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THE FLUREX PROCESS: A WET CHEMICAL METHOD FOR THE PRODUCTION OF URANIC FLUORIDE SALTS

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HANFORD LABORATORIES OPERATION

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We are preparing this paper for the Geneva Conference and we presume declassification will be requested by the OIC.

THE FLUREX PROCESS: A WET CHEMICAL METHOD FOR THE PRODUCTION OF URANIC FLUORIDE SALTS

W. W. Schulz[1], E. W. Neuvar[1], J. L. Carroll[2], R. E. Burns[1]

I. INTRODUCTION

Anhydrous uranium tetrafluoride is used as an intermediate in present industrial processes for the preparation of both uranium hexafluoride and uranium metal. Several recent investigations (4,5) have demonstrated that alkali metal and ammonium uranium(IV) double fluorides of the general formula MUF_5 may also be used as intermediates. An electrodialytic process, the Flurex Process, for the preparation of such uranic fluoride salts from aqueous uranyl nitrate - the usual end product in uranium separations processes - was proposed by Carson and co-workers in 1954 (2). Essential features of the process, as presently conceived, together with pertinent developmental data and a chemical flowsheet are briefly discussed in this paper.

II. PROCESS CONCEPT

Two major electrochemical steps are performed simultaneously in the Flurex Process; uranyl and nitrate ions of the feed solution are separated from each other, and uranyl ions are reduced at a mercury cathode to the tetravalent state. Success of the reduction step is contingent on the previous separation since nitrate ions are capable of oxidizing uranium(IV) ions.

The Flurex Process is shown in simple schematic form in Figure 1. The basic element of the process is an electrolytic cell which is divided into three compartments by an anion permeable membrane and a cation permeable membrane. Uranyl nitrate is introduced into the center (feed) compartment which is bounded by the two membranes. When a potential is applied uranyl ions are transported through the cation membrane into the cathode chamber which contains ammonium (or the appropriate alkali metal) ion and fluoride ion. Simultaneously, nitrate ions migrate through the anion

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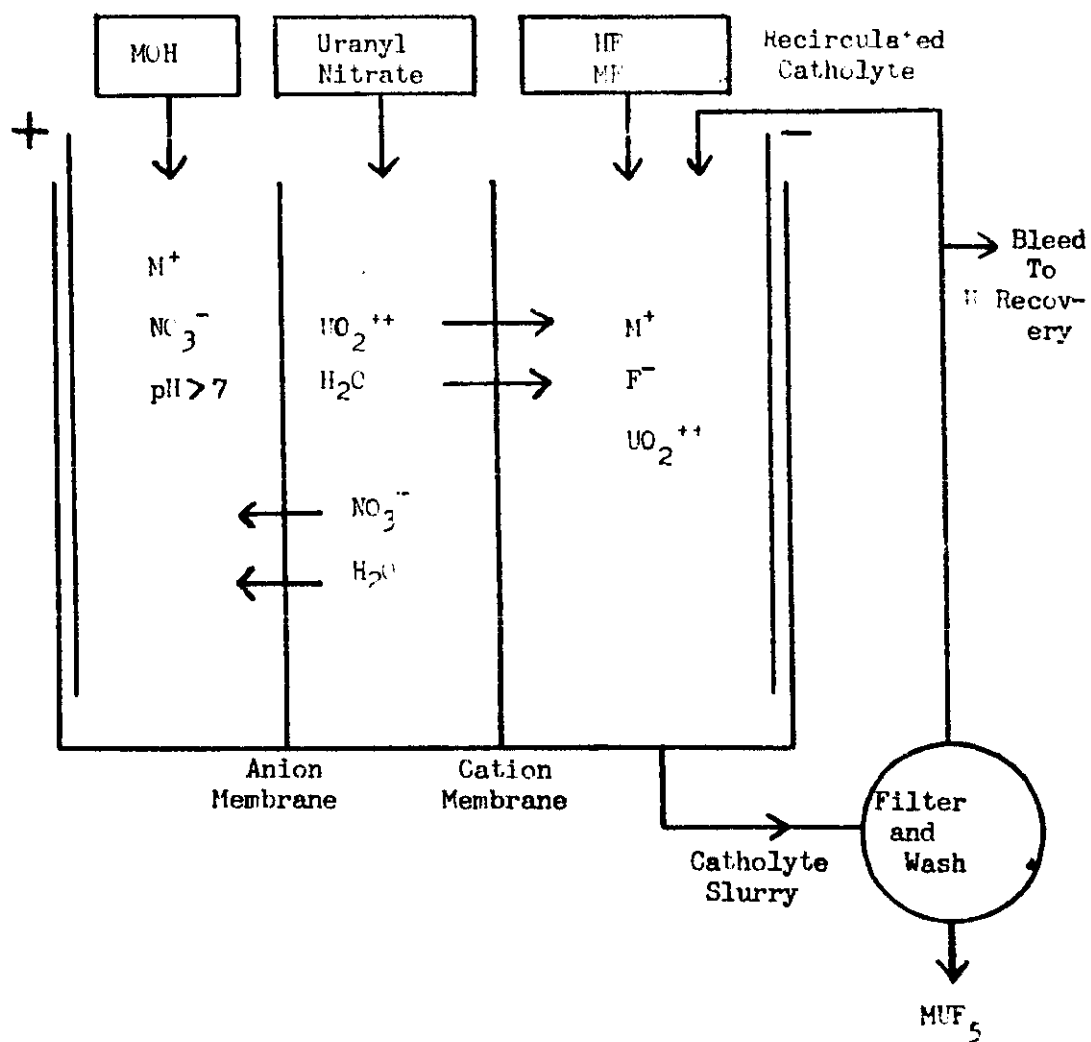(2) Department of Chemistry
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Figure 1 - BASIC FLUREX PROCESS CONCEPT
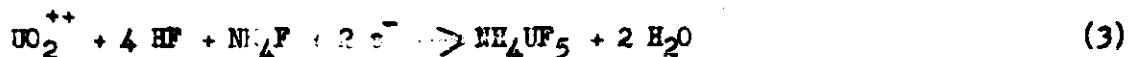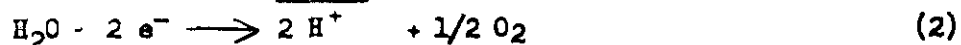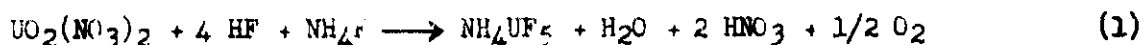
membrane to form nitric acid in the anode chamber. Water is also transported from the feed compartment with both ions. For reasons discussed later, overall current efficiencies of 80-100 percent cannot be obtained feasibly with an acid anolyte. In practice, base is continuously added to the anode compartment, and the cell is operated with an alkaline anolyte.

In the cathode chamber uranium(VI) is reduced to the tetravalent state and precipitated as a uranic double fluoride. In continuous operation solid product is removed from the catholyte external to the cell. After product removal a volume of catholyte equivalent to the volume of water introduced during cell operation is removed as a "catholyte bleed". Uranium is recovered from the bleed in a separate operation and the other constituents of the bleed are sent to waste. Alternatively, the catholyte may be continuously concentrated to remove added water with a small volume taken as a bleed and sent to waste. In both cases, the bulk of the catholyte is recycled to the cathode compartment. Hydrofluoric acid and ammonium fluoride (or alkali metal fluoride) are continuously added to the recycled catholyte.

The overall cell reaction is given in equation (1). Equation (2) represents the anode reaction and equation (3) the cathode reaction.

$$UO_2(NO_3)_2 + 4\ HF + NH_4F \longrightarrow NH_4UF_5 + H_2O + 2\ HNO_3 + 1/2\ O_2 \tag{1}$$

$$H_2O - 2\ e^- \longrightarrow 2\ H^+ + 1/2\ O_2 \tag{2}$$

$$UO_2^{++} + 4\ HF + NH_4F + 2\ e^- \longrightarrow NH_4UF_5 + 2\ H_2O \tag{3}$$

Although the equations are written for the production of NH_4UF_5, the sodium and potassium salts are prepared in a similar fashion. Greater emphasis has been placed on production of the ammonium salt since it can be readily decomposed to UF_4 (1) and ultimately converted to either metal or UF_6. The sodium and potassium salts are suitable intermediates for preparation of metal but do not appear particularly useful for preparation of UF_6.

III. PROCESS DESCRIPTION

A. MEMBRANE PROPERTIES

Ion exchange membranes for use in the process should desirably exhibit high electrolytic conductivity, high permselectivity, low hydraulic permeability. and a long useful life. A satisfactory combination of these properties is found in Permutit 3142 cation, Permutit 3148 anion (Permutit Company, New York) and in Nepton AR 111 anion (Ionics Incorporated, Cambridge, Massachusetts) membranes. The electrical resistance of these membranes under typical process conditions is in the range five to 40 ohms/cm^2. These membranes are also chemically stable in process solutions and appear to retain their electrical properties upon prolonged cell operation at temperatures as high as 60 C. The membrane property of greatest significance to overall process performance is permselectivity –

the property of the membrane to permit passage, under a potential gradient, of anions to the exclusion of cations, or the reverse. Cations which leak from the anolyte compartment across the anion membrane into the feed compartment compete with uranyl ion for transport to the cathode chamber. When the cell is at equilibrium anolyte cations are transported to the cathode compartment at the same rate at which they enter the feed compartment. Thus, the net result of such leakage is a decrease in the current efficiency for uranium transport. The same principles apply to leakage of anions from the catholyte compartment to the feed compartment. Experience shows, however, that the leakage rate of fluoride ion through the cation membrane under typical operating conditions is too small to be significant with respect to cell current efficiency.

Current efficiency decreases in the range three to 50 percent have been observed as the result of leakage of cations through the anion membrane. The rate of such leakage is known to be a function of anolyte composition and concentration, cell temperature, and membrane current density. In general, the leakage rate of a particular cation increases with increasing concentration and membrane current density and decreases with increasing cell temperature. The effect of elevated cell temperature in decreasing leakage rates is one of the important considerations in establishing a cell operating temperature of 60 C.

The relative leakage rates of ammonium, sodium, and calcium ions from alkaline nitrate anolytes (pH 8-9) and hydrogen ion from a nitric acid anolyte and the corresponding decreases in current efficiency for uranium transport are shown in Figure 2. These data were obtained with Permutit 3148 anion membrane; comparable rates were obtained with Nepton AR 111 and Nalfilm 2 (National Aluminate Company, Chicago, Illinois) anion membranes. At comparable concentrations, leakage rates for hydrogen ion are about ten times higher than those for sodium, calcium, and ammonium ions. You will note that even at 0.01 M HNO_3 (a concentration undesirably low from conductivity and anolyte flow considerations) about an 11 percent loss in current efficiency is experienced. Attainment of a feasible cell current efficiency at a practical anolyte cation concentration ($\geq$ 0.1 M) thus requires operation with an alkaline anolyte.

The increased leakage of cations through the anion membrane associated with increased membrane current densities must be considered in establishing an operating current density. Another factor which must be borne in mind is cation membrane polarization which occurs under Flurex Process conditions. Cation membrane polarization is believed to be analogous to electrode concentration polarization (5) and is illustrated for Permutit 3142 cation membrane in Figure 3. For the conditions shown the maximum or limiting membrane current density obtainable without polarization was about three amps/in². Attempts to further increase membrane current density by application of more voltage resulted in a sharp increase in membrane resistance and a decrease in membrane current density. Similar behavior was noted for Nepton CR 61 and Nalfilm 1 cation membranes except that limiting membrane current densities under Flurex Process conditions were less than one amp/in². For Permutit 3142 membrane a uniform membrane current density of one amp/in² is considered a satisfactory compromise to effect maximum utilization of available membrane area and the realization
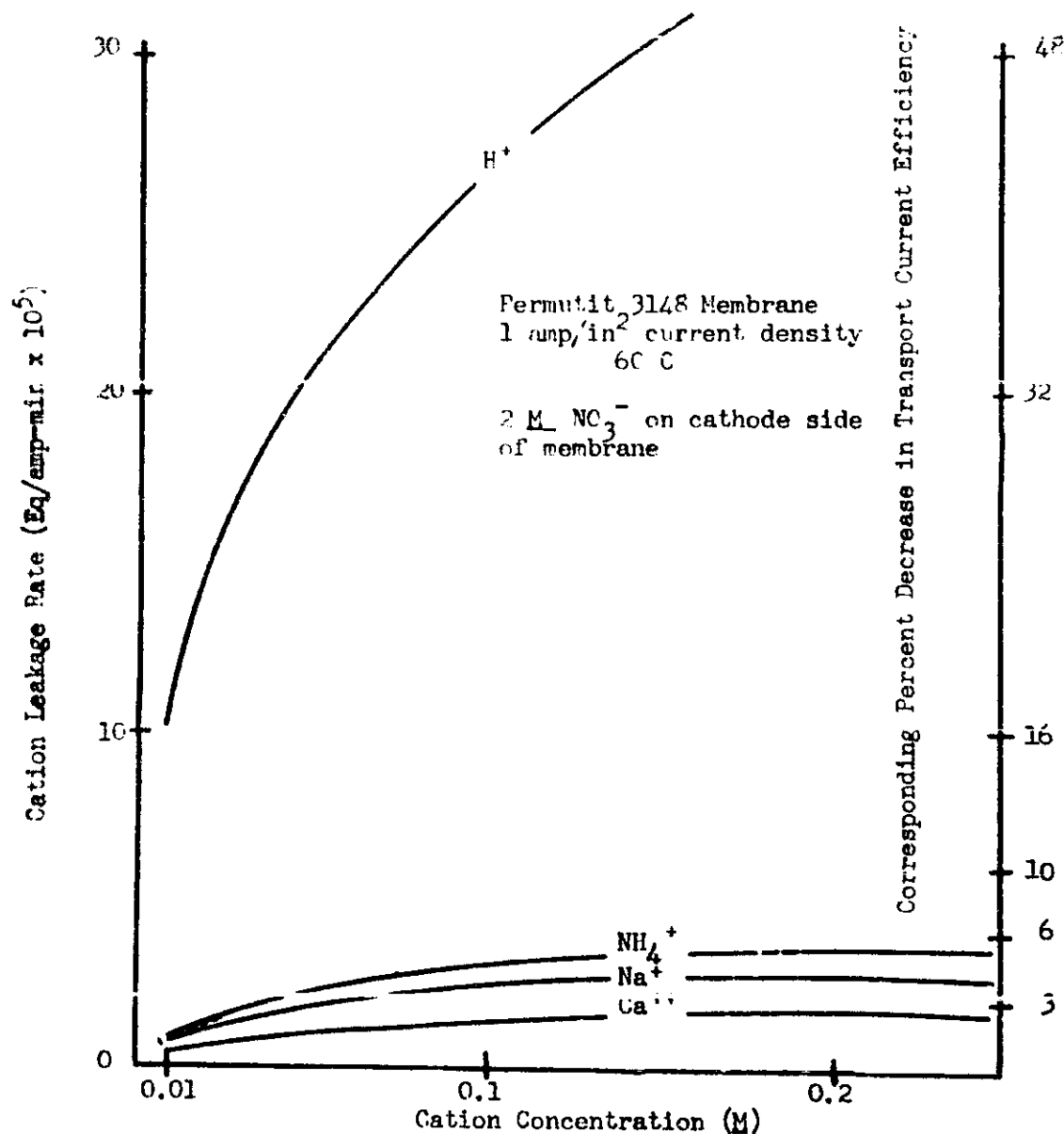
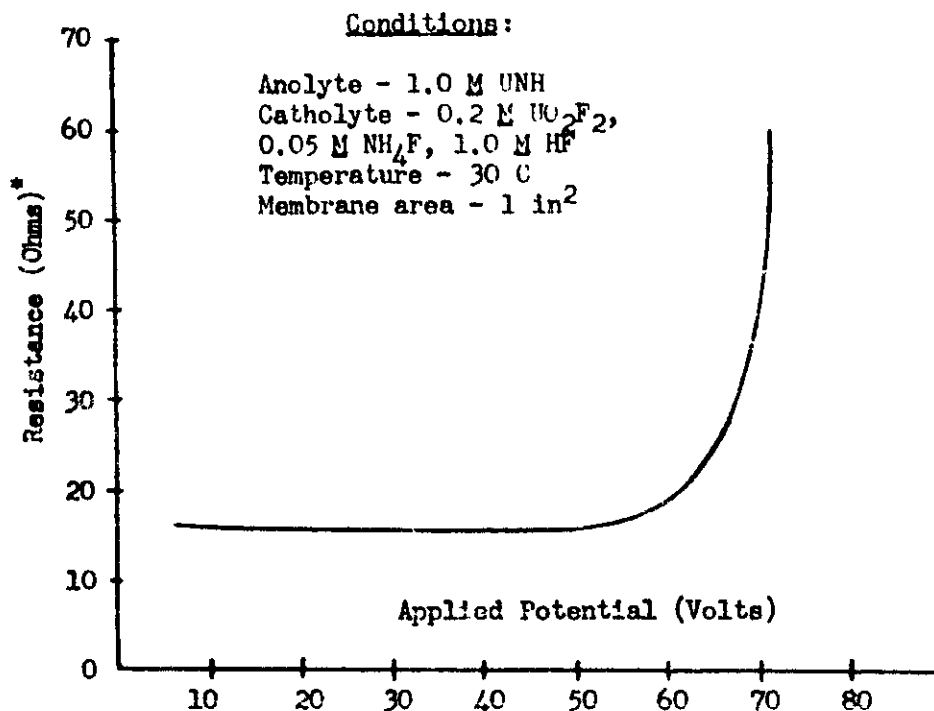Figure 2 - LEAKAGE RATES OF CATIONS THROUGH ANION MEMBRANE

Figure 3 - POLARIZATION OF PERMUTIT 3142 CATION MEMBRANE

* Resistance and potential values represent total
 resistance and total potential drop across the electrolytic
 cell. Considering that electrolyte composition, concen-
 tration, and temperature were maintained constant, the
 resistance increase is a reflection of the change in
 membrane resistance.

of a suitable overall cell current efficiency without interference from polarization effects.

B. CELL DESIGN CONSIDERATIONS

An important feature of cell design is a satisfactory arrangement of membranes and liquid mercury cathode. The choice of geometrical configuration is largely determined by the desirability of operating with minimum power requirements at an approximately uniform membrane current density of one amp/in^2. Attainment of uniform membrane current density requires a parallel arrangement of membranes and electrodes. With vertical membranes a parallel arrangement can be approximated by constructing the cathode as a series of stacked trenches, parallel to, and equidistant from the cation membrane. A laboratory model of a cell incorporating this cathode design is shown in Figure 4.

To demonstrate that a uniform membrane current density could be approximated with such a cathode arrangement the laboratory cell was fitted with a special compartmented feed chamber as shown in Figure 5. Each of the five identical feed compartments was filled with 0.6 M UNH. Anolyte and catholyte chambers were filled with solutions corresponding to typical Flurex Process conditions, and the cell was operated under a d.c. potential for a specified time. The contents of each feed compartment were then removed and analyzed for uranium. With this experimental arrangement the amount of uranium migrated from each feed compartment is a measure of membrane current density. Results in Table I show that when only the bottom trench was used, current density on the uppermost portion of the membrane was only 43 percent of that on the lowest portion of the membrane. By contrast, when all three trenches were used, membrane current density was essentially uniform.

TABLE 1

ATTAINMENT OF A UNIFORM MEMBRANE CURRENT DENSITY WITH A STACKED_TRENCH CATHODE

Number of Trenches Operated as Cathodes	Units of Uranium Migrated from Compartment No.*				
	1	2	3	4	5
Bottom Only	26	31	32	60	61
All three	41	35	37	37	39

* Feed compartments are numbered starting at top of feed chamber, cf. Figure 5.

The degree of uniformity of membrane current density obtained with stacked trenches is determined by the vertical distance between successive trenches and by the distances between cation membrane and trenches. When trenches are close to the membrane, attainment of a desired degree of uniformity of membrane current density requires that the vertical distance between
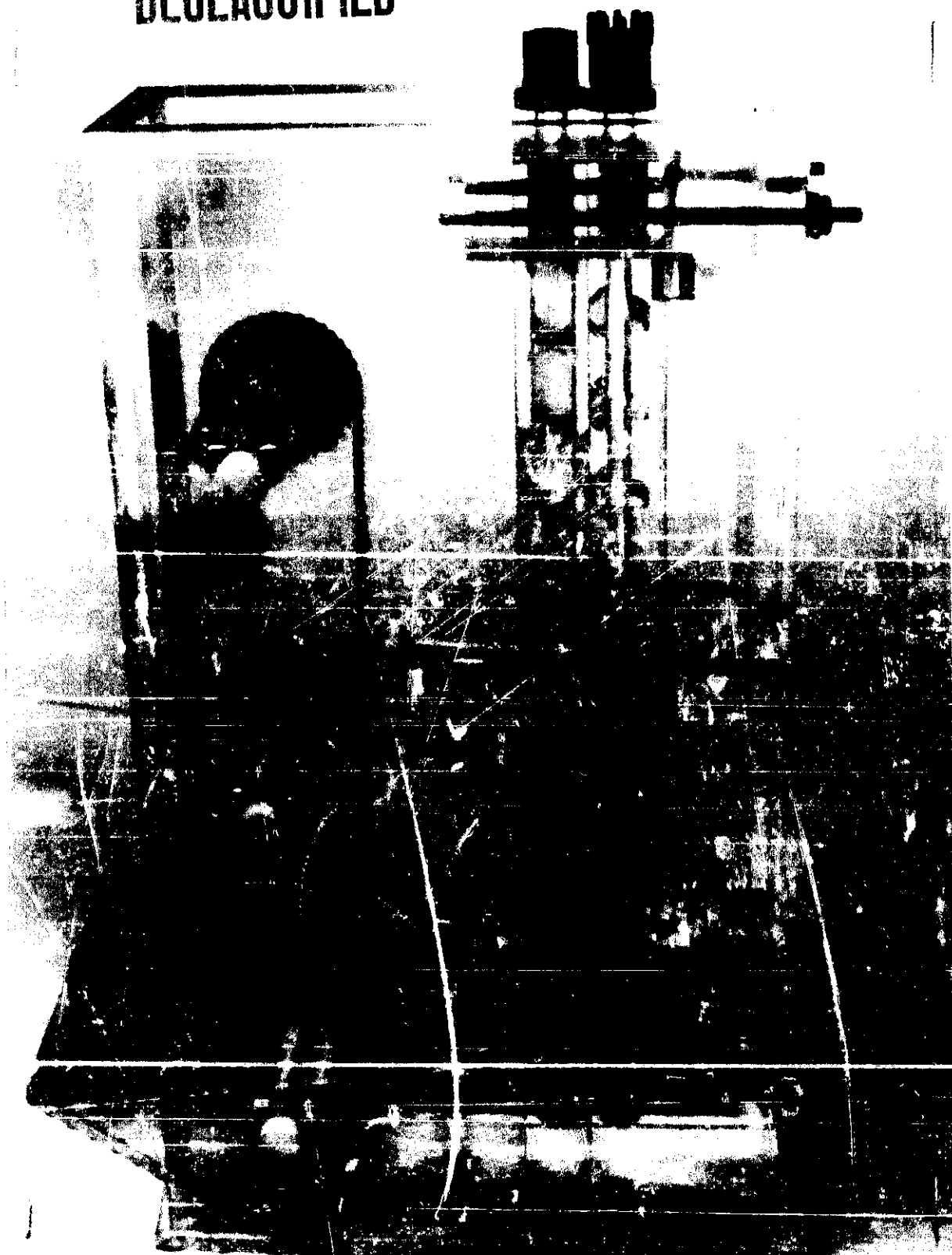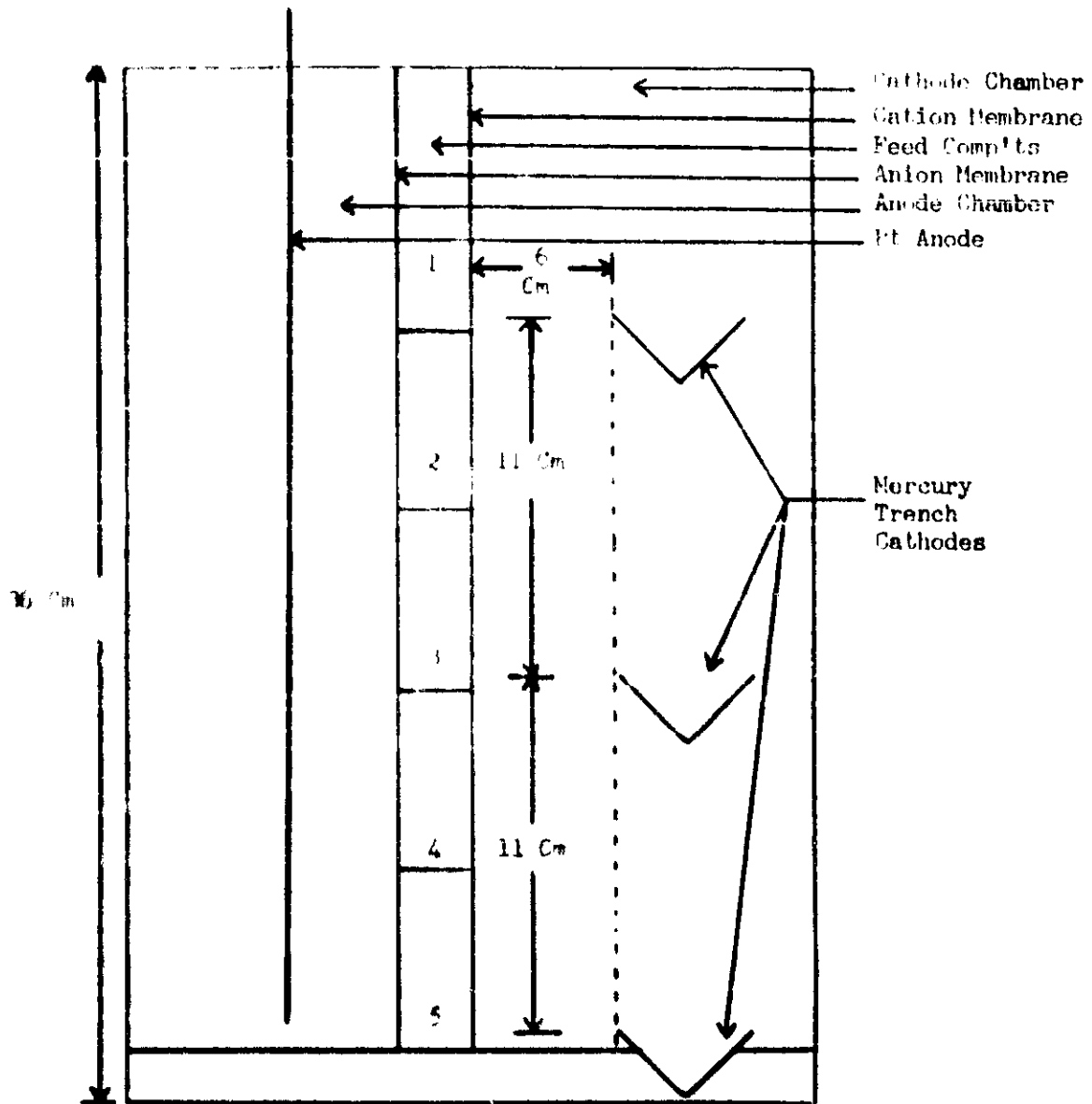
Figure 4 - LABORATORY CELL WITH TRENCH CATHODE

Figure 5 - FLOREX CELL WITH COMPARTMENTED FEED CHAMBER

successive trenches be smaller than when the trenches are farther from the membrane. On the other hand, cell resistance and voltage requirements increase as the trenches are moved farther from the membrane. Thus, a satisfactory compromise must be effected between voltage requirements and the degree of uniformity of membrane current density required. In this latter connection it should be noted that the particular configuration used in the laboratory model (Figure 5) may not represent the best compromise.

The materials of construction of cell components must be resistant to attack by any of the individual compartment solutions or by mixtures of these at temperatures at least as high as 60 C. Lucite, used in laboratory cells, appears to be suitable for construction of the cell body.

Provisions must be made in cell design for agitation of the mercury surface in each trench. In the laboratory model each trench was fitted with a paddle stirrer operated by a gear train external to the cell. Provision for agitation in each of the cell compartments to insure uniformity of solution composition also appears desirable. Means must also be provided to either dissipate heat generated in each cell compartment or to supply heat, depending on the specified operating conditions.

C. CELL OPERATING CONDITIONS

1 ANOLYTE COMPARTMENT

Because of excessive leakage of hydrogen ion through anion membranes (see Section B), the anolyte is maintained above pH 7 by continuous addition of base. Choice of the base is dictated by the product desired. Ammonia must be used for the production of pure NH_4UF_5 and, similarly, sodium hydroxide for the production of $NaUF_5$. This restriction is a consequence of the leakage of anolyte cations through the anion membrane. In addition to leakage rates of cations through the anion membrane, electrical conductivity and anolyte effluent volumes must be considered in selecting a satisfactory anolyte concentration. Anolyte cation concentrations in the range 0.1 to 0.5 $\underline{M}$ are satisfactory.

With an acidic anolyte platinum is the most satisfactory anode material yet tested. With an alkaline anolyte, however, stainless steels 304L and 347 are also satisfactory anode materials. Anodic dissolution studies indicate that the dissolution rate of SS 304L under typical Flurex process conditions is about 25 mg/amp-hr as compared to the platinum dissolution rate of about 0.06 mg/amp-hr. In view of the current relative costs of these materials, considerable economic gain in material cost is possible by using SS 304L.

2. FEED COMPARTMENT

In the present concept of the process a feed influent containing only uranyl nitrate and nitric acid as the major constituents has been assumed. In particular the feed is assumed to have been decontaminated from fission products. The Flurex process does, however, appear to be capable of giving some decontamination from fission products and other ionic impurities in

-10-

the feed. The decontamination potentialities of the process have not yet been studied in detail.

Operation of the feed compartment is most conveniently discussed in terms of factors which affect transport of uranium and of water. Three variables of importance with respect to the current efficiency for transport of uranium are (a) the free HNO_3/U ratio in the influent feed, (b) feed compartment operating temperature, and (c) leakage of cations through the anion membrane. The effects of the latter variable have been discussed earlier. The effects of feed acidity and temperature are shown in Figure 4. Note that the current efficiency for uranium transport increases slightly at elevated temperatures and decreases with an increase in feed acidity. The acidity range shown in Figure 6 is that expected for probable feeds for the process.

Water is transported from the feed by electroosmotic transfer and as hydration water of the mobile ions. The amount of water transferred with the uranyl ions increases from about two to four ml/g U as the feed compartment uranium concentration decreases from 1.5 to 0.1 $\underline{M}$. The amount of water transported with the nitrate ions is about ten percent that transported through the cation membrane.

It is possible to select operating conditions under which all the uranium and water added are transferred from the feed compartment and no effluent is necessary. However, because such operation would require precise adjustment of influent uranium concentration and flow rates, it appears more practical to operate with a small effluent from the feed compartment. Operation with a feed compartment uranium concentration of 1.5 $\underline{M}$ to decrease cell resistance and water transport, and with a feed effluent corresponding to about one percent of the influent uranium appears feasible. This feed effluent may be recycled to some previous point in the uranium separations process or processed in a separate facility for recovery of the uranium.

3. CATHOLYTE COMPARTMENT

In the catholyte compartment uranium transported from the feed compartment is reduced at a mercury cathode. Of many materials tried mercury has proved to be the only suitable cathode material at which high reduction efficiencies can be obtained at practical cathode current densities. Continuous renewal of the mercury surface by stirring or by flow is essential to achieve high reduction efficiencies.

Current efficiency for uranium reduction is primarily a function of uranium concentration and cathode current density as illustrated in Figure 7. Highest current efficiencies are obtained at high uranium concentrations and low cathode current densities. It is evident that with an all fluoride catholyte the cathode current density must be restricted to about two amps/in^2 to obtain greater than 30 percent efficiency. Operation at 60 C in the presence of a slight excess of fluoride and ammonium (or metal) ions over stoichiometric requirements also increases reduction efficiencies.
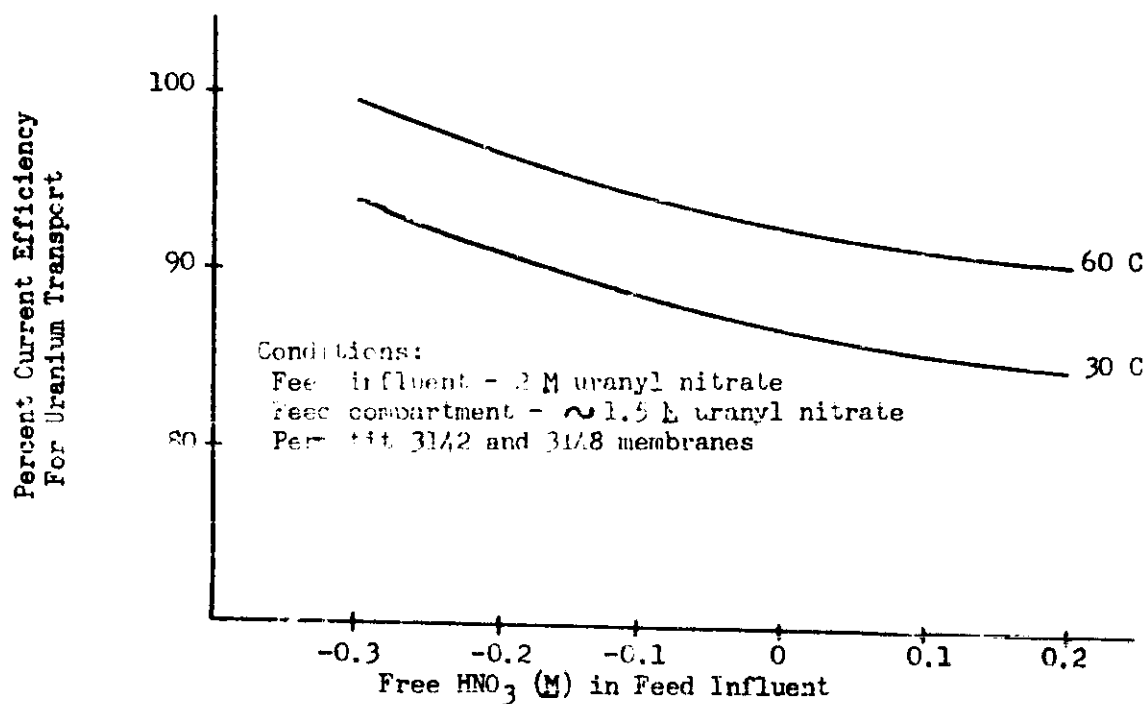
Figure 6 – EFFECT OF FEED ACIDITY AND TEMPERATURE ON
CURRENT EFFICIENCY FOR URANIUM TRANSPORT
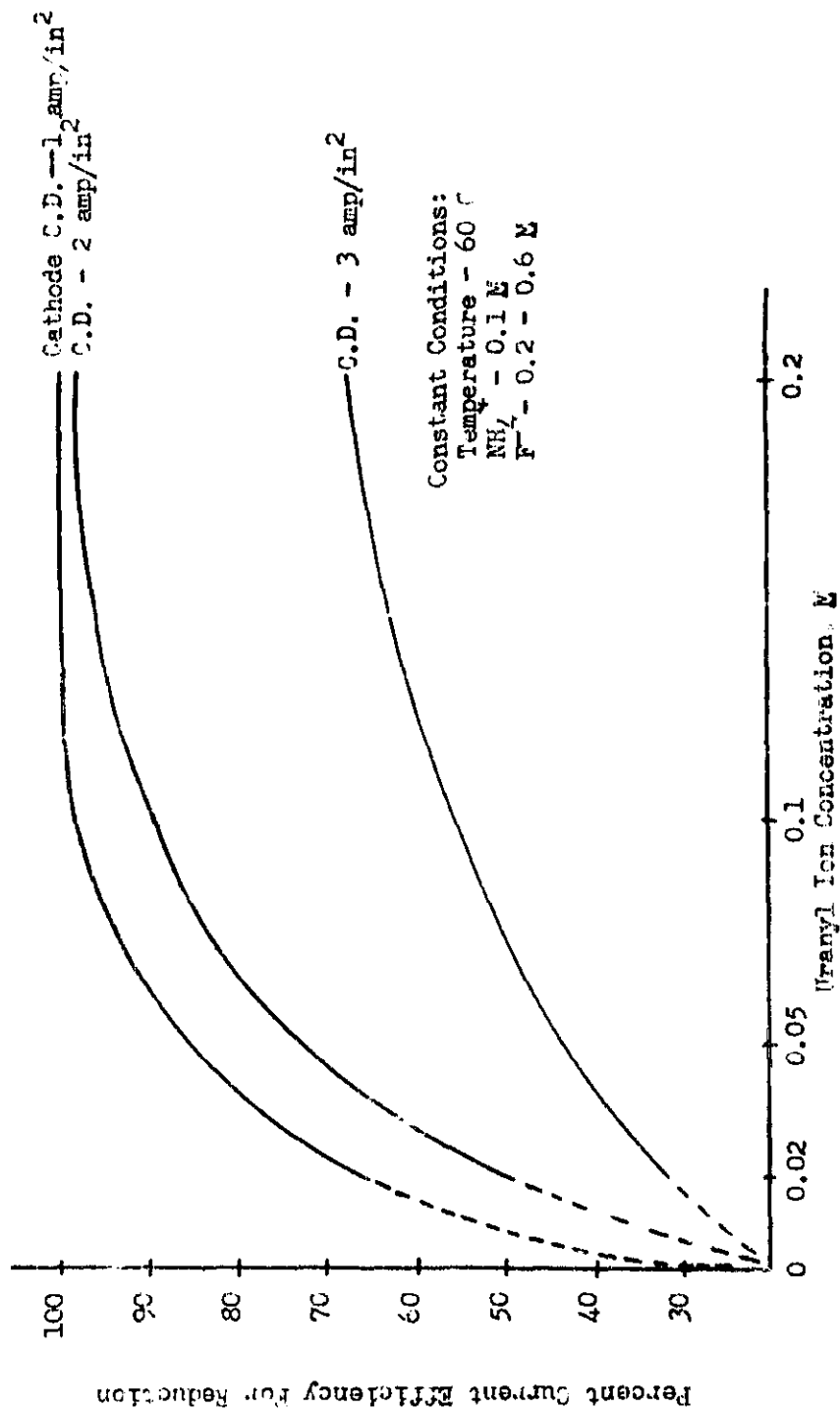
Figure 7 – VARIATIONS IN CURRENT EFFICIENCY
FOR URANIUM REDUCTION

In continuous operation with recirculation of the catholyte the equilibrium catholyte uranium concentration is determined by the relationships among current efficiency for uranium transport, current efficiency for uranium reduction, and the catholyte bleed rate. At 85 percent current efficiency for uranium transport, one amp/in^2 cathode current density, and with a bleed rate equivalent to the rate of water addition to the catholyte during cell operation, the equilibrium catholyte uranium concentration will be approximately 0.05 M. Under similar conditions except at two amps/in^2 cathode current density the equilibrium uranium concentration will be approximately 0.1 M. In both cases satisfactory operation can be realized at 0.1 M ammonium ion and 0.3-0.4 M fluoride ion in the equilibrium catholyte.

The specific resistance of catholytes of the composition 0.05-0.1 M UO_2F_2, 0.1 M NH_4F, 0.1 M HF is about 90 ohm-cm; the resistance contribution of such catholytes represents a large fraction of the overall cell resistance. Resistance of the catholyte can be decreased by minimizing the cation membrane-cathode distance or by adding to the catholyte a reagent other than a fluoride compound to avoid increasing the amount of fluoride in the catholyte bleed. Sulfuric acid is the most suitable additive of several investigated because it does not interfere with the electrochemical reduction of uranium and because the leakage rate of sulfate ion across the cation membrane is acceptably low. However, at catholyte fluoride concentrations in the range 0.16 to 0.3 M, high concentrations of sulfate ions interfere with precipitation of the reduced uranium. This latter effect is illustrated by the data in Figure 8. At 0.3 M fluoride the sulfate concentration must be limited to about 0.1 M and the cathode current density must not exceed about one amp/in^2 to achieve product yields greater than 85 percent. The specific resistance of a catholyte of the composition 0.1 M UO_2F_2, 0.1 M NH_4F, 0.1 M HF, and 0.10 M H_2SO_4 is about 20 ohm-cm.

4. PRODUCT RECOVERY

Process steps associated with product recovery and external catholyte treatment have not yet been studied in detail. A tentative procedure is as follows: Product is removed as a catholyte slurry and collected by filtration, settling, or centrifugation. The product is then washed and dried. After product removal a volume of catholyte equivalent to the volume of water introduced through the cation membrane, in the product washing step and in reagent addition is removed as a catholyte bleed. Alternatively, the catholyte may be continuously concentrated to remove added water with a small volume taken as a bleed and sent to waste. In both cases the bulk of the catholyte is recycled to the cathode compartment. In continuous operation hydrofluoric acid, ammonium fluoride (or alkali metal fluoride) and, possibly, sulfuric acid are added to the recycled catholyte to maintain constant composition.

When the catholyte is continuously concentrated, the small amount of uranium which can be sent to waste economically necessitates a relatively low catholyte bleed rate. This has the advantage of decreasing the amount of fluoride sent to waste. An important disadvantage, however, is that ionic impurities (fission products and stainless steel corrosion products) transferred from the feed compartment will build up in the catholyte to a concentration which could adversely affect the decontamination potential of the process. The decontamination potential of the process is increased when the catholyte bleed is
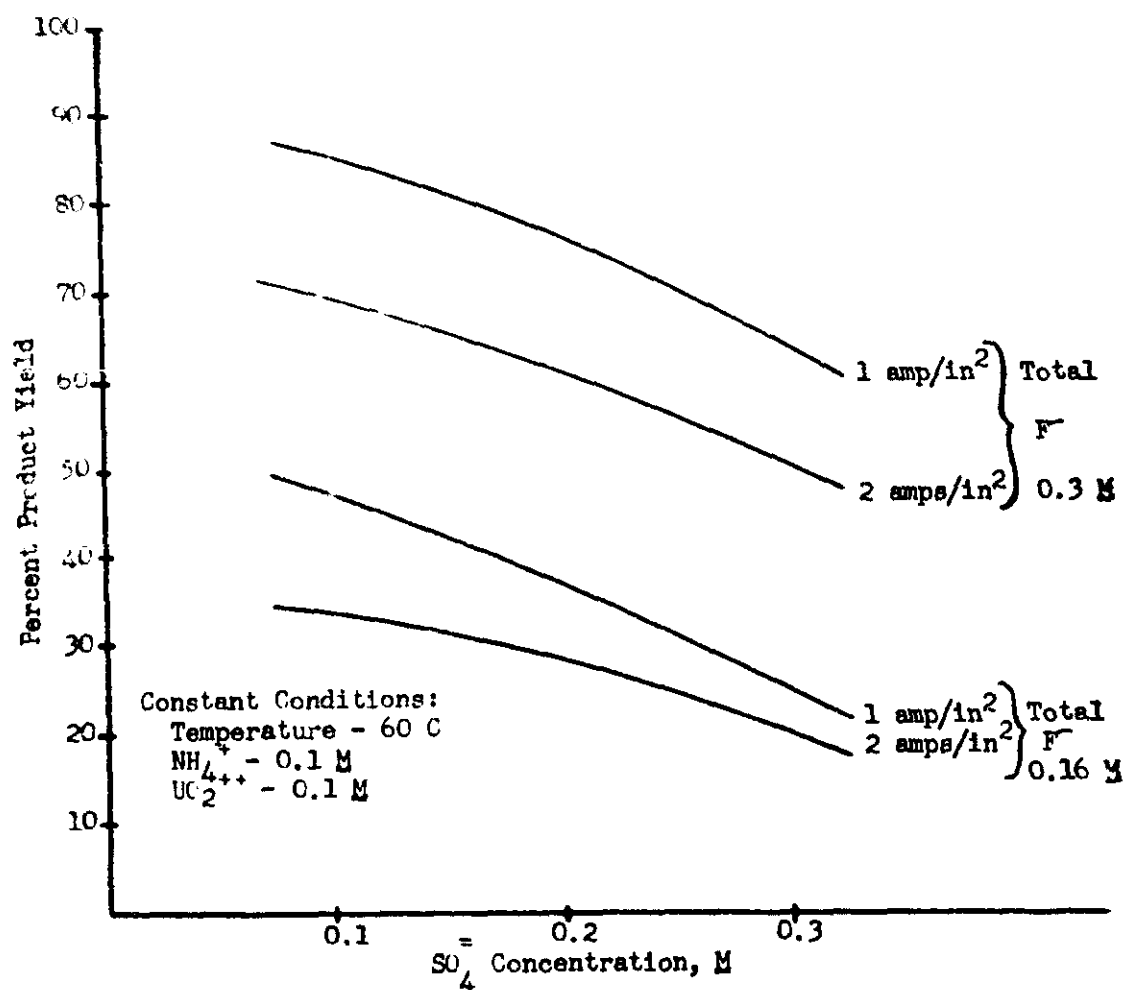
Figure 8 - EFFECT OF SULFATE ION ON PRODUCT YIELD

equivalent to the amount of water added during cell operation. Under these conditions, however, more fluoride is sent to waste and additional processing steps to recover uranium from the bleed are required. The amount of uranium in the bleed would be expected to correspond to 5-10 percent of the influent uranium to the feed compartment depending on operating parameters. It is tentatively believed that uranium may be effectively recovered from the catholyte bleed either by solvent extraction or ion exchange techniques.

D. CHEMICAL FLOWSHEET

A simplified flowsheet for the preparation of the ammonium salt is shown in Figure 9. For the conditions shown, overall current efficiencies in the range 85 to 90 percent are obtained. The concentration of ammonium nitrate shown in the feed compartment is that obtained at equilibrium as the result of leakage of ammonium ions from the anolyte. Although not indicated, traces of fluoride ion will be present in both the feed and anolyte compartments as the result of leakage of fluoride ion from the catholyte.

IV. SUMMARY

An electrodialytic process, the Flurex process, for the preparation of alkali metal and ammonium uranium(IV) double fluorides from aqueous uranyl nitrate has been investigated. Development studies have demonstrated the feasibility of the process and indicate that it has potential for becoming economically competitive, in certain applications, with present methods of converting uranyl nitrate to uranium tetrafluoride.

V. LITERATURE CITED

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Figure 9 – SIMPLIFIED FLOWSHEET FOR PREPARATION OF NH_4UF_5
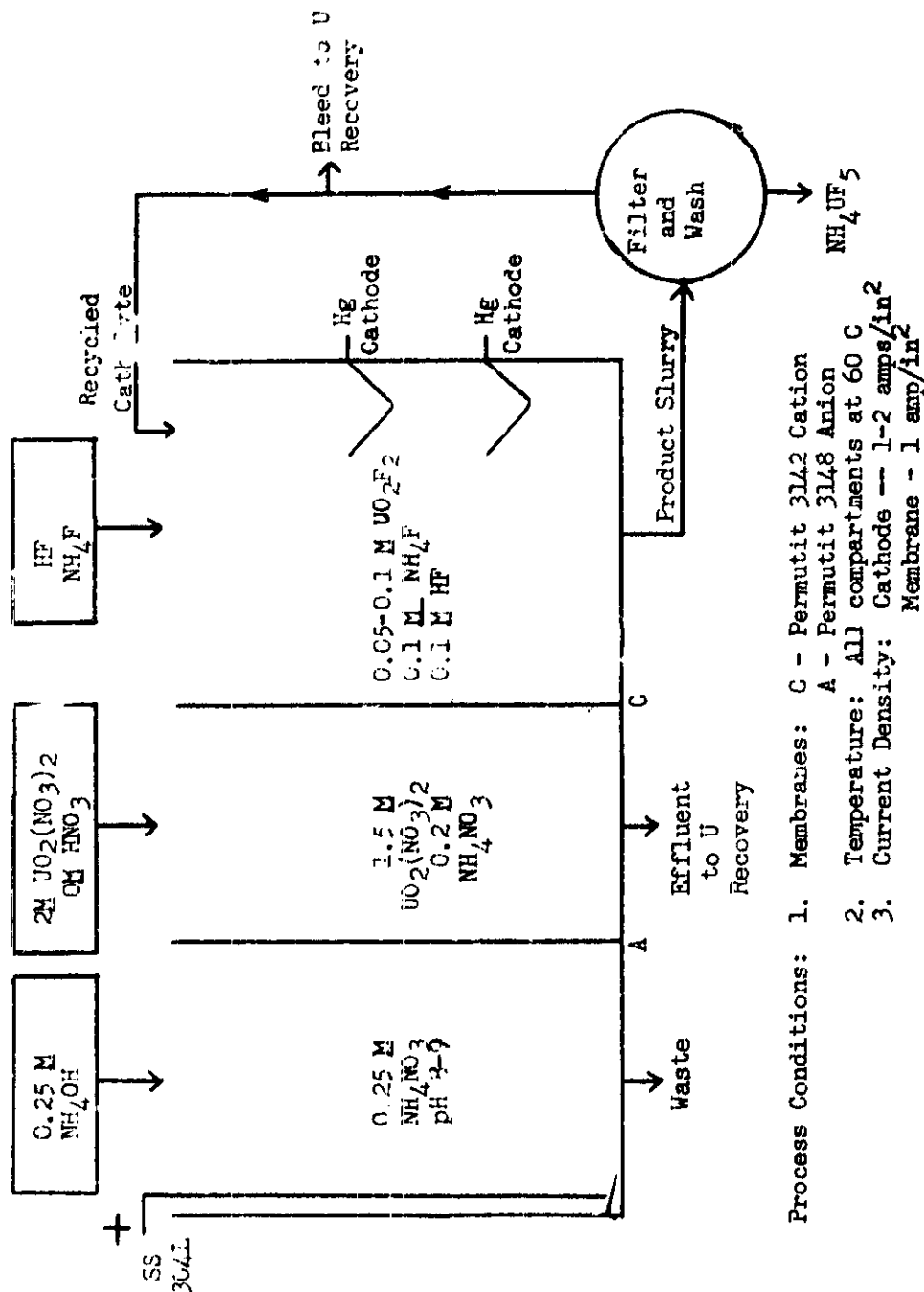
Process Conditions:
1. Membranes: C – Permutit 3142 Cation
   A – Permutit 3148 Anion
2. Temperature: All compartments at 60 C
3. Current Density: Cathode — 1-2 amps/in^2
   Membrane – 1 amp/in^2