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CRITICALITY HAZARDS CONTROL
DURING METAL FUEL ELECTROREFINING

by

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IFR TECHNICAL MEMORANDUM NO. 171

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CRITICALITY HAZARDS CONTROL DURING METAL FUEL ELECTROREFINING

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ABSTRACT

Criticality hazards control during electrorefining is concerned with three operations where accumulation of solid nuclear materials may occur. These batch operations are anodic dissolution of fuel, electrotransport of uranium to a solid cathode, and electrotransport of uranium-plutonium to a liquid cadmium cathode. In all cases the operation is controlled by electric current flow and total current (integrated current) for the batch. The transport of material follows precise known laws of electrochemistry. The maximum amount transported during any of the three operations is directly proportional to the integrated current for the batch transfer. For normal electrorefining, all nuclear material within the cell, but not in the anode feed or on the solid or liquid cathode, is dissolved in the cell liquids. The distribution and concentration of these materials follow known laws of physical chemistry and their behavior is predictable. In the development of the engineering-scale electrorefiner certain secondary indicators have been correlated to the amount of materials transported. These matters and the overall results of mass tracking of uranium during electrorefiner operations development are discussed.

I. INTRODUCTION

The process which is applied to purify IFR metal fuel is electrorefining and the apparatus in which this process is carried out is the electrorefiner or electrorefining cell. In this particular application of electrorefining, the process is carried out at 500°C. The electrolyte contained in the electrorefiner is a molten salt, LiCl-KCl eutectic, into which about 2 mol % of uranium chloride plus plutonium chloride have been dissolved. The total concentration of the heavy metal in the salt remains constant during operations, but the Pu/U ratio in the salt will vary and depends on what operations are being carried out. In electrorefining of metals, such as uranium or plutonium, the metal to be purified must be part of the cell anode, and the purified metal is collected at the cell cathode. The cell anode and cathode are submerged in the electrolyte so that an ionized liquid path exists between the two electrodes.

At the cell anode, the metal is dissolved by oxidation, that is the metal is stripped of electrons by the application of an electrical potential between anode and cathode. The metal becomes a positively charged ion which dissolves in the cell electrolyte. This is shown for uranium by Eq. (1) below. At the same time, the cathode furnishes electrons to positively charged ions in the electrolyte, this reduces the ions to metals at the cathode with the resulting metal deposit. This is shown below by Eq. (2).

where U° is uranium metal and U^{3+} is uranium tri-valent ion; the same reactions occur for plutonium (Pu).

Purification of metals by electrorefining can occur in two ways. One class of impurities (molybdenum is an example of this for U/Pu metal fuel) in the metal does not oxidize at the anode to become ions which dissolve in the electrolyte. These impurities are left in the cell anode when the U/Pu oxidizes and dissolves in the salt. Another class of impurities (cesium is an example of this for U/Pu metal fuel) oxidizes into the salt but does not reduce to metal at the cathode. These impurities are left in the cell electrolyte when the U/Pu deposits on the cathode as metal. The net result is a purification of the metal or metals being electrorefined. The applied cell potential in electrorefining is well below that required to decompose the salt by electrolysis. In electrolysis of a fused salt, negative ions, such as Cl^- in this case, give up their electrons at the anode and become chlorine gas; at the same time, metal deposits at the cathode. This contrasts markedly from electrorefining where fused salt decomposition does not take place.

Schematics of the engineering-scale electrorefining cell concept for processing IFR type metal fuel are shown in Figs. 1 and 2. The cell consists of a mild steel (or low chromium alloy steel) vessel for containing process liquids and a vessel cover for supporting components such as the anode and cathode and stirring devices. [The schematics show the various components used in process and equipment development but are not an exact model of the Fuel Cycle Facility (FCF) electrorefiner.] The operating temperature of 500°C is maintained by heaters that surround the vessel. The process liquids are the cell electrolyte which floats on top of a layer of molten cadmium at the bottom of the cell; these two liquids are immiscible. One function of the cell cadmium pool is to collect materials which fall inadvertently from either the anode or cathode.

The cadmium pool itself can be made the anode and thus Pu and U which may have escaped from the normal anode-cathode pair are not "lost" but can be transported to cathodes. The FCF electrorefiner for processing EBR-II fuel and for process demonstration, has an electrolyte pool of 230 L (nominal volume) containing 32 kg U/Pu (nominal, for a concentration of 2 mol % heavy metal in the cell electrolyte), and a cadmium pool of 125 L (nominal). This is sufficient cadmium to dissolve all the heavy metal in a nominal 20 kg batch of fuel charged to the electrorefiner.

Fig. 1. Engineering-Scale Electrorefiner Apparatus

Fig. 2. Schematic of Liquid Cathode in Electrefining Cell
(CMT/IFR Drawing No. 1007)

Electrorefining in an ionized molten salt electrolyte is governed by Faraday's laws, i.e., the mass of a substance involved in reaction at the electrodes of a cell is directly proportional to the quantity of electricity passed. The passage of one faraday of electricity, 96,494 coulombs (ampere-seconds), will change the valence of one gram mole of an ionizing substance by one unit charge. For the IFR electrorefiner electrolyte, where UCl_3 and PuCl_3 are converted to metals (and vice versa), the passage of one ampere-hour of electricity will deposit or dissolve 2.96 g of uranium-238 or 2.97 g of plutonium 239 and no more. Three important operations enter into electrorefining IFR metal fuel. These are: fuel dissolution, uranium transport with deposition on a solid cathode, and plutonium/uranium transport with deposition into a liquid cadmium cathode.

In process development for the three operations, process controls which govern the quantitative transfer of uranium and plutonium have been investigated. These operations along with experience for mass tracking of heavy metal through the electrorefining process are discussed below.

II. FUEL DISSOLUTION

Anodic dissolution is the operation for feed material input into the electrorefiner. IFR type clad fuel pins [approximately 0.25 in. (0.63 cm) clad O.D.] are chopped into 1/4-in. (0.63 cm) long cylinders and loaded into baskets similar in design to that shown in Fig. 3. The random loading of these baskets gives about 2-1/2 kg of heavy metal per basket. Four loaded baskets are mounted on the anode electrode shaft to form a cross, which completes one anode. Two anodes (20 kg of heavy metal) are the normal loading for the FCF electrorefiner. (The engineering-scale developmental electrorefiner shown in Figs. 1 and 2 has only one anode and one cathode position.) The position of the anodic dissolver during fuel dissolution is shown in the engineering-scale electrorefiner schematic (Fig. 2).

Fig. 3. Schematic of Anodic Dissolution Baskets for Engineering-scale Electrorefiner (CMT/IFR Drawing No. 1003)

The anode electrode shaft is electrically isolated from the electro-refiner cover. Each of the two anodes has its own power supply and electrical circuitry. The anode basket electrode may be hooked in the circuit with a solid mandrel or with the cell cadmium pool as cathode. Current is reversible. Normally, each anode is hooked in series with its power supply and with one solid mandrel cathode for the fuel dissolution process. A schematic diagram for anode-cathode-power supply circuit arrangement is shown in Fig. 4.

In the anodic dissolution operation, the current flow is distributed through the bed of chopped pins contained in the anode baskets because the cladding segments contact the basket inner wall surface and each other in the packed bed. The cladding segment hulls in turn contact the contained fuel surface sufficiently well to distribute current to the dissolving fuel-electrolyte interface. Dissolution of uranium (or plutonium) in this manner is represented by Eq. (1) where the metal loses three electrons to become uranium 3^+ ion and dissolves in the salt. (A simultaneous reverse reaction occurs at the cell cathode.) Zirconium, which constitutes about 30 vol % of the metal fuel, likewise oxidizes. However, it does not accumulate in the electrolyte as zirconium chloride, since the Zr cation cannot exist in the presence of uranium (or plutonium) metal. The end result of zirconium oxidation is the anodic dissolution of more U/Pu.

The anode basket and fuel cladding surface as well as the fuel surface is in contact with the cell electrolyte. Under the applied potential, U^{3+} in the salt in contact with the anode container material and cladding, (ferrous metal) surface may oxidize to form U^{4+} . A simultaneous reverse reaction can occur at the cathode, and in this case no fuel is dissolved by the action of the current. This gives a current inefficiency for the anodic dissolution process. However, anode design mitigates the effect of this reaction. The anode baskets rotate through the electrolyte so that the electrolyte containing U^{4+} is forced through the basket, where it is brought into contact with the metal fuel surface. At contact the U^{4+} is converted to U^{3+} by the reaction $U^0 + 3U^{4+} \rightarrow 4U^{3+}$ and more fuel dissolves. Experimental studies of the anodic dissolution process show that about 644 ampere-hours are required to anodically dissolve 1 kg of uranium when

the batch size is 10 kg of clad heavy metal in four baskets. This gives an electric current efficiency of 52.4 % for the anodic dissolution of a fuel batch. Completion of the dissolution process is easily recognized by a significant increase in cell voltage (difference in potential between cell anode and cell cathode). The voltage increase is caused by an increase in cell resistance from 3-4 milliohms to about 9 milliohm as the cell current is held constant by the current control. This signals the end of fuel dissolution from the baskets.

The normal mode for fuel dissolution is to transport uranium from the anode to the solid mandrel cathode rather than to the cell cadmium pool. There are two reasons for this. First, the uranium is delivered directly to its final destination (a removable cathode) instead of to the cadmium pool. If the latter were the case, the uranium would have to be subsequently transported to the removable cathode, which would require added processing time. The second reason is related to mass tracking. When the cadmium pool is used as the cell cathode, the vessel wall is also a cathode, and the wall adjacent to the electrolyte accumulates uranium solid. Liquid samples of the cell electrolyte or cadmium pool do not quantify this uranium deposit. (Plutonium deposition on the wall does not occur in a similar manner, since the thermodynamics of the reaction $\text{Pu} + \text{UCl}_3 \rightarrow \text{PuCl}_3 + \text{U}$ dictates that unless the Pu/U ratio in the salt is very high ($>10^5$) plutonium metal is reoxidized by reduction with UCl_3 as shown.) For this reason, the cadmium pool is not normally used as a cathode.

Other processes not related to electric current flow occur as the fuel dissolves at the anode. The noble metal fission products (e.g., Mo, Ru, Rh) contained in the fuel do not oxidize at the applied potential and remain as an insoluble residue. During dissolution, this residue may remain in the cladding hulls within the basket, or the residue may be washed out mechanically by flow of salt through the baskets during the dissolution process. Active fission product metals in the fuel (such as the rare earths, the alkaline earths and alkali metals) and bond sodium react chemically with uranium chloride to form uranium metal and active metal chlorides. Periodically, CdCl_2 is added to the system to keep the desired level of heavy metal chloride in the electrolyte, since the CdCl_2

reacts with uranium metal to give uranium chloride, which enters the salt, and cadmium metal, which enters the cadmium pool. (For further discussion of anodic dissolution of fuel, see Refs. 1 and 2.)

III. ELECTROTRANSPORT OF URANIUM TO SOLID CATHODE

The operation for recovery of uranium in the electrorefining process involves the collection of uranium metal on a solid steel cylindrical mandrel about 1-3/4 in. (4.4 cm) in diameter. When the uranium ion discharges at the cathode, initially, the metal formed bonds to the ferrous metal surface of the cathode, which is contacting the salt. Subsequently, as the deposit grows and covers the steel surface, the uranium ion from the salt discharges at the uranium deposit--salt interface. The metal crystals grow as dendrites as the deposit enlarges. This process at the solid cathode is represented by Eq. (2). A vertical scraper mounted on the vessel wall limits radial growth of the deposit. A horizontal scraper that is mounted on the bottom of the vessel but protrudes above the cadmium pool-salt interface limits the downward (longitudinal) growth of the dendrite deposit. The longitudinal growth in the upward direction is limited by the electrolyte level. The resultant shape of the finished cathode is a right cylinder of the desired diameter and length. Material which falls off or is scraped off the cathode during its formation dissolves in the cadmium pool and is subsequently recovered by using the cadmium pool as the anode.

A typical uranium deposit on a cathode, obtained during development work with the engineering-scale electrorefiner, is shown in Fig. 5. When the cathode is submerged in the electrolyte during its formation the porous structure is filled with electrolyte. When the cathode is withdrawn from the cell, most of this liquid drains out of the structure but some remains. Typical composition of the solid cathode product is given in Table I. The typical deposit for the engineering-scale electrorefiner is 8 in. (20.3 cm) diameter x 13 in. (33.0 cm) in length. For the 10 kg cathode deposit the average space density is about 1.0 g/cm³.

Fig. 5. Typical Uranium Deposit on Solid Cathode

The deposit from an IFR pyroprocessing electrorefiner solid cathode will contain some plutonium. The electrolyte trapped in the porous uranium solid will contain, for instance, a Pu/U ratio of 5 and a total U-Pu content of 6.8 wt %, this gives a Pu content of 5.7 wt % for the electrolyte. The salt/heavy metal (HM) in the deposit is about 0.2, so the amount of Pu (as PuCl_3) in a deposit is of the order of 100 g, about 1%. The rare earth metals (as chlorides) are also present in the electrolyte in the deposit. Their concentration in the deposit will be of the order of 0.1 wt %. In the IFR pyroprocess, the HM cathode solids will be stripped from the steel mandrel in a die press. The solids will then be vacuum melted in a cathode processor crucible. During heat up under vacuum, the chloride salts and any residual cadmium in the deposit vaporize. The vapors are cooled and solidified in the vacuum retort condenser-collector from which the material is recovered for recycle to the electrorefiner. The vacuum melting operation liquefies the heavy metal which consolidates into an ingot that is removed from the crucible-metal after cooldown.

The thermodynamic driving force minimizes the deposition of metallic plutonium on the solid cathode. In development work, no tendency was noted to form plutonium uranium alloy on the cathode or to codeposit uranium and plutonium at normal Pu/U ratios in the electrolyte [3]. The chemical equilibrium which exists at the cathode surface for the solid deposit and the electrolyte may be described by the simple equation:

where Pu and U are pure metals and PuCl_3 and UCl_3 are dissolved in the matrix electrolyte. At 500°C, the equilibrium constant is given by,

$$K_e = \frac{X_{\text{PuCl}_3} \cdot X_{\text{U}}}{X_{\text{UCl}_3} \cdot X_{\text{Pu}}} \cdot \frac{\gamma_{\text{PuCl}_3} \cdot \gamma_{\text{U}}}{\gamma_{\text{UCl}_3} \cdot \gamma_{\text{Pu}}} \quad (4)$$

where X is the mol fraction and γ is the activity coefficient of the component.

TABLE I. Composition^a of Product from
Single Mandrel Cathode Tests

Material	Concentration, ^b wt%
Uranium	77-84
LiCl-KCl-UCl ₃ Electrolyte ^c	9-15
Zirconium	0.5-0.9
Cadmium	<0.01-1.0
Aluminum	<0.01

^aDetermined from chemical analysis of samples taken from the deposits.

^bConcentrations are measured for five deposits that contained 8.2 to 10 kg uranium.

^cContained about 6.8 wt % U, 0.6 wt % Nd, 0.5 wt % Ce and 0.3 wt % Y.

Since uranium and plutonium deposit independently as solids their activities are equal to 1 and the expression for the equilibrium constant, since $X_U \gamma_U = X_{Pu} \gamma_{Pu} = 1$, becomes

$$K_e = \frac{X_{PuCl_3} \gamma_{PuCl_3}}{X_{UCl_3} \gamma_{UCl_3}}$$

From the known free energy for the reactions we compute K_e from $K_e = e^{-\Delta G/RT} = 8.8 \times 10^5$, where ΔG is the free energy, R is the gas constant and T is degrees Kelvin. The ratio $\gamma_{PuCl_3}/\gamma_{UCl_3}$ should be some value close to 1 so we have

$$\frac{X_{PuCl_3}}{X_{UCl_3}} = 8.9 \times 10^5 \quad (5)$$

For systems at equilibrium, no pure metallic plutonium can exist in contact with the electrolyte unless the Pu/U ratio in the electrolyte equals or exceeds this ratio. Normal feedstock to the electrefiner contains

uranium as well as plutonium. Therefore, the Pu/U ratio in the electrolyte will always be orders of magnitude less than that required for the existence of solid plutonium. Therefore, in the FCF electrorefiner we expect minimal metallic plutonium content in the solid cathode deposit.

As described earlier, some material which deposits on the cathode either falls or is scraped off during deposit formation. This leads to some collection losses. (The electric current efficiency for the reduction process is 100%, as demonstrated in electrochemical studies [4].) In development work, it has been found that an average 835 A h is required per kilogram of uranium in cathode deposits of 10 kg of uranium. This is a collection efficiency of about 40%. (Collection efficiency is defined as kg HM in cathode deposit/kg HM equivalent to electric current passed x 100). During formation, the cathode is rotated at 20 rpm. In the beginning, when no deposit is present on the mandrel, the cathode drive requires a power input of 3.2 W to maintain the rotation. As the deposit forms, this power requirement increases about threefold to 9.2 W for the 10 kg uranium deposit. The added power is required not only because the deposit adds to the size and weight of the starting mandrel, but as the cathode forms and fills out to the scrapers, power is consumed due to friction of the deposit surface rubbing against the scrapers. This increase in power for the cathode drive, coupled with knowledge of the ampere-hours passed, is used to estimate the size of the cathode deposit while it is still being formed.

Dissolution of the fuel continues until the end point for dissolution is indicated (i.e., the required ampere-hours is passed and the expected increase in cell resistance is observed after all the heavy metal in the anode baskets is dissolved). About 70% (~7 kg per anode) of the uranium dissolved from the anode baskets will deposit on the solid cathodes, and the remainder will collect in the cadmium pool because of the collection inefficiency of the solid cathode. (Plutonium in the dissolving fuel will not deposit on the cathode, for reasons discussed previously, but will displace uranium from the salt, increasing the Pu/U ratio in the salt.) Following this direct deposition, the electrode switching will be changed

so that the cadmium pool becomes the cell anode, and transport of uranium to the solid cathodes may continue (or uranium-plutonium transport to liquid cathode may be employed).

During the transport processes, the distribution of uranium and plutonium between the electrolyte and cadmium pool follows precise thermodynamic laws and is predictable, that is:

$$\frac{\left(\frac{\text{concentration of uranium in salt}}{\text{concentration of uranium in cadmium}} \right)}{\left(\frac{\text{concentration of plutonium in salt}}{\text{concentration of plutonium in cadmium}} \right)} = K$$

where K is a constant. Also at anytime, the sum of the concentrations of uranium and plutonium in the electrolyte is a fixed known quantity. Material balances for the distribution of heavy metals in the electrorefiner may be estimated at any time by use of the Pyro computer code developed by Ackerman [5]. This has been done for a planned sequence of operations in the FCF electrorefiner [6]. Also more information about electrorefining with solid cathodes is given in Refs. [7] and [8].

IV. ELECTROTRANSPORT OF URANIUM-PLUTONIUM TO LIQUID CADMIUM CATHODE

The chemical equilibrium for contact between a liquid cadmium cathode surface and the molten electrolyte differs markedly from that for contact between a solid metal (ferrous) cathode surface and the electrolyte. Consider the deposition of plutonium and uranium into a cadmium solution saturated with uranium and plutonium. The precipitating uranium phase is pure uranium but the precipitating plutonium phase is the intermetallic PuCd_6 . The activity of uranium $X_u \gamma_u$ is still equal to one as for the solid

cathode but the activity of plutonium $X_{Pu} \gamma_{Pu}$ for this case is 2.4×10^{-6} instead of one as for the solid cathode. If we substitute the values for the cadmium phase in Eq. (4) we get

$$\frac{X_{PuCl_3}}{X_{UCl_3}} = 2.1 \quad (6)$$

For the solid cathode, Eq. (5) the ratio of plutonium to uranium in the electrolyte must be $>10^5$ in order for plutonium metal to coexist with uranium metal on the cathode. For a liquid cadmium surface, this ratio needs to be only about 2, Eq. (6). Since the core fuel and blanket mixture for processing IFR nuclear material is largely uranium, it is impractical for plutonium removal to use an electrolyte containing only plutonium. However, it is practical to use the solid cathode to enrich the electrolyte in plutonium (by removing only uranium from the electrolyte) to a sufficient level so that plutonium metal can be removed from the electro-refining system by use of the cadmium cathode.

When the amount of plutonium in cadmium exceeds its solubility (3.62 wt % at 500°C), the solid present is the intermetallic $PuCd_6$. When the amount of uranium in cadmium exceeds its solubility (2.35 wt %), the solid present is pure uranium.

In the FCF electrorefiner design, because of space limitation considerations in the electrolyte phase, the largest possible container for the liquid cadmium cathode can accommodate up to about 30 kg cadmium. The cadmium cathode design developed for the engineering-scale electrorefiner is shown in Fig. 6, and its relative location in the electrorefining cell is shown in Fig. 2. The ceramic-insulated propeller is mounted on the shaft electrode such that the uninsulated tip of the shaft dips below the electrolyte-cadmium interface of the cadmium pool contained in the crucible. This allows current to pass to the cadmium pool within the crucible, and the liquid cadmium pool surface to become the cathode. In the design, the propeller may be moved axially with respect to the crucible-cadmium pool. The propeller may be rotated at the

Fig. 6. Crucible Assembly for Engineering-scale Cadmium Cathode
(ANL Neg. 4743)

cadmium-electrolyte interface, within the cadmium pool, and in the electrolyte phase above the cadmium level. All of these positions are used during cathode formation, to load the cadmium with heavy metal, to smooth the cadmium-electrolyte interface, to clean off materials which tend to stick to propeller surfaces, and to clean out excessive solid material trapped within the crucible above the cadmium-electrolyte interface.

The 30 kg of cadmium within the cathode crucible will contain 1.13 kg of plutonium at the solubility limit. The desired nominal batch size for plutonium is 3 kg. Thus, the cadmium cathode pool will contain the solid precipitate plutonium phase PuCd_6 (density, 9.28 g/cm^3). For the 3 kg batch size, the cadmium metal phase contains about 20 vol % solid, with the remaining volume a saturated solution of Cd-Pu-U. The presence of uranium in the cathode, even above its solubility limit, has only a small effect on the volume fraction solids since it precipitates as a pure uranium phase. For instance, the presence of 3 kg of uranium in the cathode along with the 3 kg batch of plutonium will increase the solids fraction about 10%. (The volume percent solids increases from 20 to 22.)

In laboratory-scale experiments plutonium-cadmium cathodes have been produced which contain 50 vol % plutonium solid, PuCd_6 and Pu/U-cadmium cathodes have been produced which contain 46 vol % solids with a Pu/U ratio of 1.3 [9]. This development work was carried out to explore the limits for loading PuCd_6 into the cathode. The equilibrium composition of the liquid cathode deposit is predictable and depends on the amounts of heavy metal in the cell cadmium pool, which is used as the anode for plutonium transfer, and the ratio of Pu/U in the cell electrolyte [5].

Laboratory-scale experiments have shown that uranium is much more difficult to deposit into the liquid cadmium cathode than plutonium. The uranium tends to grow as dendrites into the electrolyte phase, away from the cadmium-electrolyte interface, whereas the plutonium forms inter-metallic crystals with cadmium, which tend to mix well with the liquid cadmium. The engineering-scale development of the liquid cadmium cathode has been done with uranium alone, since a plutonium facility of sufficient size was not available. In this engineering development, electrotransport

to liquid cadmium cathodes have produced 4 kg of uranium and 18 vol % solids by the methods noted previously. Cross sections of cadmium-uranium ingots and autoradiographs of such ingots showing uranium distribution in the cadmium are given in Figs. 7 and 8. The same quantitative laws, discussed earlier, relate the maximum possible amount of heavy metal deposited into the cathode and the total electric current passed in the cathode circuit. In engineering scale cathodes made with uranium cadmium only, 873 ampere-hours was required per kilogram of uranium in the deposit; this gives a collection efficiency of 38.5%. (The electric current efficiency for the reduction process into the cadmium cathode is 100%, as demonstrated in electrochemical studies [10].) As is the case for the solid cathode, material is lost from the cathode during its formation, this occurs when the cleanout step is employed. Alternative methods of cathode formation are being developed, presently at the laboratory scale, which have shown 100% collection efficiency for plutonium and plutonium-uranium mixtures. In all cases, the ampere-hours passed, a primary measurement, is a direct indicator of the maximum possible amount of heavy metal which will form at the cathode.

Secondary indicators for the amount of heavy metal in the liquid cathode are similar to those found for the solid cathode. As the volume percent solids in the cadmium grows, the power required to stir the thickening mix within the pool increases. For instance, mixing power, for constant rpm of the mixer, increased from start to finish by about 50% for the formation of cathodes with 18 vol % solids in the finished cathode.

Fig. 7. Sectioned Product from Liquid Cadmium Cathode Test LCC-6.
Sample locations also shown. (ANL Neg. 10124)

Fig. 8. Autoradiograph of Product from Liquid Cadmium Cathode Test AD-LCC-7/7A

V. BASIS FOR MASS TRACKING

Chemical analysis of filtered salt and cadmium samples will be taken before and after each run in the FCF electrorefiner and will be used to ensure, with a large margin, that the amount of uranium and plutonium in the electrorefiner is always below the limit set by the criticality safety required operational envelope. The quantity of insoluble uranium and plutonium compounds which inadvertently may be formed in the electrorefiner will be estimated from mass balance calculations using results of the above chemical analyses, as well as chemical analysis of the product from the cathode processor.

Mass tracking calculations have been made for the developmental engineering-scale electrorefiner during 3.9 years of testing. Over this period, 324.9 kg of depleted uranium was added to the electrorefiner, and an estimated 302.1 kg of uranium was removed as cathode products. The weight of uranium in the heterogeneous cathode product was estimated from the cathode product weight and chemical analysis of samples taken from the products. Based on mass tracking calculations, the weight of uranium in the electrorefiner and removed in cathode products was underestimated by 9.8 kg (3% of the uranium input). Mass tracking using the weight of heavy metal in the product determined by weighing and sampling the product from the cathode processor (a homogeneous product), as will be done in the FCF electrorefiner, is expected to give an even better accountability of the heavy metal content of the cathode products than was obtained for the engineering-scale-developmental electrorefiner.

VI. CONCLUSIONS

The electrotransport of uranium and plutonium in the electrorefiner follows known precise laws of electrochemistry. The maximum amount of solid nuclear material which can accumulate on the collection device (solid or liquid cathode) is precisely controllable from a knowledge of the

ampere-hours used in the transport. Because of this primary control, the actual amount of material collected will always be equal to or less than that predicted by Faraday's law. The collection device for uranium is the solid cathode, and its design for the FCF electrorefiner causes collection efficiencies of less than 100%. The collection device for plutonium/uranium is the liquid cathode and its design for the FCF electrorefiner also produces collection efficiencies of less than 100%. Devices with higher collection efficiencies are under development. The uncollected solid material does not accumulate but dissolves in cell liquids and recycles. Electric current control, recording and integration with time, is the primary means for limiting and controlling accumulation of nuclear material solids within the electrorefiner during transport processes. For all other normal operations, the nuclear materials are in liquid form, and their distribution in the electrorefiner is predictable and known.

Several secondary parameters have been used to control the electrorefining process during its development. These secondary parameters have been used as end-point indicators for anodic dissolution, electrotransport of uranium to a solid mandrel cathode, and electrotransport to a liquid cadmium cathode, the three major operations of electrorefining. These secondary parameters include the following: (1) the increased cell resistance (threefold increase) at the end of anodic dissolution, (2) the increased power (threefold increase) required to rotate the solid mandrel cathode as the product is collected, and (3) the increased power (50% increase) required to rotate the mixer in the liquid cadmium cathode as heavy metal deposits. Similar correlations are needed as aids for process control in the FCF electrorefiner. These correlations will be developed from tests conducted in this electrorefiner. For the initial tests, the correlations developed in the engineering-scale electrorefiner will be used to estimate the performance expected in the FCF electrorefiner.

Continuous mass tracking calculations have been made for the engineering-scale electrorefiner during 3.9 years of operations, in which 325 kg of uranium has been processed. The running material balance is made using weights and composition of materials added and of products, and using chemical analysis of the electrorefiner cell liquids. Because the cathode

product is heterogeneous, its composition is estimated from numerous samples of the solid. Since the cathode product will be consolidated and sampled in the FCF, less error should be involved. In the development work, weight of uranium in the electrorefiner and in cathode products was underestimated by only 3% of the uranium input. A similar mass tracking procedure for the FCF electrorefiner is expected to be more accurate.

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