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PYROMETALLURGICAL PROCESSES FOR RECOVERY OF ACTINIDE ELEMENTS*

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Abstract

A metallic fuel alloy, nominally U-20-Pu-10Zr, is the key element of the Integral Fast Reactor (IFR) fuel cycle. Metallic fuel permits the use of an innovative, simple pyrometallurgical process, known as pyroprocessing, which features fused salt electrorefining of the spent fuel. Electrorefining separates the actinide elements from fission products, without producing a separate stream of plutonium. The plutonium-bearing product is contaminated with higher actinides and with a minor amount of rare earth fission products, making it diversion resistant while still suitable as a fuel material in the fast spectrum of the IFR core. The engineering-scale demonstration of this process will be conducted in the refurbished EBR-II Fuel Cycle Facility, which has entered the start-up phase.

An additional pyrometallurgical process is under development for extracting transuranic (TRU) elements from light water reactor (LWR) spent fuel in a form suitable for use as a feed to the IFR fuel cycle. Four candidate extraction processes have been investigated and shown to be chemically feasible. The main steps in each process are oxide reduction with calcium or lithium, regeneration of the reductant and recycle of the salt, and separation of the TRU product from the bulk uranium. Two processes, referred to as the lithium and salt transport (calcium reductant) processes, have been selected for engineering-scale demonstration, which is expected to start in late 1993.

An integral part of pyroprocessing development is the treatment and packaging of high-level waste materials arising from the operations, along with the qualification of these waste forms for disposal in a geologic repository. Three waste streams arise from the processing of IFR and LWR fuels: fission product gases, metallic fission products, and salt containing chloride-forming fission products. The development of suitable waste forms for each waste stream is underway.

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I. Introduction

During the Manhattan Project in the 1940s, processes were developed for recovery of actinide elements. The principal objective was the recovery and purification of plutonium from reactor-irradiated uranium for military applications. Many physical and chemical methods were investigated for the separation of uranium, plutonium, and fission products from one another. These methods included ion exchange, solvent extraction, distillation, precipitation, electrodeposition, and various metallurgical techniques. Because of the intended application and the need for hands-on work with the uranium and plutonium products, the process had to provide a high degree of separation of uranium and plutonium from high-radiation-level fission products. Precipitation, ion exchange, or organic solvent extraction from aqueous solutions provided the necessary separation and appeared to be the simplest to accomplish. By the early 1950s, aqueous processes (bismuth phosphate, Redox, PUREX, etc.) capable of achieving nearly complete recovery and decontamination had been developed. These processes were developed for recovery of military-quality fissionable material; they are complex, requiring many steps and massive installations. The development of commercial nuclear reactors in the 1950s and 1960s for electrical generation promoted further interest in the processing of nuclear fuels (mostly oxides). Today, the PUREX-type process is the principal method for processing commercial nuclear fuels as well as irradiated fuels for military applications. The process yields a high-purity plutonium product free of fission products and minor actinides (np, Am, Cm); the minor actinides are part of the aqueous waste stream along with other fission products. Transuranic extraction (TRUEX) is another aqueous process that is being developed specifically for the purpose of recovering the minor actinides from the waste stream.

As noted above, the aqueous processes for fuel recycle are complex and require massive installations. As early as the 1950s, much simpler fuel cycles were thought to be feasible for the recycle of fast reactor fuel, since higher decontamination from thermal-neutron-absorbing fission product nuclides would not be necessary. However, this would require that the fuel be processed and refabricated by remote operations. Development of such a process was undertaken by Argonne National Laboratory in the 1950s as part of the EBR-II program (Experimental Breeder Reactor number two) (1), for which the reactor was co-located with a fuel cycle facility (Fig. 1).

The method for processing the metallic spent fuel was termed the melt refining process (2, 3). This involved a melt down of irradiated fuel pins, after they were declad and chopped into short lengths in a calcia-stabilized zirconia crucible. Ten to twelve kilogram batches were melted and liquated in the crucible for three hours at 1400°C. The metal was then chill cast into an ingot by top pouring into a cold graphite mold. The average pouring yield for 500 runs was 92.3%. In melt refining, the inert gaseous fission products Xe and Kr are given off to the melting furnace atmosphere when the alloy melts. Volatile sodium, the metal fission products Cs and Rb, and volatile iodides reacted with and were trapped as solids on a fume trap, which closed off the top of the melting crucible. Rare earth and alkaline earth fission product metals reacted with the crucible wall to form a skull, which stayed in the crucible when the melt was poured. The skull trapped some metal, which became part of the skull and accounted for the 92.3% pouring yield. During 1964-1969, 5.9 metric tons of irradiated fuel pins were processed into about 35,000 new fuel elements, which were recycled to the reactor. The shortest cycle time was about 28 days, i.e., the time from discharge from the reactor until recharge in the reactor.

The skull reclamation process (4) was developed to recover the enriched uranium in the

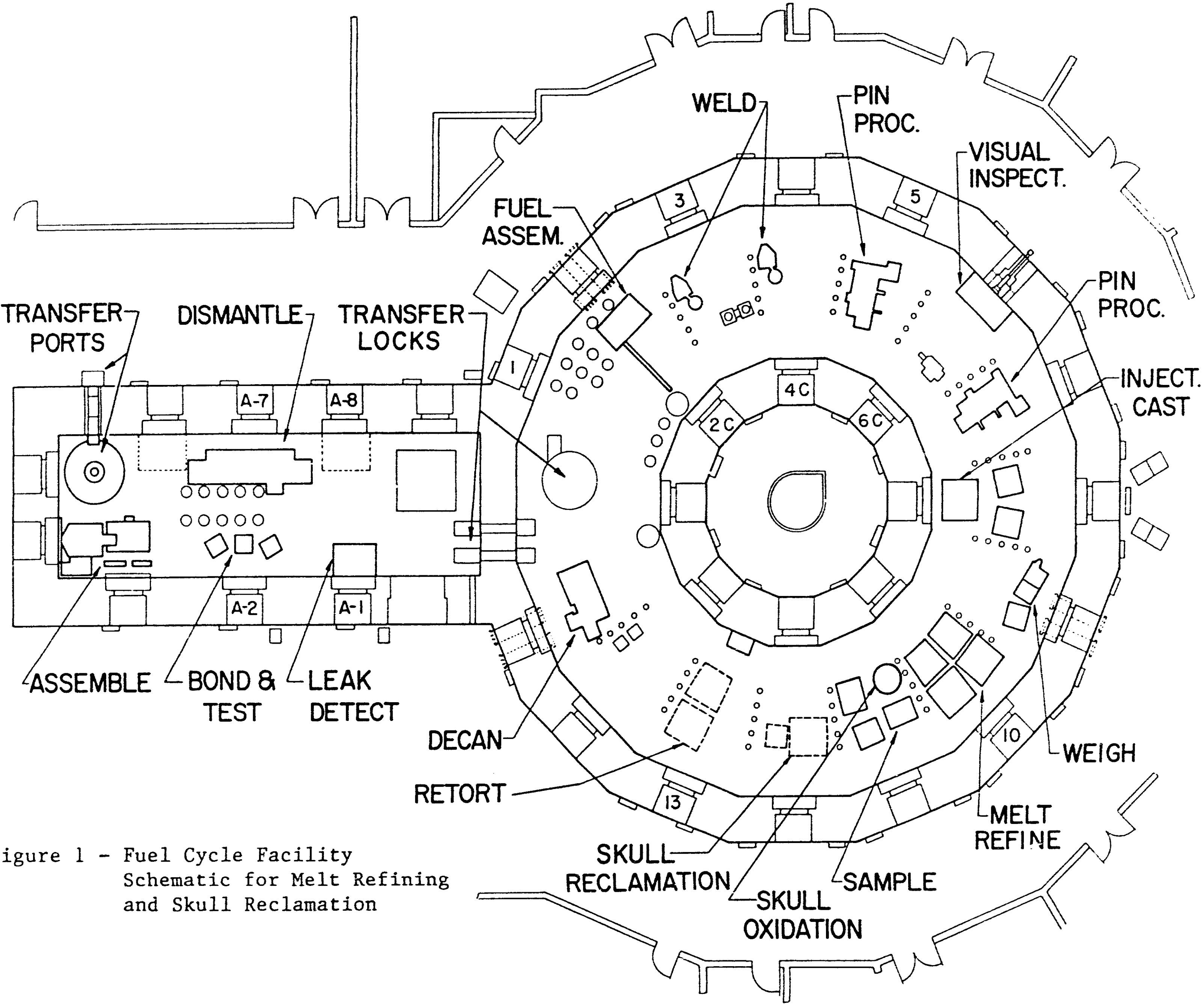


Figure 1 - Fuel Cycle Facility Schematic for Melt Refining and Skull Reclamation

crucible skulls. The melt refining skulls were oxidized within the zirconia crucible to create a free-flowing powder which was then poured from the crucible. The oxide was then mixed with a molten salt flux and liquid zinc at 750°C in a tungsten crucible. The liquid zinc phase layer containing the noble metal fission products was then removed from the crucible, and a reductant (Mg-17 at. % Zn) for uranium oxide was introduced into the tungsten crucible. Insoluble uranium metal precipitate formed, and the liquid flux and zinc phases containing fission products were removed. The uranium precipitate was dissolved in a Mg-30 at. % Zn alloy. This liquid solution was removed from the tungsten crucible and retorted, and then the residual uranium was melted in the BeO crucible from which the uranium ingot was recovered. This process required three major equipment items: a skull oxidation furnace, an oxide processing furnace with a tungsten crucible and a Mo-W liquid zinc transfer line, and a uranium retort-melter. All of these items were developed, but only the skull oxidation furnace was installed in the hot cell and used to separate the enriched uranium skull from the zirconia crucible scrap.

In 1969 fuel processing and fuel fabrication activities in the Fuel Cycle Facility ceased. At that time, the mission of EBR-II was changed from a demonstration of the integrated reactor-reprocessing complex to that of an irradiation facility, with emphasis on oxide rather than metal fuel. Interest in metal fuel was rekindled in the 1980s when metal fuel designers overcame the primary objection to metal fuel, namely, that it was limited (due to swelling) to 1% burnup or less. (Burnups of 20% have now been achieved in U-Pu-Zr fuel.) This early work in developing pyroprocesses for metal fuel emphasized uranium recovery because of the value of the enriched uranium involved. Present-day processes emphasize the recovery of plutonium since the trend is away from utilizing enriched uranium in fast reactor fuel.

The introduction of the Integral Fast Reactor (IFR) concept by Till and Chang (5) in the 1980s has generated new interest in the development of a simple, low decontamination, economical fuel cycle based on pyrometallurgical processing methods. The IFR is an advanced-reactor concept proposed by and under development at Argonne National Laboratory. Further, the fuel cycle is an integral part of the IFR, hence the basis for the name. In addition to the integral fuel cycle, the IFR concept features a sodium-cooled pool-type reactor employing a metallic alloy fuel of U, Pu, and Zr. Expected advantages of this concept are an exceptionally high degree of passive safety and competitive economics resulting from low cost for reactor construction and fuel recycle. The fuel cycle, which is a key element in the IFR concept, is based on a pyrometallurgical process which employs electrorefining with a molten salt electrolyte ($LiCl-KCl-U/PuCl_3$) at 500°C in an inert atmosphere enclosure (6, 7). Process development using simulated fuels has been conducted at Argonne-East and will be discussed in Section II. Demonstration of the fuel cycle will take place at Argonne-West in the refurbished FCF (i.e., after facility upgrade and changes in process equipment) and will utilize spent metallic fuel from EBR-II, which is located adjacent to the FCF.

Development of a unique pyrometallurgical process for the recovery of the transuranic (TRU) elements from irradiated oxide fuels was initiated in 1990 (8) as a means of providing a source of plutonium for the startup of additional IFRs. This low-decontamination process, which is discussed in Section III, will provide a plutonium alloy containing some uranium, the minor actinides, and rare earth fission products as a fuel for the IFR fuel cycle. This aspect has important beneficial implications on the disposal of commercial spent fuel. As discussed in Section IV, the treatment, immobilization, and safe disposal of waste have been important components of the IFR program from the beginning. This approach is believed to be a first in the development of nuclear reactors.

II. Pyrometallurgical Processing of IFR Metallic Fuel

The basis of the IFR concept is the metal fuel cycle, which involves irradiation of metal fuel (U-Pu-Zr alloy) in a fast reactor, reprocessing of the spent fuel, treatment and immobilization of the waste, and refabrication of fuel elements. A key element in the processing of spent fuel is a pyrometallurgical process which employs electrorefining with a molten salt electrolyte (LiCl-KCl-U/$PuCl_3$) at 500°C in a steel vessel (6, 7, 9). The abundant information developed at Argonne in the 1960s on the thermodynamics of uranium-plutonium-fission product-cadmium systems, in combination with subsequent work on molten salt batteries, provided the basis for the development of an innovative electrorefining process for the reprocessing of IFR fuels.

Although electrorefining has not been used to date in the commercial reprocessing of reactor fuels, this technology has a long history in commercial operations, the refining of aluminum being a prime example. On a lesser scale, electrorefining from molten salts has been used to prepare high-purity metallic uranium (10-12). Larger scale operations (5 to 10 kg U per batch) were conducted by Chauvin and co-workers (13, 14) in France during the early 1960s. High-purity plutonium for research purposes has also been prepared by molten salt electrorefining (15, 16). Subsequently, Mullins and co-workers at Los Alamos (17-19) developed an electrorefining process for recovery and purification of plutonium. This process has also been used at Lawrence Livermore National Laboratory (20) and at the Rocky Flats Plant (21) for the purification of plutonium. As evidenced by the above, significant research and development has been devoted to electrorefining of uranium and plutonium separately. Very little work has been done on developing electrorefining for recovery and purification of spent nuclear fuels in the U.S. In the mid-1950s electrorefining was investigated at Knolls Atomic Power Laboratory for decontamination of irradiated uranium (22, 23). Leary, et al (24) investigated electrorefining for reprocessing fuel from the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE). This fuel was successfully electrorefined at 550°C using a $LiCl\text{-}KCl\text{-}PuCl_3$ electrolyte.

The potential application of electrorefining for processing IFR metal fuel is obvious from the above discussion. However, it is important to note that IFR fuel has a complex composition, involving U-Pu-Zr alloy with associated fission products. The electrorefining process (also called pyroprocess) for IFR fuel is based on the favorable thermodynamics of the chlorides and the concomitant use of liquid cadmium as a solvent for the metal fuel and as one electrode of the electrorefining cell. A simplified schematic of the electrorefining apparatus is shown in Fig. 2. The cell vessel, fabricated from carbon steel, contains a layer of liquid cadmium with an over-layer of eutectic LiCl-KCl electrolyte (melting point ~350°C). The operating temperature is normally 500°C but can be lower (<450°C). For startup, the clad fuel elements*[Footnote: Unirradiated simulated fuel has been used in all of the process development work. Processing of irradiated fuel is scheduled for 1994 in the shielded EBR-II Fuel Cycle Facility.] are chopped and placed in perforated steel anode baskets and lowered into the electrolyte for electrochemical dissolution. Initially, the plan was to dissolve the fuel in the cadmium pool; however, this was abandoned in favor of the more rapid electrochemical dissolution (future electrorefiners may not contain a cadmium pool). With the chopped fuel in the salt, cadmium dichloride ($CdCl_2$) is added to oxidize the alkali, alkaline earth, and most of the rare earth elements to their chlorides. Additional $CdCl_2$ is added to oxidize the actinide elements to obtain a concentration of about 6 wt % actinides in the electrolyte to sustain electrotransport.

Schematic Representation of Electrorefiner Operation – Anodic Dissolution/Solid Cathode

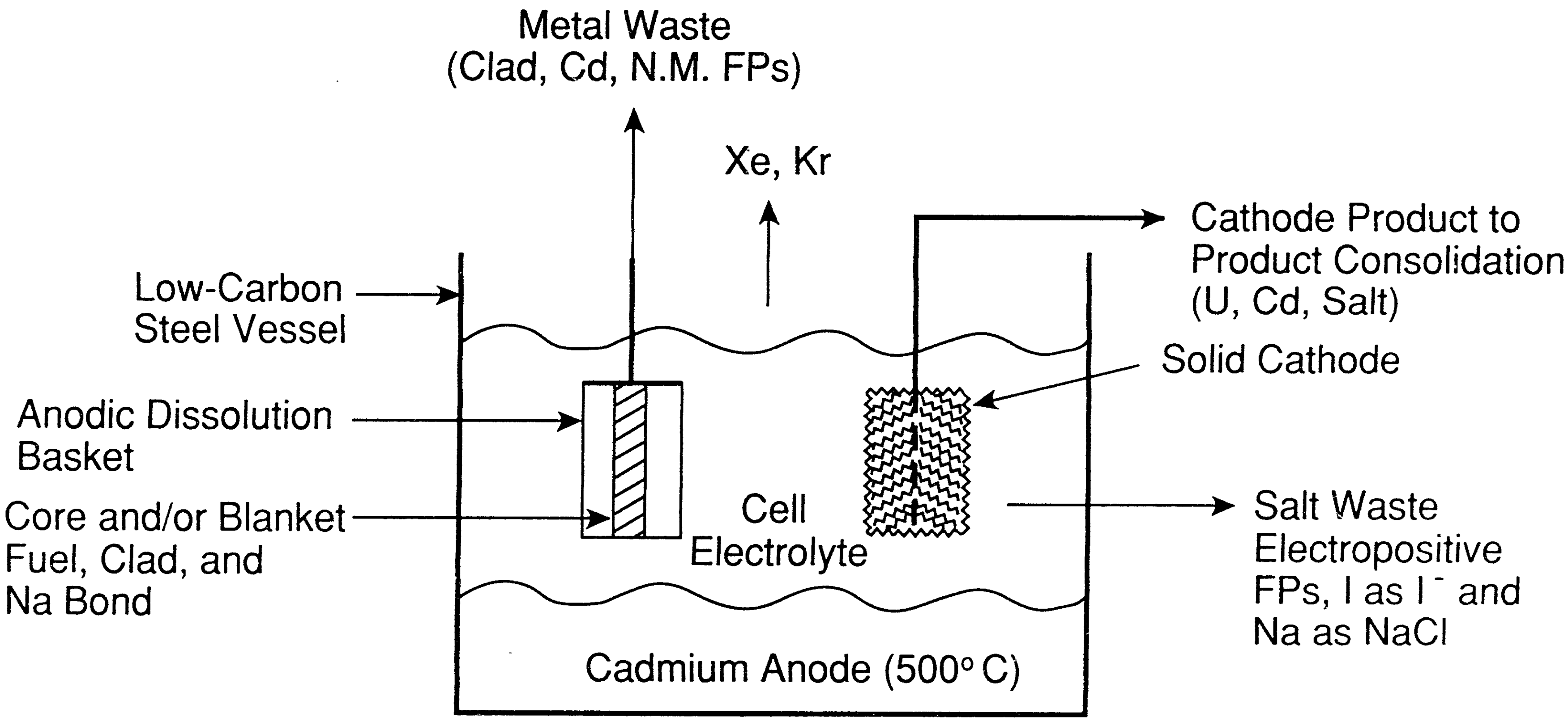


Figure 2

The partitioning of the actinides, alloy zirconium, and fission products is controlled by the thermodynamics of the respective chlorides. As indicated by the data in Table I, the free energies of formation allow separating the elements of interest into three groups: high stability, e.g., alkali, alkaline earth, and lanthanides; low stability, i.e., elements that do not form chlorides in this system; and intermediate stability, i.e., U, Np, Pu, Am, and Cm (zirconium is a borderline case). The actinide elements partition between the salt and metal phases and thus can be electrotransported. The oxidation state of the electrorefiner can be adjusted by adding an oxidant ($CdCl_2$) or a reductant (Li-Cd alloy).

Table I. Free Energies of Formation of Chlorides

at 500°C, kcal/g-equiv. chlorine

Compound	$-\Delta G_f^\circ$	*Compound*	$-\Delta G_f^\circ$
$BaCl_2$	87.9	$CmCl_3$	64.0
CsCl	87.8	$PuCl_3$	62.4
RbCl	87.0	$NpCl_3$	58.1
KCl	86.7	UCl_3	55.2
$SrCl_2$	84.7	$ZrCl_2$	46.6
LiCl	82.5	$CdCl_2$	32.3
NaCl	81.2	$FeCl_2$	29.2
$CaCl_2$	80.7	$NbCl_5$	26.7

$LaCl_3$	70.2	$MoCl_4$	16.8
$PrCl_3$	69.0	$TcCl_4$	11.0
$CeCl_3$	68.6	$RhCl_3$	10.0
$NdCl_3$	67.9	$PdCl_2$	9.0
YCl_3	65.1	$RuCl_4$	6.0

In operation, uranium is electrotransported to a steel mandrel cathode, where it deposits as metallic dendrite. A typical product is shown in Fig. 3. This product normally contains a low concentration of zirconium (1 to 2 wt %). The TRU elements do not deposit because their chlorides and uranium are in equilibrium according to the reaction,

$$UCl_3 + Pu \text{ ---> } U + PuCl_3. \qquad (1)$$

A liquid cadmium cathode is used for the recovery of plutonium and the other TRU elements. This cathode consists of a ceramic crucible containing liquid cadmium, which is suspended in the salt. Electrical contact with the cadmium in the ceramic crucible is provided by a steel electrode. The plutonium and other TRU elements are electrotransported to the cadmium in the ceramic crucible, where they form intermetallic compounds such as $PuCd_6$. The activity of the TRU elements is sufficiently decreased by the formation of intermetallics that they are stable in the presence of UCl_3 in the salt. The product obtained from this operation contains about 3 kg of plutonium; 1 kg of uranium; the associated Np, Am, and Cm (all of which behave like Pu); and a small amount of lanthanide fission products. The low decontamination of this process is beneficial since it adds a significant measure of diversion resistance. The cadmium is distilled

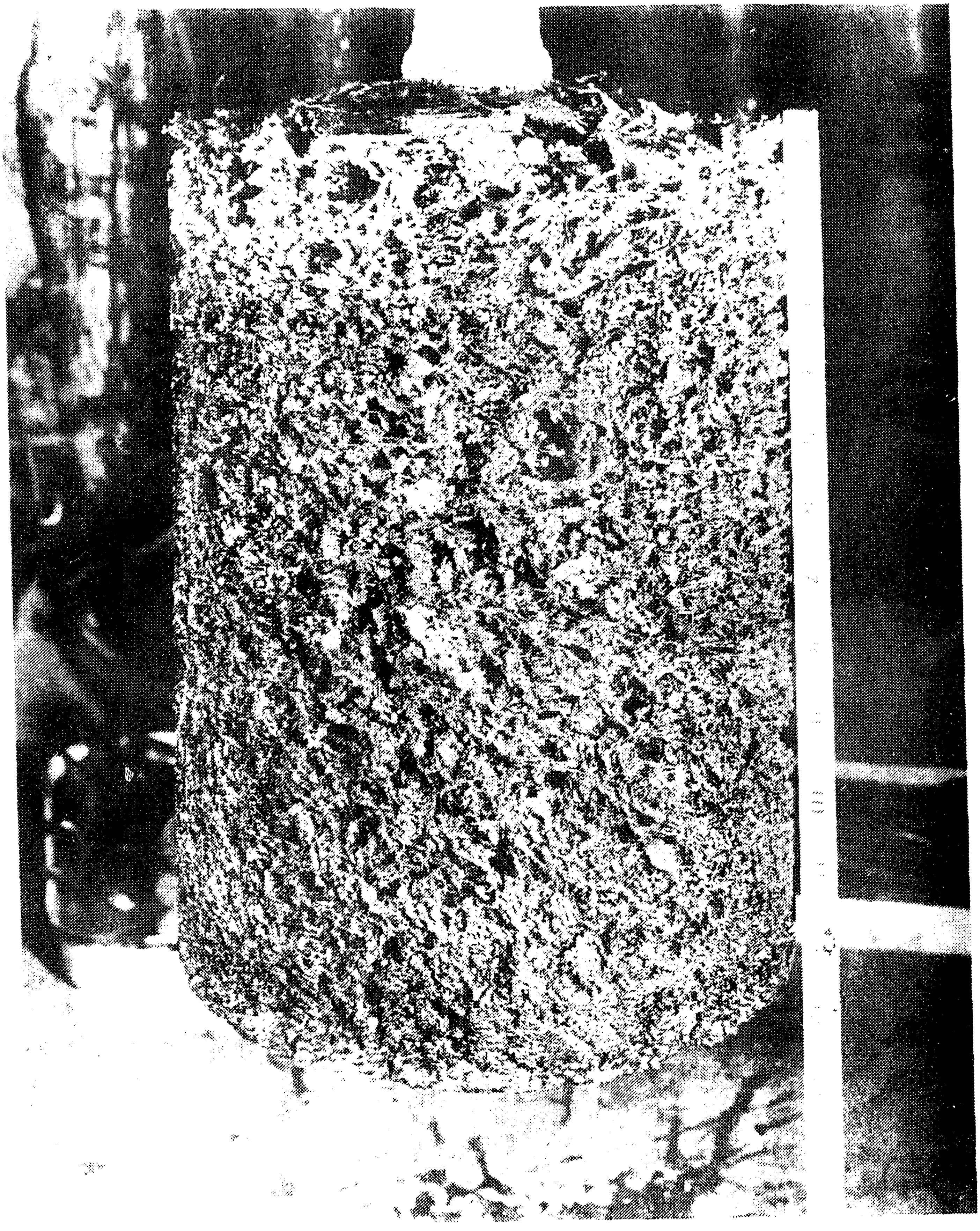


Figure 3 - Ten Kilogram Uranium Deposit

from the liquid cathode product, and the resulting plutonium-bearing alloy along with the uranium product from the solid cathode (after distilling off the adhering salt) is added to a furnace for the casting of new fuel elements.

A process model based on thermodynamic data has been developed for predicting the electrotransport of uranium, plutonium, and rare earth fission products (25). The model also predicts the composition of the solid cathode and liquid cadmium cathode. A series of experiments was conducted for model verification. The results of these experiments indicated that little or no rare earths are deposited with uranium; the uranium deposit is essentially free of plutonium and other actinides until the uranium inventory reaches a low level; the minor actinides (Np, Am, Cm) follow plutonium; and minor quantities of zirconium are electrotransported. The agreement between this observed behavior and that predicted by the model was very good.

In addition to the laboratory-scale electrorefiner used to develop process feasibility and determine process parameters, an engineering-scale electrorefiner facility (capacity of 10 kg of uranium per single solid cathode) was constructed and operated (9) to demonstrate large-scale operation, determine process parameters, and provide design information for the electrorefiner to be placed in the FCF (26). The engineering-scale electrorefiner has operated continuously at 500°C for more than 5 yr with only minor maintenance. All of the process operations (anodic dissolution, uranium deposition on solid and liquid cadmium cathodes) have been successfully demonstrated, and the operating parameters quantified. Anodic dissolution and transport to the solid cathode require about 24 h for a 10 kg batch of uranium. The FCF electrorefiner will possess two anodes and two cathodes, with an expected process rate of 20 kg of uranium in a 24 h period. Systems analyses indicate that optimization of the electrorefiner design will increase this process rate by a factor of four or more.

Electrotransport to the liquid cadmium cathode has been successfully demonstrated for uranium-plutonium (plus minor actinides) in the laboratory-scale electrorefiner and for uranium alone in the engineering-scale electrorefiner. The electrotransport rate to the liquid cadmium cathode was less than that to the solid cathode, primarily because of a smaller area for deposition. Both types of cathode products have been processed to distill off adhering salt and cadmium (liquid cadmium cathode). Analyses demonstrated that the product is essentially free of salt and cadmium impurities.

The pyroprocessing of spent IFR fuel produces three waste streams (see Fig. 2): fission product gases, a metal waste stream that contains clad hulls and noble metal fission products, and a salt waste stream that contains the rare earth, alkali, and alkaline earth fission products. The treatment, immobilization, and disposal of these wastes are discussed in Section IV.

III. Pyrometallurgical Processing of Oxide Fuel

Pyrochemical processes have been developed for extracting TRU elements from Light Water Reactor (LWR) spent fuel in a form suitable for use as feed to the IFR fuel cycle (27). This spent fuel, with a typical burnup of 33 GWd/MTIHM (gigawatt-days per metric ton initial heavy metal), contains about 97 % uranium and about 1 % TRU elements, with fission products comprising the balance. The goals of the process development include >99.9 % recovery of the TRU elements, minimum quantity of waste to be placed in a geological repository, a simple process with promising economics, and minimum risk of diversion of TRU elements to military uses. The candidate pyrochemical processes are based on work that was done at ANL in the 1960s and 1970s (28-30). Four essential features are critical to meeting the processing goals:

(1) the oxide fuel is reduced to metal components, using a reductant metal such as calcium or lithium, (2) the reductant metal oxide is dissolved in a molten salt phase, so that the reduction reaction can go to completion, (3) the reductant metal is regenerated by electrolysis to allow the molten salt to be recycled, thus minimizing wastes, and (4) the TRU metals are separated from uranium and consolidated into a product suitable for use in the IFR fuel cycle.

The generalized flowsheet for the pyrochemical process is shown in Fig. 4. The LWR spent fuel subassemblies are disassembled, and the oxide fuel is separated from most of the Zircaloy cladding before feeding to the process. The main steps in the generalized flowsheet include reduction of the oxides, regeneration of the reductant metal and recycle of the salt, separation of the TRU product from the bulk uranium, and evaporation of a solvent metal from the TRU product for consolidation into a metal ingot.

Four extraction concepts were studied: the salt transport process, the magnesium extraction process, the zinc-magnesium process, and the lithium process. Although all of these processes follow the generalized flowsheet of Fig. 4, there are important differences among them, particularly in the TRU-uranium separation method. In addition, the lithium process differs from the other three by the use of lithium as the oxide reductant. The other processes use calcium reductant.

Laboratory-Scale Experimental Studies

Many small-scale experiments were done to determine the feasibility of each step of the processes as unit operations. No attempt was made to integrate the process steps, except that reactants from some experiments were used as starting materials for subsequent steps in the process. The types of experiments and their results are summarized in the following sections.

Reductions. Reduction experiments were conducted using the molten salt and liquid metal phases for each of the process concepts. The experiments were done in MgO crucibles about 57-mm dia by 125-mm tall. In studies of the lithium process, stainless steel crucibles were used. The crucibles were well baffled to enhance mixing. The reactants (salt, metal

ACTINIDE RECYCLE PYROPROCESS CONCEPT

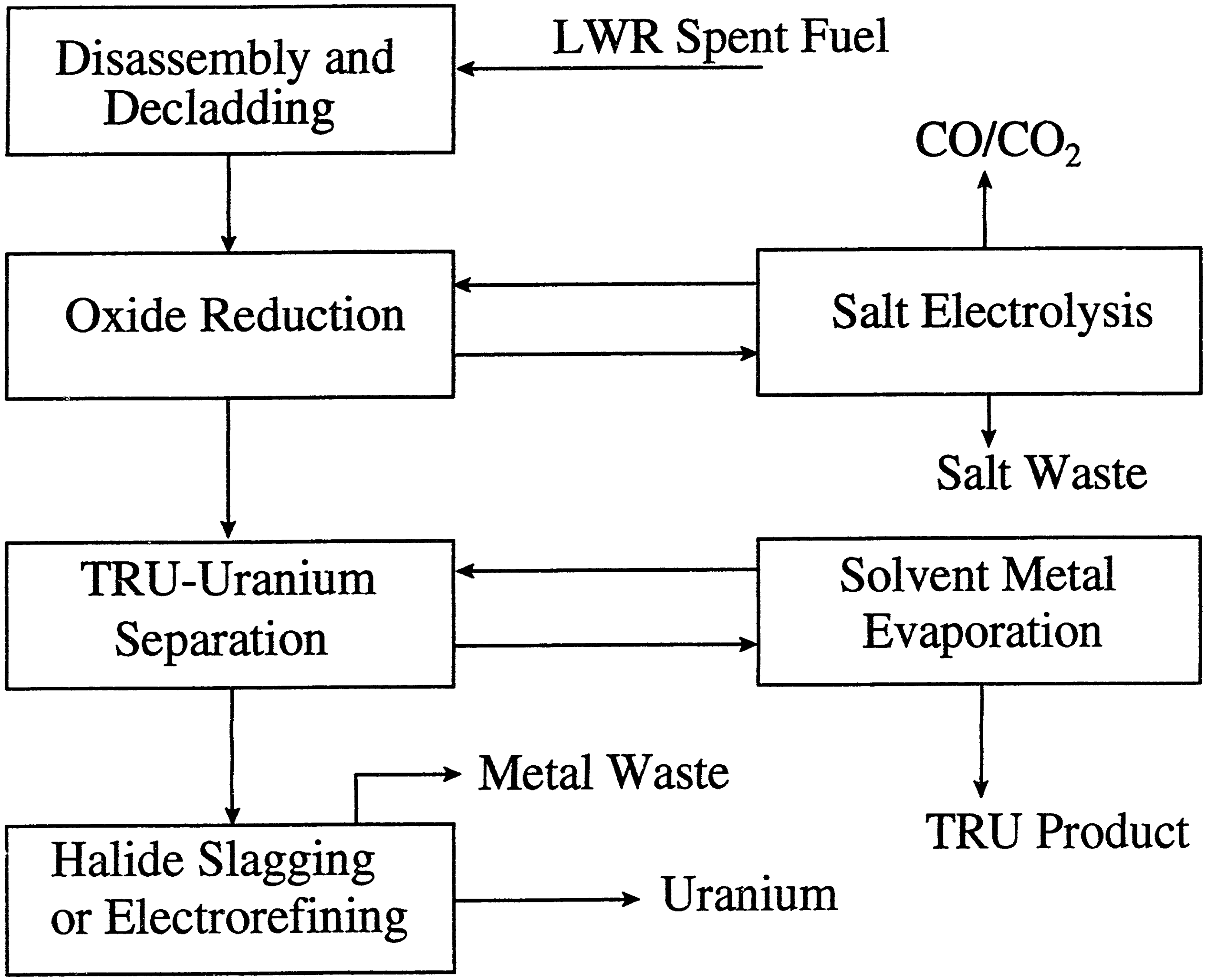


Figure 4 - Generalized Flowsheet for Pyrochemical Processing of LWR Spent Fuel

alloy, calcium or lithium, and the oxide simulated spent fuel) were loaded into the crucibles at room temperature. The simulated fuel was added as chips of high-fired UO_2 that contained prototypical quantities of Pu, Am, and nonradioactive isotopes of the fission products. The calcium reductions were conducted at 800° to 850°C in MgO crucibles, and the lithium reductions were done at 500° to 750°C in stainless steel crucibles. At the end of each experiment, filtered samples of the liquid phases were taken using tantalum sample tubes with tantalum frits welded in the ends. Table II summarizes the results achieved in many reduction experiments for each process concept. The numbers are averages of several separate experiments. The reduction step was found to be satisfactory for all of the candidate processes. A reduction "scrub" step may be needed to assure >99.9% recovery of the TRU elements.

Table II. Percent of Reductions Achieved for Each Process Concept Studied

Oxide Reduced	Salt Transport (Cu-Mg-Ca) ($CaCl_2$ Salt)	Zn-Mg Process (Zn-Mg-Ca) ($CaCl_2$ Salt)	Mg Extraction (U-Fe + Ca) ($CaCl_2$ Salt)	Lithium (Li) (LiCl-KCl Salt)
UO_2	100.0	99.9	100.0	100.0
PuO_2	99.8	99.7	99.6	99.996
NpO_2	99.8	99.6	99.8	97.5*
AmO_2	99.9	99.9	97.0**	99.982
CmO_2	99.99	-------	------	99.986

* Limited data available for NpO_2, but trends suggest >99.9% reduction under conditions similar to existing tests.

** 99.1 % in one experiment.

Uranium-Transuranium Separations. Differences among the methods used to separate TRU elements from uranium comprise the major differences among the flowsheets. As its name implies, the salt transport process uses a molten salt extraction and transport step to effect this separation. The molten salt, $MgCl_2$, is first equilibrated with the Cu-Mg reduction alloy. Since the activity coefficients of the TRU elements are relatively high in the Cu-Mg alloy and since the TRU chlorides are more stable than $MgCl_2$, the distribution of the TRU elements between the Cu-Mg alloy and the molten salt tends to favor higher concentrations of the TRU elements in the molten salt. The molten salt is then transported through a heated transfer line to a separate vessel containing Zn-Mg alloy. In the Zn-Mg alloy the activity coefficients of the TRU elements are relatively low; therefore, the distribution of the TRU elements between the Zn-Mg alloy and the molten salt tends to favor higher concentrations of the TRU elements in the Zn-Mg alloy. Thus, a net transport of TRU elements is achieved from the Cu-Mg alloy to the Zn-Mg alloy, and an equivalent amount of magnesium is transported in the opposite direction. During operation of the salt transport process, the donor vessel, the acceptor vessel, and the transfer line are all maintained at about 800°C.

The distribution coefficients of the TRU elements between Cu-Mg alloy and $MgCl_2$, between Zn-Mg alloy and $MgCl_2$, and between U-Fe alloy and Mg have been measured in several experiments. The distribution coefficient is defined as the ratio of mole fraction (or atom fraction) of the element in the salt phase (or Mg phase) to atom fraction of the element in the Cu-Mg, Zn-Mg, or U-Fe phase. These measured distribution coefficients are summarized in Table III.

Table III. Distribution Coefficients of TRU Elements between Extractants and Alloys

Actinide	$MgCl_2$/Cu-Mg	$MgCl_2$/Zn-Mg	Mg/U-Fe
Plutonium	1.6	<0.05	1.0
Neptunium	1.4	0.036	0.05
Americium	15	0.38	5.0
Curium	0.5*	-----**	-----**

* Only one measurement available.

** Not determined.

The combination of relatively high values for the $MgCl_2$/Cu-Mg system and relatively low values for the $MgCl_2$/Zn-Mg system indicates that the salt transport process should provide efficient separation of the TRU elements from the bulk uranium. A small quantity of uranium is transported with the TRU elements. Extraction of neptunium was found to be very poor in the Mg/U-Fe system, as indicated by the low distribution coefficient. These data, combined with the observation that the U-Fe alloy is very corrosive and difficult to contain in normal materials of construction, led to the decision to eliminate the magnesium extraction process from further consideration as a practical concept. Subsequent work concentrated on the remaining three concepts.

In the lithium process the precipitated metal is separated from the reduction salt by filtration or decanting of the molten salt from the crucible. At the end of the reduction step, the uranium and TRU elements are present as metal precipitates at the bottom of the reduction crucible, along with the transition metal and noble metal fission products. The metal precipitate is transferred to an electrorefiner, and the uranium-TRU separation is done by the electrorefining process, as discussed in Section II.

Salt Recycle. Two types of electrochemical cells have been tested for regeneration of the calcium and lithium reductant metals: (1) a liquid Cu-Mg or Zn-Mg cathode and a carbon anode and (2) a liquid lithium cathode and a carbon anode. Since lithium has a lower density than the molten salt, it floats on the surface, whereas the calcium cathodes have a higher density than the molten salt and remain on the crucible bottom.

Electrochemical reactions at carbon anodes have been shown to produce carbon dusting. Because carbon reacts with uranium and TRU metals to form very stable carbides, methods for controlling this carbon dust had to be developed. A porous ceramic (MgO) shroud to surround the carbon anode was found to adequately contain the carbon dust and prevent it from recycling with the salt. At the end of the salt regeneration step, the porous shroud was raised out of the molten salt and allowed to drain. The shroud was placed in a dry air environment and heated to ignite the carbon. The carbon dust burned off and the shroud was clean enough for reuse in the process.

The results of many experimental tests of these types of electrochemical cells are summarized in Table IV. The current densities were higher for the zinc-magnesium cathode than for the Cu-Mg cathode because the activity coefficient of calcium in the Zn-Mg alloy is lower than in the Cu-Mg alloy. This lower activity coefficient decreases the theoretical decomposition potential, thus increasing the available potential for the reaction. The current density for the lithium process is higher than the other two processes because the difference between the LiCl and Li_2O decomposition potentials is greater than the difference between $CaCl_2$ and CaO; thus, the working potential is higher and the current density is greater. A current density of 500 mA/cm^2 would be required for a practical full-scale system, and any of the systems shown in Table IV could achieve that level with proper cell design. The differences in current efficiencies are not well understood. Current losses may be due to chemical short-circuiting reactions that are diffusion limited. Current efficiency is not an important parameter because the electricity costs are low relative to other operating costs.

Table IV. Results of Electrolysis of CaO and Li_2O in Molten Salt Systems

Parameter	Salt Transport	Zinc-Magnesium	Lithium
Cathode Material	Cu-Mg	Zn	Li
Temperature,(°C)	800	800	650
Current Density (mA/cm^2)	170	250	540
Current Efficiency (Percent)	70	85	91

Process Selection. Based on the performance of the process steps compared to the goals of the process, the lithium process was selected as the reference flowsheet. The advantages of the lithium process include lower operating temperature, less corrosive environment allowing use of common materials of construction, and a salt waste that is compatible with the IFR salt waste, eliminating the need for development of a separate waste form. The salt transport process will be retained as a backup because it is well understood and the most reliable in terms of chemical performance. As stated above, the magnesium extraction process was rejected because of poor extraction of neptunium by magnesium from the U-Fe alloy, and because of the corrosive nature of the U-Fe liquid alloy. The zinc-magnesium process was rejected because it produces more salt waste than the others and because achieving clean separation of the Zn-Mg alloy from the uranium precipitate may be difficult.

Engineering-Scale Process Development

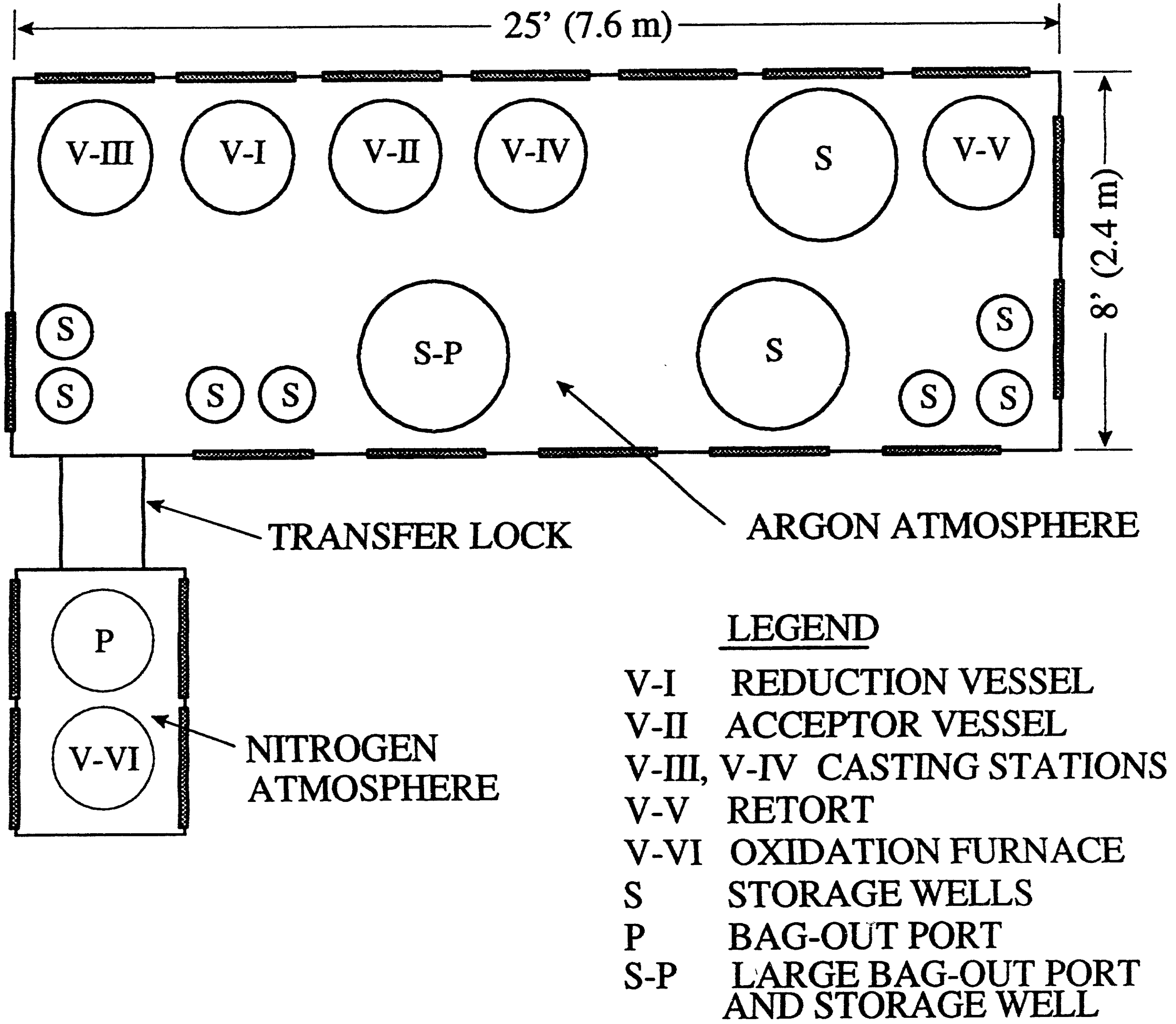
The processes that were developed in laboratory-scale experiments are being scaled up for demonstration at a scale that is a significant fraction of a full-scale plant. The scale that was chosen for this demonstration is 20 kg batch size. This scale is about 10 % of a full-scale plant module, and such a design would address most of the engineering issues associated with heating, containing, and transferring high-temperature process fluids and reagents.

The engineering-scale experiments will be done in an inert gas (argon) environment to prevent reaction of the molten salt, liquid metals, actinide metals, etc. with oxygen or moisture. The argon enclosure, or glovebox, is shown in Fig. V., along with a small nitrogen glovebox that is connected by means of a vacuum transfer lock. The gloveboxes are shown in plan view, and the location of the process equipment is indicated in the legend. The system design is flexible so that a variety of flowsheet concepts and equipment can be tested.

IV. Waste Management

An integral part of pyroprocessing development is the treatment and packaging of the high-level wastes arising from the pyroprocessing operations, along with qualification of these wastes for disposal in a geologic repository. Because the actinides are virtually absent from the pyroprocess waste streams, the radiological toxicity of the pyroprocess waste is greatly reduced beyond the 300-400 year period during which the shorter-lived fission products disappear by radioactive decay. This could represent a significant advantage in the disposal of nuclear wastes, making it easier to provide assurance of complete containment of the radionuclides present in the waste (31). As pointed out by Ramspott et al. (32), the removal of actinides provides an ability to predict future effects regarding the release of materials from

ENGINEERING-SCALE PROCESS GLOVEBOX



LEGEND

V-I	REDUCTION VESSEL
V-II	ACCEPTOR VESSEL
V-III, V-IV	CASTING STATIONS
V-V	RETORT
V-VI	OXIDATION FURNACE
S	STORAGE WELLS
P	BAG-OUT PORT
S-P	LARGE BAG-OUT PORT AND STORAGE WELL

Figure 5 - Equipment Designations and Locations in the Engineering-Scale Process Gloveboxes

a mined geologic repository that is unchallengeable; if the actinides are not present in the waste, they cannot cause an effect.

The fission products extracted from spent fuel by pyroprocessing will be placed in stable, leach-resistant waste forms with acceptable mechanical integrity for repository disposal. These fission products appear in various waste streams: in the electrorefiner wastes and in the waste salt from the reduction process used for recovery of actinides from the spent oxide fuel. The pyroprocess waste treatment operations will concentrate these fission product wastes and then immobilize them into the final waste forms. These operations are summarized below.

As spent fuel batches are processed in the electrorefiner, fission products accumulate in the electrorefiner vessel. Fission products of the alkaline earth, alkali metal, and rare earth groups build up in the electrolyte salt. The transition metals (i.e., the more electrochemically noble metals) tend to concentrate in the cadmium pool, remain 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 increases until it exceeds facility or equipment design limits. At that point, it is necessary to remove the heat-generating elements. First, the heavy metals present in the salt are recovered in a form suitable for subsequent reintroduction to the electrorefiner, by a process known as "drawdown." After the drawdown operation, which reduces the heavy metal content in the salt to less than 0.01 wt %, the salt and metal phases are removed for treatment to recover the remaining TRU elements and remove a sufficient quantity of fission products that the salt and cadmium can be recycled.

The spent salt (i.e., the salt phase after drawdown, or the salt from the oxide reduction process) will contain fission products (such as Cs, Sr, I) and the rare earth elements, all in the form of chlorides. This salt is first sent to an extraction step, where the molten salt is reacted with a liquid U-Cd alloy. The extraction of the TRU elements is carried out in a multi-stage centrifugal contactor at a temperature of 500°C. The (depleted) uranium reduces the chlorides of the TRU elements, which are present at low concentrations in the salt, with the TRU elements partitioning into the metal phase in metallic form. The TRU-bearing cadmium is returned to the electrorefiner, where the TRU elements are subsequently recovered by electrotransport from the cadmium pool. Initial experiments are in progress (33) to characterize the separation efficiency of a single-stage contactor.

After extraction of the transuranics, the spent salt is sent to a stripping operation in which the salt is reacted with a liquid Cd-Li alloy, again at a temperature of 500°C. The lithium is a strong reductant and reduces all of the rare earth chlorides present in the salt; the rare earths concentrate in the cadmium phase, which becomes a waste material, and most of the salt can be recycled to the electrorefiner until the decay heat load builds up to such a level that the alkaline earth and alkali metal fission products must also be removed. The removal of the rare earth elements from the salt is necessary to reduce the heat load in the electrorefiner; because they can be electrotransported with the actinide elements, the rare earths in the salt must be maintained at comparatively low concentrations to avoid excessive contamination of the heavy metal product. Experiments with the salt stripper have been completed and reported recently (34). The results showed that the stripping process is effective in reducing the concentration of rare earth fission product elements to very low levels.

The stripped salt is next sent to an immobilization step, where the molten salt is infiltrated through a zeolite column. The zeolite sorbs the fission products by two processes: ion exchange and occlusion of salt molecules in the molecular cage of the zeolite structure. The effluent salt is virtually free of fission products and can be recycled to the electrorefiner. Initial measurements have shown that high fission product loadings in the zeolite can be obtained: up to 25 wt % fission products is possible. After sorption of the fission products, the waste-loaded zeolite pellets are subjected to a stream of hot argon gas to remove adherent surface salt. Then, a small quantity of anhydrous zeolite powder is added to immobilize any residual surface salt, and the waste-loaded zeolite is hot pressed. The hot-pressing operation can be done with a small amount of added low-melting glass frit to serve as an encapsulating and binding medium for the zeolite powder particles, or the zeolite can be pyrolyzed to form a solid monolithic mineral waste, sodalite. The release of fission products from the zeolite-based mineral waste under conditions of groundwater impingement appears to be acceptably small. Representative leach rates for various elements from the glass-bonded composite zeolite are shown in Table V, where it is seen that the normalized elease rates are all lower than the screening criterion of 1 g/m^{2}d.

Table V. Normalized release rates, L, for various constituents present in glass-bonded zeolite waste form (35). Standard test in deionized water at 90°C, for 28 days.

Element	L, g/m^{2}d		Element	L, g/m^{2}d
Cs	0.52		B	0.53
Sr	0.15		Ba	0.11
Al	0.26		Li	0.60
Si	0.22		K	0.45

A similar comparison is not yet available for the leach resistance of the sodalite version of the waste form, but tests with unconsolidated sodalite powders have shown leach rates even lower than those obtained with the glass-bonded composite (35).

The spent cadmium from the electrorefiner and from the salt stripping step is also treated in the IFR pyroprocess. These two streams are combined in a partitioning process where the fission product-bearing cadmium is contacted with a molten Al-Cu alloy having little solubility for cadmium. The fission products tend to precipitate in the Al-Cu phase as intermetallic compounds, leaving the cadmium phase virtually free of fission products. The cadmium is recovered by retorting and then recycled to the electrorefiner. The Al-Cu alloy, now containing the transition metal, rare earth, and noble metal fission products, can be cast directly into a waste container for repository disposal.

An alternative version of the metal waste form, also under development at this time, incorporates the cladding hulls as the matrix material. Depending on starting fuel type, this material can be either stainless steel or zirconium alloy. With this approach, a substantial fraction of the original fuel assembly hardware can also be included in the waste form while achieving minimum packaged waste volume for disposal.

Although the IFR waste treatment and packaging processes are at a relatively early stage of development, they appear to be technically feasible and fully amenable to DOE initiatives on waste volume minimization. These processes will ultimately be developed and demonstrated at a large scale with simulated fission products, with confirmation of the processes carried out on a somewhat smaller scale as part of the IFR Fuel Cycle Demonstration.

V. Summary

Development of the technology for pyrometallurgical processing of spent fuel from the Integral Fast Reactor (or Advanced Liquid Metal Reactor) is progressing well. The technology demonstration phase, in which recycle will be demonstrated with irradiated fuel from the EBR-II reactor, has been initiated in the refurbished EBR-II Fuel Cycle Facility. Methods for recovering actinides from spent LWR fuel are at an earlier stage of development but appear to be technically feasible. The processes developed for recycling valuable spent fuel materials promise to provide substantial economic incentives for future applications of the technology, perhaps including the treatment of the DOE spent fuel that is now awaiting permanent disposal.

Although the waste treatment and packaging processes are at a relatively early stage of development, they appear to be technically feasible and fully amenable to DOE initiatives on waste volume minimization. These processes will be developed and demonstrated at a large scale with simulated fission products, with confirmation of the processes carried out on a somewhat smaller scale as part of the IFR Fuel Cycle Demonstration.

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