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FEED MATERIALS PROCESSING STATUS REPORT FOR NOVEMBER, 1956

R. E. Blanco
J. C. Bresee

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CONTENTS

		Page
1.0	Fluorox Process	3
2.0	Excer Process	4
3.0	Ore Processing	5

All studies reported here are preliminary and conclusions are subject to change. The information is published as a formal report only to permit ready dissemination of data to interested persons.

ABSTRACT

Fluorox Process. The UF_6 scrubbing column was operated with incomplete recovery of UF_6. Column modifications are being made. UF_4 was successfully fluidized with nitrogen at 600°C.

Excer Process. Electrolytic reduction cells with cathodes other than mercury were studied. Initial results on chemical reduction with iron or aluminum were promising.

The electrolytic cell flow system was modified.

Ore Processing. One hundred and eighty tons of 0.3% uranium ore was processed in a 13-day test of the 12-in.-dia Higgins contactor at Grand Junction, Colorado with an average uranium recovery of 99.8%.

1.0 FLUOROX PROCESS

In the Fluorox process, UF_4 is prepared by simultaneously reducing and hydrofluorinating uranium oxide. The UF_4 product of this reaction may be either reduced to metal or oxidized to UF_6.

1.1 Larger-scale Studies (J. C. Bresee, J. B. Adams)

Oxidation. In initial tests recovery of UF_6 from the cold trap by scrubbing with water in a packed column were unsuccessful. At a water flow rate of 6000 lb/hr/ft^2, a white mist appeared in the off-gas from the column at all gas flow rates attempted, including extremely low rates. The gas-inlet nozzle clogged soon after startup and was kept clear only with difficulty. The inlet is being redesigned, the monel ferrule packing is being replaced with 1/4-in. nickel raschig rings, and provision is being made for somewhat higher liquid flow rates. If water alone is not sufficient as a scrubbing agent with the improved tower design, a solution of aluminum nitrate or possibly sodium carbonate will be used.

The fluidized-bed reactor was operated for several hours at temperatures up to 675°C, with -40 mesh sand being fluidized with air. Operation was simple and bed temperature control was satisfactory. The maximum steady-state bed temperature attainable with the present equipment is believed to be at least 750°C. Homalite plastic sight glasses mounted on the top flange plate allowed

direct visual observation of the top of the bed. Above 600°C no external light source is required, the red hot walls providing sufficient light. The sight glasses are far enough from the reaction zone to prevent damage by excessive temperatures. A procedure for sampling the bed through a plug valve was demonstrated on sand at 600°C.

UF_4 was fluidized in dry nitrogen for several hours at 500°C to 600°C. A 35 by 100 mesh fraction was prepared from 1/8- by 3/16-in. UF_4 pellets made in the experimental 4-in.-dia reduction-hydrofluorination moving-bed reactor. The procedure involved passing the pellets 3 times through a roll crushing mill followed by screening out the desired fraction. Fluidization was accompanied by some dusting, possibly as a result of some further grinding in the bed.

2.0 EXCER PROCESS

In the Excer process, uranium is converted by ion exchange to a form suitable for electrolysis and is then electrolytically reduced. When the process is applied to ore leach pulps, the unfiltered pulp may be fed directly to the ion-exchange column. With some relatively pure solutions the ion-exchange step may be omitted and the solution electrolyzed directly.

2.1 Laboratory-scale Studies (I. R. Higgins, W. J. Neill)

Ion-exchange Purification. Sorption of UO_2^{++} from a UO_2Cl_2 ore concentrate on a cation-exchange column and elution with HCl followed by electrolysis gave a UF_4 product with no detectable molybdenum. When the cation-exchange step was omitted, UF_4 produced from the same UO_2Cl_2 solution contained 3-38 ppm of molybdenum.

Reduction. Further studies were made on electrolytic reduction of a uranic salt to uranous and precipitation of UF_4 outside the cell. Reductions were performed in cells with nickel or lead cathodes and lead or platinum anodes and a cation-exchange membrane and with a cell using porous carbon electrodes with no ion exchange membrane. Chemical reduction of UO_2Cl_2 with iron and no electrolysis was rapid, complete, and efficient. UF_4 precipitated from a $U(SO_4)_2$ solution contained 4700 ppm of sulfate compared to 70 ppm when precipitated from UCl_4. It is not apparent why sulfate does not wash out easily.

Dehydration. The water in a sample of dehydrated UF_4 exposed to the laboratory atmosphere was:

After	0	hr	0.09% H_2O	After	5	hr	0.40% H_2O
	2		0.26		24		0.14
	3		0.26		72		0.55

2.2 Use of Excer Product in Homogeneous Reactor Studies (C. E. Schilling)

Uranous oxalate for use in preparing uranium-thorium slurries for a homogeneous reactor experiments was prepared from an Excer strip solution of uranous chloride. The uranous chloride was diluted to a uranium concentration of 50 g/liter and heated to 60°C. With vigorous stirring, 1 M oxalic acid was

added slowly. The resulting product was easily filtered, washed on the filter, and air-dried. The product contained 45.2% uranium; the theoretical for uranous oxalate is 45.7%. The chief contaminant was 37 ppm of molybdenum.

2.3 Larger-scale Studies (C. W. Hancher, G. K. Ellis)

Reduction. The new electrolytic reduction cell (ORNL-2209, Sec. 3.2) was provided (Fig. 1) with means for recycling the cell effluent through a separate settler and thickener at 5-10 times the net aqueous feed rate. Mercury may be recycled across the cathode screen surface from the settler at 2-3 times the previous recycle rates in an effort to minimize UF_4 adherence. In the new cell a pressure probe is used to control a liquid level control valve for withdrawing concentrated UF_4 slurry from the system as product. Orifice type flow meters complete with differential pressure cells and water purge are being fabricated and will be used to control the aqueous recycle rate.

A summary of data obtained in completed large-scale reduction runs in the old cell is given in Table 1.

Dehydration. Results of completed dehydration runs, not previously reported, are given in Table 2.

3.0 ORE PROCESSING (C. W. Hancher)

3.1 12-in.-dia Ion-exchange Contactor

In a 5-day test the 12-in.-dia Higgins contactor at the National Lead installation at Grand Junction, Colorado operated at a slurry feed rate of 5 gpm (~6 tons of ore per day, 10% slime). Uranium recovery was 99.25%.

In a 13-day test, made in two parts, 130 tons of Dysart's shaft ore (0.3% uranium) was processed. In the first part of the test, under steady-state conditions, the rate was 7 gpm (580 gal/hr/ft^2, 12 tons of ore per day) and the average recovery in 50 hr was 99.82%. The conditions were:

	Flow Rate (gpm)	Flow Rate (gal/hr/ft^2)	U_3O_8 Conc. (g/liter)	Other Components
Feed	7.0	580	0.98	
Feed wash	0.96			
Strip	0.44	150		0.9 M NH_4NO_3--0.1 M HNO_3
Strip wash	0.57			
Acid wash	0.08			0.5 M H_2SO_4
Waste	8.20		0.002	
Slip water	0.30			
Product	0.60		12.1	
Resin	0.095		65	

Flow balance	101%
Uranium material balance	104%
Slip water ratio	3.2
Pulse frequency	1 every 5 min

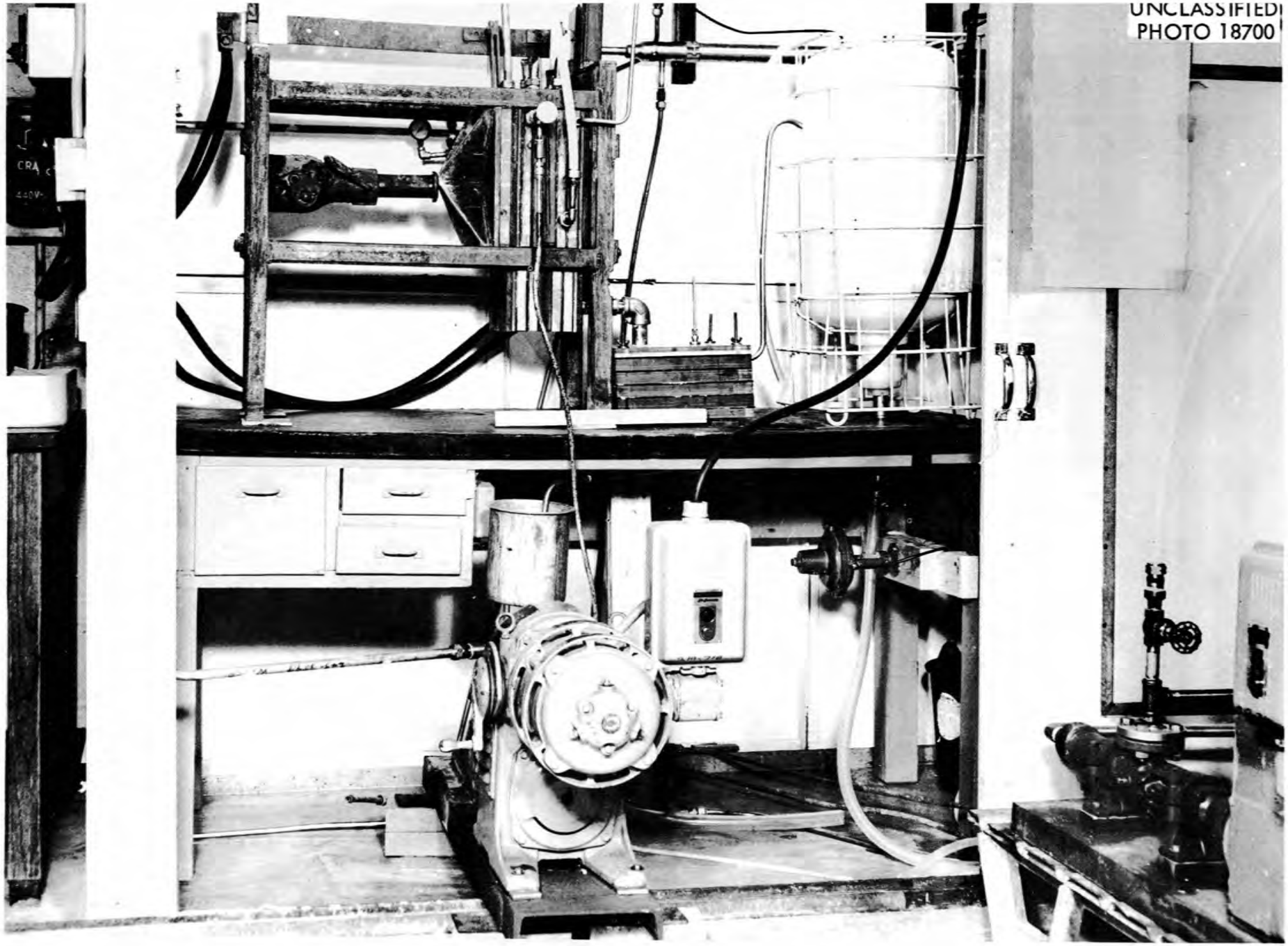

Fig. 1. Auxiliary Equipment for Excer Cell.

Table 1. Excer Process Electrolytic Reduction Cell Runs

Cell cathode: 8 by 8 in.
Anolyte flow rate: 150 ml/min

Run No.	Feed Composition (g/liter) U	Feed Composition (g/liter) SO_4	Feed Composition (g/liter) F	Feed Flow Rate (ml/min)	Current (amp)	Voltage (volts)	Waste (g/liter) U	Waste (g/liter) F	Anolyte Composition (g/liter) Feed and Waste SO_4	Anolyte Composition (g/liter) Waste F	Anolyte Composition (g/liter) Waste U	Product Composition (%) U	Product Composition (%) U(IV)	Product Composition (%) F	Product Composition (%) AOI*	Product Density (g/cc)	Current Efficiency (%)	Reduction Efficiency (%)
1	59.7	42	29	330	300	12.4	14.6	10.0	60	0.19		73.9	65.8	22.6	0.56	2.6		
2	51.5	41	22	300	220	10.4	37.0	25.9	53	0.14						2.0		
3	46.9	50	25	130	240	10.2	40.4	11.6	60	0.23				21.1		2.0		
4	118.5	97	44	180	250	12.0	83.9	29.0	50				65.5			1.6		
5	132	142	54	150			82.9	32.4	50			67.7	65.5	20.1	0.05	2.0		
6	56.5	48	33	100			27.8	16.0	50			69.2	68.2	21.1	0.19	2.6		
7	90.0	48	52	100			51.0	31.2	120	0.54		69.1	68.5	21.7	0.30			
10	139	40	19	100	200	12.0	89.8			0.20	0.04	68.5	68.5	21.7			34	32
11	139	57	15	150	220	13.5	128.0			0.15	1.00	57.5	59.5				8	10
12	109	46	53	150	150	12.0	69.0			0.11	0.23	65.6	66.3	20.8			36	53
14	102	42	39	150	160	14.0	60.8		128	0.12	0.04	70.4	71.4	20.4			42	55
15	103	51	46	150	250	11.5	25.5		202	0.16	0.13	69.4	67.9	22.6			74	63
16	103	68	50	150	240	8.0	51.8			0.19	0.04	70.8	70.0	22.4			48	43
17	98.0	67	22		240	11.2	62.7		162	0.32	0.66	68.2	68.4	22.4			36	33
18	109	56	44		220	11.5	68.7		238	0.22	0.19	71.3	71.0	22.9			37	41
19	106	57	42		250	10.2	85.0		238	0.88	1.39	71.5	71.8	22.4			20	18

* Ammonium oxalate insoluble

Table 2. Excer Dehydration Data

Run No.	Feed Rate (lb/hr)	Feed Composition (%) U	U(IV)	F	H_2O	AOI*	Temp. (°C) Zone 1	Zone 2	Zone 3	Tap Density (g/cc) Original	Final	Sweep Gas (cfm)	Product Wt (lb)	Product Composition (%) U	U(IV)	F	AOI*	H_2O
1	3.4	72.42	70.99	23.0	3.48	0.61	125	250	380	1.9	2.5	0.4		75.24	72.95	22.0	0.58	1.47
2	2.5	73.63	73.35	23.0	3.67	0.10	125	250	380	1.9	2.3			75.24	69.70	23.0		0.45
3	2.4				3.30		125	250	380	1.9	2.4			75.86	71.99		7.50	0.51
4	3.2				3.50		125	250	380	1.9	2.3	0.3						0.37
5	1.5	75.24	75.00		3.50		125	250	380	2.3	2.4	0.3			71.60		0.10	0.56
6		72.81	72.30	22.1	3.41	0.24	125	250	380					76.25	73.90	23.0	7.20	0.26
7	4.0	72.40	72.70		3.50	0.34	125	250	380			0.2		75.14	73.90		0.33	0.65
8	4.4	72.26	74.52		3.26	0.24	125	250	380			0.3		75.52	74.42		0.14	0.51
9	1.8	75.23	70.56	22.7	3.67	0.57	125	250	380			0.34		72.61	71.48	23.1	0.13	0.37
10	1.9	72.40	69.88	22.7	3.58	0.14	125	250	380			0.34		75.71	70.73	23.3	0.23	0.48
11	4.8	74.36			3.50				378			0.34			70.97	22.8	0.15	0.63
12	3.2	67.40	63.83	21.1	9.03	0.25			375			0.34		74.27	60.47	22.8	0.16	0.80
13	2.6	67.35	63.37	20.9	6.90	0.10			385			0.34		73.08	65.53	20.8	0.41	1.10
14	1.8	66.88		20.1	7.07	0.18			370			0.34		72.35	65.04	22.0	0.23	0.67
15									400									
16	0.8	70.90	69.92	22.1	3.90	0.41			400			0.41		72.52	62.30	20.7	0.89	2.32
17	0.8	70.36	70.01	22.2	4.65	0.36			400			0.41		74.00	69.74	22.6	0.59	0.33
18	0.4	70.82	70.11	22.1	3.30	0.29			400			0.41		74.41	67.41	22.5	0.26	0.43
30	2.0		67.8	21.8	3.4	3.3	200	275	390			0.4	8.0					
31	2.4	75.3	73.7	23.5	0.50	0.07	220	320	370			0.4	20.5	69.1	69.7	21.7	2.9	0.54
32	2.9	74.3	73.8	23.0	0.32	0.09	205	300	360			0.4	16.5	73.9	67.6	22.3	1.3	0.47
33		75.5	74.1	22.9	0.27	1.13	205	300	360			0.4	4.5	75.0	67.2	22.0	1.1	0.03
34	0.9	74.8	71.4	23.2	0.43	1.14	210	305	400			0.4	3.3	76.0	71.5	23.1	0.87	0.14
35	2.7	75.1	68.3	22.6	0.21	0.58	210	300	400			0.4	8.0	76.2	69.1	22.5	0.69	0.27

Pure UF_4 = 75.8% U(IV), 24.2% E
Pure $UF_4 \cdot 3/4H_2O$ = 72.7% U(IV), 23.2% F, 4.1% H_2O

*Ammonium oxalate insoluble

In the second part of the test, made to determine the upper limit of the feed flow rate, the concentration profiles of the two sections of the column did not change at a feed rate of 10 gpm (860 gal/hr/ft^2, 16 tons of ore per day):

Distance from top of leading section (ft)	U Conc. (g/liter)
0	0.090
1	0.920
2	0.650
3	0.230
4	0.031
5	0.004
6	0.001
Outlet	0.001

At this rate the pressure drop through the contactor was the limiting factor, about 45 psi in the loading section. The product concentration was somewhat lower because of the undersized slip-water takeoff.

3.2 36-in. dia Resin Test Loop

Installation of the 36-in.-dia resin test loop was completed. The loop has a resin volume of 125 ft^3 and is filled with Permutit SK resin, 10-20 mesh.