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# ELECTRODIALYTIC CONVERSION OF URANYL NITRATE TO URANIC FLUORIDE SALTS

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## HANFORD ATOMIC PRODUCTS OPERATION
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## PRELIMINARY REPORT

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## ELECTRODIALYTIC CONVERSION OF URANYL NITRATE TO URANIC FLUORIDE SALTS

## 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 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 (2,3). 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 electrodialytic 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 uranim(IV) ions.

The electrodialytic 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 the appropriate alkali metal (or ammonium) ion and fluoride ion. Simultaneously, nitrate ions migrate through the

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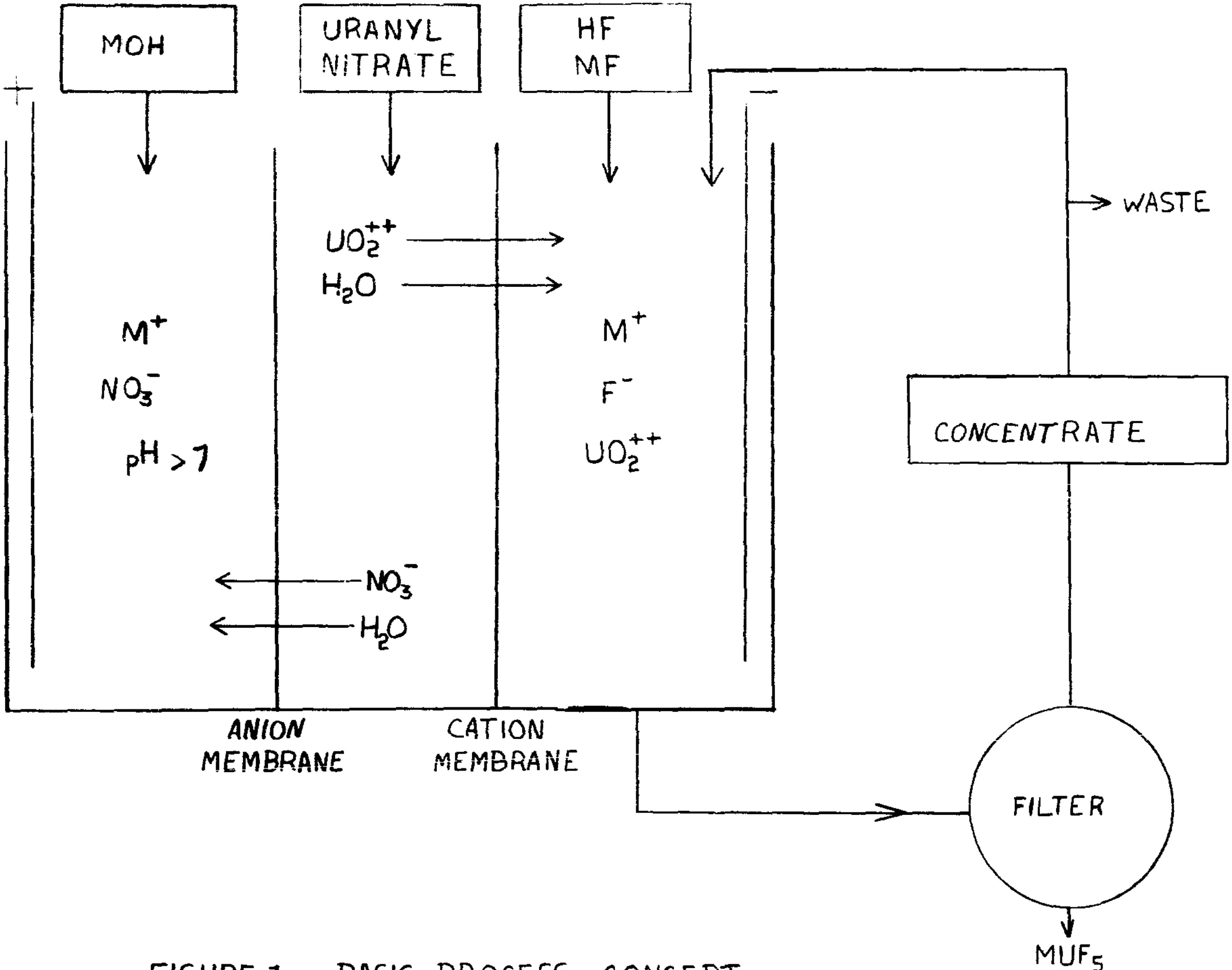

FIGURE 1 BASIC PROCESS CONCEPT

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anion 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 in the desired range, 80-100 per cent, 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. The catholyte is continuously concentrated to remove water introduced during cell operation and is then recycled except for a small fraction sent to waste. Hydrofluoric acid and alkali metal (or ammonium) ions 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.

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

$$H_2O - 2\ e^- \longrightarrow 2\ H^+ + 1/2\ O_2 \qquad (2)$$

$$UO_2^{++} + 4\ HF + NH_4F + 2\ e^- \longrightarrow \underline{NH_4UF_5} + 2\ H_2O \qquad (3)$$

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

### 1. 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 leaking from the anolyte compartment across the anion membrane into the feed compartment compete with uranium for current. 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 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 per cent 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.

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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 uranium transport efficiency 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 $\underline{M}$ $HNO_3$ (a concentration undesirably low from conductivity and anolyte flow considerations) about an 11 per cent loss in current efficiency is experienced. Attainment of a feasible cell current efficiency at a practical anolyte cation concentration ($\geq$ 0.1 $\underline{M}$) thus requires operation with an alkaline anolyte.

The increased leakage of cations through the anion membrane associated with an increased membrane current density must be considered in establishing an operating current density. Other factors which must be borne in mind are the adverse effects of increased current density on membrane useful life and the decrease in current efficiency for uranium reduction at increased cathode current densities. Current densities above two amps /in$^2$ have been observed, in some instances, to cause excessive membrane deterioration. A uniform membrane current density limited to one amp /in$^2$ is considered a satisfactory compromise to effect maximum utilization of available membrane area without undue damage and the realization of a suitable overall cell current efficiency.

2. Cell Operating Conditions

a. Anolyte Compartment

The anolyte is maintained above pH 7 by continuous addition of base.

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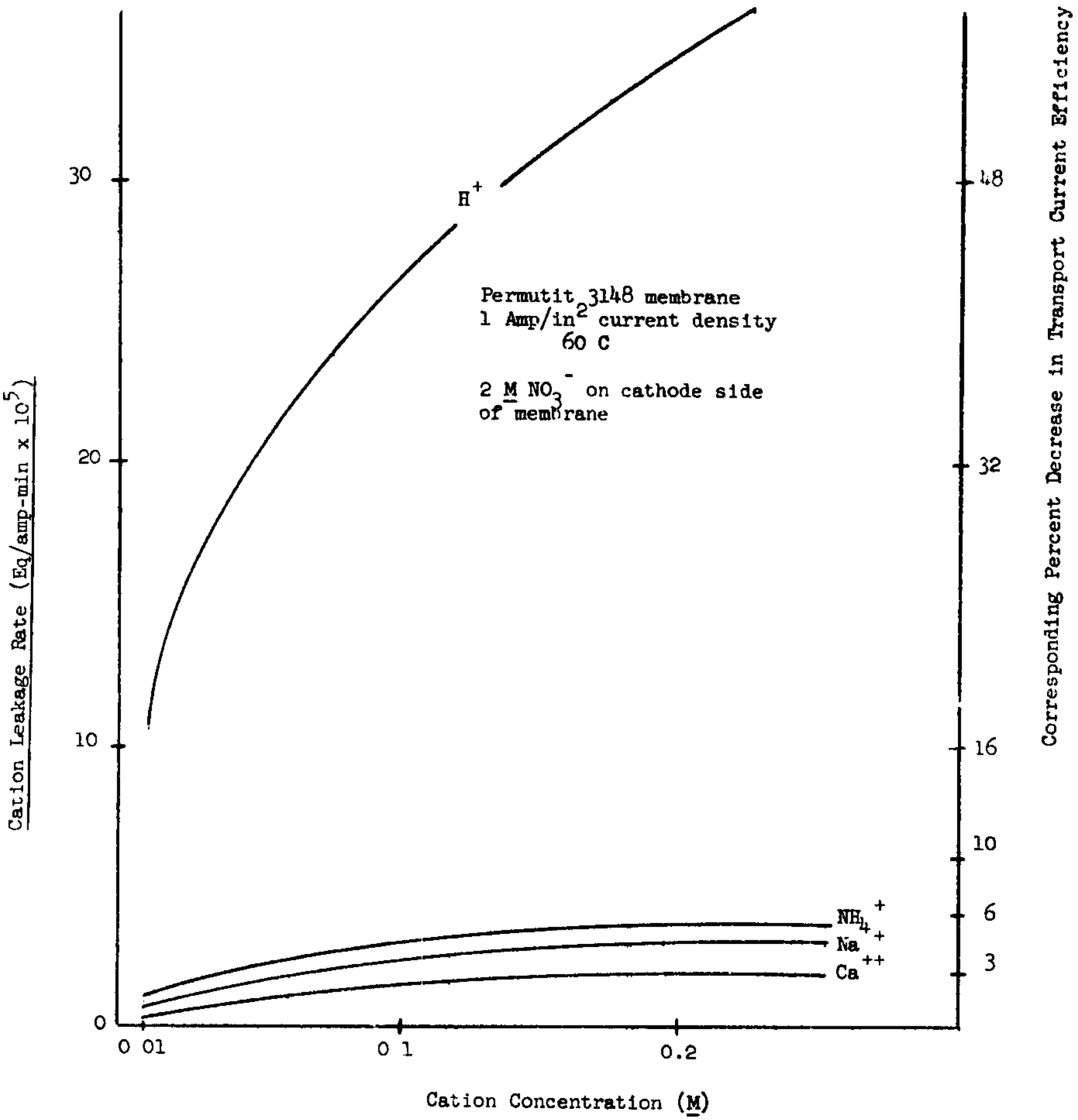
FIGURE 2

LEAKAGE RATES OF CATIONS THROUGH ANION MEMBRANE



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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 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 molar are satisfactory.

Platinum is the most satisfactory anode material yet tested. Anodic dissolution rates for platinum average 0.05 mg/ampere-hour over a wide range of probable operating conditions in the anolyte compartment. Recent results indicate that stainless steels 304L and 347 may also be satisfactory anode materials in an alkaline medium .

b. 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.

Operation of the feed compartment is most conveniently discussed in terms of factors which affect transport of uranium and of water. Three primary 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 3. You will note that current efficiency for uranium transport is increased slightly at 60 C, another reason for operating the cell at this temperature. Current efficiency decreases with an increase in feed acidity.

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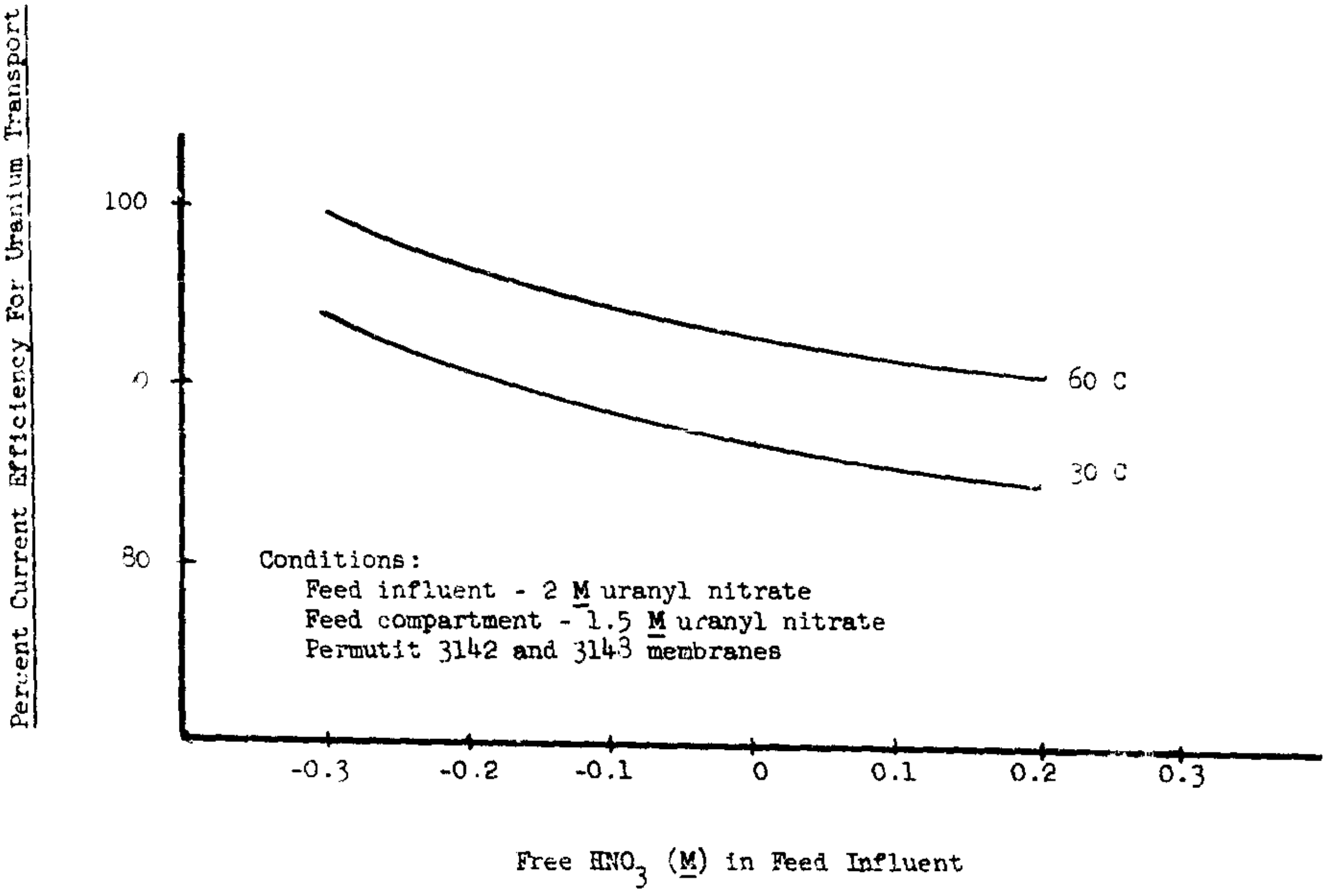
FIGURE 3

## EFFECT OF FEED ACIDITY AND TEMPERATURE ON CURRENT EFFICIENCY FOR URANIUM TRANSPORT



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The acidity range shown in Figure 3 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 ion increases from about two to four ml/g U as the feed compartment uranium concentration decreases from 1.5 molar to 0.1 molar. The amount of water transported with the nitrate ion is about ten per cent that transported through the cation membrane.

In terms of feed compartment operation, it is possible to select operating conditions under which all the uranium and water added are transferred. However, such operation requires 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 molar to decrease cell resistance and with a feed effluent corresponding to one per cent of the influent uranium is presently envisioned. 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.

c. Catholyte Compartment

In the catholyte compartment uranium transported from the feed compartment is reduced at a mercury cathode. Mercury has proven 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 4. Highest current efficiencies are obtained at high uranium concentrations and

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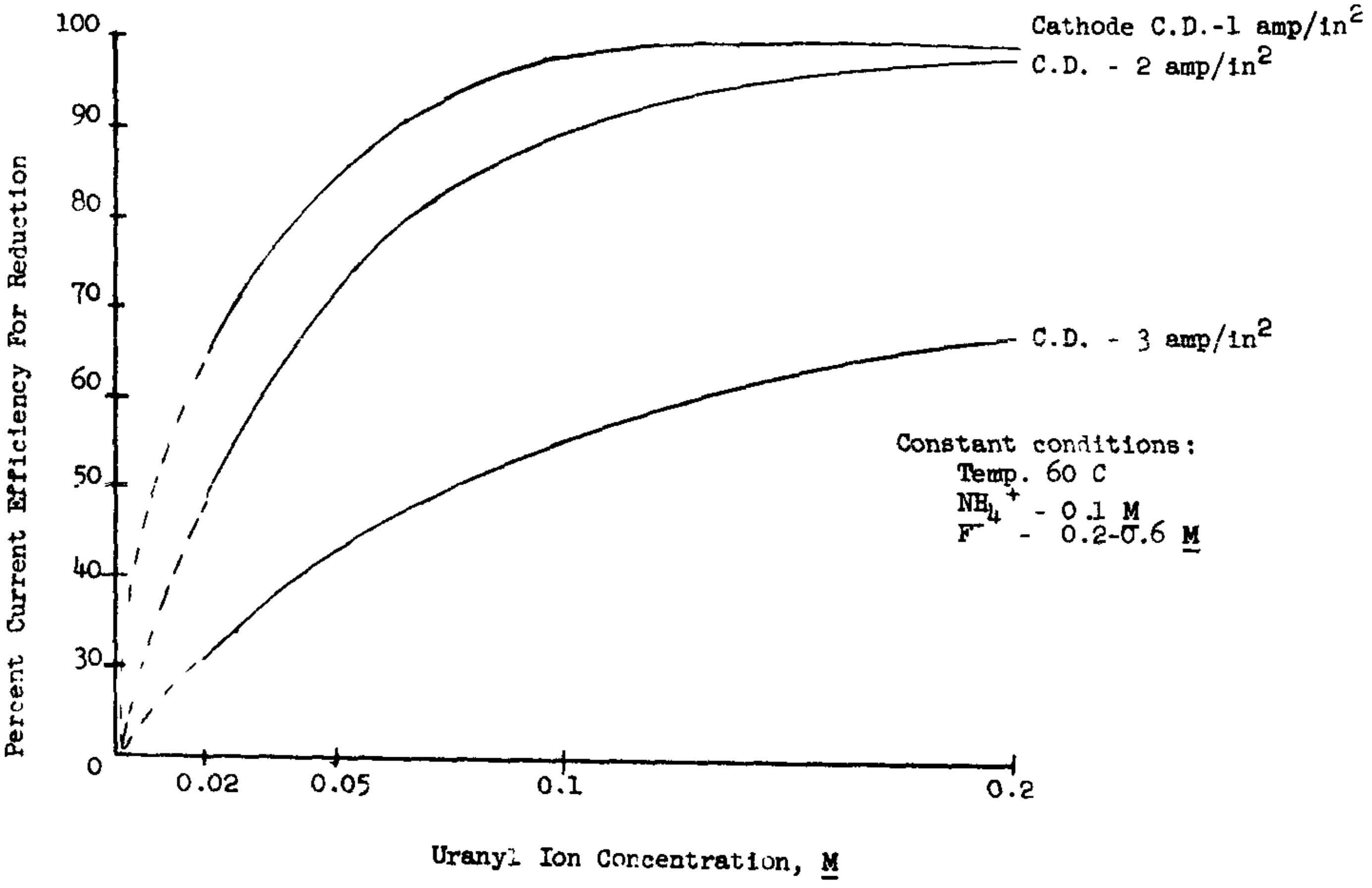
FIGURE 4

## VARIATIONS IN CURRENT EFFICIENCY FOR URANIUM REDUCTION



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low cathode current densities. It is evident that cathode current density must be restricted to about two amps/in$^2$ to obtain greater than 80 per cent efficiency. Operation at 60 C in the presence of a slight excess of fluoride and metal (or ammonium) ions over stoichiometric requirements also increases reduction efficiencies.

d. 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. A small volume of the catholyte and wash liquids are sent to waste while the bulk is concentrated to remove water introduced through the cation membrane and in the product washing step. After cooling to the desired temperature, the catholyte is then recirculated to the catholyte compartment. In continuous operation hydrofluoric acid and the appropriate alkali metal (or ammonium) ion are added to the catholyte to maintain constant composition.

In this external catholyte treatment, the small amount of uranium which can be sent to waste economically necessitates a relatively low catholyte bleed rate. As a consequence, ionic impurities (fission 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. An alternative procedure would be to remove catholyte equivalent to the volume of water introduced during cell operation. Additional processing steps to recover uranium from the bleed would be required but these may be compensated for by an increased decontamination potential.

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e. 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 a 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 5. The degree of uniformity of membrane current density in such a cell is determined by the vertical distance between successive trenches.

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.

f. Chemical Flowsheet

A simplified flowsheet for the preparation of the ammonium salt is shown in Figure 6. For the conditions shown overall current efficiencies

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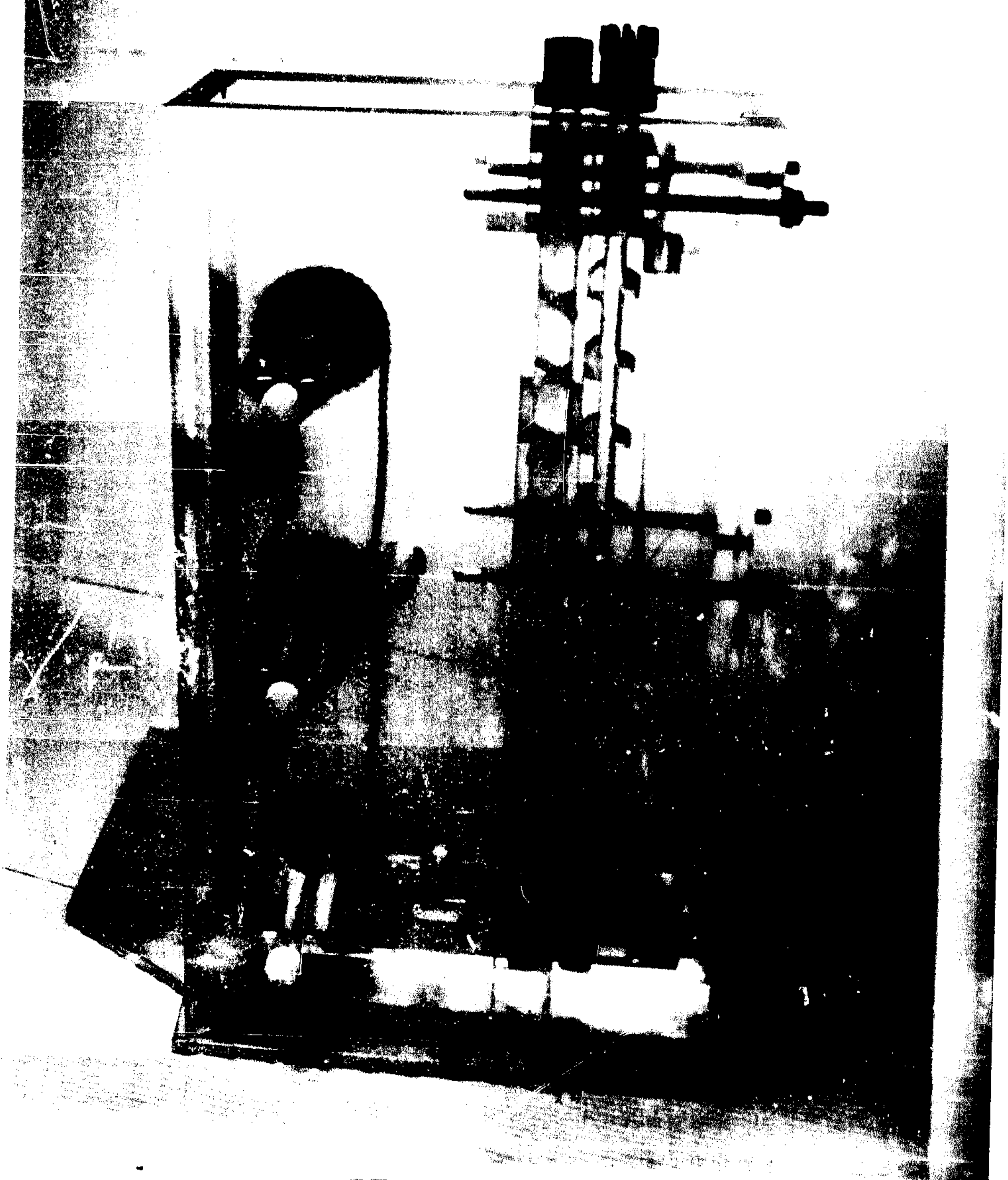

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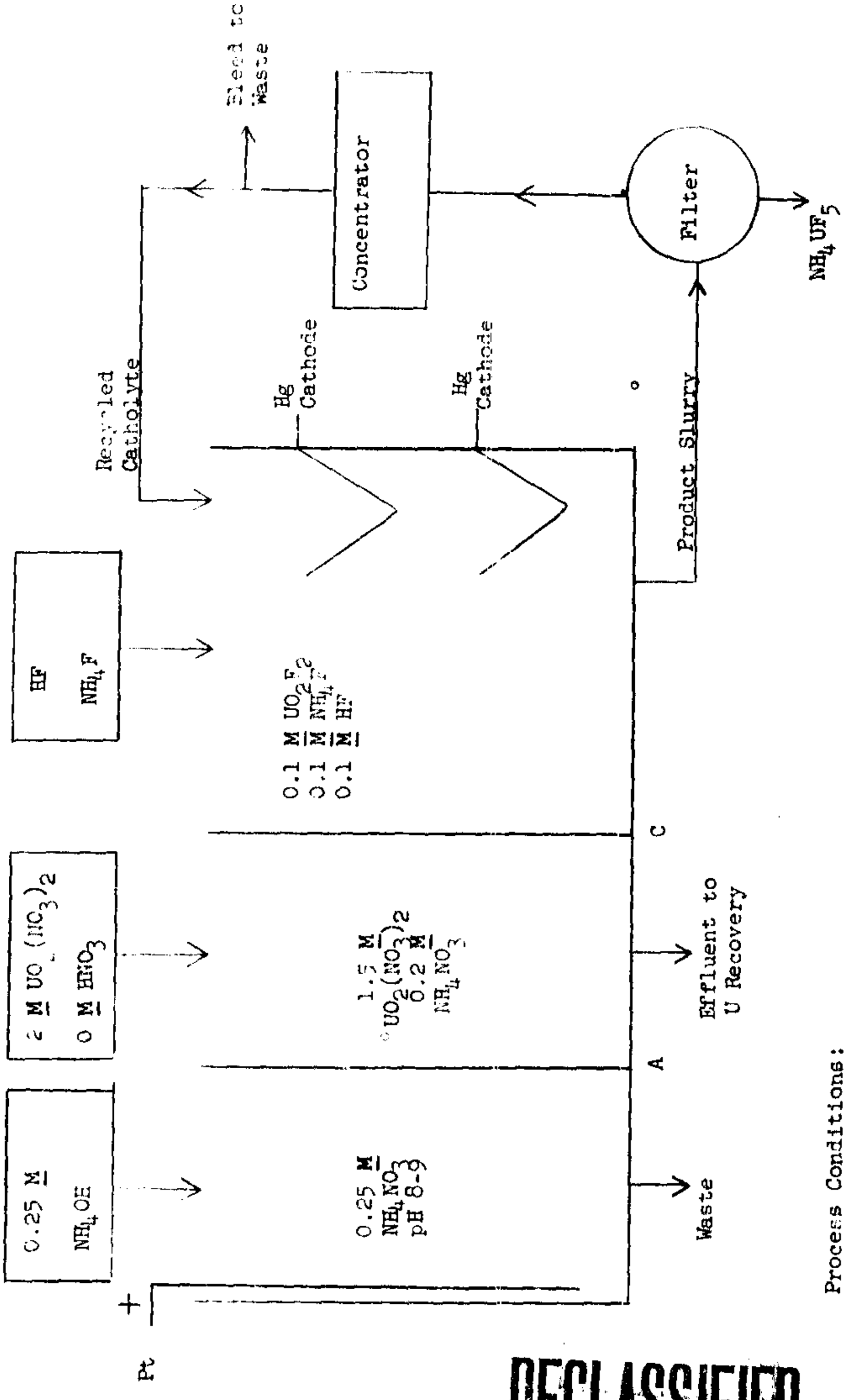
FIGURE 6

## 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 - 2 amps/$in^2$
   Membrane - 1 amp/$in^2$

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in the range 85 to 90 per cent are obtained. The concentration of ammonium nitrate shown in the feed compartment is that obtained at equilibrium as the result of leakage of ammonium ion 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 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

1. Bernhardt, H. A., Gustison, R. A. and Posey, J. C., Thermal Decomposition of the Compound Uranium Tetrafluoride-Ammonium Fluoride, K-410, June 1, 1949. Declassified.

2. Carson, W. N., Jr., A Single Step Process for Conversion of Aqueous UNH into Uranium Tetrafluoride, HWIR 538, HW-32144, June 15, 1954. Confidential.

3. Carson, W. N., Jr., and Van Meter, W. P., Flurex Process - Interim Report, HW-39457, October 11, 1955. Declassified.

4. Marinsky, J. A. and Giuffrida, A. J., Development of the Excer Process II, ORNL 1979, April 17, 1956. Unclassified.

5. Tolley, W. B., Precipitation of Uranium Ammonium Fluoride from UNH Solutions as an Intermediate in the Preparation of Uranium Tetrafluoride, HW-35814, February 1, 1955. Declassified.

[redacted]