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Author(s):

Kent D. Abney
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Kent D. Abney (CST-11), Larry R. Avens (NMT-6), P. Gary Eller (NMT-6), and Edward D. Arthur (NMSM-PO)

Laboratory Directed Research and Development Program
Los Alamos National Laboratory
Los Alamos, NM 87544

ABSTRACT

The objective of this project is to review the status of advanced nuclear processing technologies and approaches developed after 1977 that can minimize or eliminate key negative characteristics associated with aqueous (PUREX) processes—separated plutonium streams, complexity, waste generation, and economics. The impetus behind this review is to determine what nuclear fuel processing activities have occurred since the Carter decision to split defense and commercial fuel cycles. This review is also an attempt to begin updating the Brookhaven National Laboratory review of alternative processing options published in 1977.[1]

Since 1977, the only major programs that have attempted to develop alternate nuclear fuels processing methods are the Argonne National Laboratory Integral Fast Reactor Program with its associated spent fuel reprocessing flowsheet and the Oak Ridge National Laboratory molten salt fluoride volatility process flowsheet. (The latter was actually begun earlier then 1977 and was nearly complete by this time.) The information derived from reviewing these programs will be an important element in efforts to convince policy makers that a reconsideration and change in the current U.S. position on spent fuel processing should occur.

BACKGROUND

For the past 50 years or more the PUREX process flowsheet has been the baseline separation process for recovery and purification of plutonium and uranium to be used in everything from nuclear weapons production to commercial nuclear power generation. The merits and efficiency of this process are undeniable since it ultimately produces highly purified plutonium and uranium which both can be easily converted into metal. The PUREX process is however not without disadvantages. The generation of copious quantities of high activity fission product-bearing aqueous and non-aqueous wastes is one aspect of this process which has reduced its use at present. This process also requires large production sites and equipment for it to be performed on a production scale. The inherent ability of this process to generate highly purified plutonium and uranium fractions also contributes to nonproliferation issues not easily resolved in today’s political climate.

The development of alternative nuclear fuel processing schemes must overcome many of the disadvantages of the PUREX process while still remaining economically viable over the single use geological repository approach currently being considered and planned for spent nuclear fuels. Any new process must also recover the plutonium and uranium in forms that are acceptable for reuse in a nuclear reactor but in a form unacceptable for weapons of mass destruction and terrorist application. This process must be performed in a manner to which minimum floor space is needed for processing thus reducing chances for diversion and must be amenable to accurate accounting of the nuclear material content.

Based upon the criterion described above only two major process alternatives have been developed since the 1970’s which overcome most of these hurdles. The U.S. Department of Energy Integral Fast Reactor (IFR) Project at Argonne National Laboratory is one program that has overcome many of the technical and political hurdles associated with spent nuclear fuels processing. The Oak Ridge National Laboratory (ORNL) molten salt fluoride volatility is another which has also made significant advances toward solving these same issues.

This review is the first of several describing these two major programs and several other smaller efforts. Within this report we discuss the merits and issues associated with the IFR preprocessing flowsheet. Future reports will discuss the ORNL process and others.

IMPORTANCE TO LANL'S SCIENCE AND TECHNOLOGY BASE AND NATIONAL R&D NEEDS

The efforts supported under this project are key to Laboratory initiatives in identifying strategies and technologies applicable to dealing with, and solving, the global Plutonium Legacy. They also support the Nuclear Vision effort by providing data and arguments as the basis for spent fuel recycling, and most importantly, allow concrete information to be provided concerning more attractive materials processing methods applicable to future global nuclear fuel cycle scenarios.

IFR PROCESS DISCUSSION

The IFR project and its predecessor the Experimental Breeder Reactor (EBR) in its conception was designed and built to breed plutonium to reduce the perceived shortage of uranium so that mixed plutonium and uranium oxide fuels could replace standard $^{235/238}U$ fuels for commercial power generation. It was also recognized that the neutronics of this reactor could be modified to change it from a plutonium breeder into a burner of nearly all of the transuranium elements (TRU). This configuration would allow burnup of the TRU component of spent nuclear fuels from the commercial sector as generally described in Figure 1. In this scenario a variety of spent nuclear fuel types would be sent to fuel reprocessing. The uranium would be removed and stored until the economics of this material require it reuse. The fission product fraction would continue to be sent to a high level waste (HLW) repository. (Another option for the fission products would be burnup in an accelerator-based transmutation system.) The TRU component of spent nuclear fuel would then be sent to IFR fuel processing after which the energy content of this fraction could be utilized and converted into a nonproliferant fission product form. Because of this new mission, detailed investigations into spent nuclear fuel processing, IFR fuels processing (actinide metal production and recycle), pyrochemical waste processing, and reactor performance and optimization continues.

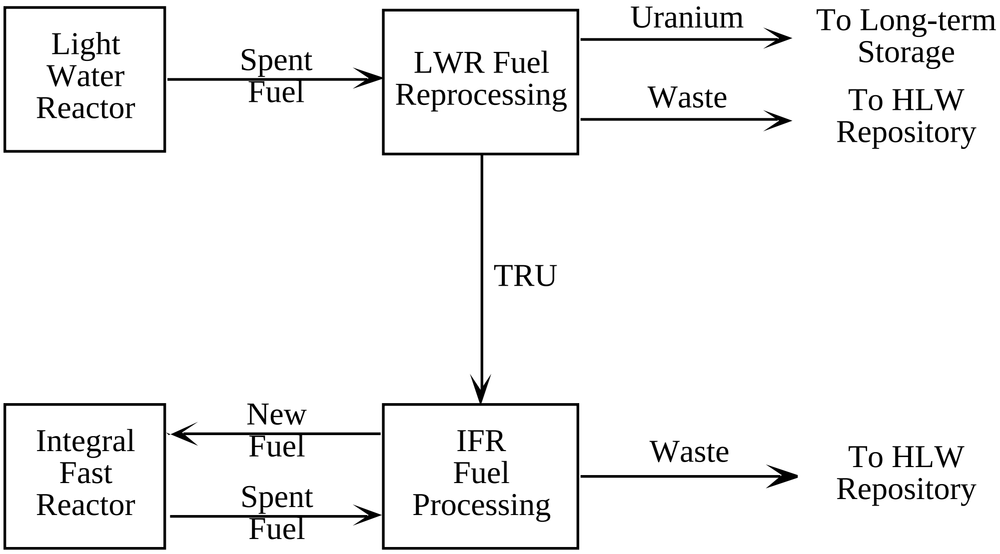

Figure 1. Spent nuclear fuel/IFR fuel cycle for actinide transmutation.[2]

While the detail of the IFR neutronics are beyond the scope of this review, it is important and informative to understand the underlying design of the reactor core and the separation requirements for the actinides based upon this configuration. The IFR core is small and compact which permits a high flux, high energy neutron spectrum. The result of this neutron spectrum is an increase of the fission cross sections for the actinides relative to their capture cross sections. Likewise, the fission product capture cross sections change little or may even decrease at these high energies thus conserving the neutrons for actinide burnup. The major components of the core shown in Figure 2 are the boron carbide shield, a steel neutron reflector, radial and internal blankets, and a driver fuel. In all cases the driver and blankets will contain actinides in their metallic state. The reactor can be driven under several scenarios. In a self-sufficient mode, more likely for energy generation and very slow TRU element transmutation, natural or depleted uranium is converted to plutonium. The plutonium generation rate is slightly larger than consumption thus having a breeding ratio of > 1. In this instance the radial and internal blankets contain 90 wt % U and 10 % Zr, and the driver fuel contains 70 wt % U, 20 % Pu and 10 % Zr. The blankets contain approximately 3900 kg of uranium and require nearly 500 kg per year for makeup. The reactor can also be used to burn plutonium and the minor actinides or used in a manor which converts the minor actinides to ^{239}Pu. In these latter two modes the blankets are removed and plutonium/uranium/zirconium metal alloys are used as the fuel. In this instance nearly 4000 kg is needed to load the driver and 350 kg per year (88% Pu) is needed as makeup. The makeup quantity is equivalent to the plutonium generated from a single 1000 MW(e) Light Water Reactor annually.

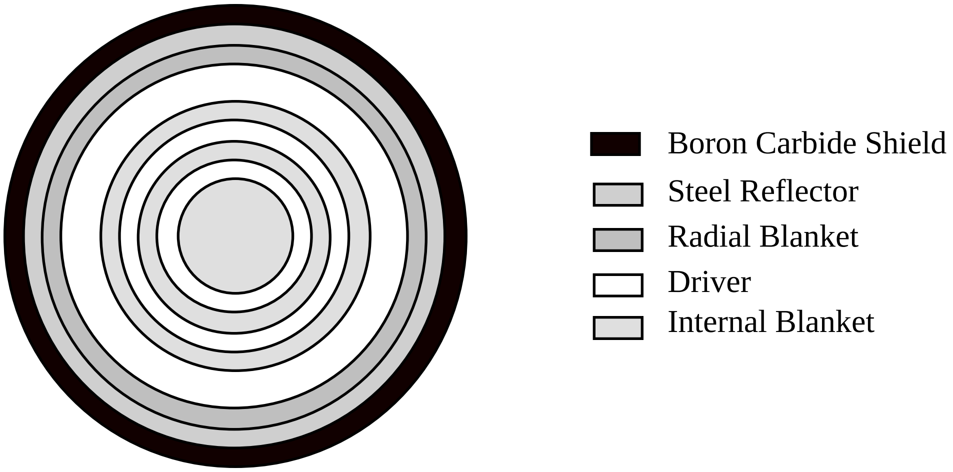

Figure 2. IFR Core Design.

The spent nuclear fuel reprocessing step in preparation for IFR fuel preparation must be sufficiently flexible to accommodate a number of spent fuel types beyond the metal oxides of Light Water Reactors. Other potential fuels for reprocessing include metals, carbides, and nitrides. Metal fuels are easily fed directly into the IFR pyrochemical flowsheet for recovery of the transuranium element fraction. In the case of carbides and nitrides, strict limitations on carbon and nitrogen have been imposed due to their actinide complex formation ability and the inability of the pyrochemical flowsheet to overcome this issue. Thus pretreatment steps like calcination and/or aqueous-based chemical conversion are required to remove these impurities.

The overall spent fuel process flow diagram is shown in Figure 3.[3] In the initial step the spent nuclear fuel from the Light Water Reactor is declad and the fuel extruded. Zircalloy or aluminum cladding materials are minimized within the process flowsheet.[4] The spent fuel oxide is then reduced to metal in a KCl/LiCl eutectic mixture having a melting point of 356 °C. Lithium metal and lithium chloride react with the oxides of plutonium, uranium, and the other TRU elements to form zero valent actinide metals and Li_2O. Any losses at this juncture are due to incomplete reaction and formation of actinide oxychlorides. Within the salt there exists a mixture of metal halides and oxyhalides for virtually the entire periodic table. One advantage to this process is the formation of relatively non-volatile tellurium, iodine, and noble metal chlorides, all of whom present off-gas treatment issues for classical PUREX or other aqueous processes. The removal of oxygen from the reduction salt and its subsequent recycle is performed by reduction of the Li_2O to O_2 which subsequently migrates into a carbon anode forming CO and CO_2. In this manner the oxygen is continually removed from the salt and the reaction to form actinide metals is driven to completion.

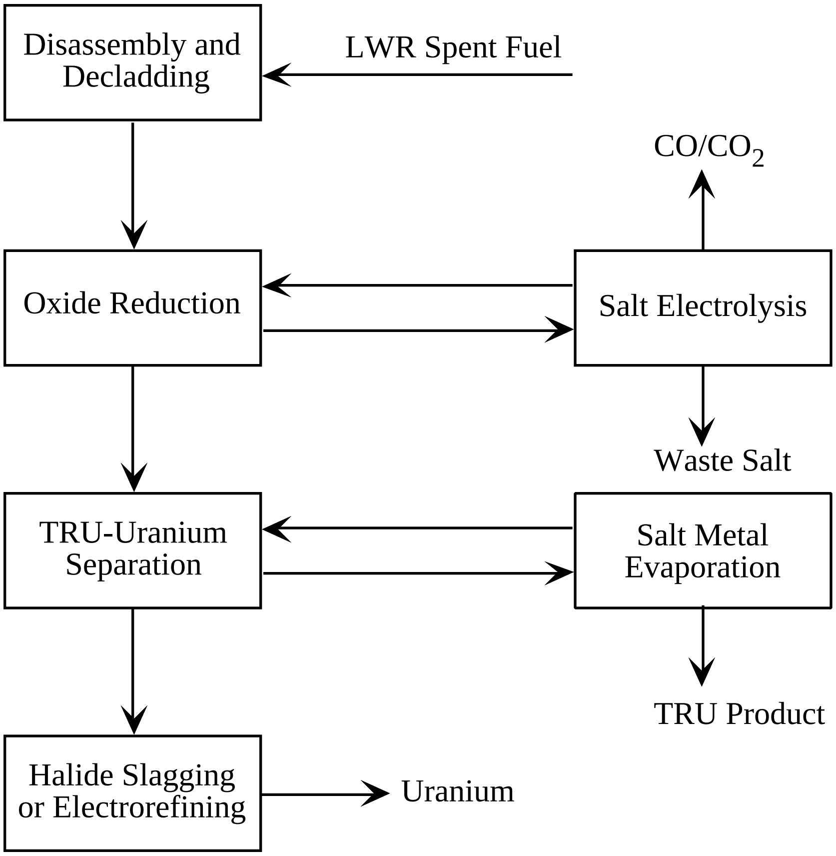

Figure 3. Spent nuclear fuel reprocessing flow diagram.

Subsequent to the oxide reduction step is the separation of uranium and the TRU elements from the fission products.[5] This is then followed by a separation of uranium from the TRU elements. Sequential electrorefining steps are capable of accomplishing these goals. Electrorefining by transport of metal ions through the salt phase is performed using the 350 °C melting KCl/LiCl eutectic operating at 500 °C. The declad fuels pins are assembled into a basket and dropped into the vessel for heating. At the bottom of this vessel is a layer of cadmium metal which melts at 321 °C containing cadmium chloride that serves to oxidize the metals for transport, Equations 1 and 2. Initial separation of the majority of the uranium is accomplished by use of a stainless steel solid cathode with the basket containing the fuel pins serving as the anode. The anode oxidizes the zero valent metals and allows dissolution and transport of the ions through the salt matrix. The stainless steel solid cathode electrochemical potential is set at 1 volt to collect uranium and some rare earth elements. Once the amount of uranium is reduced such that the ratio of Pu:U is greater than 2-3, the plutonium is deposited within a second cathode, in this instance a ceramic crucible containing liquid cadmium. The plutonium and other TRU element fraction accounts for < 1 % by mass of the spent nuclear fuel weight. Removal of the uranium dendrites from the stainless steel cathode is accomplished by high temperature (> 1200 °C) extrusion into a button. The removal of the plutonium is likewise recovered using a 700 °C melting process.

$$2\,U + 3\,CdCl_2 \longrightarrow 2\,UCl_3 + 3\,Cd \tag{1}$$

$$2\,Pu + 3\,CdCl_2 \longrightarrow 2\,PuCl_3 + 3\,Cd \tag{2}$$

The spent salt can be regenerated by a number of processes including treatment with depleted U-Cd alloys to reduce the remaining TRU elements into a metallic cadmium phase for additional electrorefining and by treatment with Cd-Li alloy to reduce residual rare earths into another cadmium waste phase. The cadmium is then recovered by distillation. Additionally, another technique under development for the regeneration of spent electrorefining salt involves the removal of fission products such as cesium, strontium, and the rare earths by ion exchange through a zeolite column. In this case zeolite A has been shown to effectively remove these elements and can be vitrified into a glass matrix for final disposal.[6]

TECHNOLOGY STATUS

Technology Maturation and Applicability to Present Day Spent Fuel Reprocessing[7,8]

The IFR pyrochemical process flowsheet as applied to spent nuclear fuels continues to be one of the few alternative processes under development today. It offers a new approach to the traditional PUREX process flowsheet. This EBR and IFR programs offer over 30 years of technology development for the total nuclear fuel cycle from neutronics to process chemistry to waste management. This review cannot obviously cover the entire spectrum of technology development. Yet within the limited scope of this review process some questions discussing the limitations of the IFR process remain unanswered or at least undiscovered within the documents located to date. For instance the recovery of plutonium and other TRU elements from the spent fuel reprocessing scheme is approximately 99 %. Yet PUREX is purportedly able to recover 99.99 %. The optimization of the IFR process flowsheet must be clearly described and the total yields documented before its effects upon the total spent nuclear fuel plutonium inventory can be determined. Additionally, the ability to separate the TRU elements from the rare earths (typically difficult for aqueous processes) must have further elaboration to determine this effect upon the IFR fuel recycle and chemistry efforts. The reduction of spent nuclear fuels from oxides to their metallic still is in the process of optimization. Experimental progress has been made on uranium and plutonium oxides. However, the noble metals and their technetium alloys are typically difficult to process under aqueous conditions. Occlusions within these nodules could reduce the overall plutonium recovery efficiency. Another limitation of the IFR process is the continued used of cadmium for molten salt ion transport. This RCRA listed material has the potential to generate extensive quantities of mixed waste similar to the PUREX process. From a facility perspective, significant progress has been made upon scale-up of many of the unit operations. In 1996 the electrorefiner throughput was reported as 42 kg per hour. That rate has now been reported as 1000 kg uranium per day. These improvement will hopefully continue for this and other chemical operations and should be benchmarked against the backlog of existing spent nuclear fuel.

Safeguards, Nonproliferation, and Plutonium Management[9,10,11]

The safe and accountable control of nuclear material with particular attention to fissionable materials constitutes the basis for IAEA standards of nonproliferation. While the use of reactor-grade plutonium and its commensurate isotopic distribution has been demonstrated to be of sufficient quality to produce a nuclear weapon, the existence of high radiation combined with the presence of depleted uranium and poor plutonium isotopics all add to a large degree of difficulty in using spent fuels as a source of bomb materials. Thus all questions of safeguards and nonproliferation are measured against at least these three issues. For the IFR fuel cycle it is clear that complete separation of uranium from plutonium is not required or performed and more importantly that the other TRU elements are not separated from plutonium. Additionally, high gamma radiation sources such as the rare earths and the alkali metals contribute substantially to the specific activities of many of the process solutions requiring hot cells for safe handling and lowering the possibilities for diversion. Finally, the chemical species found within the IFR process flowsheet and the specific activities both contribute to additional barriers to covert diversion and reprocessing. The PUREX process does not handle safely the zirconium-actinide alloys found in the IFR process. Likewise the tributyl phosphate PUREX extractant was designed for handling spent fuels cooled for greater than two years. Degradation of this extractant results in plutonium hold-up in the organic phase and causes significant criticality concerns. The IFR process is designed to continuously handle irradiated reactor fuel thus reducing the possibility for diversion.

Conversely, actinide purification to pure plutonium using the IFR electrorefining technique relies strictly on the electrochemical potential across the electrodes. Thus like PUREX, this process flowsheet still has the ability to generate highly purified plutonium. The compact design of many of the IFR fuel cycle processes also increases the likelihood of operating this plant in a covert fashion. Thus while many facets of the IFR fuel processing program contribute to nonproliferation, they may also be used to thwart this effort.

The ability to run the IFR at a low conversion ratio also lowers safeguard concerns over time. Plutonium inventories in currently existing spent nuclear fuel could be significantly reduced over time. The plutonium inventories based upon the continued growth of nuclear power internationally could at a minimum be held at current levels depending upon the IFR deployment level. Present estimates show that each IFR is capable of burning the TRU elements produced by a 1000 MWe/y LWR annually. Further optimization and deployment of IFR's could dramatically shorten the time period required to work off all plutonium inventories.

CONCLUSIONS

The IFR program is the latest and only currently funded U.S. government initiated reactor development program. Technology development for fuel recycle constitutes only a small fraction of the entire IFR program. Because of the Carter decision to not support spent nuclear fuel reprocessing, the erosion of nuclear competence especially in the area of fuel cycles continues. This loss of competence has both short term and long term safety and capability consequences. First, the DOE currently owns spent (irradiated) nuclear fuels under wet storage that are know to have had their cladding layer corroded, damaged, and leaking. Nuclear Materials and Environmental Management Programs within the DOE are focused upon stabilization and inventory management issues to develop solutions to this problem. Second, the short and long term resolution of both defense and commercially produced spent fuels has not been clearly defined. The continued delay of these technical and political decisions makes it more imperative to understand the potential application of existing processing options and their limitations. Third, the PUREX aqueous-based process has reached technical maturity. Even with the significant financial backing it received, this maturation process required nearly 50 years. Given the limited resources for technology investment today, the IFR program cannot be expected to reach optimum performance in significantly less time. Still this leaves only one option in an environment where multiple feedstreams, waste issues, and applications are needed in the nuclear field.

Given this result, the IFR program offers our best and only hope at present for solving the myriad of nuclear energy and spent fuel plutonium management issues for today and the future. However, even the IFR program has serious technology and proliferation hurdles if applied to spent nuclear fuel processing. These include i) limited capacity under the current plant design, ii) waste generation problems due to cadmium use, iii) the ability to generate pure plutonium if needed thus adding to proliferation questions, and iv) lack of economic analyses. This obviously presents a situation not conducive to solving the problems associated with the nuclear energy field.

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