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PROCESS DEVELOPMENT QUARTERLY REPORT, PART II

by

W. M. Leaders and Pilot Plant Personnel

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GENERAL INTRODUCTION

During the third quarter of 1953, major emphasis of the development program was on metal quality projects and development of processing methods for new refinery feeds.

Casting of large uranium ingots has been accomplished to determine their adaptability to the FMPC rolling mill.

Satisfactory methods have been developed for extracting Rand ore refinery feeds.

A new investigation has been started with the objective of producing ingot shapes directly from uranium bomb reductions. As a beginning step, uranium tetrafluoride bomb charges up to 650 pounds have been fired in the pilot plant.

Experimental work on projects concerned with other process operations have been continued. These include further refinement of the slag liner grinding circuit, pilot plant testing of the Waxco process, cooperative testing of new development by production personnel, alloy production, and initial operation in the ceramics pilot plant.

The laboratory program for the third quarter of 1953 is reported in Process Development Quarterly Report, Part I, NYO-1357.

CONCLUSIONS

1. Satisfactory uranium recovery from Rand ore digest slurries containing 3 lbs/gal uranium was obtained by addition of calcium and magnesium nitrates to an ionic strength of the salt background of 7. Scaling problems encountered in extraction of Rand ore has been severe, especially when attempting to recycle raffinate to reduce salting agent requirements. The use of iron as an additional salting agent has been necessary to reduce the problems encountered with Rand ore.
2. Satisfactory uranium recovery from MCW raffinates has been obtained in pilot plant testing of the Waxco process. Major problems to be resolved are: type of contacting method to minimize cost, and improvement of the physical properties of the Waxco agent.
3. In the bomb reduction of uranium much of the difference between theoretical and actual yield is made up of small pellets of metal trapped in the slag. Pilot plant development has demonstrated that these pellets can be readily separated from the slag in the proposed slag grinding circuit. Development work during this quarter indicates the feasibility of internal recycle of these pellets in the reduction bombs thereby effectively increasing bomb yields.
4. Preliminary investigation of large uranium tetrafluoride reduction bombs was made. Successful reduction of 650 pounds per bomb was accomplished in slag lined reactors.
5. Development and production of uranium alloys by co-reduction has continued. These alloys included: uranium-molybdenum, uranium-zirconium, uranium-chromium, uranium-niobium, uranium-vanadium, and uranium-tungsten. Some of these were cast into ingot form.
6. The use of "Hotop" molds consistently produces best ingots from the standpoint of internal soundness. Pilot plant casting of nominal 1000 pound ingots has revealed many design changes that will be required if these large ingots are to be produced in production equipment to increase plant capacity. The geometry of these large ingots should simplify the problem of securing complete soundness.
7. Production scale testing of Black Oxide feeds salted with calcium and magnesium nitrates has demonstrated the feasibility of such operation with or without partial raffinate recycle. These tests emphasized the necessity for more careful control of both feed makeup and extraction column operation when using straight salted Black Oxide feed.

ETHER EXTRACTION OF URANYL NITRATE USING A FOUR-INCH JET MIXER COLUMN

by

J. L. Corder

A. M. Kirby

I. Introduction

Current processing of uranium bearing ores at Mallinckrodt Chemical Works includes a two cycle diethyl ether extraction of aqueous uranyl nitrate solutions. The first cycle extraction achieves uranium recovery with gross purification from solutions prepared by the nitric acid digestion of the raw feed material. The second cycle extraction is a purification of the first cycle product based on the relative solubility of uranyl nitrate and contaminating ions in ether and water.

A prime requisite for satisfactory uranium recovery during the first cycle extraction is the presence of various soluble metallic nitrates in the uranium solution to serve as salting agents. Past, and some current, feed materials for plant use have contained sufficient nitric acid soluble metallic compounds to satisfy this salting agent requirement. Blending of various salted and unsalted feeds provided a means for processing the several feeds received at the MCW refinery. However, an increase in the proportion of unsalted feed materials indicated that additional salting agent would be required.

An investigation of salting agent requirements for various unsalted feeds was initiated in the fall of 1952, and has continued to be of major importance through this quarter.

The investigations completed this quarter have included several series of runs to determine the extraction efficiency and physical operation in a four inch glass jet-mixer column when:

- 1) Extracting salted Rand digest slurries,
- 2) Extracting Vitro Black Oxide digest liquors and,
- 3) Using dolomite as a source of salting agent.

Operational and analytical data for all runs and a glossary are included in the appendix.

The description and discussion of previous investigations are included in earlier reports^{1,2,3}

¹ Rueble, A. E., and Leaders, W. M., Research and Development Progress Report, Mallinckrodt Chemical Works, January 15, 1953, (NYO 1352), p. 25 - 46.

² Leaders, W. M., and Miller, E. I., Process Development Quarterly Report, Part I, Mallinckrodt Chemical Works, April 15, 1953, (NYO 1353), p. 8 - 45.

³ Leaders, W. M., and Miller, E. I., Process Development Quarterly Report, Part II, Mallinckrodt Chemical Works, July 15, 1953, (NYO 1356), p. 76 - 112.

II. Experimental Equipment

The pilot plant jet-mixer column is constructed of four inch, Pyrex glass pipe and a 12 inch stainless steel decanting section assembled as shown in figure 1. The central four, four inch glass tees are mixing sections and are separated by three foot lengths of four inch Pyrex glass pipe which serve as separating sections for the ether and aqueous phases.

Details of a typical mixing section are shown in figure 2. From the $\frac{3}{16}$ inch stainless steel flange on each mixing tee a $\frac{3}{4}$ inch portable pump driven by a $\frac{3}{4}$ HP, 3600 rpm, class I, group D explosion proof motor. This pump discharges through a $\frac{1}{2}$ inch line to a rotometer and, thence, back through the mixing tee flange to a "splash plate" mixing device in the column (see figure 3). The flow rate can be controlled from about 2 to 10 GPM by means of a valued, $\frac{1}{2}$ inch recycle line on the outlet of each pump and a valve on the pump discharge line re-entering the column. The discharge line is also equipped with a 0 to 60 psi, pressure gauge, and a $\frac{1}{4}$ inch sample tap. An orifice with a $2\frac{1}{2}$ inch diameter hole is installed above each mixing tee as shown in figure 3. This orifice is an inverted frustrum of a hollow cone and acts as a funnel to direct all of the aqueous phase into the area of maximum agitation.

The bottom of the column, below the last 3 foot glass settling section, consists of a 4 inch Pyrex glass pipe tee containing a stainless steel float. This float maintains an aqueous-organic interface at the bottom of the column by activating a compressed air control valve on the $\frac{3}{4}$ inch line discharging raffinate from the column to an ether stripper. Ether feed, pumped from a brine cooled storage tank with a $\frac{3}{4}$ -CG-1 Worthington pump, is metered through a rotameter and introduced into the bottom of the column through a $\frac{1}{2}$ inch line. Introduction at a point several inches above the aqueous-ether interface prevents formation of emulsions.

A 4 foot long, 12 inch diameter, stainless steel decanting section is located above the top mixing tee. A mixture of aqueous feed and organic phase are introduced into the column at this decanter as shown in figure 4. A $\frac{3}{4}$ inch stainless steel line leads from the side of the decanter at a point 12 inches from the top, to the suction of a $\frac{3}{4}$ inch portable pump powered by a $\frac{3}{4}$ HP, 3600 RPM, class I, group D explosion proof motor. This pump discharges through a $\frac{1}{2}$ inch line and a rotameter to a 5 ft. shell and tube heat exchanger where the ether is cooled. From this heat exchanger, the ether is jetted past the bottom of a Pyrex glass mixing chamber constructed of a 4 inch glass tee and cross assembled as shown in figure 4.

Aqueous feed, pumped from a 200 gallon feed tank by a $\frac{3}{4}$ -CG-1 Worthington pump, is introduced through a $\frac{1}{2}$ inch line into the bottom of a constant head tank. A 1 inch overflow line recycles feed slurry from this tank back to the feed tank. The height of the liquor in the head tank is varied by means of an adjustable, 2 inch diameter standpipe, feeding the 1 inch overflow line, so as to control the feed rate discharging from the constant head tank through an orifice into the glass mixing chamber.

FIGURE-1
PILOT PLANT JET MIXER EXTRACTION COLUMN

FIGURE-2
TYPICAL MIXING SECTION ON JET MIXING COLUMN

FIGURE-3

FIGURE - 4

FEED INTRODUCTION SYSTEM ON JET MIXER COLUMN

The ether-aqueous feed mixture is drawn from the bottom of this mixing chamber through a $\frac{3}{4}$ inch line to the suction of a $\frac{3}{4}$ inch portable pump. An automatic valve on the $\frac{1}{2}$ inch discharge line from this pump is actuated by a float which maintains a constant head of liquor in the mixing chamber. From the pump, the ether-aqueous mixture enters a brine cooled double pipe heat exchanger, and after being cooled, is introduced into the decanter through a $\frac{1}{2}$ inch line discharging tangentially along the wall about 2 feet from the top of the decanting section.

Above the decanting section is a 4 foot length of 4 inch Pyrex pipe and at the top of the column, a 4 inch Pyrex glass tee. A $\frac{1}{4}$ inch stainless steel pipe, extending from the top of the column about 3 feet down into the 4 foot length of glass pipe, serves to introduce a scrub water spray into the exit ether extract to reduce the carry over of impurities with the ether extract. The ether extract overflows through a $\frac{3}{4}$ inch line on the side outlet of the tee at the top of the column to a re-extraction column where the uranyl nitrate is removed by a water strip and the ether recycled to a storage tank for re-use.

Both the extraction column and the mixing chamber are vented to relieve any pressure developing in the system. A 0 to 60 psi, pressure gauge is installed at the bottom of the column as a further safeguard. Korosel gaskets with painted cast iron or aluminum flanges are used in assembling the column.

III. Experimental Procedure

The procedure for starting and operating the jet-mixer extraction column is outlined below:

The desired aqueous feed is pumped into the ether pilot plant feed tank from a storage tank where it has been agitated for at least one hour at a temperature of about 150°F.

The column is filled with diethyl ether, the continuous phase, and the ether rotameter is set to establish the desired flow rate. Brine is introduced to all coolers in the ether system. All the column mixing pumps, including the organic recycle pumps on the feed system, are started and adjusted to the proper flow rates.

The desired scrub water flow rate is set with the rotameter to feed scrub water to the top of the extraction column.

The proper orifice is installed in the constant head feed tank and the overflow standpipe adjusted to give the proper aqueous feed rate. The aqueous feed pump is started to deliver aqueous feed to the constant head tank. The feed pump discharge valve is regulated to establish an overflow from the constant head tank free from surges. Aqueous feed flows from the constant head tank into the ether-aqueous mixing chamber and is immediately entrained with the stream of recycle ether from the decanter section of the column. The ether-aqueous mixture is pumped through a brine cooled double-pipe heat exchanger to remove the heat of mixing and fed into the decanter section. A level control valve in the

mixing chamber adjusts the recycle flow rate and thus maintains a constant head above the ether-aqueous mixture pump.

The aqueous phase passes through the column and collects in the bottom tee. When the proper ether-aqueous interface is established, an interface control float operates the raffinate discharge valve to maintain the interface and to discharge raffinate into the stripper. When the raffinate starts to flow, entrained ether is removed in a countercurrent steam-heated raffinate stripper. The ether is condensed and recycled. The stripped raffinate discharges by gravity into a storage tank.

The ether extract overflows at the top of the extraction column to the bottom of a re-extraction column. When the re-extraction column is about half filled with ether extract, water is sprayed into the upper portion of the column at the flow rate necessary to completely strip the uranyl nitrate from the ether. The stripped ether overflows the top of the column to an ether storage tank. This stored ether drains by gravity through a water separator to the ether feed tank from which it is recycled to the extraction column.

The aqueous phase, containing the uranyl nitrate, collects at the bottom of the re-extraction column. When the proper interface is established, the aqueous phase flow to a steam-heated ether stripper is controlled by an interface control float similar to the raffinate control valve. The ether free aqueous phase then flows to a storage tank. The vaporized ether is condensed and returned to the ether storage tank.

During the entire run (normally of four hours duration) operating conditions are checked periodically. The operating data tabulated below (together with typical values) are recorded every half hour:

	Type of Feed	
	Filtrate	Slurry
1) Ether Flow Rate	72 GPH	72 GPH
2) Organic Overhead Recycle Rate	225 GPH	216 GPH
3) Scrub Water Rate	1.2 GPH	1.2 GPH
4) Column Mixing Pump Rate	3 GPM	3 GPM
5) Aqueous Feed Flow Rate (Calculated from periodic measurement of the volume in the feed tank)	45 GPH	36 GPH
6) Column Mixing Pump Pressure	20-30 psi	20-30 psi
7) Re-extracted Ether Specific Gravity at 70°F	0.708-0.720	0.708-0.720
8) Aqueous Feed Density at 100°F	58-64° Be	58-64° Be
9) Raffinate Density at 80°F	30-40° Be	30-40° Be
10) Ether Feed Temperature	60°F	60°F
11) Aqueous Feed Temperature	100-110°F	100-110°F

	Type of Feed	
	Filtrate	Slurry
12) Ether Recycle Temperatures		
Before Cooling	80°F	80°F
After Cooling	70°F	70°F
13) Ether-Aqueous Mixture Temperatures		
Before Cooling	80°F	80°F
After Cooling	70°F	70°F
14) Column Mixing Pump Temperatures		
No. 1 (bottom pump)	85°F	85°F
No. 2	90°F	90°F
No. 3	90°F	90°F
No. 4 (top pump)	85°F	85°F
15) Final Raffinate Temperature	215-225°F	215-225°F

After one hour of operation to establish equilibrium in the extraction column, a measured quantity of each of the samples listed below is taken every half hour for the duration of the of the run. A composite of each group of samples is made and a portion submitted for the analyses as tabulated below:

<u>Sample Source</u>	<u>Analyses Requested</u>
1) Ether Feed	U
2) Aqueous Feed	U, HNO ₃ , SO ₄ , PO ₄ , Fe, Ca, Mg
3) Ether Extract	U
4) Raffinate	Soluble U, Insoluble U, HNO ₃ , Ether
5) Aqueous Phase from the top of the Extraction Column	Soluble U, Insoluble U, HNO ₃ , Ether

Correlation of results by comparison of raffinate uranium values must be restricted to runs in a single series because variations in feed material change the equilibrium distribution coefficient. A more extensive correlation of results between series of runs is accomplished by an ether extraction of each raffinate to obtain the following information:

- 1) The amount of uranium left in the raffinate after one additional stage of extraction.
- 2) A distribution coefficient for the raffinate which might be compared with that of other raffinates.

The raffinates extraction procedure is as follows:

One hundred fifty milliliters of unde-etherized raffinate is shaken with 300 milliliters of neutral diethyl ether in a separatory funnel. The two layers are allowed to separate after each of two shakeout periods of about three minutes. The final volume of each layer and emulsion, if any, are noted. Both the ether and aqueous phases are analyzed for uranium content.

A distribution coefficient is calculated for each raffinate by dividing the grams per liter of uranium in the ether phase by the grams per liter of uranium in the aqueous phase. A distribution coefficient of 1.0 or more indicates that the raffinate was still chemically extractable, but that the uranium was not extracted due to physical characteristics. A low distribution coefficient (<1.0) indicates satisfactory extraction mechanically with little potential chemical extractability.

IV. Experimental Results

A. Extraction of Rand Ore Digest Liquors

Rand ore is the uraniferous product from the recently developed process for reworking African gold mine residues. A brief description of the process is given:

The finely ground cyanide tailing from the gold refinery is digested in sulfuric acid. The soluble uranium in the filtrate is then extracted on an ion exchange resin. Uranium is washed from the resin with an ammonium nitrate solution and then precipitated from the solution with ammonia. The precipitated ammonium salts of uranium are then filtered, pelletized, dried, and calcined to obtain the final product.

Analyses of three lots of Rand ore received at the Mallinckrodt Chemical Works Refinery are tabulated below:

Assay	Lot SA-2	Lot SA-10	Lot SA-22
Calcination Temp., °C	Around 700	Around 700	Around 500
% U	74.4	73.9	68.0
% H ₂ O, dried at 100°C	0.99	-	0.96
% SO ₄	6.31	6.50	9.14
% NH ₃	0.13	-	2.64
% SiO ₂	1.41	1.37	1.07
% PbO	-	<0.01	-
% P ₂ O ₅	0.07	0.08	0.04
% V ₂ O ₅	-	0.06	-
% Fe	0.50	0.44	0.27
% MoO ₃	-	<0.01	-
% CaO	-	0.22	-
B ppm	<10	<5.0	<10

A laboratory investigation^{4,5} of various Rand ore samples indicated that some form of silicious gel produced during nitric acid digestion caused emulsification during ether extraction.

⁴ Rueble, A. E., and Shepardson, J. U., Process Development Quarterly Report, Part II, Mallinckrodt Chemical Works, April 15, 1953, (NYO-1354), P. 22-23.

⁵ Rueble, A. E., and Shepardson, J. U., Process Development Quarterly Report, Part I, Mallinckrodt Chemical Works, July 15, 1953, (NYO-1355) p. 16-19.

Additional study showed that emulsion difficulties might be partially alleviated by proper calcination. However, calcination at temperatures above 500°C was reported as possible of rendering some of the uranium insoluble in nitric acid.

A shipment of Rand ore Lot SA-10 was received for pilot plant study about the time this laboratory investigation was completed. Scheduling of Rand ore as a plant feed material beginning September 1, 1953, necessitated initiation of pilot plant investigation before any additional laboratory work could be accomplished.

1. Extraction of Rand Ore Lot SA-10

Rand ore Lot SA-10 was a heterogeneous mixture of dark green to light yellow pellets. The variation in color was probably due to variation in temperature within the furnace during calcination.⁶ Beaker digestion of this material indicated that a warm nitric acid digestion (120-130°F) would produce a final slurry containing less wet solids than a hot digestion (190-200°F). Since past work has indicated that emulsification increased with increased wet solids, warm digestion was used for most of the pilot plant aqueous feed preparations.

An exploratory series of runs was made to determine the optimum salting agent requirement. The successful use of $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ as salting agent in black oxide slurries⁷ suggested that these salting agents might be used with this ore. Feed slurries were prepared to contain 340-360g U/l plus $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ at various total ionic strengths⁸ of the salt background. The calcium to magnesium ratio was maintained at a constant 3:1 (molar basis). A description of each aqueous feed and raffinate uranium values is given in Table I, series 1.

The best extraction of Rand slurry was obtained using calcium nitrate and magnesium nitrate at a total ionic strength of 7. The soluble uranium content of raffinate for Run No. 222, salted at an ionic strength of 7, was 1.52g U/l. Decreasing the ionic strength of the salt background to 5 or 6 resulted in higher uranium losses (5.7 and 4.6g U/l respectively). Increasing the ionic strength of the salt background to 8 also reduced the extraction efficiency producing a raffinate with 3.9g soluble U/l.

Filtration of a Rand slurry, to determine the effect of removing the silicious solids from this feed, resulted in a 50 percent reduction of uranium in the raffinate. Run No. 221, using filtrate salted to an ionic strength of 6, yielded a raffinate containing 2.3g U/l as compared to Run No. 220, using slurry salted to an ionic strength of 6, which produced a raffinate containing 4.6g U/l.

⁶ Memorandum from Bitzer, E. C., to Rueble, A. E., "South African Concentrate at Mallinckrodt Chemical Works", June 18, 1953.

⁷ Op. cit., NYO 1356

⁸ Op. cit., NYO 1356

Table I

Neutral Ether Extraction of Rand Ore Lot SA-10
Digest Liquors Salted with $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$

Run No.	Aqueous Feed Description	Ionic Strength of Salt	Raffinate Analyses		
		Back-ground	Sol. U g/l	Insol. U g/l	Ether Wt. %
Series I					
223	Rand slurry salted with Ca and Mg	5	5.7	0.27	0.6
220	Rand slurry salted with Ca and Mg	6	4.6	0.08	0.4
222	Rand slurry salted with Ca and Mg	7	1.52	0.21	0.3
230	Rand slurry salted with Ca and Mg	8	3.9	0.4	14.8
221	Rand filtrate salted with Ca and Mg	6	2.3	<0.05	0.3
Series II					
224	Rand slurry salted with Ca and Mg	7	3.5	0.22	0.6
227	Rand slurry salted with Ca and Mg				
	and 60% recycle raffinate from Run #224	7	10.0	0.25	0.2
228	Rand slurry salted with Ca and Mg and				
	60% recycle raffinate from Run #227	7	17.0	0.14	1.1
229	Rand slurry salted with Ca and Mg and				
	60% recycle raffinate from Run #228	7	5.0	0.49	0.2
231	Rand slurry salted with Ca and Mg and				
	60% of filtered raffinate from Run #229	7	26.0	0.2	0.3
Series III					
232	Rand slurry salted with Ca and Mg				
	Hot Digestion (190-200°F)	7	4.7	<0.1	0.1
233	Rand slurry salted with Ca and Mg cold				
	digestion followed by 4 hr. hot holding				
	period	7	1.2	0.1	<0.1

Another series of runs was made to determine if a reduction in total salting agent cost might be affected by recycling salted raffinates in successive aqueous feeds. Successful recycling of 75 percent of each salted black oxide raffinate has been demonstrated in previous pilot plant work⁹. A 60 percent recycle was chosen for this series because of the greater amount of wet solids in Rand material over those contained in the black oxide slurries used in the earlier work.

⁹ Op. cit., NYO-1356

A series of runs was completed in which successive aqueous feeds, each containing 340-360g U/l, were salted with 60% recycled raffinate and sufficient calcium nitrate and magnesium nitrate to maintain an ionic strength of the salt background at 7. A description of each aqueous feed and the raffinate uranium values are given in Table I, series 2.

The results of this series of runs indicated a decrease in extraction efficiency with successive raffinate recycles. The wet solids content of the initial aqueous feed (Run No. 224) was 1.17 lbs/gal while that of the final aqueous feed (Run No. 228) was 2.14 lbs/gal. This increased wet solids in the aqueous feed, was postulated to be contributing to the decrease in extraction efficiency by hindering the mixing of the ether and aqueous phase.

A final run, in which filtered raffinate was recycled, also gave poor extraction (26g U/l in the raffinate). This indicated that the build up of wet solids in the aqueous feed was not the only source of decreased extractability.

Inadequate feed supply prevented another series of runs with this lot of ore, but two additional runs were made to check the effect of hot Rand ore digestion. The aqueous feeds were prepared to contain 340-360g U/l and were salted with calcium nitrate and magnesium nitrate to an ionic strength of the salt background of 7.

A description of aqueous feeds for these runs and the raffinate uranium analyses are given in Table I, series 3. The aqueous feed which was digested at 125°F and held at 200°F for one hour (Run No. 233) appeared to give better extraction than the slurry which was digested at 190-200°F (Run No. 232).

The increase in wet solids content and emulsification tendency, expected as a result of hot digestion temperature, was not observed.

2. Extraction of Composite of Rand Ore Digest Slurries

Rand Ore Lot SA-10 was not representative of the future feed material expected to be received by the MCW refinery. The calcination temperature had been dropped from about 700°C to 500°C after several lots (including Lot SA-10) had been processed because of furnace deterioration encountered at the higher temperatures. The remainder of the extraction study was made using feed material purported to be representative of the current production in South Africa. A composite of equal weights of Rand Ore Lots SA-16, SA-18, SA-19, SA-21 and SA-22 was digested to yield an aqueous feed containing 340-360g U/l for subsequent runs.

The first series of runs was made to determine the effect of various digestion procedures on the extraction characteristics and the insoluble uranium and wet solids

of the aqueous feed. Digestions were made permuting the order of addition of the ore and salting agent source and the digestion temperature. Calcium nitrate and magnesium nitrate were used for salting agents. Digestions were made at either 120-130°F or 190-200°F.

A description of each aqueous feed and the raffinate analyses are given in Table II.

Table II

Neutral Ether Extraction of Rand Ore Composite
Digest Liquor Salted with $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$

Run No.	Digestion Procedure	Aqueous Feed Description					Raffinate Analyses		
		Wet Solids lbs/gal	Ca g/l	Mg g/l	Fe g/l	μ	Sol. U g/l	Insol. U g/l	Ether Wt. %
237	Digestion at 120-130°F salting agent added first	1.02	54	14	-	7	2.74	0.08	0.14
238	Digestion at 120-130°F ore added first	1.29	53.0	13.8	-	7	1.36	0.05	0.23
239	Digestion at 190-200°F salting agent added first	1.24	54	14	-	7	1.03	0.06	<0.07
240	Digestion at 190-200°F ore added first	0.94	56.8	14.6	-	7	1.2	0.09	<0.07
242	Digestion at 190-200°F ore added first	1.18	51.0	13.8	-	7	1.8	<0.05	0.08

The extraction achieved with the four different digestion procedures was equally good (1 to 2g U/l in the raffinates). No appreciable difference in the insoluble uranium in the four raffinates indicated that neither the order of ore and salting agent addition nor the digestion temperature affected the solubility of the ore.

The digestion temperature did not alter the quantity of wet solids in the aqueous feeds. The wet solids which were produced did not promote stable emulsions in any of the runs as indicated by the low ether contents of the raffinates (less than 0.25%).

The major difficulty encountered during these runs was a rapid scale deposition in the extraction column and related equipment. The scale was analytically determined to be mainly CaSO_4 , probably resulting from the reduction in solubility of CaSO_4 in the aqueous phase as the uranyl nitrate was extracted.

A second series of runs was made using the Rand ore composite in another recycle raffinate study. A previous series of runs using Lot SA-10, in which 60% of the salted raffinates were recycled to succeeding runs, indicated that this procedure was not feasible because of degeneration of extractability with each successive run. Filtration of the raffinate before recycle might eliminate some or all of the deleterious effects. The series of runs was made using the initial feed salted with calcium nitrate and magnesium nitrate to an ionic strength of about 7. Each succeeding run was salted with an 80% recycle of filtered raffinate from the preceding run and an additional amount of calcium nitrate and magnesium nitrate to compensate for the 20% bleed off.

A description of each aqueous feed and the raffinate analyses are given in Table III.

Table III

Neutral Ether Extraction of Rand Composite Digest Liquors
Salted with $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ and Filtered Recycle Raffinate

Aqueous Feed Description						Raffinate Analyses			
Run No.	Digestion Procedure	Wet				Insol.			
		Solids lbs/gal	Ca g/l	Mg g/l	Fe g/l	μ	Sol. U g/l	U g/l	Ether Wt. %
244	Digestion at 190-200°F ore added first	0.75	59.2	15.0	-	6.3	1.94	0.14	0.07
247	Digestion at 190-200°F 80% of salting agent from filtered Run #244 raffinate	0.11	41.2	13.0	-	4.7	12.8	0.08	0.07
249	Digestion at 190-200°F 80% of salting agent from filtered Run #247 raffinate	0.57	32.8	11.6	-	3.9	35.0	0.20	0.02

No buildup of solids or emulsification was observed during the series of runs. However, the rapid decline in extractability, from 2g U/l to 35g U/l in the raffinate after only two recycles, appears to eliminate this method of processing. A partial explanation for the decrease in extractability might be the net loss in salting agent and the increase in sulfate concentration. Calcium losses occurring due to precipitation of CaSO_4 as scale were not accounted for in the aqueous feed preparation for Runs 247 and 249. An increase in amount of scale deposition during each succeeding extraction was also a result of the increase in sulfate concentration in the aqueous feeds containing recycled raffinates.

Attention was next directed to the major problem of scaling which occurred as a result of using calcium nitrate in combination with magnesium nitrate for salting of

Rand ores (containing 6 to 9 percent SO_4). Elimination of the use of calcium nitrate was tried in a first attempt at scale prevention. Two aqueous feeds were prepared in which magnesium nitrate was the only salting agent added. A description of each aqueous feed and the raffinate analyses are given in Table IV, series 1.

Table IV

Neutral Ether Extraction of Rand Ore Composite Digest Slurries
Salted with $\text{Mg}(\text{NO}_3)_2$ or $\text{Mg}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_2$

Aqueous Feed Description		Wet				Raffinate Analyses			
Run No.	Digestion Procedure	Soluble lbs/gal	Ca g/l	Mg g/l	Fe g/l	μ	Sol. U g/l	Insol. U, g/l	Ether Wt. %
Series I									
245	Digestion at 120-130°F salting agent added first	1.1	-	54.0	-	7	20.0	0.09	5.3
246	Digestion at 120-130°F salting agent added first	1.2	-	64.0	-	8	28.6	0.3	0.16
Series II									
248	Digestion at 120-130°F salted Fe:Mg::1.5:55 ionic basis	0.46	2.4	41.8	16.2	7	2.4	0.08	1.8
256	Digestion at 120-130°F Fe:Mg::1:6 ionic basis	1.2	-	46.0	11.4	7	7.22	0.04	2.6
257	Digestion at 120-130°F Fe:Mg::2:5 ionic basis	1.2	-	41.2	21.6	7	3.49	0.03	1.6
258	Digestion at 120-130°F Fe:Mg::3::4 ionic basis	2.6	-	31.8	31.8	7	4.40	0.04	0.1

The aqueous feeds salted with magnesium nitrate at total ionic strengths of 7 or 8 extracted poorly. (20g U/l and 28.6g U/l in the raffinate respectively.)

Distribution coefficients determined for Runs No. 245 and 246 raffinates were low (0.55 and 0.37 respectively) indicating that the potential extractability of these raffinates was quite low. This lack of potential extractability was born out when a plant extraction experiment, run in parallel and at the same uranium and salting agent concentrations as Run 245 aqueous feed, produced a raffinate of 17 to 18g U/l of raffinate.

These results verified earlier data indicating that combinations of two or more salting agents were usually necessary for good extraction. Use of calcium or magnesium nitrate alone as salting agents did not result in satisfactory extraction in most cases.

The sulfate content of the Rand ore slurry was also suspected as being a contributing factor to the poor extraction.

Previous laboratory work¹⁰ has shown that ferric nitrate will improve extraction in uranium solutions containing sulfate. The beneficial effect is thought to be the result of an iron sulfate complex ion in combination with the usual salting agent effect. Substitution of iron nitrate for calcium nitrate as a second salting agent was tried in a second attempt at scale prevention on the basis of these results.

A series of Rand composite feed slurries was extracted to determine the effect of varying the proportions of iron nitrate and magnesium nitrate at a total ionic strength of 7. A description of the aqueous feeds and the raffinate analyses for these runs are given in Table IV, series 2.

Salting of the Rand composite with iron nitrate and magnesium nitrate resulted in good extraction with little scale deposition. An iron content of about 20 g/l produced the best extraction (1.74g U/l in the raffinate).

B. Extraction of Vitro Black Oxide Digest Liquors

Vitro Black Oxide is a current Mallinckrodt Chemical Works Refinery raw feed material which assays 40 to 60% U. This feed has been processed in the past by blending with MgX slurries in small quantities due to:

- 1) The presence of a large amount of nitric acid insolubles in the ore.
- 2) The need for additional salting agent.
- 3) The tendency towards emulsification observed in laboratory ether extractions.

A future replacement feed (Congo Ion Exchange Product) for MgX ore has necessitated the investigation of the future disposition of Vitro Black Oxide.

One plant experiment was run to investigate the single stage neutral ether extraction of filtrate from a Vitro Black Oxide digest slurry. Little additional consideration was given to this method of processing Vitro Black Oxide because:

- 1) The large amount of nitric acid insoluble material in the ore hindered filtration.
- 2) The high iron content of the filtrate (5 to 15% in the ore) might represent a source of contamination of the OK Liquor.

A series of pilot plant digestions and extractions was made to study possible methods of processing Vitro Black Oxide. Processing of Vitro as an individual feed stream and in blended ore batches was tried. A summary of the raffinate analyses together with a description of each feed is given in Table V.

¹⁰ Rueble, A. E., and Leaders, W. M., *Process Development Quarterly Report, Mallinckrodt Chemical Works, October 15, 1953, (NYO-1349), p. 10-37.*

Table V

Neutral Ether Extraction of Vitro Black Oxide Digest Liquors

Run No.	Aqueous Feed Description*	Raffinate Analyses		
		Sol. U g/l	Insol. U g/l	Ether Wt. %
209	Vitro Black Oxide slurry	Inoperable due to solids & scale		
210	Vitro Black Oxide Filtrate			
	Organic to Aq. Rates 1.6/1	1.8	1.4	1.9
212	Vitro Black Oxide Filtrate			
	Organic to Aq. Ratio = 2/1	Inoperable excessive scaling		
211	Vitro B.O. and V-20 are combined on a 1:1 U basis. Filtered	0.6	7.6	24.4
213	Vitro B.O. and V-20 ore combined on a 1:3 U basis. Filtered	41	72	0.2
214	Vitro B.O. and Fernald B.O. combined on a 1:9 U basis. Salted with Ca and Mg	4.2	0.28	9.7
219	Vitro B.O. and Fernald B.O. combined on a 1:3 U basis. Salted with Ca and Mg	12.6	0.24	1.34

* Each aqueous feed contained 340-360g U/l.

An attempt was made to extract a Vitro Black Oxide digest slurry salted with calcium nitrate and magnesium nitrate (Run No. 209). Operation of the pilot plant extraction equipment was impossible because of large solid particles in the feed and excessive scale deposition.

The salted slurry was then filtered and a four hour run was completed. The extraction efficiency during this run (Run No. 210) was good with respect to the soluble uranium but the insoluble uranium left in the raffinate was high (1.4g U/l). This insoluble uranium compound was probably a part of the flocculent precipitate observed forming in the extraction column during the run.

A second run (Run No. 212) using a Vitro Black Oxide filtrate salted with calcium and magnesium nitrates, was inoperable due to blockage of pipelines from excessive scale deposition and the flocculent precipitate in the extraction column.

Two runs (Runs 211 and 213) were made using the filtrate from Vitro Black Oxide blended with V-20 ore. Results indicated that this combination was not feasible because of high insoluble uranium left in the raffinate (7.6 and 72g U/l respectively).

Fair extraction of Vitro Black Oxide and Fernald Black Oxide mixtures (Runs 214 and 219) were obtained. Results indicated that Vitro Black Oxide might be processed by

blending small quantities with Fernald Black Oxide. Distribution coefficients for the Run 214 and Run 219 raffinates were 3.6 and 3.3 respectively. This indicates good potential extraction with lower uranium content raffinates possible in plant equipment. No precipitation or scale deposition occurred in the extraction column during the Vitro-Fernald slurry runs.

Additional work is indicated before a good processing method for Vitro Black Oxide can be proposed.

C. Use of Dolomite as a Source of Salting Agent

Calcium nitrate and magnesium nitrate salting agents are currently prepared by dissolving calcium hydroxide and magnesium oxide in nitric acid. These sources were chosen because all three items were relatively inexpensive, easily digested, and readily available in the refinery.

An economical source of the same salting agents might be dolomite which is usually a 1:1 molar ratio of calcium oxide and magnesium oxide. A less expensive source of better salting agent might be iron contaminated dolomite. The combined salting agent effect should enhance the extractability of the aqueous feeds.

Several runs were made using black oxide or Rand Ore slurries to determine the applicability of using dolomite as a source of salting agent. Each aqueous feed was prepared to contain 340-360g U/l. A description of each aqueous feed and the raffinate analyses are given in Table VI.

Table VI

Neutral Ether Extraction of Digest Liquors Salted with $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$
Prepared from Nitric Acid Digestion of Dolomite

Run No.	Aqueous Feed Description	Wet Solids lbs/gal	Ca g/l	Mg g/l	Fe g/l	μ	Raffinate Analyses		
							Sol. U g/l	Insol. U g/l	Ether Wt. %
234	Fernald B.O. slurry with salting agent from dolomite	0.04	50.0	29.4	-	8	16.7	0.2	34.4
235	Fernald B. O. slurry with salting agent from dolomite	0.08	44.4	27.2	-	7	<0.5	<0.1	<0.08
241	Rand Lot SA-2 slurry with salting agent from dolomite	1.5	45	28.2	-	7	5.1	0.1	<0.7
243	Rand Lot SA-2 slurry with salting agent from dolomite SO_4 =ppt'd with BaCO_3	2.7	46.2	28.6	-	7	8.4	0.10	9.4
251	Rand Composite slurry with salting agent from dolomite and iron	1.6	37.0	22.2	20	7	0.42	0.05	0.08
255	Rand Composite slurry with salting agent from dolomite and iron	1.04	37.0	22.2	15.87		2.64	0.07	0.02

Low raffinate uranium content ($<0.5\text{g U/l}$) for Run No. 235 indicates that dolomite might be a satisfactory source of salting agent with black oxides. The high uranium in the raffinate from Run No. 234 (16.7g U/l) was attributed to emulsification as indicated by the raffinate ether content of 34.4% (by weight). The emulsion appeared to be caused by a finely powdered, insoluble foreign material in the black oxide. Similar emulsification has occurred when extracting other Fernald Black Oxide digest slurries.

Salting of Rand Ore Lot SA-2 with nitric acid digested dolomite was fair, producing a raffinate with a uranium content of 5.1g U/l (Run No. 241). An identical Rand SA-2 slurry, with the sulfate precipitated with BaCO_3 (Run No. 243) handled fairly well and yielded fair extraction (8.4g U/l). The raffinate ether content of 9.4% (by weight) indicates some emulsification occurred. The use of BaCO_3 eliminated the scale deposition observed in the first run with dolomite alone.

Distribution coefficients for both raffinates from Rand Lot SA-2 slurries salted with dolomite were high (3.7 and 4.45) indicating that both were potentially extractable in large scale equipment. The wet solids in both slurries probably hindered extraction.

The two Rand composite ore extractions (Runs 251 and 255), made to determine the effect of combining iron and dolomite as salting agent sources, yielded good raffinates (0.42 and 2.61g U/l respectively). Scale deposition during these runs appeared to be moderate but might be excessive in plant equipment.

V. Discussion of Results

The imminent addition of Rand ore as a major source of feed material at the MCW Refinery necessitated rapid development of a digestion and extraction procedure amenable to plant production equipment. An initial laboratory study of the digestion of Rand ore indicated that the uranium salts were completely soluble in nitric acid. However, subsequent ether extractions of these digest slurries were hindered by the formation of stable emulsions.

The emulsification was attributed to the presence of bulky gelatinous solids resulting from some form of silica present in the ore. Calcination of the ore at 450 or 700°C was shown to alleviate the emulsification. A possibility existed, however, that ore calcination at the higher temperature might render some of the uranium insoluble in nitric acid. On this basis, the laboratory tentatively recommended calcining the Rand ore at about 400°C before digestion in nitric acid.

Initial Rand ore production in Africa included calcination at about 700°C . After several lots had been processed, this temperature was reduced to around 500°C primarily because of excessive deterioration of the calcination furnaces at the high temperature.

The reported calcination temperature was a nominal value with considerable fluctuation from the measured value possible at a given point in the furnace. The temperature variation in

in the furnace was apparent from the gradation in color in the ore received at the MCW refinery. The ore was a heterogeneous mixture of yellow to olive green pellets, dependent on the extent to which calcination had occurred.

Initial pilot plant studies were made using an ore lot calcined at 700°C ; later work was done using a composite of ore lots calcined at 500°C . Ore digestions were made in 45 percent nitric acid at either 125 or 200°F . Salting agents (calcium and magnesium nitrates) were included by dissolving MgO or $\text{Ca}(\text{OH})_2$ in the acid either before or after addition of the ore.

Satisfactory extraction of Rand ore was observed for slurries salted with calcium and magnesium nitrates to yield a total ionic strength of the salt background of 7. No emulsification occurred during the entire series of runs, nor were appreciable amounts of insoluble uranium observed. The absence of insoluble uranium, even for the ore lots calcined at high temperature, might be a result of a lower average calcination temperature than actually reported due to variations in furnace temperature.

The only significant problem observed during the series of runs was scale deposition in the extraction column. This scale, which is primarily calcium sulfate on the basis of spectrographic analysis, was probably deposited as a result of decreased scale solubility in the aqueous phase with decreasing uranium and nitric acid concentrations during extraction.

Elimination of the scaling problems was attempted in several pilot plant runs by omitting calcium nitrate as a salting agent. No scale was observed for these runs using magnesium nitrate alone as salting agent. However, less efficient extraction was obtained resulting in a ten fold increase in raffinate uranium content. These results corroborated earlier laboratory studies showing that sulfate hindered extraction if not removed from the system either as a precipitate or a complex.

Two possible methods for removing sulfate from the system were next investigated:

- 1) Precipitation of the sulfate with barium carbonate
- 2) The use of ferric ion as a sulfate complexing agent

Pilot plant extraction showed that scale deposition was eliminated by precipitating the sulfate as barium sulfate, but the increased wet solids in the aqueous feed caused stable emulsions during extraction. Removal of the barium sulfate precipitate should allow the sulfate free liquor to be extracted with no emulsion formation. Since the additional equipment for filtration of the slurry was not readily available, this possibility was dropped to permit investigation of the use of iron as a complexing agent.

The use of iron and magnesium nitrates as salting agents was studied using various iron-magnesium ratios at a total ionic strength of the salt background of 7. Adequate extraction of salted Rand slurries with no scaling was obtained for all ratios. A decrease in raffinate

uranium content with an increase in iron content up to 20 g/l indicated that sufficient iron to complex the sulfate was necessary for optimum extraction.

Plant production of Rand digest batches was initiated using iron and magnesium nitrates. Satisfactory extraction has been obtained using 20g Fe/l and 40g Mg/l.

Economy of salting agent prompted a pilot plant investigation of the possibility of recycling salted Rand raffinate to successive aqueous feed batches. Series of runs were made recycling both filtered and unfiltered raffinates from feeds salted with calcium and magnesium nitrates. Both schemes proved to be impractical because of the decrease in extraction efficiency with each successive recycle of raffinate. The unsatisfactory extraction was attributed in part to a wet solid buildup in the aqueous feed but was probably principally the result of the increase in sulfate content in feeds containing recycle raffinates.

Recycling of raffinates from aqueous feeds salted with iron and magnesium nitrates might be feasible. An investigation of this possibility will be made.

Although the major emphasis this quarter was on the digestion and extraction of Rand ores, exploratory investigations were made on two additional problems:

- 1) Extraction of Vitro Black Oxide digest liquors and
- 2) Use of dolomite as a source of salting agent

Extraction of salted Vitro Black Oxide slurries was impossible because of large quantities of acid insoluble material in the aqueous feed and a flocculent precipitate which formed in the extraction column. The same type of flocculent precipitate prevented continuous operation during extraction of a salted Vitro Black Oxide filtrate.

Filtration of a digest slurry containing a blend of Vitro Black Oxide and V-20 ore produced satisfactory physical operation but the formation of an insoluble uranium precipitate in the extraction column created an excessive loss of insoluble uranium in the raffinate.

Processing of Vitro Black Oxide by blending with a high assay black oxide, such as Fernald Black Oxide, was shown to have possibilities if the proportion of Vitro was 10 percent or less of the total uranium. However, additional study of this problem is needed before a definite procedure can be recommended.

Dolomite was used successfully in the salting of both a black oxide and a Rand slurry. The combination of iron and dolomite in a Rand digest liquor resulted in better extraction than dolomite alone.

Further study is indicated to determine the reliability and optimum concentration of dolomite for use in salting black oxide slurries. The possibility of salting Rand slurry with digested

dolomite appears to be remote since the calcium present would tend to aggravate the scaling tendencies. However, if sufficient iron were present to complex the sulfate, dolomite might be used satisfactorily. An investigation to determine the degree to which iron inhibits CaSO_4 scaling will be made.

VI. Conclusions

Satisfactory uranium recovery from Rand Ore digest slurries containing 3 lb/gal uranium was obtained by addition of calcium and magnesium nitrates to an ionic strength of the salt background of 7.

Severe calcium sulfate scale deposition occurred when Rand Ore digest slurries were salted with calcium nitrate.

The best extraction of Rand Ore digest slurries containing 3 lb/gal uranium was obtained by addition of iron and magnesium nitrate (2:5 ratio, ionic basis) to an ionic strength of the salt background of 7.

Recycling of filtered or unfiltered Rand raffinates containing calcium and magnesium nitrates was impractical because of increased scale deposition and raffinate uranium content with each succeeding aqueous feed.

Vitro Black Oxide was blended with Fernald Black Oxide in small quantities (up to 10 percent of uranium in content) without excessive uranium losses in the raffinate.

Dolomite was used successfully as a source of salting agent in some black oxide and Rand digest liquors.

Appendix

Operational Data of Pilot Plant Neutral Ether Extractions

Run Number	Aqueous Feed Rate gallons/hour	Ether to Aqueous Ratio	Ether Feed Rate gallons/hour	Ether Acidity Normality	Total Throughput gallons/hour	Organic Recycle to Aqueous Feed Ratio	Organic Overhead Recycle Rate, gallons/hour	Mixing Pump Rate gallons/minute	Scrub Water Rate gallons/hour	Strip Water Rate gallons/hour	Temperatures - °F									
											Aqueous Feed	Ether Feed	Organic Recycle		Org. - Aq. Mixture Recycle		Pump No. 1	Pump No. 2	Pump No. 3	Pump No. 4
													Before Cooler	After Cooler	Before Cooler	After Cooler				
210	45.0	1.60	72	0.0	1345	5.00	225	3	1.2	17	108	72	82	71	84	74	92	92	92	92
211	36.8	1.96	72	0.0	1250	5.87	216	3	1.2	40	106	60	76	68	78	69	80	84	88	88
213	33.0	2.18	72	0.0	1210	6.54	216	3	1.2	45	106	62	78	70	78	68	80	91	91	84
214	45.0	1.60	72	0.0	1345	5.00	225	3	1.2	45	104	60	80	69	82	72	82	85	86	84
219	45.5	1.58	72	0.0	1350	4.45	216	3	1.2	45	110	60	85	69	85	77	92	92	94	95
220	35.6	2.02	72	0.0	1230	5.90	210	3	1.2	44	110	61	84	73	84	73	90	92	94	98
221	37.7	1.91	72	0.0	1265	5.73	216	3	1.2	42	105	60	83	71	84	72	88	92	90	90
222	35.8	2.01	72	0.0	1235	5.81	208	3	1.2	42	108	61	80	70	82	72	84	89	90	88
223	36.0	2.00	72	0.0	1240	5.98	216	3	1.2	45	106	58	79	68	82	71	83	90	91	87
224	34.6	2.08	72	0.0	1220	5.49	190	3	1.2	42	109	59	79	68	81	68	87	90	92	86

Appendix

Operational Data of Pilot Plant Neutral Ether Extractions, (Cont'd.)

Run Number	Aqueous Feed Rate gallons/hour	Ether to Aqueous Ratio	Ether Feed Rate gallons/hour	Ether Acidity Normality	Total Throughput gallons/hour	Organic Recycle to Aqueous Feed Ratio	Organic Overhead Recycle Rate, gallons/hour	Mixing Pump Rate gallons/minute	Scrub Water Rate gallons/hour	Strip Water Rate gallons/hour	Temperatures -- °F									
											Aqueous Feed	Ether Feed	Organic Recycle		Org. - Aq. Mixture Recycle		Pump No. 1	Pump No. 2	Pump No. 3	Pump No. 4
													Before Cooler	After Cooler	Before Cooler	After Cooler				
227	36.5	1.97	72	0.0	1245	5.89	216	3	1.2	41	105	60	77	67	80	71	88	91	90	88
228	36.5	1.97	72	0.0	1245	5.89	215	3	1.2	40	108	61	82	71	81	74	85	88	90	88
229	35.4	2.04	72	0.0	1230	6.08	216	3	1.2	40	107	58	79	70	82	71	78	82	84	84
230	34.8	2.07	72	0.0	1225	6.18	216	3	1.2	43	110	60	79	69	82	72	87	90	91	89
231	33.0	2.18	72	0.0	1210	6.48	216	3	1.2	42	104	60	79	71	82	72	84	88	84	83
232	34.7	2.08	72	0.0	1220	5.85	203	3	1.2	40	111	59	80	71	83	72	87	90	90	89
233	33.0	2.18	72	0.0	1205	6.54	215	3	1.2	40	105	57	77	70	82	71	84	88	88	87
234	33.9	2.12	72	0.0	1215	6.35	215	3	1.2	43	105	60	78	70	82	72	84	87	89	90
235	34.4	2.10	72	0.0	1220	6.25	215	3	1.2	40	105	59	75	70	81	72	80	88	88	86
237	36.3	1.98	72	0.0	1242	5.95	216	3	1.2	45	110	62	80	67	82	72	84	91	91	92

Appendix

Operational Data of Pilot Plant Neutral Ether Extraction (Cont'd.)

Run Number	Aqueous Feed Rate gallons/hour	Ether to Aqueous Ratio	Ether Feed Rate gallons/hour	Ether Acidity Normality	Total Throughput gallons/hour	Organic Recycle to Aqueous Feed Ratio	Organic Overhead Recycle Rate, gallons/hour	Mixing Pump Rate gallons/minute	Scrub Water Rate gallons/hour	Strip Water Rate gallons/hour	Temperatures - °F									
											Aqueous Feed	Ether Feed	Organic Recycle		Org. - Aq. Mixture Recycle		Pump No. 1	Pump No. 2	Pump No. 3	Pump No. 4
													Before Cooler	After Cooler	Before Cooler	After Cooler				
238	37.7	1.91	72	0.0	1259	5.73	216	3	1.2	43	110	59	78	68	83	70	82	90	90	86
239	36.0	2.00	72	0.0	1240	6.00	216	3	1.2	43	110	60	82	70	84	74	86	90	92	93
240	34.8	2.06	72	0.0	1223	6.20	216	3	1.2	45	110	59	82	70	84	74	84	88	88	88
241	36.0	2.00	72	0.0	1240	6.00	216	3	1.2	45	108	58	80	67	82	70	81	88	91	88
242	38.5	1.87	72	0.0	1269	5.60	216	3	1.2	45	105	62	86	71	84	74	84	89	92	92
243	37.0	1.94	72	0.0	1250	5.83	216	3	1.2	45	107	60	81	70	84	74	82	86	88	88
244	37.3	1.92	72	0.0	1253	5.78	216	3	1.2	45	105	61	86	74	88	75	87	91	92	90
245	35.4	2.03	72	0.0	1232	6.07	215	3	1.2	45	108	58	72	65	78	67	82	88	88	86
246	35.7	2.02	72	0.0	1235	6.02	215	3	1.2	44	105	59	75	68	82	70	78	84	86	80
247	34.5	2.08	72	0.0	1223	6.15	212	3	1.2	43	106	60	77	64	83	68	83	90	91	86

Appendix

Operational Data of Pilot Plant Neutral Ether Extraction (Cont'd.)

Run Number	Aqueous Feed Rate gallons/hour	Ether to Aqueous Ratio	Ether Feed Rate gallons/hour	Ether Acidity Normality	Total Throughput gallons/hour	Organic Recycle to Aqueous Feed Ratio	Organic Overhead Recycle Rate, gallons/hour	Mixing Pump Rate gallons/minute	Scrub Water Rate gallons/hour	Strip Water Rate gallons/hour	Temperatures - °F									
											Aqueous Feed	Ether Feed	Organic Recycle		Org. - Aq. Mixture Recycle		Pump No. 1	Pump No. 2	Pump No. 3	Pump No. 4
													Before Cooler	After Cooler	Before Cooler	After Cooler				
248	36.0	2.00	72	0.0	1240	5.96	215	3	1.2	47	102	59	74	68	81	69	78	83	84	80
249	35.6	1.97	72	0.0	1244	5.96	212	3	1.2	43	105	58	82	71	84	72	84	90	91	90
251	36.0	2.00	72	0.0	1240	5.94	214	3	1.2	44	103	58	79	71	83	72	83	90	90	88
254	35.2	2.04	72	0.0	1235	6.14	216	3	1.2	45	102	58	78	70	82	71	85	90	92	88
255	35.2	2.04	72	0.0	1235	6.14	216	3	1.2	45	108	60	79	68	82	71	84	90	92	88
256	36.7	1.96	72	0.0	1250	5.89	216	3	1.2	45	106	60	79	70	82	72	84	90	90	86
257	36.5	1.97	72	0.0	1250	5.92	216	3	1.2	45	109	61	79	69	83	72	82	89	90	84
258	36.2	1.99	72	0.0	1245	5.97	216	3	1.2	45	107	59	76	68	81	70	76	82	83	80

AQUEOUS FEED DESCRIPTION

<u>Run No.</u>	<u>Description</u>
210	The filtrate from a Vitro Black Oxide slurry salted with calcium nitrate and magnesium nitrate.
211	The filtrate from a combined slurry of Vitro Black Oxide and V-20 ore (1:1 uranium basis). The black oxide was salted with calcium nitrate and magnesium nitrate.
213	The filtrate from a combined slurry of Vitro Black Oxide and a V-20 ore (B.O.:V-20::1:3 uranium basis). The black oxide was salted with calcium nitrate and magnesium nitrate.
214	A Vitro Black Oxide-Fernald Black Oxide slurry combined on a 1:9 uranium basis. The slurry was salted with calcium nitrate and magnesium nitrate.
219	A Vitro Black Oxide-Fernald Black Oxide slurry combined on a 1:3 uranium basis. The slurry was salted with calcium nitrate and magnesium nitrate.
220	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength of the salt background of six.
221	The filtrate from a Rand ore slurry which was salted with calcium nitrate and magnesium nitrate to an ionic strength of the salt background of six.
222	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength of the salt background of seven.
223	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength of the salt background of five.
224	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength of the salt background of seven.
227	Rand ore slurry salted with 60% of the raffinate from Run No. 224 and enough calcium nitrate and magnesium nitrate to compensate for that lost in the 40% bleedoff.
228	Rand ore slurry salted with 60% of the raffinate from Run No. 224 and enough calcium nitrate and magnesium nitrate to compensate for that lost in the 40% bleedoff.

AQUEOUS FEED DESCRIPTION (cont'd.)

<u>Run No.</u>	<u>Description</u>
229	Rand ore slurry salted with 60% of the raffinate from Run No. 228 and enough calcium nitrate and magnesium nitrate to compensate for that lost in the 40% bleedoff.
230	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength of the salt background of eight.
231	Rand ore slurry salted with 60% of the filtered raffinate from Run No. 229 and enough calcium nitrate and magnesium nitrate to compensate for that lost in the 40% bleedoff.
232	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength in the salt background of seven. The ore was digested at 190 - 200° F.
233	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength in the salt background of seven. The ore was digested at 120 - 130° F. and then held at 200° F. for one hour before being cooled to the standard aqueous feed operating temperature (100 - 110° F.)
234	Fernald Black Oxide slurry salted with dolomite to obtain an ionic strength of the salt background of eight.
235	Fernald Black Oxide slurry salted with dolomite to obtain an ionic strength of the salt background of seven.
237	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength of seven. The salting agent was digested and then the ore was digested at 120 - 130° F.
238	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength of seven. The ore was digested first at 120 - 130° F. The salting agent was then digested at 120 - 130° F.
239	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength of seven. The salting agent and then the ore were digested at 190 - 200° F.
240 and 242	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength of seven. The ore was digested first at 190 - 200° F. The salting agent was then digested at 190 - 200° F.

AQUEOUS FEED DESCRIPTION (cont'd)

<u>Run No.</u>	<u>Description</u>
241	Rand ore slurry salted with dolomite to obtain an ionic strength of the salt background of seven.
243	Rand ore slurry salted with dolomite to obtain an ionic strength of the salt background of seven. The sulfate was precipitated by addition of BaCO_3 and left in the aqueous feed.
244	Rand ore slurry salted with calcium nitrate and magnesium nitrate to an ionic strength of seven.
245	Rand ore slurry salted with magnesium nitrate to an ionic strength of the salt background of seven.
246	Rand ore slurry salted with magnesium nitrate to an ionic strength of the salt background of eight.
247	Rand ore slurry salted with 80% of the filtered raffinate from Run No. 244 and enough calcium nitrate and magnesium nitrate to compensate for that lost in the 20% bleedoff.
248	Rand ore slurry salted with ferric nitrate (ionic strength=1.5) and magnesium nitrate (ionic strength = 5.5).
249	Rand ore slurry salted with 80% of the filtered raffinate from Run No. 247 and enough calcium nitrate and magnesium nitrate to compensate for that lost in the 20% bleedoff.
251 and 255	Rand ore slurry salted with ferric nitrate and nitric acid digested dolomite. The ionic strength of the salt background was about seven.
256	Rand ore slurry salted with ferric nitrate (ionic strength = 1) and magnesium nitrate (ionic strength = 6).
257	Rand ore slurry salted with ferric nitrate (ionic strength = 2) and magnesium nitrate (ionic strength = 5).
258	Rand ore slurry salted with ferric nitrate (ionic strength = 3) and magnesium nitrate (ionic strength = 5).

Analytical Data of Pilot Plant Neutral Ether Extractions

Run No.	Ether Extract		Raffinate						Ether Feed		Aqueous Feed								Raffinate Shakeout			Aq. Phase from top of Extraction Column				
	U, g/l		de-etherized			Ether, Wt. %	Wet Solids, lbs/gal	Baume at 100°F	U, mg/l		U, g/l	HNO ₃ , g/l	SO ₄ , g/l	PO ₄ , g/l	Fe, g/l	Ca, g/l	Mg, g/l	Be ' at 100°F	Wet Solids, lb/gal	U in Aq. Phase, g/l	U in Ether Phase, g/l	Distribution Coefficient	Sol. U, g/l	Insol., g/l	HNO ₃ , g/l	Ether, Wt. %
			Sol. U, g/l	Insol. U, g/l	HNO ₃ , g/l																					
210	152		1.8	1.4	16.1*	1.9	3.17	37.6	30		334	64	19.2	17.4	14.2	-	-	62.0	0.10	-	-	-	1.9	0.18	20.2	1.2
211	161		0.6	7.6	2.2*	24.4	1.54	33.4	5		384	93	24.6	9.4	8.4	-	-	63.0	0.00	20	2.9	0.15	2.9	0.14	39.1	2.4
213	112		41.0	72.0	5.7*	0.2	0.00	26.2	10		390	79	17.8	6.6	6.4	-	-	58.4	0.08	42	2.8	0.07	148	0.17	37.5	0.1
214	163		4.2	0.28	3.8*	9.7	0.0	34.6	5		336	86	2.4	3.6	3.2	-	-	61.8	0.40	0.36	1.3	3.61	45	0.05	23.9	0.3
219	140		12.6	0.24	4.7*	10.3	1.34	34.6	29		332	67	2.6	6.0	7.6	-	-	61.2	1.04	1.0	3.3	3.3	3.2	2.7	26.1	1.5
220	155		4.6	0.08	2.2*	0.4	1.44	29.2	17		194	71	25.0	2.8	3.0	54	12	61.6	1.10	0.6	1.0	1.67	59	0.1	29.6	0.3
221	165		2.3	<0.05	0.6	0.3	0.55	25.4	7		153	78	12.0	3.8	3.2	42	11	60.2	0.01	0.86	0.75	0.87	6.3	<0.05	37.5	0.1
222	161		1.52	0.21	4.7*	0.3	1.70	31.4	5		354	80	28	0.4	3.2	46.4	13.3	62.2	1.22	0.03	0.46	15.3	60.5	3.71	25.5	0.1
223	147		5.7	0.27	2.2*	0.6	1.50	27.4	43		336	70	28	0.38	3.0	41	16.2	59.0	1.18	1.95	1.70	0.87	43.7	4.79	26.5	<0.1
224	131		3.5	0.22	0.06	0.63	1.57	30.0	<5		238	70	29.6	0.40	2.8	58.4	12.8	60.0	1.17	0.61	0.76	1.25	78	0.83	26.5	0.69

* Acid Deficient

Analytical Data of Pilot Plant Neutral Ether Extractions

Run No.	U, g/l	Ether Extract	Raffinate						Ether Feed	Aqueous Feed									Raffinate Shakeout			Aq. Phase from top of Extraction Column			
			De-etherized			Ether, Wt. %	Wet Solids, lbs/gal	Baume at 100°F		U, g/l	HNO ₃ , g/l	SO ₄ , g/l	PO ₄ , g/l	Fe, g/l	Ca, g/l	Mg, g/l	Be at 100°F	Wet Solids, lb/gal	U in Aq. Phase, g/l	U in Ether Phase, g/l	Distribution Coefficient	Sol. U, g/l	Insol., g/l	HNO ₃ , g/l	Ether, Wt. %
			Sol. U, g/l	Insol. U, g/l	HNO ₃ , g/l																				
227	151		10.0	0.25	0.16	0.17	1.88	29.0	<4	310	67	41.4	0.46	1.0	51.0	10.6	59.4	1.75	3.96	1.56	0.40	104	1.30	30.1	0.47
228	113		17.0	0.14	0.13	1.1	2.48	29.0	6	385	77	52.6	0.72	1.5	53.6	12.4	62.0	2.14	3.55	4.66	1.31	174	4.8	49.5	5.1
229	142		5.0	0.49	7.79*	0.19	3.20	32.0	<5	215	47	156.6	1.86	4.2	56.8	3.6	62.6	2.22	1.43	1.53	1.07	165	1.51	36.2	0.08
230	180		3.9	0.40	0.28	14.8	1.40	34.6	30	360	72	33.6	0.88	0.8	45.0	24.4	63.4	0.63	0.22	0.60	2.73	63.0	0.1	20.6	<0.08
231	160		26.0	0.20	0.00	0.3	1.80	27.0	5	400	71	39.6	1.0	1.4	36.4	10.2	62.2	0.90	12.3	4.9	0.40	147	0.1	30.1	1.1
232	154		4.7	<0.1	1.13	0.1	1.90	30.4	60	320	64	34.2	0.8	0.8	56.8	13.5	61.0	0.95	1.05	0.47	0.45	828	1.4	23.3	0.8
233	160		1.2	0.1	0.00	<0.1	-	31.2	<5	326	68	33.5	0.8	0.8	55.1	13.0	62.6	1.30	0.20	0.36	1.80	-	-	-	-
234	141		16.7	0.2	3.09	34.4	0.10	32.0	30	290	62	1.6	0.4	0.1	50.0	29.4	61.0	0.04	0.46	1.98	4.3	24.6	20.1	13.6	0.47
235	181		<0.5	<0.1	1.01	<0.08	0.06	29.6	10	310	68	1.9	0.7	0.2	44.4	27.2	60.4	0.08	0.05	0.09	1.8	7.0	0.2	18.6	0.15
237	143		2.7	0.08	0.3	0.14	1.60	33.0	<5	348	74	35.8	1.16	1.72	54	14.0	60.8	1.02	0.52	1.2	2.31	48	0.06	20.8	<0.07

* Acid Deficient

Analytical Data of Pilot Plant Neutral Ether Extractions

Run No.	Ether Extract U, g/l	Raffinate						Ether Feed U, mg/l	Aqueous Feed									Raffinate Shakeout			Aq. Phase from top of Extraction Column			
		De-etherized			Ether, Wt. %	Wet Solids, lbs/gal	Baume at 100°F		U, g/l	HNO ₃ , g/l	SO ₄ , g/l	PO ₄ , g/l	Fe, g/l	Ca, g/l	Mg, g/l	Be' at 100°F	Wet Solids, lb/gal	U in Aq. Phase, g/l	U in Ether Phase, g/l	Distribution Coefficient	Sol. U, g/l	Insol., g/l	HNO ₃ , g/l	Ether, Wt. %
		Sol. U, g/l	Insol. U, g/l	HNO ₃ , g/l																				
238	150	1.4	0.05	<0.3	0.23	1.60	31.2	10	380	75	28.8	2.50	1.78	53.0	13.8	60.2	1.29	0.78	1.2	1.54	31.0	<0.05	24.6	<0.07
239	164	1.0	0.06	<0.3	<0.07	2.03	33.0	3	344	80	38.8	3.14	1.56	54	14	61.6	1.2	0.26	0.88	3.39	29.0	<0.05	25.2	0.29
240	158	1.2	0.09	4.7*	<0.07	1.60	33.2	<3	324	65	21.0	2.0	1.58	56.8	14.6	62.2	0.94	0.24	0.50	2.08	40.5	0.05	17.3	<0.08
241	170	5.1	0.1	2.8*	<0.07	3.10	33.4	3	350	69	24.0	0.70	1.82	45.0	28.2	63.4	1.5	0.62	2.3	3.71	65.5	0.1	14.2	1.8
242	161	1.8	<0.05	2.5*	0.08	2.01	32.0	<5	374	74	25.2	0.58	2.50	51.0	13.8	61.6	1.18	0.26	0.89	3.42	77	0.07	24.6	<0.07
243	181	8.4	0.10	2.8*	9.4	1.46	39.0	<5	338	69	7.8	0.66	4.50	46.2	28.0	65.4	2.7	0.90	4.0	4.4	58.4	0.09	19.8	3.2
244	198	1.94	0.14	3.2*	0.07	1.17	35.0	<5	344	67	20.8	0.66	2.50	59.2	15.0	62.4	0.75	0.20	0.9	4.5	66.3	<0.05	20.5	0.22
245	152	20.0	0.09	3.5*	5.3	1.3	33.0	<5	312	70	41.6	0.62	20	-	54.0	60.0	1.1	10.5	5.8	0.55	39.7	0.05	14.5	0.08
246	154	28.6	0.3	3.5*	0.16	1.1	35.8	6	348	70	37.2	0.64	2.50	-	64.0	61.0	1.2	14.0	5.2	0.37	63.1	0.4	11.7	<0.08
247	140	12.8	0.07	3.8*	0.07	1.3	27.6	<5	315	76	28.0	0.42	3.6	41.2	13.0	57.6	0.11	5.20	0.08	0.02	27.5	0.6	38.7	4.4

* Acid Deficient

Analytical Data of Pilot Plant Neutral Ether Extractions

Run No.	Ether Extract		Raffinate						Ether Feed	Aqueous Feed								Raffinate Shakeout			A q. Phase from top of Extraction Column					
	U, g/l	Sol: U, g/l	De-etherized			Ether, Wt, %	Wet Solids, lbs/gal	Baume at 100°F		U, mg/l	U, g/l	HNO ₃ , g/l	SO ₄ , g/l	PO ₄ , g/l	Fe, g/l	Ca, g/l	Mg, g/l	Be' at 100°F	Wet Solids, lb/gal	U in Aq. Phase, g/l	U in Ether Phase, g/l	Distribution Coefficient	Sol. U, g/l	Insol., g/l	HNO ₃ , g/l	Ether, Wt. %
			Insol. U, g/l	HNO ₃ , g/l																						
248	152	2.4	0.08	5.4*	1.8	0.44	32.0	<4	380	88	29.6	0.28	16.2	2.4	41.8	60.4	0.46	0.54	1.9	3.52	48.6	<0.05	18.0	0.7		
249	163	35.0	0.20	0.0	0.08	1.7	28.6	15	336	73	31.6	0.50	4.6	32.8	11.6	59.0	0.57	18.3	8.0	4.37	87.0	1.07	34.7	0.07		
251	167	0.42	0.05	14.5*	0.08	1.8	33.2	3	376	75	28.6	0.28	20.0	37.0	22.2	60.2	1.6	0.32	0.4	1.25	44.4	<0.05	19.5	<0.07		
254	155	9.71	<0.03	7.0	0.2	0.80	31.4	15	360	61	47.8	0.50	15.6	-	38.4	61.6	0.82	4.40	2.8	0.64	77.2	<0.03	14.0	0.1		
255	155	2.64	0.07	3.47	0.2	1.92	30.6	<3	344	71	43.8	0.30	15.8	37.0	22.0	61.0	1.04	-	-	-	54.0	<0.03	24.7	0.2		
256	161	7.22	0.04	2.39	2.6	0.33	31.4	<3	332	61	44.8	0.34	11.4	-	46.0	60.2	1.2	2.50	1.90	0.76	66.2	0.09	21.4	0.2		
257	154	3.49	0.03	3.78	1.6	0.61	31.6	<3	336	66	41.0	0.38	21.6	-	41.2	60.0	1.2	0.50	0.71	1.42	51.5	0.07	17.6	0.2		
258	151	4.44	0.04	3.7*	0.1	0.76	30.4	4	328	64	39.8	0.34	28.6	-	31.8	60.0	2.6	1.21	1.90	1.58	75.0	0.05	17.0	2.6		

* Acid Deficient

GLOSSARY

Black Oxide -	A concentrated uranium bearing feed material, principally U_3O_8 .
Congo Ion Exchange Precipitate -	A high assay uranium bearing feed material prepared by a magnesium hydroxide precipitation of the uranium in a strip liquor from anion exchange beds. The precipitate is filtered and dried. This material is scheduled to replace MgX ore as a feed material in the near future.
Jet - Mixer Column -	An open column with pumps spaced at intervals to remove the continuous phase from the column for reintroduction through a mixing device to produce agitation.
MgX Ore -	A uranium bearing feed material prepared by magnesium hydroxide precipitation of filtrate from a sulfuric acid leach of low grade pitchblende ores.
MgX Slurry -	A prepared aqueous feed slurry for the ether extraction process. The current MgX slurry includes 28.5 percent black oxide ore, 39.2 percent V-20 ore, and 34.1 percent MgX ore (all on a uranium basis) digested in 45 percent nitric acid at 100 to 150° F. in the order named.
Pitchblende Ore -	A naturally occurring ore of uranium and radium.
Pitchblende Filtrate -	An acid solution of uranyl nitrate and other metallic nitrates resulting from filtration of a slurry obtained by digesting pitchblende ore in 45 percent nitric acid. Recovery cake from the plant sump and other miscellaneous materials are usually added to this slurry.
Rand Ore-	A uranium bearing feed material obtained from a sulfuric acid leach of gold refinery cyanide tails. The uranium is stripped from the leach liquor on an ion exchange bed and then washed off and precipitated with ammonium nitrate. The precipitate is filtered, dried, and calcined.
Salting Agent -	Any metallic nitrate present in an acid solution of uranyl nitrate which increases the uranium distribution coefficient in favor of the ether phase in the ether-water system.
V-20 Ore -	A concentrated uranium bearing feed material, principally sodium diuranate, resulting from processing of low content uranium-vanadium ores.

PILOT PLANT STUDIES OF THE WAX COMPLEX (WAXCO) EXTRACTION PROCESS

by

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I. Introduction

Production of uranium at Mallinckrodt Chemical Works involves a two-cycle ether extraction of aqueous uranium solutions -- the first cycle to obtain a gross purification and recovery from solutions prepared from uranium-bearing ores, the second to obtain a final purification of the first-cycle product. The uranium recovery obtained in the first cycle is adequate; however, this recovery can still be improved.

Several possibilities for improvement of the recovery of uranium from this first-cycle extraction raffinate have been studied by MCW personnel in recent months. Considerable emphasis has been placed on the use of strong uranium complexing agents, such as tributyl phosphate, which are capable of highly efficient uranium recovery. A solid-liquid extraction technique was developed to overcome emulsification encountered with kerosene. The solid-liquid extraction process has been named the wax-complex (Waxco) extraction process.

The Waxco Process utilizes the novel method of incorporating the uranium complexing agent with a wax to obtain a solid extraction agent. The wax extraction agent in the form of flakes, spheres, cubes, etc. may then be contacted with uranium-bearing liquors in a packed column, by slurring, by containing the wax agent in a basket or by some other suitable method. After contact with the raffinate, the wax agent can be stripped with water or some other suitable stripping agent.

Although emphasis has been placed on recovery of uranium from MCW raffinates, consideration has been given to other possible applications of this process. In general, this process might be applied to the recovery of any uranium-bearing acid solutions that have a suitable salt background. Specifically, this process could be used for uranium recovery from digest slurries of low grade ores.

Earlier laboratory work on this process has been published.^{1, 2, 3} Current laboratory work is being issued in a separate report.⁴ This report covers a continuation of pilot plant investigations⁵ of this process.

¹ Rueble, A. E., and Leaders, W. M., Research and Development Progress Report, Mallinckrodt Chemical Works, January 15, 1953 (NYO-1352), p. 8-24.

² Rueble, A. E., and Shepardson, J. U., Process Development Quarterly Report, Part II, Mallinckrodt Chemical Works, April 15, 1953, (NYO-1354), p. 7-13.

³ Rueble, A. E., and Shepardson, J. U., Process Development Quarterly Report, Part I, Mallinckrodt Chemical Works, July 15, 1953 (NYO-1355), p. 8-15.

⁴ Rueble, A. E., and Shepardson, J. U., Process Development Quarterly Report, Part I, Mallinckrodt Chemical Works, October 15, 1953 (NYO-1357), p. 18-31.

⁵ Leaders, W. M., and Miller, E. I., Process Development Quarterly Report, Part II, Mallinckrodt Chemical Works, July 15, 1953 (NYO-1356), p. 113-129.

The initial pilot plant work indicated that development of a continuous process for extraction of raffinate slurry with a wax agent would be difficult. Disintegration of wax particles to form a colloidal suspension imposed many limitations upon a method of contacting and separating. Thus, study of a continuous process was continued using filtered raffinate.

Application of the Waxco process for uranium recovery from slurries would be desirable since difficulty is frequently encountered in filtration. The potential usefulness of such a process to handle slurries prompted investigation of a multiple-stage countercurrent batch process.

These investigations have covered the following points:

1. Extraction and stripping efficiencies obtainable by both processes.
2. Chemical and physical stability of the wax agent with repeated contracting and stripping.
3. Uranium capacity of the wax agent with repeated contacting and stripping.

II. Experimental Equipment

Earlier pilot plant investigations⁶ have shown that the physical properties of the wax agent impose limitations upon the equipment design. Operating pressures and the depth of unsupported wax are limited in the continuous process by concretion of the wax agent particles. Contacting methods of wax agent with raffinate in a batch process are limited since even nominal agitation results in disintegration of the wax agent to form colloidal dispersions. Separation of a slurry of wax agent and raffinate is very difficult due to entrainment of wax agent particles in the raffinate.

The equipment described and illustrated in this section resulted from modifications made, as the work progressed, to overcome these limitations imposed by the wax agent.

A. Continuous Contacting Equipment

The continuous contacting equipment used in these investigations was a bed of wax agent. This filter bed has been modified from the apparatus described in a previous report⁷ to the equipment as shown in Figure 1. The piping has been changed so that solutions can be passed in either direction through the bed. A rotameter has been placed in the feed line to control flow rates; however, all throughputs are calculated from the volume processed during a given length of time. A removable screen has been placed in the center of the bed to prevent packing of the wax agent. A removable screen has been placed on the top of the bed to prevent flotation of the wax agent during upward flow of solutions through the bed.

⁶ *Op. cit.*, (NYO-1356).

⁷ *Op. cit.*, (NYO-1356).

FILTER BED APPARATUS

FIGURE - I

B. Batch Contacting Equipment

1. Single-Stage Churn Apparatus

The batch contacting equipment described here was developed to yield sufficient contact with a minimum of agitation. A basket was designed to contain the wax agent to facilitate separation and minimize wax agent disintegration. Contact with the raffinate was accomplished by churning the basket in a container of raffinate. This equipment is illustrated in Figure 2.

The basket consisted of a ring of 14 guage stainless steel 3 inches high by 6 inches in diameter. A $\frac{1}{2}$ inch pipe coupling was supported in the center of the ring by a web of four $\frac{5}{8}$ inch by $\frac{1}{8}$ inch pieces of stainless steel flat. The open ends of the basket were covered with 102 Vinyon-N cloth. The cloth was clamped on the basket by $\frac{1}{2}$ inch wide 14 guage stainless steel bands tightened by means of a bolt. A 12 inch length of $\frac{1}{2}$ inch pipe extended from the coupling in the center of the basket. The top cloth was sealed around this pipe by means of two washers.

The pipe from the basket was attached to a Bellows Co., model BCAM-5 reciprocating air cylinder. The air cylinder was bolted to an adjustable supporting apparatus made of pipe and structural steel.

2. Four-Stage Churn Apparatus

The single-stage churn apparatus was modified for four-stage contacting as shown in Figure 3. Four $\frac{1}{2}$ inch pipe couplings were welded to the bottom of a $2\frac{1}{2}$ inch channel 42 inches long for attachment of four baskets. The channel was in turn fastened to the air cylinder for reciprocation.

Two guides were provided to prevent rotation of the channel during operation.

III. Experimental Procedure and Results

A. Continuous Process Experiments

Work on the continuous process with the filter bed was continued. The investigation of wax agent stability upon repeated extraction and stripping was emphasized by using the same portion of wax agent (50 percent tributyl phosphate - Mekon Y-20) that was used in earlier work.

Five runs were made using raffinates of varied uranium concentration. The raffinate was passed downward through the bed in four runs and upward through the bed in one run. The stripping of uranium from the bed was accomplished with either water or a portion of strip liquor from a previous run. Four stripping operations were carried out with flow counter-current to, and one with flow co-current with that used for extraction operations.

FIGURE - 2

FIGURE - 3

The operating procedure was essentially the same for both extraction and stripping operations.

A known volume of feed liquor was placed in the feed tank, and in the case of uranium-bearing liquors, sampled for uranium analysis. The feed liquor was fed to the filter bed by means of an air-driven pump. A constant flow rate was maintained with a rotameter (about 14-15 gal/hr-sq. ft. for extraction and 10-12 gal/hr-sq. ft. for stripping). For downward flow, valves A, B, D and E were open and valve C was closed (see Figure 1). In this case, the liquor was sprayed over the bed, trickled through by gravity, and was collected in the receiving tank. For upward flow, valves A, B, and C were open, and valves D and E were closed. In this case, liquor entered the bottom of the filter bed and overflowed at the top into a receiving tank. The wax agent was prevented from floating in upward flow by a screen which was locked in place at the top of the bed.

Progress of the run was followed by taking:

1. Periodic grab samples of the discharge liquor for uranium analysis.
2. Composite samples of measured volumes of liquor in the receiving tanks for uranium analysis.

Extraction efficiencies and wax agent uranium concentrations were determined for different operating conditions using varied uranium concentration raffinates. The experimental results obtained in run No. 8 (using downward flow) are typical (see Table I). The run was tabulated in portions to show the decrease in extraction efficiency as the bed approached saturation. Flow counter-current to the extraction flow was used during stripping operations. The first two portions of the stripping cycle were made with the last two portions of strip liquor from run No. 7.

A summary of the data obtained in all five runs is presented in Tables II and III.

The effect of different uranium concentration raffinates on extraction efficiency and wax agent uranium concentration was observed by a comparison runs Nos. 8 and 5. Operating conditions for these runs were identical. The cumulative extraction efficiency is plotted as a function of wax agent uranium concentration in Figure 4. At a wax agent uranium concentration of 70 mg/g uranium, the extraction efficiency was 66 percent for a 6 g/l uranium raffinate as compared with 91 percent for a 1.8 g/l uranium raffinate.

Run No. 6 was made to observe the operating characteristics of upward flow during the extraction cycle. The low extraction efficiency and low wax agent uranium concentration was a result of channeling and bed concretion.

Table I

Experimental Data - Filter Bed Run No. 8

Extraction Cycle

Portion No.	Volume of Raffinate Processed, gal.	Time Required to Process, hrs.	Average Flow Rate, gal/hr-sq. ft.	Solution Uranium Analyses, g/l		Uranium Extracted, g	Recovery Efficiency, %	Wax Agent Uranium Concentration, mg/g
				Initial	Final			
1	20.0	4.0	14.3	5.60	0.28	403	95.5	24.9
2	20.0	4.0	14.3	6.20	1.36	364	78.0	47.4
3	20.0	4.0	14.3	5.60	3.15	185	44.0	58.9
4	20.0	4.1	14.0	6.35	3.23	236	49.2	73.4
Totals	80.0	16.1	14.2	5.94	2.00	1188	67.0	73.4

Stripping Cycle

								Cumulative Recovery Efficiency, %
1	8.0	2.0	11.5	0.82	24.3	712	60.0	60.0
2	10.0	2.5	11.5	0.51	12.1	452	38.2	98.2
3	10.0	2.5	11.5	0.00	2.60	99	8.3	106.5
4	10.0	2.2	13.0	0.00	0.51	19	1.6	108.1
Totals	38.0	9.2	11.9	0.33	9.08	1284	108.1	108.1

⁸ Based on uranium extracted in extraction cycle.

Table II

Extraction Cycle Data Obtained in Filter Bed Runs Nos. 5-9

Run No.	Volume of Raffinate Processed, gal.	Time Required to process, hr.	Average Flow Rate gal/hr-sq. ft.	Feed Raffinate Uranium Analyses, g/l			Processed Raffinate Uranium Analyses, g/l			Uranium Extracted, g	Extraction Efficiency, %	Wax Agent Uranium Concentration, mg/g
				High	Low	Average	High	Low	Average			
5	165.3	42.4	11.2	2.10	1.65	1.87	0.57	0.04	0.17	1039	91.2	69.5
6	187.4	40.6	13.2	2.25	0.83	1.34	0.92	0.05	0.44	642	67.2	42.2
7	300.0	61.9	13.9	1.22	0.86	1.04	0.91	0.11	0.45	664	56.7	40.8
8	80.0	16.1	14.1	6.35	5.60	5.94	3.23	0.28	2.00	1188	67.0	73.4
9	120.0	28.0	12.2	1.64	1.64	8.86	23.1	0.11	4.50	1973	51.6	122

Table III

Stripping Cycle Data Obtained in Filter Bed Runs Nos. 5-9

Run No.	Volume of Liquor Processed, gal.	Processing Time, hr.	Average Flow Rate gal/hr-sq. ft.	Feed Solution Uranium Analyses, g/l			Processed Solution Uranium Analyses, g/l			Uranium Recovered, g	Recovery Efficiency, %	Comments
				High	Low	Ave.	High	Low	Ave.			
5	63.2	17.2	10.0	0.0	0.0	0.0	18.0	0.15	4.24	1015.4	97.8	Co-current with Extraction Flow
6	51.6	13.5	10.6	0.0	0.0	0.0	11.05	0.51	3.74	726.0	112.9	Counter-current with Extraction Flow
7	41.6	8.3	14.4	0.0	0.0	0.0	11.85	0.44	4.08	683.1	102.9	"
8	38.0	9.2	11.9	0.82	0.0	0.33	24.3	0.51	9.08	1284	108.1	"
9	40.4	10.3	11.3	2.16	0.0	0.57	44.4	0.47	13.08	1911	96.8	"

FIGURE 4

VARIATION OF EXTRACTION EFFICIENCY WITH WAX
AGENT URANIUM CONCENTRATION FOR 2 RAFFINATES

Run No. 7 was made with raffinate filtrate from a slurry which had been acidified to 3 N excess nitric acid. This run was made to determine the effect of acidification on filter bed extraction efficiency and insoluble uranium in the raffinate slurry. The decreased extraction efficiency for run No. 7 may be observed by comparison with run No. 5. The effect of acidification to 3 N excess nitric acid on insoluble uranium in the raffinate slurry can be observed from the data in Table IV:

Table IV

The Effect of Acidification to 3 N Excess Nitric Acid
on Insoluble Uranium in Raffinate Slurry

Cake Description	Cake Analyses		
	Soluble Uranium, %	Insoluble Uranium, %	Moisture, %
1st Batch Before Acidification	0.06	0.04	57.9
1st Batch After Acidification	0.06	0.01	58.1
2nd Batch Before Acidification	0.11	0.04	56.0
2nd Batch After Acidification	0.08	0.03	58.3

A slight reduction of insoluble uranium in raffinate slurries was obtained by acidification to 3 N excess nitric acid.

The stability of the wax agent after 8 extraction and stripping cycles was demonstrated in run No. 9. The uranium content of the raffinate was varied from 1.6 g/l uranium initially to as high as 33 g/l uranium during the last portion of the run. This high uranium content feed resulted in poor overall extraction efficiency, but produced a wax agent uranium concentration of 122 mg/g (about 60 percent higher than any of the other runs).

Stripping efficiencies in general were high for all five runs. Stripping efficiencies of greater than 100 percent for runs Nos. 6 through 8 may be explained by inefficient stripping during earlier runs compounded by cumulative errors in analyses and material balances. The more efficient stripping obtained during this quarter was attributed to reversal in the direction of liquor flow through the bed for stripping operation. The effect of countercurrent flow may be observed by a comparison of run No. 8 with run No. 5. Complete stripping was obtained with less than 40 gal. of liquor during run No. 8 (counter-current flow) whereas more than 60 gal. of liquor was needed for complete stripping during run No. 5 (parallel flow).

Operational difficulties that were encountered during last quarter and the early part of this quarter were:

1. Plugging of the filter bed with solids which had precipitated in the raffinate filtrate.

2. Cementation of wax agent particles due to evaporation and crystallization of raffinates held in the bed during shutdown periods.
3. Plugging of the filter bed due to compaction of the wax agent particles under their own weight or excessive pressures.

Elimination of raffinate filtrate crystallization to prevent plugging of the bed was attempted, with only partial success, by raffinate filtrate dilution, by acidification, and by filtration at lower temperatures. Bed plugging was finally prevented by clarification of the filtrate immediately before extraction.

Cementation of the wax agent particles during shutdown periods was prevented by flushing and flooding the filter bed with water prior to shutdown. The bed was allowed to stand for one week in this condition, between the extraction and stripping cycles of run No. 5, with no indication of wax agent cementation.

Elimination of bed plugging due to solids in the raffinate during the latter portion of run No. 5 revealed a problem of bed plugging due to wax agent concretion under its own weight. A similar concretion was observed during upward flow on run No. 6 as a result of the great difference in specific gravity between raffinate (sp gr 1.3) and the wax agent (sp gr 0.9) combined with the greater flow pressure needed with upward flow. This problem was solved with the installation of a supporting screen in the center of the bed. This screen reduced bed weight on the bottom screen to a point where concretion was no longer a problem.

B. Batch Process Experiments

1. Single-Stage Batch Process Experiments

Earlier investigations⁹ of a batch process have indicated that a minimum of agitation would be necessary to eliminate wax agent disintegration. An attempt to eliminate disintegration of wax agent was made by confining the wax agent in a basket which could be churned in a container of raffinate slurry.

Three experiments were performed to determine the extraction efficiency of such a process. Extractions were made by:

- a. Slurrying the wax agent directly in raffinate.
- b. Churning a basket of wax agent in a container of raffinate slurry.
- c. Agitating a container of raffinate slurry in which was suspended a basket of wax agent.

The data obtained are tabulated in Table V.

⁹ *Op. cit.*, (NYO-1356).

Table V

Comparison of Three Different Contact Methods
Using an Eight g/l Raffinate at Contact Ratios of 0.5 and 1.0 lb of
50 Percent Tributyl Phosphate-Mekon Y-20/gal of Raffinate

Contact Method	Contact Ratio, lb/gal	Extraction Efficiency, Percent	Wax Agent Uranium Concentration, mg/g
Direct Slurrying	0.5	53.4	64.2
	1.0	75.4	46.7
Churn Apparatus	0.5	42.5	55.4
	1.0	68.1	42.5
Basket in Agitated Raffinate	0.5	21.1	29.2
	1.0	23.9	16.4

Churning of a basket of wax agent in raffinate resulted in only a 10-20 percent reduction of extraction efficiency from that of direct slurrying. Confining of the wax agent in a stationary basket suspended in agitated raffinate resulted in a 55-65 percent reduction of extraction efficiency. The churn apparatus was adopted for further experimental work on the basis of this low reduction in extraction efficiency and the ready means of separation of the wax agent from the raffinate slurry that was offered.

A series of runs was then made to determine the effect of variation of the wax agent weight to raffinate volume ratio on extraction efficiency and wax agent uranium concentration. Runs were made at contact ratios of 0.1, 0.5, 1.0 and 2.0 lbs. of wax agent/gal of raffinate using raffinate slurries ranging from 1-8 g/l uranium. The data obtained are presented in Table VI. A graph of extraction efficiency vs. contact ratio with raffinate uranium as a parameter appears in Figure 5.

These data showed that efficient uranium recovery could be obtained at high contact ratios. However, the accompanying low wax agent uranium concentration would yield low uranium concentration liquors on subsequent stripping operations. Thus, a multiple-stage extraction was indicated as a requisite for obtaining efficient extraction with high wax agent uranium concentrations.

Another series of experiments was performed to determine the maximum wax agent uranium concentration obtainable in a four-stage extraction process. The same portion of wax agent was contacted for one hour each with four batches of the same raffinate. Runs were made using raffinates ranging from about 2-8 g/l uranium. The data obtained are given in Table VII.

Table VI

One Hour Contacts of 50 Percent Tributyl Phosphate-Mekon V-20 at Varying Contact Ratios With Varying Uranium Concentration Raffinates

Range of Raffinate Uranium Content, g/l	Contact Ratio, lb/gal.	Volume of Raffinate Processed, ml	Weight of Wax Agent, g	Solution Uranium Analyses, g/l		Weight of Uranium Transferred, g	Extraction Efficiency, %	Wax Uranium Concentration, mg/g
				Initial	Final			
1-2	0.1	16,600	200	1.54	1.20	5.6	22.1	28.3
	0.5	10,000	600	1.71	0.35	13.6	79.5	23.7
	1.0	5,000	600	1.72	0.12	8.0	93.1	13.3
	2.0	2,500	600	1.88	0.12	4.4	97.6	7.3
6-7	0.1	16,600	200	6.53	5.92	10.1	9.1	50.5
	0.5	10,000	600	6.71	3.19	35.2	52.4	58.6
	1.0	5,000	600	6.90	1.14	28.2	83.5	48.1
	2.0	2,500	600	6.90	0.24	16.6	96.6	27.8
7-8	0.1	16,600	200	7.61	6.62	16.6	13.1	83.1
	0.5	10,000	600	7.80	4.48	33.2	42.5	55.4
	1.0	5,000	600	7.66	2.44	26.1	68.1	42.5
	2.0	2,500	600	8.08	1.29	17.0	84.0	28.3
8-9	0.1	16,600	200	8.96	8.39	9.5	6.4	47.5
	0.5	10,000	600	8.75	6.67	20.8	24.8	34.8
	1.0	5,000	600	8.39	3.46	24.6	59.0	41.0
	2.0	2,500	600	8.98	1.00	19.9	88.6	34.2

FIGURE 5

EXTRACTION EFFICIENCIES FOR VARIOUS CONTACT RATIOS
WITH RAFFINATES OF VARYING URANIUM CONCENTRATIONS

Table VII

Four-One Hour Contacts of Varying Uranium Concentration Raffinates At a Contact Ratio of 0.5 lb/gal

Range of Raffinate Uranium Content, g/l	Contact No.	Volume of Raffinate Processed, ml	Weight of Wax Agent, g	Solution Uranium Analyses, g/l		Weight of Uranium Transferred, g	Extraction Efficiency, %	Wax Agent Uranium Concentration, mg/g
				Initial	Final			
1-2	1	10,000	600	1.76	0.35	14.1	80.5	-
	2	10,000	↓	1.80	0.54	12.6	70.2	-
	3	10,000	↓	1.65	0.90	7.5	44.5	-
	4	10,000	↓	1.72	1.18	5.4	31.4	55
6-7	1	10,000	600	6.86	3.42	3.44	49.9	-
	2	10,000	↓	6.65	5.41	12.4	18.7	-
	3	10,000	↓	6.95	6.08	8.7	12.5	-
	4	10,000	↓	8.11	6.80	13.1	8.4	85
7-8	1	10,000	600	7.27	4.14	31.3	43.1	-
	2	10,000	↓	7.18	6.16	10.2	14.2	-
	3	10,000	↓	7.25	7.25	1.0	1.4	-
	4	10,000	↓	7.45	7.05	4.0	5.4	76
8-9	1	10,000	600	8.05	5.01	30.4	37.8	-
	2	10,000	↓	8.15	7.25	9.0	11.0	-
	3	10,000	↓	8.25	7.50	7.5	9.1	-
	4	10,000	↓	8.39	7.62	7.7	9.2	94

These data show that wax agent uranium concentrations from 55 mg of uranium/g of wax agent for a 1.8 g/l uranium raffinate to 95 mg uranium/g of wax for an 8 g/l uranium raffinate were obtained in four successive contacts.

2. Four-Stage Countercurrent Batch Process Experiments

A four-stage countercurrent batch process was studied on the basis of earlier data indicating that multiple-stage extraction would be necessary to obtain high wax agent uranium concentrations with efficient extraction. Four-stage countercurrent extraction runs were made as follows:

- a. Four baskets were filled with a weighed amount of known moisture content wax agent.
- b. Four buckets were filled with a measured volume of raffinate slurry which had been sampled for uranium analysis.
- c. The baskets were attached to the channel and a bucket placed under each basket.
- d. The apparatus was lowered to immerse the baskets in the raffinate.
- e. The air cylinder was started and the baskets churned up and down in the raffinate for one hour.
- f. The apparatus was raised and the baskets were allowed to drain for ten minutes.
- g. The basket in the first stage was removed from the channel and the remaining three baskets were moved to the next lower stage in number.
- h. The wax agent in the removed basket was weighed and sampled for uranium and moisture analyses.
- i. A basket containing the same amount of wax agent as in (a) was attached to the channel in the fourth stage.
- j. The bucket in the fourth stage was removed and sampled for uranium analysis.
- k. The three remaining buckets were moved to the next higher stage in number.
- l. A bucket containing the same volume of raffinate as in (b) was placed in the first stage.
- m. The procedure from part (d) to (l) was repeated for the desired number of contacts.

A total of six runs has been made in the study of the four-stage countercurrent batch process. Runs were made using raffinate slurries varying in uranium content from one to five g/l uranium. Initial wax agent weight to raffinate volume ratios were estimated by assuming that adequate extraction in a four-stage process would be obtained at that ratio which yielded 60 percent extraction in a single-stage.

The experimental data obtained in run No. 4 are typical (see Table VIII). The final results of all six runs are listed in Table IX.

Better than 80 percent extraction was obtained in all runs except run No. 5 which was made using raffinate slurry acidified to 3 N excess nitric acid. The 54 percent extraction efficiency observed for this run verifies similar reduction of extraction efficiency observed for filter bed run No. 7 using 3 N excess nitric acid raffinate filtrate. No difficulty was encountered with wax agent disintegration during these runs. Entrainment of raffinate solids in wax agent particles was observed due to improper fitting of the cloth seal clamps or solids leakage through the cloths.

C. Comparison of Hot vs. Cold Stripping

Considerable work has shown that the uranium distribution coefficient between tributyl phosphate in kerosene and water increases in favor of the water phase with increase in temperature. An investigation was made to determine if similar behavior was observed in water stripping of uranium from a tributyl phosphate impregnated wax agent.

Three runs were made -- 2 runs using 50 percent tributyl phosphate - Acrawax C (melting point 252°F); 1 run using 50 percent tributyl phosphate - Mekon Y-20 (melting point 172°F). Acrawax C was used to obtain a higher melting point wax agent which would not soften and agglomerate at 150°F.

The experimental procedure was the same for all three runs.

A uranium loading on the wax agent was obtained by slurring the wax agent in raffinate filtrate. The wax agent-raffinate slurry was separated by filtration on a Buchner funnel. The wax agent was washed with a small amount of water while in the Buchner funnel to remove adsorbed salts. The wax agent was homogenized and divided into two portions on a weight basis. One portion was slurried in water at 85°F while the other was slurried at 150°F.

The experimental data obtained are tabulated in Table X. These data indicate that stripping at 150°F gives 10-15 percent greater efficiency than stripping at 85°F.

Table VIII

Four-Stage Countercurrent Batch Run No. 4 at 0.45 Lb. of 50 Percent Tributyl Phosphate-Mekon Y-20/gal of 5 g/l Raffinate

Contact No.	Volume of Raffinate Processed, ml	Initial Solution Uranium Analyses, g/l	Solution Uranium Analyses After Contact, g/l				Wax Weight, g		Wax Analyses	
			1st Stage	2nd Stage	3rd Stage	4th Stage	Before Contact	After Contact	Uranium, mg/g	Water, %
1	10,000	4.66	-	-	-	3.36	540	848	35	24
2	10,000	4.85	-	-	-	0.86	540	712	52	-
3	10,000	5.00	-	-	-	0.37	540	660	57	-
4	10,000	4.66	-	-	-	0.13	540	702	56	-
5	10,000	4.66	-	-	-	0.54	540	686	44	22
6	10,000	4.80	-	-	-	0.42	540	649	59	-
7	10,000	4.90	-	-	-	0.56	540	634	49	-
8	10,000	5.22	4.37	3.64	2.48	0.52	540	678	49	-
9	10,000	5.05	-	-	-	1.08	540	621	44	-
10	10,000	5.18	-	-	-	0.90	540	661	47	22
11	10,000	5.09	-	-	-	0.97	540	694	46	-
12	10,000	5.04	4.57	3.94	2.58	0.73	540	689	43	-
13	10,000	5.09	-	-	-	1.02	540	671	40	-
14	10,000	4.90	-	-	-	0.90	540	732	43	-
15	10,000	5.78	-	-	-	1.18	540	-	45	18
16	10,000	5.40	5.04	4.50	3.18	1.15	540	593	53	-
17	10,000	5.04	-	-	-	1.07	540	736	46	-
18	10,000	4.84	-	-	-	0.88	540	708	48	-
19	10,000	5.31	-	-	-	0.93	540	723	38	-
20	10,000	5.65	4.66	4.44	3.22	0.89	540	605	58	10
Average	10,000	5.06	4.66	4.13	2.86	0.86	540	672	47.0	19.2

Table IX

Experimental Data Obtained in Four-Stage Countercurrent Batch Run Nos. 1-6

Run No.	Number of Contacts	Contact Ratio, lb. Wax Agent per gal. of Raffinate	Volume of Raffinate, ml	Initial Raffinate Uranium Analyses, g/l	Solution Uranium Analyses				Wax Agent		Wax Agent		Calculated by Material Balance on Solution	
					After Contact, g/l				Before Contact, g	After Contact, g	Analyses		Wax Agent Uranium Concentration mg/g	Extraction Efficiency, %
					1st Stage	2nd Stage	3rd Stage	4th Stage			Uranium, mg/g	Water, %		
1	12	0.25	10,000	2.23	1.71	0.90	0.30	0.10	300	-	37.7	25.5	71.0	95.5
2	15	0.10	10,000	0.87	0.74	0.68	0.43	0.16	120	-	35.2	24.3	59.2	81.6
3	20	0.10	10,000	0.99	0.88	0.68	0.52	0.19	120	-	40.1	27.3	66.7	80.8
4	20	0.450	10,000	5.06	4.66	4.13	2.86	0.86	540	672	47.0	19.2	77.7	83.0
5	20	0.20	7,500	1.69	1.64	1.48	1.16	0.77	180	190	28.2	8.0	38.3	54.4
6	20	0.61	6,850	3.50	1.96	0.84	0.56	0.42	500	661	37.2	11.4	42.2	88.0

Table X

Comparison of Hot and Cold Stripping of Tributyl Phosphate Impregnated Wax Agents

Wax Agent	Process	Volume of Solution, ml	Weight of Wax Agent, g	Solution Uranium Analyses, g/l		Weight of Uranium Transferred, g	Extraction Efficiency, %	Wax Agent Uranium Concentration, mg/g	Temperature, °F
				Initial	Final				
50 Percent Tributyl Phosphate Acrawax	Extraction	8000	1362	1.85	0.13	13.76	93.0	10	-
	Wash	300	1008	0.0	1.36	0.41	-	-	-
	Cold Stripping	3780	504	0.0	1.57	5.93	88.8	1.9	88
	Hot Stripping	3780	504	0.0	1.90	6.97	104.3	0	147
50 Percent Tributyl Phosphate Acrawax	Extraction	8000	914	7.00	0.13	55.0	98.0	60	-
	Wash	400	980	0.0	2.02	0.8	-	-	-
	Cold Stripping	3940	490	0.0	6.15	24.2	89.5	6.8	85
	Hot Stripping	3570	490	0.0	7.05	25.2	92.5	4.7	150
50 Percent Tributyl Phosphate Acrawax	Extraction	8000	1000	7.00	0.56	51.5	92.0	51.5	-
	Wash	566	964	0.0	8.76	4.9	-	-	-
	Cold Stripping	3960	482	0.0	3.82	15.1	65.0	14	85
	Hot Stripping	3700	482	0.0	5.13	19.0	81.5	4.2	150

IV. Discussion of Results.

Pilot plant work on the Waxco process has continued in two directions:

1. The investigation of a continuous process contacting filtered raffinate with a bed of wax agent.
2. The development of a four-stage countercurrent batch process to contact wax agent with raffinate slurries.

Work during this quarter has demonstrated that satisfactory extraction of uranium from a raffinate filtrate can be accomplished in a filter bed. Operational problems involving crystallization of raffinate filtrate and compaction of wax agent were solved satisfactorily. The chemical and physical stability of the wax agent upon repeated extraction and stripping through nine cycles was demonstrated. Complete recovery of uranium from the wax agent was shown to be possible. No gross loss of tributyl phosphate or wax agent extraction capacity was observed.

Extraction efficiencies and wax agent uranium concentrations in the four-stage countercurrent batch process were found to be comparable to those observed in filter bed operations. Satisfactory physical operation was obtained in the pilot plant batch unit. However, since this unit is not readily adaptable to plant use, considerable development work is anticipated for development of such a process.

Continued investigation of the application of the Waxco process to low uranium content slurries will be stressed in future work because of the obvious advantages inherent to such a process. Emphasis will be placed on a study of contacting methods with various forms of wax extraction agent.

V. Conclusions

1. Satisfactory extraction of uranium from MCW raffinates was obtained in a filter bed containing 50 percent tributyl phosphate-Mekon Y-20 wax agent.
2. Complete recovery of extracted uranium from this bed was possible.
3. Chemical and physical stability of the wax agent upon repeated contacting and stripping has been demonstrated through nine cycles.
4. Filter bed stripping flow countercurrent to extraction flow has been demonstrated to be more efficient than co-current flow.
5. Wax agent extraction by churning of a basket of wax agent in raffinate resulted in only a 10-20 percent reduction of extraction efficiency from that of slurring.

6. Extraction efficiencies and final wax agent uranium concentration in the four-stage countercurrent batch process were found to be comparable to those observed in filter bed operations.
7. Acidification of raffinates to 3 N excess nitric acid decreases the insoluble uranium content of the slurry; however, wax agent extraction efficiencies using acidified raffinate were much lower than with unacidified raffinate.
8. Stripping of uranium from wax agent with water at 150°F produces 10-15 percent greater stripping efficiency than stripping at 85°F.

CERAMICS PILOT PLANT

by

W. G. Weber

It is anticipated that the newly formed ceramics pilot plant will be in operation by the end of November. All of the major equipment has been received with the exception of the induction furnace instrumentation which is expected shortly. All of the old equipment has been removed and the area has been prepared for the installation of the new equipment.

In the meantime some of the equipment has been set up temporarily in order to learn something of slip casting techniques. Several slips with MgO have been made of 2½ inch diameter 6 inch high crucibles. Also a 5 inch diameter 13 inch long ceramic sleeve insert for a "hotop" mold has been successfully slip cast from Los Alamos formulation AL-4 consisting of

240 gm Kentucky Ball Clay,
360 gm Georgia Kaolin,
1200 gm 1518 Al₂O₃, Norton Alundum Cement,
200 gm T-61 Champion Spark Plug Alumina,
640 cc Water,
4.56 gm Na₂SiO₃,
4.56 gm Na₂CO₃,

The sleeve was then fired in the pilot plant vacuum induction furnace in a graphite susceptor. Firing procedure constituted heating to 2400° F. for one-half hour, and cooling to 300° F. in eleven hours. Results were excellent and the sleeve will be used in the top of a "hotop" mold to prevent graphite seizure.

URANIUM METAL BY BOMB REDUCTION

by

W. Knecht

G. Kerr

L. Weber

I. Introduction

The history of the development of the use of magnesium fluoride slag as a liner material for bombs in which uranium tetrafluoride is reduced to metal has been traced in a series of reports.^{1,2,3,4,5,6}

This development is now being incorporated into the manufacturing methods for uranium metal by the design and installation of a production grinding plant and other necessary changes. These changes will probably be completed in the early part of 1954.

In connection with the use of slag as a liner material for producing pure uranium metal, an increasing amount of experience has been gained in the use of this liner material in the formation of uranium alloys. These alloys have been made by co-reducing a salt of the particular metal and uranium tetrafluoride with magnesium.

II. Crushing and Grinding of Magnesium Fluoride Slag

The magnesium fluoride slag that is formed in the reduction of uranium tetrafluoride with magnesium is crushed, ground, and classified to yield satisfactory liner material. The process by which this is accomplished has been previously described.⁷ The development work during this quarter has been limited to refinements for the operation of the production grinding facilities to be installed in St. Louis. Since these are not of general interest they will not be reported here.

¹ Weber, L. G., Pilot Plant Studies of Liner Hardening, Mallinckrodt Chemical Works, June 24, 1952, (NYO 1344).

² Anderson, T. O., Pilot Plant Studies of Slag Liner, Mallinckrodt Chemical Works, November 14, 1952, (NYO 1348).

³ Rueble, A. E., Leaders, W. M., et al, Research and Development Progress Report, Mallinckrodt Chemical Works, October 15, 1952, (NYO 1349), p. 102 - 115.

⁴ Rueble, A. E., Leaders, W. M., et al, Research and Development Progress Report, Mallinckrodt Chemical Works, January 15, 1953, (NYO 1352), p. 104 - 119.

⁵ Leaders, W. M., Miller, E. I., et al, Process Development Quarterly Report, Part I, Mallinckrodt Chemical Works, April 15, 1953, (NYO 1353), p. 67 - 91.

⁶ Leaders, W. M., Miller, E. I., et al, Process Development Quarterly Report, Part II, Mallinckrodt Chemical Works, July 15, 1953, (NYO 1356), p. 8 - 37.

⁷ Leaders, W. M. and Miller, E. I., et al, *Op. cit.* (NYO 1356), p. 8 - 14.

However, some small scale work has been done on methods of removing the small metallic particles of uranium from the discard slag by wet concentration methods. These efforts have indicated the ease of recovery offered by these methods, and additional work with laboratory scale equipment is planned for the next quarter.

A sampling program for this discard slag is also planned for the next quarter. The purpose of these tests will be the determination of the minimum sample size to provide a representative sample for accountability purposes.

III. Reduction Operation Using Slag Liners

When the magnesium fluoride has been suitably ground and classified, it is then jolted into a liner for bomb reduction of uranium tetrafluoride. This material is admirably suited as a liner for the reduction bombs since it is formed from very pure material and also adequately resists the high temperatures achieved inside the bomb when it "fires".

The use of additives to the uranium tetrafluoride charge when slag is used as a liner has been widely discussed.^{8,9,10,11} The most desirable additive that has been tested to date is uranium trioxide (UO₃).

A. The Use of Uranium Pellets with Uranium Trioxide

It has also been noted previously¹² that much of the difference between theoretical and actual yield of metal in a reduction bomb is made up of those small particles of uranium that were trapped in the solidifying slag before they could coalesce into the derby. These pellets exist as reduced metal and are potentially useful as such. Attempts to separate these pellets have been fairly successful but no practical usefulness had been found prior to this work. Attempts to melt these pellets in vacuum pointed out the presence of excessive quantities of volatile magnesium and magnesium fluoride.

The alternatives to casting these pellets were to

1. Recycle them to the bomb or,
2. Recycle to the refinery for dissolving.

⁸ Rueble, A. E., Leaders, W. M., et al, *Op. cit.* (NYO 1349).

⁹ Rueble, A. E., Leaders, W. M., et al, *Op. cit.* (NYO 1352).

¹⁰ Leaders, W. M., Miller, E. I., et al, *Op. cit.* (NYO 1353).

¹¹ Leaders, W. M., Miller, E. I., et al, *Op. cit.* (NYO 1356).

¹² Leaders, W. M., Miller, E. I., et al, *Op. cit.* (NYO 1356), p. 25 - 26.

The first alternative is the more economical so efforts were concentrated there. Earlier results of recycling these pellets to the reduction bomb^{13, 14} were rather discouraging. Then a test was attempted in which the pellets were subjected to a light nitric acid pickle. These results were promising and led to an extended series of tests in which "pickled pellets" and uranium trioxide were added to the charge in varying amounts.

The results of these experiments are summarized in Figure 1 in which each point represents the average of two or more runs. If the weight of "pickled pellets" charged to the bomb (W_i) is divided by the weight of uranium charged that is not recovered as massive metal (W_L), it follows that when this ratio equals unity ($\frac{W_i}{W_L} = 1.0$), the net result is approximately 100% yield from the green salt. The losses $\left(\frac{W_i}{W_L}\right)$ would be the inefficiency of the recovery of metal from slag and the loss of metal due to pickling.

It will be noted from Figure 1 that several combinations of "pickled pellets" and uranium trioxide not only yield ratio values equal to unity but greater than unity. The value of W_L includes the uranium charged as uranium trioxide and as "pickled pellets" together with that charged as uranium tetrafluoride in the total amount of uranium theoretically recoverable as massive metal.

While the data plotted in Figure 1 are not sufficiently definitive to indicate as smooth curves, they do point out the obvious advantages in overall yield of using the combinations of "pickled pellets" and uranium trioxide that fall above the "breakeven point" $\frac{W_i}{W_L} = 1.0$.

Preliminary work has also indicated that the curves shift to the right at higher furnace temperatures so that a set of conditions that yields a value of the W_i/W_L ratio greater than unity at one temperature will not produce the same effect at a higher temperature. The firing time of these bombs at 1225° F. has been about three hours and twenty minutes.

An average spectrographic analysis for thirty-five of these derbies is as follows:

Fe	Mn	B	Mg	Ag	Ni	Co
34	7.9	<0.10	85	<1	26	<10

All values are in parts per million.

¹³ Ibid.

¹⁴ Leaders, W. M., Miller, E. I., et al, Op. cit. (NYO 1353), p. 72.

FIGURE 1

Two experimental castings were made with these derbies. Except for an increased amount of "boiling" in the crucible in each case, these derbies behaved well in casting and yielded acceptable ingot metal.

However, when "pickled pellets" were melted experimentally, the amount of volatiles was excessive. Condensed magnesium and magnesium fluoride covered the entire inside of the vacuum furnace, and several fires started when the furnace lid was removed. The pickling of the pellets did not help here since the problem is in the removal of the volatile slag from the pellets.

Since Figure 1 indicates an ability to operate well above the 1.0 line, another source of uranium metal was investigated. When the melted derbies are cast into ingots, a certain amount of sawing is necessary on the finished metal. The sawdust from this operation was degreased and mixed in with the bomb charge.

When sawdust was substituted for the "pickled pellets", the yield dropped very low in two cases and the W_i/W_L ratios were 0.60 and 0.38. In these cases, four pounds of sawdust were added with two pounds of uranium trioxide. However, when the combination of two pounds sawdust, three pounds of "pickled pellets" and three pounds of UO_3 was blended with the charge, the results were more encouraging. The W_i/W_L ratios were 1.28 and 1.06 in each of two cases indicating the possibility of using such a blend.

It should be pointed out that a considerable fire hazard exists when handling finely divided uranium metal, and the necessary safety precautions should be observed. The processing advantages of the use of these small pieces of metal as a recycle stream back to the bomb dictate more investigation during the next quarter, especially on methods of recovery from the slag.

B. The Effect of Water on Yields

When magnesium fluoride is used as a liner material, it does not carry with it the amount of water that is found in fused dolomite liners. This was investigated early in the development of slag as a liner material and has been previously reported.¹⁵ In order to determine the effect of water on the behavior of these bombs, a series of tests was made. A measured volume of water was introduced into the bomb by pouring the water into the bottom of the liner before charging. The results are shown in Table I.

¹⁵ Anderson, T. O., *Op. cit.* (NYO 1348), p. 13.

Table I

The Effect of Water on Bombs

<u>Water Added,</u> <u>ml</u>	<u>Cases,</u> <u>number</u>	<u>Average Yield,</u> <u>%</u>	<u>Time,</u> <u>Hrs:Min.</u>
12	4	97.5	2:40
18	5	96.1	2:41
25	4	97.5	2:32
32	5	97.0	3:14
37	4	97.0	3:16
50	5	97.4	3:20

Although these results indicate no marked improvement in yield with increasing amounts of water, they also indicate no very bad effects. The firing time tends to increase, however, with increased concentration of water.

C. The Effect of Density of the Charge

Several series of experiments have been run in an attempt to evaluate the effect of the packing of the charge on bomb behavior. Some bombs have been tightly packed (charge density about 200 lbs/ft³) and some have been packed loosely (about 185 lbs/ft³). The first experiments in this investigation indicated the experimental difficulty in packing a charge loosely, especially after the cap was put on, since packing the cap tends also to pack the charge.

The first two sets of experiments directly contradicted each other, but when the method of capping was perfected, another set of runs was made as shown in Table II.

Table II

Preliminary Data on the Effect of Charge Packing

<u>Packing</u>	<u>Yield, %</u>	<u>Time, Hrs:Min.</u>
Tight ¹⁶	96.3	3:21
Loose ¹⁷	96.9	2:25
Standard ¹⁸	97.1	3:13

Conditions: 163 pounds UF₄, 1150° F. furnace temperature.
Each result is the average of three cases.

¹⁶ Charge packed as tightly as possible by hand.

¹⁷ Charge poured into bomb.

¹⁸ Charge partially packed by hand.

These data indicate that loose packing of the charge tends to shorten the firing time without appreciably effecting the yield.

The same effect may be noted in some parallel work in which the effects of gasketing were also included in the study. An asbestos gasket was used in the runs noted to prevent gas leakage into or out of the bomb. These bombs were all loaded in air. See Table III.

Table III

Preliminary Data on Effects of Packing and Gasketing on Bomb Behavior

<u>Conditions</u>	<u>Tight Packing</u>		<u>Loose Packing</u>	
No Gasket	95.8	2:46	96.6	2:34
Gasket	94.7	3:04	95.6	2:36

163 pounds UF_4 ; 1225° F.; each result is the average of five cases.

D. The Use of Sodium Fluoride in Advanced Generation¹⁹ UO_3 Bombs

The addition of sodium fluoride to advanced generation bombs in which UO_3 had been used has been reported.²⁰ The yields improved on addition of sodium fluoride in one generation but continued to fall off again when uranium trioxide was added. These data are shown in Table IV where each result represents the average of six cases.

Table IV

Advanced Generation Slag

<u>Generation</u>	<u>Yield, %</u>	<u>Time, Hrs:Min.</u>	<u>Comments</u>
11	98.1	3:06	4 pounds NaF added to each bomb
12	98.0	4:00	1 pound UO_3 added to each bomb
13	97.6	3:28	1 pound UO_3 added to each bomb
14	97.0	3:59	1 pound UO_3 added to each bomb

170 pounds UF_4 ; 4% magnesium excess; 1225° F.

¹⁹ Advanced generation means continued recycling of slag for liner material.

²⁰ Leaders, W. M., Miller, E. I., et al, *Op. cit.* (NYO 1356), p. 22.

An evaluation of uranium trioxide in plant operation will be made during the next quarter on a limited production scale.

E. Mandrel Studies

Throughout the development of the "slag liner" process, a rubber mandrel has been used to form the liner. It was originally thought to have two advantages in that it would pack the liner harder, and withdraw from the liner easier than a steel mandrel. In production tests, it was found that a small amount of torque on the centering screw used to center the top of the mandrel would be enough to cause the mandrel to bend and touch the shell wall. This caused thin liners and difficult mandrel withdrawal.

As a result, a series of tests was run to determine whether the rubber mandrel actually did pack a harder liner than the steel mandrel. In the first four cases, a liner was made first with the rubber mandrel and then tested for hardness; then the liner was destroyed and the same material used for making a liner with the steel mandrel. This liner was then charged and fired. In the second four cases, the procedure was reversed. See Table V.

Table V

Mandrel Study

<u>Steel Mandrel</u>	<u>Rubber Mandrel</u>	<u>Yield, %</u>	<u>Time, Hrs:Min.</u>
105	107	95.3	2:18
73	66	96.8	2:22
101	101	95.7	2:23
78	74	96.7	2:30
	Average Steel	96.1	2:23
77	84	97.5	2:39
100	102	98.2	2:24
99	106	98.0	2:17
75	75	96.5	4:30
	Average Rubber	97.6	2:57

These data show that there is relatively little difference between the packing of liners with rubber or steel mandrels and that differences in liner material are much more pronounced. The steel mandrel used was one-half inch smaller in diameter at the top than the rubber mandrel so that the liners were one-fourth inch thicker at the top when the steel mandrel was used.

F. Ignition Attempts

Several attempts have been made to fire a bomb before it would normally fire by using a hot wire trigger technique. In this method a resistance wire was placed in the top of the charge surrounded by uranium tetrafluoride and magnesium fines (<50 mesh). Thirty amperes were passed through this wire at a selected time before the normal firing time. It was thought that the wire would initiate the reaction locally and the reaction would then propagate itself through the rest of the charge. This technique was tried with normal bombs and with bombs containing uranium trioxide (UO_3). In all cases the attempts at ignition by this method failed.

G. Shell Materials

The change in original dimensions of the bomb shells that are used to contain the reduction reaction has been noted many times in production operations. A study of several materials for bomb shell construction has been previously reported²¹ Table VI is a summary of the dimension changes in these shells to date. In this table under the maximum change in dimension title are listed two axes. The diameter of the shell is measured at several levels of the shell and measured along the two diameters which are 90° from each other. The measurements indicate the maximum change in dimension from the original dimension - whether this is a bulge (B) or a shrink (S) - and the distance above the bottom of the shell where this maximum deformation has occurred.

Table VI
Behavior of Shell Materials

Shell No.	Material	No. of Times Used	Maximum Change in Dimension	
			Axis A	Axis B
TT 45	$\frac{1}{4}$ " SAE 4130 Steel	111	$\frac{3}{16}$ " - S - 18"	$\frac{3}{16}$ " - S - 18"
TT 61	$\frac{3}{8}$ " SAE 4130	25	$\frac{1}{16}$ " - S - 18"	$\frac{1}{32}$ " - B - 20"
TT 62	$\frac{3}{8}$ " SAE 4130	23	$\frac{9}{64}$ " - S - 18"	$\frac{1}{16}$ " - B - 10"
TT 55	$\frac{1}{2}$ " Mild Steel	60	$\frac{5}{16}$ " - S - 16"	$\frac{5}{32}$ " - B - 14"
TT 56	$\frac{1}{2}$ " Mild Steel	30	$\frac{3}{32}$ " - S - 18"	$\frac{3}{32}$ " - B - 22"
TT 57	$\frac{1}{2}$ " Mild Steel	36	$\frac{5}{64}$ " - S - 18"	$\frac{3}{32}$ " - S - 5"
TT 58	$\frac{1}{2}$ " Mild Steel	44	$\frac{11}{64}$ " - S - 16"	$\frac{1}{16}$ " - B - 24"
TT 59	$\frac{1}{4}$ " Stainless Steel	59	$\frac{1}{8}$ " - S - 20"	$\frac{5}{64}$ " - B - 12"
TT 60	$\frac{1}{4}$ " Stainless Steel	36	$\frac{5}{32}$ " - B - 10"	$\frac{3}{32}$ " - S - 8"
			$\frac{3}{64}$ " - S - 24"	$\frac{3}{32}$ " - B - 26"
TT 53	$\frac{1}{4}$ " 410 Stainless Steel	64	$\frac{7}{32}$ " - B - 18"	$\frac{5}{32}$ " - B - 6"
				$\frac{3}{32}$ " - S - 18"
TT 54	$\frac{1}{4}$ " 410 Stainless Steel	72	$\frac{13}{64}$ " - S - 14"	$\frac{3}{32}$ " - B - 14"
			$\frac{1}{8}$ " - B - 20"	$\frac{13}{63}$ " - S - 20"

²¹ *Ibid.*, p. 29.

It will be noted that the shell made of $\frac{1}{4}$ " SAE 4130 steel plate has given good service in over 100 runs.

H. Large Bombs

A program of investigation of the geometry of uranium reduction bombs has been initiated and the first work has been reported.²² Some work has continued on the "pot-bellied bomb" but current emphasis has shifted to the use of larger charges.

An investigation of the use of 2.3 pounds of sodium bifluoride as an additive to the 210 pounds of "green salt" in the "pot-bellied" bomb did not show much promise. However, in one of these bombs the fuse in the furnace blew out and no power was supplied for two hours. During this time the bomb remained in the furnace and when the furnace started up again, the bomb fired, after six hours and thirty minutes in the furnace. The yield was 98.2%. This seems to indicate that if the bomb charge were allowed to soak up more heat, the yield might be improved.

Experimental work on magnesium excesses in this bomb was carried out at the same time. Five cases fired at 1190° F. with a 2% magnesium excess yielded one dud and four derbies with very bad tops. These derby tops had considerable slag included so that the yield results are meaningless. This same effect was noted when the magnesium excess was held at the same weight of magnesium as in a 170 pound UF_4 charge.

Quite a few magnesium flange fires had occurred when the 210 pound charge was used. When the charge size was reduced to 190 pounds, the cap on the bomb was thicker and these flange fires stopped. Nine runs were made at 1190° F. and 4% excess magnesium using the 190 pound charge but the yields were very erratic, ranging from 74 - 104%. The derby tops were again a mixture of slag and metal, which explains the higher than theoretical yield.

Further work with this bomb was suspended when a vanadium bomb blew out and damaged the lid.

Another bomb shell has been fabricated and some testing completed. This shell is 24 inches in diameter by 29 $\frac{5}{8}$ inches tall. It is heated in the same Rockwell furnace used for the "pot-bellied bomb". The charge cavity is large enough to hold 700 pounds of uranium tetrafluoride and the derby produced is 22 inches in diameter by about 1 $\frac{1}{4}$ inches tall. It is believed that the largest piece of massive uranium metal ever produced as a derby has been made using this shell.

²² *Ibid.*, p. 33 - 35.

Magnesium fluoride slag has been used as liner material in this bomb and has behaved very well under more strenuous service than slag as a liner has ever before seen. The liner material is one inch thick at all points. Breakout has been very easy. The bomb has been turned over and tapped lightly in order to get the contents out.

Yields in this "cartwheel" (so named because of the shape of the derby) bomb have been erratic but only a few runs have been attempted. Some tests have included the use of small amounts of iodine. This has been used as a "filming agent" rather than as a booster. The data from these early runs are shown in Table VII.

Table VII

Results from "Cartwheel" Bomb

Run	UF ₄ , lbs.	I ₂ , gms.	Mg xs %	Derby Weight, lbs.	Yield %	Time Hrs:Min.
2282	450	-	4	271.4	79.5	5:07
2283	650	-	1.8	411.0	83.2	4:15
2284	650	75	1.8	450.5	91.1	5:10
2285	650	75	3	401.5	81.5	4:55
2286	650	150	3	470.0	95.3	4:42
2287	650	150	3	437.5	88.6	4:15
2288	650	200	3	391.0	79.2	4:25
2290	650	200	3	451.5	91.3	5:26

All runs at 1225° F. except 2290 which was held at 1000° F. for four hours and then raised to 1225° F.

In run 2290 the derby was formed in two pieces by building a small divider of slag on the bottom of the liner. This considerably eases the handling problems with this type of derby.

These results indicate that charges of uranium tetrafluoride almost four times larger than in current production operations can be safely contained in slag lined bomb shells. The reduction reaction is seemingly complete in these larger charges since clean white slag is produced. The failure to attain present production yields can probably be ascribed to incomplete phase separation. The large surface area of this derby creates opportunity for large losses at the interface.

A shell of approximately the same size, but which will produce a derby six inches tall, six and one-half inches wide and eighteen inches long, is currently being tested. This derby will be pickled and rolled without casting as a test of a "derby ingot".

IV. Uranium Alloys by Co-reduction

The formation of uranium alloys by the simultaneous magnesium reduction of uranium tetrafluoride and other metallic salts has been studied for some time. Large quantities of several uranium alloys have been supplied to other A.E.C. installations.

A. Small Scale Reduction Studies

The limitations that are imposed by the co-reduction process on the types of metallic salts that are useful are quite severe. The reaction of many of the physically suitable salts with magnesium is usually unknown. As a result a series of experiments to test the reaction temperature of each of several metallic salts with magnesium has been made. About twenty grams of the metallic salt was mixed with an excess of magnesium fines (50 mesh) and heated in an Armco crucible. This crucible was placed at the bottom of a sealed length of two inch pipe. Two thermocouples, inside stainless steel thermowells, were inserted through a rubber stopper. One thermocouple was placed outside the crucible and the other was placed inside the crucible. A static atmosphere of helium was introduced. As heating progressed, the outer thermocouple indicated a higher temperature than the inner thermocouple. When the reaction occurred, the exothermic reaction caused the inner temperature to rise higher than the outside temperature. The point at which these two temperatures were equal was called the reaction temperature. These reaction temperatures are shown in Table VIII where the average reaction temperatures are listed.

Table VIII

Reaction Temperatures of Metal Salts with Magnesium

Compound	Number of Trials	Average Reaction Temperature, °F.
UF ₄	3	1045
Cr ₂ O ₃	3	1125
V ₂ O ₅	2	1190
V ₂ O ₃	3	1130
VF ₃	1	1560
ZrF ₄	3	1185
MoO ₃ ²³	2	1195
Cb ₂ O ₅ ²⁴	2	1355

²³ Explosive.

²⁴ Using -10 +50 mesh magnesium.

Metal was detected by X-ray diffraction in the residues from vanadium pentoxide, vanadium trioxide, vanadium trifluoride and columbium pentoxide. Not all of the samples were tested since it is known that UF_4 , ZrF_4 , and MoO_3 are reduced to the metal.

The magnesium reduction of both molybdic oxide and vanadium pentoxide were quite violent.

B. Large Scale Co-reduction Studies

Several alloy derbies and two alloy ingots were produced during this quarter with varying degrees of success as outlined below.

1. Molybdenum Alloys

Alloys of uranium with molybdenum up to five w/o molybdenum have been produced in large quantities at this site for several years. However increased concentrations of molybdenum in these alloys present increasingly difficult problems. It has been reported²⁵ that alloys of 10 and 12 w/o molybdenum have been successfully produced. During this quarter an extension of this work to a 14 w/o molybdenum alloy has been made. In the first attempt molybdic oxide and molybdenum metal each contributed an equal amount of molybdenum. Even though the calculated heat release of this bomb was held to 72,500 BTU (25° C. calculations), this first bomb was a blowout. However, two further attempts were successful. In each case, equal weights of molybdenum metal and molybdic oxide were used. These bombs gave crude yields of 87.4% and 91.4%, but the derby tops were very rough and were removed by sawing down far enough to expose clean metal.

Segregation in molybdenum alloys is not as pronounced as in other alloys. Segregation in the 10, 12, and 14 w/o molybdenum alloys is shown in Table IX.

Table IX

Segregation in Molybdenum Alloy Derbies

Run	Desired Alloy	Chemical Analysis, Mo	
		Top, %	Bottom, %
1899	10 w/o Mo	8.75	7.97
1910	10 w/o Mo	9.28	9.42
1911	12 w/o Mo	8.99	12.06
1918	12 w/o Mo	12.17	10.61
1920	14 w/o Mo	13.79	13.28
1921	14 w/o Mo	13.71	12.16

²⁵ Leaders, W. M., Miller, E. I., et al, *Op. cit.* (NYO 1356), p. 36.

Incomplete reduction can be noted in several cases where the chemical analysis shows that less molybdenum appeared in the derby than was put in the charge.

An attempt was made to reduce molybdic oxide (MoO_3) to molybdenum dioxide (MoO_2) and metal (Mo) by heating in an hydrogen stream. Several pounds of molybdic oxide (MoO_3) were placed on a tray and heated in a batch furnace. The temperature was held at 900 - 1000° F. for two and one-half hours and then raised to 1650° F. for five hours. This treatment yielded a product which had a total molybdenum content of 89.9%. If this is a mixture of molybdenum metal and molybdenum dioxide (MoO_2), it amounts to approximately 60% molybdenum metal. This mixture was fired in a two w/o molybdenum alloy bomb giving a yield of 98.0% in two hours and twenty-eight minutes, and with a normal derby top.

2. Zirconium Alloys

Four zirconium alloy derbies were co-reduced using zirconium tetrafluoride as the source of zirconium metal. These runs are described in Table X.

Table X

Zirconium Alloys

Run	Desired Composition % Zr	Yield %	Time Hrs:Min
2026	2.0	95.4	2:26
2027	2.0	98.2	2:22
2028	2.0	95.1	2:00
2029	2.8	92.2	2:25

Although it is known that considerable segregation occurs in zirconium alloy derbies, no analyses were made since these derbies were immediately cast into a special bottom gated mold. Previous casting experience²⁶ had established 2.3 w/o as a good starting point to produce a 2.0 w/o zirconium ingot. This is apparently caused in part by the formation and liquation of the very stable carbide and nitride of zirconium.

In this run, the average zirconium content of the derbies charged was 2.2%. The melted charge was poured at 2700° F. through a three-fourths inch diameter pour hole into a one and one-half inch diameter downsprue which was gated into the bottom of four three and three-eighths inch diameter ingot molds through gates

²⁶ Leaders, W. M., Miller, E. I., et al Op. cit. (NYO 1353), p. 156.

measuring three-fourths inch by three-fourths inch. The mold was made from one block of graphite with a graphite plate bolted to the bottom.

The four ingots had some deep folds near the top but otherwise had good surfaces. The distribution of zirconium, carbon, and nitrogen in these ingots is shown in Table XI and Figure 2 and indicates the liquation of zirconium encountered.

Table XI

Segregation in Two w/o Zirconium Alloy Ingot

<u>Sample No.</u>	<u>Zirconium, %</u>	<u>Carbon, %</u>	<u>Nitrogen, %</u>	<u>Density</u>
1	5.84	0.296	0.0146	15.27
2	6.24	0.309	0.0150	15.59
3	5.05	0.265	0.0094	15.66
4	3.06	0.156	0.0059	17.38
5	1.90	0.066	0.0020	18.25
6	1.61	0.022	0.0030	18.45
7	1.64	0.006	0.0012	18.51
8	1.72	0.006	0.0011	18.51

See Figure 2 for origin of samples.

3. Chromium Alloys

The method of production of chromium alloy derbies has been discussed previously.²⁷ A pronounced tendency toward segregation in chromium alloys, especially in ten w/o chromium alloys, can be noted from the data of Table XII.

Table XII

Chromium Distribution in Alloy Derbies

<u>Run</u>	<u>Desired Composition</u>	<u>Chemical Analysis, Cr</u>	
	<u>% Cr</u>	<u>Top, %</u>	<u>Bottom, %</u>
1865	5	8.68	4.22
1866	5	5.30	5.18
1916	10	10.22	3.33
1917	10	7.52	3.83
1966	10	8.66	4.79

²⁷ Leaders, W. M., Miller, E. I., et al, *Op. cit.* (NYO 1356), p. 37.

SHADED AREAS ARE THE POSITIONS AT WHICH SAMPLES WERE TAKEN

ZIRCONIUM ALLOY INGOT

FIGURE 2

Again, in the case of chromium, incomplete reduction of the metal salt is evident from the chemical analyses, especially at the ten w/o chromium level.

4. Niobium (Columbium) Alloys

A series of alloy derbies containing approximately 4, 8, 12, and 16 w/o niobium have been made by the co-reduction process using niobium pentoxide (Nb_2O_5) as the metal salt. The reaction

can be shown to be thermodynamically possible and exothermic, yielding 2800 BTU per pound of niobium.

The addition of niobium metal to uranium increases the melting point quite rapidly. While pure uranium melts at 1133°C , the four w/o niobium alloy has a melting point of approximately 1300°C , and the 16 w/o niobium alloy melts at about 1630°C . These melting points are points on the liquidus of the uranium-niobium phase diagram.²⁸

The increased melting point of the metal and the increased melting point of the slag, since reduction of niobium pentoxide adds magnesium oxide to the magnesium fluoride slag, both tend to make separation of metal and slag more difficult than in a normal uranium reduction. In all cases when niobium pentoxide was used, the derbies had rough tops and had to be "cropped" to expose clean metal. In the case of the 12 and 16 w/o alloys, an attempt will be made to melt and cast the derbies without cropping.

Several variations in technique were tried with the niobium alloys. The chemical energy release was limited to 70,000 - 80,000 BTU by reducing the charge size. The bombs were allowed to "soak" at 1190°F . for two and one-half hours and then the furnace temperature was raised to 1400 or 1500°F . until the bomb fired. Four pounds of sodium fluoride were added to each of the 12 and 16 w/o runs in order to reduce the melting point of the slag somewhat. The yield data are presented in Table XIII.

²⁸ Buzzard, R. W., and Cleaves, H. E., "The Binary Alloys of Uranium", *Journal of Metallurgy and Ceramics*, 1, 33, (1948), (TID-65).

Table XIII

Niobium Alloys

Run	Desired Composition, % Nb	Crude Yield, %	Time Hrs:Min.
2192	4	92.7	1:58
2217	4	90.6	3:12
2246	8	85.1	2:14
2247	8	84.9	5:30
2251	12	69.4	2:33
2252	12	79.3	3:05
2264	16	54.0	--
2265	16	51.6	--

The decrease in crude yield with increasing concentrations of niobium is evident from these data. The increasing melting points of both metal and slag predict this behavior.

Niobium analyses on the two-four w/o derbies were 3.40% and 6.86% at top and bottom respectively on run 2192 while the other derby (Run 2217) analyzed 4.30% and 2.90%, top and bottom.

5. Vanadium Alloys

The initial difficulties in producing vanadium alloy derbies have been discussed.²⁹ In the first two attempts to co-reduce vanadium pentoxide and uranium tetrafluoride with magnesium to form a five w/o vanadium alloy, the bombs both blew out. In the next attempt, the magnesium excess was increased to 7%. This bomb reacted very slowly and no derby was formed. Small droplets of metal were distributed through a "black slag".

Another attempt was made to produce this alloy in which the charge size was reduced to produce a theoretical yield of 85 pounds, the furnace temperature was increased to 1300° F. and four pounds of sodium fluoride was added to the charge. This run produced a derby but only a 54.5% yield.

A second five w/o vanadium alloy derby was produced by allowing the bomb to "soak" in the furnace at 1190° F. for two and one-half hours. The temperature was then increased to 1400° F. until the bomb fired. This run gave a crude yield of 76.8%.

²⁹ Leaders, W. M., Miller, E. I., et al, *Op. cit.* (NYO 1356), p. 37.

The same heating technique was used on the first 10 w/o vanadium alloy run and six pounds of sodium fluoride was added to the charge. This bomb blew out at the flange, but did produce a small derby (35.5% yield). Further work on the production of vanadium alloys will use vanadium metal as a supplementary source of vanadium. If the future demand for vanadium alloys is sufficient, some investigation into the use of combinations of the trifluoride, the trioxide, and the metal will be made.

6. Tungsten Alloys

Five tungsten alloy derbies were produced at the 1.3 w/o tungsten level and cast into an ingot. Tungsten was added to the bomb as metal, and no difficulty was encountered in producing these derbies. The average yield for the five derbies was 95.5%.

The addition of tungsten to uranium increases the melting point sharply. The 1.3 w/o alloy melts at 2300 - 2400° F.³⁰ These derbies were pickled in nitric acid to remove about five percent of their weight, and melted in a graphite crucible. The melt was poured at 2700° F. into a normal uranium production mold. The crucible charge was completely melted at 2350° F., and the ingot produced had a very good surface. No analytical data are available on segregation in this ingot although little segregation would be expected since tungsten has a very high density (19.3 g/cc).³¹

Several thousand pounds of this alloy were produced as routine production following this investigation.

Future work in the field of uranium alloys will, at present, be directed towards the investigation of suitable metallic salts as sources of alloying ingredients for several alloys in which a good deal of interest is being currently shown by other A.E.C. installations. The process of co-reduction possesses some advantages over the co-melting process and undoubtedly an increasing number of alloys will be studied using this process.

³⁰ Buzzard, R. W., and Cleaves, H. E., *Op. cit.*, p. 48.

³¹ Perry, J. H., editor, "Chemical Engineer's Handbook", Third Edition, p. 127, McGraw-Hill Book Company, New York (1950).

THE CASTING OF URANIUM METAL (PILOT PLANT)

by

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I. Introduction

Improvement of metal quality has again been the main objective of this work.^{1,2,3} Metal soundness improvement by means of "hotop" mold techniques and metal purity improvements by refinement of the present casting procedures are described in this section of the report.

II. Metal Quality Studies

Metal quality studies include both metal soundness work which is directed toward removing the macro and micro size voids in ingot metal, and metal purity work which is directed toward reducing the amount of impurities and inclusions in ingot metal.

Casting of derby metal was possible during this period and comparison runs showed there was no appreciable difference in ingot soundness when using either derby metal or recast metal. Ingot soundness again was determined by radiographic methods.

1. Nominal Five Inch "Hotop" Molds

Only a limited amount of work has been done with the molds which produce approximately 5 inch diameter by 45 inch long ingots. This is due in part to the unfavorable geometry for producing sound metal, and also this shape will of necessity be obsolete if the present trend for making larger melts is adopted for full scale plant production. Larger diameter molds would have to be used if melt size is increased by any appreciable amount.

Previous reports⁴ have shown the inferior quality metal with respect to axial cavities that is produced in unheated production shape molds and the somewhat improved quality of metal that is produced in the heat taper hotop molds. A limited amount of more recent work has been done with a double tapered hotop mold. Ingots produced in the double tapered hotop mold showed no improvement over those produced in heat taper, hotop molds. A typical ingot from the double taper hotop mold is shown in Figure 1.

¹ Ruehle, A. E., Leaders, W. M., et al, Research and Development Progress Report, Mallinckrodt Chemical Works, January 15, 1953, (NYO 1352), p. 66 - 96.

² Leaders, W. M., Miller, E. I., et al, Process Development Quarterly Report, Part I, Mallinckrodt Chemical Works, April 15, 1953, (NYO 1353), p. 92 - 119.

³ Leaders, W. M., Miller, E. I., et al, Process Development Quarterly Report, Part II, Mallinckrodt Chemical Works, July 15, 1953, (NYO 1356), p. 38 - 70.

⁴ Ruehle, A. E., Leaders, W. M., et al, Op. cit. (NYO 1352), p. 66 - 96, and (NYO 1353), p. 92 - 119.

HEAT- 303

FIVE INCH HOTOP MOLD
DOUBLE TAPER

FIGURE - I

Axial cavities were always present from four to twelve inches from the bottom and also about thirty-three inches from the bottom and extending to the top of the ingot. Mold temperatures of 2100° F. and 2200° F. and holding times of two to ten minutes at those temperatures were tried but no appreciable difference was noted in the ingot quality.

2. Six Inch Diameter "Hotop" Riser Molds

Development work for determining the proper mold geometry and temperature gradients for producing sound metal has been continued for the six-inch diameter "hotop" riser molds. More extensive work has been done with this shape of mold because the present rolling mill equipment can be readily adapted to ingots produced from this type of mold.

The temperatures for the "hotop" section of the mold have been studied in the range of 1900 - 2200° F. When the mold is heated in this range, there is a tendency for the molten uranium to react with the graphite, thus making it difficult to remove the mold after the metal has solidified. This problem is called "graphite seizure" and is much more pronounced as the temperature increases. The optimum mold temperature is one that will produce sound metal with a minimum amount of damage to the graphite. It now appears that mold life will be somewhat shorter with the heated molds, regardless of temperature; although the lower the temperature, the longer the life of the mold. Mold life data are now being obtained.

The results obtained with mold temperatures of 1900, 2000, 2100, and 2200° F. show that 1900° F. is too low to produce sound metal and 2200° F. is too high because it greatly increases the problem of graphite seizure. The optimum temperature is in the range of 2000 - 2100° F. and the temperature that is best depends somewhat upon the mold design and amount of insulation that is used around the mold. Figure 2 illustrates how the internal soundness of the ingot is affected by changes in the maximum temperature on the mold. The type "C" mold was used for these ingots, and will be discussed later in this report. The illustration in Figure 2 is intended to show only the effect of mold temperature on ingot soundness.

The regular six-inch double tapered hotop mold produces an ingot which is approximately 31 inches long. A modification of this mold, called type "B", produces an ingot which is approximately 35 inches long. The type "B" mold requires a 675 pound charge for the ingot and "hotop" riser as compared to 640 pounds for the regular mold. It has been found that the additional length of the ingot from the type "B" mold does not appreciably effect the soundness of the metal. Figure 3 shows the dimensions of the two molds and the betatron results of the ingots made under the same conditions. It should be pointed out that the ingot in the type "B" mold extends up into the induction field in the regular six-inch hotop mold. The ability to reproduce results is about the same for each type of mold.

(DOUBLE TAPER-TYPE
"C" MOLD SHOWN)

EFFECT OF MOLD TEMPERATURE ON
INTERNAL SOUNDNESS

FIGURE 2

HEAT-313
DOUBLE TAPER MOLD

HEAT-359
DOUBLE TAPER TYPE "B" MOLD

COMPARISON OF DOUBLE TAPER & DOUBLE
TAPER TYPE "B" MOLDS

Another mold known as the type "C" has been studied briefly. This mold is the same as the regular six-inch double tapered hotop mold except the outside diameter at the bottom has been reduced from 11½ inches to 10 inches. The amount of outside taper or heat taper was reduced to determine what effect that would have on the internal soundness and also to reduce the actual weight of the bottom mold section. The bottom section of a regular six-inch double tapered hotop mold actually weighs 108.5 pounds which makes it rather difficult to handle. The bottom section of the type "C" mold weighs only 79 pounds.

Results with the type "C" mold show that it can be used to make sound metal if it is properly insulated. This is shown in Figure 4. The run conditions were the same in both heats except for the amount of insulation and the use of a bottom heat exchanger on heat 396. The use of more insulation and a bottom heat exchanger to aid in promoting directional solidification makes a pronounced difference in the quality of the ingot that is produced in this type of mold.

3. Melting of Larger Charges

In a previous report⁵ melt sizes ranging up to 835 pounds were described. No additional work has been done with this particular melt size, but several melts have been made with a crucible charge of 1000 to 1040 pounds of metal. It was desired to make melts of this size in order to determine the operational problems that would be involved and also to produce some larger ingots for rolling tests at F.M.P.C.

The molds used for these large melts had a seven and one-half inch inside diameter and produced an ingot that was 34 inches long. The mold design was a heat tapered hotop riser mold made out of 12 inch graphite electrodes. The mold setup and the betatron results of the ingot from heat 357 are shown in Figure 5. The actual weight of the ingot and riser was 977 pounds with crucible holdup accounting for the remainder of the 1010 pounds of the pickled derby charge.

Considerable difficulty was encountered in melting the large charges with the small induction coil that was available in the pilot plant furnace. The technique for melting the large charges involved the fabrication of a graphite extension to fit on the regular production crucible in order to accommodate the unmelted charge. This extension projected above the induction coil for a distance of about 14 inches so insulation was necessary to avoid excessive heat losses. No other changes were made in the crucible design for the first few runs. The wall thickness of this crucible was seven-eighths of an inch which is standard for production crucibles. CS-312 grade of graphite was used.

⁵ Leaders, W. M., et al, *Op. cit.* (NYO 1356), p. 38 - 70.

HEAT 353
NO INSULATION - NO HEAT EXCHANGER

HEAT 396
WITH INSULATION - WITH HEAT EXCHANGER

EFFECT OF INSULATION AND HEAT EXCHANGER ON
INTERNAL SOUNDNESS IN TYPE "C" MOLD

FIGURE 4

HEAT - 357

ONE THOUSAND POUND HEAT

FIGURE - 5

The first two attempts to melt 1010 pounds of metal in the crucible just described were unsuccessful. In both runs metal started leaking out of the crucible a few minutes after the metal had melted. Inspection of the crucibles revealed that the metal had permeated the sides and run out through several small (approximately one-eighth inch diameter) holes. This undoubtedly was caused, in part at least, by the increase in hydrostatic pressure with the larger melts. The height of molten metal was about 13 inches for 640 pounds of metal but the height for 1010 pounds of metal was about 20 inches. This additional hydrostatic pressure apparently was enough to cause the metal to permeate weak spots in the graphite. After these runs, the wall thickness was increased to one and one-sixteenth inches, but after five runs with this type of crucible similar trouble developed. Wall thickness was finally increased to one and three-eighths inches.

In addition to difficulties with wall thickness several leaks were experienced around the shear plug at the bottom of crucible. This, too, was probably a result of the increased hydrostatic pressure. Also, some trouble was found with shifting of the metal as it started to melt, and this shifting cracked one crucible. A heat of this size required nine derbies to be stacked vertically in the small crucible. It is not surprising, then, that some shifting would occur in the metal as it melts. Increasing the wall thickness was also helpful with this problem since it gave additional mechanical strength to the crucible. A faster heating cycle was also found to be beneficial in reducing the amount of shifting during the melting cycle.

It finally became necessary to increase the outside diameter of the crucible to that of the graphite sleeve which holds the zircon grog in place in the furnace and thus eliminate the sleeve entirely. The increased outside diameter permitted the increase in wall thickness and also a slight increase in inside diameter to lower the level of the molten metal. Three successive heats were made with this design and no trouble was encountered. However, this solution was not a good one from the operational point of view as it required that zircon grog be placed around the crucible before each run. A new larger diameter induction coil, which will accommodate larger crucibles, will have to be designed for satisfactory operation with melts of 1000 pounds and larger.

Changing the melt size from 640 pounds to 1025 pounds is about a 60% increase. The actual increase in furnace time, i.e. the time required to pump down the furnace, melt, pour and cool the ingot, is only about 28% more when using the larger charge and when "hotop" molds are used in both instances. Actually, the only appreciable increase is in the cooling of the ingot. The cooling time for a 640 pound ingot is about three hours and twenty minutes in a "hotop" mold, and about four hours and fifty minutes are required to cool a 1025 pound ingot in a "hotop" mold. The results for the larger charges are based on a limited number of runs and may be subject to some change when more data

are available. Just for comparison purposes, it might be well to point out that the cooling cycle for a 640 pound ingot in an unheated, uninsulated mold is only about two hours. It was mentioned in a previous report⁶ that the cooling cycle will be somewhat lengthened if "hotop" mold techniques are used in place of the unheated molds, but better quality metal would be produced.

4. Horizontal Hotop Mold

The method normally used for producing ingot metal is to cast the ingot with the long axis in a vertical position. In order to produce metal free of axial cavities with this type of mold, a reserve of molten metal must be available at the top to feed down as the solidification proceeds. In the case of the production ingot, the metal must feed the length of the ingot or a distance of approximately 45 inches. One run was made with a mold which had the long axis in the horizontal position with the mold being fed through an open riser in the top of the mold at the center. The riser extended up into the induction coil that is normally used for hotop work so that it would be possible to use it as a "hotop" riser. The graphite mold had a square cross section, 5 inches x 5 inches, and was 35 inches long. The mold with riser was designed to hold the standard size charge of 640 pounds.

An ingot produced from this horizontal mold was found to be free of all voids except for one extending into the ingot directly below the riser. The mold for this run was insulated at the top and sides to within eight inches of the ends and the riser was heated to 2100° F. before the pour. A pouring temperature of 2450° F. was used with a one inch diameter pour hole in the crucible. The ingot, however, did become warped during the cooling cycle.

5. Modified "Hotop" Molds

Additional work has been done with molds that have been elevated to contact or nearly contact the pour block on the bottom of the crucible. The reasons for using this technique were described in a previous report⁷.

A six-inch double tapered riser mold used in this manner did not produce an ingot which is entirely free of axial cavities. See Figure 6. This is due to the fact that not enough heat is transferred to the mold before the pour is made. Our present method of elevating the mold gives very poor contact between the mold and crucible and thus reduces the amount of heat that is transferred. The maximum temperature with a normal "hotop" mold is 2000 - 2100° F. while this modified "hotop" mold has a maximum temperature of 1500 - 1600° F. prior to the pour. Radiographic results show that these conditions in the elevated mold are not adequate to produce sound ingot metal.

⁶ Leaders, W. M., et al, *Op. cit.* (NYO 1356), p. 38 - 70.

⁷ Leaders, W. M., et al, *Op. cit.* (NYO 1356), p. 38 - 70.

HEAT - 352

MODIFICATION OF "HOTOP" METHOD

FIGURE - 6

6. Carbon as a Mold Material

The design for a mold which produces a sound ingot must include some method for cooling the ingot at a faster rate at the bottom than at the top. Normally, the procedure in the pilot plant work has been to heat taper the mold at the bottom, insulate and heat by induction at the top of the mold. Both top and bottom sections of the mold were made of graphite which has a very high thermal conductivity. In view of the fact that carbon has a thermal conductivity of about one-tenth that of graphite, it was decided to try carbon as a material for the top mold section in order to retard the cooling at the top.

Carbon top mold sections were machined from carbon electrodes for a production type mold and for a six-inch "hotop" riser mold. When the pour was made into the unheated production mold, the carbon top section developed longitudinal cracks immediately, thus indicating that the carbon could not withstand the thermal shock. Unfortunately, a crucible leak developed when using the "hotop" carbon mold and no information was obtained. Additional work is planned for this type of mold.

Carbon electrodes machine with much greater difficulty than the graphite electrodes. This is a very definite disadvantage for using carbon as a mold material, and as yet it has not been determined whether it would be more suitable than graphite from the standpoint of producing sounder metal.

7. Problems in Metal Soundness Work

a. Graphite Seizure

The problem of the ingot adhering to the mold in the "hotop" section is still present although it diminishes rapidly as the mold temperature decreases. It now appears that mold temperatures of 2000 - 2100° F. are necessary to produce sound metal and graphite seizure has been found to occur rather frequently at these temperatures. This is undesirable because it greatly reduces the life of the mold and causes poor surfaces on the upper part of the ingot.

Attempts to eliminate graphite seizure by using different types and heavier applications of mold dressings have been largely unsuccessful. However, the use of ceramic inserts in the "hotop" section shows considerable promise of being a satisfactory solution to this problem. Two alumina sleeves, approximately five and three-sixteenths inches inside diameter by six inches high with five-sixteenths inch walls, were supplied by the Norton Company for use as inserts in the mold. When these ceramic pieces were used in the mold there was no evidence of any reaction between the uranium metal and the inserts. In fact, the ingot surface was slightly better in the ceramic section than the adjacent area that was bounded by graphite. In both cases, the inserts were found to be cracked after the ingot was removed from the mold. The cracking occurred after the metal had solidified since there were no metallic fins on the ingot. This indicates that the inserts could be used only once.

Further work will be done using ceramic inserts fabricated by the ceramics pilot plant.

b. Lengthened Cooling Cycle

As mentioned earlier, the time required for the ingot to cool to a temperature where excessive oxidation will not occur is considerably longer for a "hotop" mold. The length of the cooling varies with the size of the ingot, the temperature to which the mold was heated, the amount of insulation on the mold and whether a bottom, water cooled heat exchanger is used. It has been demonstrated that the bottom heat exchanger is effective in reducing the overall cooling cycle by about 10%. The cooling cycle for a six-inch "hotop" mold is about two hundred minutes without a heat exchanger and about one hundred and eighty minutes with one. The cooling cycle is measured by the amount of time required for the surface temperature of the mold at the "hotop" section to reach 400° F. Surface oxidation of the ingot is not excessive when the furnace is opened at this time.

c. Mold Life

As stated above, graphite seizure shortens the life of a mold considerably. However, it has been found that the bottom mold also has a shorter life when "hotop" techniques are used. The reasons for the shorter life are not clear since the bottom mold receives very little heat from the "hotop" section. Temperature of the bottom mold normally does not exceed 500° F. before the pour. Data are currently being obtained on the expected life for both top and bottom mold sections but indications are that it will be somewhat shorter than for unheated molds.

d. Surface Cracks or "Hot Tears" on the Ingot

Surface cracks still are occasionally found on ingots that are produced in "hotop" molds. This problem like graphite seizure is somewhat dependent upon mold temperatures and decreases as the temperature decreases. The exact cause of these cracks still has not been determined and as a result no method has been found for preventing their occurrence. Actually, the problem is not too serious since the cracks occur near the top of the ingot or on the riser itself and can be "cropped off". It is estimated that the cracks occur on about 10% of the heats although only limited data are available at this time.

8. Metal Purity

a. Mechanical Stirring of the Melt

As stated in a previous report⁸, it should be possible to remove more of the volatile materials from a melt if the melt is agitated. Attempts to stir the melt by electrical methods were unsuccessful so a mechanical stirring mechanism was used.

⁸ Leaders, W. M., et al, *Op. cit.*, (NYO 1353), p. 114.

The stirring mechanism consisted of a four inch disk of graphite which was connected to a twenty-five inch length of a two inch diameter graphite rod. A stainless steel connecting rod passed up through a Wilson vacuum seal which was bolted to a central flange on the lid of the furnace. The melt was agitated by manually raising and lowering the connecting rod. No lid was used on the crucible.

Stirring of the melt was started at 2350° F. and after most of the usual boiling had ceased. After 10 minutes of agitation the melt was again allowed to become quiet. This procedure was repeated two more times, then the temperature was raised to 2450° F. and pour was made after 10 minutes at this temperature.

During each stirring period there was some additional boiling which continued for a short time after the stirring was stopped. There was the usual thin layer of dark "slag" on the surface of the melt but the metal stirred easily and seemed to be very fluid.

Another heat was made in which conditions of the above run were duplicated except the melt was not stirred. A comparison of the metallographic results and chemical analyses for the two heats will be made to determine if stirring of the melt is beneficial in removing the volatile impurities. No results are available at the present time.

b. Effect of the Heating Cycle on Removal of Volatile Impurities

The amount of volatile impurities that distill from a melt is a function of the temperature and time when furnace pressure is held constant. Carbon pickup from a graphite crucible is also dependent upon the same two factors. An investigation is now in progress to determine, if possible, the holding temperature of the molten metal which will give maximum removal of volatile impurities and yet not give excessive carbon pickup.

At the same time, an effort is also being made to determine what effect, if any, the crucible cover has upon the removal of volatile impurities. Normal casting practice is to use a crucible cover which has a two inch diameter hole through which the volatile impurities must escape. It is believed that this small hole offers considerable resistance to the flow of impurities from the crucible. It also is not uncommon to find this hole almost completely closed by material which volatilized from the melt and condensed at the hole. This happens only when the charge is composed of normal "derby" metal. It never happens when "pickled derby" metal is used. The study will include heats made with and without a regular crucible cover.

The production plant is currently using a holding temperature of 2450° F. and holding for a period of twenty minutes at this temperature before making the pour. The pilot plant study included holding temperatures of 2359° F., 2450° F., and 2550° F. for periods of twenty minutes. Heats were made with and without covers on the crucible.

Evaluation of the heats is being made by metallographic examination and by chemical analysis. Complete results are not available at the present time.

c. Experimental Crucible Dressings

The production plant uses magnesium oxide as a dressing for the graphite crucible. The magnesium oxide is slurried to a spraying consistency with Aerosol solution and sprayed on the crucible. An investigation has been started to develop a dressing which would be superior to the present magnesium oxide dressing that is now used. The ideal dressing should have the following properties:

- a. Be easy to apply,
- b. Be chemically inert to uranium metal,
- c. Be capable of preventing carbon pickup in the melt,
- d. Be adherent so as not to cause inclusions in the melt.

The evaluation of the crucible dressing is accomplished by metallographic examination and chemical testing. Metallographic results are particularly useful for determining inclusions and chemical testing reveals the amount of carbon pickup and other impurities that may be introduced with a particular dressing.

The following materials have been tried as crucible dressings:

- a. Magnesium Oxide (Production dressing),
- b. Two-coat Dressing
 - 1) Sodium Silicate-Magnesium Oxide
 - 2) Magnesium Oxide-Magnesium Sulfate (This is the dressing used on graphite molds),
- c. Magnesium Oxide-Magnesium Chloride,
- d. AL-4 (Los Alamos formulation),
- e. AL-5 (Los Alamos formulation very similar to AL-4),
- f. Uranium Dioxide,
- g. Zirconium Sulfate,
- h. Zirconium Oxide,
- i. Thorium Dioxide,
- j. T.A.M. Zirconite,
- k. Mullite.

The general method of application has been to reduce the particle size to 200 mesh or less, slurry the powder with water until a spraying consistency is obtained and spray the slurry on the unheated crucible. In some cases a dispersing agent is necessary to keep the particles suspended during the spraying operation.

Some of the dressings have been pre-fired in an effort to sinter the dressing. It has been possible to sinter several of the dressings but scaling occurs at some point in the firing cycle.

Complete results on the performance of the various dressings will be given in a later report.

III. Miscellaneous Work

1. Use of Castable Refractories in a Vacuum Induction Furnace

Four commercial castable refractories were tested to determine their suitability for use as insulation in the casting furnace. The trade names of the refractories were 3000 Degree Castable, Kast Set, Chrisco Baffle and Tasil Hydrocast.

Of the four materials tested only the 3000 Degree Castable manufactured by Laclede-Christy held up at temperatures of 2800° F. and under a high vacuum. The refractory material is cast, allowed to air dry, then fired at 1250° F. before being used in a vacuum furnace. When treated in this manner the amount of out-gassing is not a troublesome factor.

Castable refractories are useful in fabricating special shapes which are often temporarily needed in experimental work.

2. Observations of Melts During the Pouring Cycle

It was considered desirable to obtain information about the amount of mixing or vortexing that occurs in the melt during the actual bottom pouring operation. The elimination of a vortex in the melt is desirable because this action causes the impurities that normally liquate to the surface to become mixed throughout the melt. Solidification proceeds rapidly in the mold and there probably is not much time for liquation of the impurities.

The casting furnace was equipped with a large sight glass directly above the melt and another at the side of the furnace for observing the stream of molten metal as it leaves the crucible. By eliminating the crucible cover it was possible to observe both the surface of the melt and the stream during a pouring operation. Observations of the pour from the top reveal that there is no visible vortex in the melt until the last few seconds of the pour. This was true for one-half inch, one inch, and one and one-quarter inch diameter pour holes. Observations from the side confirm the fact that a vortex develops near the end of the pour. This is noted by a tendency for the stream to "fan out" near the end of the pour.

Work with a scale model crucible using mercury as the liquid aided in this pour study. A full scale graphite crucible using water and various other liquids was also used to make the pour study.

3. Estimation of the Kinematic Viscosity of Uranium at 2450° F.

The kinematic viscosity of a liquid may be determined by measuring the time required for a definite volume of the fluid to discharge through an orifice at the bottom of a vessel.

The kinematic viscosity of uranium at 2450° F. as measured by this method is 0.55 centistokes. A calibration curve was made for a crucible using liquids of known kinematic viscosities. Uranium at 2450° F. was then poured from this crucible to determine pour time and the kinematic viscosity value was taken from the calibration curve.

4. Chromium Plating of Power Hack Saw Blades

In the work to date, it has not been possible to extend the life of the blade by chromium plating. Work will be continued on this project.

PRODUCTION OF SEVERAL ALLOYS OF URANIUM

by

W. O. Powers

Introduction

Over the past several years, numerous orders for experimental quantities of various uranium base alloys have been produced in the metal production plant. Most of the earlier alloys were supplied to the consumers in the form of derby metal (the result of the bomb reduction of UF_4). More recently, several alloys were cast into ingots. The production of 2 weight percent zirconium ingots was reported previously¹. During the past quarter, the alloy work has been extended to include several alloys that had not been attempted previously in the metal plant. This work is described herein.

Zirconium Alloys

A series of zirconium-uranium alloy castings were produced at zirconium concentrations of from 2 to 5 weight percent. The castings were $3\frac{3}{4}$ inches in diameter and about 45 inches long before cropping. Uranium tetrafluoride and zirconium tetrafluoride were co-reduced to derby metal for the casting charges. The metal was melted and poured in the production furnaces using regular graphite crucibles and molds.

The first few derbies were 6 weight percent zirconium and were produced using two types of liners for the reduction bombs; fused dolomitic lime and ground slag. These derbies were to be 6 weight percent zirconium which was much greater than any previous zirconium alloy reductions and the two types of liners were used to determine if one might produce a better derby than the other. The derbies produced in ground slag liners were of a much better quality than those produced in the dolomite lime liners. The lime liner derbies had very bad tops. There was an inch thick layer of slag-metal mixture on top of the derby. This slag-metal cap could be removed by use of a pneumatic chisel which is used to clean regular derbies. This slag-metal derby top did not occur on the slag liner derbies. Consequently, the rest of the derbies were produced in slag lined reduction bombs. The reduction data are summarized in Table I.

Table I

Summary of Reduction of Zirconium Alloys

<u>Zirconium Content</u>	<u>No. of Derbies</u>	<u>Type Liner</u>	<u>Firing Time</u>	<u>Derby Yield</u>
4%	5	slag	3 hrs. 12 min.	98.3%
5%	6	slag	2 hrs. 34 min.	98.7%
6%	2	lime	2 hrs. 12 min.	100.8%
6%	4	slag	2 hrs. 58 min.	98.2%
7%	5	slag	3 hrs. 11 min.	100.8%

¹ W. M. Leaders, E. I. Miller, et al, "Process Development Quarterly Report, Part II", April 15, 1953, NYO-1353, pp. 155-158

The large amount of slag in the lime liner derby tops is reflected in the higher derby yield shown in Table I. Derby yields are based on the weights of the chipped derbies. The same phenomenon occurred with the slag liner derbies at 7 weight percent concentration at which point the sluggish derby top characteristic developed.

As casting heats were for the most part made up of 2½ derbies each, it was necessary to bisect a number of derbies. This afforded the opportunity to observe the internal structure of the derbies. All the alloy derbies were more porous and contained more slag inclusions than normal derby metal. This characteristic increased with increasing zirconium content. The porosity concentrated in the upper part of the derby but when the zirconium content reached 7%, the area of porosity had extended down from the top of the derby nearly to the bottom. It appears that reduction of zirconium alloys of greater than 7 weight percent would result in very poor derbies and that at some zirconium concentration, not too much greater than 7 weight percent, the derbies would be uncastable. Reduction techniques can probably be varied to increase the maximum zirconium content in castable derbies.

Eleven 3¼ inch diameter ingots were cast from derby and crop metal. Casting yields were quite low and the ingots had to be cropped severely to produce finished ingots with acceptable zirconium uniformity. Table II summarizes the casting data.

Table II

Summary of Casting Uranium-Zirconium Alloys

<u>No. of Heats</u>	<u>Type</u>	<u>Zirconium in Charge</u>	<u>Furnace Cycle</u>	<u>Casting Yield</u>	<u>Casting Efficiency*</u>
2	Derby	4%	Held 40 min. at 2650° F	74.4%	49.8%
2	"	5%	Held 40 min. at 2650° F	79.7%	53.4%
2	"	6%	Held 20 min. at 2600° F	72.9%	42.2%
2	"	7%	Held 40 min. at 2650° F	70.0%	53.9%
3	Crop	-	Held 30 min. at 2650° F	83.9%	53.0%

* Defined as finished ingot weight divided by charge weight.

The two charges of 6 weight percent zirconium derbies were melted and cast first. The resulting ingots had very large primary pipes and were porous down through the ingot to within 20 and 28 inches from the bottom of the two ingots. The porosity concentrated near the periphery of the ingots. These first two heats were heated to 2600° F, held 20 minutes and poured. Table II shows that the heating cycle was changed in the rest of the castings. The temperature was increased to 2650° F and the holding time was increased to 40 minutes, 30 minutes in case of crop heats. The increases in holding temperature and time improved the ingot quality. Porosity was no longer a problem, but primary pipe was still excessively large - about 8 - 10 inches deep.

The casting yields were much lower than regular production yields. This was probably due to the poorer derby quality as compared with regular derby metal, and to the scavenging action of zirconium. The zirconium combines with nitrogen and liquates in the crucible. Much of these nitrides and carbides apparently remained in the crucible when the metal was poured and held back a large quantity of uranium with it. It is significant that the casting on the 7 weight percent zirconium derby metal show a further decrease in yield. This is consistent with previous comments about the poorer quality of these derbies.

Three of the ingots were non-destructively radiographed by metal pilot plant personnel using the betatron. They reported that the internal soundness was as good as or better than that of regular production ingots.

The upper third of the ingot was cropped and if the ingot was sound, which they were with the exception of the first two, the top and bottom ends were sampled and analyzed for zirconium and other elements. If the zirconium variation from top to bottom of the ingot was large, the ingot was recropped and the top sampled again. The analytical data on the finished ingot are shown in Table III.

Table III
Analyses of Zirconium Alloy Ingots

Heat	Charge	Sample	Zirconium, %	Density, g/cc	Nitrogen, ppm	Carbon
6383	6% Zr	Bottom	4.94	17.47	34	
	Derbies	Top	5.41	17.23	69	
6438	6% Zr	Bottom	4.88	17.69	14	
	Derbies	Top	4.13	17.70	17	
6479	5% Zr	Bottom	4.89	17.68	20	30
	Derbies	Top	4.87	17.24	29	460
6517	5% Zr	Bottom	4.17	17.78	14	60
	Derbies	Top	4.30	17.45	26	360
6827	7% Zr	Bottom	4.48	17.39	19	
	Derbies	Top	5.10	16.96	44	
6845	7% Zr	Bottom	4.78	17.46	37	
	Derbies	Top	4.79	17.26	28	
6919	Crop	Bottom	2.27	18.29	9	30
		Top	2.30	17.54	15	20
7034	4% Zr	Bottom	2.56	18.15	28	
	Derbies	Top	2.81	17.73	47	
7044	4% Zr	Bottom	2.89	18.12	8	50
	Derbies	Top	3.46	17.65	51	710
7284	Crop	Bottom	3.66	17.88	18	
		Top	3.68	17.73	12	
7299	Crop	Bottom	2.45	18.33	10	
		Top	2.19	18.28	10	
Average		Bottom			19	40
		Top			31	390

Spectrographic Analyses
Average of 11 Heats

Sample	Fe, ppm	B, ppm	Mn, ppm	Mg, ppm	Ni, ppm
Bottom	84	<0.10	9.2	1.4	22
Top	95	<0.10	10.2	200	25

It is difficult to accurately estimate the zirconium content of cast ingots based on the zirconium content of the charge as there are large and unpredictable zirconium losses in the casting process. This can be seen by comparing the zirconium in the casting charges and the zirconium in the resulting ingots.

The data in Table III indicate that there will probably have to be changes in techniques to produce castings with greater than 5 weight percent zirconium. The ingots from 7 weight percent zirconium derby charges contained no more zirconium than the ingots from 6 weight percent zirconium derby charges, actually a little less. The 7 weight percent zirconium charges were heated hotter and held longer (Table II) which allowed more liquation of zirconium carbides and nitrides. This problem of excessive zirconium losses with increasing zirconium content can probably be solved by improving reduction method to produce better quality derbies at the higher zirconium levels.

The high iron content of the ingot metal was traced back to the zirconium fluoride. One sample of zirconium fluoride was analyzed and found to contain 0.21% iron.

Molybdenum Alloys

Several production requests for 2 weight percent molybdenum alloys in both derby and ingot form have been filled during this quarter. The processing problems associated with zirconium alloys did not exist in the case of molybdenum. Derby yields were somewhat lower than regular production yields and the derby tops tended to contain more occluded slag. There was no problem of molybdenum segregation or losses during casting.

Table IV shows data from a recent production of 3000 lbs. of 2 weight percent molybdenum-uranium alloy derby metal. The alloy was produced by co-reduction of UF_4 and MoO_3 with some powdered molybdenum added to reduce the heat of reaction to a value comparable to that of the reduction of UF_4 .

Table IV
Summary of Reduction of Molybdenum Alloys

Charge	Reaction Time	Derby Yield	Typical Mo Analyses of 2 Derbies		
			Derby	Top	Bottom
167 lbs. UF_4 1.30 lbs. Mo 1.95 lbs. MoO_3 28.2 lbs. Mg	2 hrs. 28 min. at 1230°F	95.3%	122,193 122,206	1.95% 1.91%	2.08% 2.05%

Another alloy order of approximately 14,000 lbs. of ingot metal 2 weight percent molybdenum and 98 weight percent depleted uranium was completed. The depleted UF_4 used as raw material was produced at Fernald by the de-fluorination of UF_6 . This material behaved rather erratically during reduction. Many derbies were of excellent quality, while some were quite poor with slaggish tops. The depleted UF_4 had a packed bomb charge density that was 10% greater than that of normal UF_4 charges. Table V summarizes the reduction and casting data.

Table V
Summary of Reduction and Casting Data
2 Weight Percent Molybdenum - Depleted Uranium Alloy

<u>Charge</u>	<u>Reaction Time</u>	<u>Derby Yield</u>	<u>Casting Yield</u>
170 lbs. UF_4	2 hrs. 53 min.	87.1%	96.0% (80.9-98.7%)
3.94 lbs. MoO_3	at 1150°F		
29.8 lbs. Mg			

The derby yields with depleted UF_4 were improved over normal UF_4 derby yields from Table IV. The casting yields varied widely, generally the low casting yields were associated with derbies that had slaggish tops.

The ingots were cut into 5 inch sections starting at the bottom of the ingot. The bottom of the bottom section and the top of the top section were sampled. This resulted in the top sample being cut anywhere from 1 to 6 inches from the top of the ingot. The analytical data are summarized in Table VI.

Table VI
Summary of Analyses of 2 Weight Percent Molybdenum-Depleted Uranium Alloys

	<u>Top Sample</u>			
	<u>Average</u>	<u>Range</u>	<u>Average</u>	<u>Range</u>
Molybdenum %	2.01	1.90 - 2.09	2.00	1.84 - 2.09
Density g/cc	18.51	18.21-18.60	18.51	18.44-18.58
Nitrogen ppm	20	5 - 32	20	6 - 38
Carbon ppm			650	560 - 750

The metal was quite uniform. The nitrogen content was about half that of normal production ingot metal, while carbon was about twice as great. Low nitrogen is characteristic of ingots produced from de-fluorinated UF_6 . The high carbon content may be due to carbon in the UF_4 .

Several heats were analyzed spectrographically and the results were typical of regular metal with the exception of nickel which was high (25-40ppm).

Tungsten Alloy

Approximately 5000 lbs. of 1.3 tungsten alloy ingots were produced in the metal plant. Powdered tungsten was added to the bomb reduction charge of UF_4 and Mg. The resulting derbies were given a 5 weight percent pickle in 45% HNO_3 and then cast into 5 inch diameter ingots in a manner similar to regular production casting. Forty-five derbies and nine castings were involved.

The alloy processed very well. The derby yields averaged 97.6% which was slightly higher than the regular production yields at that time. The derbies were clean and unusually free of slag.

The casting yields averaged 96.7% which is a little lower than yields usually obtained when regular pickled derbies are cast. The ingots have not been analyzed for tungsten as the laboratory does not have an adequate method for W-U alloys. Some other analytical data is shown in Table VII.

Table VII

Analyses of 1.3 Weight Percent Tungsten Alloy (Average of Nine Heats)

Sample	Density	N, ppm	Spectrographic, ppm				
			Fe	B	Mn	Mg	Ni
Top of Ingot	18.92	66	34	0.17	11	19.8	12.8
Bottom of Ingot	18.94	51	36	0.14	11	8.9	<10

Table VII shows the ingots to be very uniform with respect to chemical impurities. Boron is slightly higher than normal while nickel is slightly lower than normal.

ETHER EXTRACTION OF SALTED BLACK OXIDE SLURRIES

by

H. L. Boyce

I. Introduction

Black oxide feed materials, as received at the MCW uranium refinery, unlike pitchblende and MgX, contain relatively small amounts of metallic impurities which might serve as salting agents in the ether extraction. Therefore, in order to satisfactorily extract uranium into ether from nitric acid digested black oxide slurries, salting agent must be added to the slurry before extraction. This can be conveniently accomplished by dissolving enough lime and magnesium oxide in nitric acid to give the desired concentration of calcium and magnesium in the final prepared feed.

Because of the added cost to the process of dissolving calcium and magnesium in nitric acid for use as salting agent, it would be economical to recycle part of the raffinate resulting from the ether extraction of the uranium from this type of feed. Therefore, this experiment was designed to test the extraction of salted black oxide slurries in the plant, using recycled raffinate as part of the salting agent requirements.

II. Experimental

The experimental runs were set up and carried out as part of regular production requirements with pilot plant personnel taking special samples and observing the extraction operations.

The feed batches were intended to contain approximately 2.5 - 3.0 pounds per gallon of uranium, 0.67 pounds per gallon of added calcium, 0.12 pounds per gallon of added magnesium, and a nitric acid concentration of 0.6 pounds per gallon, with the final slurry density at 60° - 64° Be. The black oxide used analyzed 75% - 80% uranium.

For the first batch the necessary salting agent was supplied by dissolving 2000 pounds lime and 333 pounds of magnesium oxide in 60% nitric acid and mixing with the dissolved black oxide. For each succeeding batch, the salting agent was supplied by collecting 80% of the raffinate resulting from the ether extraction of the preceding batch, concentrating it, and adding 400 pounds lime and 66 pounds of magnesium oxide with an equivalent amount of nitric acid.

Eleven batches were made up and extracted in this manner, with samples of the raffinate taken every half-hour. Table I shows the pertinent data.

Digestion and Extraction Data for Salted Black Oxide Batches Using Recycled Raffinate

The first batch, using no recycled raffinate, extracted well, confirming the pilot plant experience concerning the efficiency of the calcium-magnesium mixture as salting agent.

Examination of the table will show low slurry ^0Be for the second and third runs, and consequent poor extraction. As a result the recycled raffinate was concentrated further to give a higher slurry density in the final feed. This action improved the extraction efficiency in the subsequent runs, but the results were erratic because of operating difficulties, due in part to the nature of the black oxide slurry. These difficulties included sanding of lines and rotameters, resulting in fluctuating flow rates, shutdowns, and emulsions.

For the eighth run, a fresh batch of salting agent was made up as in the first run. It will be observed that again the extraction was good. Batches nine and ten, with recycled raffinate, were also satisfactory. Batch eleven extracted poorly, probably because of serious emulsion difficulty.

As has been emphasized in previous quarterly reports, experimental work done in the plant is subject to run variations from batch to batch, and it is difficult to strictly compare different runs. Such things as the number of jet mixer pumps running, and the scaled condition of the column plus the differences in feed batch make-up all contribute to successive run variations.

III. Conclusions

From the data gathered in these runs, the following conclusions may be drawn:

1. Black oxide slurry salted with calcium and magnesium can be successfully extracted.
 2. Black oxide slurry with 80% of the raffinate from the previous extraction may be successfully extracted, provided careful control is kept on the slurry density and ether column operation. However, the black oxide with recycled raffinate does tend to produce more emulsion difficulty, and further work should be done before the recycling method is made standard operating procedure.
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