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AN INVESTIGATION OF METHODS FOR THE RECOVERY OF URANIUM
FROM ~~RETAILERS~~ OBTAINED DURING THE MANUFACTURE OF PURE
URANIUM DIOXIDE

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AN INVESTIGATION OF METHODS FOR THE RECOVERY OF URANIUM
FROM RESIDUES OBTAINED DURING THE MANUFACTURE OF PURE
URANIUM DIOXIDE

I. INTRODUCTION

When Mallinckrodt first started to produce highly purified uranium dioxide for the Office of Scientific Research and Development, and later the Manhattan Project, the material to be processed was a refined grade of U_3O_8 containing only small amounts of impurities. Later, because of a deterioration in quality of the U_3O_8 and also because it became necessary to use large quantities of impure sodium uranate as starting material, the amount of uranium containing residues from the process increased sharply. By June of 1943, the weight of accumulated residues totalled about 180,000 pounds of which approximately 90,000 pounds was uranium.

Because of the amount of residues on hand, and also because it was thought that the quality of raw material might become worse, giving still greater quantities of residues, it seemed worthwhile to attempt to devise a process to recover the uranium from this material.

The investigations were done by several workers at intervals during a period of about two years.

II. DISCUSSION

In general, residues from the manufacture of uranium dioxide fall into one of two general classes.

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- (1) Material from which most of the uranium can be extracted by leaching with water or nitric acid to produce a uranyl nitrate liquor pure enough to be used in the batch-ether extraction step.
- (2) Material which must be treated more drastically to separate the uranium from other elements in the residues so that it can be treated with nitric acid to make uranyl nitrate liquor suitable to use in the batch-ether extraction step.

The latter class of residues is the one with which this paper is concerned. An outline of the source, and the process by which these residues are obtained, is given in Figure 1. About 65 to 75 per cent of the residues come from the iron-uranium-phosphate press cake, (tank 7 cake) the remainder from dissolving raw material (acid press cake). A typical analysis of the residues is given in Table 1.

TABLE 1.
TYPICAL ANALYSIS OF CLASS 2 RESIDUES

<u>Analyzed for:</u>	<u>Results in Per Cent</u>
U	55 - 65
MoO ₃	0.08
Na	2.5
V ₂ O ₅	2.0
Fe	1.0
PO ₄	7.0
SiO ₂	8.0

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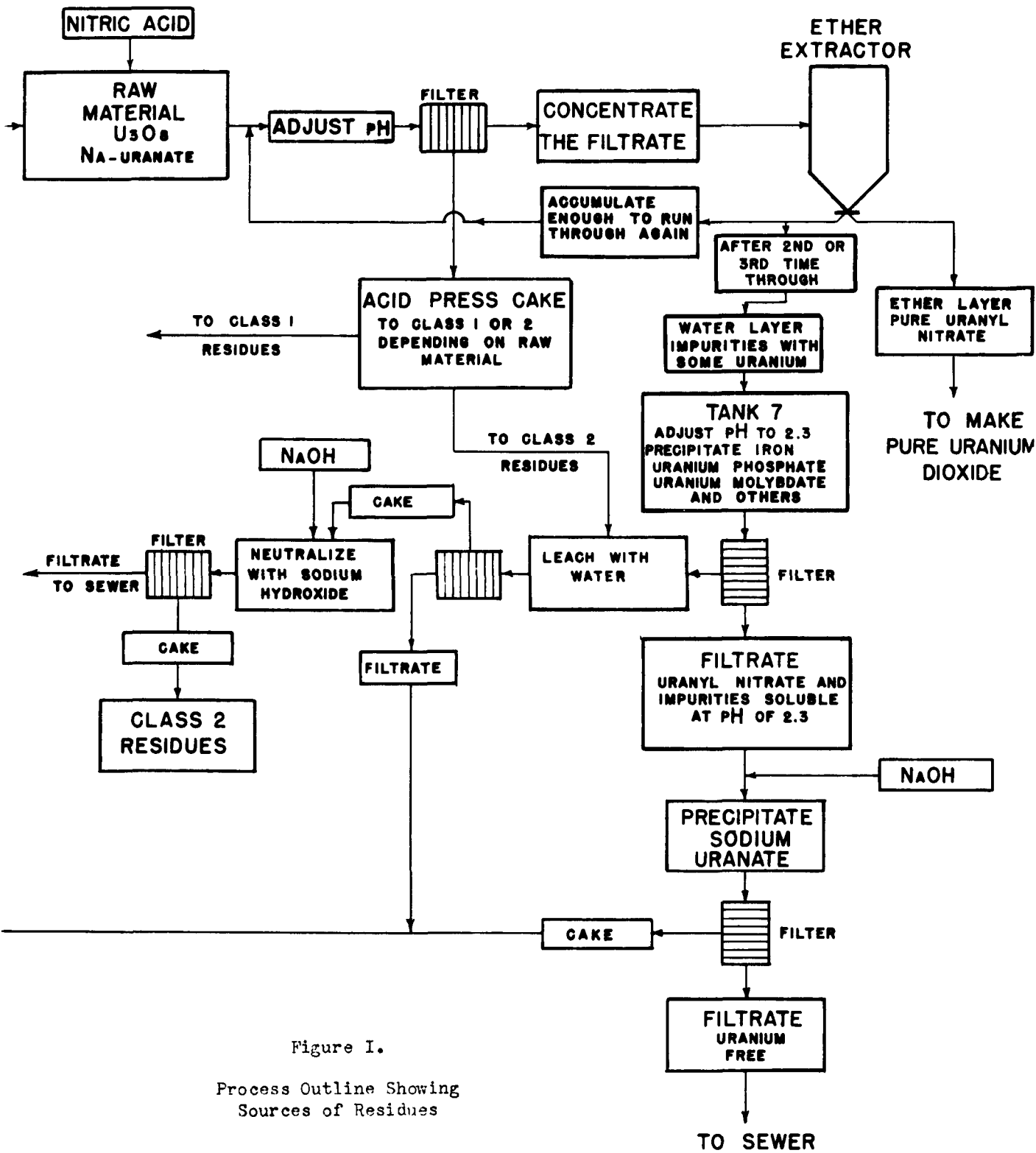


Figure I.
Process Outline Showing
Sources of Residues

Assuming one uranium per phosphate group as uranyl phosphate, about thirty-five per cent of the uranium in the residues is present as uranyl phosphate. It appeared then that the main problem was one of separating uranium from phosphate, and, if possible, from vanadium and molybdenum at the same time. Removal of silica, iron and sodium was not expected to be troublesome.

Several methods for recovering the uranium were tried, but were later dropped because they seemed to be chemically unworkable or economically unsound, or because another method was proposed for trial.

These methods were:

- (1) Dissolve residues in nitric acid, mix the liquor with sodium carbonate solution to form soluble sodium uranyl carbonate, add lead or barium salts to precipitate phosphate, molybdate, and vanadate, filter, and recover the uranium as sodium uranate by neutralizing the filtrate with nitric acid and boiling off carbon dioxide.
- (2) A variation of (1) involving the precipitation of uranium peroxide from the filtered liquor after treatment to remove phosphate.
- (3) Dissolve in nitric acid and add iron to precipitate phosphate.
- (4) Dissolve in nitric acid and precipitate uranium peroxide without preliminary treatment to remove phosphate.
- (5) Leach with sodium sulfide solution and filter to remove dissolved phosphate, followed by dissolving the leached cake in nitric acid to make liquor for extraction.

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- (6) Leach with strong sodium hydroxide solution to convert phosphate to sodium phosphate and uranium to sodium uranate, filter off the solution containing sodium phosphate, and dissolve the cake in nitric acid to make liquor for extractor.

The sodium hydroxide leach does not remove all of the phosphate, possibly because of the coating over of the uranyl phosphate particles with sodium uranate. About one-fourth of the original amount remains. Because of this, the acidity of the uranyl nitrate liquor made by dissolving the leached cake in nitric acid, must be greater than usual to keep the uranium in solution in the presence of phosphate ion. This acid liquor cannot be used efficiently in the batch-ether extractor.

However, because of the development of a continuous extractor using a salting agent, it is possible to use liquors of considerably greater acidity than can be used in the batch process. This new development makes the sodium hydroxide leach method for treatment of phosphate containing residues sufficiently interesting to warrant further investigation.

Of all the methods tried, the one which gave greatest indication of usefulness as a manufacturing process included as the main step a high temperature reduction with carbon or illuminating gas. The work done on this process is the basis for this report.

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In addition to work done with the regular plant residues, (principally tank 7 press cake) some experiments were done to test the adaptability of the reduction process to other uranium containing materials, such as:

- (1) Press cake obtained from the filtration of liquor made by dissolving the uranium bearing raw materials in nitric acid.
(Acid Press Cake)
- (2) Sodium uranate containing as much as 10% Na_2O made by neutralizing uranyl nitrate liquors so impure that they could not be used in the extractor (N.G. Sodium Salt).

Outline of Process

- (1) Remove nitrate from the residues by a water leach or by igniting to drive off oxides of nitrogen.
- (2) Mix nitrate free cake with
 - (a) Carbon - and ignite in absence of air.
 - (b) Carbon and Sodium Carbonate and ignite in absence of air.
 - (c) Sodium Carbonate - and ignite in atmosphere of illuminating gas.

This step changes the uranium to U_3O_8 and converts phosphate to soluble sodium phosphate (same reaction with molybdate and vanadate).

- (3) Leach the ignited cake with water to remove soluble salts, leaving mostly U_3O_8 , reduced iron, and silica.
- (4) Re-ignite the cake in the presence of air to burn off the carbon and oxidize the iron so that the iron will be less soluble in nitric acid.

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- (5) Dissolve the re-ignited cake in nitric acid to make uranyl nitrate solution for the ether extraction step. Filter the solution to remove insoluble matter.

It was found that the reaction which forms U_3O_8 by reduction with carbon is reversable. That is, U_3O_8 can be converted to sodium uranate by mixing it with sodium carbonate and heating the mixture in air. Thus it is necessary, as outlined above, to leach out soluble salts before re-igniting the cake.

If the leached cake is dissolved in nitric acid without re-ignition, two things happen:

- (1) A large amount of iron goes into solution.
- (2) The liquor is very hard to filter.

These conditions do not occur if the iron is oxidized prior to the nitric acid dissolving step.

In order to test the extractability of the uranyl nitrate liquor made from reduced residues, an extraction test was devised. It was found by testing plant liquors, that their behavior in the plant extractor could be fairly well predicted from the results of this test. The test is done as follows:

In a separatory funnel place 175 ml. of ethyl ether. Cool the funnel and contents in an ice bath to $3-4^{\circ}C$. Add 100 ml. of uranyl nitrate solution which has been concentrated to a boiling point of $118^{\circ}C$. and cooled to about $80^{\circ}C$. Mix thoroughly by vigorous shaking. Observe:

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- (a) Separation time of the two layers
- (b) Any tendency to form stable emulsions
- (c) Appearance of each layer (suspended matter, color, etc.)
- (d) Specific gravity of ether layer.

The general conclusion based on results from the experimental work done on the reduction process is that ninety-two to ninety-nine per cent of the uranium in residues can be recovered in uranyl nitrate liquor suitable for use in the batch-ether extractor.

III. EXPERIMENTAL DETAILS

Details and results of the experiments are given in Table 2. The quantities in this table are not the actual quantities used in most cases, but are calculated from the results of analyses and experimental measurements, and are based on amounts which would be present if no samples had been removed during the procedure. Therefore the table presents a material balance rather than actual experimental data.

All the experiments done on this problem are not reported. Instead several experiments considered typical are given to illustrate some of the variations in the methods, and in types of residues used.

Experiment 13J

The starting material for this experiment was residues which had been ignited for four hours at 800° C. to remove nitrates by driving off oxides of nitrogen. The ignited residues assayed 63% U.

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Experiment 22

In this experiment the residue, a mixture of 15% acid press cake and 85% tank 7 cake, taken as wet cake directly from the factory filter presses (See Figure 1), was leached with hot water, filtered and washed on the filter to remove nitrates. The leached cake was then dried and milled to pass a 30 mesh screen. This material, which was produced in the factory about three months later than the residues used in 13J and may have been from different raw material, assayed 67% U.

Experiments 33, 34 and 35

To obtain starting material for these experiments, wet press cake from tank 7 was slurried with water and neutralized with 20% sodium hydroxide solution to a pH of about 7. During the neutralization the slurry thickened considerably, indicating that more precipitate was forming, presumably, sodium uranate. The neutralized slurry was then filtered in a small filter press and washed with water until the effluent was practically free of nitrate when tested with indigo carmine. The washed cake was dried and milled to pass a 30 mesh screen, after which a sample was assayed and was found to contain 66% U.

Experiments 18, 18D1-4, and 21

These experiments were done using treated acid press cake as starting material. The cake was taken wet from a factory press, slurried with water and neutralized with 20% sodium hydroxide solution until the pH was 9.1, measured with a glass electrode meter. The slurry was filtered on a large suction funnel, re-

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slurried with 1% sodium hydroxide solution and filtered again. The cake was then dried, milled to pass a 60 mesh screen, and assayed. Found 50% U.

Experiment 17

The starting material used in this experiment (N. G. sodium salt) was made by neutralizing with sodium hydroxide, extractor water layer which had been through the extractor four times, resulting in a many-fold concentration of the impurities. This N. G. sodium salt was ignited at 800° C. for three hours to decompose nitrate and remove the oxides of nitrogen. The cool ignited cake was milled, and then assayed. Sixty-eight per cent uranium was present.

As an example of the actual experimental procedure, one experiment, No. 33, is given in detail.

Reduction

A mixture of 1200 grams of powdered residue and 120 grams of powdered carbon (Darco) was placed in a stainless steel tray. A stainless cover was put on the tray, after which it was inserted in an electrically heated muffle furnace at 800° C. After two hours heating the tray was removed from the muffle and allowed to cool. The reduced cake weighed 1122 grams; a loss of 15% during the reduction. Samples of the cake were tested qualitatively for chloride and sulfate--chloride absent, sulfate present.

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Leaching

One thousand grams of reduced cake was mixed with 4000 ml. of water which had been heated to 70° C. The slurry was stirred mechanically, while heating at 70° C. was continued for one hour. Then the slurry was filtered on a suction funnel, and the cake washed on the funnel with 400 ml. of water. The cake was re-slurried twice more with 2000 ml. of water at 70° C. and filtered. Each of the three filtrations was slower than the previous one. The filtrates were tested qualitatively for uranium but none was found. The cake which was glossy black, was dried and weighed. Its weight was 913 grams, a loss of 8.7%.

Re-ignition

The dried cake was easily crushed to form a powder. In order to oxidize the iron and burn off any carbon, 850 grams of this powder was placed in an open nickel tray and heated in a muffle at 800° C. for one hour during which time it was stirred occasionally with a stainless rod. After the powder was cool, it was weighed. The final weight was 820 grams; a loss of 30 grams or 3.5%.

Dissolving

Seven hundred grams of the re-ignited cake were dissolved at 90° C. in 600 grams of 38° Be. nitric acid which had been diluted with 160 ml. of water. A large amount of oxides of nitrogen was liberated during the reaction. All acid seemed to have been neutralized before the cake was completely dissolved, so an additional

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50 grams of 38° Be. nitric acid was added, and the mixture reheated to 90° C. Then the liquor was diluted until the Beaume measured 63°.

The pH of a sample of this solution which had been diluted with 99 volumes of water was 3.5. By adding 115 grams of 38° Be. nitric acid the pH was adjusted so that a diluted sample measured 2.7. The mixture was then ready for filtration, which was done on a suction funnel. The filtration was slow. The cake was re-slurried twice with water and filtered to remove soluble uranium salts, after which it was dried and weighed. The weight was 51.5 grams; 7.4% of the re-ignited cake.

Extraction

The filtrate was red colored indicating dissolved iron. This condition would result from a poor re-oxidation which could be accounted for by the presence of sulfur in the cake. The filtrate was evaporated to a boiling point of 118° C. and then allowed to cool to 90° C. One hundred ml. of this liquor was mixed with 175 ml. of cold (3° C.) ether in a separatory funnel and the mixture shaken vigorously. The layers separated in three minutes to give a clear ether layer and a cloudy red water layer. The specific gravity of the ether layer was 1.40. The liquor is extractable.

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TABLE 2.

DETAILS OF REDUCTION EXPERIMENTS

Conditions	Experiment Number								
	13J	22	33	34	35	18	18D1-4	21	17
1. Wt. Dry Cake (Nitrate Free) g	1000	1000	1000	1000	1000	1000	1000	1000	1000
2. Wt. Carbon Added g	100	100	100	100	None	100	100	100	100
3. Wt. Na ₂ CO ₃ Added g	None	None	None	100	100	None	None	150	None
4. Total Wt. Charge g	1100	1100	1100	1200	1100	1100	1100	1250	1100
5. Temp. of Heating °C.	800	800	800	800	800	800	800	800	800
6. Time of Heating Min.	60	60	120	120	120	60	60	60	60
7. Atmosphere	No air	No air	No air	No air	illum. gas.	No air	No air	No air	No air
8. Wt. Ignition Loss g	75	187	165	152	115	228	228	171	41
9. Per Cent (of 4) Loss	6.8	17	15	13	10.5	20.7	20.7	13.7	3.7
10. Wt. Ignited Cake g	1025	913	935	1048	985	872	872	1079	1059
11. Wt. Leach Water g	4500	4000	4100	4000	3900	3900	3900	5300	4500
12. Temp. of Leach °C.	70	80	70	75	70	65	65	70	70
13. Wt. Re-leach Water g	None	None	3700	2000	3300	None	None	None	None
14. Temp. of Re-leach °C.	XX	XX	70	30	50	XX	XX	XX	XX
15. Wt. Leach Loss g	182	22	81	173	207	31	31	197	160
16. Per Cent (of 10) Leach Loss	17.8	2.4	8.7	16.5	21	3.5	3.5	18.3	17.0
17. Wt. Leached Cake (Dry) g	843	891	854	875	778	841	841	882	879
18. Temp. of Re-ignition °C.	800	800	800	800	800	None	800	None	None
19. Time of Re-ignition Min.	60	60	60	60	60	XX	60	XX	XX
20. Atmosphere	Air	Air	Air	Air	Air	XX	Air	XX	XX
21. Wt. Loss Re-ignition g	30	6	30	38	Gain in Wt.	XX	34	XX	XX
22. Per Cent (of 17) Re-ignition Loss	3.6	0.7	3.5	4.4	1.5	XX	4.0	XX	XX
23. Wt. Re-ignited Cake g	813	885	824	837	790	XX	807	XX	XX
24. pH in HNO ₃ Soln. (1-100)	2.35	2.5	2.7	2.6	2.55	2.85	2.85	2.85	2.95

Conclusions and Discussion

The residues used in the first five experiments listed in Table 2 were approximately the same composition. There is no significant difference in the results although there is rough correlation between loss on leaching and recovery of uranium. The loss on leaching results, of course, from dissolving out soluble salts produced during the ignition by the action of sodium with impurities such as phosphate, and from dissolving out soluble salts present before the ignition was done, these salts either being present as a result of sodium hydroxide neutralization or as sodium carbonate added to the reaction mixture. Table 3 shows this correlation and indicates that the greater the excess of sodium carbonate (or hydroxide) the better the recovery of uranium.

Table 3.

CORRELATION OF EXCESS SODIUM WITH RECOVERY OF URANIUM

<u>Expt. No.</u>	<u>Uranium Recovery</u>	<u>Loss on Leaching</u>	<u>Na₂CO₃ added</u>	<u>Indication of Amount Excess Sodium</u>
22	95.8	2.4	None	Residues leached to remove nitrates. <u>Could also remove soluble sodium.</u>
33	96.0	8.7	None	Residues neutralized to pH of 7 with NaOH. Then leached to remove nitrates. <u>Soluble sodium removed.</u>
34	99.1	16.5	100 g.	Same as 33.
13J	99.2	17.8	None	Ignited instead of leached to remove nitrates from neutralized cake. <u>Sodium is not removed.</u>
35	99.6	21	100 g.	Same as 33.

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