ABSTRACT

This paper provides a brief overview of the Los Alamos accelerator-driven transmutation system, a description of the pyrochemistry technology base and the fuel cycle for the system. The pyrochemistry technology base consists of four processes: direct oxide reduction, reductive extraction, electrorefining, and electrowinning. Each process and its utility is described. The fuel cycle is described for a liquid metal-based system with the focus being the conversion of commercial spent nuclear fuel to fuel for the transmutation system. Fission product separation and actinide recycle processes are also described.

I. INTRODUCTION

The accelerator-driven transmutation system (ATW) being studied at Los Alamos National Laboratory (LANL) consists of a high power linear proton accelerator coupled to a liquid lead spallation neutron source that drives a subcritical liquid lead cooled nuclear system. The neutron spectrum in the system can either be fast or thermal; the choice of the spectrum depends on whether transuranic burning, fission product transmutation, or both are needed. Fissile material and select fission products dissolved in liquid metal are contained in transmutation canisters, similar to conventional fuel rods, and placed in the active region of the nuclear system where they undergo fission or transmutation. This type of system could be used to essentially eliminate the transuranics and hazardous long-lived fission products present in spent nuclear fuel that is destined for storage and, used as such, enhances the viability of a permanent nuclear waste repository.

II. SYSTEM OVERVIEW

Key components of the ATW system are the linear accelerator, the nuclear transmutation system, and the spent fuel treatment facility. High-power accelerator technology is being developed by the Accelerator Production of Tritium (APT) Project at Los Alamos. Current design

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considerations are focusing on normal conducting systems, with particle energies in the range of 1300 MeV, 100 mA beam current, and normal conducting / superconducting hybrid systems, with particle energies in the range 1300 - 1700 MeV, 100 mA beam current. Both systems are moderate extensions of existing accelerator technology. Interest in the hybrid system stems from the potential of lower capital and operating cost as compared to the normal conducting system. An APT-class accelerator, 1700 MeV - 100 mA, could be used to drive four or five 3000 MWt subcritical transmutation systems.

Nuclear system technology is based on fast reactor technology (e.g., Advanced Liquid Metal Reactor) with the substitution of liquid lead coolant for the traditional sodium coolant and modification of the system to accept a proton beam transport system. Russian nuclear powered submarines have successfully used a lead-bismuth eutectic mixture as a reactor coolant. Extension of this technology to a pure lead system is under investigation at LANL. Using lead or lead - bismuth eutectic as the coolant for the system eliminates some of the safety concerns associated with the use of sodium. For example, in the case of a coolant leak lead does not react violently with water or air, lead has a high boiling point - almost twice that for sodium, and lead based systems can possess a negative void coefficient of reactivity. More importantly, the lead coolant also serves as the target for the production of spallation neutrons. Thus, a complex target structure is not needed; only a proton beam transport pipe is required to deliver the beam to the core region of the transmutation canisters where the spallation neutrons drive the system.

The spent fuel treatment facility and technologies are based on those developed at US National Laboratories for Pu production and nuclear fuel reprocessing. A prototype treatment facility has been designed and costed for the recycle of spent nuclear fuel in a conventional fast reactor system. The facility needed for the LANL ATW system would be derived from the information presented in this report and the design and operating experience of the LANL Plutonium Processing Facility (i.e., TA-55). Pyrochemical treatment technologies are the preferred method for the conversion of spent nuclear fuel to fuel for the ATW system. They are potentially less expensive and offer enhanced Pu proliferation or diversion resistance over current aqueous technologies. Central to the development of the LANL ATW system is the identification of the specific pyrochemical technologies needed for fuel preparation and fission product removal processes, and the design of a fuel cycle. A summary of the pyrochemistry technology base and fuel cycle for the system is presented below.

III. CHEMISTRY TECHNOLOGY BASE

The pyrochemistry technology base consists of four processes: direct oxide reduction, reductive extraction, electrorefining, and electrowinning. While a detailed account of the processes is beyond the scope of this paper, a brief description of each process and its utility follows.

Direct Oxide Reduction: Direct oxide reduction is the conversion of a metal oxide into a metal by reaction of the metal oxide with a more active metal. The reaction is driven by the free energy

difference between the reactant and product oxide materials. The process is described by the equation:

\[ \text{MO}_{n/2} (s) + \frac{n}{2} \text{Ca} (1) = \text{M} (s) + \frac{n}{2} \text{CaO} (1, \text{in CaCl}_2), \]  

where \( \text{MO}_{n/2} \) is a metal oxide of metal valence \( n \) and \( \text{M} \) is the product metal. Approximately 20 mol% calcium oxide is soluble in calcium chloride at 1100 K. LANL uses the process to produce impure Pu metal from plutonia.\(^6\) The solvent molten salt can be regenerated and recycled by sparging HCl or Cl\(_2\) gas through the salt converting the CaO to CaCl\(_2\).\(^7\) LANL has also explored the possibility of regenerating Ca from CaO by electrolytic methods. Argonne National Laboratory (ANL) uses this type of process for the conversion of uranium oxide based nuclear fuel to metal.\(^8\) ANL uses Li instead of Ca as the reductant and either a LiCl or LiCl-KCl eutectic mixture as the solvent molten salt. Lithium metal is regenerated from the lithium oxide produced during the reduction process by electrochemical methods and the chloride salt is recycled. Both LANL and ANL have demonstrated the process on the kilogram scale.

**Reductive Extraction:** Reductive extraction is the process by which a more active metal, dissolved in a solvent liquid metal, displaces a less active metal, dissolved in a molten salt as a metal halide. Again, the reaction is driven by the free energy difference between the reactant and product metal halides and alloys. Oak Ridge National Laboratory (ORNL) investigated the reductive extraction process as a means to separate lanthanide fission products from actinides during the Molten Salt Reactor Experiment program.\(^9\)-\(^11\) The extraction process consists of contacting the molten salt, which contains lanthanides and actinides, with a liquid bismuth stream containing a small quantity of lithium, for example 0.1-1 at% Li. The equation that describes the process is:

\[ n \text{Li} (1, \text{in Bi}) + \text{MF}_n (1, \text{in Li}_2\text{BeF}_4) = \text{M} (1,\text{in Bi}) + n \text{LiF} (1) \]  

where \( \text{MF}_n \) is an actinide or lanthanide fluoride of valence \( n \) dissolved in the molten salt and \( \text{M} \) is the actinide or lanthanide metal dissolved in liquid bismuth. This type of process is also commonly used in the purification of metals. For example, LANL uses this process to remove americium contamination from plutonium.\(^12\) The process is described by the equation:

\[ 3 \text{Am} (1, \text{in Pu}) + n \text{PuCl}_3 (1, \text{in CaCl}_2) = 3 \text{AmCl}_3 (1, \text{in CaCl}_2) + n \text{Pu} (1) \]  

where \( n \) is the valence of americium, either +2 or +3. Americium contamination in plutonium can be reduced down to the ppm impurity level with this process. ANL used this type of process for the separation of fission products and actinides contained in spent nuclear fuel. In addition, they have developed a centrifugal pyrocontactor that operates at about 3000 rpm and temperatures up to 850 K.\(^13\) This device is a compact mixer / separator that greatly reduces the time required to achieve optimum separations.

Electrorefining: Electrorefining is the process by which a pure element or class of elements is produced by the electrotransport of that element or class of elements from an impure anode material to a cathode. It is commonly used in the purification of metals such as copper and nickel using an aqueous transport process, and beryllium using a molten salt transport process. LANL uses electrorefining to produce purified plutonium metal from impure feedstock. The general equations that describe the process are:

\[ \text{Pu (impure, l)} = \text{Pu}^{n+} (l) + ne \text{ (anode)} \]  

and

\[ \text{Pu}^{n+} (l) + n e = \text{Pu (pure, l)} \text{ (cathode)} \]

where the plutonium is oxidized at the anode and transported to the cathode as a Pu\(^{3+}\) chloride. The LANL process uses a NaCl-KCl eutectic salt mixture, doped with a small quantity of PuCl\(_3\), as the transport medium. The process is typically used to purify three to four kilograms of Pu. LANL has also investigated various solvent anode materials (e.g., Bi, Cd, Ga) for use in this process. ANL is investigating electrorefining techniques to separate uranium from nuclear fuel. The proposed process is a two step process, first U is electrotransported to a solid cathode which, after U deposition, is removed from the system, then the transuranics are transported to a Cd solvent cathode. They use a LiCl-KCl eutectic salt mixture, doped with a small quantity of CdCl\(_2\), that reacts with the active metals and produces MCl\(_n\), as the transport medium. Currently, ANL is stabilizing metallic nuclear fuels by using electrorefining methods to recover U from the fuel.

Electrowinning: Electrowinning is the electrolytic production of a metal from a metal-bearing species dissolved in a molten salt. The process is commonly used in the production of aluminum and magnesium but has also been used to produce lithium and calcium. As previously mentioned, ANL uses electrowinning to produce Li from the Li\(_2\)O generated in the direct oxide reduction process. The electrochemical cell consists of either a carbon or Pt-Rh anode and a Li or Bi-Li alloy cathode. Carbon oxides or oxygen are produced at the anode and Li is produced at the cathode. They have demonstrated the process on the 100-200 g scale. LANL explored the possibility of using electrowinning to regenerate calcium from the CaO produced in the direct oxide reduction process. This method could also be used to separate transition metal fission products from lanthanide fission products and actinides.

IV. FUEL CYCLE

In this concept the fissile material and fission products are contained in a liquid metal solvent, bismuth, inside transmutation canisters similar to conventional pins. Fuel canisters are designed so that they can be shuffled in the nuclear system for optimum transuranic burn-up and stored after irradiation to allow for cooling prior to fuel treatment. The system does not require on-line presented at Global ‘97 International Conference on Future Nuclear Systems, Yokohama, Japan, Oct. 5-10, 1997.
chemical processing but spent ATW fuel is treated periodically via batch processes. A description of the front-end and back-end of the fuel cycle is given below.

**Spent Fuel Feed:** Spent nuclear fuel is converted to fuel for the ATW system by a two-step process. After the spent oxide fuel is decladded and crushed, the oxide powder is mixed into a CaCl$_2$ molten salt which contains calcium metal at 1100 K. The calcium metal reduces the metal oxides and produces a mixture or solid solution of metals (U, Pu, etc.). Equation (1) describes the process. Fission product gas released during this process and the fuel crushing process is collected in a gas handling system. The system consists of a series of getter beds: a silver alloy to collect iodine, a Fe-V-Ni alloy to collect tritium, and activated carbon or molecular sieves to collect noble gases. The metals produced by the reduction process are treated with the electrorefining process.

Electrorefining is the centerpiece of the chemical processing and is used to separate the transuranics and long-lived hazardous fission products from U for destruction in the ATW system. The metals produced by the calcium reduction process serve as the anode in the electrorefining cell. In general, equations (4) and (5) describe the transport process. The transport media is a LiF - NaF - KF eutectic molten salt, at 1023 K, spiked with a small concentration of a weak metal fluoride, perhaps bismuth fluoride, that oxidizes a small quantity of the active metals. Deposition of the uranium and transuranics is completed sequentially and is controlled by an external power supply. Two cathodes are required to achieve separation between U and Pu so that no additional plutonium is produced in ATW by neutron absorption in U-238. The first cathode is a bare metal rod or wire mesh attached to a rod and it serves as a place for uranium to deposit. After U deposition is complete, the U-bearing cathode is removed from the molten salt and the Bi solvent cathode is inserted into the system. The liquid bismuth cathode is used to collect the transuranic elements as alloys. The solubility of Pu in liquid Bi ranges from 0.5 to 7.0 at% at temperatures in the range 673 - 973 K. Cadmium could be used in place of the Bi but its vapor pressure is 650 torr at 1023 K compared to 0.025 torr for Bi. In addition to its desirable chemical properties, Bi is also a good solvent because of its low neutron absorption cross section. Active metals such as Cs and Sr remain in the molten salt along with the lanthanide elements. Transition metal elements remain at the anode. The bismuth - transuranic alloys are transferred to fuel canisters, constructed from Mo, Ta, or Ta alloys, and transferred to the ATW system for irradiation. Uranium, after re-enrichment, is recycled to conventional reactor fuel.

Technetium is removed from the spent fuel feed anode heels and sent to the ATW system for transmutation. Separation of Tc from the anode is accomplished by oxidation of the anode metals followed by the distillation and condensation of Tc$_2$O$_7$. Tc$_2$O$_7$ is converted to pure Tc metal by a direct oxide reduction process. No molten salt flux is required for this process. The pure Tc metal could be dissolved in the liquid bismuth - transuranic alloys or made into targets and prepared for irradiation. The remaining transition metal oxides are stored in a repository.

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Fuel and Fission Product Clean-Up: The fuel canisters remain in the transmutation system for about 12 months after which time they are removed from the system, allowed to cool, and transferred to the treatment plant for fission product removal. The fission product removal process is based on the electrorefining process described in the spent fuel feed step. Changes to the process include the use of a liquid Bi alloy solvent anode rather than the solid metal anode, and since no uranium is present in the spent fuel only the single solvent cathode is required. Volatile fission products released during the fuel decladding process must be adsorbed in getter beds similar to those described for the spent fuel feed system. Partitioning of the fission products is the same as that previously described. Reprocessed Bi-transuranic alloys are recycled to the ATW system for further irradiation.

Removal and recycle of remnant transuranics contained in the molten salt used in the electrorefining process is accomplished by a reductive extraction process. This process is required because of the similarity of the solubility and physical properties of the transuranics and lanthanide fission products. The process for removing the lanthanides from the molten salt is a liquid-metal process, derived from that researched previously at ORNL, and potentially made faster through the application of the centrifugal pyrocontactors developed at ANL. The extraction process consists of contacting the molten salt, which contains lanthanides and actinides, with a liquid bismuth stream containing a small quantity of lithium. Equation (2) describes the process. The proposed process is a two-stage reduction process. In the first step, the lithium concentration (0.10 at% Li) in the bismuth is selected so that the transuranics are preferentially extracted from the salt phase into the liquid metal phase where they remain in solution as liquid metals. The transuranics are preferentially extracted from the fuel salt into the bismuth because they form thermodynamically less stable fluorides than the lanthanides, the separation is not absolute and approximately 10% of the original lanthanide load in the salt will be extracted into the bismuth phase. The liquid Bi-transuranic alloys are placed in canisters and sent to the ATW system for further irradiation. A different, higher lithium concentration (1.0 at% Li in bismuth) is selected for use in the second step, so that the lanthanides are removed from the fuel salt and transferred into a second bismuth phase where they remain in solution. Lanthanides in the liquid Bi stream are allowed to precipitate as solid Bi alloys and are removed from the liquid Bi by filtration. The solid alloys are oxidized and disposed of in a repository. The remaining Bi is recycled, after Li make-up, back to the reductive extraction system. Cesium and strontium are not extracted from the salt.

Active metals, such as Cs, could be periodically removed from the electrorefining salt by electrowinning methods. The recovered metals are oxidized, placed in engineered containers, and sent to a repository for storage.

Transition metals are removed from the Bi solvent anode heel by oxidation followed by a slagging process. Residual Tc is separated from the other transition metals by the aforementioned distillation process. The remaining transition metal oxides are placed in storage containers and sent to a repository for storage. The bismuth solvent is recycled back to the

V. CONCLUSIONS

Development of the fuel cycle for the LANL ATW system is progressing well and is guiding the experimental research program in which the reductive extraction and solvent anode/cathode electrorefining processes are being investigated. Pyroprocessing is the preferred method for recovering and separating transuranic elements from uranium and fission products and, in some cases, the technologies are developed to an advanced stage. Future fuel cycle work will also focus on waste forms and understanding the interface between ATW and a permanent repository. Continued development and subsequent implementation of an ATW system could lead to more complete utilization of fissile materials and destruction of hazardous long-lived fission products thus enhancing the viability of a permanent nuclear waste repository.

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