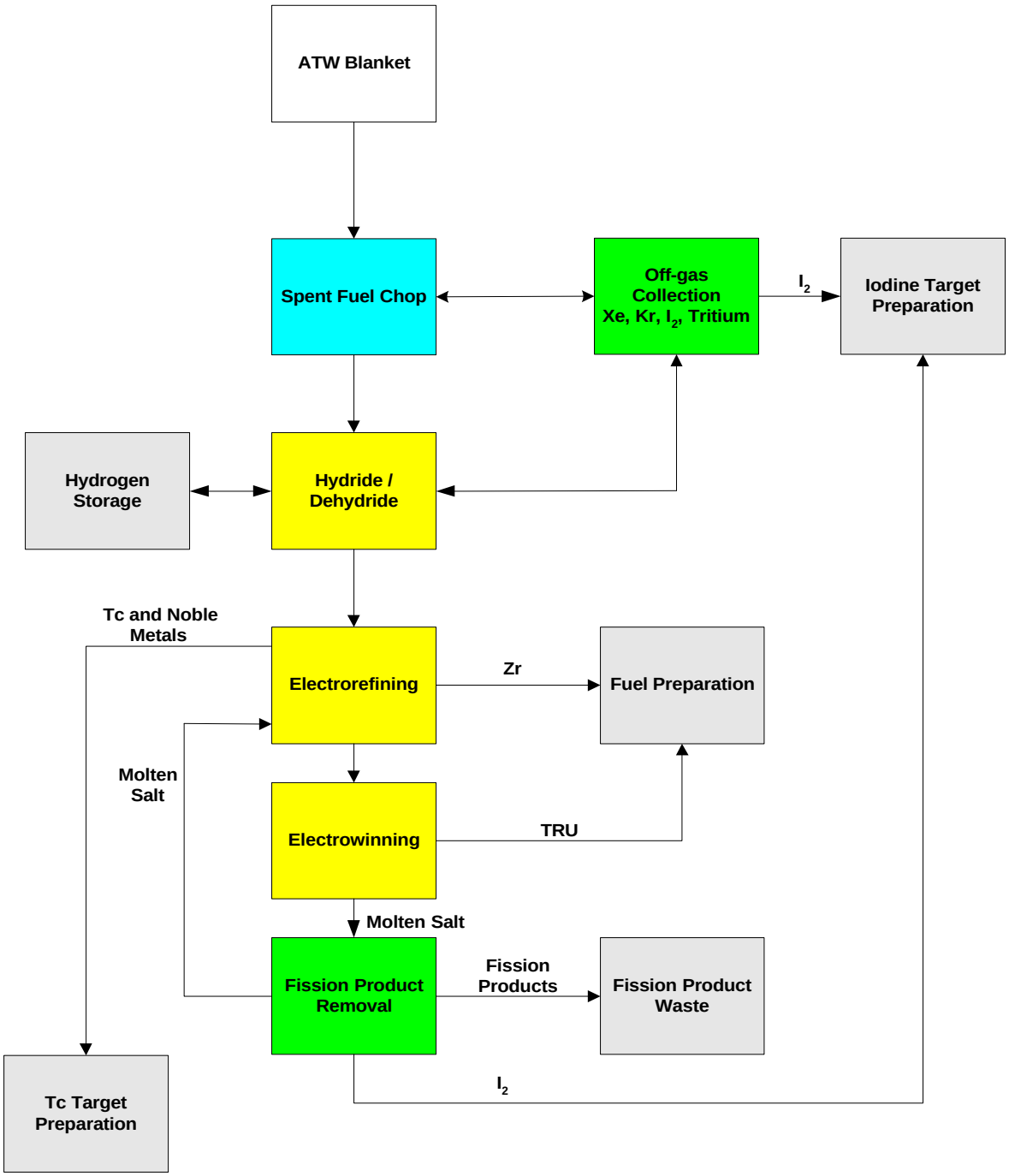


Figure 8. Electrometallurgical backup option flowsheet for ATW fuel processing.

Spent Fuel Chopping/Shredding: Chopping of metallic spent nuclear fuel is being demonstrated at the pilot-scale as part of the program for the Electrometallurgical Treatment of Spent Nuclear Fuel currently being conducted by ANL. Industrial-scale experience exists for chopping oxide fuels at large reprocessing facilities in Europe. Both technologies are directly applicable to ATW. Shredding of metallic spent nuclear fuel is not a demonstrated technology.

Off-Gas System: Industrial-scale experiences exist for the recovery of xenon, krypton, iodine, and other off-gases at large reprocessing facilities in Europe and US National Laboratories (i.e., INEEL and SRS). Several options, for example cryogenic distillation or zeolite adsorption, are currently available for use. Iodine target production has been studied at the bench-scale at US National Laboratories. Both technologies are directly applicable to ATW.

Chloride Volatility Process: The chloride volatility process is commonly used for the industrial-scale production of zirconium metal. Batch operations are currently within the desired scale for the plant-scale ATW system. Although thermodynamic calculations and chemical periodicity based arguments indicate the process is viable for the treatment of ATW fuel, no experience exists with zirconium-based spent nuclear fuels that contain fission products and TRUs. No experience exists with the MSCVP approach to spent fuel treatment. Chloride volatility technology must be modified and demonstrated for ATW applications.

TRU Electrowinning: Bench-scale experience exists at US National Laboratories (i.e., ANL and LANL) for uranium and plutonium extraction from nuclear fuels and molten salt systems. This technology is directly applicable to ATW fuel treatment.

Fission Product Removal: Reductive extraction, electrowinning and other pyrometallurgical processes have been demonstrated at the bench- to pilot-scale at US National Laboratories (i.e., ANL, LANL, LLNL, and ORNL). Each technology is directly applicable to ATW.

Magnesium Chloride Electrowinning: Industrial-scale experience exists for the production of magnesium by the electrowinning process. In addition, chlorine getter technology is commonly employed on the industrial scale both in magnesium production, and in chlorine gas technology. Both technologies are directly applicable to ATW but will require modification to deal with potential fission product or TRU contamination.

Hydride / Dehydride: Metal hydriding and dehydriding is common practice in the specialty metal industry and the nuclear industry. The process is usually used to produce fine powders from large slugs or ingots. It is demonstrated on the pilot- to industrial-scale for many different metals. The accompanying hydrogen storage technology is also demonstrated on the industrial-scale. Both technologies are directly applicable to ATW fuel treatment.

Electrorefining: Electrorefining of zirconium-based materials is a common method by which zirconium metal is produced and purified on the pilot- to industrial-scale. No experience exists in the treatment of zirconium-based spent nuclear fuel. However,

electrorefining is an established process for the separation of uranium and TRUs from spent nuclear fuel and the purification of uranium and plutonium. It has been demonstrated at the pilot-scale at US National Laboratories (i.e., ANL and LANL). Combining the industrial and National Laboratory experience base enables the direct application of these technologies to the treatment of spent ATW fuel.

Iodine Separation: Bench-scale experience exists in the separation of iodine from molten salt systems. This process is different from the off-gas recovery system in that the iodine is recovered from a molten salt matrix. The technology is applicable to ATW.

3.3 Target-State of Technology

The target-state for the plant-scale treatment of ATW fuel, whether it is by chloride volatility or electrorefining, is 100-200 kg of ATW fuel per day. It is essential that the TRUs be extracted as a group from spent ATW fuel and recycled to make fresh fuel. A recovery efficiency of greater than 99.9% is the target for TRU processing. Technetium and iodine are also both recovered from spent ATW fuel, fabricated into targets, and used to produce transmutation assemblies. These two fission products are to be recovered with greater than 95% efficiency. In the case of the classic chloride volatility approach, the technetium is recycled with the zirconium and becomes an integral component of the fuel. No additional technetium recovery process is needed. In addition to the recovery of TRUs, technetium and iodine, the processing media must be recycled numerous times to minimize the amount of waste discharged to the repository. Pyrometallurgical processes allow for multiple recycle of the reagents and are easily designed to produce waste materials that are compatible with either the ceramic or metallic waste form.

The main treatment processes for both the baseline and back-up options must be demonstrated at the following scales during the lab- and pilot-scale stages of the program: lab-scale 1-10 kg ATW fuel and pilot-scale 10-25 kg of ATW fuel. Each auxiliary process must be demonstrated at a scale proportionate to the appropriate main process. The demo-scale facility target-state is for the treatment of 3,000 kg of TRU per year or about 13 MT (total fuel mass) ATW fuel per year. Although the material throughput requirement is not great for the demo facility, it is a completely integrated processing facility operating at about half the scale of a deployable plant serving eight ATW burners.

3.4 Key Technical Barriers

In general, the key technical barriers for the processing of irradiated ATW fuel are much the same as those encountered in other nuclear chemical engineering environments. They include optimization of the TRU separation efficiency and select fission product recovery, process scale and parameter optimization, waste minimization, and materials compatibility and lifetime in corrosive, high temperature, and radiation environments.

Specific technical barriers associated with components of the baseline option of the ATW fuel processing include: (1) spent fuel chopping/grinding system reliability at high throughput; (2) optimization of the interface between the off-gas and chloride volatility systems; (3) chemical and metallurgical behavior of technetium and the TRUs in the

chloride volatility system; (4) americium, curium, and technetium electrochemical behavior in the TRU electrowinning process; (5) the development of pilot- to demo-scale iodine separation processes; and (6) the compatibility of process residues with the desired waste forms.

The specific technical barriers for the back-up option of the ATW fuel processing are: (1) the adaptation of zirconium electrorefining experience to the treatment of zirconium-based nuclear fuels, which includes studies of the chemical behavior of the TRUs and technetium in the process; (2) the compatibility of the process residue with currently proposed waste forms; (3) the development of waste forms capable of accepting fluoride-based molten salts; and (4) the development of pilot- to demo-scale iodine separation processes.

3.5 R&D Needs

The RD&D needs for both the baseline and back-up options proposed for the treatment of ATW fuel are presented. First, the general requirements for each of the RD&D phases will be discussed. Then, specific RD&D needs are presented for both the baseline and back-up options.

3.5.1 Laboratory-Scale R&D. The general RD&D needs for the lab-scale studies of ATW fuel processing are: (1) establish the process chemistry and separation efficiency for the species targeted by the process; (2) obtain a preliminary material balance for each process; (3) optimize process chemistry parameters utilizing both experimental and modeling tools; and (4) establish materials behavior, compatibility and estimates of material lifetime for each process system. These studies will utilize unirradiated materials but the work will include the use of TRU elements. The results of the lab-scale studies will be used to establish a preliminary engineering design and test program for the pilot-scale studies.

3.5.2 Pilot-scale Research, Development and Demonstration. The RD&D requirements for the pilot-scale studies of ATW fuel processing include: (1) determining a moderately detailed material balance for each process and constructing theoretical estimates of the material balance for an integrated process system; (2) continued development of optimized process parameters at moderate batch sizes and equipment scales; (3) verification of species separation efficiencies in larger scale batch processes; and (4) establish more detailed information regarding materials compatibility and lifetime. Process chemistry and metallurgy studies will also continue through the pilot-scale studies. Initially, the studies will use unirradiated materials that contain the TRU elements. However, the later stages of the pilot-sale studies will involve the treatment of irradiated ATW fuel. This assumes that hot cell facilities will be available for the studies. Treatment of irradiated fuel also allows for studies related to decay heat management and the effect that a high radiation environment has on the process and processing equipment. The flow sheet used in the demo-scale studies will be selected at the end of the pilot-scale studies. In addition, the results of these studies will be used to produce a detailed engineering design for the demo-scale integrated processing system.

3.5.3 Demonstration-Scale Activities. The RD&D needs for the demo-scale studies of ATW fuel treatment are: (1) establishing a very detailed material balance for the integrated processing system; (2) verification of pilot-scale separation efficiencies at demo-scales; (3) optimization of unit and integrated process system parameters; and (4) the evaluation of processing equipment materials lifetimes. Ultimately, the results of the demo-scale studies will be used to produce an optimized integrated engineering design of the first plant-scale ATW chemical processing system.

ATW fuel processing activities and waste form development must be well integrated throughout each stage of the RD&D program. This integrated process ensures that the ATW processing residues are kept to a minimum and those that are produced are compatible with qualified waste forms.

The process specific RD&D needs for the baseline option are: (1) verification of chopping blade lifetime and high throughput system reliability for spent fuel chopping / grinding; (2) establishing iodine and chlorine chemistry in the chloride volatility process; (3) establishing TRU, technetium, and fission product chemistry and metallurgy in the chloride volatility process; (4) verification of the TRU, technetium, and fission product behavior in the electrowinning system; (5) electrowinning cell system design optimization; and (6) waste minimization / waste form compatibility studies.

Specific process RD&D needs for the back-up option are; (1) adaptation of the zirconium electrorefining technology to spent nuclear fuels; (2) establishing the behavior of TRUs and fission products in the process; (3) waste minimization / waste form compatibility studies; and (4) molten salt solvent system optimization. In addition, iodine sparge chemistry and the associated process system must be optimized for the removal of iodine from the molten salt medium.

3.6 R&D Linkages

The lab-scale RD&D studies must be complete and the fundamental chemical process engineering established for each of the proposed batch processes before design of a pilot-scale system can be completed. Both the chloride volatility and zirconium electrorefining options must be studied through the laboratory-scale development phase.

Pilot-scale RD&D studies will be demonstrated first for surrogate spent fuel materials and then for irradiated ATW fuel. New hot cell facilities must be available or existing facilities refurbished for treatment of the irradiated fuel. Selection of the flow sheet for use in the demo-scale facility is made in the last stages of pilot-scale operations.

4.0. Waste Treatment and Production of HLW Forms

4.1. Summary

The separations technologies described in the LWR and ATW fuel processing sections of this report require limited development of high-level waste forms that are similar to waste forms being produced under the aegis of other programs. The baseline UREX process for LWR fuel treatment is designed to remove high purity uranium from the spent fuel that may then be disposed as a Class C low-level waste. The cladding hulls from this process will constitute a high-level waste stream. All other high-level waste will be carried through to the pyrochemical treatment process along with the burnable materials to be separated for ATW fissioning and transmutation.

There will be secondary wastes (e.g., protective clothing, crucibles, and process solutions) that will be handled using standard low-level waste treatment methods such as grouting and volume reduction. It is assumed that this will be true for all secondary waste from each treatment step. In all cases, secondary waste streams are to be minimized.

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.

For the first three years of this development program, backup processing options will be considered. One of the backup LWR spent fuel processing methods contains a TRUEX step which, if incorporated, will produce aqueous raffinate solutions and other miscellaneous waste that will contain residual technetium, iodine, and other fission products. This waste stream would require a different high-level waste form, such as borosilicate glass. High level waste form materials must be selected, developed, and evaluated for the backup processing options to provide a basis for comparison to the baseline processes.

4.2. Current State of Technology

The principal step in the electrometallurgical process is the electrorefining of uranium metal in a molten salt electrolyte. Two distinct high-level waste streams emanate from the electrorefiner: (1) fission products and actinides extracted from the electrolyte salt that are processed into a ceramic waste form, and (2) metallic wastes that are consolidated into a metal waste form. The ceramic and metal waste form technology

developed for electrometallurgical treatment (EMT) provides a technical foundation for the ceramic and metal waste forms that have been postulated for the ATW.

The EMT ceramic waste form is designed to immobilize halides as well as actinide, alkali, alkaline earth, and rare earth elements (e.g., Cs, Sr, Ba, Ce, and Nd) retained as ionic solutes in the molten salt. These salt-borne fission products and 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 naturally converts to sodalite.

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-live fission products (e.g., Cs, Sr, Ba, and the rare earths), but TRU isotopes will not be a waste disposal issue.

The EMT metal waste form comprises remnant metallic constituents that are electrochemically noble (inert) in the electrorefiner; these metals are melted and cast into alloy waste forms. The metallic waste includes cladding hulls from the spent fuel assemblies (which may be steel or Zircaloy), noble metal fission products (e.g., Ru, Re, Pd, Nb, Mo, and Tc), zirconium metal from the ATW fuel matrix, and remnant uranium metal. Since cladding hulls represent 85 to 99 wt % of the EMT 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.

In the early stages of EMT development, two SS-Zr compositions were selected: (1) stainless steel-15 wt % zirconium (SS-15Zr) for stainless steel-clad fuel and (2) Zircaloy-8 wt % stainless steel (Zr-8SS) for Zircaloy-clad fuel. The SS-15Zr waste form is now a well-characterized waste form material with well-understood properties. Behavior characterization and qualification testing is well underway for the EMT demonstration at Argonne National Laboratory. The Zr-8SS development was stopped after preliminary investigations were complete because there was no near-term mission to treat Zircaloy-clad fuel. The preliminary data for Zr-8SS properties and behavior were quite favorable for application as a waste form and it may be a better match for the ATW metal waste form. However, development work is still needed to bring Zr-8SS technology to an appropriate level of maturity.

4.3 Target State of Technology

The target state for the waste treatment process is two-fold. First, processing methods and equipment designs must demonstrate the viability of treating the waste from processing LWR spent fuel and recycling ATW fuel. Second, the high-level waste form

materials must be well–characterized and ongoing performance assessment and qualification testing efforts must support repository disposal of the high-level wastes.

To keep pace with the expected annual spent fuel throughput of nearly 170 MTHM LWR spent fuel per year and 26 MT ATW fuel per year per ATW station [assuming 8.5 ATW stations of 8x840 MWt each], the waste form production facilities must produce ~60 MT per year per station (~24 m^3 per year) of the ceramic waste form and ~65 MT per year per station (~8 m^3 per year) of the metal waste form. These waste form fabrication processes and the resulting waste forms must be developed and evaluated under strict quality controls to satisfy regulatory and repository-specific requirements for geologic disposal.

During the first three years of the program, the ATW salt-borne waste stream will be quantified and representative waste form materials will be fabricated for qualification testing. Processing alternatives will be evaluated and the best method available after 3 years will be demonstrated at the pilot-scale (~25%). Similarly, the ATW metal waste stream will be quantified and representative Zr-8SS waste form alloys will be fabricated for behavior testing. After 3 years, the development of Zr-8SS must be completed so that a selection may be made regarding the waste form composition. Processing methods and qualification testing plans will be comparable to the methods developed for EMT, and demonstration equipment will be scaled to achieve the target throughput.

4.4 Key Technical Barriers

The key technical barriers for the ceramic waste form are (1) the definition of the waste stream composition, (2) the development of full-scale processing methods, (3) the development of waste minimization and salt recycling technology, and (4) the definition of process residuals that must go to the waste form (e.g., waste from vapor release). The full-scale processing methods must be capable of processing ~75 MT (~33 m^3) of the qualified ceramic waste forms per year for each operating ATW station.

The key technical barriers for the metal waste form are (1) the definition of the waste stream composition, (2) the characterization and qualification of Zr-8SS waste form, (3) the development of full-scale processing methods for salt removal and casting, and (4) the definition of process residuals that must go to the waste form (e.g., residual technetium, if any). The full-scale processing methods must be capable of processing ~55 MT (~7 m^3) of the qualified metal waste forms per year for each operating ATW station.

The definition of both waste streams is strongly dependent on the front- and back-end treatment processes. It is not possible to declare up-front what these waste streams will be since they will be defined as the LWR and ATW fuel processing technologies mature. The metal and ceramic waste forms were selected as the baseline ATW approach because they are flexible enough to accept a wide variety of waste for immobilization in a high level waste form.

4.5 Research Needs

4.5.1 Ceramic Waste Form

4.5.1.1 Laboratory-Scale R&D. This phase will focus on expanding the fundamental understanding of the salt waste treatment processes being developed for the EMT system and the development of advanced salt treatment and waste form processing methods for scale-up to ATW processing equipment. During this phase, the waste form qualification activity will be initiated at a low level of effort because of the extensive, long-term nature of qualification testing.

The following research activities will be required: (1) the salt-zeolite exchange behavior needs to be fully characterized and modeled to enable the simulation of the waste treatment process; (2) salt treatment methods must be demonstrated for concentrating the fission products and recycling the salt electrolyte; (3) high-throughput fabrication methods must be demonstrated for all processing steps and reference methods must be selected for pilot-scale equipment; and (4) waste form characterization and qualification testing must be carried out to evaluate the developing methods and to initiate the database for repository assessment activities.

4.5.1.2 Pilot-Scale Research, Development and Demonstration. This phase will focus on the design, construction and operation of pilot scale facilities. In addition to this engineering task, the following research will continue: (1) modeling the salt treatment processes to simulate the waste treatment process; (2) basic research on the waste form material to support the modeling effort and designs for pilot-, demonstration- and full-scale equipment; and (3) waste form qualification testing and modeling for repository assessment activities.

4.5.1.3 Demonstration-Scale Activities. This phase will focus on the design, construction and operation of an ATW demonstration plant.

4.5.2 Metal Waste Form

4.5.2.1 Laboratory-Scale R&D. This phase will focus on expanding the fundamental understanding of the metal waste treatment processes being developed for the EMT system and the development of advanced waste form processing methods for scale-up to ATW processing equipment. During this phase, the waste form qualification activity will be initiated at a low level of effort because of the extensive, long-term nature of qualification testing.

The following research activities will be required: (1) the Zr-8SS alloy must be fully characterized to evaluate its merit as a waste form material (SS-15Zr is a viable backup); (2) high-throughput fabrication methods must be selected for the design of pilot-scale equipment; and (3) waste form characterization and qualification testing must be carried out to evaluate the developing methods and to initiate the database for repository assessment activities.

4.5.2.2 Pilot-Scale Research, Development and Demonstration. This phase will focus on the design, construction and operation of pilot scale facilities. In addition to this engineering task, the following research will continue: (1) modeling the casting and salt removal processes to simulate the waste treatment process; (2) basic research on the waste form material to support the modeling effort and designs for pilot-, demonstration- and full-scale equipment; and (3) waste form qualification testing and modeling for repository assessment activities.

4.5.2.3 Demonstration-Scale Activities. This phase will focus on the design, construction and operation of an ATW demonstration plant. It will consist of a conceptual and final design for the demonstration plant.

4.5.3 Waste Forms for Backup Processes

4.5.3.1 Laboratory-Scale R&D. Some of the backup treatment options (e.g., TRUEX) will require the fabrication of an additional waste form. For example, TRUEX would require a vitrified glass waste form to handle its raffinate solution waste and a fluoride-based pyroprocess would require a different mineral than sodalite to immobilize the waste. These alternative waste forms must be developed along with the backup options to provide a clear basis for comparison with the baseline processes. The development R&D needs for these waste forms would be similar to the needs described for the ceramic and metal waste forms.

4.5.3.2 Pilot-Scale Research, Development and Demonstration. There are no backup options after 3 years. If a "backup" waste form becomes part of the ATW pilot-scale operations, the R&D needs would be similar to the needs described for the ceramic and metal waste forms.

4.6 R&D Linkages

The waste form R&D is strongly linked to the LWR and ATW-fuel treatment R&D. The final waste streams cannot be defined until the final processes are selected and developed.

In addition, materials handling issues are linked to the waste form R&D. For example, the off-gas treatment system may need to feed vapor traps and filters into one, or both, of the waste form processing systems.

And finally, the waste form R&D is also the point where the tail-end of the ATW fuel cycle returns to the HLW repository. Therefore, the waste form research is strongly linked to the repository interface of the ATW program.

5.0 Schedule

A top-level schedule for the development of ATW separations technologies and waste forms is located in the Microsoft Project™ file ***ATWseparations5.mpp***.

6.0 Costs

The projected costs for the RD&D program necessary to develop the separations technologies and waste form production processes for the ATW system are summarized below. A greatly increased level of detail is provided in the projected cost tables included in Appendix B.

It should be noted that these cost projections are preliminary; there has not yet been an attempt to smooth the cost profiles or to tailor the cost ramp-ups to make them more realistic with project initiation activities. The principal purpose of the cost estimates in this document is to provide the decision-maker with an understanding of the general magnitude of cost involved in developing and demonstrating the ATW separations and waste forms technologies. The costs shown in Appendix B are readily separable into three main components: (1) research and development, (2) pilot-scale engineering demonstration, and (3) full-scale demonstration. Multiple decision points included in the overall program plan make the real separation of these costs possible; i.e., proceeding with the R&D stage does not carry with it a commitment to expend funds for demonstration activities.

It should also be noted that the cost projections begin with U.S. fiscal year 2000. This is a matter of convenience; if the project start is at a different year, FY2000 in these tables can simply be referred to as Project Year 1.

Table I. ATW Separations Technologies and Waste Forms Projected Annual Costs (000)

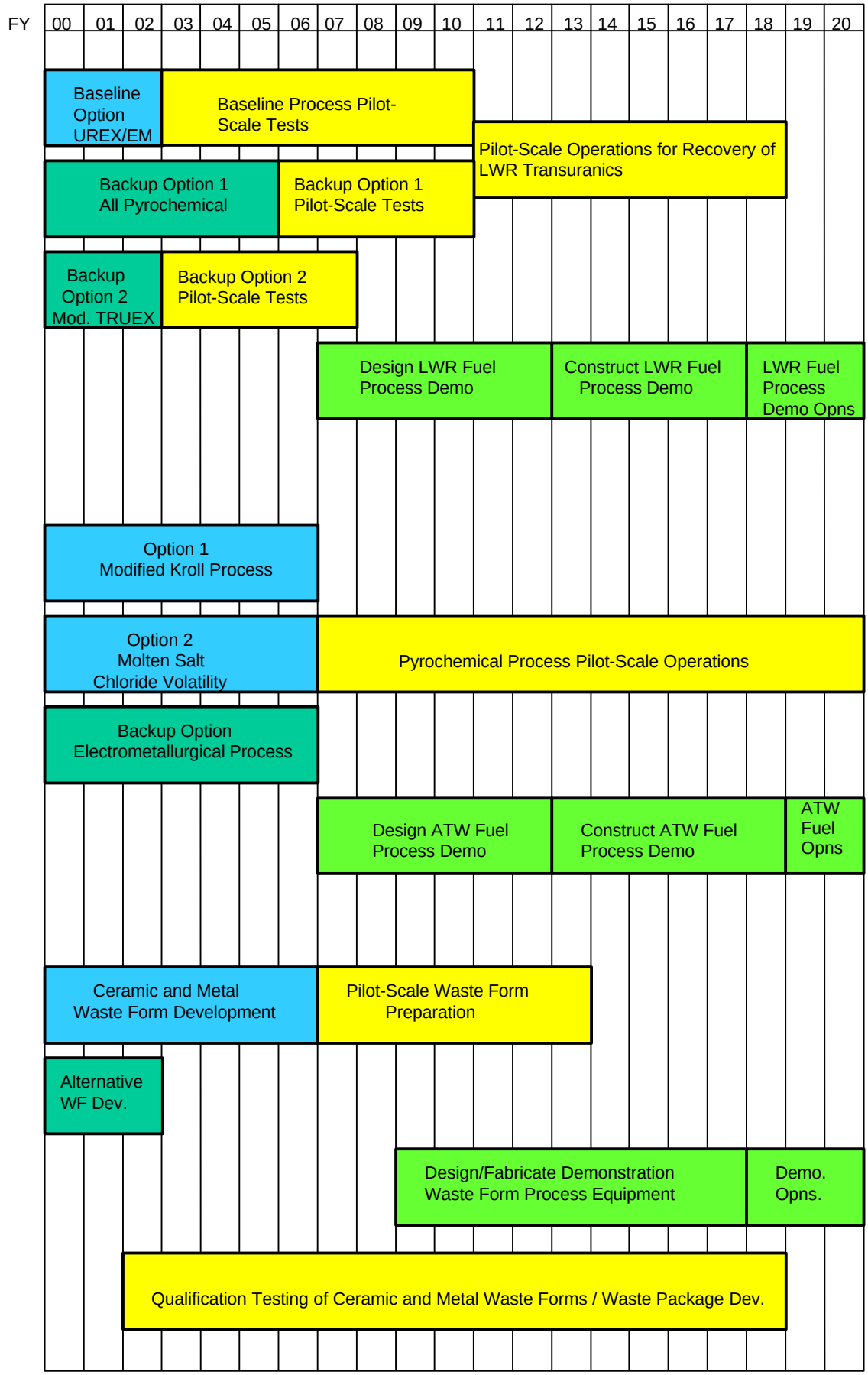
	LWR Fuel Processing		ATW Fuel Processing		Waste Form Development		TOTALS		
Year	Operating	Capital	Operating	Capital	Operating	Capital	Operating	Capital	TOTAL
2000	$7,835	$0	$6,475	$0	$5,150	$0	$19,460	$0	$19,460
2001	$10,335	$0	$9,525	$800	$5,125	$200	$24,985	$1,000	$25,985
2002	$13,830	$0	$12,525	$1,600	$6,550	$1,400	$32,905	$3,000	$35,905
2003	$9,285	$1,075	$13,775	$2,150	$6,650	$1,550	$29,710	$4,775	$34,485
2004	$12,140	$1,015	$14,775	$2,150	$6,550	$1,400	$33,465	$4,565	$38,030
2005	$10,415	$2,000	$14,800	$1,350	$6,550	$1,000	$31,765	$4,350	$36,115
2006	$9,145	$2,000	$12,650	$1,050	$6,050	$200	$27,845	$3,250	$31,095
2007	$7,700	$100	$10,400	$0	$7,200	$0	$25,300	$100	$25,400
2008	$12,375	$0	$13,700	$500	$7,200	$0	$33,275	$500	$33,775
2009	$13,950	$100	$13,700	$2,500	$7,150	$0	$34,800	$2,600	$37,400
2010	$12,300	$0	$13,465	$3,000	$7,150	$0	$32,915	$3,000	$35,915
2011	$9,050	$0	$10,990	$5,000	$7,150	$0	$27,190	$5,000	$32,190
2012	$10,250	$0	$10,590	$3,250	$8,800	$0	$29,640	$3,250	$32,890
2013	$6,450	$60,000	$9,925	$45,150	$8,300	$0	$24,675	$105,150	$129,825
2014	$7,700	$95,000	$13,800	$65,000	$8,300	$0	$29,800	$160,000	$189,800
2015	$10,200	$130,000	$19,050	$80,000	$8,300	$0	$37,550	$210,000	$247,550
2016	$17,700	$125,000	$19,300	$85,000	$8,300	$0	$45,300	$210,000	$255,300
2017	$56,450	$100,000	$56,245	$35,000	$8,300	$0	$120,995	$135,000	$255,995
2018	$49,200	$0	$35,500	$250	$5,800	$0	$90,500	$250	$90,750
2019	$54,950	$0	$35,500	$200	$0	$0	$90,450	$200	$90,650
2020	$58,200	$2,000	$32,500	$100	$0	$0	$90,700	$2,100	$92,800
TOTAL	$399,460	$518,290	$379,190	$334,050	$134,575	$5,750	$913,225	$858,090	$1,771,315

7.0 Separations Technology Roadmap

The basic research program for development of separations technologies described above has been summarized as a roadmap in Figure 9. The roadmap shows three technology options being carried for the LWR Fuel Processing function through the pilot scale. In FY 2007 a technology selection decision will be made as the design basis for the LWR demonstration facility. In light of the lesser state of maturity, the ATW Fuel Processing function will carry two technology alternatives for a longer period of time. The technology selection decision will not be made until 2010. The two major waste forms, glass-bonded sodalite and Zr-metal have already been selected. Alternative waste forms will also be studied in order to deal with the potential waste streams that may be generated by the LWR backup option 2. The detailed research and design activities associated with the separations technology and waste form roadmap are highlighted in previous chapters.

8.0

Figure 9. ED&D Roadmap



8.0 Material and Isotope Balance

A preliminary mass and isotope balance has been prepared to assist the Separations Technology and Waste Forms TWG size the LWR Fuel and ATW Fuel processing plants and to estimate waste volumes and radionuclide inventories that may be sent to the repository. The material and isotope balance is shown as Figure 10 and the assumptions used to develop the balance are as follows:

- 87,000 MTHM Spent LWR Fuel
- 60 year operating life
- 1 Prototype Station
- 4x840 MW transmuters in prototype station
- 8 ATW full-sized stations
- 8 x 840 MW transmuters per full-sized station
- System will process 1,450 MTHM/yr
- Nominal Characteristics of LWR Fuel
  - 94.6% U
  - 1.04% TRU
  - 0.084% Tc
  - 0.024% I
  - 4.25% Other FP
  - 0.29 tons hulls per MTHM
- 99.9% Recovery of TRU in overall system
  - 0.1 % TRU lost to ceramic waste form
- 99.94% Recovery of TRU from LWR fuel treatment
- 95% Recovery of I from LWR fuel treatment
  - 4.95% of I is lost to the scrubber media
  - 0.05% of I is lost to ceramic waste form
- 95% Recovery of Tc from LWR Fuel Treatment
  - 5% of Tc remains with hulls and becomes part of Zr metal waste form
- 99.94% Recovery of TRU by ATW Fuel Recycle
  - "Lost " TRU goes to ceramic waste
- 95% recovery of new Tc formed from fission of TRU in burner
  - 5% of Tc lost to Zr metal waste form
- 95% recovery of new I formed from fission of TRU in burner
  - 5% of new I lost to ceramic waste form
- Losses of radionuclides in the course of fuel or transmutation assembly fabrication have not been considered

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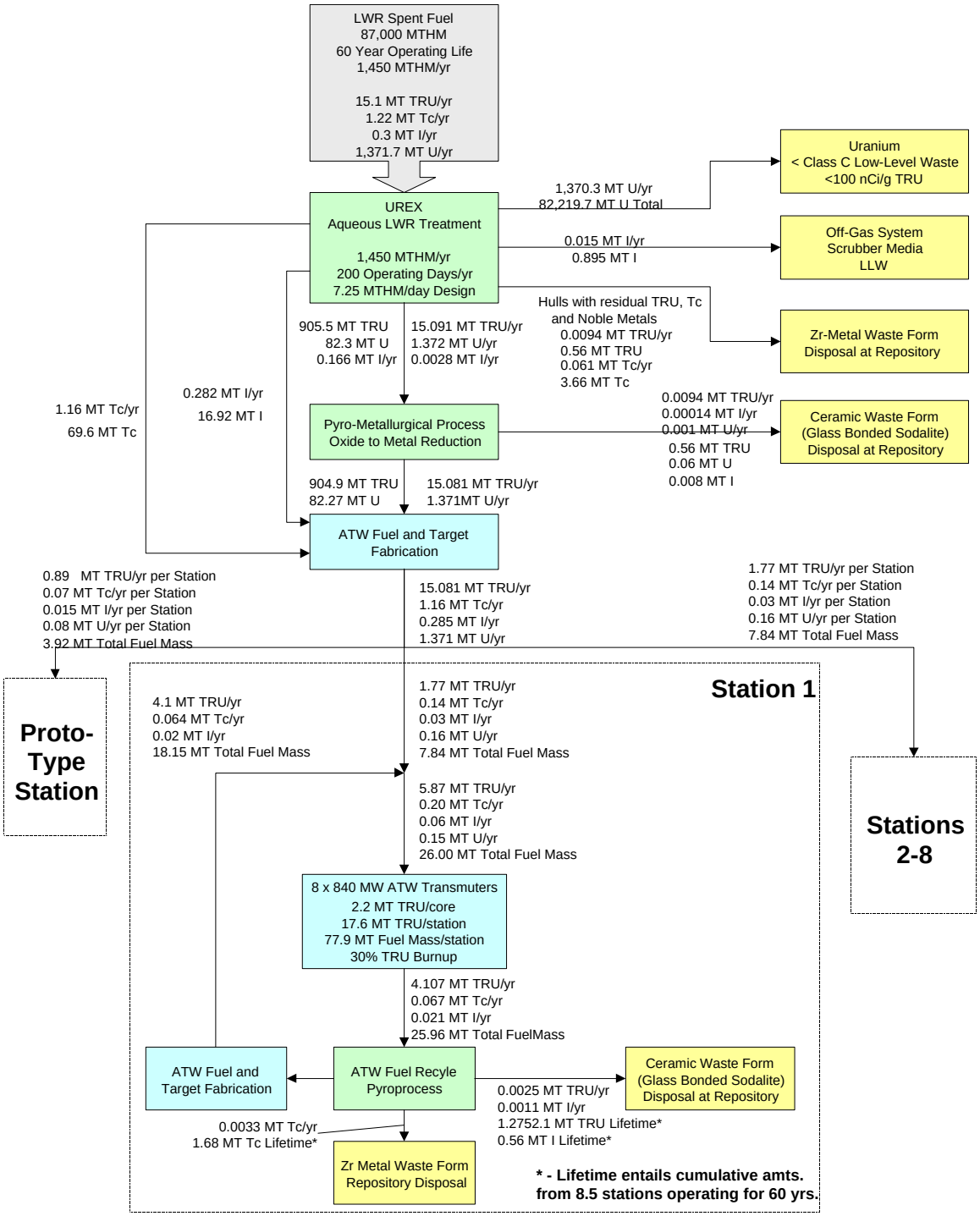
- Characteristics of Transmuter
  - 8 x 840 MW ATW Transmuters per station
  - 2.2 MT TRU per core (before burnup)
  - 17.6 MT TRU per station (before burn-up)
  - 22.6 wt% TRU in fuel
  - 77.9 MT Total fuel mass in core per station (17.6 MT ÷ 22.6%)
  - 1/3 of core discharged per year
  - 30% TRU burn-up at discharge
  - 5% of fission TRU becomes Tc and I
    - 76% becomes Tc
    - 24% becomes I
  - Tc and I Targets are not removed and recycled

Figure 10. Preliminary ATW Material and Isotope Balance



9.0 Contributors to this Report

The following individuals, listed in alphabetical order, contributed to this report as members of the ATW Separations Technology and Waste Forms Technical Working Group.

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Appendix A. Potential Solvent Extraction Processes for Separation of TRU from Acidic Waste Stream

DHDECMP Process: Similar to the TRUEX process except the active extractant is dihexl-N,N-diethylcarbamoylmethylphosphonate which is a weaker extractant than the CMPO in the TRUEX process. Domestic availability of the extractant could be an issue for testing and production scale operations. The TRU and lanthanides are extracted by the solvent and stripped together. Thus the end product stream includes TRU material and lanthanides. This process has been successfully tested on a pilot scale (5.5 cm centrifugal contactors) with simulated tank waste at the INEEL.

Phosphine Oxide Process: Uses a phosphine oxide derivative as the active extractant. Developed jointly between the INEEL and the Khlophin Radium Institute in Russia. The TRU and lanthanides are extracted by the solvent and stripped together. Thus the end product stream includes TRU material and lanthanides. The process has been successfully demonstrated (<99.5% TRU removal) with actual tank waste at the INEEL using 2-cm diameter centrifugal contactors in a shielded and remotely maintained hot cell facility (RAL).

TRPO Process: Developed as a cooperative program between the Tsinghua University in China and the European Institute for Transuranium elements in Germany. Uses trialkyl phosphine oxides as the active extractant. Operates most effectively with a waste acidity < 2.0 M HNO_3. The TRU and lanthanides are extracted by the solvent and stripped together. Thus the end product stream includes TRU material and lanthanides. The process has been demonstrated with actual commercial HLW solution, diluted ten-fold, in centrifugal contactors in China. Greater than 99.97% of the Am was extracted and a D.F. of > 1400 was obtained for ^{99}Tc.

DIDPA Processes: Developed by the Japan Atomic Energy Research Institute. Uses diisodecyl phosphoric acid as the active extractant. This process has the potential for selective stripping of the actinides from the lanthanides and requires a waste acidity of < 0.5M HNO_3. This low acidity may require dilution which will increase processing time and possibly waste generation. The DIDPA process was successfully tested in Japan with actual commercial HLW (denitrated with formic acid) in mixer settlers. Greater than 99.99% of the Am was extracted.

DIAMEX Process: The DIAMEX process was first developed at the CEA Fontenay-aux-Roses Research Center (France) and the University of Reading (UK).The active extractant in the DIAMEX process is di-methyl-di-butyltetradecylmalonamide. The DIAMEX solvent is fully incinerable and is not adversely affected by radiolytic and hydrolytic degradation. The process requires a waste acidity of greater than 3M. The TRU and lanthanides are extracted by the solvent and stripped together. Thus the end product stream includes TRU material and lanthanides. Technetium is not extracted with this process. This process has been successfully tested with actual waste in France.

If separation of TRU elements and lanthanide fission products is required for ATW fuel fabrication, the following separation processes are also under development:

TPTZ: Being developed by the CEA Fontenay-aux-Roses Research Center (France) and the University of Reading (UK). The process uses a tripyridyltriazine ligand to selectively extract the TRU material (valence III) from the lanthanides (valence III). This process has been successfully tested with simulated waste in France.

CYANEX 301™: Being developed in the People's Republic of China and by the ITU of Karlsruhe, Germany. Uses bis (2,4,4-trimethylpentyl) dithiophosphonic acid to selectively separate TRU material (valence III) from the lanthanides (valence III). The aqueous solution must be adjusted to a pH of 3.5 to 4. This process has been successfully demonstrated on a bench scale with radioactive waste in China.

Appendix B. Projected Costs by Program Element for the Period from FY2000 through FY2020 (project years 1 through 21)

(Please see Microsoft Excel™ file ***ATWsepcostest.xls***)