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The Application of Electrorefining

for

Recovery and Purification of Fuel Discharged

from the

Integral Fast Reactor

by

L. Burris, R. K. Steunenberg, and W. E. Miller

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439

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MASTER

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ABSTRACT

An electrorefining process employing a molten salt
electrolyte and a molten cadmium anode is proposed for the
separation of uranium and plutonium from fission products and
cladding material in discharged IFR driver fuel. The use of a
liquid cadmium anode, which is the unique feature of the
process, permits selective dissolution of the fuel from the
cladding and prevents electrolytic corrosion of the steel
container and contamination of the product by noble metal
fission products.

I. Introduction

Electrolysis is a key operation in a proposed process for recovery and
purification of uranium and plutonium present in the uranium-based metal
fuel materials discharged from a type of fast reactor known as the Integral
Fast Reactor. In the electrolysis operation, uranium and plutonium are
selectively transported from an anode to a cathode, leaving impurity
elements, mainly fission products, either in the anode compartment or in a
molten chloride salt electrolyte. Because of the considerable purification
of uranium and plutonium that is realized, the operation is called electro-
refining.

Electrorefining was chosen for processing discharged IFR fuel materials because of its compact nature, its capability of providing adequate purification of the uranium and plutonium products in one step, and the direct production of uranium and plutonium metals, suitable, after composition adjustments, for fabrication of new fuel elements for return to the reactor.

In the electrorefining step, the discharged fuel is first dissolved in cadmium contained in a low-carbon steel vessel. The liquid cadmium phase becomes the anode of the electrorefining cell. Uranium and plutonium are electrolytically transported through a molten salt electrolyte to a suitable cathode, e.g., a cylindrical metal probe, or liquid cadmium contained in a ceramic crucible. The electrolyte salt is composed of very stable chlorides (e.g., $CaCl_2$, $BaCl_2$, $LiCl$, and $NaCl$) and some UCl_3 and $PuCl_3$, which are installed in the salt to facilitate the electrotransport of uranium and plutonium. The use of a liquid cadmium anode, which is a unique feature of the process, allows use of low-carbon steel or a chrome steel as the container material. These materials are not attacked by cadmium, and cadmium prevents corrosion of steel because its chloride is more stable than iron chloride.

Now in the early stages of development, the process, if successfully developed, will be installed and demonstrated in a fuel cycle facility adjacent to the Experimental Breeder Reactor No. 2 (EBR-II) located in Idaho near Idaho Falls (see Fig. 1).

Fig. 1. EBR-II Reactor and Fuel Cycle Facility
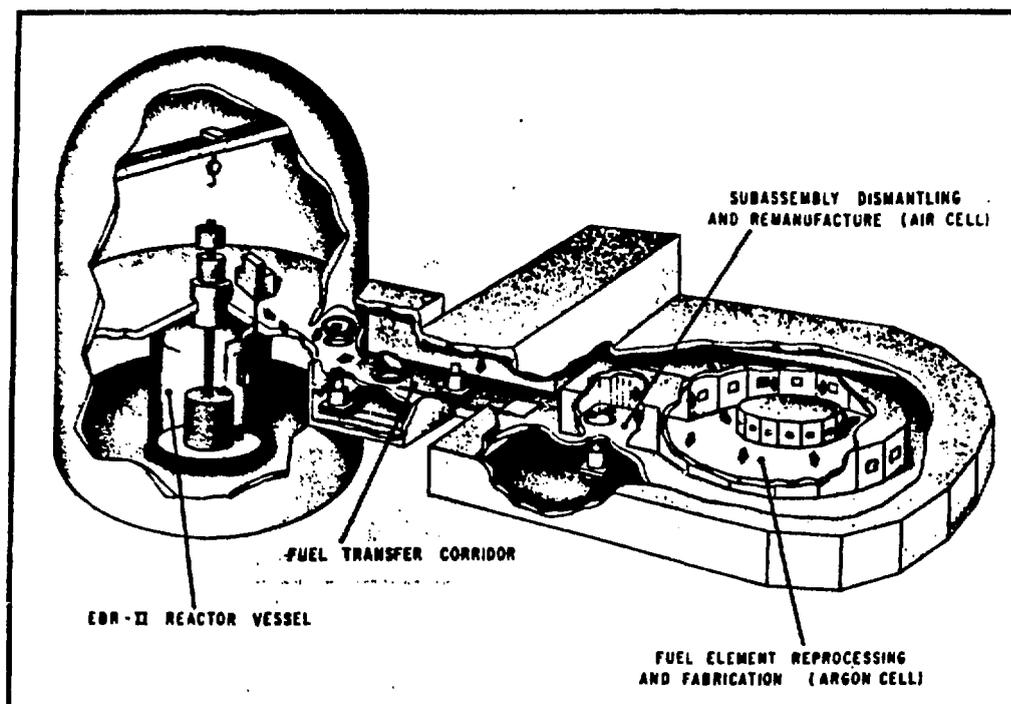
II. Background Information

Although electrorefining has not been used to date in the commercial reprocessing of reactor fuels, a substantial amount of information is available in the literature as a result of earlier laboratory work on the electrodeposition and electrorefining of uranium in molten halide salt media. A list of workers in this area and their accomplishments (including work on electrorefining of plutonium) is presented in Table 1. The preparation of metallic uranium by electrowinning from molten salts was reported in 1930 by Driggs and Lilliendahl.[1] In the 1950s, Marzano and Noland[2] and Blumenthal[3] prepared small amounts of high-purity uranium for research purposes by electrorefining, using molten chloride electrolytes. Metal of very high purity, >99.99%, was obtained.

Table 1. Technology Base - Electrorefining

1930   Driggs & Lilliendahl (Westinghouse Lamp Co.)
        o Electrolytic preparation of U

1953   Marzano & Noland (Argonne National Lab.)
        o High-purity U from electrorefining

1955   Blumenthal (Argonne national Lab.)
        o >99.993% U from electrorefining

1956   Niedrach & Glamm (Knolls Atomic Power Lab.)
        o U decontamination by electrorefining

1958   Mullins, Leary, et al. (Los Alamos National Lab.)
        o Pu purification by electrorefining

1960   Blumenthal & Brodsky (Argonne National Lab.)
        o High-purity Pu from electrorefining

1961   Chauvin, et al. (Commmissariat a l'energie atomique)
        o High-purity U from electrorefining, 1000 kg/yr

1963   Mullins, Leary, et al. (Los Alamos National Lab.)
        o Decontamination of Pu-Fe alloy by electrorefining

1982   Mullins, et al. (Los Alamos National Lab.)
        o Pu purification by electrorefining, 6-kg scale

1982   Coops, et al. (Lawrence Livermore National Lab)
        o Pu purification by electrorefining

1982   Baldwin & Navratil (Rocky Flats Plant)
        o Pu purification by electrorefining

In a much larger scale of operation (5-10 kg U per batch), Chauvin and co-workers in France employed electrorefining to prepare high-purity uranium for basic metallurgical studies.[4-8] In their apparatus, uranium was transported from an impure uranium metal anode through a molten LiCl-KCl eutectic salt containing 3 mol % UCl_3 to a molybdenum cathode rod, where the uranium deposited as a bushy, dendritic, crystalline mass. The containment vessel, which held 200 kg of electrolyte, was silica (SiO_2). The salt was removed with nitric acid, and the metal was consolidated by melting into a high-purity ingot.

High-purity plutonium for research purposes was also prepared by electrorefining (Kolodney,[9] Blumenthal and Brodsky,[10] and Brodsky and Carlson[11]). Subsequently, Baker, Mullins, Leary, and others[12-14] at Los Alamos developed an electrorefining process for recovery and purification of plutonium from scrap and aged, weapons-grade plutonium being recycled for removal of americium. This process, which has been used at Los Alamos in production operations for over 20 years,[15] is also used at the Lawrence Livermore Laboratory[16] and the Rocky Flats Plant[17] for the purification of plutonium.

Very little work has been done on the application of electrorefining to recovery and decontamination of discharged nuclear fuel materials. In the mid 1950s, Niedrach and Glamm[18-20] of the Knolls Atomic Power Laboratory investigated electrorefining for decontamination of irradiated uranium. Operating with a molten $CaCl_2$-UCl_3 electrolyte at 950°C, they deposited uranium on a nickel or manganese cathode. The uranium and the cathode material formed a low-melting liquid metal alloy, which dripped from the cathode into a collector. Overall fission-product decontamination factors of about 200 were realized.

In the 1960s, Mullins and Leary[21] investigated electrorefining for
reprocessing fuel from the Los Alamos Molten Plutonium Reactor Experiment
(LAMPRE). This fuel, which was molten at reactor operating temperatures,
was successfully electrorefined at 550°C using a LiCl-KCl-PuCl$_3$
electrolyte. Use of an iron cathode resulted in the formation of the Pu-Fe
eutectic alloy, which, being a liquid at the 550°C operating temperature,
dripped from the cathode into a tantalum crucible. Fission-product
removals were similar to those obtained previously for irradiated uranium
by Niedrach and Glamm.

The above results pointed to the potential application of electro-
refining for recovery and purification of IFR fuel. Processing of IFR fuel
poses two important differences from the uranium and plutonium work
described above. The first is that both uranium and plutonium are present,
which requires attention to the difference in the free energies of forma-
tion of their chlorides. The second is the concomitant use of liquid
cadmium as a solvent for the IFR metal fuel and for the anode of the
electrorefining cell. Fortunately, there is a wealth of information,
developed at Argonne in the 1960s, on the thermodynamics of uranium-,
plutonium-, fission product-cadmium systems, and on the handling of liquid
cadmium solutions.

III. Process Description

The objectives of the IFR process are given in Fig. 2. For the core
material, the objectives are adequate (not necessarily high) removal of all
fission products, replacement of the plutonium consumed by fission for
generation of power by fresh plutonium generated in the blanket, and

Fig. 2.   IFR Process Objectives

Core Fuel
- ● **Removal of fission products**
- ● **Reenrichment**
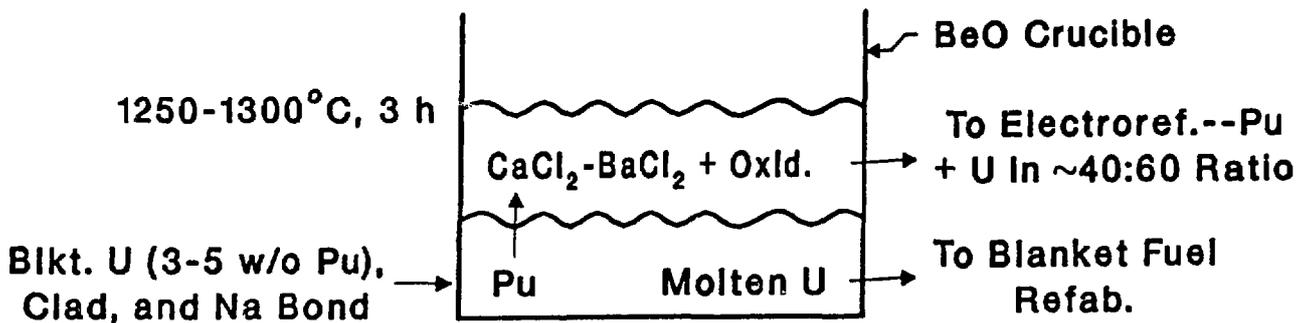- ● **High recovery -- >98%**

Blanket Fuel
- ● **Provide plutonium for reenrichment of core fuel**
- ● **Adequate recovery of plutonium -- >95**

reasonably high recovery of uranium and plutonium (>98%). For the blanket
the objective is a plutonium-uranium concentrate, production of which
requires upgrading the concentration of plutonium from 2 to 5 wt % in
discharged blanket material to a concentration greater than approximately
25 wt %, i.e., sufficiently high so that, when the product fraction is
added to the core, the nominal core plutonium concentration of 19 wt % will
be restored.

The two major steps that have been devised for these purposes are
electrorefining and halide slagging. The main purposes of electrorefining
are purification of uranium and plutonium and direct production of a metal
product concentrate that can be consolidated into a product ingot, which,

after composition adjustments, can be used to fabricate new fuel for the reactor. The purpose of halide slagging is enrichment of the plutonium bred in the blanket. As shown in Fig. 3, this is accomplished by melting the blanket alloy in a beryllia crucible, which is highly resistant to attack (in fact, not even wetted), and then preferentially extracting the plutonium into an overlying molten salt composed of $BaCl_2$ and $CaCl_2$ by oxidizing the plutonium, using UCl_3 as the oxidant. This salt extract, in

Fig. 3.   Halide Slagging for Recovery of Plutonium
from Blanket Uranium.

1250-1300°C, 3 h

BeO Crucible

$CaCl_2$-$BaCl_2$ + Oxid.

To Electroref.--Pu + U In ~40:60 Ratio

Blkt. U (3-5 w/o Pu),
Clad, and Na Bond

Pu   Molten U

To Blanket Fuel Refab.

which the Pu-to-U ratio is much higher that that in the blanket, is added to the electrolyte of the core electrorefiner to effect reenrichment of the core material with plutonium. The electrorefining step is shown schematically in Fig. 4.

Cadmium is used as a liquid metal anode in the electrorefining step. Fuel contained in fuel pin segments about 1/4-in. in length is first dissolved in cadmium at 500°C. The fuel pin segments are charged to the electrorefiner in an anode basket through which cadmium is circulated to leach out the fuel. The anode basket then becomes the container for the

Fig. 4. Electrorefining for Recovery
of Plutonium and Uranium.
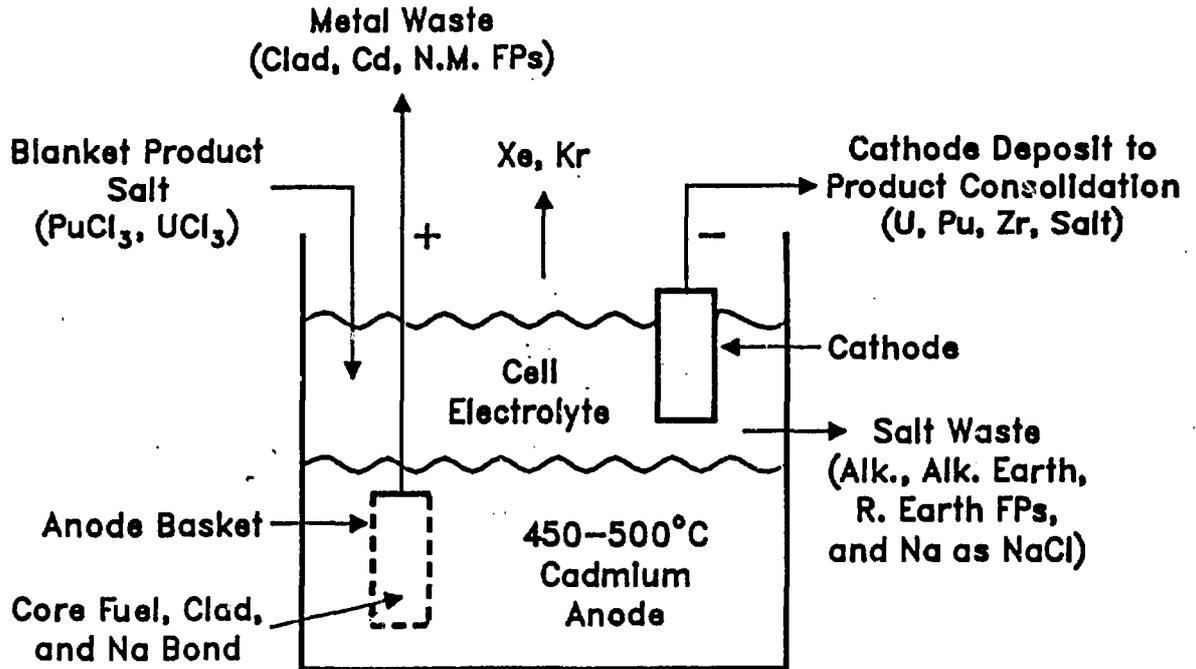
fuel pin cladding hulls, which is discarded as a process waste. Thus, the
electrorefining vessel functions also as a dissolver for the core and
blanket fuel materials.

Because mechanical decladding of the blanket is deemed infeasible,
chemical decladding of the blanket alloy is also achieved by leaching the
fuel out of pin segments with cadmium. This requires, for product
recovery, electrotransport of the uranium and plutonium. The electro-
transport operation provides removal of fission products but, because of
the low burnup of plutonium in the blanket, fission-product removal is
incidental to the main purpose--product recovery.

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The two main process steps, electrorefining and halide slagging, have been integrated into the process flowsheet previously described by Burris[22] (see Fig. 5). They are preceded by disassembly of reactor subassemblies to yield chopped fuel pins, and are followed by steps to consolidate the electrorefiner products and separate any accompanying electrolyte from them.

Fig. 5. Pyrochemical Process for IFR Core and Blanket
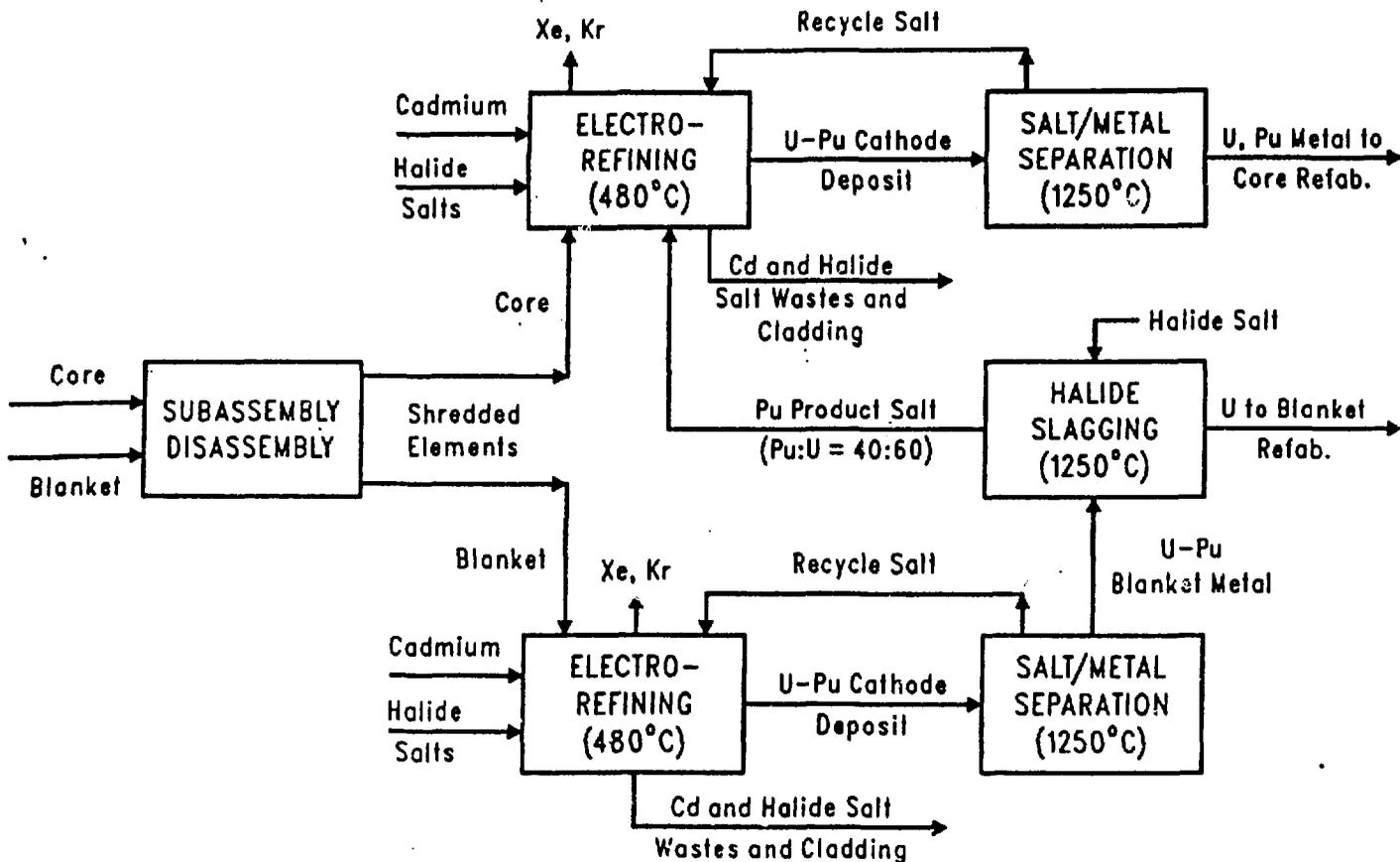
Fission products are removed in three streams: (1) gaseous fission products that are released when the fuel pins are chopped into segments and also when the fuel is dissolved; (2) the electrolyte salt, which contains electropositive fission products, such as the rare earth elements; and (3) the cadmium anode solution, which contains noble metal fission products.

In the part of this paper that follows, only the electrorefining step will be discussed.

IV. The Electrorefining Step

As stated previously, uranium and plutonium are transported, under a voltage gradient, from solution in the liquid cadmium anode to a suitable cathode, which will be described later. Essentially, uranium and plutonium are oxidized to their trichlorides at the anode. At the cathode, these trichlorides are reduced to metals. The major components of the electrolysis unit, anode, electrolyte, and cathode, are discussed below. Important in the discussions of them are the relative free energies of formation of the chlorides of uranium and plutonium, other transuranic elements, fission-product elements, cadmium, and container material elements such as iron. These are given in Table 2.

A.   Cadmium Anode

Cadmium has been chosen as the anode for the electrolysis unit for the reasons listed below:

(1) Plutonium and uranium have reasonably high solubilities in cadmium at the proposed cell operating temperature of 500°C (3.6 wt % and 2.3 wt %, respectively). Thus, cadmium is a good medium in which to dissolve IFR fuel materials and to establish the good electrical contact required for efficient electrotransport of uranium and plutonium.

Table 2. Free Energies of Formation of
Chloride at 1000°K

$-\Delta G^\circ$, kcal/g-equiv. Cl					
$BaCl_2$	83.4	$CmCl_3$	58.8	$CdCl_2$	30.4
KCl	81.4	$PuCl_3$	58.5	$FeCl_2$	26.6
RbCl	81.2	$MgCl_2$	57.7	$NbCl_5$	24.6
$SrCl_2$	81.0	$NpCl_3$	54.1	$MoCl_2$	8.0
CsCl	80.0	UCl_3	51.8	$TcCl_3$	7.0
$SmCl_2$	80.0	$ZrCl_2$	49.2	RhCl	5.8
LiCl	78.8			$PdCl_2$	3.8
$CaCl_2$	77.9			$RuCl_3$	1.4
NaCl	75.7				
$LaCl_3$	67.0				
$PrCl_3$	66.3				
$CeCl_3$	66.3				
$NdCl_3$	64.2				
YCl_3	61.2				

(2) Cadmium can be readily contained in low-carbon steels. The
solubility of iron in liquid cadmium at 480°C is 2.8×10^{-4} wt %. Because
low-carbon steels are also resistant to attack by molten chloride salts,
they are convenient and attractive container materials for the electro-
refining vessel and other appurtenances (stirrers, thermocouple wells,
etc.).

(3) Cadmium is a good material for retaining noble metal fission
products, and may be a satisfactory medium in which to ultimately dispose
of them. Most of the noble metal fission products (molybdenum, ruthenium,

rhodium, palladium, and zirconium) have low solubilities in cadmium. As a
result, the portion of the anode removed to waste after each run will
contain precipitates of these elements as cadmium intermetallics. Figure 6
gives the solubilities of metals in liquid cadmium at 500°C.

Fig. 6. Solubilities of Metals in Liquid Cadmium (500°C)
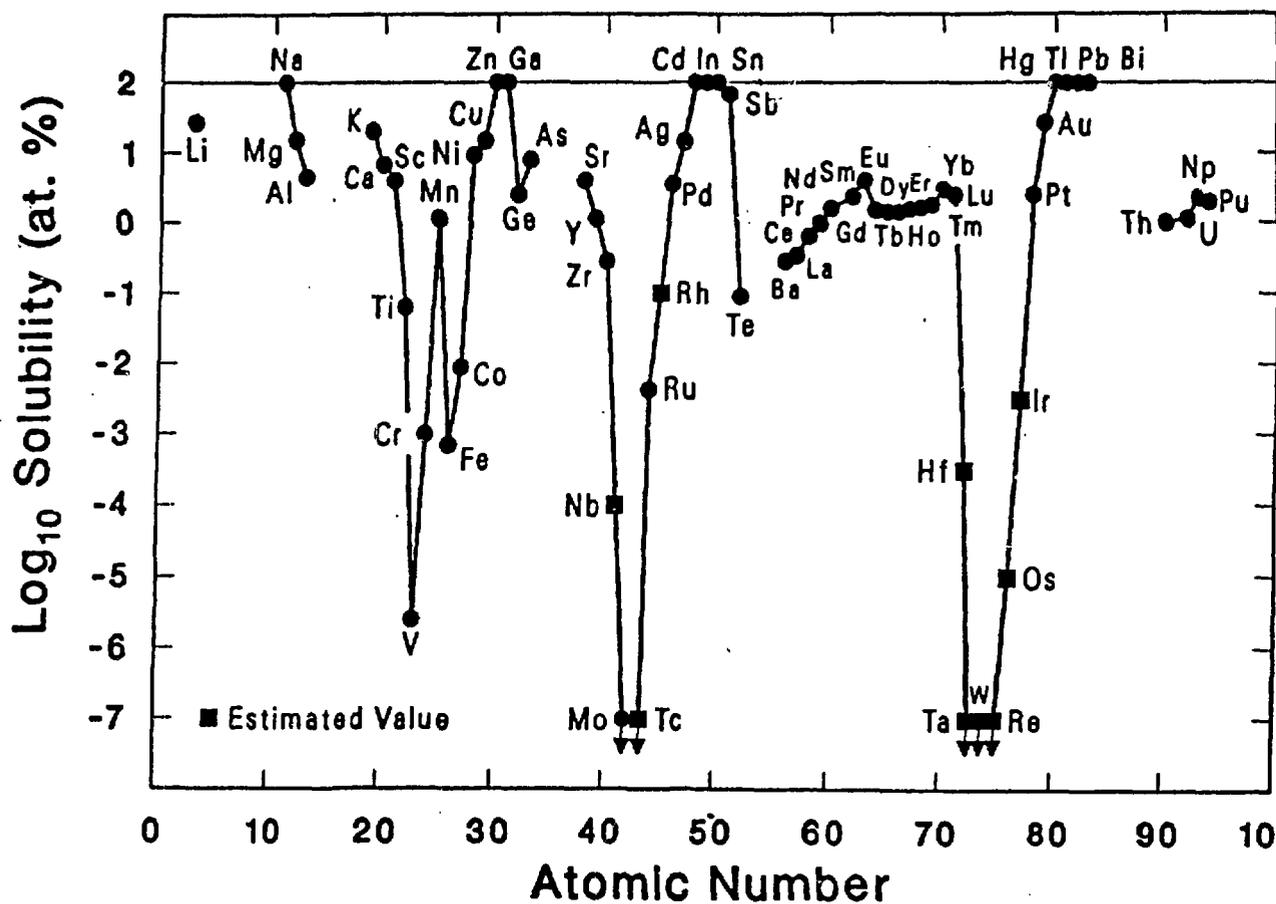
(4) With a boiling point of 767°C at 1 atm pressure, cadmium has a
reasonably high volatility, which enables its complete removal by vapori-
zation from the uranium-plutonium product alloys, which are consolidated by
melting at about 1300°C. However, the high volatility of cadmium limits
the practical operating temperature of the electrorefining unit to less
than approximately 500°C.

A concern in the use of low-carbon steels as a container material
for the cadmium and the chloride salt electrolyte is whether the applied
voltages during electrorefining could lead to anodic oxidation of iron to
produce $FeCl_2$. The free energy of formation of $FeCl_2$ is -26.8 kcal/g atom
of chlorine, which is small compared to the free energies of formation of
UCl_3 and $PuCl_3$ (-52 and -59 kcal/g atom of Cl, respectively). Translation
of these free energies into voltages required for anodic oxidation after
99% transfer of uranium and plutonium, an extreme condition, gives the
following:

$$U \quad -0.16 \text{ V}$$
$$Pu \quad -0.49 \text{ V}$$
$$Fe \quad -1.26 \text{ V}$$

Thus, a large negative voltage increase, which is readily detectable, would
be required to cause anodic oxidation of the iron. In addition, the system
also includes a large quantity of cadmium, which would begin to oxidize at
about -1.08 V. The cadmium serves as a buffer because nearly all of it
would have to be oxidized before oxidation of iron can begin, making, for
all practical purposes, anodic oxidation of the iron impossible. In the
electrorefining process a cutoff potential of -1.0 V has been adopted.

Experience with electrorefining experiments in the Mark I apparatus has confirmed the above arguments that no significant corrosion of low-carbon steel will occur. Figure 7 shows the condition of a low-carbon steel stirrer and a thermocouple tube after holding the electro-refining apparatus at temperature (500°C) with the cadmium and salt present for a period of about four months, during which time several electro-refining runs were made. At the end of this period, no corrosion of stirrer blades or other steel components was detectable.

B. The Electrolyte

The base constituents of the electrolyte salt are $BaCl_2$ (35.5 mol %), $CaCl_2$ (19.5 mol %), LiCl (37.0 mol %), and NaCl (8.0 mol %). The $BaCl_2$ and $CaCl_2$ come from the halide slagging operation, for which high-stability, low-vapor-pressure chlorides are required. Sodium chloride results from oxidation of sodium present in the fuel elements as a thermal bond. Lithium chloride is used at the indicated concentration to give, in conjunction with the other constituents, a salt composition having a low melting point. The use of LiCl is also advantageous because lithium often is used as a reductant, for example, to adjust the concentration of $(U + Pu)Cl_3$ in the electrolyte or, if a fraction of the electrolyte is being discarded to waste, to reduce $(U + Pu)Cl_3$ from it. The byproduct of the reaction is LiCl, a normal constituent of the electrolyte. To make possible electrotransport of uranium and plutonium, UCl_3 and $PuCl_3$ must be present in the electrolyte at a reasonable concentration—say, 6 mol % of $(U + Pu)Cl_3$. These chlorides facilitate electrotransport of uranium and plutonium. As an atom of uranium or plutonium is oxidized at the anode, a

Fig. 7. Eleclytically Deposited Uraniun

(Note dendritic structure.)

molecule of UCl_3 or $PuCl_3$ is reduced at the cathode. Thus, no change in the total $(U + Pu)Cl_3$ concentration in the electrolyte will occur as uranium and plutonium are being transferred.

Because the negative free energy of formation of $PuCl_3$ is greater than that of UCl_3 by about 21 kcal/mol, calculations of the $PuCl_3$-to-UCl_3 ratio in the electrolyte for the ideal case (plutonium and uranium activity coefficients of one in the salt and metal phases) give a $PuCl_3$-to-UCl_3 ratio in the salt of nearly 60,000 (see Table 3). Fortunately, the difference in free energies is counterbalanced by a high uranium activity coefficient in cadmium (88.4) and a low plutonium activity coefficient (1.4×10^{-4}). This results in a $PuCl_3$-to-UCl_3 ratio of 1:4, which is favorable for simultaneous transport of uranium and plutonium.

Table 3. Effect of Activity Coefficients on
Electrorefining. Temperature 500°C.

Ideal Case

$$\gamma_U = \gamma_{Pu} = 1$$

$$\frac{X_{PuCl_3}}{X_{UCl_3}} = 5.9 \times 10^4$$

Actual Case in Liquid Cadmium

$$\gamma_U = 88.4$$

$$\gamma_{Pu} = 1.39 \times 10^{-4}$$

$$\frac{X_{PuCl_3}}{X_{UCl_3}} = 1.4$$

The UCl3 and PuCl3 are charged to the electrolyte salt by oxidizing the necessary amounts of uranium and plutonium from the cadmium phase, using CdCl2 as the oxidant. The byproduct of this reaction, cadmium, simply becomes part of the bulk cadmium phase. Once the initial investment of (U + Pu)Cl3 is in the electrolyte, only minor adjustments of the concentration of (U + Pu)Cl3 are required as successive batches of fuel are processed.

On oxidation of the necessary amounts of uranium and plutonium to install their chlorides in the electrolyte, all of the fission-product and transuranic elements whose chlorides are more stable than UCl3 are also oxidized into the electrolyte (see Table 2). Thus, the alkali, alkaline earth, rare earth, and most of the americium and curium are oxidized into the electrolyte. Their concentrations are allowed to build up to steady state levels that are many fold higher than would result from processing one batch of fuel. If the fuel batch sizes and burnup do not vary significantly, the steady state concentrations of the fission product and actinide elements are set by the fraction of the electrolyte salt removed to the waste process after each run. An equivalent amount of fresh salt is added before the next run, making this a "feed and bleed" operation. A similar procedure is used to establish and control the level of noble metal fission products in the cadmium phase.

From the foregoing, it is clear that the salt is a complex mixture of base constituents (BaCl2, CaCl2, NaCl, and KCl), chlorides of the electropositive fission product elements, and actinide element chlorides. Moderately low concentrations of (U + Pu)Cl3 were arbitrarily chosen with

two factors in mind: (1) avoidance of saturation, although their solubilities in this complex salt have not been determined; and (2) minimization of the $PuCl_3$ inventory of the salt. A higher $(U + Pu)Cl_3$ concentration would facilitate electrotransport of uranium and plutonium. Optimization of the salt concentration is a worthwhile subject for future work.

C. The Cathode

The direct deposition of uranium on a cylindrical iron cathode is straightforward. As experienced by other investigators, the uranium deposit is highly dendritic, as shown in Fig. 7. Through proper agitation, reasonably high rates of uranium transport [about 1 g/(h) (sq cm of bare cathode] can be achieved at good current efficiencies (~70%). About 10 kg of uranium can be deposited on a cathode in 16 hours.

The electrotransport of plutonium at 700°C and its deposition on a molybdenum cathode, from which it drips into a collector, is also straight-forward, as demonstrated at Los Alamos where electrolysis has been used for about 20 years to refine impure plutonium.

However, deposition of both uranium and plutonium on the same cathode is much more difficult than dealing with them individually. The reason for this difficulty is the difference in the chemical stabilities of their chlorides. As a result, under current control with the voltage being allowed to "float," uranium and plutonium will deposit sequentially, with uranium depositing first. The deposition of plutonium is further complicated by the fact that plutonium metal deposited on the cathode is vulnerable to oxidation by UCl_3 in the electrolyte by the reaction:

$$Pu + UCl_3 \longrightarrow PuCl_3 + U.$$
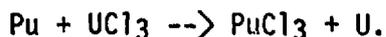
Conditions for plutonium deposition are improved as UCl3 is replaced by
PuCl3. Figure 8 shows the pattern of one run for sequential deposition of
uranium and plutonium onto a solid cathode, followed by transfer of them
back to the anode (stripping) by reversing the voltage.

Fig. 8. Electrodeposition and Stripping of
Uranium and Plutonium
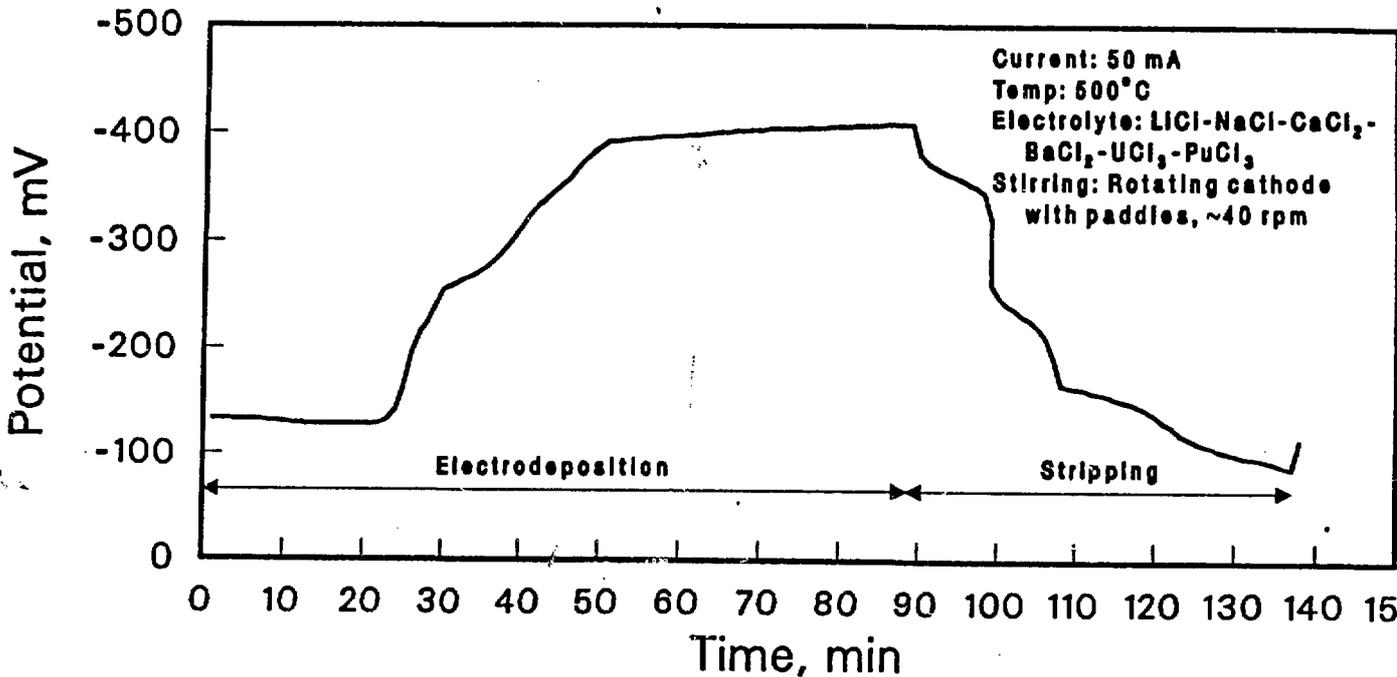
The plutonium converted to PuCl3 is not lost because, after the next
batch of U-Pu fuel is charged to the electrorefiner, "excess" plutonium in
the salt phase is returned to the cadmium anode. Thus, the two major con-
sequences of plutonium oxidation are a higher average plutonium inventory
in the salt and chemical reduction of some of the UCl3.

In principle, plutonium and uranium can be codeposited by using, from the outset, a voltage high enough to deposit the plutonium. This does not, however, remove the vulnerability of deposited plutonium to oxidation by UCl_3, but it could diminish the magnitude of the oxidation.

The appearance of a deposit containing both uranium and plutonium is substantially different from that of a uranium-only deposit. In contrast to the dendritic structure characteristic of a uranium deposit, a uranium-plutonium deposit is amorphous, seems to consist of fine-grained metal particles in a salt matrix, and adheres poorly to a cathode substrate (see Fig. 9). Adherence of the amorphous deposit can be improved by using a roughened or knurled mandrel.

Another cathode option is liquid cadmium, in which case uranium and plutonium are electrolytically transported from a liquid cadmium anode to a liquid cadmium cathode, and the cell functions as a concentration cell. Because both the anode and cathode use liquid cadmium as a solvent metal, the activity coefficients of uranium are identical in the two electrodes; the same is true for the activity coefficients of plutonium. Under these conditions, the thermodynamic relationships are such that only a small voltage is required for uranium and plutonium transport and they can be transferred from anode to cathode together. The volume of cadmium in the cathode compartment can be very small, and uranium and plutonium can be "pumped" into the cadmium in amounts that far exceed their solubilities, uranium precipitating as uranium metal, plutonium as $PuCd_6$. The precipitates will settle to the bottom of the cathode receiver. As illustrated in Fig. 10, the volume of the uranium-plutonium-cadmium product phase will be about the same as that of a uranium-plutonium deposit on a solid cathode mandrel.
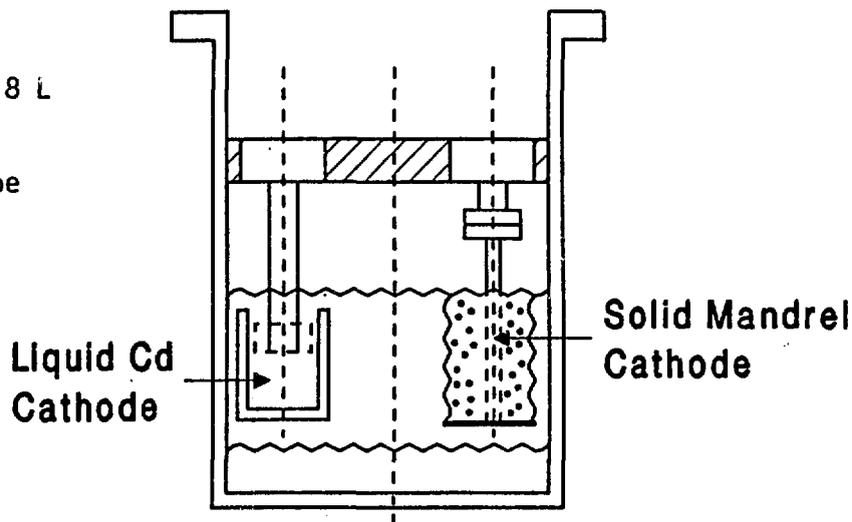
Fig. 9.   Electrodeposited Uranium-Plutonium

Fig. 10. Cathodes for Collection of 7.5 kg Heavy Metal (Core)

Space for
1. Solid cathode deposition - 8 L
2. Liquid Cd cathode - 1.6 L
    (Volume of container will be larger.)

Liquid Cd Cathode

Solid Mandrel Cathode

Recovery of uranium and plutonium from a cadmium cathode requires vaporization of the cadmium and melting of the uranium and plutonium into a product ingot. In the case of a solid cathode product, the uranium and plutonium must be coalesced into an ingot and separated from the accompanying salt electrolyte. Removal of electrolyte or removal of cadmium are probably operations of comparable difficulty.

The capability of depositing uranium selectively and uranium and plutonium together, either on a solid mandrel or into cadmium, provides considerable flexibility for process design. For example, enrichment of plutonium in uranium in the anode, as required for processing the blanket uranium of a breeder reactor, can be accomplished by selectively electro-transporting uranium to a solid cathode. A charge of core material can then be dissolved in the anode and the combined amounts of uranium and

plutonium can be codeposited into a cadmium cathode, thereby effecting
reenrichment of the core and removal of fission products. The same result
could be achieved by either sequential or codeposition of uranium and
plutonium on a solid mandrel cathode. A flowsheet utilizing selective
electrotransport for the plutonium enrichment required for the blanket and
codeposition of uranium and plutonium required for the core is illustrated
in Fig. 11. Elimination of halide slagging provides considerable process
simplification.

Fig. 11. Optional Electrorefining Process for
IFR Core and Blanket
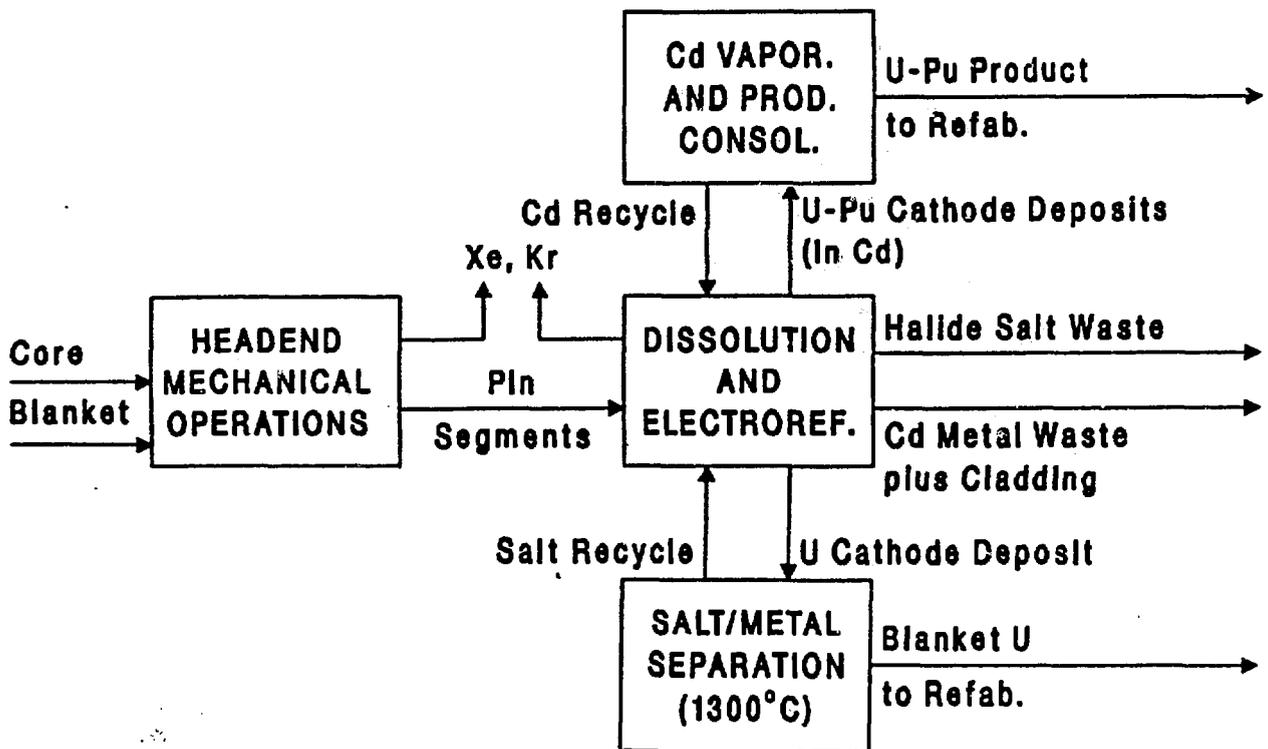
V. Laboratory Support Studies

Concentrations of (U + Pu)Cl$_3$ in the salt electrolyte suitable for efficient transport of uranium and plutonium can be achieved either by oxidation of uranium and plutonium to the electrolyte with CdCl$_2$ or reduction of (U + Pu) Cl$_3$ from the electrolyte with lithium (in a lithium-cadmium alloy). The distribution of uranium and plutonium between the salt and metal phases is in excellent agreement with theoretical predictions based on previously determined activity coefficients of uranium and plutonium in cadmium (see Tables 4 and 5).

Table 4. Equilibrium Data for Electrorefining

UCl$_3$ (salt) + Pu (Cd) $\rightleftharpoons$ PuCl$_3$ (salt) + U (Cd)
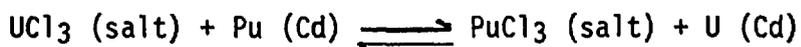
Salt Matrix: LiCl-NaCl-CaCl$_2$-BaCl$_2$
Temperature: 500°C

Laboratory-scale Experiment	Calculated Value	Experimental Result
Pu (salt), g	2.43	2.39
U (salt), g	2.88	2.92
Pu (Cd), g	4.46	4.50
U (Cd), g	7.34	7.25

The cathodic reduction of Pu(III) and U(III) has been studied by cyclic voltammetry. For studying reactions and identifying species, cyclic voltammetry is to the electrochemist what spectroscopy is to the aqueous chemist. A typical cyclic voltammogram for Pu(III) is shown in Fig. 12.

Table 5. Equilibrium Data for Electrorefining

UCl$_3$ (salt) + Pu (Cd) $\rightleftharpoons$ PuCl$_3$ (salt) + U (Cd)
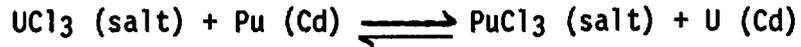
Salt Matrix: LiCl-NaCl-CaCl$_2$-BaCl$_2$
Temperature: 500°C

Bench-Scale Engineering Run	Calculated Value	Experimental Result
Pu (salt), g	16.25	16.29
U (salt), g	51.17	51.14
Pu (Cd), g	25.50	25.46
U (Cd), g	111.3	111.3

Fig. 12. Cyclic Voltammogram for Pu(III) Reduction

Working electrode: Steel
Apparent area: 0.079 cm^2
PuCl$_3$ concentration: 1.11 mol %
Temp: 435°C
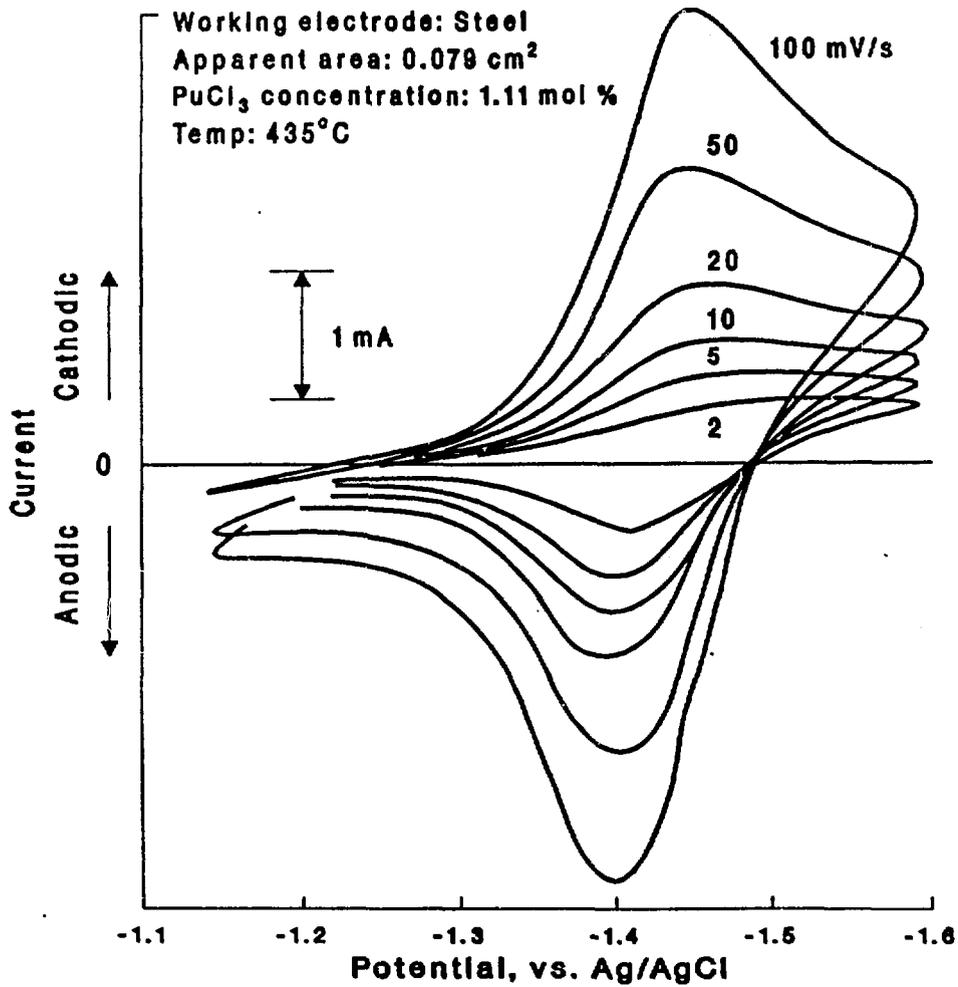
Considerable information can be obtained by analysis of these voltammo-grams. Cyclic voltammetry results for PuCl$_3$ are given in Table 6, the most important ones being that the reduction reaction involves three electrons and that it is rapid and reversible.

Table 6. PuCl$_3$ Cyclic Voltammetry Results

o Electrochemical reduction of plutonium is a rapid, reversible
  reaction

o Reduction rate is controlled by diffusion mass transfer

o Rate increases with increasing PuCl$_3$ concentration

o Reduction reaction involves three electrons

o Diffusion coefficients are 2.4 to 5.4 x 10^{-6} cm^2/sec at 452
  and 520°C, respectively; activation energy of diffusion is
  about 10 kcal/mole

o Potentials for Pu(III)/Pu(0) are -1.45 to -1.75 V vs. Ag/AgCl,
  depending on PuCl$_3$ concentration

VI. Experimental Results

A. Recovery of Uranium and Plutonium

Electrotransport of greater than 95% of the uranium in a cadmium anode has been readily achieved. With additional experience, higher percentages of uranium transport may be achieved. However, the amount of uranium left in the anode does not constitute a uranium loss--merely a heel that is carried through successive runs. If a small portion of the cadmium

is to be transferred to waste, the uranium in that cadmium can be oxidized to the electrolyte and temporarily stored there for return later to the bulk cadmium phase. In principle, uranium transport to a cadmium cathode should be straightforward, but it remains to be demonstrated.

While both uranium and plutonium have been deposited on the same cathode, either sequentially or simultaneously, the extent maximum of plutonium transfer has not been established. Conditions for minimizing the side reaction, oxidation of plutonium to $PuCl_3$ by UCl_3 in the electrolyte, and thereby maximizing plutonium recovery have not been studied. Plutonium should also be effectively transferred to a cadmium cathode, but, as was the case for uranium, plutonium recovery by transferring it to a cadmium cathode has not been demonstrated.

B. Fission Product Removals

One of the major purposes of the electrorefining step is removal of fission products. As pointed out earlier, fission products are removed in three major streams - fission-product gases, which are released to the cell atmosphere; the cadmium anode; and the salt electrolyte. The non-gaseous fission products behave in accord with their chemical stabilities (see Table 2). That is, the noble metal fission products, e.g., molybdenum, ruthenium, rhodium, and palladium, whose chlorides have low stabilities relative to that of UCl_3 remain in the cadmium anode. Zirconium has several chlorides ($ZrCl$, $ZrCl_2$, $ZrCl_3$, and $ZrCl_4$) whose free energies are near that of UCl_3, but experiments have shown that, when uranium is present in cadmium, no zirconium is in the electrolyte. Thus, zirconium, too, behaves as a noble metal and is retained in the cadmium

anode (see decontamination factors in Table 7). The behavior of zirconium
is important because it is both a fission product and an alloying element
in both the blanket and core fuel materials. The highly electropositive
fission products, such as the rare earths, the alkaline earths, and the
alkali metals, whose chlorides are more stable than $PuCl_3$, should transfer
to the electrolyte. These expectations are borne out by the fission-
product decontamination factors given in Table 7. The data in Table 7 were
determined for the steady state concentrations of fission products and
deposition of the uranium and plutonium on a low-carbon steel cathode.
Clearly, fission product removals are adequate.

Table 7. Decontamination Factors for Electrorefining of U-Pu

(Inactive fission-product elements)

| Fission-product Element	Decontamination Factor
Strontium	>2,000
Barium	>1,500
Yttrium	>1,000
Cerium	>250
Neodymium	>1,500
Zirconium	~1,000

Not shown in Table 7 is the decontamination factor for iodine.
Previous work has shown that iodine will report to the electrolyte salt as
a stable iodide, possibilities being NaI, CsI, etc. Bromine would be
similarly removed. Decontamination of uranium and plutonium from iodine
should be very high.

The free energies of formation of chlorides of the transuranic elements, americium, curium, and neptunium, are not well known. Estimates, shown in Fig. 13, show that neptunium is likely to accompany uranium and plutonium. The behavior of americium and curium is uncertain, but not important, since no difficulty is introduced by recycling these with the uranium and plutonium.

VII. Summary

Electrorefining is an attractive processing step for recovery and purification of uranium-plutonium-zirconium alloys, which are the reference fuel materials for reactors of Integral Fast Reactor type. The molten-salt, cadmium-electrode systems are easily contained in electrorefining vessels made of low-carbon steel. Adequate removal of fission products is readily achieved. There are several product deposition methods, which can be selected to fulfill different process objectives, and which provide flexibility in the application of electrorefining. For example, uranium can be separated sufficiently from plutonium to meet an objective of the processing of a fast reactor blanket. Alternatively, uranium and plutonium can be deposited together, as required for processing of the reactor core. Additional work is required to select optimum product-deposition methods.

Fig. 13.   Free Energies of Formation of Chlorides
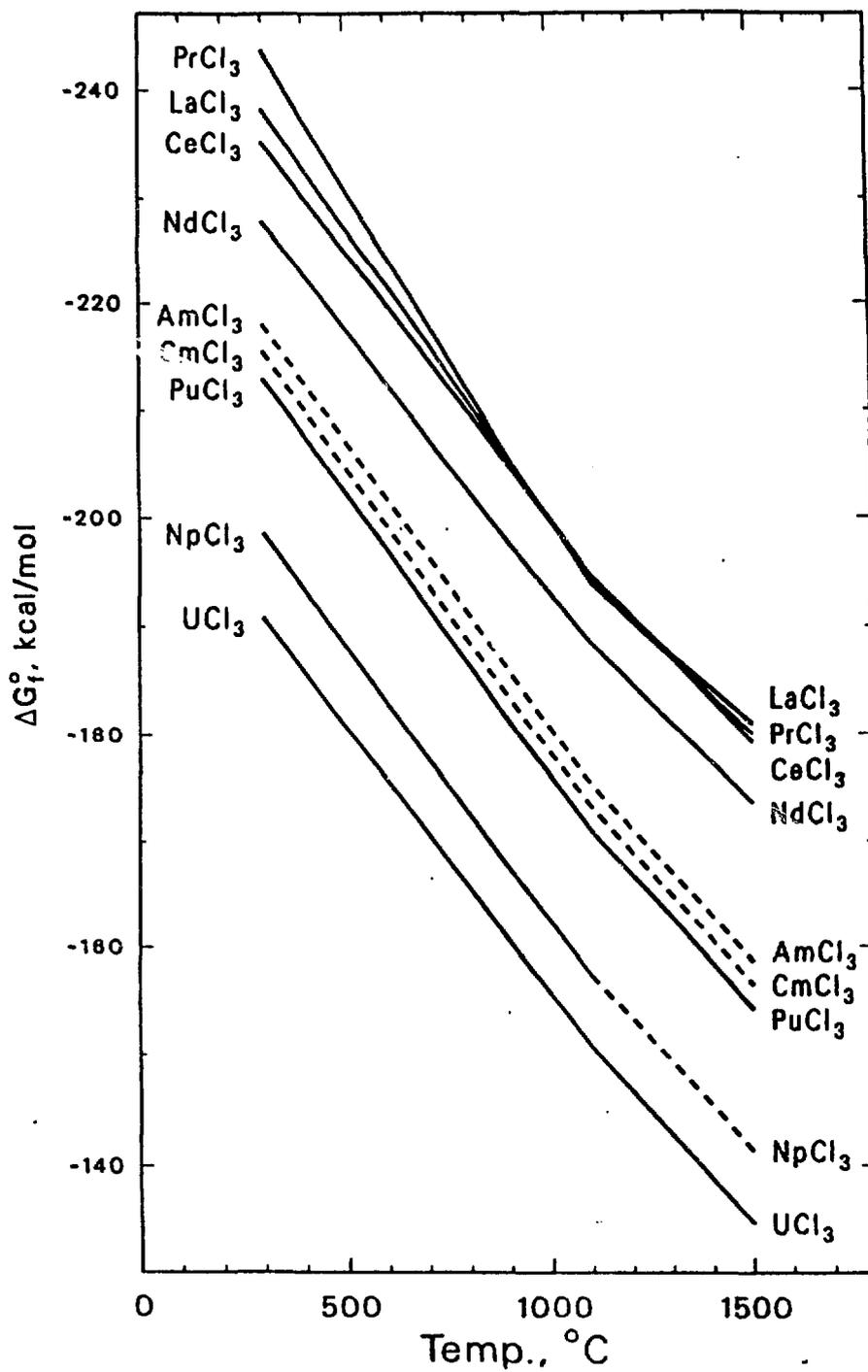
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