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Basics of Electrorefining in the Fuel Cycle Facility

October 2025

R D Mariani

Idaho National Laboratory

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by R. D. Mariani

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BASICS OF ELECTROREFINING
IN THE FUEL CYCLE FACILITY

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ABSTRACT

The basic electrochemical concepts that are relevant to the Fuel Cycle Facility electrorefiner (FCF ER) are discussed. Key points are developed in the report that equip the reader to examine the literature for the ER process, and these points are clearly identified. Basic electrochemical concepts are presented and definitions are given prior to a discussion of the energetics and rates of electrorefining. A brief **explanation** of power supply operation for the electrorefining operation is then given, followed by an elementary discussion of chemical equilibrium. With this background information, FCF ER operations are described in terms of typical operations, their sequence, and the attending chemical reactions.

SUMMARY

Several key points that are developed in this report are listed below. These points equip the reader to discuss and evaluate the electrorefiner process. Each point will be identified by bold-face type in the body of the report as it is developed.

1. The electrorefining process transports actinides from fuel elements (in the fuel dissolution baskets) to refined deposits (either solid or liquid cathodes) leaving zirconium, bond sodium, and the **fission** products in the electrorefiner.
2. The integrated current is related to the mass of actinide being dissolved at the fuel dissolution baskets or being deposited at the liquid or solid cathodes.
3. The reference mode of operation for the power supply to the electrorefiner cell is controlled current.
4. The cutoff voltage restricts the electrochemical reactions to actinide electrorefining.

S. Actinides may be electrorefined by direct transport operation or by a two-step operation.

6. Pure plutonium metal cannot deposit on the solid cathodes in the presence of $UC1_3$ dissolved in the salt phase. Plutonium is harvested in liquid cadmium cathodes.
7. Thermodynamics dictate the distribution of actinides and rare earths between the salt phase and the cadmium pool in the electrorefiner.
8. $CdC1_2$ is used as the oxidant to compensate for bond sodium, active metal fission products, and a fraction of rare earth fission products introduced by the fuel.
9. It is important to exclude oxygen-bearing impurities (such as water vapor) from the electrorefiner because they will react to form actinide compounds unavailable to the electrorefiner process.
10. To lower the actinide content of the salt phase, Lied intermetallic compound is added to the electrorefiner in the fuel dissolution baskets.

I. INTRODUCTION

The criticality safety evaluation of the Fuel cycle Facility electrorefiner requires the safety analyst to understand the electrorefiner equipment design, the electrorefiner operational strategy, electrochemical laws, and the laws of thermodynamics as well as the principles of reactor physics and criticality safety. This breadth of knowledge is needed to integrate the scientific, engineering, and administrative aspects into a safety strategy for the electrorefiner. Hence this report is intended to provide the reader with the basic chemical and electrochemical principles governing the operation of the electrorefiner.

A thorough description of the laws of chemistry and thermodynamics that govern the heavy metal operations in the electrorefiner and their distribution within the electrorefiner has been given.[1] Moreover, the chemistry of the electrorefiner operation and the operating characteristics of the electrorefiner have been demonstrated (e.g., normal and off-normal conditions) in the engineering-scale electrorefiner facility.[1,2] Knowledge of the heavy metal operations and their distribution in the electrorefiner lays the foundation for the electrorefiner criticality safety strategy. Actual operations will employ a "normal operations envelope"[3,4] and a process control strategy[5] to ensure criticality safety. A criticality safety analysis has been performed that encompasses the chemical and thermodynamic laws, the operating strategy, experimental data, and equipment design of the Fuel Cycle Facility electrorefiner. The analysis[6,7] demonstrated that a large safety margin to criticality safety exists for the Fuel Cycle Facility electrorefiner.

In this report, basic electrochemical concepts are then introduced, and the electrorefining process is discussed in terms of the energetics and gross rates of electrode processes. The basic use of a power supply for an electrorefiner is then presented. A brief introduction to chemical equilibrium reactions in the electrorefiner is given followed by a review of typical electrorefiner operations planned for the Fuel Cycle Facility. The primary chemical reactions in the electrorefiner are addressed next, followed by a discussion of possible secondary reactions. Finally, the sequence of operations in the electrorefiner are highlighted.

II. **BASIC** ELECTROCHEMICAL CONCEPTS AND DEFINITIONS

All electrochemical cells characteristically have an external circuitry, an electrolyte, and two electrodes (at least). The external circuitry may include a power supply. The electrolyte always contains ions that carry the current through an electrochemical cell. Ions are species, e.g., an element, a compound, or a compound fragment, with a net positive or negative charge. Anions are negatively charged species; cations are positively charged species. The ions may be dissolved in a solvent-like table salt dissolved in water, or they may be pure ions, with molten KCl being an example. The ions are able to carry the current through an electrochemical cell because they have significant mobility; they are not fixed in space as they would be in a crystal. The two electrodes are always electronic conductors, such as an iron rod or liquid cadmium, and connect to the power supply via wire leads.

In electrochemical cells, the reactions of interest are confined to the electrode/electrolyte interface where a transformation of a species occurs (Fig. 1). In the external circuit and the electrodes, electrons carry the current. In the electrolyte, ions carry the current. In order to maintain overall electroneutrality and complete the circuit, one electrode must be giving up electrons to one species while the other electrode is taking electrons from another (or the same) species.

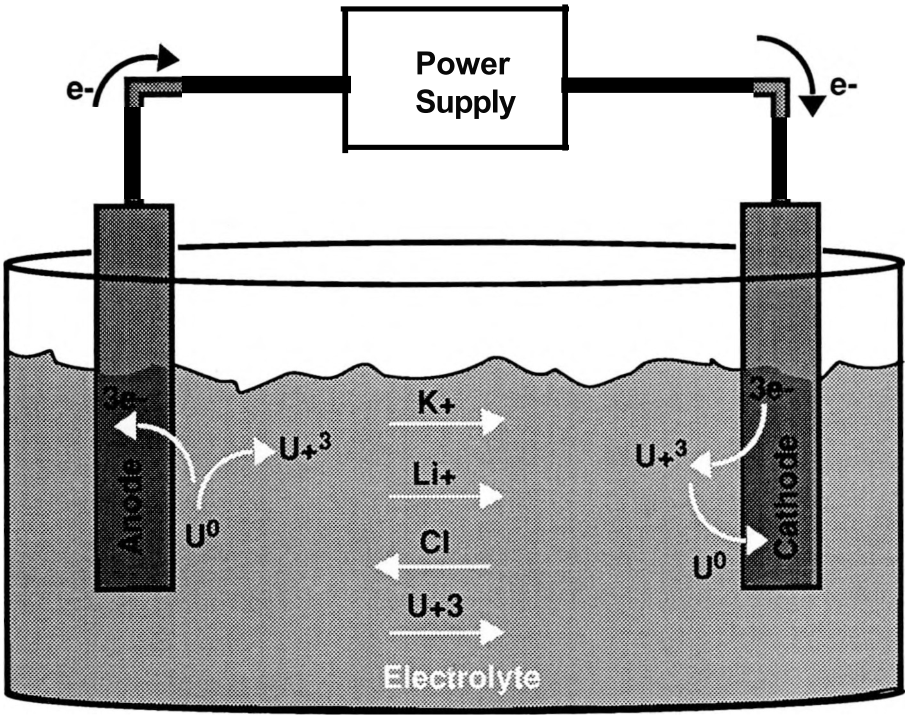


Fig. 1. Electrode Reactions and Ion Transport During Uranium Electrorefining

The electrode that gives up electrons to a species is the cathode; the process at the cathode is called reduction. The valence of a species is reduced at the cathode. The electrode taking electrons from a species is the **anode**; the process occurring at the anode is called oxidation. When a **species is** oxidized, its valence is raised.

The electrorefining process depicted in Fig. 1 **shows** uranium being oxidized at the anode, e.g., a uranium rod or irradiated fuel. The anode takes three electrons from uranium metal oxidizing it to $u+^{3}$ which dissolves in the salt solution. The valence on uranium being oxidized at the anode is being raised from zero to +3. The electrons that the uranium metal lost are conducted through the external circuit to the cathode. At the cathode (e.g., a steel rod) the supply of electrons are used to reduce $u+^{3}$ in the salt. The cathode gives three electrons to $u+^{3}$ in the immediate vicinity of the electrode to reduce $u+^{3}$ to uranium metal which precipitates on the cathode. The valence of the uranium at the cathode is reduced from +3 to zero.

In Fig. 1, the arrows associated with ions in the center of the vessel illustrate the current-carrying role of the ions. Anions (chloride ions here) always carry current in the electrolyte in the direction of electron flow: clockwise in Fig. 1. Cations (K+, Li+, and $u+^{3}$ ions here) always carry current in the electrolyte in the direction opposing electron flow.

Reactions for the example in Fig. 1 may be written as

cathode:

$$u+^{3} + 3\,e- \rightarrow u, \text{ and} \qquad (1a)$$

anode:

$$\mathbf{U \rightarrow U^{+3} + 3\,e^{-}}, \qquad (1b)$$

whence summing the reactions cancels everything; there is no net reaction. **This is the basis of electrorefining: actinides are electrotransported from fuel elements to refined deposits.** The immediate implication is that no energy is required for electrorefining because there is no net reaction, but this is not so. Firstly, heat energy is expended in the form of electrical resistance in the electrolyte and in the external circuit. Secondly, the anode is substantially less pure than the cathode, so they are not exactly in the same state. In other words, alloyed uranium and pure uranium are different species, and an energy difference is associated with these two different states of uranium. Thirdly, the electron transfer event at the interface may be impeded. For example, an oxide scale on an electrode surface can induce a greater resistance to the electron-transfer event.

Besides the electrical resistance, a significant **mass** transfer resistance can be **associated** with getting the $u+^{3}$ across the cell. Thus an electrochemical cell designed to move uranium from an anode to a cathode, **i.e.**, electrorefine uranium, should have a significant concentration of $u+^{3}$ **ions dissolved** in the electrolyte. If no $u+^{3}$ w6re initially present in such a cell, the rate of deposition of U+l at the cathode would be severely restricted during the early stages until the $u+^{3}$ concentration built up in the vicinity of the cathode, emphasizing that the reactions of interest are confined to the electrode/electrolyte interface. It is worth noting that the concentration of the salt does not change because the amount of pure uranium deposited is the same amount of uranium that was oxidized into the salt at the anode. When U/Pu are dissolving but only uranium depositing, then the Pu/U ratio in the salt is changing, although the $Pu+^{3}$ and $u+^{3}$ total concentration is constant.

III. ENERGETICS AND RATES OF ELECTROREFINING

The current passing in an electrochemical cell indicates the reaction rate, and the voltage indicates the relative energy of the electrons in the electrode. The voltage of an electrode also indicates what reactions are possible at electrodes because electrons, whose energy is controlled by the voltage, prefer to be in the more stable state. Figure 2a depicts the oxidation process and shows that as the electrode becomes more positive, electrons are attracted to it.

When the electron's energy level in an electrode is slightly lower than the energy level of the highest filled orbital of a species (Fig. 2a), then the electron in the species transfers to the electrode because this is a lower energy state for the electron. An orbital **is a** distinct energy level that electrons may occupy. Uranium metal has 92 electrons, so there are an additional 45 energy levels or orbitals (not illustrated in Fig. 2) below the highest filled orbital, each with two electrons. The highest filled orbital has the electrons of highest energy of a species, so these electrons will be the first to transfer to an electrode in an oxidation process.

Just above the highest filled orbital in Figs. 2a through 2c is the energy level of the lowest unfilled orbital. When the electron's energy level in an electrode is slightly higher than the energy level of the lowest unfilled orbital of a species (Fig. 2b), the electron in the electrode will transfer to the species because the unfilled orbital is a lower energy state.

An unfilled orbital is the next available energy level that an electron may occupy for a species. The process depicted in Fig. 2b is called reduction, and this figure shows that the electrode needs to become more negative to repel electrons from it.

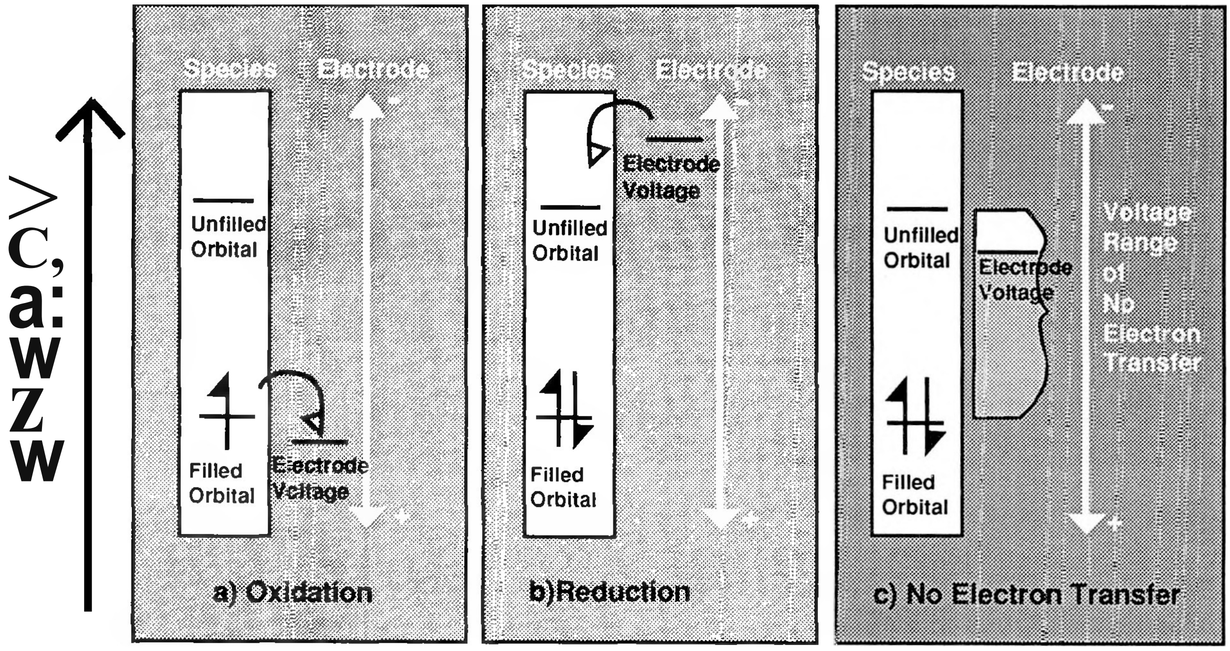


Fig. 2. Energetics of Oxidation, Reduction, and Stabilization of a Chemical at an Electrode. Curved arrow with single hook represents transfer of a single electron.

When the electron's energy level in an electrode is between the highest-filled and lowest-unfilled orbitals of a species, no electron transfer takes place because the energy levels available upon transfer are at a higher energy (Fig. 2c). The chemical is stable over this voltage range. Electron transfer does not occur at the electrodes in this voltage range no matter how the voltage is changed. The only current that may flow with voltage changes that stay in this range is a capacitive charging current in the external circuit up to the electrode interface; current does not flow through the cell, and neither oxidation nor reduction take place. This is precisely the situation occurring in a capacitor.

The bulk electrolyte should have a broad voltage range over which it is stable where only capacitive currents flow so that electrochemistry can be done on some other species, besides the electrolyte, dissolved in the electrolyte. In other words, the bulk electrolyte should not be reduced or oxidized when the voltage difference of the electrodes is changed over a broad potential range. This range is characteristic of the bulk electrolyte.

Consequently, the electrochemical reduction and oxidation of other **species** besides the electrolyte may be performed without interferences from the electrolyte itself. In the electrorefiner, the bulk electrolyte, molten eutectic LiCl/KCl, provides a broad voltage range over which it is stable so that uranium and plutonium may be electrorefined in the molten eutectic. Thus the voltage range over which the LiCl/KCl eutectic is stable against electron transfer encompasses the voltages corresponding to uranium and plutonium electron **transfers** thereby enabling the electrorefining process in the LiCl/KCl eutectic.

When uranium and plutonium are electrorefined, the current flowing through the cell indicates the rate of an electrochemical reaction because the current is directly proportional to the flux of electrons at the electrode/electrolyte interface. The current is integrated over some time frame to give the number of coulombs of charge that transferred across the electrode/electrolyte interface during that time frame. Electroneutrality (Kirechoff' e Law) requires that the number of coulombs passing at the anode is equal to the number of coulombs passing at the cathode.

The number of coulombs that **pass** is proportional to the amount of electrochemical reaction caused by the flow of current; this is Faraday's Law. Consequently, Faraday' e Law can be used to calculate how much actinide is discharged from the anode or deposited on the cathode:

Mase (g) = [Q*MW*EffJ/(n*F) (2)

where

Q is the number of coulombs of charge passed,

MW is the g molecular weight,

Eff is the efficiency,

n is the number of electrons in the electron-transfer reaction, and

Fis Faraday's constant, the charge on one mole of electrons.

Thus, aonitoring the couloabs passed, i.e., the integrated current, provides an active aeans of aonitoring the extent of the electrorefining process.

IV. POWER SUPPLY OPERATION MODES

When the electrorefiner is operating, a power supply is connected to an anode and a cathode. Typically, power supplies are switchable in their mode of controlling the cell so that the output of the power supply is either a controlled current or a controlled voltage. It is not possible to dictate simultaneously both the voltage and the current being output by the power supply because the electrolyte acts like a linear circuit element that obeys Ohm's Law (V=IR). Since the cell resistance is characteristic of the cell components, reactions, and geometry (but may not be constant), controlling the current at the power supply makes the voltage the dependent variable, and vice versa.

If the power supply is used to control the current passing through a cell, the electrodes will adopt whatever voltage difference is necessary to sustain the current that is dictated. **This is the reference position for Fuel Cycle Facility electrorefiner power supply operation: controlled current.** The voltage difference that the electrodes adopt indicates what reactions are possible in the cell. Since only certain electrochemical reactions are desired, it would be useful to limit somehow the voltage that the electrodes may adopt, thus preventing any undesired reactions. In the controlled current mode of operation, a cutoff voltage is used for this purpose. The power supply output is interrupted if the cutoff voltage is reached.

During the course of electrorefining, the voltage typically increases toward the cutoff voltage. The voltage slowly increases at a given current level because the cell resistance slowly increases with the diminishing supply of feed uranium at the anode. Basically, the mass transfer resistance, introduced earlier, is increasing. Electrorefining beyond the cutoff voltage could cause the anode hardware, such as the fuel dissolution baskets, to dissolve anodically (and the process would not be electrorefining any longer). In this way, the cutoff voltage limits the possible reactions **during electrorefining.**

The alternate method of power supply operation is controlled voltage. If the voltage is controlled, then any current that flows will conform to Ohm's law. This method is not widely used industrially because controlled voltage does not dictate the rate of the electrochemical reaction while controlled current does.

V. CHEMICAL EQUILIBRIUM REACTIONS IN THE FUEL CYCLE FACILITY ELECTROREFINER

The electrorefiner contains two liquid phases that can dissolve chemical **species**: the salt phase and the cadmium pool. The less-dense salt phase is nominally 12 in. deep and sits above the 6 in. deep cadmium phase at the bottom of the electrorefiner. Species introduced to the electrorefiner in the fuel, such as actinides, zirconium, fission products, and bond sodium, may dissolve in the salt phase, in the cadmium pool, or in both. Chemical equilibrium reactions in the electrorefiner specifically concern species that are dissolved simultaneously in both the salt phase and the cadmium pool.

Species that dissolve in both the salt and cadmium phases in the electrorefiner obey equilibrium thermodynamics. For species that are in both **phases**, equilibrium thermodynamics dictate the distribution, or partitioning, of a given element between the two phases. Under ordinary electrorefining conditions, chemical equilibrium reactions involve the rare earth and actinide +3 cations dissolved in the salt phase coexisting with the rare earth and actinide metal atoms dissolved in the cadmium pool.

Species that dissolve exclusively in the salt phase are metals more active than the rare earths and actinides and do not participate in the equilibrium reactions. An active metal is one that is easily oxidized, such as sodium. Sodium metal is easily oxidized by oxygen or water; hence, sodium metal, like all active metals, is absent from the earth's crust, and sodium compounds are present.

Species that dissolve exclusively in the cadmium phase are more noble metals than the rare earths and the actinides and, likewise, do not participate in the equilibrium reactions. Noble metals, such as palladium, are difficult to oxidize. Noble metals are typically found as the metals in the earth' s crust, and their compounds are rare or nonexistent. In the electrorefiner, the metals referred to as noble metals are not all strictly noble, in the same sense that palladium and gold are noble; however, all of the metals that are dissolved exclusively in the cadmium pool under ordinary electrorefining conditions are referred to as noble metals in the electrorefiner process. Hence, metals such as zirconium and niobium are being classed with palladium as noble metals in the electrorefiner process for convenience, even though this is not strictly appropriate.

Figure 3 illustrates the relative stabilities of the metal chlorides common to electrorefiner operations with the more negative free energies of formation indicating greater stability. With rare earths and actinides distributed between the salt and cadmium phases, all the metal chlorides in Fig. 3 with more negative free energies than the rare earths and actinides will be present as cations (as the chlorides) dissolved exclusively in the salt phase. The metals below the rare earths and actinides in the figure are more active than the rare earths and actinides. On the other hand, all the metal chlorides represented in the figure with less negative free energies than the rare earths and actinides will be present as metal atoms dissolved exclusively in the cadmium phase. The metals above the rare earths and actinides in Fig. 3 are more noble than the rare earths and actinides.

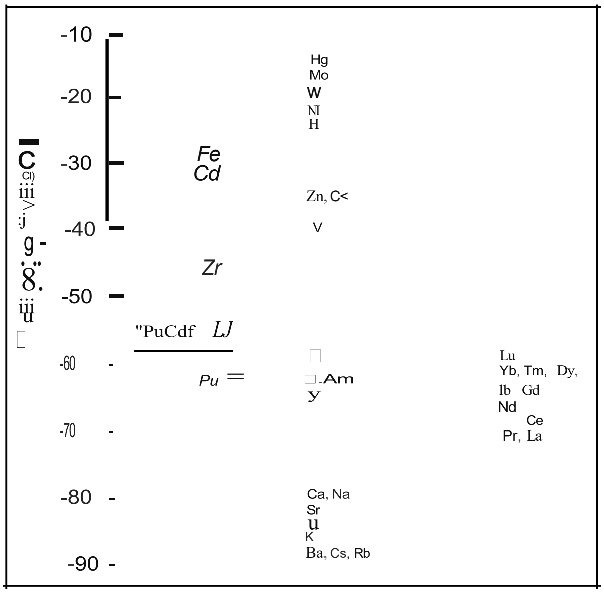


Fig. 3. Free Energy of Formation of Various Chlorides at 500°c

The significance of Fig. 3 is that the relative stability of the metal chlorides provides the basis for obtaining purified actinide deposits from the electrorefiner process. Noble metals cannot be reduced at the cathode because they do not exist in measurable concentrations in the salt phase; hence they do not transport. Active metals will not deposit at the cathode because they are more stable as the chlorides at electrode voltages corresponding to actinide electrorefining.

VI. TYPICAL ELECTROREFINING OPERATIONS

Actinides may be electrorefined by one of two schemes: either direct transport, or a two-step electrorefining scheme. In either electrorefining scheme, a uranium product may be obtained or a mixed actinide product may be obtained. **In the reference electrorefining scheme (Fig. 4), heavy metal is electrotransported directly from the fuel dissolution baskets to the product cathode.** This scheme is referred to as direct transport.

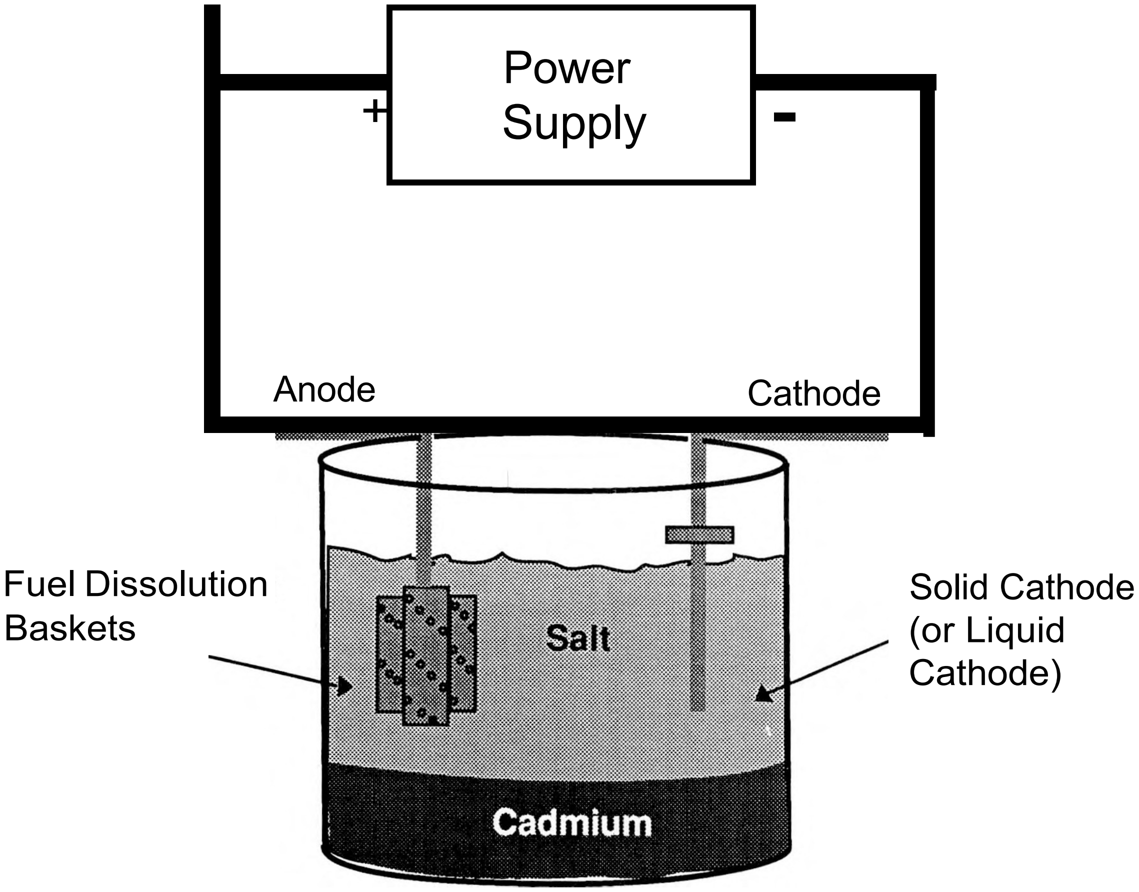
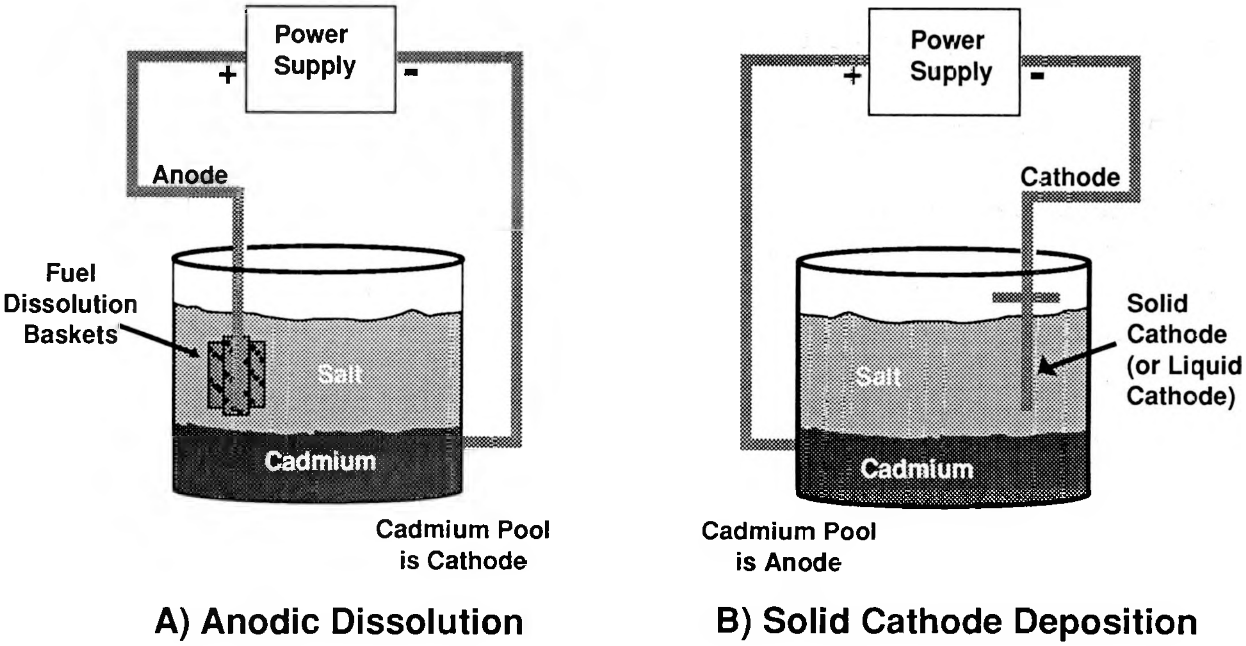


Fig. 4. Schematic of Direct Transport: One-step Electrorefining

In either electrorefining scheme, products may be collected on solid cathodes or in liquid cadmium cathodes. A solid cathode is used to obtain a refined uranium product. It consists of a steel or uranium mandrel onto which the uranium deposits. A liquid cadmium cathode, or liquid cathode for brevity, is used to obtain a refined, mixed actinide product, primarily plutonium and uranium. It consists of a crucible containing liquid cadmium into which the uranium and plutonium deposit. Both cathodes are positioned in the electrolyte during the deposition process.

The alternate ■ch-e for electrorefining actinides i■ a two-step process (Fig. 5), in contra■t to direct transport which i• a ■ingle ■tap. In the first step (Fig. Sa) of the two-step process, the actinides are electrotransported to the cadmium pool. In the second step (Fig. Sb), the actinides are electrotransported to the product cathode. The first step is commonly referred to as anodic dissolution. In the first step, the fuel dissolution baskets are the anode, and the cadmium pool in the electrorefiner is the cathode.



A) Anodic Dissolution

B) Solid Cathode Deposition

Fig. 5. Schematic of Two-step Electrorefining

The second step is commonly referred to as solid or liquid cathode deposition. In the second step (Fig. 5b), the cadmium pool in the electrorefiner is the source of the actinide; therefore, it is the anode. The actinides are electrotransported to the liquid or solid cathode for product recovery. The possible electrode configurations discussed are summarized in Table I by operation.

TABLE I. Electrode Configurations for Typical Electrorefiner Operations

Scheme	Step	Operation	Anode	Cathode
Direct Transport	N/A	Direct Transport	Fuel Dissolution Basket	Solid or Liquid Cathode
Two-Step	1	Sanodic Dissolution	Fuel Dissolution Basket	Cadmium Pool
	2	Solid Cathode Deposition	Cadmium Pool	Solid Cathode
	2	Liquid Cathode Deposition	Cadmium Pool	Liquid Cathode

The liquid cathode is necessary for electrorefining actinides in addition to the solid cathode because plutonium will not deposit on a solid cathode while UCl_3 is present in the salt phase. Plutonium is a more active metal than uranium; therefore, if plutonium metal were to deposit anywhere, the UCl_3 in the salt phase would react with it to form uranium metal and $PuCl_3$:

$$Pu + UCl_3 \rightarrow PuCl_3 + U. \qquad (3)$$

The single arrow indicates the reaction goes to completion (at least one reactant is completely consumed). The solid cathode, therefore, collects uranium exclusively because UCl_3 is present in the salt phase preventing plutonium deposition. (Rare earths and other actinides do not deposit on the solid cathode for the same reason plutonium does not.)

Plutonium deposition is made possible in the FCF ER by using the liquid cadmium cathode. Plutonium and cadmium happen to form an intermetallic compound, $PuCd_6$, at **SOO**^{0}c when plutonium reaches its solubility limit in cadmium (3.62 wt% plutonium). The existence of this intermetallic compound demonstrates a definitely more stable state than the pure plutonium metal (otherwise it would not form), and the net stabilization of plutonium metal in $PuCd_6$ renders the plutonium in $PuCd_6$ a less active metal than pure plutonium. Moreover, plutonium simply dissolved in cadmium is stabilized even if the plutonium has not reached its solubility limit (when $PuCd_6$ forms) because a significant interaction of plutonium with cadmium is already taking place.

The net stabilization of plutonium dissolved in cadmium vs pure plutonium is quite sizable, given approximately by the free energy of formation of $PuCd_6$· On the other hand, uranium in cadmium is stabilized only very little compared to uranium metal because uranium does not form an intermetallic compound with cadmium at electrorefiner operating temperatures. (Uranium dissolved in cadmium must be stabilized relative to the uranium metal at least a little or it would not dissolve.) This fact and the stabilization of the incipient Puc� renders the plutonium in cadmium about as noble as uranium in cadmium. Consequently, it is possible to collect plutonium and uranium simultaneously in a liquid cadmium cathode in the presence of UCl_3 in the salt phase. (Recall that it is impossible to collect plutonium on the solid cathode with UCl_3 present in the salt.)

The relationship between uranium and plutonium in the liquid cathode and the salt phase can be summarized as

PuinLCCd + UCl1maa1, .. PuCl3maa1, + UinLCCd' (4) where the subscript LC Cd signifies liquid cathode cadmium. Here, the double arrow indicates an equilibrium reaction where each **species** in the reaction is present in measurable quantities. The relative amounts of reactants or products in the equilibrium can be adjusted by adding one of the reactants or products. For example, addition of $PuC1_3$ would favor formation of the reactants: $UC1_3$ and plutonium in the liquid cadmium cathode. **Thie** behavior reflects LeChatelier'e Principle, •a system will respond to a stress so as to relieve that stress.•

The corresponding equilibrium expression for the above reaction is

$$\text{[PuC1}_3\text{h,u1, * [UlinLCCd / [Pu)inLCCd * [UC1}_3\text{Jmu1,} = \mathbf{K,\ a}\ \text{constant.} \qquad (5)$$

The bracketed quantities in the expression can be related to their concentrations. K is the equilibrium constant, which **is a** function only of temperature. This expression shows that controlling the ratio of $PuC1_3$ to $UC1_3$ will change the ratio of plutonium to uranium being harvested in the liquid cadmium cathode. As in the example above, adding $PuC1_3$ to the electrorefiner would cause a liquid cathode to be richer in its plutonium harvest and poorer in its uranium harvest in order to satisfy the expression. The equilibrium expression is a quantitative statement of LeChatelier' s Principle. Liquid cathode product compositions are being planned to range from about 1:1 to around 6:1 plutonium to uranium.

VII. COMPLETE CHEMICAL REACTIONS IN THE ELECTROREFINER

The chemical equilibria established in the electrorefiner are based upon the chemical compositions within the electrorefiner. The chemical equilibrium state of the electrorefiner can be altered by chemical additions to induce a new equilibrium state. For example, if an active metal such as sodium were added to the electrorefiner, the amount of sodium added would reduce the corresponding amount of $UC1_3$ in the salt:

$$3\ Na + UC1_3 \rightarrow 3\ NaCl + \text{Uin}_{\text{e�fino,}}\ \text{Cd}_{\text{pool}}\cdot \qquad (6)$$

Now less actinide ions would be in the salt. Thie reaction is complete in that all of the sodium is consumed in the formation of uranium metal and NaCl. The equilibrium constant for a liquid cathode in the electrorefiner would still apply as in

$$[PuCl_3]_{\text{in salt}} * [U]_{\text{in LC Cd}} / [Pu]_{\text{in LC Cd}} * [UCl_3]_{\text{in salt}} = K, \qquad (7)$$

but the total amount of +3 actinide ions in the salt phase would be diminished. Consequently, the distribution of actinides between the salt and cadmium phases has been altered amounting to a new equilibrium state for the electrorefiner.

If just the right amount of sodium metal were added to the electrorefiner, all of the actinide +3 ions in the salt would be reduced and driven out of the salt. The dissolved rare earths and actinides would reside exclusively in the cadmium phase because they would have all been reduced, and the equilibrium position of the electrorefiner contents would be altered to a different state. If excess sodium metal were added, then the excess sodium would dissolve in the cadmium, and now sodium would be distributed between the salt phase (as ions) and cadmium phase (as atoms).

For the chemical reaction described above, the sodium is a reducing agent or **a** reductant. It reduces the valence of uranium from +3 to zero in the same sense that electrons reduce uranium from +3 to zero at the cathode. With the addition of a chemical reductant however, the total amount of metal in the salt phase (as dissolved metal ions) is decreased while the total amount of metal in the cadmium phase (as dissolved metal atoms) is increased. The electrode reactions that have been discussed so far do not have this property. Thus, a chemical reductant changes the redox (reduction-oxidation) level of the electrorefiner, i.e., the relative proportion of species that is present in oxidized form. In the electrorefiner, the oxidized form is +3 actinide ions which would be diminished from the salt phase upon addition of sodium whereupon the reduced actinide metal atoms deposit in the cadmium pool.

Irradiated fuel happens to contain bond sodium metal and active metal fission products such as barium and rubidium. These metals will reduce the $u+^{3}$ in the salt to actinide metal and will themselves be oxidized, thereby diminishing the uH concentration in the salt. Without compensatory actions, there would eventually be no $u+^{3}$ left in the salt, and the electrorefining process could hardly work.

To circumvent this situation, an oxidizing agent or an oxidant is added to the electrorefiner. An oxidant is a chemical acting in reverse of a reductant. An oxidant oxidizes or raises the valence of uranium from zero to +3 in the same sense that an anode oxidizes uranium from zero to +3; however, an oxidant alters the redox level of the electrorefiner contents (in the reverse of a reductant), while the electrode reactions do not. An oxidant can restore the redox level of the electrorefiner that was altered by the bond sodium and active metal fission products.

The oxidant used in the electrorefiner is $CdCl_2$. $CdCl_2$ **dissolves** in the salt to react with uranium metal which is dissolved in the cadmium pool. The reaction occurs at the cadmium/salt interface:

3 CdC12inoalt + 2 U inCdpool → 2 UCl3 inNlt + 3 Cd. (8)

Thus, $CdCl_2$ is used to restore the redox level of the electrorefiner and maintain the actinide (U^{+3} and Pu^{+3}) salt concentration at about 7 wt,.

Not only will $CdCl_2$ be used to compensate for the bond sodium and active metal fission products, but it **will also be used to compensate for a fraction of the rare earth fission products and actinide activation products**. Any rare earth fission products or activation products that end up in the salt phase as cations do so by reducing actinide ions in the salt to actinide metals. Consequently, $CdCl_2$ must be used to oxidize the actinide metals back into the salt phase that were reduced by rare earth metal fission products. This is the same situation as for the bond sodium and active metal fission products; however, it is unnecessary to compensate for the entire amount of the rare earth metal fission products because the rare earths do not completely react like the sodium does. The rare earths and the actinides participate in simultaneous chemical equilibrium reactions.

Simultaneous equilibrium reactions involving the rare earths and actinides exist in the electrorefiner for the exact same reasons that plutonium can be harvested with the liquid cadmium cathode. The rare earth metal fission products, plutonium, and other actinides are all stabilized by the electrorefiner cadmium pool just as the plutonium is stabilized by the liquid cathode cadmium. Without the cadmium pool, the rare earth fission products would completely react with the UCl_3 just as sodium does. The added complication of several elements being simultaneously present in both the cadmium pool and the salt phase is referred to as simultaneous equilibria. The simultaneous equilibrium reactions involving plutonium, uranium, and neodymium are given as

PuinelcMm,fisrOlpool + UCl3 • PuCl3 + U ine-fincrCdpool• and (9a)

$$Nd_{\text{in electrorefiner Cd pool}} + UCl_3 \leftrightarrow NdCl_3 + U_{\text{in electrorefiner Cd pool}}. \qquad (9b)$$

These reactions have equilibrium constants associated with them (K for the former reaction is identical with that for the liquid cathode), so that the new distribution of rare earths and actinides between the salt phase and cadmium pool can be predicted after fuel is added. Hence, the amount of

[Type here]

$CdCl_2$ necessary to compensate for the rare earth metal fission products is easily calculated from the equilibrium constants that dictate what fraction of the rare earth fission products and actinide activation products end up in the salt phase.

VIII. SECONDARY REACTIONS AND BY-PRODUCTS

All secondary reactions during the electrorefining process render the location of actinides less distinct, and some make actinides in the electrorefiner unavailable to the electrorefining process. One secondary reaction occurs during the anodic dissolution step of the two-step electrorefining scheme; it only obscures the location of uranium temporarily. The remaining secondary reactions make actinides unavailable to the electrorefiner process; typically these reactions involve actinides and impurities that produce undesirable by-products.

When uranium is being electrorefined under the two-step scheme, some of the uranium deposits neither in the cadmium pool nor on the solid cathode, but on the side wall of the electrorefiner. This secondary reaction is possible only during anodic dissolution operations when the fuel dissolution baskets are the anode and the cadmium pool is the cathode. In anodic dissolution operations, the electrorefiner vessel is an electronic conductor in contact with the cadmium pool, and it is basically at the same potential as the cadmium pool. Consequently, uranium that is electrotransporting to the cadmium pool can take an alternate route to deposit on the electrorefiner side wall as well as in the cadmium because they are at the same potential: both the cadmium pool and the electrorefiner side wall are cathodes in the operation. This secondary reaction is not possible during direct transport operations because the vessel is electrically isolated from the fuel dissolution baskets (anode) and solid cathodes.

Note that during anodic dissolution operations uranium can deposit on the side wall of the electrorefiner but plutonium cannot, for the same reason that plutonium does not deposit on the solid cathode. Plutonium is a more active metal than uranium and is therefore unstable in the presence of UCl_3. In practice, any uranium that deposits on the electrorefiner side wall will form dendrites as it does on the solid cathode. It will be distributed on the side wall near the fuel dissolution baskets because this provides the path of least resistance through the salt. While uranium is present on the side wall of the electrorefiner, its location is inferred and is therefore indistinct.

Any uranium on the electrorefiner side wall can be recovered during solid cathode deposition operations. In this operation, the uranium dissolved in the cadmium pool is transported from the cadmium pool anode to the solid cathode. For the same reasons as given above, the cadmium pool and the electrorefiner side wall will be at basically the same potential. Consequently, any uranium on the electrorefiner **side** wall will be electrotransported whenever uranium is electrotransported from the cadmium pool. Note that transport from the electrorefiner **side** wall is slightly favored thermodynamically because a pure metal **has a** higher activity than that same metal in solution.

The secondary reactions that make actinides unavailable to the electrorefiner process typically involve oxygen or oxygen-bearing impurities that react with actinides. The unavailable actinide products are the actinide oxides such as $U0_2$and $Pu0_2$. Consequently, actinide oxides contribute to holdup of actinides in the electrorefiner. The oxygen-bearing species can be H_20 (water vapor), 011, and metal oxides such as CdO and Na_2O (in the bond sodium). **ne actinide oxides that form are unavailable because they cannot be collected on any cathode without participating in a reduction at the cathode, and they cannot be reduced at the cathode because they do not have a significant solubility in the electrolyte**. Moreover, any actinide oxides that form may not be represented in cadmium or salt samples, and therefore the location of the actinide oxides is indistinct.

Actinide by-products unavailable to the electrorefiner **process** can be produced by reaction of actinides with gaseous or solid impurities added with reagents or fuel. These reactions are typically redox reactions and, as discussed, involve a change in valence for the actinides and the impurities as in

$$4\ U^{+3} + O_2 \rightarrow UO_2 + 3\ UCl_4. \qquad (10)$$

Here the valence of uranium changes from +3 to +4, and the valence of oxygen changes from zero to -2. Since $UC1_4$ is not stable in the presence of uranium metal, it will react as in

$$3\ UC1_4 + U \rightarrow 4\ UC1p \qquad (11)$$

These reactions may be summed to give an example of an overall reaction with **a gaseous** impurity:

$$U + O_2 \rightarrow UO_2. \qquad (12)$$

Solid impurities introduced with the fuel would typically be **Na:z().** Sodium oxidation to give **Na_20** results from exposure of the bond sodium in the chopped fuel pins to0_2 and H:z() impurities in the argon cell atmosphere. An impurity that might be introduced with the reagents is CdO on the surface of **cadmium** metal. CdO on the surface of the cadmium pool would react with uranium metal in the cadmium pool according to:

$$U + 2\,CdO \rightarrow U0_2 + 2\,Cd. \qquad (13)$$

Any actinide oxides that are produced will locate somewhere above the cadmium pool because the oxide flocculi will form at a density considerably less than theoretical. Additionally, it is possible that the oxides could form a suspension in the salt phase because of turbulence or because of colloidal properties.

In addition to the actinide oxides that may result from secondary reactions, actinide nitrides and actinide carbides may also form. The actinide nitrides may form upon reaction of the actinide metals with pure nitrogen (which does not exist in the Fuel Cycle Facility or electrorefiner atmosphere). The actinide carbides can be introduced with the fuel, having formed in the graphite crucibles at high temperatures during the cathode processor or casting operations; however, the actinide oxides are so much more stable than either the nitrides or carbides that the oxides will form at the **expense** of nitride or carbide formation.

IX. SEQUENCE OF OPERATIONS IN THE ELECTROREFINER

During initial operations, the LiCl/KCl eutectic salt and the cadmium must be loaded into the electrorefiner. Thereafter, the salt must be charged with u^{+3} ions ($UC1_3$). This latter step is accomplished by contacting uranium metal in the fuel dissolution baskets with $CdC1_2$ that is added to the salt. The $CdC1_2$ dissolved in the salt oxidizes the uranium metal to U+l, and is itself reduced to cadmium metal. The u^{+3} dissolves in the salt, and cadmium metal **sinks** to and deposits in the cadmium pool.

Three manual operations make up the routine electrorefining operation: 1) the introduction of the fuel to the electrorefiner, 2) the addition of $CdC1_2$ to compensate for u^{+3} displaced from the salt phase by the more active metals, and 3) the removal of the refined actinide products. Each of these steps has been discussed. It is worth reiterating that the $CdC1_2$ addition mentioned here is to maintain the actinide (UH and Pu+l) concentration at some prescribed level. These repetitive $CdC1_2$ additions can conceivably occur just prior to introducing the fuel, after introducing the fuel but before electrorefining, or just after product removal.

At some point the contents of the electrorefiner must undergo waste processing. Waste processing of the electrorefiner salt and cadmium phases becomes necessary when: 1) the heat load of the fission products becomes excessive, 2) the accumulation of actinide holdup in the electrorefiner becomes comparable to the level specified in the Criticality Hazards control Statement, or 3) the product quality becomes unacceptable. The electrorefiner operation that initiates waste processing is called drawdown because it removes the vast majority of actinides from the salt and cadmium phases. Drawdown also removes the bulk of the rare earth fission products from the salt phase. The drawdown operation may also be used anytime it is desired to lower the actinide inventory in the salt phase.

Once the actinides in the cadmium phase and any reduced metal on the side wall of the electrorefiner are virtually removed from the electrorefiner, drawdown operations can begin. The objective now is to remove the bulk of the actinide ions from the salt phase. To **lower the actinide content of the salt phase**, LiCd **intermetallic** compound is added to the **electrorefiner in the fuel dissolution baskets**. Lied intermetallic is solid at the electrorefiner operating temperature.

The lithium in LiCd is a reductant toward actinide +3 ions in the salt phase and will react spontaneously; however, the reaction will produce actinide metal at the Lied surface only to have the actinide metal atoms sink to and dissolve in the cadmium phase:

$$3\ \text{LiinUC<111loy} + u^{3} \rightarrow 3\,\text{Li+} + \text{uinadmium}\cdot \qquad \textbf{(14)}$$

Since the current drawdown strategy involves removal of the actinides from the electrorefiner, having the actinides collect directly on cathodes for removal from the electrorefiner is preferred over letting them deposit in the cadmium pool.

To collect the actinides on cathodes, a circuit is connected where the fuel dissolution baskets are the anodes and a solid or liquid cathode or the cathodes, and without a power supply driving the electrotransport. Then the actinides will spontaneously deposit at the cathodes while the lithium is oxidized at the anode. In this situation, the electrorefiner acts just like **a** battery and could supply a small amount of electrical power to a load; however, the lithium is rather dilute in the solid LiCd, and the electrodes are too far apart (to be a good battery). Consequently, the reaction at the anode (fuel dissolution baskets) will be slow.

To accelerate the drawdown operation the current will be controlled at the power supply as if the electrorefiner were not acting like a battery, as if fuel were being electrorefined. The current which is set at the power supply then can dictate a somewhat higher rate and drive the reaction for the Lied oxidation and actinide reduction.

The addition of Lied in the fuel dissolution baskets with simultaneous collection of actinides on solid or liquid cathodes is repeated as often as necessary to exhaust the salt phase of actinides. Then waste processing to remove rare earth fission products or inventory activities may proceed. At this point, actinide electrorefining is no longer possible in the electrorefiner. To continue actinide electrorefining after a drawdown operation, procedures similar to startup that restore the uranium and plutonium concentrations in the salt phase will need to be performed.

X. CONCLUSIONS

In general, electrorefiner operations, equilibria, and reactions are more complex than what has been discussed. The presentation was simplified in order to identify the key features of the electrorefiner process and still offer **a basis** for understanding the process. This report should serve as an introduction and guide to the more detailed documents extant and **as a** refresher for the key features of the electrorefiner process.

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