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PYROCHEMICAL PROCESSING OF DOE SPENT NUCLEAR FUEL*

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ABSTRACT

A compact, efficient method for conditioning spent nuclear fuel is under development. This method, known as pyrochemical processing, or "pyroprocessing," provides a separation of fission products from the actinide elements present in spent fuel and further separates pure uranium from the transuranic elements. The process can facilitate the timely and environmentally-sound treatment of the highly diverse collection of spent fuel currently in the inventory of the United States Department of Energy (DOE). The pyroprocess utilizes elevated-temperature processes to prepare spent fuel for fission product separation; that separation is accomplished by a molten salt electrorefining step that provides efficient (>99.9%) separation of transuramics. The resultant waste forms from the pyroprocess are stable under envisioned repository environment conditions and highly leach-resistant. Treatment of any spent fuel type produces a set of common high-level waste forms, one a mineral and the other a metal alloy, that can be readily qualified for repository disposal and avoid the substantial costs that would be associated with the qualification of the numerous spent fuel types included in the DOE inventory.

I. INTRODUCTION

Pyrochemical processing, or "pyroprocessing," is a dry chemical processing method that has the potential for effective application in the conditioning of DOE spent nuclear fuel prior to final disposal. The pyroprocessing system has been under development for nearly ten years in an application involving the recycle of spent metallic fuel in a liquid metal cooled fast reactor, the EBR-II. A more rudimentary version of the pyroprocess was used in the 1964-1969 period in a demonstration of the liquid metal reactor fuel cycle, when 35,000 EBR-II fuel rods

were processed. In its contemporary embodiment, the pyroprocess is a compact, simple system that has the attributes of low operating and capital costs and minimal waste volumes. Because the pyroprocess does not produce a separate stream of pure plutonium, it also offers the benefits of a non-proliferant technology that can be utilized without compromising the U.S. position on such matters.

It appears that the pyroprocess can be used effectively in the conditioning of the wide variety of fuel types that make up the DOE spent nuclear fuel inventory. This paper will address the incentives for conditioning spent fuel and describe the operations that constitute the pyroprocessing system. Application of this system to major fuel classes will be discussed, as will the various waste products that arise from such applications.

II. INCENTIVES FOR CONDITIONING SPENT NUCLEAR FUEL BY PYROPROCESSING

There are a number of fuels in the DOE inventory that differ in very significant ways from the rather larger inventory of commercial reactor spent fuel in the United States. Because of these differences, it is not reasonable to expect that the disposal of all of the DOE spent fuels can proceed in the same manner planned for commercial spent fuel. Over 130 different fuel designs are represented in the DOE inventory; these can be grouped into 53 different categories according to common design features such as composition, cladding material and enrichment level. The fuel can be further reduced into six categories according to fuel composition: metal, oxide, graphite, cermet, hydride, and aluminum alloy. Much of the fuel is chemically reactive, to the point that it cannot

safely be exposed to air for preparation of the fuel for final disposal or for extended dry storage. A great deal of the fuel is highly enriched in either ^{235}U or plutonium, making the final disposition of the spent fuel in a geologic repository problematic under present government regulations. The process of qualifying such a large number of fuel types for repository disposal, which will probably be necessary for those fuel types differing substantially from zirconium alloy-clad low-enrichment oxide fuel (i.e., commercial light water reactor spent fuel), can be prohibitively expensive.

The DOE spent fuel is presently in storage in a variety of facilities, many of which do not meet the current standards of safety and environmental protection required of commercial spent fuel storage facilities. In some of the DOE facilities, the spent fuel has begun to degrade significantly¹ and prompt action is necessary. Current DOE planning would place the spent fuel in interim dry storage until such time, some 40-60 years hence, that the means are available for permanent geologic disposal of this material. While this interim step would serve to prevent serious environmental consequences that could result from containment failures in existing storage facilities, it cannot be regarded as the final answer to the spent fuel disposal problem.

Some of the DOE spent fuels cannot be expected to retain their integrity or to remain stable over an extended period of wet or dry storage. An example is the fuel from sodium-cooled fast reactors: when this fuel is washed to remove external adhering sodium, traces of caustic material remain to initiate the process of intergranular stress-corrosion cracking, culminating in breach of the fuel cladding. This process has been observed to occur over relatively short (i.e., a few years) time periods. Although some of the more stable spent fuel can probably be placed in interim storage in suitable containers and then eventually transferred to a permanent repository safely, the fuels that are inherently unstable or of questionable long-term integrity will require extensive conditioning before repository disposal is possible. Placing spent nuclear fuel in a well-engineered surface dry storage facility must be done with recognition of the possibility of a future decision to make such storage permanent, especially if legal and political barriers threaten to prevent the commissioning of a geologic repository for the disposal of commercial spent nuclear fuel and defense wastes. Such a decision would defer the

problem to later generations, in all likelihood exacerbated as a consequence of further deterioration of the less stable fuels during the period of dry storage. Permanent dry storage of the certain highly-stable spent fuel types might be feasible, even for the 300- to 400-year period during which most of the fission products present in the spent fuel will decay to stable isotopes. Assuring the protection of the public from the long-lived actinide elements, however, is much more difficult, particularly so if the concentration of fissionable isotopes in the spent fuel is high.

A promising solution to this multi-faceted dilemma is the use of a pyrochemical processing technique, developed by the Argonne National Laboratory, for conditioning the collection of DOE spent nuclear fuel types for ultimate disposal. This process is applicable in its current stage of development to 99% of the DOE spent fuel inventory and offers the advantages of a simple, compact system that is both economical and technically sound. The pyrochemical process produces a separation of the fission products present in spent fuel from the transuranic elements that represent the greatest threat to public health and safety. Pure uranium is separated from the transuranic elements and can be disposed of as a low-level waste, being free of fission products. The transuranic elements can be recovered and stored in a secure surface repository for future use as a fuel material, or they can be alloyed with the structural materials present in the spent fuel elements and placed in ultra-long life containers for repository disposal. The pyrochemical process was initially designed for application in a commercial fast reactor fuel cycle, and has therefore been subject to overriding emphasis on safety, economics, and environmental soundness. It deserves serious consideration as a potential means for dealing with the responsible disposition of DOE spent nuclear fuel.

III. PYROCHEMICAL PROCESSING

Pyrochemical processing, or pyroprocessing, refers to the complete set of unit operations required to separate the actinide elements from fission products present in spent fuel and to place the waste products in stable forms suitable for disposal. In the case of most spent fuel types, these operations begin with the dismantling of the irradiated fuel assembly and the removal of individual fuel elements. These fuel elements are sent to a chopper, where they are chopped into pieces suitable for the next

operation. The process then follows the flowsheet shown in Figure 1. If the fuel is metallic, regardless of the cladding type or any internal components such as hardware or heat transfer media, it is sent directly to the electrorefiner for electrotransport of the actinides to appropriate electrodes where they are collected for further processing. If the fuel is oxide, it is first sent to a reduction step where the oxide compounds of actinides and fission products are reduced to the metallic state by reduction with metallic lithium. The reduced metal product is then transferred to the electrorefiner for separation into the various product streams. If the fuel is of a type other than metal or oxide, it must first be treated in a head-end operation to convert the fuel materials to metals or oxides, which can then be processed as above.

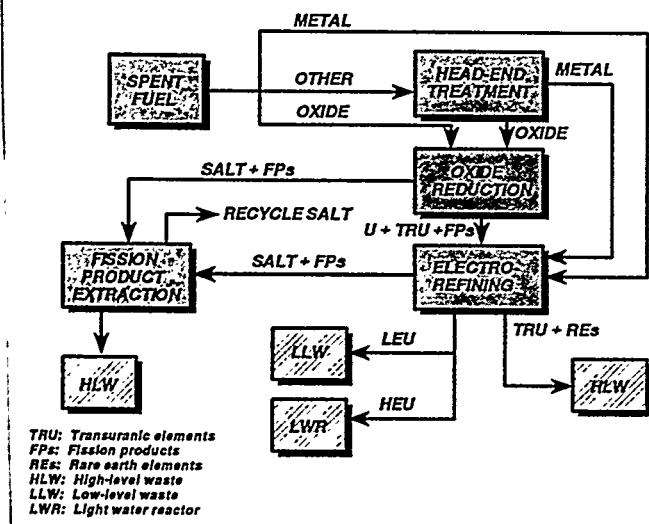


Fig. 1. Simplified flowsheet illustrating the treatment of various spent fuel types by means of the pyrochemical process. The process yields three product streams: a mineral high-level waste form that contains the majority of the highly radioactive fission products; a metal high-level waste form that is an alloy of the transuranic elements, lanthanide fission products and cladding materials; and a third stream that is pure uranium. If the uranium is highly enriched in the ^{235}U isotope, it can be blended down to lower enrichment levels with depleted or normal uranium and recycled to commercial light water reactor fuel fabricators; if it is not significantly enriched in ^{235}U , the uranium can be calcined to produce a low-level waste form with composition U_3O_8 or UO_3 .

The key element of the pyroprocess is the electrorefining step where the actinide elements are separated from the fission products present in the spent fuel. The process is the same as the electrorefining process used for many years in the minerals industry: an impure metal is made the anode, and it is deposited at a cathode in a condition of greater purity by electrotransport through a suitable electrolyte. In the pyrochemical processing electrorefiner, virtually pure uranium is collected at a solid mandrel cathode and a mixture of plutonium, americium, neptunium, curium, uranium, and some rare earth fission products is collected at a liquid cadmium cathode suspended in the electrolyte salt. The noble metal fission products and the cladding hulls remain in the electrorefiner anodic dissolution baskets. The alkaline earth and alkali metal fission products remain in the electrolyte salt, from which they are later extracted.

The cathode deposits are recovered after the desired amount of material has been collected and are then sent to a cathode processor, which is basically a high-temperature vacuum furnace. The deposits are consolidated in the cathode processor by melting; in the process, any volatile materials that were included in the cathode deposits are removed by vaporization. These include the electrolyte salt in the case of the solid mandrel uranium deposits, and cadmium in the case of the liquid cadmium cathode deposits. The distillates from the process crucible are transported to the condenser region of the cathode processor, where they are collected for recycle to the electrorefiner. The metal ingots resulting from the cathode processing operation are then directed to the final step in the pyrochemical process, waste form production. All of these operations are performed remotely, in a highly shielded hot cell facility, because the decontamination factor for fission products in the transuranic product is inherently low. Low decontamination provides self-protection for the waste form and affords a high degree of diversion resistance to the nuclear materials contained therein.

The electrorefining process is shown schematically in Figure 2. In the pyroprocess, electrorefining is carried out in a high-purity inert gas (argon) atmosphere in a steel vessel; current engineering-scale vessels are about 1 m in diameter and 1 m high. The electrolyte salt is a eutectic mixture of LiCl and KCl (melting point 350°C). The cell is operated at a temperature of about 500°C.

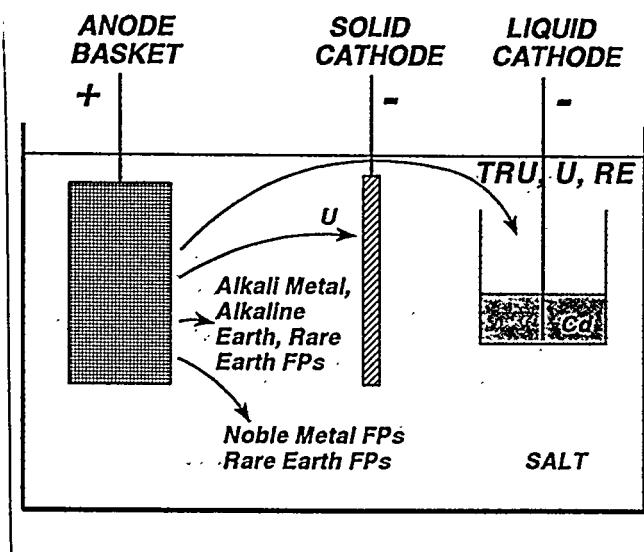


Fig. 2. Schematic diagram of electrorefining process. Spent fuel segments are placed in the anode basket and anodically dissolved. Pure uranium deposits on the solid cathode, while a mixture of transuranic (TRU) elements, uranium and rare earth (RE) fission products deposit in the liquid cadmium cathode. Other fission product (FP) elements distribute between the salt and cadmium phases according to the stability of their chlorides.

The chopped spent fuel segments are placed in perforated steel anode baskets and lowered into the electrolyte salt for electrorefining. The actinides from the spent fuel are transported from the anode baskets to two kinds of cathodes by means of an applied electric current; in the process, all the constituents of the chopped fuel, including the cladding hulls, come into chemical equilibrium with the electrolyte salt. The chemistry of the electrorefiner operation and the operating characteristics of the electrorefiner (e.g., normal and off-normal conditions) have been demonstrated during more than six years of operation of an engineering-scale electrorefiner facility.

The concepts of equilibrium thermodynamics provide necessary insight into the electrorefining process.² It is experimentally observed that the distribution of the various elements among the anode baskets, the salt, and the two kinds of cathodes can be calculated with good accuracy from equilibrium constants; from this it can be inferred that reactions of the metal phases with the molten salt are rapid with respect to processing rates. Further,

thermodynamic activities of the metals from the spent fuel can be manipulated to provide product streams that have adequate--but by no means complete--separations of the actinide elements from fission products and from each other, and to provide waste streams that are essentially free of the transuranium actinides Np, Pu, Am, and Cm.

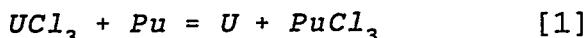
Table 1 presents an ordered list of the stabilities of the chlorides of the key elements involved in pyroprocessing, expressed as standard free energies of formation at a temperature of 500°C. The chloride electrolyte system was selected for pyroprocessing use because the stabilities are arranged in this particularly convenient manner. As seen in Table 1, the elements can be conveniently grouped into three thermodynamic classes, based on chloride stabilities. The first class, the noble metals, includes cadmium, the cladding hull constituents, and the transition metal fission products. These metals have chlorides of such low stability that they react immediately when used as reagents, or are never formed under pyroprocess conditions. These elements are removed mechanically from the electrorefiner, either in the anode baskets after electrotransport or by filtration. The second class comprises the salt and those fission products that form highly stable chlorides, mainly europium, samarium, and the alkali metal and alkaline earth elements. These are permanently and completely oxidized to chlorides that are found only in the salt. The halogen, chalcogen, and pnictide fission products are found as anions that also remain in the salt; they are also included in this class. Elements from this class are periodically removed from the salt into the waste form by means of ion exchange using zeolite A. The third class is of greatest interest. It includes the remaining rare earth fission products and all of the actinides. At various stages in the pyroprocess, elements of this class exist in equilibrium as both metals and as chlorides. This property makes them amenable to selective electrotransport in the electrorefining cell.

Two kinds of cathodes are used for electrotransport. On solid steel cathodes, uranium collects in the form of a dendritic deposit containing a small amount of occluded electrolyte salt. Any dendrites which break off fall to the bottom of the electrorefiner, where they are recovered on a screen. Uranium deposited on a solid cathode is essentially pure because the transuranium actinides and the rare earths cannot be deposited in the presence of UCl_3 in the electrolyte salt. The chlorides of

Table 1. Standard free energies of formation of fission product, actinide element, and electrolyte chlorides at 500°C, kcal/mole.^{3,4}

Relatively Stable	ΔG_f°	Electro-Transportable	ΔG_f°	Relatively Unstable	ΔG_f°
CsCl	-87.8	CmCl ₃	-64	ZrCl ₄	-46.6
RbCl	-87	PuCl ₃	-62.4	CdCl ₂	-32.3
KCl	-86.7	AmCl ₃	-62.1	FeCl ₂	-29.2
SrCl ₂	-84.7	NpCl ₃	-58.1	NbCl ₅	-26.7
LiCl	-82.5	UCl ₃	-55.2	MoCl ₂	-16.8
NaCl	-81.2			TcCl ₄	-11
LaCl ₃	-70.2			RhCl ₃	-10
PrCl ₃	-69			RuCl ₄	-6
CeCl ₃	-68.6				
NdCl ₃	-67.9				
YCl ₃	-65.1				

plutonium and uranium are in equilibrium according to reaction [1].



Because the chloride of plutonium, per Table 1, is substantially more stable than the chloride of uranium, and because both chlorides of uranium and plutonium are present in similar concentrations in the electrolyte salt, any plutonium metal which tends to deposit on the solid cathode immediately reacts with UCl₃ and the reaction [1] is driven strongly to the right. The deposition of pure uranium is calculated to occur in the presence of PuCl₃:UCl₃ ratios even well in excess of 1000. Experimentally, deposition of essentially pure uranium has been demonstrated⁵ up to bulk PuCl₃:UCl₃ ratios of at least 13.

In order to enable the collection of plutonium (and the minor actinides Am, Np, and Cm, which behave like plutonium), it is necessary to reduce their activities. This is done by electrotransporting them to a liquid cadmium cathode, where stabilization occurs by formation of intermetallic compounds with cadmium. Although rare earth metals are similarly stabilized, their chlorides are much more stable than those of the actinides, and thus only small amounts of rare earths are deposited in the cadmium cathode.

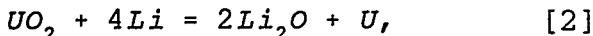
Cadmium cathodes consist of a small amount of liquid cadmium at the bottom of a ceramic crucible. The crucible is suspended in the salt phase, and electrical contact is made to the cadmium. When current is passed, Pu, Am, Np and Cm deposit as intermetallic compounds, MCd₆, at the interface between the cadmium and salt in the ceramic crucible, along with some metallic uranium. The relative amounts of uranium and transuranium actinides that deposit depends on the MCl₃:UCl₃ concentration ratio in the salt and the amount of metal deposited relative to the amount of cadmium used. Once the proper concentration ratio (roughly 3) has been established in the electrolyte salt, the solid cathodes and liquid cadmium cathodes can be operated either simultaneously or sequentially. The desired salt composition is maintained by controlling the amount of charge passed to each cathode so that the desired amount of uranium is deposited at solid cathodes and the desired amount of other actinides are deposited at cadmium cathodes. A typical liquid cadmium cathode deposit in the current engineering-scale equipment contains approximately 4 kg Pu and minor actinides, together with about 1 kg of uranium and a small quantity (several hundred ppm) of the rare earth fission products. The companion solid cathodes collect about 10 kg of uranium each, with essentially no rare earths or transuranium actinides. Collection efficiencies close to 100% have been achieved in laboratory-scale tests of the liquid cadmium cathode.

In the present electrorefiner design configuration, a solid cathode deposit of 10 kg uranium per electrode is obtained in a period of about 24 hours. Efforts are underway to optimize the anode/cathode geometry, so that the deposition rates can be increased; improvement factors between twenty and fifty appear to be easily achievable by appropriate modifications of the collector geometry, as demonstrated in initial experiments. Improved collection rates are considered to be an essential step in the large-scale application of this technology to the treatment of DOE spent fuels such as the inventory of N-Reactor fuel.

IV. TREATMENT OF OXIDE SPENT FUEL

A method for processing oxide spent fuel, fully compatible with the pyrochemical process for metal fuels, is at an advanced stage of development.^{6,7} Basically, the process for oxide fuels involves the reduction of the

oxides to metallic form, followed by the standard electrorefining process for separation of fission products and the separation of the uranium from the transuranic elements. The oxide fuel head-end flowsheet is shown in Figure 3; the oxides are reduced by contacting chopped spent fuel segments with metallic lithium in a LiCl carrier salt in a stainless steel vessel operated at a temperature of 500-650°C. The reduction reactions, as typified by the reaction



are rapid and complete. The reduction reactions for U, Np, Pu, Am and Cm have been observed to be more than 99.99% efficient over the stated temperature range. At the lower end of the temperature range, the reduction product is micron- or submicron-sized particles, whereas the particles are a few millimeters in diameter at the higher end of the range. The metallic product is collected at the bottom of the reduction vessel on a screen and transferred to an electrorefiner where it is placed in an anode basket for electrorefining. The uranium, which represents the bulk of the product in most oxide spent fuels, is electrotransported to a solid mandrel cathode where it collects as pure uranium, free of fission products. Because of the large tonnages of uranium that must be collected, a uranium electrorefiner, intended for uranium collection only, has been designed to operate at very high throughput rates, 500-1,000 kg heavy metal per day. A typical uranium deposit contains a small amount (less than 2 wt. %) of electrolyte salt, which must be removed by vacuum distillation. The transuranic elements are left in the electrolyte salt until their concentration builds up to the point that it becomes necessary to remove them for purposes of assuring a critically-safe operation. The salt is then pumped into a second, smaller electrorefiner that maintains a critically-safe geometry, and the transuranics are recovered by electrotransporting them to a liquid cadmium cathode. The transuranic deposit will typically contain 30% uranium, 1% lanthanide fission products, and the balance the transuranic elements Np, Pu, Am, and Cm. The liquid cadmium cathode deposit is consolidated by vacuum melting, during which process the cadmium in which the deposit forms is distilled off and collected for recycle. Typical consolidated liquid cathode deposits contain less than 0.0001% cadmium.

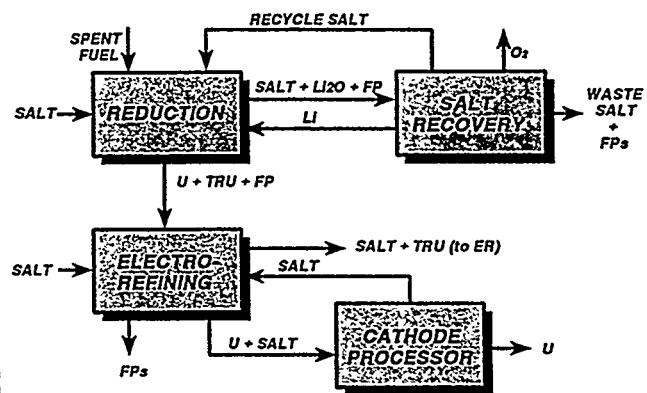


Fig. 3. Flowsheet for the lithium process for reduction of oxide spent fuel to the metallic state and subsequent separation of the fission products from actinide elements. Pure uranium is removed in a high-throughput electrorefiner and consolidated into ingot form in the cathode processor. The transuranic elements are retained in the electrolyte salt, which is transferred to a fissile electrorefiner (ER) for removal of the transuranics together with minor amounts of uranium and fission products. The bulk of the fission products are removed in the electrorefining process and sent to the pyrochemical process waste form production step.

The lithium converted to Li_2O in the reduction reaction is recovered and recycled by means of an electrowinning operation that is carried out in the same vessel used for the reduction process. An inert anode (e.g., Pt) installed in a porous shroud is placed in the reduction salt and metallic lithium floats to the top of the salt bath where it is collected for the next batch reduction operation. Oxygen is evolved at the anode and ducted out of the reduction vessel for venting. The reduction salt contains the active metal fission products and some rare earth fission products, and is periodically bled off for removal of these heat-generating fission products.

V. TREATMENT OF OTHER DOE SPENT FUEL TYPES

The pyrochemical process can be applied with great effect to the problem of DOE spent fuel disposition.

Because the process has been developed for use with metal or oxide fuel, it can be easily adapted for the processing of virtually all of the DOE spent fuel types: metal, oxide, graphite, hydride, cermet, etc. Aluminum-clad metal or oxide fuels can easily be pyroprocessed, but aluminum-matrix fuels are perhaps better treated by conventional aqueous methods, because the aluminum tends to form stable intermetallic compounds with the actinide elements and makes their removal more difficult and hence more expensive. A cermet fuel containing oxide fuel particles in a metallic matrix would be treated by electrolytic dissolution and deposition of the matrix material, followed by high-efficiency filtration of the electrolyte salt to recover the fuel and fission product oxides. The oxide phase, collected in a porous stainless steel filter, can then be treated by the lithium reduction process and the balance of the flowsheet would not differ from that for ordinary oxide fuels. Graphite fuel such as that used in the Fort St. Vrain reactor would be treated by removal of the fuel compacts from the graphite blocks, roll-crushing to expose the fuel kernels, and oxidation to convert the (Th,U) carbides to oxides. Again the balance of the flowsheet would be the same as that for any oxide fuel. The pyrochemical process, because it is carried out in an inert atmosphere, is well-suited for the treatment of hydride fuels and any other reactive fuel materials.

The use of pyroprocessing for DOE spent fuel management has a number of benefits: (1) the recovery of actinide elements, such as highly-enriched uranium, for subsequent re-use in power generation; (2) a substantial reduction in packaged waste volume for ultimate disposal; and (3) the production of a common waste form regardless of starting fuel type. Processing can be done with a common basic process, with common equipment and procedures. This would result in greatly improved economics of waste management. The transuramics recovered in the course of pyroprocessing are co-deposited and contaminated with rare earth fission products so that there is no production of a separate stream of weapons-usable material.

VI. WASTE MANAGEMENT

An integral part of the pyrochemical process development effort is the treatment and packaging of high-level waste materials arising from the pyroprocess operations, and the qualification of these wastes for disposal in a geologic repository. As spent fuel batches

are processed in the electrorefiner, fission products accumulate in the vessel. Fission products of the alkaline earth, alkali metal, and rare earth groups build up in the electrolyte salt phase. The transition metal fission products (more electrochemically noble metals) tend to concentrate as a sludge in the anode basket, or remain with the cladding hulls. As these fission products accumulate, the heat load due to their radioactive decay processes increases until it exceeds facility or equipment design limits. At that point, it is necessary to remove the heat generating elements. The electrolyte salt is removed for treatment to recover the TRU elements and remove a sufficient quantity of fission products that the salt can be recycled.

The removal of fission products from the electrorefiner (and the reduction vessel, for the case of oxide fuel conditioning) is done in two ways. The metallic fission products, together with the structural materials (i.e., cladding) from the chopped spent fuel elements, collect at the bottom of the electrorefiner anode basket on a screen and are transferred to a melting furnace where the deposits are combined with the transuranic deposits collected at the liquid cathode and melted under reduced pressure. The alloy of metallic fission products, cladding material, uranium and transuranic elements has a nominal composition Fe-15Zr-3U-5STRU-2FP or Zr-16Fe-3U-5STRU-2FP, depending on the composition of the cladding material [here, TRU represents the transuranic elements and FP means fission product elements]. This metal alloy has excellent corrosion resistance and is intended to be encapsulated in a normal stainless steel repository container for geologic disposal as a high-level waste form. Because of its small volume, the metal waste form could be economically packaged in a "super container" to provide added assurance against release of transuranic elements to the biosphere.

Treatment of the salt from the electrorefiner and the oxide reduction vessel is only slightly more complicated. The salt is first treated in a series of centrifugal contactors operating at 500°C to remove any actinide elements present; the actinides are returned to the electrorefiner as chlorides for subsequent electrotransport and collection. The molten salt effluent from the centrifugal contactors is passed through a set of zeolite columns where the fission products are immobilized in the zeolite pellets by a combination of ion exchange and

molecular occlusion. The salt exiting from the zeolite columns is free of fission products and is recycled to the electrorefiner. The loaded zeolite pellets, containing up to 25 wt.% fission products, are mixed with anhydrous zeolite powder to adsorb any salt adhering to the surface of the zeolite pellets; the mixture is then hot-pressed at 700-725°C to convert the mixture to a solid monolithic mineral form having the composition of the natural aluminosilicate mineral, sodalite. It is then intended that the sodalite blocks be loaded into standard repository containers for disposal as a high-level waste. Standardized leach tests with waste-loaded sodalite have shown this waste form to be comparable in its resistance to groundwater leaching to the standard borosilicate glass waste form.⁸

The final product of the pyrochemical processing operations is pure metallic uranium. If this product is highly enriched in the ^{235}U isotope, the metal product can be blended with depleted or natural uranium for recycle to commercial reactor fuel manufacturing processes. If the uranium is low in ^{235}U content, it can be calcined to convert the product to U_3O_8 or UO_3 for disposal as a low-level waste.

The packaged volume of high-level wastes arising from the pyrochemical process is considerably less than the volume of the original fuel if it were to be packaged for direct disposal. Current estimates of the high-level waste volume are about 0.2-0.5 m³ per metric ton of initial heavy metal present in the fuel.

VII. CONCLUSIONS

Pyrochemical processing offers an economical and expeditious means for dealing with the ultimate disposal of spent nuclear fuels presently in the custody of the Department of Energy. It is a simple, compact process that can accommodate nearly 99% of the DOE inventory, and it produces three common waste forms regardless of the fuel type being treated. Pyrochemical processing places the hazardous transuranic elements in a stable, corrosion-resistant alloy of minimal volume and separates the highly radioactive fission products in a mineral waste form that is stable under long-term irradiation and resistant to leaching by groundwater.

VIII. ACKNOWLEDGMENT

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REFERENCES

1. T. O'Toole, "Spent Fuel Working Group Report on Inventory and Storage of the Department's Spent Nuclear Fuel and other Reactor Irradiated Nuclear Materials and their Environmental, Safety and Health Vulnerabilities," U. S. Department of Energy, Volume I (1993).
2. J. P. Ackerman, "Chemical Basis for Pyrochemical Reprocessing of Nuclear Fuel," *I&EC Research* **29**, pp. 141-145 (1991).
3. L. Pancratz, "Thermodynamic Properties of Halides," United States Department of the Interior, Bureau of Mines, Bulletin 674, (1984)
4. J. Fuger, V. Parker, W. Hubbard, and F. Oetting, "The Chemical Thermodynamics of Actinide Elements and Compounds, Part 8, The Actinide Halides," International Atomic Energy Agency, Vienna, Austria, 1983.
5. Z. Tomczuk, J. P. Ackerman, R. D. Wolson, and W. E. Miller, "Uranium Transport to Solid Electrodes in Pyrochemical Processing of Nuclear Fuel" *J. Electrochem. Soc.* **139**, pp. 3523-3528 (1992).
6. J. J. Laidler, "Pyrochemical Recovery of Actinides," Proceedings, *American Power Conference* 55-II, Illinois Institute of Technology, pp. 1074-1078 (1993).
7. C. C. McPheeers, R. D. Pierce, D. S. Poa, and P. S. Maiya, "Pyrochemical Methods for Actinide Recovery from LWR Spent Fuel," Proceedings, *GLOBAL 93 Conference*, American Nuclear Society, pp. 1094-1101 (1993).
8. C. Pereira, Argonne National Laboratory, private communication (1994).