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TECHNOLOGY—FEED MATERIALS

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ABSTRACT

Metallex Process. Preliminary experiments indicated that aqueous washing of the thorium amalgam may be eliminated by dissolution of the thorium mercuride in the mercury phase and filtering while hot to separate it from undissolved impurities. Further work with antioxidants in an aqueous wash solution showed that they consistently lower the quality of the metal.

X-ray diffraction studies of thorium amalgam showed that the species of thorium mercurides produced are dependent on time and temperature, but not on washing technics.

Installation of the interim facility for larger-scale production of thorium quasi amalgam by the dry salt flowsheet was completed.

Fluorox Process. The rate of oxidation of UF_4 by air increased rapidly as the temperature was increased from 700 to 800°C. In preliminary oxidation runs in the lined moving-bed reactor, in which graphite pellets were used as the source of the heat, the UF_4 pellets fused. An unlined fluidized bed was designed in which temperature control should be more precise.

Excer Process. The high decontamination factors obtained in electrolysis of a solution of crude ore concentrate produced by solvent extraction indicated that in some cases the ion-exchange step may be omitted.

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1.0 METALLEX PROCESS

In the Metallex process, thorium is recovered from thorium chloride by reduction of the chloride with sodium amalgam; concentration of the thorium amalgam, thus formed, by filtration and pressing; and separation by distilling off the mercury, to leave sintered thorium metal. In processing of thorium metal, the process could start with dissolution of the thorium in boiling mercury^{*} to form thorium amalgam, with the rest of the processing steps the same.

1.1 Laboratory-scale Studies (O. C. Dean, C. P. Johnston)

Dissolution of Metal. To check earlier work, an experiment was carried out to determine the rate of solution of metallic thorium immersed in boiling mercury (356°C). Over a 24-hr period, with time intervals of 1 to 1.66 hr, the dissolution rate averaged 0.143 mg/min/cm².

Amalgam Washing. The use of magnesium or hydrazine dihydrochloride as antioxidants in the wash solution has resulted in high porosity and oxide contents of the sintered metal. Results of preliminary attempts to eliminate the washing step by heating the amalgam to dissolve the thorium mercuride in the mercury and filtering while hot were encouraging.

The addition of 0.03 wt % magnesium to the amalgam, after reduction but prior to washing, increased the reduction step yield from 70-75% to 85-90%. Recovery by immediate filtration or centrifugation was 90-97%. Three experiments were carried out in which dry ThCl₄ was reduced at 130°C with 3.4 M sodium amalgam, agitated at 1700-2000 rpm. Magnesium was added in two of these, and the thorium amalgam was washed with two passes of 3 M aqueous HCl and two passes of water. However, only 10-12% of the magnesium was washed from the amalgam. Of that remaining, 90% followed the amalgam filtrate, and 10%, or 3480 ppm, stayed in the quasi amalgam. Since the boiling point of magnesium is 1110°C, this residue boiled off late in the sintering and not only left 45-1200 ppm magnesium in the metal but increased the free voidage from 10% to 25-30% and the oxide from 1% to 2-4%. In a second series of six runs, results were similar.

* A similar process for recovering uranium from scrap metal is described in power reactor fuel processing reports, CF-56-5-101, CF-56-6-101, etc. (Hermex process).

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The use of 5 g of hydrazine dihydrochloride per liter of wash solution increased the reduction yield to 79%. Thorium recovery was 98% of that reduced. The bulk density of the resulting sintered metal was 8.0 g/cc, the apparent density 11.5 g/cc, the free voidage 30%, and the total voidage 31%. The sintered metal had an inferior appearance, but difficulty in the pressing step caused undue exposure to air and cracking of the cold compact; hence it is not certain that the poor quality of the sinter was related to the use of hydrazine.

The replacement of water by methanol for washing apparently reduced the particle size of thorium mercuride so that filtering and cold pressing were difficult. In addition, the free voidage and the oxygen content of the sintered metal were increased.

In one experiment on elimination of washing, 3.5 wt % thorium amalgam produced by dry sodium amalgam reduction of ThCl_4 was heated to 356°C and the free-flowing liquid decanted while hot.⁴ Approximately 60% of the thorium remained in the vessel as a thick quasi amalgam, while ~40% was either dissolved or suspended in the fluid phase, whose thorium concentration was 1.86 wt %. Centrifugation of the cooled fluid phase gave a supernatant containing 0.31 wt % thorium and a bottom quasi-amalgam phase containing 9.95 wt % thorium. In a second experiment, ThCl_4 was reduced by an 80% excess of sodium in sodium amalgam at 356°C. At the end of the agitation the hot mixture was filtered under argon through a coarse sintered glass filter. The bulk of the mercury passed through the filter, leaving a residue containing dark gray solids and a small amount of quasi amalgam. Centrifugation of the cooled filtrate isolated a small quantity of quasi amalgam at the bottom of the tubes, showing that some of the thorium had passed the hot filter. Large excesses of sodium are known to hinder thorium separation by filtration or centrifugation, and it was not known whether the filter remained at 356°C during the filtration.

Nature of Amalgam. In preliminary work, two species of thorium mercuride were found in thorium quasi amalgam produced by sodium amalgam reduction of ThCl_4 and washing with either aqueous or anhydrous reagents to remove by-products. In the amalgam produced at 250°C and above, ThHg_3 is predominant, but in that produced at 50-150°C, an X phase, whose composition and structure are unknown, with Bragg angles (2θ) of 28° and 58°, is predominant. In further experiments, the method of preparation and aging of the amalgam appeared to determine the species produced; the washing technic appeared to have no effect:

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Amalgam Preparation	Aging Time (days)	Wash Solution	% of total X Phase	ThHg ₃
Dry reduction of ThCl ₄ at 1300C	0	1 M HCl	95	5
	0	Distilled H ₂ O	95	5
	0	Anhydrous methanol	95	5
	7	1 M HCl containing (NH ₂) ₂ ·2HCl	95	5
Dissolution of thorium metal in boiling mercury (3560C)	14	None	5	95
	1-3	None	-	> 99
	1-3	Distilled H ₂ O	-	> 99
	1-3	1 M HCl	-	> 99

Sintering. In two series of vacuum retorting runs by the Metallurgy Division, slow, rather than rapid, elimination of mercury between 140 and 2250C improved the physical appearance and decreased the free voidage of the sintered thorium metal.

1.2 Larger-scale Studies (J. C. Suddath)

The 1.5-gal Dispersall contactor and related equipment have been installed and leak-tested with mercury, water, and helium gas. The facility will be used to study production of thorium quasi amalgam by the dry process.

2.0 FLUOROX PROCESS

In the Fluorox Process, UF₄ is prepared by simultaneously reducing and hydrofluorinating uranium oxide. The UF₄ product of this reaction may be either reduced to metal or oxidized to UF₆.

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2.1 Laboratory-scale Studies (J. E. Savolainen, L. M. Ferris)

Oxidation of UF_4 . The rate of oxidation of UF_4 to UF_6 (plus UO_2F_2) with dry air increased rapidly as the reaction temperature was increased from 700 to 800°C:

Temp. (°C)	UF_4 Wt. Loss in 1 hr (%)	UF_4 Oxidized in 1 hr (%)
600	0.19	3.2
700	0.97	2.7
800	23.5	37.5

UF_5 was identified, possibly as an intermediate in the oxidation reaction. U_2OF_8 , which has chemical and physical properties similar to those of UF_5 , could not be found in the product by x-ray analysis.

For the experiments, about 18 g of UF_4 was placed in a platinum boat in a quartz tube, which was heated to the desired temperature while being flushed with helium. Dry air was then passed over the UF_4 for 1 hr at a time at a flow rate of about 300 cc/min. After the oxidation, the UF_4 was allowed to cool in a helium atmosphere.

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

Pelleting. Procedures for making uranium oxide pellets that will hold up through all subsequent processing steps are being evaluated. Results of preliminary tests indicated that satisfactory pellets can be formed from mixtures of UO_3 , UO_2F_2 , starch, hydrated UO_3 fines, and water (Table 1). The hydrated UO_3 fines had little effect on the pellet strength, but the water content appeared to be critical. New pellets containing no UO_2F_2 were definitely less stable than those containing this compound. The relative instability of the UO_3-H_2O pellets (sample 1) prepared in these experiments compared to those prepared earlier (sample 5) is postulated to be due to some hydration of the UO_3 used in present tests, which probably occurred during a long storage time.

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Table 1. Results of Feed-pelleting Experiments

Sample No.	Amount (g)					Pellet Strength		
	UO ₃	UO ₂ F ₂	Hydrated UO ₃ Fines	Starch	H ₂ O	H ₂ O in Mix (%)	Shaking Time (min)	Survival (%)
Series I: To Determine Optimum Water								
1	50	--	--	--	9	15.2	5	10
2	50	50	--	--	14	12.3	20	72
3	46	46	--	8	14	12.3	20	76
4a	45	45	2	8	15	13.0	20	75
4b	44	44	4	8	15	13.0	20	77
4c	42	42	8	8	14	12.3	20	80
5*	--	--	--	--	--	--	20	90
Series II: To Determine Minimum Water								
1a	50	--	--	--	8	13.5	5	27
1b	50	--	--	--	8	13.3	10	61
1c	50	--	--	4.2	11	16.6	10	54
2	50	50	--	--	10	9.1	15	48
3	46	46	--	8	11	9.9	20	82
4a	45	45	2	8	11	9.9	20	80
4b	44	44	4	8	10	9.1	15	54
4c	42	42	8	8	10	9.1	15	67
4d	38	38	16	8	12	10.7	20	82

Pellet stability was measured by a simple attrition-impact test. Weighed portions of 6 x 8 mesh pellets were placed in 3/4-in.-dia by 3-in.-high sample bottles and shaken in a horizontal plane with 200 3-in. strokes per minute. The stability was measured by the number of surviving +6 mesh pellets. A similar test has been described elsewhere. It should be noted that in this test, because of the long strokes, destruction by impact was accentuated over destruction by attrition more than would be the case in a moving-bed system.

* A sample of UO₃-starch-H₂O pellets prepared at ORNL during a large-scale pelleting run in 1955.

** C. J. Rodden et al., NYO-2043, p. 78.

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Oxidation of UF_4 . The temperature in the oxidation reactor must be in the range 700-900°C because the oxidation rate is very slow at lower temperatures, the reaction is endothermic at higher temperatures, and the melting point of UF_4 is 960°C. An unlined direct-heating fluidized-bed reactor is being investigated for this reaction because of temperature-control problems encountered in the lined, indirectly heated moving-bed reactor (CF-56-6-100, Fig. 3). Contrary to previous belief, there is now some indication that inconel might withstand the corrosive attack of O_2 and UF_6 at 850°C, which may allow elimination of the liner. This would permit precise monitoring of the wall temperature, and would avoid bed overheating since the wall temperature would be the highest in the reactor. In addition, it would permit direct use of the UF_4 , as it comes from the reduction-hydrofluorination reactor, as feed rather than having to adjust its carbon content.

The fluidized-bed reactor (Fig. 1) is to be constructed of schedule 40 inconel pipe. The main reactor section will be a 3-in.-dia pipe, with totally enclosed clamshell heaters covering a 2-ft length of the reactor. Thermocouples welded to the center reactor surface, plus a movable thermocouple well entering through the reactor top will be used to control the bed temperature. Oxygen will enter the reactor through a 1-in.-dia pipe, and the bed will be supported by a porous stainless steel plate flanged to the bottom of this pipe. The reactor will be fed intermittently through the top flange plate, and solids samples will be withdrawn through a 0.5-in.-dia line near the bottom of the reactor. Two of the three top pipe connections will be equipped with transparent eyepieces (probably Homalite plastic) so that the characteristics of the fluidization may be seen. The third connection will be an off-gas connection with a movable thermocouple well for internal bed temperature measurements.

In preliminary corrosion tests, an inconel thermocouple well survived four runs but during a fifth run burned through 3 in. from the end. The tip, which was at all times kept below 850°C, was not badly corroded.

In preliminary fluidization tests with UF_4 of 1- to 10- μ particle size, the bed expanded but fluidization did not occur even with superficial gas velocities of 0.1-0.6 fps. These velocities are far in excess of fluidization velocities calculated from existing correlations based on experimental data for larger-sized particles. This anomalous behavior of fine powders has been noted before.*,** Gas flow appeared

* R. H. Wilhelm, M. Kwauk, Chem. Eng. Prog., 44: 201 (1948).

** L. J. Jolley, J. E. Stanton, J. Appl. Chem., 2, Suppl. issue 1: 562 (1952).

FIGURE 1
EXPERIMENTAL FLUIDIZED BED
OXIDATION REACTOR

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to be restricted chiefly to fissures through the expanded bed. Intense, erratic bubbling and channeling occurred from time to time in the bed, with spouting noticeable at the bed surface. Material at the wall was usually quiescent, though bubbles could occasionally be seen. Slugs of material that rose several inches before disintegrating were noted. There was some indication of the effects of static electricity, with material clinging to the walls over large areas of the tube. Successful fluidizing of coarser particles with nitrogen has been demonstrated,* and coarser material is being obtained for testing.

These tests were made in a 3-in.-dia glass reactor with a fritted glass distributor and support plate. Auxiliary equipment included a rotameter for metering dry nitrogen gas, differential manometer across the column, and a bag filter at the top of the column to prevent dust loss.

In the moving-bed reactor, a refractory liner was used to prevent corrosion of the inconel walls. The liner cannot be made leaktight, and heat is supplied internally. The exothermic oxidation of hydrogeneous matter cannot be used to supply heat since the water vapor formed would convert the UF_6 to UO_2F_2 .

In preliminary tests, combustion of the small amounts of carbon, 0.1-1 wt %, remaining in the UF_4 from the reduction reaction gave insufficient heat. Even when finely divided carbon was added to 2%, moving-bed temperatures did not exceed $500^{\circ}C$. In several short runs with a 50-50 mixture of UO_2F_2 pellets and graphite pellets, the feed was easily ignited when preheated to $500-600^{\circ}C$ and dropped into dry oxygen at $100-200^{\circ}C$. However, even though control thermocouples never read higher than $850^{\circ}C$, the pellets fused.

Since thermocouples mounted at the reactor liner surface would not record the maximum temperature of the bed, an inconel thermocouple-probe was mounted through the top, along the axis of the reactor, and connected to an individual indicator-recorder rather than to the multi-point instrument used for all other thermocouples measuring temperatures in the same unit. The temperatures recorded by the thermocouple-probe could be controlled smoothly by controlling the oxygen feed rate to the reactor, but this apparently was a very poor indication of the highest temperature in the bed. It is probable that with the large, discrete carbon particles, regions immediately adjacent to the carbon are several hundred degrees hotter than the thermocouple within the probe. The more uniform the dispersion of carbon through the uranium,

* R. W. Blandell, RDB(s)-TN-2083 (1953).

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the less likely is overheating to occur. The problem of detecting bed temperature precisely enough for control still remains. The thermocouple-probe will be supplemented by an optical pyrometer to allow reading of the bed surface temperature.

The screw feeder used to meter feed from the preheating section to the reactor proper was calibrated. A delivery rate of 1/15 lb per revolution was found to be approximately constant for rates of 4-13 lb/hr. To permit lower feed rates with sufficient power to maintain a constant delivery rate, the diameter of the pulley drive on the feed screw shaft was increased from 3 in. to 5 in.

A report was prepared, "Fluorox Moving-bed Process for Producing UO_3 , UF_4 , and UF_6 : Bibliography," J. E. Moore, ORNL-2117 (35%).

3.0 EXCER PROCESS

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

3.1 Laboratory-scale Studies (I. R. Higgins)

High decontamination factors were obtained in anion-exchange and electrolysis processing of synthetic sulfate leach pulp:

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Contaminant	Amount (ppm)		
	In Feed	In Ion-exchange Product	In Electrolysis Product
Fe	26,000	310	15
Al	36,700	16	19
Mg	880,000	8	5
B	367	2	4
Mn	183,000	0.5	0.3
Cu	36,700	445	11
Cd	18,300	< 40	Not detected
V	110,000	105	Not detected
Ca		500	350
Cr		2	3
Mo		330	10
Na		1,890	13
Ni		2	2
Si		3	Not detected
Hg			Not detected
Pb			Not detected
Ag			4

The experiments were made in the 2-in.-dia continuous contactor. The uranium was sorbed on Permutit SK resin, sulfate was removed with 8 M HCl, the UO_2Cl_2 was eluted with water, HF was added, and the $\text{UO}_2\text{Cl}_2\text{-HF}$ solution was electrolyzed.

Decontamination in the electrolysis step alone was great enough that in some cases elimination of the anion-exchange step may be possible:

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Contaminant	Amount (ppm)		
	In Feed	In Electrolytic Product	In Product of Anion Exchange and Electrolysis
Fe	65,000	141	78
Al	27,500	2,280	88
V	7,350	48	Not detected
B		66	11
Ca	1,060	75	173
Cd			Not detected
Cu	298		160
Mg	78	9	0.3
Mn	1,130		5
Mo	21,000	44	2
		1,400	7
Na	14,200		
Ni			350
Si	490	4	1
K		11,000	
Cr	375	15	Not detected
Ag			
Hg			Not detected
Pb			7
Ce		< 330	
La		< 330	< 1
Gd		< 33	
Y		67	3
Yb		33	1
Dy		< 67	Not detected

For these experiments, part of a strong HCl solution of ore concentrate (Bureau of Mines, Salt Lake City, Dow organic phosphate process) to which HF had been added was electrolyzed directly. Another portion was sorbed on Permutit SK resin and eluted with water before the HF was added. Analysis of the 60% HF used showed it to contain 55 ppm of boron. Copper in the products probably came from a copper coil used to preheat the solution and nickel from a stainless steel cathode support that was not sufficiently protected. No explanation is offered for the high calcium.

Photo-17855
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Fig. 2

Excer Electrolytic Cell II, 128-in.² Cathode

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Fig. 3

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Fig. 4 Water in UF_4 Product as a Function of Time.

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3.2 Larger-scale Studies (C. W. Hancher)

Reduction. An electrolytic reduction cell (cell II) with a 128-in.² cathode, anode, and membrane was constructed (Fig. 2). It has a capacity of 65 lb of UF_4 per day with 95% current efficiency. Feed is introduced in a parallel manner at the top, and the catholyte and $\text{UF}_4 \cdot 3/4\text{H}_2\text{O}$ slurry are removed together from the bottom and separated outside the cell. The anolyte is fed to the anolyte compartments in series. The falling-film mercury cathode consists of metal screen inserted into a mercury header. Mercury is pumped into this header, forming a film cathode to distribute the current from the cell and a surface for the UF_4 to be plated onto, from which it can be easily removed. UF_4 adheres strongly to the metal surface, and has a high resistance to current flow. In cases where the mercury flow stopped and allowed the UF_4 to plate on the screen (Fig. 3), the cell resistance became too high for operation. Shakedown runs on the equipment have been made, and the cell is operating satisfactorily.

A similar cell, with a rated capacity of 240 lb of UF_4 per day at 95% current efficiency, is being designed by Ionics, Inc. It has a 450-in.² cathode, and will be designed to operate at 2 amp/in.² For a plant producing 5000 tons of UF_4 per year, 160 such cells would be needed, with a total current load of 144,000 amp.

Dehydration. In 14 test runs in the 3-in.-dia, 6-ft-long nickel ribbon-flite dehydrator (CF-56-7-100, Fig. 3), UF_4 product with less than 0.5% water has been obtained in 90 min heating (Fig. 4). The specification aimed at is 0.03%. The first foot of the tube was kept at 125°C, the next 2 ft at 250°C, and the last 3 ft at 280°C. In the five products for which analyses have been completed, tap densities have varied from 1.9 to 2.3 in the feed and from 2.3 to 2.5 g/cc in the product. Both UO_2 and UO_2F_2 have been high in the products, probably as a result of insufficient washing of the hydrate after filtration and incomplete sweeping of oxygen from the dehydrator prior to the start of the runs. The scatter in the data for heating time vs. H_2O remaining in the product may be due to less efficient mixing in the thicker beds that result as the feed rate increases.

MWG/lk

Previous reports in this series were CF-56-5-100 for May (30¢), CF-56-6-100 for June (30¢), and CF-56-7-100 for July (30¢). The next will be CF-56-9-100 for September (25¢).

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