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PURDUE PILOT PLANT STUDIES ON THE RECOVERY OF
URANIUM FROM SYNTHETIC β -GUNK

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Purdue Pilot Plant Studies on the Recovery of

Uranium from Synthetic β -Gunk

The Purdue Pilot Plant was designed and operated to study the recovery of uranium from synthetic β -gunk and its conversion to uranium (IV) chloride by known processes and by processes developed through research. The Purdue unit was similar in size to those used in commercial production. The aims of the work carried out in the pilot plant were to determine the uranium recoveries obtainable by the equipment and process under study, to find the sources of losses, and to develop methods and equipment to overcome the losses.

Attempts to accomplish these aims led to the study of a Standard Process involving liquid-phase chlorination of calcined uranium peroxide with carbon tetrachloride. Variations of this process in both equipment and mode of operation were investigated. A process involving the preparation of uranium (IV) chloride by vapor-phase chlorination with carbon tetrachloride and one using hexachloropropene in the liquid phase as the chlorinating agent were also studied. Since the removal of uranium from effluents was a major problem in recovering uranium from β -gunk, evaporation of effluents, thorium peroxide treatment of effluents, and ammonia treatment of effluents were studied. (Analytical methods were studied and developed in order to determine accurately the recovery of uranium obtained by the various procedures.)

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Section A

The Standard Process

A Standard Process following closely in scale, in equipment, and in operation the process used by the Tennessee Eastman Corporation was adopted for the pilot plant studies at Purdue University. This process may be described briefly as follows.

- Step 1 - Preparation of synthetic β -gunk;
- Step 2 - Precipitation of uranium (VI) peroxide;
- Step 3 - Centrifugation of the uranium (VI) peroxide slurry;
- Step 4 - Removal of the uranium (VI) peroxide from the centrifuge bowl by scraping;
- Step 5 - Dehydration and calcination of the uranium (VI) peroxide to uranium oxides;
- Step 6 - Liquid-phase chlorination of uranium oxides to uranium (V) chloride by carbon tetrachloride;
- Step 7 - Thermal decomposition of uranium (V) chloride to uranium (IV) chloride.

A schematic flow sheet of the Standard Process is shown in Figure 1. Complete operational details will be given in later paragraphs of this report.

The recovery of uranium by the Standard Process was studied step-wise. The steps of the process were investigated to learn the operational details by taking a sample of uranium through the necess-

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Figure 1

Standard Process Flow Sheet

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Figure 1 Cont'd.

UCl₄

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ary steps. The amount of uranium charged and the amount recovered were determined by the analytical procedures discussed in Section J.

In order to obtain values for the recovery of uranium for which the analytical error was low and which would represent what can actually be done in repeating the steps many times, a series of ten-cycle runs was carried out. In each of these runs, a batch of synthetic β -gunk was prepared and the steps under study were performed. The main product and any uranium-containing solutions were then charged to a new batch of contaminants and the necessary steps repeated for a total of ten times. The amount of uranium recovered at the end of the run was determined and the over-all recovery and average recovery per cycle were calculated.

Apparatus and Operational Details.

Preparation of Synthetic β -Gunk.

Synthetic β -gunk was prepared in a 200 gallon glass-lined jacketed kettle fitted with a stainless steel cover. A stainless steel propeller-type stirrer was used to agitate the liquid. A diagram of apparatus is shown in Figure 2; the lower kettle was the one normally used.

The synthetic β -gunk had the composition shown in Table 1. The values given in Column A were used for pilot plant runs P-1 through P-51 and those in Column B for runs P-52 through P-92.

A batch of synthetic β -gunk having the composition shown in Column A of Table 1 was prepared in the following manner. One

- LEGEND**
- **STAINLESS STEEL OR GLASS LINED VALVE**
 - **GLOBE VALVE**
 - **GATE VALVE**
 - **CHECK VALVE**
 - **STRAINER**

Figure 2.

PRECIPITATION, CENTRIFUGATION, AND EVAPORATION APPARATUS

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Table 1

COMPOSITION OF SYNTHETIC β -GUNK

<u>Constituent</u>	<u>Constituent, %</u>	
	<u>A</u>	<u>B</u>
U	0.11	0.22
Fe	0.03	0.06
Cu	0.15	0.30
Cr	0.005	0.01
Ni	0.002	0.004
Cl	0.07	0.14
NO ₃	1.00	2.00
SO ₄	0.002	0.004

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hundred and twenty-five gallons of tap water was metered into the kettle. To this water was added 2850 ml of concentrated nitric acid, 10 ml of concentrated sulfuric acid, 1026 g of iron (III) nitrate nonohydrate, 2698 g of copper (II) nitrate trihydrate, 181 g of chromium (III) nitrate nonahydrate, and 47 g of nickel (II) nitrate hexahydrate. These materials were mixed thoroughly by stirring and a weighed quantity of a solution of uranium (VI) oxide in concentrated hydrochloric acid was added. The amount of uranium charged to the batch was determined accurately from the weight of solution charged and the amount of uranium per unit weight of the solution as determined by analysis. In making up synthetic β -gunk according to the specifications of Column B, Table 1, the amount of water used was the same and the amounts of the other materials were doubled.

Precipitation of Uranium (VI) Peroxide.

Uranium was precipitated from synthetic β -gunk with hydrogen peroxide in the following manner. Stirring was continuous throughout this step. The pH of the synthetic β -gunk was adjusted to 2.2 with 10-15% calcium hydroxide slurry prepared from a low-silicate calcium hydroxide in the copper tank of Figure 2. The pH was determined by a Beckman pH meter (Industrial Model M) on samples dipped from the synthetic β -gunk. The solution was then cooled by brine circulating through the kettle jacket. The brine was cooled by ice in a 400 gallon tank and circulated by a pump as shown in.

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Figure 2. To prevent corrosion of the brine lines, brine treated with sodium dichromate was used.

When the temperature of the synthetic β -gunk reached 10°C, 50 ml of a 27.5% hydrogen peroxide solution was added. Fifty milliliter portions of the hydrogen peroxide solution were added at temperatures of 8°C, 7°C, and 6°C. At a temperature of 5°C, 19 liters of the hydrogen peroxide solution was added and the slurry was allowed to age for one hour at 0-5°C.

Centrifugation of the Uranium (VI) Peroxide Slurry.

The uranium (VI) peroxide was removed from the slurry by a No. 16 Sharples Super Centrifuge. A stainless steel pipe connected the glass-lined valve at the bottom of the kettle to the bottom of the centrifuge. A short section of Koroseal tubing in this line was used to provide flexibility sufficient to prevent excessive wear in the centrifuge drag. The effluent from the centrifuge passed into a 400 gallon stainless steel blowcase. A vacuum of 10-25 inches of mercury was maintained upon the blowcase by means of a steam ejector while the effluent was being discharged from the centrifuge. This equipment is shown in Figure 2.

The steps in the operation were as follows: The steam ejector was turned on, the centrifuge started, the kettle stirrer turned off, and the bottom valve on the kettle opened wide as soon as the centrifuge was running at top speed. After all the slurry had passed into the centrifuge, the kettle was washed with 3 gallons of a

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2% hydrogen peroxide solution acidified with nitric acid to a pH of about 2. This solution also washed the centrifuge cake. About one hour was required for the centrifugation. The centrifuge was allowed to spin 10 minutes after the last of the wash water had passed through. The centrifuge was then stopped and the centrifuge drainings run from the centrifuge bowl through the drag into a stainless steel pan. These drainings and the drag washings were submitted for uranium analysis.

The effluent from the centrifugation was blown by air pressure from the blowcase through a Koroseal tube to the upper 200 gallon jacketed glass-lined kettle shown in Figure 2. The precipitation kettle was washed with nitric acid and the blowcase was washed with water. These solutions were added to the effluent and the resulting solution thoroughly mixed by rapid stirring. This solution was then weighed by draining portions into a steel drum on a scale. A portion of the solution was removed for uranium analysis.

Removal of Uranium (VI) Peroxide from the Centrifuge Bowl.

Two methods were used to remove uranium (VI) peroxide from the centrifuge bowl. The first method, dissolution in nitric acid, was developed by the Purdue Pilot Plant Staff. The second method, scraping, was the standard technique used in commercial operation.

The dissolution method was developed to study the recovery of uranium in the steps of the Standard Process prior to the scraping of the uranium (VI) peroxide from the bowl and to furnish a

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procedure for a simpler and more complete removal of uranium from the centrifuge bowl. Research at Purdue showed that the uranium (VI) dioxynitrate solution obtained by the dissolution method can be readily converted to uranium (IV) chloride.

The apparatus originally used for the dissolution consisted of a Glas-Col blanket wrapped around the centrifuge bowl containing uranium (VI) peroxide. Nitric acid was added to the bottom-stoppered bowl and the bowl heated. The uranium (VI) dioxynitrate solution so formed was poured from the bowl. A water wash removed all the remaining uranium solution from the bowl. The successful operation of this equipment led to the design and construction of the apparatus shown diagrammatically in Figure 3. The centrifuge bowl was stoppered at the bottom and the split iron rings fastened as shown in the centrifuge bowl detail of Figure 3. A charge of 500 ml. of concentrated nitric acid (if about 500 g of uranium had been used) was poured into the centrifuge bowl through one of the effluent outlets. The centrifuge bowl was then placed in the iron tube. The apparatus was inclined slightly from the horizontal so that the solution would not run out of the effluent outlets. At the end of one-half hour of heating and rotating at five rpm, the was removed from the apparatus, the solution was poured out, and the bowl rinsed with water. The solution was then ready for analysis or further processing.

The scraping of uranium (VI) peroxide from the centrifuge bowl

FIGURE 3
DISSOLUTION APPARATUS

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was done on a stainless steel table, a diagram of which is shown in Figure 4. The liner from the liquid phase chlorination apparatus was placed under the funnel of the table (Section C-C, Figure 4). The bowl was removed from the centrifuge, the bottom was loosened, and the bowl was placed in the center section of the table. The uranium (VI) peroxide was scraped from the bowl bottom and from the lower section of the bowl with spatulas. The three-wing was pulled from the bowl and cleaned by scraping. Most of the uranium (VI) peroxide remaining in the bowl was removed by scoops. The uranium (VI) peroxide was dropped into the liner through the guide hole of the plate in the funnel. After the scraping was completed, the liner was replaced by a beaker. The bowl was then placed in the tube in the upper end of the table. Approximately 2.5 l of 10% nitric acid was placed in the acid egg (Detail A of Figure 4) and heated nearly to boiling by steam. The acid egg was then closed and the air pressure turned on. The nitric acid was sprayed into the bowl in approximately 750 ml portions by opening the valve between the acid egg and the sprayer.

The three-wing, bowl-bottom, tools and table were cleaned with hot dilute nitric acid from wash bottles. The bowl was removed from the tube and any spots of uranium (VI) peroxide remaining were removed by nitric acid. All the uranium-containing solutions were combined and designated as the centrifuge bowl washings and analyzed for uranium.

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STEAM
HNO₃
STEAM
AIR PRESSURE

DETAIL A

1/32 HOLES-4 EVERY 2 IN.

SECTION B-B

FLOOR LINE

SECTION C-C

Figure 4.

CENTRIFUGE BOWL CLEANING TABLE

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Calcination of Uranium (VI) Peroxide.

The wet uranium (IV) peroxide was converted to a mixture of uranium oxides by dehydration and thermal decomposition. The liner containing the uranium (VI) peroxide was placed in the calciner. A diagram of the calciner is shown in Figure 5. The electrically-heated furnace contained a stainless steel boot which had a thermocouple well, an outlet, and a lid. The outlet was attached to two traps and from there to a stainless steel water aspirator. A slight vacuum was maintained on the system during the calcination. The furnace was heated to a temperature of 500°C and the liner placed in the boot. The temperature was maintained at 500°C for approximately five hours. The lumps in the material were broken with a stainless steel rod at the end of two hours and then again at the end of three hours. The product, uranium oxides, was a red-brown finely-divided solid.

Preparation of Uranium (V) Chloride.

The mixture of uranium oxides from the calcination step was chlorinated by carbon tetrachloride in the liquid phase to produce uranium (V) chloride. The apparatus used for the chlorination is shown in Figure 6. The drag type stainless steel stirrer was placed in the liner containing the uranium oxides. A charge of 2700 ml of carbon tetrachloride was added and the liner placed in the reactor so that the ears on the liner fitted the slots. The reactor head was bolted to the reactor and the stirrer was turned to about 30 rpm. The bleed valves were closed and water was started through

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22 fig. 5

Figure 5.

CALCINING APPARATUS

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Figure 6,

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the jacket of the carbon tetrachloride trap. Steam was turned into the jacket of the reactor and, when the pressure inside the reactor reached 100 lb / sq in, the steam was turned off. The pressure was allowed to rise and was maintained at approximately 300 lb / sq in for 10-15 minutes by the introduction of steam or water into the reactor jacket.

The reaction mixture was cooled to 130°C and the reaction gases and excess carbon tetrachloride were bled from the reactor. The rate of bleeding was controlled by the bleed valves so that 10-20 minutes were required to reduce the pressure in the reactor to atmospheric pressure. The excess carbon tetrachloride was condensed from the gases from the reactor by the carbon tetrachloride trap. The uncondensed gases passed into two pyrex tubes packed with Berl saddles and filled with water, and then into a caustic soda scrubber. A 5% caustic soda solution was circulated through this scrubber which was packed with brick fragments. Any gases remaining were vented.

After the bleeding was completed, air was passed through the entire system for 30-45 minutes to dry the material. After run P-68, the air was dried by passage through the tube packed with anhydrous calcium chloride (Figure 6). The temperature was maintained at 100-130°C during this operation. At the end of this time, the reactor was cooled by passing water through the jacket.

The liner was removed from the reactor and the product transferred. The liner, stirrer, reactor head, bleed lines, carbon tetra-

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chloride trap, and water scrubbers were cleaned with water. The washings were submitted as equipment washings for uranium analysis.

The liquid-phase reactor was fitted with a bursting diaphragm, a pressure relief valve, and an expansion tank to prevent the pressure in the reactor from becoming dangerously high. A diagram of this apparatus is shown in Figure 6. The outlet of the expansion tank was connected to the caustic soda scrubber.

Preparation of Uranium (IV) Chloride.

The uranium (V) chloride was converted to uranium (IV) chloride by thermal decomposition. The apparatus used is shown diagrammatically in Figure 7. A stainless steel funnel was attached to a Hastelloy bank bottle (as shown in A, Figure 7) and placed over the liner from the liquid-phase reactor containing the uranium (V) chloride. This assembly was then turned over and uranium (V) chloride flowed into the Hastelloy bank bottle. As much of the material as possible was shaken from the liner. Any large lumps that did not pass through the funnel into the box were broken in the funnel and put into the box. The adapter shown in Figure 7 was fastened to the box and the nitrogen inlet tube attached to the adapter. This assembly was then inserted in and bolted to a stainless steel box which fitted closely in the small muffle furnace. This furnace could be raised or lowered as desired. The vent connection was made and nitrogen was started through the apparatus.

The furnace temperature was maintained at about 600°C. At the

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Figure 7.

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URANIUM PENTACHLORIDE DECOMPOSER

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start of the decomposition, the furnace was raised so that one-half of the Hastelloy bank bottle was in the furnace and was held there for 10 minutes. The furnace was then raised all the way. The furnace heat was controlled so that the temperature in the bank bottle as measured by a thermocouple in a well next to it reached 525°C in not less than 35 minutes. The maximum temperature was held for 15 minutes and the furnace then lowered. The decomposing unit was allowed to cool.

When the bottle was cool, the apparatus was dismantled. The uranium (IV) chloride was removed from the bottle and the entire unit cleaned.

Experimental Data.

The Standard Process was studied in the Purdue Pilot Plant by steps. Each step was investigated by several single-cycle runs and by a ten-cycle run. In all cases, the study of any one step included the operation of all steps of the Standard Process from Step 1 through the step under investigation.

Dissolution of Uranium (VI) Peroxide in the Centrifuge Bowl.

The first three steps of the Standard Process were investigated as a unit. The recovery of uranium from synthetic β -gunk by precipitation as uranium (VI) peroxide followed by centrifugation was studied by dissolving the uranium (VI) peroxide in the centrifuge bowl with nitric acid as described for the apparatus shown in Figure 3. It was thought that if reasonable care were exercised,

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no loss would occur using this method of removing the uranium (VI) peroxide from the bowl.

Data from runs in which the dissolution method was used are given in Table 2. Several runs were made with the original dissolution apparatus which has been previously described. Runs made with the apparatus shown in Figure 3 are so indicated in Table 2. In single-cycle runs, all samples were prepared in the manner previously described and uranium analyses performed. For the ten-cycle run, P-41, a batch of synthetic β -gunk was prepared and the Standard Process carried through the centrifugation step. The uranium (VI) peroxide was dissolved in nitric acid in the centrifuge bowl and the resulting solution and the centrifuge drainings were charged to a fresh batch of contaminants to form synthetic β -gunk. These operations were repeated a total of ten times. The peroxide effluents were sampled as described previously. At the end of the tenth cycle all uranium-containing solutions were submitted for analysis.

The uranium recoveries obtained in single-cycle runs and in a ten-cycle run indicate that if care is used, little or no loss occurs in the operation of the first three steps of the Standard Process. An average uranium recovery of 99.996% per cycle was obtained in the ten-cycle run.

Scraping of Uranium (VI) Peroxide from the Centrifuge Bowl.

The Standard Process through the step involving the scraping

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Table 2

RECOVERY OF URANIUM THROUGH THE CENTRIFUGATION STEP OF THE STANDARD PROCESS

Run No	P-23	P-26	P-28	P-32	P-38	P-40 ^a	P-41 ^a	P-50 ^a	P-53 ^a
U charged, g	423.9	414.1	425.5	390.5	506.0	504.8	503.0	550.1	910.2
U recovered, g									
in solution	422.3	412.2	421.6	381.7	495.0	494.1	474.4	543.9	888.9
in peroxide effluent	1.1	1.7	2.9	2.9	3.9	3.9	3.46	4.3	5.8
							1.91		
							2.48		
							2.49		
							3.24		
							0.91		
							3.82		
							2.98		
							0.94		
							5.29		
in centrifuge drainings	---	---	0.4	5.9	7.0	6.8	3.72	2.2	7.6
in salvage	---	---	---	---	---	---	0.14	---	6.3
Total U recovered, g	423.4	413.9	424.9	390.5	505.9	504.8	505.8	550.4	908.6
%	99.9	100.0	99.9	100.0	100.0	100.0	99.96	100.1	99.8 ^b
average per , %							99.996		
cycle									

(a) Apparatus of Figure 3 used.

(b) A few drops of solution was spilled.

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of the uranium (VI) peroxide from the centrifuge bowl was investigated with respect to uranium recovery. The data from pilot plant runs in which this technic was used are shown in Table 3. In single-cycle runs, the uranium (VI) peroxide was dissolved in the nitric acid centrifuge bowl washings. All other analytical samples were prepared as previously described. For the ten-cycle run, P-48, uranium (VI) peroxide was precipitated from synthetic β -gunk, centrifuged from the slurry, and scraped from the centrifuge bowl. A nitric acid solution of the uranium (VI) peroxide, the table, bowl, and tool washings, and the centrifuge drainings were charged to a fresh batch of contaminants to form synthetic β -gunk. The procedure was repeated until ten-cycles had been completed. The necessary solutions were then submitted for uranium analysis. The peroxide effluents were sampled separately.

The recovery of uranium through the scraping step of the Standard Process was excellent if care was used in all operations. An average uranium recovery of 99.994% per cycle was obtained in the ten-cycle run.

Calcination of Uranium (VI) Peroxide.

The recovery of uranium from synthetic β -gunk through the calcination of the uranium (VI) peroxide step of the Standard Process was investigated in a series of pilot plant runs. The data for these runs are shown in Table 4. The single-cycle runs were carried out in the usual manner. In the ten-cycle run, P-68,

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Table 3

RECOVERY OF URANIUM THROUGH THE BOWL CLEANING STEP OF THE STANDARD PROCESS

Run No	P-43	P-44	P-45	P-46	P-48	P-51	P-52
U charged, g	504.9	506.4	507.0	538.9	553.5	551.1	1023.0
U recovered, g							
in uranium (VI) peroxide	487.8	498.0	498.9	533.1	503.5	549.1	994.4
in peroxide effluent A	2.8	4.6	3.0	3.1	4.89	4.0	4.8
B					4.40		
C					3.63		
D					4.57		
E					2.20		
F					5.04		
G					4.10		
H					2.44		
I					7.53		
J					4.53		
in centrifuge drainings	14.5	4.2	3.2	1.2	2.12	0.7	23.3
in salvage	---	---	---	---	4.15	---	---
Total U recovered, g	505.1	506.8	505.1	537.4	553.2	553.8	1027.5
%	100.0	100.1	99.6	99.6	99.94	100.5	100.0
average per, %					99.994		
cycle							

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Table 4

RECOVERY OF URANIUM THROUGH THE CALCINATION STEP OF THE STANDARD PROCESS

Run No.	P-54	P-60	P-61	P-62	P-63	P-68
U charged, g	936.2	919.7	1096.0	1116.0	1100.5	1013.0
U recovered, g						
in uranium oxides	819.6	841.3	925.3	983.3	997.0	888.3
in centrifuge bowl washings	92.4	44.1	109.2	116.1	75.7	21.3
in peroxide effluent A	6.4	1.9	7.5	8.8	7.8	5.50
B						3.55
C						3.61
D						5.70
E						4.56
F						6.28
G						12.93
H						11.40
I						9.65
J						8.70
in centrifuge drainings	11.7	32.8	51.0	6.1	14.5	22.9
in salvage	--	0.1	0.9	0.7	0.1	0.34
Total U recovered, g	930.1	920.2	1093.9	1115.0	1093.1	1004.7
%	99.4	100.1	99.8	99.9	99.3	99.18
average per cycle, %						99.92 ^{2.6}

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the product of the first cycle, the uranium oxides, was dissolved in nitric acid and charged to a fresh batch of contaminants. The centrifuge drainings and the table, bowl, and tool washings were also added to the batch. The procedure was repeated for a total of ten times.

The results shown in Table 4 indicate that some loss did occur. Only a very small amount of uranium, about 4-20 mg per cycle, was found in the traps of the calcining apparatus shown in Figure 5. The total amount of uranium found in the traps at the end of the ten-cycle run was 0.04 g. The average recovery of uranium as shown by the ten-cycle run was 99.92% per cycle.

Preparation of Uranium (V) Chloride.

A series of runs was carried out to investigate the recovery of uranium by the Standard Process through the liquid-phase carbon tetrachloride chlorination step. The data from these runs are given in Table 5. The single-cycle runs were made in the manner described to learn operational technic. For the ten-cycle run, P-67, a batch of synthetic β -gunk was prepared and the precipitation, centrifugation, scraping, calcination, and liquid-phase chlorination steps carried out in the normal manner. The final product, uranium (V) chloride, was dissolved in nitric acid and, together with the centrifuge drainings, and the table, centrifuge bowl, and tool washings, was charged to fresh contaminants making a new batch of synthetic β -gunk. The process was repeated

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Table 5

RECOVERY OF URANIUM THROUGH LIQUID-PHASE CHLORINATION STEP OF THE STANDARD PROCESS

Run No	P-55	P-56	P-57	P-58	P-59	P-67
U charged, g	909.8	890.8	918.0	907.8	921.7	1105.8
U recovered, g						
in uranium (V) chloride	769.6	619.9	608.9	764.2	664.1	844.7
in equipment washings	23.5	140.0	136.3	71.6	169.7	48.2
in centrifuge bowl washings	88.4	102.0	133.0	47.3	63.1	103.0
in peroxide effluent A	6.2	5.9	4.8	4.0	6.1	7.56
B						9.70
C						8.84
D						3.78
E						10.38
F						8.91
G						8.22
H						9.40
I						8.29
J						7.65
in centrifuge drainings	17.0	15.4	22.0	11.3	18.0	9.1
in salvage	0.7	3.7	4.8	3.0	0.7	1.1
Total U recovered, g	905.4	886.9	909.8	901.4	921.7	1088.8
%	99.5	99.6	99.1	99.3	100.0	98.46
average per cycle, %						99.85

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for a total of ten times. After the third, sixth, and ninth cycles, the water scrubbers of the liquid-phase unit were emptied, cleaned, and refilled. The carbon tetrachloride was drained from the carbon tetrachloride trap and extracted with dilute nitric acid. These solutions were added to the batch for the fourth, seventh, and tenth cycle. After ten cycles, all equipment was cleaned and all uranium-containing materials were submitted for analysis.

The results as shown in Table 5 indicate that some loss of uranium does occur in the liquid-phase chlorination step of the Standard Process. The average recovery of uranium per cycle, as shown by the ten-cycle run, was 99.85%. The amount of uranium found in the calciner traps was 0.05 g and that found in the caustic soda scrubber was 0.20 g for the ten-cycle run.

Preparation of Uranium (IV) Chloride.

The Standard Process for the recovery of uranium from synthetic β -gunk and its conversion to uranium (IV) chloride was studied in its entirety in both single-cycle runs and in a ten-cycle run. The data for these runs are presented in Table 6.

In the ten-cycle run, P-74, uranium (VI) peroxide was precipitated from synthetic β -gunk, centrifuged from the slurry, scraped from the centrifuge bowl, and calcined to uranium oxides which were then converted by liquid-phase chlorination to uranium (V) chloride. This was transferred to the bank bottle and decom-

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Table 6

RECOVERY OF URANIUM THROUGH THE FORMATION OF URANIUM (IV) CHLORIDE BY THE STANDARD PROCESS

Run No	P-69	P-70	P-71	P-72	P-73	P-74
U charged, g	1073.0	1033.0	1047.0	1039.0	1047.8	1041.0
U recovered, g						
in uranium (IV) chloride	504.2	520.5	919.1	847.8	951.8	857.2
in uranium (IV) chloride	---	333.0	---	---	---	---
in equipment washings	517.7	116.6	70.4	124.6	39.9	84.9
in centrifuge bowl washings	34.0	31.5	40.0	41.5	43.9	21.3
in peroxide effluent A	9.3	7.1	7.9	7.9	10.8	8.03
B						8.94
C						6.41
D						4.32
E						3.36
F						5.45
G						7.55
H						2.48
I						2.39
J						4.25
in centrifuge drainings	5.8	18.7	7.8	14.7	2.5	13.7
in salvage	1.6	0.6	0.1	0.1	1.4	7.12
Total U recovered, g	1072.6	1028.0	1045.3	1036.6	1050.3	1037.4
%	100.0	99.5	99.9	99.8	100.2	99.65
average per cycle, %						99.965

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posed to uranium (IV) chloride. The final product, uranium (IV) chloride, was dissolved in nitric acid and charged to fresh contaminants. Also added were the centrifuge drainings, the decomposer washings, the liquid-phase chlorination liner, stirrer, and head washings, and the centrifuge bowl, table and tool washings. The process was then repeated until ten cycles had been completed. After every third cycle, the water scrubbers and the carbon tetrachloride trap of the liquid-phase chlorinator were cleaned and the uranium-containing solutions added to the batch. At the end of the tenth cycle, all equipment was thoroughly cleaned and the analyses performed.

The results of the ten-cycle run show that the average recovery of uranium per cycle was 99.965%. This value is higher than that obtained by the ten-cycle run through calcination or by the ten-cycle run through the preparation of uranium (V) chloride. The additional loss found in these runs as compared to the complete process is thought to be caused by dusting during solid transfers. The calcined uranium oxides and the uranium (V) chloride were finely-divided powders and dusting during transfers was noticed. In the ten-cycle runs in which these materials were the products, the solid was poured from the liner into a beaker for later dissolution in nitric acid. In the ten-cycle run in which uranium (IV) chloride was the final product, no transfer was necessary between calcination and chlori-

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nation, and the uranium (V) chloride was transferred to the bank bottle through the stainless steel funnel. The use of the funnel decreased the loss of material by dusting since the system was essentially closed during the transfer of solid from the liner to the bank bottle.

Analysis showed that there was 0.039 g of uranium in the traps from the calciner and 0.10 g of uranium in the caustic soda scrubber after the ten-cycle run.

Summary.

The Standard Process for the recovery of uranium from synthetic β -gunk and its conversion to uranium (IV) chloride has been investigated with regard to the recovery of uranium. Steps of the Standard Process were studied individually. The average recoveries of uranium per cycle as obtained by a series of ten-cycle runs are shown in Table 7. Each value is for the Standard Process from the preparation of synthetic β -gunk through the step under consideration. The analytical error for the result is given. Excellent uranium recoveries have been obtained by the operation of the Standard Process. The average uranium recovery per cycle of the Standard Process was found to be 99.965%.

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Table 7

RECOVERY OF URANIUM BY THE STANDARD PROCESS

<u>Step</u>	<u>Cumulative Average Recovery Per Cycle, %</u>
1. Preparation of β -gunk.	---
2. Precipitation of uranium (VI) peroxide	---
3. Centrifugation.	99.996 $\pm 0.010\%$
4. Scraping of uranium (VI) peroxide from the centrifuge bowl.	99.994 $\pm 0.017\%$
5. Calcination.	99.92 $\pm 0.01\%$
6. Liquid-phase chlorination with carbon tetrachloride.	99.85 $\pm 0.02\%$
7. Conversion of uranium (V) chloride to uranium (IV) chloride.	99.965 $\pm 0.002\%$

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Section B

Variation of the Standard Process

A large number of runs in which uranium peroxide was removed from the centrifuge bowl by dissolution in nitric acid using the apparatus shown in Figure 3 have been reported in Section A of this report. Excellent recoveries of uranium were obtained. Research at Purdue had shown that uranium (VI) dioxynitrate solutions were easily converted to uranium oxides by evaporation and calcination. It seemed desirable to determine if these uranium oxides could be converted to uranium (V) chloride by liquid-phase carbon tetrachloride chlorination.

In pilot plant runs P-64 and P-66, uranium, as uranium (VI) peroxide, was removed from cold synthetic β -gunk by centrifugation as described for the Standard Process. The centrifuge bowl containing 1000 ml of concentrated nitric acid was placed in the dissolution apparatus shown in Figure 3 and was heated and rotated for one-half hour. The uranium (VI) dioxynitrate solution so formed was poured into the liner of the liquid-phase chlorinator (Figure 6) and the liner containing the solution was placed in the calcining furnace (Figure 5). Under slightly reduced pressure, the solution was evaporated to dryness and the cake so formed was calcined to uranium oxides.

The liner containing the uranium oxides and 2700 ml of carbon tetrachloride was charged to the liquid-phase chlorinator (Figure 6)

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and the chlorination carried out in the normal manner. The reaction proceeded smoothly and in a manner similar to that resulting if uranium oxides prepared by drying and calcining uranium peroxide were used. Recoveries of uranium of 99.5% and 99.4% were obtained as shown by the data given in Table 8. These uranium recoveries are similar to those obtained in single-cycle runs using the scraping technique for the removal of uranium (VI) peroxide from the centrifuge bowl followed by the preparation of uranium (V) chloride by liquid-phase chlorination with carbon tetrachloride (recoveries of 99.5%, 99.6%, 99.1%, 99.3% and 100.0% in pilot plant runs P-55 through P-59, Table 5).

Dissolution of the uranium (VI) peroxide in the centrifuge bowl offers several advantages over the scraping technic for the removal of the uranium peroxide from the centrifuge bowl. Less labor is involved and a more nearly complete removal of uranium is obtained. This results in a subsequent increase in the conversion of uranium to the final product.

Section C

Use of the Purdue Cleaning Table in the Standard Process

In the early stages of the work at the Purdue Pilot Plant before the regular scraping table (Figure 4) had been installed, the first four steps of the Standard Process were studied using the Purdue Cleaning Table. The data of the runs are summarized in Table 9. The average uranium recovery per cycle of these runs

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Table 8

RECOVERY OF URANIUM THROUGH THE FORMATION OF
URANIUM (V) CHLORIDE

Run No	P-64	P-66
U charged, g	1100.0	1098.0
U recovered, g		
in uranium (V) chloride	969.0	987.5
in equipment washings	61.8	72.4
in centrifuge bowl washings	4.4	9.4
in peroxide effluent	12.0	10.3
in centrifuge drainings	47.8	11.0
in salvage	0.4	1.1
Total U recovered, g	1095.4	1091.7
%	99.5	99.4

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Table 9

RECOVERY OF URANIUM USING THE PURDUE CLEANING TABLE

Run no	P-1	P-5	P-7	P-13	P-14	P-15 and P-17	P-18	P-19
Uranium charged, g	494.5	552.5	497.5	502.9	496.6	947.8	434.3	407.9
Uranium recovered, g								
in uranium (VI) peroxide solution	465.6	536.7	437.1	491.4	486.4	936.2	427.6	395.1
in peroxide effluent A	27.8	5.4	19.9	10.3	3.1	3.8(P-15)	2.5	2.9
B	--	--	7.5	--	--	2.3(P-17)	--	1.5
C	--	--	22.8	--	--	--	--	1.5
D	--	--	--	--	--	--	--	1.5
in salvage	--	--	0.1	0.3	--	--	--	--
Total uranium recovered, g	493.4	542.1	487.4	502.0	489.5	942.3	430.1	402.5
%	99.8	98.1	98.2	99.3	98.6	99.4	99.1	98.7
average per cycle, %			99.6			99.7		99.7

was 99.45%.

The Purdue Cleaning Table consisted of a V of stainless steel sheeting having an over-all length of 48 inches and a width of 21 inches. The total height of the V was 2 inches. This V was mounted on a wooden table so that it had a 6-inch slope. A container was placed under a spout fixed at the lowest point of the table surface.

The recovery of uranium from synthetic β -gunk was studied using the Purdue Cleaning Table and the Standard Process. The uranium in cold synthetic β -gunk was precipitated with hydrogen peroxide and the uranium (VI) peroxide so formed was removed from the slurry by centrifugation as described for the Standard Process. The centrifuge bowl containing the uranium (VI) peroxide was placed on the Purdue Cleaning Table and the bowl bottom removed. The uranium (VI) peroxide was scraped with spatulas and scoops from the bowl bottom, the bowl, and the three-wing into the container placed under the spout of the table. The centrifuge bowl, three-wing, table, and scraping tools were sprayed with hot dilute nitric acid from wash bottles to remove the remaining uranium peroxide. These washings were placed in the container holding the uranium (VI) peroxide and the mixture heated until dissolution of the solid occurred. The centrifuge drainings were then added and the final solution submitted for uranium analysis. The uranium content of the solution is recorded in Table 9 under the heading "in uranium (VI) peroxide solution".

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The effluents from the centrifugation of the uranium (VI) peroxide slurry were treated in various ways. In pilot plant runs P-1 and P-7, the effluent was allowed to flow from the top 200 gallon kettle of Figure 2 into the evaporator and was concentrated to approximately 3 gallons by evaporation. The resulting material was submitted for uranium analysis. In pilot plant run P-5, ammonium hydroxide was added to the effluent until a pH of 5 was reached, one pound of tannic acid was added, and the pH was then raised to 9 with ammonium hydroxide. The mixture was aged 65 minutes and was then centrifuged. The centrifuge cake was removed from the bowl in the normal manner and was dissolved in dilute nitric acid. The effluent was evaporated to a final volume of about 3 gallons. Uranium determinations on the solutions showed 5.3 g of uranium in the ammonia precipitate and about 0.1 g of uranium in the evaporated effluent. In the other runs presented in Table 9, the effluent was weighed and aliquoted for uranium analysis.

Considerable loss of uranium (average recovery, 99.45%) occurred in the use of the Purdue Cleaning Table in the first four steps of the Standard Process and the losses were somewhat erratic (range 98.1%-99.8%). It was thought that most of the loss occurred in the cleaning of the centrifuge bowl. In an attempt to overcome this loss, the dissolution technique and apparatus were developed as reported in Section A. The experience gained in carrying out the precipitation and centrifugation was very valuable in the later work on the Standard Process.

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Section DThe Vapor-Phase Chlorination Process

The production of uranium (IV) chloride by reactions involving carbon tetrachloride in the vapor-phase has been studied in the laboratories of the Tennessee Eastman Corporation. The recovery of uranium from synthetic β -gunk and its conversion to uranium (IV) chloride by vapor-phase chlorination were studied in the Purdue Pilot Plant.

The vapor-phase chlorination process for the recovery of uranium from synthetic β -gunk and its conversion to uranium (IV) chloride may be described briefly as follows.

- Step 1 - Preparation of synthetic β -gunk;
- Step 2 - Precipitation of uranium (VI) peroxide;
- Step 3 - Centrifugation of the uranium (VI) peroxide slurry;
- Step 4 - Removal of the uranium (VI) peroxide from the centrifuge bowl by scraping;
- Step 5 - Vapor-phase treatment,
 - Step 5a- Dehydration and calcination of the uranium (VI) peroxide,
 - Step 5b- Reduction with absolute ethyl alcohol,
 - Step 5c- Chlorination of the reduced oxides to uranium (IV) chloride with carbon tetrachloride;
- Step 6 - Transfer of the uranium (IV) chloride from the reactor to a bank bottle.

The process followed closely in scale, in equipment, and in operation the process proposed for commercial production by the

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Tennessee Eastman Corporation.

A schematic flow sheet of the vapor phase chlorination process is shown in Figure 8. Operational details are given in later paragraphs of this report.

The recovery of uranium was studied using this process. The amount of uranium charged and the amount recovered were determined by the analytical procedures described in Section J.

Apparatus and Operational Details.

Preparation of Synthetic B-gunk.

The synthetic B-gunk used for the study of the vapor-phase chlorination process had the composition shown in Column B of Table 1. It was prepared as described for the Standard Process in Section A of this report.

Precipitation of Uranium (VI) Peroxide.

Uranium was precipitated from synthetic B-gunk with hydrogen peroxide as described for the Standard Process.

Centrifugation of the Uranium (VI) Peroxide Slurry.

Uranium (VI) peroxide was removed from the slurry by centrifugation using the equipment and procedure previously described for the Standard Process.

Scraping of Uranium (VI) Peroxide from the Centrifuge Bowl.

Uranium (VI) peroxide was scraped from the centrifuge bowl into the vapor-phase reactor shown in Figure 9. The scraping table shown in Figure 4 was used. The method of operation was the same as described for the Standard Process.

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Figure 8

Vapor-Phase Chlorination Process Flow Sheet

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Figure 8 (continued)

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Figure 9.

VAPOR-PHASE REACTOR

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Vapor-Phase Treatment.

The conversion of uranium (VI) peroxide to uranium (IV) chloride involved three steps. The uranium (VI) peroxide was dehydrated and calcined to uranium oxides, these uranium oxides were reduced with absolute ethyl alcohol, and the reduced uranium oxides were converted to uranium (IV) chloride by treatment with carbon tetrachloride.

These procedures were carried out in the apparatus shown in Figures 9 and 10. Uranium (VI) peroxide was scraped into the stainless steel reactor (Figure 9) and the head bolted. The reactor was then placed in its mounts and fastened securely by unions. The furnace, which consisted of two halves, was rolled into position and closed. The furnace was electrically heated and the temperature was controlled by a Capacitrol activated by a thermocouple placed in a well through the furnace and touching the surface of the reactor. The reactor was turned at one r p m through a chain and sprocket arrangement with a gear-head motor. A banger was operated from a cam fastened to the reactor so that the banger fell three times per minute on the reactor. This served to loosen material from the sides of the reactor.

The gases from the reactor passed into the scrubbing system. Two scrubbing systems were used and are shown diagrammatically in Figures 11 and 12. The scrubbing system shown in Figure 11 was used for pilot plant runs P-76 through P-85 and that of Figure 12 was used for run P-91. Water was used in the first Berl saddle-packed tower of Figure 11 and a 5% caustic solution was used in

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Figure 10.

VAPOR-PHASE REACTOR-INTRODUCTION SYSTEM

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BERL
SADDLES

Figure 11.
SCRUBBING SYSTEM

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Figure 12.

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the second tower. The rate of flow was controlled from separatory funnels at about one liter per hour. The scrubbing system shown in Figure 12 was patterned after those to be used in commercial production. Water was used in the first tower and a 10% caustic solution in the second tower. The rate of flow was about 1.5 liters per hour.

a. Dehydration and Calcination

The dehydration and calcination of the uranium (VI) peroxide was carried out in the following manner in the apparatus shown in Figures 9 and 10. Nitrogen was passed through a flowmeter at 2.5 liters per minute into the boiler and thence into the reactor. The nitrogen was dried by passage through Drierite and was de-oxygenated by passage through a stainless steel tube packed with copper turnings and maintained at about 600°C.

The temperature of the reactor was raised to 275°C and was maintained at 275°C for one hour, at 300°C for the second hour, and at 350°C for the third and final hour of dehydration and calcination.

b. Reduction

The uranium oxides from the dehydration and calcination were reduced with absolute ethyl alcohol in the same apparatus. The temperature of the reactor was maintained at 350°C. Nitrogen was passed through the reactor during the reduction. Alcohol was passed from the reservoir (Figure 10) through a calibrated rotameter at 8 cc per minute into the electrically heated boiler.

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The boiler was maintained at about 150°C . Reduction was continued for one hour.

c. Chlorination

The reduced uranium oxides were chlorinated by carbon tetrachloride in the same apparatus that was used for the reduction. The temperature of the reactor was maintained at 350°C for the first 2 hours of chlorination, at 375°C for the third hour, and at 400°C for the fourth and last hour. Carbon tetrachloride was introduced from its container into a boiler maintained at 15°C through a calibrated rotameter. The rate of flow was adjusted at 10 cc per minute for the first hour of chlorination, at 12 cc per minute for the second hour, at 15 cc per minute for the third hour, and at 10 cc per minute for the fourth hour. Nitrogen flow was stopped during the chlorination. After the addition of carbon tetrachloride was complete, the nitrogen flow was started. The temperature of the reactor was maintained at 400°C for 15 minutes. The furnace was then removed from the reactor and the reactor was cooled. Cooling was facilitated by means of a fan.

Transfer of Uranium (IV) Chloride to a Bank Bottle.

The reactor was disassembled and the system (Figure 13) placed on the end of the reactor. The uranium (IV) chloride was allowed to flow slowly into the bank bottle. The rate of flow was adjusted with the pinch clamp.

The uranium (IV) chloride was poured from the bank bottle into a beaker and the entire quantity submitted for uranium analysis.

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Figure 13.

VAPOR-PHASE REACTOR-TRANSFER SYSTEM

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The reactor, the bank bottle, the transfer equipment, the solutions from the scrubber, the washings of the scrubbing system, and the extract of the excess carbon tetrachloride were combined and submitted for uranium analysis as equipment washings.

Experimental Data

The recovery of uranium from synthetic β -gunk and its conversion to uranium (IV) chloride using the vapor-phase chlorination process was studied by several pilot plant runs. The data for these runs are given in Tables 10 and 11.

The uranium (IV) chloride prepared in the runs summarized in Table 10 was not transferred to the bank bottle but was poured from the reactor into a beaker and submitted for uranium analysis. The product prepared by these runs was a dark amorphous-appearing material. The average uranium recovery in these four runs was 99.54%.

Five pilot plant runs, single-cycle only, were carried out and the uranium (IV) chloride was transferred to the bank bottle as described. The product was weighed and sampled. The latter sample was analyzed for uranium and for chlorine. The main bulk of the sample was dissolved in nitric acid. A small part did not dissolve; this was thought to be mainly carbonaceous material. The average uranium recovery for the five runs was 99.33%. The products varied considerably in color, in chlorine and uranium contents and ratio, and in insolubles. No explanation can be given for the variance in products.

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Table 10

RECOVERY OF URANIUM BY THE VAPOR-PHASE CHLORINATION PROCESS

Run no	P- 76	P-77	P-78	P-80
Uranium charged, g	1056.0	1016.5	1032.0	972.7
Uranium recovered, g				
in uranium (IV) chloride	936.2	916.5	886.2	847.0
in equipment washings	9.65	17.43	12.85	15.17
in centrifuge bowl washings	61.0	58.5	99.4	79.43
in centrifuge drainings	16.5	13.7	17.2	17.4
in peroxide effluent	9.35	6.8	8.47	5.89
in salvage	15.2	1.6	4.15	2.37
Total uranium recovered, g	1047.9	1014.5	1028.3	967.3
%	99.23	99.80	99.67	99.44

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Table 11

RECOVERY OF URANIUM BY THE VAPOR-PHASE CHLORINATION PROCESS

Run no	P-81	P-82	P-83	P-84	P-85	P-91
U charged, g	987.4	989.2	992.0	985.5	994.3	978.2
U recovered, g						
in uranium (IV) chloride	858.5	881.0	869.7	859.3	880.6	829.6
in equipment washings	23.43	34.08	12.5	49.0	45.78	43.2
in centrifuge bowl washings	86.0	53.4	47.0	50.7	47.0	33.6
in centrifuge drainings	7.55	6.36	7.3	13.3	4.95	6.35
in peroxide effluent A	8.25	3.09	25.9	7.36	8.15	7.19
B						5.79
C						5.37
D						4.65
E						3.48
F						5.09
G						4.74
H						5.35
I						5.34
J						2.90
in salvage	0.51	0.53	23.71	0.25	0.19	0.18
Total uranium recovered, g	984.2	978.5	986.1	979.9	986.7	962.83
%	99.68	98.92	99.40	99.43	99.23	98.43
average per cycle, %						99.843
Uranium (IV) chloride quality						
U, %	63.2	62.4	60.64	63.09	63.38	---
Cl, %	36.8	36.7	35.9	36.1	36.0	---
Cl:U ratio	3.90	3.95	3.97	3.84	3.82	---
insolubles, %	1.23	0.79	3.85	0.22	0.14	---
Color	Dark green	Medium green	Black	Light green	Dark green	---

In order to obtain a value for the recovery of uranium for which the analytical error was low and which would represent what could actually be done in repeating the process over and over, a ten-cycle run, P-91, was carried out. The data are given in Table 11. A batch of synthetic β -gunk was prepared and the vapor-phase chlorination process carried out. The product was dissolved in nitric acid, the insoluble material was removed by filtration, and the resulting solution was charged to a new batch of contaminants. The vapor-phase equipment was cleaned and the resulting solutions were filtered and added to the batch. The scrubber solutions, the centrifuge bowl washings, and the centrifuge drainings were also added to the batch. The process was then repeated for a total of ten times. The residue from the filtration was ashed over burners, dissolved in nitric acid, and added to a later cycle. The amount of uranium recovered at the end of the tenth cycle was determined.

Data in Table 11 show that 98.43% of the uranium charged to the first cycle was recovered at the end of the tenth cycle. The average uranium recovery per cycle was 99.843%.

The results obtained by the vapor-phase process can be compared with those obtained by the Standard Process in a ten-cycle pilot plant run, number P-74, Table 6. This run showed an average uranium recovery per cycle of 99.965%. The average uranium recovery obtained by the Standard Process was 0.122% per cycle higher than that obtained by the vapor-phase process.

It is believed that the losses which occurred in the vapor-phase process may be due to leaks through the packing glands and

unions of the reactor. These leaks were caused mainly by flooding of the scrubbing towers and by dusting of the finely divided uranium (IV) chloride during transfers. The rate of flow of liquid through the scrubbers had to be very low to prevent flooding but even with extremely low rates of flow, some flooding did occur during the chlorination step of the vapor-phase treatment. Most of the losses that occur in the vapor-phase process are due to the vapor-phase treatment since previous results (Table 7) have shown almost quantitative uranium recoveries through the scraping step.

Section E

The Hexachloropropene Process

The preparation of uranium (IV) chloride by the reaction between ~~hexachlor~~ hexachloropropene and various uranium compounds has been studied in great detail by the Research Group at Purdue. These reactions are completely described in other reports. Some of these reactions and techniques were used in the Purdue Pilot Plant. The results of these runs are summarized in Table 12. However, no exhaustive study of any of the technics was undertaken in the pilot plant.

In pilot plant run P-4, uranium was removed from cold synthetic β -gunk as uranium (VI) peroxide by means of centrifugation as described for the Standard Process. The wet uranium (VI) peroxide was scraped from the centrifuge bowl into a three-neck 5-l glass flask. The flask was fitted with a thermometer, a stirrer, and a reflux condenser. Two liters of hexachloropropene was added to the flask, the reflux condenser was removed, and the wet uranium (VI)

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Table 12

RECOVERY OF URANIUM FROM SYNTHETIC β GUNK
CHLORINATIONS WITH HEXACHLOROPROPENE

Run no	P-4	P-10	P-47	P-49
Uranium charged, g	521.9	476.0	519.4	553.5
Uranium recovered, g				
in uranium (IV) chloride	459.0	433.2	476.7	523.1
in uranium (IV) chloride equip- ment washings	--	2.3	2.2	11.2
in centrifuge bowl washings	32.3	8.0	---	---
in organic layer	2.0	0.4	13.7	7.1
in centrifuge drainings	--	--	9.9	6.0
in peroxide effluent	24.5	11.5	5.6	5.3
in salvage	0.1	--	---	---
Total uranium recovered, g	517.9	455.4	508.1	552.7
%	99.2	95.6	98.0	99.9
Uranium charged found				
in uranium (IV) chloride, %	87.9	91.0	91.8	94.5
in organic layer, %	0.4	0.1	2.6	1.3
Uranium (IV) chloride quality				
U, %	62.3	43.1	62.0	62.4
Cl, %	37.3	37.4	37.1	37.0
Cl:U ratio	4.02	5.8	4.05	3.97

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peroxide was dried by codistillation of the water with hexachloropropene. The reaction started violently at 150°C and some uranium was lost by spraying. After the reaction subsided, the run was continued by adding 500 ml of hexachloropropene and refluxing the reaction mixture for 2 hours.

The reaction mixture was then filtered through a sintered glass filter-funnel. The solid was washed with carbon tetrachloride and dried by the passage of dry air through the cake. A small sample of the cake was degassed and analyzed for uranium and chlorine content. The remainder of the cake was dissolved in nitric acid and all uranium-containing solutions submitted for analysis. Analytical data show that the uranium recovery was 99.2%, that the conversion to uranium (IV) chloride was about 88%, and that the product was of satisfactory quality.

In pilot plant run P-10, uranium was recovered from synthetic β -gunk as uranium (VI) peroxide by centrifugation as in the Standard Process. The centrifuge bowl containing the wet uranium (VI) peroxide was attached by means of a different bowl bottom to a stainless steel pot which contained 3 l of hexachloropropene and was heated by blast burners. The hexachloropropene was boiled into the centrifuge bowl. Reaction occurred vigorously when the temperature in the pot reached 202°C. White fumes issued from the centrifuge bowl and after they had stopped, the reaction mixture was refluxed for 1 hour.

The uranium (IV) chloride was filtered from the reaction

mixture by a sintered glass filter-funnel and a sample taken for uranium and chlorine analysis. The remainder of the product was dissolved in nitric acid for uranium analysis. A layer of uranium (IV) chloride remained on the inside of the centrifuge bowl. Considerable corrosion occurred in the bowl during this reaction.

Some of the reaction mixture sprayed from the end of the centrifuge bowl during the reaction. The uranium (IV) chloride produced contained a large amount of iron. These facts explain the results shown in Table 12.

In pilot plant run P-47, the precipitation of uranium (VI) peroxide and its centrifugation from synthetic β -gunk was carried out as in the Standard process. Nitric acid was added to the centrifuge bowl and the uranium peroxide was dissolved using the apparatus shown in Figure 3. The solution so formed was poured from the centrifuge bowl into a 4 l glass beaker. By heating the beaker on a hot-plate, the solution was evaporated to dryness, and the resulting cake calcined until brown fumes were no longer given off. Two liters of hexachloropropene were added to the beaker and the mixture heated with stirring until the reaction subsided, and then the reaction mixture was refluxed for 1 hour.

The uranium (IV) chloride was removed from the reaction mixture by filtration on a special sintered glass filter-funnel and was washed with carbon tetrachloride. The product was degassed in the filter-funnel at 350°C to give a dry powder, readily transferred to another vessel. Pilot plant run P-49 was carried out in a similar manner.

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The results of the two runs are shown in Table 12. The quality of the uranium (IV) chloride was satisfactory in both runs. The recovery of uranium was nearly quantitative in run P-49. The low uranium recovery for run P-47 was probably due to inexperience in using the procedure. Excellent conversions to uranium (IV) chloride were obtained.

The hexachloropropene process was examined with regard to uranium recovery by a three cycle run, pilot plant run P-92. The general procedure is as follows.

The uranium in cold synthetic β -gunk was precipitated with hydrogen peroxide and the uranium (VI) peroxide so formed was removed by centrifugation. The bottom of the centrifuge bowl was stoppered and one liter of nitric acid added to dissolve the centrifuge cake. Solution was facilitated by heating and by rotating (Figure 3) the bowl and its contents. The resulting solution was poured directly into a stainless steel reactor used for further treatment. The centrifuge bowl was then rinsed with water and the rinsings added to the contents of the reactor. The reaction vessel and its contents were heated by means of a hot plate to remove water and other volatile compounds. A syrup ~~was formed~~ which decomposed ^{upon} further heating to give solid uranium oxides. Heating was continued until fumes of nitrogen oxides were no longer evolved. This operation was carried out over-night. Little or no spattering occurred. When evaporation and decomposition was complete, a hard orange-brown porous crust remained.

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After cooling to about room temperature, 3 liters of hexachloropropene, prepared by the Hooker Electrochemical Company, was added to the reaction vessel. The reactor head, equipped with stirrer and condenser, was allowed to set loosely on top of the vessel. Heat was again applied to the reactor. At about 60°C. white fumes were evolved from the reaction mixture. These fumes gradually became more voluminous and dense as the temperature rapidly rose to a maximum of about 160°C (25 min). The temperature remained at its maximum value for about 5 minutes and then dropped slowly as the initial reaction subsided. At this time, the reactor head was bolted tightly to the reaction vessel and stirring was begun. The reaction mixture was then heated at 155-160°C with stirring, to distill the volatile products of the reaction. Relatively small amounts of distillate were collected, and in no case was more than 500 ml of organic material obtained in the receiver. A period of about 2 hours was required for distillation.

After cooling to room temperature, the head of the reactor was removed and about one liter of carbon tetrachloride was added to the mixture of reaction products. Cooling was hastened by surrounding the reactor in an ice bath. The slurry was filtered on a special sintered glass funnel. The uranium (IV) chloride on the filter was washed with about one liter of carbon tetrachloride. When the filtration and washing operations were complete, the filter, containing uranium (IV) chloride, was placed in a large

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tube furnace for degassing. The filtration apparatus was evacuated and heated. The pressures under which the uranium (IV) chloride was degassed varied considerably due to the vaporization of organic materials. As the organic materials were driven off, the pressure in the system gradually dropped. The pressures at which most of the degassing was conducted ranged from 33-50 mm Hg. The maximum temperatures were 260-280^o C, and the operation required about 1.5 hours.

The uranium (IV) chloride was transferred from the degassing apparatus into a Hastelloy bank bottle by means of a stainless steel funnel. The product was weighed and then was ready for further treatment.

The equipment used to prepare and to degas the uranium (IV) chloride was cleaned with water and nitric acid. The resulting solution was filtered to remove a tar-like material which had covered the inside of the reactor. The filter paper containing this material was digested with concentrated nitric acid and the resulting mixture was filtered. The residue was ashed and submitted for uranium analysis. The uranium (IV) chloride was poured from the bank bottle into a beaker and was dissolved in concentrated nitric acid. These uranium containing solutions and the centrifuge drainings were charged to a fresh batch of contaminants making a new batch of synthetic β -gunk. The entire procedure was then repeated. After three cycles had been completed, all equipment was cleaned and the necessary samples were submitted for analysis.

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The data from this run are shown in Table 13. An overall recovery of uranium of 98.60% was obtained. The average uranium recovery per cycle was 99.53%.

The use of hexachloropropene for the preparation of uranium (V) chloride offers certain advantages over the use of carbon tetrachloride in the liquid-phase, such as the use of atmospheric pressure equipment and the non-existence of phosgene as a by-product.

Section F

Evaporation of Uranium (VI) Peroxide Effluents

Some of the effluents from the centrifugation of the uranium (VI) peroxide slurry were concentrated by evaporation. Since uranium recoveries were not quantitative in the early runs, it was decided to test the efficiency of the evaporation step. The effluents from the centrifugation were blown by air pressure from the 400 gallon blow tank to the 200 gallon jacketed kettle and allowed to flow to the evaporator through a hose. A diagram of this apparatus is shown in Figure 2. High pressure (150 lb./sq.in.) steam was passed through the stainless steel coils in the evaporator to heat the solution.

The recovery of uranium in the evaporation procedure was studied in several ways. Data from these tests are presented in Table 14. The synthetic effluent used in run P-11 was prepared in the manner used for preparing a normal batch of synthetic B-gunk except for the addition of the uranium solution. A uranium

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Table 13

RECOVERY OF URANIUM FROM SYNTHETIC B-GUNK-PILOT PLANT RUN P-92

Uranium charged, g	766.7
Uranium recovered, g	
in uranium (IV) chloride	612.6
in equipment washings	111.6
in centrifuge drainings	15.0
in peroxide effluent A	9.36
B	2.80
C	3.38
in salvage	1.23
Total uranium recovered, g	755.97
%	98.60
Average uranium recovery per cycle, %	99.53

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Table 14

RECOVERY OF URANIUM THROUGH EVAPORATION OF PEROXIDE EFFLUENT

Run no	P-11	P-12	P-15	P-17	P-18	P-22	P-25	P-26	P-43	P-44
Source of effluent	Synthetic	Synthetic	Actual	Actual	Actual	Synthetic	Synthetic	Actual	Actual	Actual
Uranium charged, g	13.33	9.84	3.66	2.25	2.37	8.96	6.12	1.7	2.71	4.55
Uranium recovered, g	8.04	9.69	3.7	1.7	1.77	8.84	6.09	1.8	2.67	4.55
%	60.3	98.5	101	75	75	99	100	106	99	100

solution containing about 14 g of uranium was added. The pH was adjusted to 2.2 with lime slurry and 5 gallons of a 27.5% solution of hydrogen peroxide was added. As the solution was evaporated to 3 gallons, considerable solid separated. A 60% recovery of uranium was obtained.

The synthetic effluent used in run P-12 was prepared in a manner similar to that for P-11 except that no copper, iron, chromium, or nickel salts were used. Only a very small amount of solid separated during the evaporation. The recovery of uranium was 98.5%.

The effluents from runs P-15, P-17, and P-18 were weighed into the evaporator after an aliquot had been taken for analysis. The evaporation was carried out in the usual manner. A large amount of solid was present in the concentrate. The uranium recoveries were 101%, 75% and 75% for these three runs.

Run P-22 was similar to run P-11. The uranium recovery was 99%. Very little solid was found in the concentrate.

Since it was believed that the uranium in the solid formed during the evaporation might not be separated by the analytical procedures used, a synthetic effluent free of uranium was prepared and evaporated in run P-25. A sample of a uranium solution was added to the concentrate. Approximately 100% of the uranium added was found.

An attempt to prevent formation of solid during the evaporation was made by adding two liters of concentrated nitric

acid to the evaporator at the start of the evaporation. Nearly quantitative recoveries were obtained in runs P-26, P-43, and P-44 using this procedure. Very little solid was formed. Thus uranium peroxide effluents can be concentrated in the Purque evaporator without loss of uranium and without an appreciable amount of solid formation if the acidity of the effluent is increased before evaporation.

Section G

Recovery of Uranium from Uranium (VI) Peroxide Effluents with Thorium (IV) Peroxide

A procedure for the removal of uranium from uranium (VI) peroxide effluents using thorium (IV) peroxide as a carrier has been developed by the research group of the Tennessee Eastman Corporation. The procedure consists essentially of adding 1 g of thorium, as a 10% aqueous solution of thorium (IV) nitrate for each liter of effluent to the uranium (VI) peroxide effluent at a temperature of about 5°C, a pH of 2.0, and a hydrogen peroxide content of about 0.05 M. The thorium (IV) peroxide is removed from the slurry by centrifugation. The uranium is separated from the thorium and returned to another batch of β -gunk and the thorium is reused for the treatment of other effluents. It was requested that part of this procedure be tested in the Purdue Pilot Plant. Hence, three runs were made; analytical data for these runs are given in Table 15.

The synthetic β -gunk used for these runs had the composition

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Table 15

RECOVERY OF URANIUM FROM URANIUM (VI) PEROXIDE
EFFLUENTS WITH THORIUM (IV) PEROXIDE

Run no	P-75	P-76	P-77
Uranium in uranium (VI) peroxide effluent,			
p p m	90 $\pm$ 1	32.2 $\pm$ 0.3	12.2 $\pm$ 0.1
total, g	----	18.2 $\pm$ 0.2	6.8 $\pm$ 0.1
Uranium in thorium (IV) peroxide effluent,			
p p m	6 $\pm$ 0.4	0.32 $\pm$ 0.05	0.12 $\pm$ 0.03
total, g	----	0.18 $\pm$ 0.03	0.07 $\pm$ 0.02
Uranium in thorium (IV) peroxide cake in nitric acid,			
mg/g soln	12.5 $\pm$ 0.1	3.0 $\pm$ 0.1	1.33 $\pm$ 0.03
total, g	53.5 $\pm$ 0.5	18.2 $\pm$ 0.5	6.8 $\pm$ 0.2
Uranium in thorium (IV) peroxide effluent, concentrate,			
mg/g soln	----	0.010 $\pm$ 0.002	0.0016 $\pm$ 0.0008
total, g	----	0.26 $\pm$ 0.04	0.04 $\pm$ 0.02

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shown in column B, Table 1. The solution used for run P-75 had turned brown on standing several days. Even though this solution was acidified with nitric acid and the pH readjusted to 2.20 with lime slurry, the color remained brown. A normal hydrogen peroxide precipitation, as described for the Standard Process, was carried out using this batch. The uranium (VI) peroxide slurry was centrifuged, but a cloudy effluent resulted. Recentrifugation cleared this effluent slightly. The uranium content of this effluent was much higher than usual. The pH of the uranium (VI) peroxide effluent was adjusted to about 2.0 with lime slurry and 5 gallons of a 27.5% solution of hydrogen peroxide and an aqueous solution containing 1200 g of thorium (IV) nitrate were added. The pH was readjusted to about 2.0 and the slurry was aged with stirring for 45 minutes.

The thorium (IV) peroxide slurry was centrifuged in 87 minutes. The rate of slurry flow through the centrifuge was too rapid as shown by the slow formation of solid in a sample of the effluent taken toward the end of the centrifugation.

The thorium (IV) peroxide centrifuge cake was scraped from the centrifuge bowl using the table shown diagrammatically in Figure 4. The centrifuge bowl, scraping table, three-wing, tools, and bowl bottom were cleaned with hot dilute nitric acid. The cake, orange in color and waxy in appearance, nearly filled the centrifuge bowl.

The thorium (IV) peroxide treatment reduced the uranium content

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of the uranium (VI) peroxide effluent from about 90 to about 6 ppm even though the rate of slurry feed through the centrifuge was too rapid for complete clarification.

The precipitation and centrifugation of uranium (VI) peroxide from synthetic B-gunk were carried out in the normal manner in run P-76. A solution of uranium (VI) oxide in hydrochloric acid equivalent to about 10 g of uranium was added to the uranium (VI) peroxide effluent. Two gallons of a 27.5% solution of hydrogen peroxide and an aqueous solution containing 1200 g of thorium (IV) nitrate were added. The pH was adjusted to about 2.0 both before and after the addition of the thorium (IV) nitrate solution. The reaction mixture was aged, with stirring, for 60 minutes.

The thorium (IV) peroxide slurry was centrifuged in 100 minutes. No solid deposited in 30 minutes from samples of the effluent taken every half hour during the centrifugation. However, after standing for several hours, a very small amount of solid precipitated from the effluent. The thorium (IV) peroxide effluent was concentrated to approximately one-thirtieth of its original volume by evaporation. The thorium (IV) peroxide centrifuge cake was treated as in run P-75. The cake weighed about 20.3 kg and nearly filled the centrifuge bowl.

Run P-77 was carried out in the manner described for run P-76, except that no uranium was added to the uranium (VI) peroxide effluent. The thorium (IV) peroxide slurry was centrifuged in

120 minutes. No solid deposited from the effluent even upon long standing. The centrifuge cake was similar to those previously obtained and weighed about 19 kg.

Analytical data for runs P-76 and P-77 (Table 15) indicate that the concentration of uranium in the effluents was decreased by about one hundred fold by the thorium (IV) peroxide treatment. Uranium balances in these runs are fairly good.

That part of the thorium (IV) peroxide procedure for the removal of uranium from effluents which was tested in the pilot plant seemed rather simple to operate. The thorium (IV) peroxide precipitate was bulky and was easily removed from the glass kettle with water. The thorium (IV) peroxide centrifuge cake was well packed, and fairly dry and was scraped from the centrifuge bowl with less difficulty than the uranium (VI) peroxide centrifuge cake.

Section H

Recovery of Uranium from Uranium (VI) Peroxide

Effluents by Ammonia Treatment

The recovery of uranium from uranium (VI) peroxide effluents by precipitation with ammonium hydroxide was studied. Ammonium hydroxide also precipitates iron (III) and chromium (III) hydroxides and forms soluble complex ions with copper (II) and nickel (II) ions.

The ammonia treatment of uranium (VI) peroxide effluents in the presence of tannic acid was used for three pilot plant runs. Effluents from the centrifugation of a uranium (VI) peroxide slurry

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prepared from synthetic β -gunk were allowed to warm to room temperature. The synthetic β -gunk used had the composition shown in column A, Table 1. The pH of the rapidly-stirred effluent was raised to about 5 with ammonium hydroxide, then tannic acid was added after which the pH was raised to about 9 with ammonium hydroxide, and the slurry was aged. Centrifugation followed. In runs P-3 and P-4, the precipitate was contained in one centrifuge bowl. Even though the rate of slurry feed to the centrifuge was reduced toward the end of the centrifugation, there was some solid present in the final effluent. In run P-5, two centrifuge bowls were used to collect the ammonia precipitate.

The centrifuge cake was very dark in color, well packed and fairly dry. The cake was scraped from the centrifuge bowl using the Purdue Cleaning Table (Section C) and then dissolved in nitric acid. The centrifuge bowl and accessories and the tools used to remove the cake from the bowl were cleaned with hot dilute nitric acid. The resulting solutions were combined and analyzed for uranium. In runs P-4 and P-5, the final effluent was evaporated to about 5 gallons and analyzed for uranium. In run P-3, the effluents were sampled for uranium analysis. The data are summarized in Table 16. These data show that the uranium content of the uranium (VI) peroxide effluent was greatly decreased by the ammonia treatment.

The ammonia treatment of effluents was tried further in four runs. Synthetic effluents, which approached in concentration

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Table 16

RECOVERY OF URANIUM FROM URANIUM (VI) PEROXIDE

EFFLUENTS BY AMMONIA TREATMENT

Run no	P-3	P-4	P-5
U in original effluent, p p m	78.3	49.1	10.7
U in treated effluent, p p m	1.6	0.86	0.11
Tannic acid used, g	200	200	450
Ageing time, min	90	15	65

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effluents from uranium (VI) peroxide slurries, were prepared by adding the necessary amounts of salts and acids to 125 gallons of water to make the final solution 0.30% in copper (II), 0.01% in chromium (III), 0.004% in nickel (II), 0.045% in chloride, 2.0% in nitrate, and 0.004% in sulfate ions. Various amounts of iron (III) nitrate and uranium (VI) dichloride in hydrochloric acid solution were then added. The pH of the rapidly-stirred solution was adjusted to 2.20-2.25 with lime slurry. After the temperature of the solution had been reduced to 6°C by ice-cooled brine circulating through the kettle jacket, 5 gallons of a 27.5% solution of hydrogen peroxide was added and the mixture was aged 15 minutes.

The temperature of the synthetic effluent was raised to about 25°C by the introduction of steam into the solution. The solution was then sampled for uranium analysis. Ammonium hydroxide was added until the pH was 9.5-9.6 and the slurry was aged 30 minutes.

The slurry was then centrifuged. In run P-86, the precipitate completely filled the centrifuge bowl. Toward the end of the centrifugation, the rate of slurry feed through the centrifuge had to be greatly decreased to obtain a relatively clear effluent. The effluent from this run contained considerable solid. In run P-87, the centrifugation was carried out at the normal rate and a clean bowl was used when solid appeared in the effluent. The first bowl was almost full and the second was one-third to one-half full. In runs P-88 and P-89, the precipitate was divided

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almost evenly between the two bowls.

The centrifuge cake was removed from the centrifuge bowl by dissolution in nitric acid using the apparatus shown by diagram in Figure 3. The centrifuge bowl bottom was stoppered, concentrated nitric acid was added, and the bowl was heated and rotated for one-half hour. The resulting solution was then poured from the bowl. Two treatments with 1000 ml of nitric acid were required to remove the centrifuge cake formed in run P-86. Fifteen hundred milliliters of nitric acid was used to remove the cake from the first bowl used in run P-87 while 1000 ml was used for the second bowl. One thousand milliliters of nitric acid was sufficient for each bowl used in runs P-88 and P-89.

The treated effluent was analyzed for uranium. The data for these runs are given in Table 17. Considerable reduction in the uranium content of the effluent was accomplished by this treatment. Samples of the treated effluent were polished by filtration and the uranium content was determined. This polishing procedure greatly decreased the uranium content of the effluent. A uranium balance was determined for run P-88. Data are given in Table 18.

The recovery of uranium from uranium (VI) peroxide effluents by the ammonia procedure described can be made nearly complete by the use of a polishing device beyond the centrifuge. The precipitate is very bulky. The centrifuge cake was dark and well packed and was easily removed from the centrifuge bowl by

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Table 17

RECOVERY OF URANIUM FROM URANIUM PEROXIDE

EFFLUENTS BY AMMONIA TREATMENT

Run no	P-86	P-87	P-88	P-89
Uranium in synthetic effluent, p p m	30	26.1	8.7	83.8
Uranium in treated effluent, p p m	3.1	0.49	0.18	1.19
Uranium in treated effluent, polished, p p m	---	0.06	0.01	0.08
Iron in synthetic effluent, %	0.03	0.05	0.05	0.05

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Table 18

RECOVERY OF URANIUM FROM URANIUM (VI) PEROXIDE

EFFLUENTS BY AMMONIA TREATMENT---

URANIUM BALANCE

Run no	P-88
Uranium in synthetic effluent, g	4.73
Uranium recovered, g	
in centrifuge cake	4.64
in treated effluent	0.098
in centrifuge drainings	0.004
in salvage	0.002
Total U recovered, g	4.74
%	100.2

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dissolution in nitric acid.

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Section I

Miscellaneous Pilot Plant Runs

All Purdue Pilot Plant runs were numbered consecutively from P-1. A large number of these runs have not been reported in the previous sections. They may be accounted for in the following manner. Runs P-2, P-3, and P-9 were lost because of mechanical failures of equipment or breakage of glassware containing analytical samples. Runs P-6, P-8, P-33, P-34, P-36, P-65, P-79, and P-90 were salvaged. The reasons for salvaging these runs ranged from mechanical difficulties with apparatus to errors made in operational details.

In order to prepare pilot plant products for use in research by the Purdue Group, runs P-16, P-20, P-21, P-24, P-27, P-29, P-30, P-31, P-35, P-37, P-39, and P-42 were carried out.

Section J

Analytical Methods Used for the Purdue Pilot Plant

Part A

Sample Treatment

Hydrochloric Acid Solutions of Uranium (VI) Dioxychloride Used for Pilot Plant Charge. Approximately 17 l of solution was prepared containing about 600 g of dissolved uranium (VI) oxide and 680 ml of c p concentrated hydrochloric acid per liter of solution. This solution was well mixed in a 20 l bottle and 2 l samples were aliquoted by weight for each pilot plant charge.

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These samples were weighed in a stoppered 2 l volumetric flask to the nearest 0.1 g on a 10 kg analytical balance. The amount of uranium per charge was calculated from the weight of solution charged and the number of grams of uranium per gram of solution. The number of grams of uranium per gram of charge solution was determined by transferring a 10 ml aliquot of solution from the stock bottle to a weighed 100 ml volumetric flask. The flask plus the solution was then weighed, the solution was diluted with distilled water to the mark and then the flask and its contents reweighed. Weighed aliquots were withdrawn from this flask for the determination of uranium content. Analyses were always obtained upon duplicate samples of stock solution. Analytical methods used for this and other determinations are summarized in Part B of this section.

Nitric and Hydrochloric Acid Solutions of Pilot Plant Uranium (VI) Peroxide, Calcined Uranium Oxides, Uranium (IV) Chloride and Uranium (V) Chloride. The solid bulk samples were dissolved in 4 l covered beakers. The uranium (VI) peroxide samples were dissolved in 4 l covered beakers. The uranium (VI) peroxide samples were dissolved in nitric acid and the calcined uranium oxide samples were dissolved in a mixture of nitric and hydrochloric acids. The samples of uranium (IV) chloride and of uranium (V) chloride were dissolved in nitric acid. The nitric acid oxidized the uranium to uranium (VI). A quantity of acid slightly in excess of the stoichiometric amount for conversion to uranium

(VI) dioxynitrate or chloride was used. The samples, after dilution to 2500 ml, were filtered with suction through paper on a large Buchner funnel into a 4 l suction flask. The solution was transferred to a weighed stoppered 4 l Erlenmeyer flask and weighed to the nearest 0.5 g on a 10 kg analytical balance. Weight aliquots were used for the determination of uranium. The filter paper and residue were combined with any pilot plant salvage and ignited in a porcelain crucible; the ash was leached with concentrated nitric acid. The resulting solution was filtered and analyzed colorimetrically.

Combined Miscellaneous Samples. Nitric acid solutions from the centrifuge bowl wash, equipment washes, and centrifuge drainings were evaporated to 500 ml each. One milliliter aliquots were withdrawn and extracted with diethyl ether in a separatory funnel using a nitric acid-calcium nitrate solution as a "salting out" agent and were submitted for colorimetric analysis. From these analyses a fairly accurate ($\pm 3\%$) determination of the uranium in each separate sample was made. The amount of uranium contained in these aliquots was added as salvage to the final material balance. The main portions of all miscellaneous samples were combined and diluted to volume in a 2 l volumetric flask, aliquoted, and submitted for ether extraction and titrimetric determination. In this manner, the bulk of the material balance was derived from three master samples: the charge material, the main product, and the combined miscellaneous samples.

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Uranium (VI) Peroxide Effluents. The total effluent (approximately 1200 lb) was blown into a glass-lined 200 gallon kettle and stirred for 15 minutes. The solution was drained into 55 gallon drums and weighed on a balance sensitive to 1/16 lb. The overall weighing error was not over 1 lb. A 2 to 3 gallon sample was weighed and set aside for analysis after the first drum had been weighed. This sample was well-shaken and one-liter portions were withdrawn, weighed to the nearest gram, and submitted for ether extraction and colorimetric analysis.

If thorium was present in the effluent, the sample for ether extraction was treated with oxalic acid in about 5% nitric or hydrochloric acid solution. The thorium (IV) oxalate was removed by filtration and the filtrate submitted for colorimetric analysis for uranium.

Evaporated Uranium (VI) Peroxide Effluents. The volume of the sample as it came from the evaporator was 4 to 5 gallons. This solution was transferred to a weighed 5 gallon carboy and weighed. All weighings were made to $\pm 1/16$ lb. The solution sometimes contained suspended particles which settled on standing; therefore, the solution was well shaken immediately before withdrawing each aliquot. One-hundred-milliliter aliquots were withdrawn, weighed to ± 0.1 g and submitted for ether extraction and colorimetric analysis.

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Part B

Analytical Procedures

The procedures used in the analysis of pilot plant samples are summarized in this section. These procedures are described in greater detail in the Analytical Volume of the Manhattan Project Technical Series.

The Separation of Uranium by Extraction with Diethyl Ether.

Samples to be purified by extraction with diethyl ether were evaporated to incipient crystal formation. Then a sufficient quantity of 1:1 nitric acid was added to dissolve the crystals. Silver nitrate was added to remove chloride ions. The sample was transferred to a continuous extractor using a saturated calcium nitrate solution 10% by volume in nitric acid. A period of 1-1.5 hours, the exact time depending upon the amount of uranium present, was required for the extraction. The residue remaining after evaporation of the ether was used for subsequent analysis.

Zinc Amalgam Reduction-Titrimetric Method. Before reduction, the sample was fumed with sulfuric acid and hydrogen peroxide to remove nitrates and organic matter. The fumed sample was made 5% sulfuric acid and the solution boiled with zinc amalgam and mossy zinc to reduce the uranium. After completion of the reduction as indicated by the red color of uranium (III) ions, the solution was cooled and separated from the amalgam by decantation. Air was bubbled through the solution to oxidize

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uranium (III) to uranium (IV). The uranium was determined by titration with standard 0.1 N potassium dichromate solution in the presence of ferric alum and phosphoric acid using barium di-phenylamine sulfonate as the indicator. The iron content was determined colorimetrically on a separate aliquot and the appropriate correction made. This correction is necessary since iron titrates as uranium. The precision and accuracy is about 1-2 parts per thousand.

Mercury Cathode Cell Reduction-Potentiometric Titrimetric Method. Solutions containing uranium in 1 N sulfuric acid were simultaneously purified and reduced using a mercury cathode diaphragm cell. The uranium (III) was air-oxidized to uranium (IV). The potential change during the oxidation was followed potentiometrically to prevent over-oxidation. The final potentiometric titration with potassium dichromate solution was done at room temperature in the presence of iron (III) ions. When a water-jacketed chamber-buret was used, a precision of 1 part in 2000 was obtained.

Zinc-Hydrochloric Acid Reduction-Titrimetric Method. A large sample of uranium was freed of nitrates and organic matter by evaporation and ignition to 500 °C. The ignited oxides were dissolved in sulfuric acid and hydrogen peroxide. The solution was freed of contaminants by electrolysis in a mercury cathode cell. After purification the large sample was diluted and aliquoted into smaller samples. The small samples were reduced

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with granulated zinc and concentrated hydrochloric acid.

Uranium (III) was oxidized to uranium (IV) by air. To prevent over-oxidation the potential change was followed with a platinum-tungsten bimetallic electrode system. The uranium was determined by titration with potassium dichromate using barium diphenylamine sulfonate indicator. Iron remaining in the sample was determined colorimetrically on a separate aliquot and the appropriate correction applied. This method is rapid and gives accurate and precise results.

The Determination of Chloride. The chloride content of uranium (IV) chloride samples was determined by the Volhard method.

The Colorimetric Determination of Uranium. Samples to be analyzed for their uranium content were purified by extraction with diethyl ether. The extracted portion was evaporated to dryness and ignited to destroy organic material. The ignited residue was dissolved in nitric acid and the resulting solution neutralized with sodium hydroxide and sodium carbonate. The pH was then adjusted to 11-14 by adding sodium hydroxide. After adding hydrogen peroxide, the solution was diluted to volume and the transmittancy was measured at 400 m μ .

The Colorimetric Determination of Iron. The pH of a sample containing 0.025-0.25 mg of iron was adjusted to 3.9. To avoid precipitation of uranium, the pH must not be above 3.9. Iron (III) ions were reduced to iron (II) ions by hydroxylamine hydrochloride. An aliquot was used in the reference beam and another aliquot, equal in volume, was treated with 2-2'-bipyridine.

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The optical density was measured at 522 m μ . A blank determination was made on the hydroxylamine hydrochloride and the appropriate correction applied before determining the amount of iron present from the calibration curve.

Part C

Precision and Accuracy of Uranium Balance

Since the start of the Purdue Pilot Plant work, the analytical methods used have been constantly tested and improved. From time to time there has been a complete change in method of analysis. Without exception the charge material and the main bulk sample from the pilot plant on any run were analyzed by the same method.

The zinc amalgam reduction procedure was used in the analysis of bulk samples from runs P-1 - P-57 inclusive, P-60, P-61, P-62, and P-63. The average precision was 1 part per 850. The mercury cathode reduction procedure was used in the analysis of bulk samples from runs P-68 through P-92, with an average precision of 1 part per 2600.

A typical uranium balance as determined on pilot plant run P-41, which was a ten-cycle test of the uranium (VI) peroxide precipitation and centrifugation steps of the Standard Process, is as follows in Table 19.

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Table 19

RECOVERY OF URANIUM FROM SYNTHETIC β -GUNK

PILOT PLANT RUN P-41

Uranium charged, g	506.0 $\pm$ 0.2
Uranium recovered, g	
in uranium (VI) peroxide	474.4 $\pm$ 0.5
in centrifuge drainings	3.72 $\pm$ 0.01
in effluent A	3.46 $\pm$ 0.04
B	1.91 $\pm$ 0.03
C	2.48 $\pm$ 0.01
D	2.49 $\pm$ 0.03
E	3.24 $\pm$ 0.04
F	0.91 $\pm$ 0.03
G	3.82 $\pm$ 0.04
H	2.98 $\pm$ 0.09
I	0.94 $\pm$ 0.05
J	5.29 $\pm$ 0.09
rinse solution	0.06 $\pm$ 0.002
residues	0.08 $\pm$ 0.002
Total uranium recovered, g	505.82 $\pm$ 0.53
%	99.96 $\pm$ 0.10
average per cycle, %	99.996 $\pm$ 0.01
Iron in peroxide cake, g	0.53

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97Section KAcknowledgements

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