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by Continuous Ion Exchange and Electrolysis

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ABSTRACT

Steps in uranium recovery and purification by continuous ion exchange and electrolysis (the Excer process) are summarized.

1.0 INTRODUCTION

Uranium recovery and purification by continuous ion exchange and electrolysis, either independently or jointly in a single process, are being studied.¹⁻³ The function of the ion exchange step is to concentrate, partially purify, and prepare uranium in a suitable chemical form for the subsequent purification step. The function of electrolysis is to provide more purification and reduce UO_2F_2 to $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$. A number of chemical process steps are used for uranium processing, whether from ores to concentrates, to pure metal or hexafluoride, or from spent reactor fuels back to purified uranium. The ion exchange and electrolysis steps described in this report are proposed as shorter and less expensive routes in this uranium cycle. Even these steps may be complicated by attempts to adapt them to the chemistry of existing processes. For this

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reason all uranium sources, or starting materials, will be grouped as follows:

1. Sulfate leach of ores or scrap with uranium the minor acid-consuming material.
2. Chloride leach of concentrates or scrap with uranium the major acid-consuming material.
3. Uranyl nitrate product from solvent extraction processes.

The purpose of this report is to orient interested groups and bring them up to date with laboratory developments. At ORNL a 2-in.-dia. Higgins contactor is installed for anion exchange and a 1-in.-dia. contactor for cation exchange treatment. The electrolytic cell is 6 by 6 in. with 1-in. spacings between the lead anode, membrane, and mercury film cathode. The $UF_4 \cdot 3/4 H_2O$ product is filtered on paper and dehydrated in a magnesium or nickel tube 1.5 by 18 in. long. Synthetic feeds are being used, but any uranium source, including ore leach pulps, may be tested.

This report covers laboratory development only. Filtration and dehydration of $UF_4 \cdot 3/4 H_2O$ are being investigated by C. W. Hancher. Design of a large-scale electrolytic cell is being studied by Ionics, Inc., at Cambridge, Mass.

2.0 ANION-EXCHANGE RECOVERY, PURIFICATION, AND CHEMICAL PREPARATION FOR ELECTROLYSIS

Various uranium eluting agents are used for anion-exchange resins, depending on corrosion conditions, cost, and problems of coupling to adjoining processing steps. For example, nitrates are used instead of chlorides because stainless steel construction may be used. On the other hand, sodium chloride is attractive because of its low cost. Slightly acidified salts are used to decrease the alkali consumption in the subsequent diuranate precipitation.³ To avoid the intermediate precipitation step now required, it is desirable to elute the uranium relatively free from bulk salt or contaminants; the low-bulk-salt eluate can be fed directly to the electrolytic cell. By using concentrated

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brine, 5 M NaCl, or about 8 M HCl, it is possible to displace sulfate and leave the uranium on the resin as a chloride-anion complex. This anionic species is broken by dilution and is eluted with water. Product solutions with uranium concentrations greater than 100 g/liter, as UO_2Cl_2 , have been obtained, with NaCl contamination as low as 0.05 M. Sodium chloride has been used because of low cost and low metal corrosion, but hydrochloric acid is preferred because sodium decontamination is then not required.

Sulfuric acid is used for leaching whenever uranium is a minor acid-consuming element, for example, with Colorado Plateau type ores. In this situation the uranium processing rate is limited by the rate at which the feed volume can be handled, and the sulfate-chloride exchange can be carried out leisurely (Fig. 1).

When uranium concentrates are processed, feed volumes are small because of the high uranium contents, and the sulfate-chloride exchange could limit the production rate. Therefore, the uranium crudes are dissolved in hydrochloric acid and sorbed as the anionic complex directly, which makes a faster treatment cycle. It may be desirable to use the barren waste for makeup liquid to maintain a high chloride concentration. In order to prevent accumulation of sulfate, fluoroide, or phosphate, lime or CaCl_2 may be added to the barren waste and centrifuged (Fig. 2).

3.0 CATION-EXCHANGE PURIFICATION OF URANYL SALTS AND CONVERSION TO URANYL FLUORIDE

The high-degree-of-purification step now used for ore concentrates and spent reactor fuels is solvent extraction in a nitrate system. Cation exchange is particularly suitable for a nitrate system because uranyl ion may be sorbed from $\text{UO}_2(\text{NO}_3)_2$ with low uranium loss and elimination of the nitrate ion. Hydrofluoric acid is a very effective eluting agent for uranium on cation-exchange resins and the uranyl fluoride is readily adjusted for electrolysis. A uranyl chloride solution may be treated as effectively. If conversion of the uranyl salt form is not necessary, at least the cation-exchange step provides significant decontamination¹

Fig. 1. Continuous Anion-exchange Contactor for Treatment of Ore or Scrap Sulfate Leach in Recovery of Uranium.

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Fig. 2. Continuous Anion-exchange Contactor for Treatment of Ore Concentrates and Scrap Chloride Leach in Recovery of Uranium;

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from noncationic impurities (Fig. 3).

If it is desirable to use concentrated NaCl instead of HCl for elution of an anion-exchange column, sodium must be removed by the cation-exchange resin also. Hydrofluoric acid selectively elutes uranium, leaving sodium on the resin. However, enough sodium is removed that a H-form resin scrub is required (Fig. 4).

4.0 ELECTROLYTIC REDUCTION OF URANYL FLUORIDE TO HYDRATED URANIUM TETRAFLUORIDE

In the final design of an electrolytic cell for the Excer process, a cation-exchange membrane was used to prevent fluoride attack on the anode. A plate-and-frame type construction was used for easy maintenance. Engineering development of the cell is continuing. For the laboratory production the following cell (Figs. 5 and 6) was used:

Cell size: 6 by 6 in.

Cathode area: 55 in.²

Cathode material: Falling mercury film on monel screen

Cation exchange membrane: Ionics Inc.

Anode: lead

Electrode spacing: 1 in. between membrane and anode and
between membrane and cathode

Catholyte: usually 0.5 M UO_2F_2 , 2 M HF, and 1 N H_2SO_4
or HCl

Catholyte rate: 40-60 ml/min

Anolyte: 0.5 M H_2SO_4

Anolyte rate: 40-60 ml/min

Temperature: 92-98°C

Current: 100 amp

Voltage: 7-8 volts

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Fig. 3. Continuous Cation-exchange Contactor for Treatment of Solvent-Extraction $UO_2(NO_3)_2$ Product or Anion-exchange UO_2Cl_2 Product in Recovery of Uranium.
Uranium loss, 0.01%.

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Fig. 4. (A) Continuous Cation-exchange Contactor, Na-H-form Resin, and (B) Fixed-bed Cation-exchange Contactor, H-form Resin; Used When 5 M $NaCl$ Is Substituted for 8 M HCl in Anion-exchange Step.

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Fig. 5. Laboratory-scale Electrolytic Cell for Production of $\text{UF}_4 \cdot \frac{3}{4} \text{H}_2\text{O}$ from UO_2F_2 .
Cathode area, 55 in.^2 ; current, 100 amp; voltage, 7-8 volts; temperature, $92-98^\circ\text{C}$.

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Fig. 6 A Three-Stage Electrolytic Cell

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5.0 EXPERIMENTAL WORK

This report is being issued for orientation purposes preliminary to a final experimental demonstration. A 2-in. continuous contactor is being operated to produce UO_2Cl_2 product from synthetic contaminated leach solution. Sulfate feeds have been run and chloride feeds are to be run. Three anion elution systems have been used so far: (1) concentrated brine recycled after removing sulfate as CaSO_4 by adding CaCl_2 , (2) concentrated brine with no recycle, and (3) 8 M HCl with no recycle.

A 1-in.-dia. continuous cation-exchange contactor is on standby for converting UO_2Cl_2 to UO_2F_2 . So far, a fixed bed has been used to save time.

Electrolytic cell decontamination of uranium and preparation of UF_4 was carried out in the cell described in Sec. 4.0.

The $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$ was dehydrated in a magnesium pipe in a tube furnace in a nitrogen atmosphere. Heating from 200 to 400°C was extended over a 2-hr period.⁴

6.0 REFERENCES

1. I. R. Higgins, J. T. Roberts, "Development of the Excer Process. I," ORNL-1696 (March 19, 1956).
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3. I. R. Higgins, "Development of the Higgins Ion Exchange Contactor for the Treatment of Ore Leach Pulps," ORNL-1918 (in press).
4. L. L. Annas, "Dehydration of $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$," CF-56-6-125 (in press).

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7.0 APPENDIX

The following data were obtained from fixed bed or a combination of fixed bed and continuous contactor runs preliminary to a final continuous demonstration.

Experiment No. 1

Feed: Utex diuranate cake, containing 63.6% U; prepared from Utex pulp in 2-in.-dia contactor (see ORNL-1918); dissolved in H_2SO_4 , EMF adjusted to 550 mv (calomel electrode), spiked with fission products

Anion-exchange column: Permutit SK regular, sulfate form, used; 12 M HCl used to convert sulfate to chloride; uranium eluted as UO_2Cl_2 by water

Cation-exchange column: Dowex 50W, 8% cross linked, 50-100 mesh, used; UO_2Cl_2 from anion column made 0.1% in oxalic acid fed to column; eluted with 4 M HF

Electrolysis cell: platinum anode and horizontal mercury cathode, batch operated

Dehydration: in magnesium tube furnace, N_2 atmosphere

Final product:

U(IV)	74.6%	H_2O	0.19%	Ag, Mg, Na, Si	trace
U(VI)	0.73%	Ca	> 100 ppm	B, Al, Ni, Cu, Sn	faint trace
UO_2	2.5%	Fe	10 ppm	Pb	strong
F	23.1%				

Experiment No. 1 (cont'd)

Fission Products	Decontamination Factors			
	Anion Exchange	Cation Exchange	Electrolysis	Total
Gross γ	105	83	8.7	7.6×10^4
Total rare earths	153	9.8×10^3	(background)	1.5×10^6
Zirconium	11.7	> 5.8	(background)	> 68
Niobium	14.7	> 102	(background)	> 1480
Strontium	525	(background)	(background)	> 525
Cesium	7600	(background)	(background)	> 7600
Ruthenium	75	37	(background)	> 275

Experiment No. 2

Feed: Synthetic anion-exchange column product, i.e., UO_2Cl_2 solution prepared from pure UO_3 and HCl ; containing

U	61 g/liter	Fe(III)	0.63 g/liter	Ca	0.29 g/liter
Na	6.9 g/liter	B	1.0 g/liter		

Cation column No. 1, fixed bed: Dowex 50W, 8% cross linked, 50-100 mesh; eluted with 4 M HF; Product, UO_2F_2 , 120 g U per liter, containing

Na	4.25 g/liter	Fe	1.34 g/liter
Ca	0.154 g/liter	HF	1.0 M

Cation column No. 2, fixed bed: Dowex 50W, 8% cross linked, 50-100 mesh, hydrogen form; fed with product from first column; product, UO_2F_2 , 92 g U per liter, containing

Na	0.01 g/liter	Fe	0.89 g/liter
Ca	0.10 g/liter	HF	1.0 M

Electrolysis cell: 6- by 6-in., Ionics membrane, lead anode; operated continuously.

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Experiment No. 2 (cont'd)

Dehydration equipment: magnesium tube furnace; N₂ atmosphere

Final product: tap density 3.4 g/cc

Total U	74.54%	Ca	133 ppm	Al	35 ppm
U(IV)	73.95%	Mg	1.6 ppm	Cr	0.68 ppm
UO ₂	0.27%	Hg	Not detected	Cu	2.6 ppm
H ₂ O	1.08%	Pb	Not detected	Mn	0.1 ppm
F	23.9%	Fe	4.3 ppm	Ni	< 0.4 ppm
Na	112 ppm	B	104 ppm	Si	1 ppm

Experiment No. 3

Feed: synthetic sulfate ore leach containing

U	5 g/liter	B	0.05 g/liter	Th	1 g/liter
V	1 g/liter	Mo	0.1 g/liter	SO ₄	15 g/liter
Fe	50 g/liter	SiO ₂	0.1 g/liter	PO ₄	4.6 g/liter
Mg	2.4 g/liter	Cu	0.1 g/liter	H ⁺	0.1 M
Ca	0.1 g/liter	Mn	0.5 g/liter	EMF	440 mv
Al	0.5 g/liter				

Anion-exchange column, fixed bed: XE-123 resin used; sulfate removed with 5 M NaCl saturated with CaSO₄; uranium eluted with water; product, UO₂Cl₂, 10.4 g U per liter, containing

Ca	2.90 g/liter	Fe	0.078 g/liter
Na	7.1 g/liter		

Cation-exchange column No. 1, fixed bed: Dowex 50W, 8% cross linked, 50-100 mesh, used; eluted with 4 M HF; product, UO₂F₂, 86.0 g U per liter containing

Ca	0.31 g/liter	Na	2.56 g/liter
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Cation column No. 2, fixed bed: hydrogen-form Dowex 50W, 8% cross linked, 50-100 mesh, fed with product from first cation-exchange column; product, UO₂F₂, 57.0 g U per liter, containing

Ca	0.172 g/liter	Fe	0.58 g/liter
Na	0.35 g/liter		

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Experiment No. 3 (cont'd)

Electrolysis cell: 6- by 6 in., Ionics membrane, lead anode; operated continuously (electrolysis mostly below 90°C and product was fluffy $\text{UF}_4 \cdot 2.5 \text{H}_2\text{O}$)

Dehydration equipment: magnesium tube furnace, N_2 atmosphere

Final product:

				Ni	12 ppm	
U(IV)	73.6%	Fe	110 ppm	Mn	2.2 ppm	
UO_2	0.56%	Ca	80 ppm	Cr	12 ppm	
H_2O	1.11%	Mg	5.5 ppm	V, B, Mo,	} not reported	
F	24.0%	Al	12 ppm	SiO_2 , Th		
Na	12.5 ppm	Cu	9 ppm	SO_4 , PO_4		

Experiment No. 4

Feed: synthetic sulfate ore leach; EMF = 450 mv (calomel electrode); containing

U	3.3 g/liter	B	0.002 g/liter	Th	0.2 g/liter
Fe	6.8 g/liter	V	2.5 g/liter	Mg	1.6 g/liter
Al	0.2 g/liter	Mn	1.1 g/liter	PO_4	0.2 M
Mo	0.02 g/liter	Cu	1.6 g/liter	H_2SO_4	0.1 M

Anion-exchange column, 2-in.-dia continuous contactor: Permutit SK regular used; sulfate eluted with 5 M NaCl saturated with CaSO_4 ; uranium eluted with water; product, UO_2Cl_2 , 45 g U per liter, containing

Na	33 g/liter	Ca	2.63 g/liter
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Cation-exchange column No. 1, fixed bed: Dowex 50W, 8% cross linked, 10-50 mesh, used; fed with anion contactor UO_2Cl_2 product, eluted with 4 M HF ; product, UO_2F_2 containing

Na	3.50 g/liter	Cu	0.22 g/liter
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Cation-exchange column No. 2; fixed bed: hydrogen-form Dowex 50W, 8% cross linked, 50-100 mesh, used; fed with UO_2F_2 product from first cation-exchange column; product, UO_2F_2 , 84 g U/liter, containing

Na	0.007 g/liter	Ca	0.120 g/liter
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Experiment No. 4 (cont'd)

Electrolysis cell: 6- by 6 in. continuously operated

Dehydration equipment: magnesium tube furnace, N₂ atmosphere

Final product: tap density, 2.3 g/cc; specific surface area, 2.50 m²/g

Total U	73.4%	Na	465 ppm	Th	12	
U (IV)	71.4%	Ca	270 ppm	B	35	
H ₂ O	1.08%	Mg	1.3 ppm	Ni, Hg,	} not detected	
UO ₂	0.14%	Al	160 ppm	Pb, Mn		
F	22.5%	Cu	10.5 ppm			
Fe	27.6 ppm	Cr	3.7 ppm			

Experiment No. 5

Feed: synthetic sulfate ore leach, EMF 550 mv (calomel electrode), containing

U	5 g/liter	Mn	0.4 g/liter	Mg	1.2 g/liter
Fe	0.14 g/liter	V	0.2 g/liter	Cu	0.5 g/liter
Al	0.2 g/liter	Cu	0.2 g/liter	Ni	0.01 g/liter
Mo	0.01 g/liter	Th	0.2 g/liter	Co	0.01 g/liter
B	0.002 g/liter				

Anion-exchange column, 2-in.-dia continuous contactor: Permutit SK, regular, used; sulfate removed with 5 M NaCl containing no CaSO₄, no recycle; eluted with water; product UO₂Cl₂, 77.9 g U per liter, containing

Fe	0.02 g/liter	Al	0.022 g/liter
V	0.021 g/liter	Na	4.5 g/liter

Cation-exchange column No. 1, fixed bed: Dowex 50W, 12% cross linked, 50-100 mesh, used; eluted with 6 M HCl; product UO₂F₂, 131.6 g U per liter, containing 2.2 g Na per liter

Cation-exchange column No. 2, fixed bed: hydrogen-form Dowex 50W, 8% cross linked 50-100 mesh; fed with product from first cation-exchange column; product, UO₂F₂, 140 g U per liter, containing

Al	0.003 g/liter	Na	0.105 g/liter
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Electrolysis cell: 6- by 6 in. operated continuously

Dehydration equipment: magnesium tube furnace, N₂ atmosphere

Final product: tap density, 3.1 g/cc; specific surface area, 1.1 m²/g

Total U	76.34%	Ca	130 ppm	Ni	2.1 ppm
U(IV)	75.1%	Fe	3.9 ppm	Cr	0.25 ppm
UO ₂	0.64%	Al	30 ppm	B	49 ppm
H ₂ O	0.345%	Mg	6.8 ppm	V	< 5 ppm
F	22.8%	Hg	< 13 ppm	Mn	< 0.25 ppm
SO ₄	0.37%	Pb	60 ppm	Si	0.5 ppm
Na	48 ppm	Cu	1.2 ppm		

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