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URANIUM METAL INVESTIGATIONS -

THE PREPARATION OF PURE URANIUM OXIDE

BY

R.E. Wilmshurst

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THE PREPARATION OF PURE URANIUM OXIDE

ABSTRACT

A process has been developed for purification of South Australian Uranium Oxide. The freshly precipitated crude oxide is leached in 5 percent ammonium carbonate solution, and the uranium recovered by boiling the filtered leach solution. Some impurities may be precipitated as phosphates before boiling. The product contains some boron but should be suitable for electrolytic production of reactor grade uranium metal.

1. SUMMARY

An ammonium carbonate leaching procedure was investigated for refining South Australian Crude Uranium Oxide. It was found that freshly precipitated crude oxide was readily leached in 5 percent ammonium carbonate solution, 95 percent extraction of uranium being achieved in a single stage and 98 to 99 percent in two stages. Drying of the crude oxide before leaching made extraction difficult.

The uranium was precipitated completely by boiling the leach solution to destroy the ammonium carbonate. The ammonia was recoverable but some loss of carbon dioxide was indicated by its presence in the precipitate.

The product was a mixture of uranyl carbonate and uranates of the alkali and alkaline earth metals. Introduction of a subsidiary purification step, using phosphate or oxalate as precipitant removed some calcium and magnesium from the solution, and gave a higher grade product which after ignition contained up to 95 percent U_3O_8. Varying the strength of ammonium carbonate solution from 2 to 10 percent did not improve the product purity.

The principal impurities in the ignited product were calcium, magnesium, sodium, and up to 100 parts per million of boron. It is believed that these elements would not interfere in an an electrolytic process for metal manufacture, and the purified oxide should be suitable for production of reactor grade metal.

2. INTRODUCTION

Investigations by Canning (1957 a,b) and by the author (1957) demonstrated that production of reactor grade uranium metal from South Australian crude oxide was not easily accomplished by simple processes. This led to a search for a suitable process for refining the crude oxide prior to its use in metal production.

The conventional large scale process for uranium metal production involves the preparation of a pure oxide by a solvent extraction technique. When considered in the light of its application to South Australian crude oxide, this process has a number of disadvantages. Capital cost for a small plant to treat the whole of this State's oxide may not be prohibitive, but reagent costs are very much higher than those overseas and the process may not be economic. It was felt that some effort to develop an alternative process was justified.

Canning (loc.cit) studied a partial chlorination process which produced a purified uranium dioxide. While this product was suitable for use as a feed for an electrolytic process, it was not ideal for any wet process since the dioxide is not soluble in acids except under strongly oxidising conditions. A refining process which could produce a tri-oxide would have some advantage in that this product would be more readily soluble.

The crude oxide itself is freely soluble in any mineral acid but purification by a selective acid leach is probably not practicable. A carefully controlled precipitation from acid solution is unlikely to give a high purity product since co-precipitation of other elements occurs. An alkaline carbonate leach is much more selective and should separate most of the iron which is the major impurity in the crude oxide. For this reason a carbonate leaching procedure was chosen for investigation.

It is well known that ammonium carbonate solution is a selective solvent for uranium tri-oxide and forms the basis of an analytical separation. Precipitation of the dissolved uranium can be brought about by neutralisation but not by addition of ammonium hydroxide. However, ammonium carbonate decomposes in boiling water, and it was expected that precipitation would occur on boiling. and that the volatilised ammonia and carbon dioxide would be readily recoverable.

3. RAW MATERIAL

3.1 Crude Uranium Oxide

A large batch of crude oxide produced from Radium Hill concentrates during Pilot Plant operations was used as raw material. Table 1 gives a complete analysis of this oxide, including the distribution of lanthanons.

TABLE 1

COMPLETE ANALYSIS OF CRUDE OXIDE

UO_3	70.96%	ThO_2	0.21%
CO_2	1.22	Sc_2O_3	0.21
H_2O	9.38	Y_2O_3	0.053
Fe_2O_3	5.32	CaO	3.96
Al_2O_3	0.03	MgO	3.69
TiO_2	0.75	Na_2O	1.90
Cr_2O_3	0.04	K_2O	0.08
V_2O_5	0.04	SiO_2	1.20
CuO	0.01	NiO	0.025
PbO	0.18	MnO	0.04
Cl	0.03	F	0.02
P_2O_5	0.04	SO_3	0.42
Li_2O	2.5 p.p.m.	BaO	3 p.p.m.
CoO	20	BiO	<10
CdO	<3	ZnO	<50
B_2O_3	60	As_2O_3	<1
Sb_2O_3	<50	MoO_3	<10

TABLE 1 (Cont^{d})

WO_3	$<$ 75 p.p.m	La_2O_3	1500 p.p.m
Ce_2O_3	500	Pr_2O_3	30
Nd_2O_3	70	Sm_2O_3	15
Eu_2O_3	0.7	Gd_2O_3	25
Tb_2O_3	17	Dy_2O_3	65
Ho_2O_3	55	Er_2O_3	150
Tm_2O_3	130	Yb_2O_3	150
Lu_2O_3	17		

Total reported	100.09%
Less O equivalent to Cl & F	0.01%
Total	100.08%

3.2 Freshly Precipitated Crude Oxide

For much of the experimental work a freshly precipitated oxide was required. This was prepared by dissolving the crude oxide in a mixture of sulphuric and hydrochloric acids, neutralising to pH2 with sodium hydroxide and precipitating at pH 6.5 with magnesia slurry. The suspension was filtered and the washed precipitate used without drying

4. ANCILLARY MATERIALS

4.1 Ammonium Carbonate

All ammonium carbonate was of analytical reagent quality. Three different batches were used at different times and the composition of each is given in Table 2.

TABLE 2

COMPOSITION OF AMMONIUM CARBONATE

Source	Form	% NH_3	%CO_2	p.p.m.Boron
British Drug Houses	Lump	32.1	47.5	21
" " "	Granular	31.4	48.6	n.d.
Hopkin & Williams	Lump	$\not<$ 31	n.d.	2

n.d. = not determined

4.2 Magnesia

B.D.H. Laboratory reagent light magnesium oxide was used. It was activated before use by soaking overnight in distilled water.

4.3 Other Reagents

All other materials were of analytical reagent quality.

5. EXPERIMENTAL PROCEDURE

5.1 Leaching of Crude Oxide

The oxide was stirred for some hours in an appropriate volume of ammonium carbonate solution. Initial tests were carried out at room temperature, but later a thermostatically controlled water bath was used to maintain the solution at a constant temperature. 10 ml samples of the suspension were taken as required and the washed solids dried and analysed for uranium by the method of Canning and Dixon (1955).

5.2 Purification of Solution

This step was not used in the initial experiments.

When phosphate was introduced to precipitate impurities a 10 percent aqueous solution of diammonium phosphate was added to the filtered leach solution until a definite excess was detectable by the stannous chloride-ammonium molybdate method. The solution was then allowed to stand for at least four hours before filtration.

When other anions were used as precipitants they were added as their ammonium salts in amount equivalent to the quantity of phosphate normally used.

5.3 Recovery of Uranium

The solution was boiled for a prolonged period to destroy the ammonium carbonate. A heavy precipitate formed soon after boiling commenced and "bumping" was troublesome when boiling on a hot plate. This was minimised by filtering off the precipitate at intervals. When no more ammonia was being evolved from the solution and the pH value of the condensed vapours had fallen to 7, boiling was discontinued. Each precipitate was washed, dried, and ignited at 800°C for not less than one hour.

5.4 Recovery of Ammonia

One test was carried out to determine the proportion of ammonia recoverable.

25 grams of ammonium carbonate was dissolved in 500 ml of water and a small sample of the solution taken for analysis. The bulk of the solution was stirred for one hour with 50 grams of crude oxide then filtered and the residue washed well.

The uranium solution and washings were placed in a flask which was part of a "Quickfit" assembly for steam distillation. The solution was boiled by steam injection and the distillate absorbed in water. At the end of the test the distillate was made up to a suitable volume and sampled for analysis.

5.5 Standard procedure for Preparation of Purified Oxide

The procedure as outlined in the preceding paragraphs was modified in the light of the results obtained. The final procedure which was adopted for preparation of purified oxide is described below.

200 grams of crude oxide were dissolved and reprecipitated as in 3.2 above. The wet filter cake was divided into two equal parts and each was leached for 5 hours at 40°C in 2 litres of 5 percent ammonium carbonate solution, using stainless steel equipment. The leach solutions were filtered and the residues combined and leached for 5 hours in a further litre of fresh carbonate solution. This second solution was filtered and combined with the previous 4 litres.

The combined solutions were purified by addition of phosphate as in paragraph 5.2.

4 litres of the purified solution were boiled in a large stainless steel beaker by "Vitreosil" immersion heaters. The remaining solution was added as required to maintain a constant volume. When all the purified solution was added, distilled water

was used as"make-up" until the vapours evolved were neutral to litmus. The precipitate was then filtered washed, dried and ignited at 800°C

6. RESULTS

6.1 Test No.2

210 grams of crude oxide was stirred for one hour in one litre of 5 percent carbonate solution. Analysis indicated that 34 percent of the uranium was extracted. The filtered solution was alternately boiled and filtered to recover the uranium. The first precipitate was a bright yellow colour, the others being progressively darker until the last one was orange. After ignition, the difference was more marked, the first precipitate being nearly black, the others being orange and unchanged. The weights of the ignited products and their uranium content are listed in Table 3.

TABLE 3

OXIDE PRODUCTS FROM TEST 2

No.	Weight g.	U_3O_8 %
1	39.2	94
2	5.2	92
3	2.8	91
4	4.0	73
5	1.2	-

The first precipitate was analysed for some other elements with the results shown in Table 4. The figures for iron and titanium are from a spectrographic analysis.

TABLE 4

PRODUCT FROM TEST 2

U_3O_8*	95.2%	Ca	1.20%
Fe	0.04%	Mg	0.24%
Ti	0.02%	Na	0.29%

* By cellulose column method.

The results of a spectrographic determination of scandium, yttrium and the lanthanons in this precipitate are shown in Table 5. All figures are expressed as parts per million with respect to uranium. The corresponding values for the crude oxide are also given together with the ratio

$$\frac{\text{concentration in crude oxide}}{\text{CONCENTRATION IN PRODUCT}}$$ for each element

TABLE 5

LANTHANONS IN REFINED OXIDE FROM TEST 2

Element	Refined Oxide p.p.m.	Crude Oxide p.p.m.	Ratio
Ce	0.7	720	1000
Eu	< 0.04	1	> 25
Gd	< 0.2	36	> 180
Ho	0.17	81	470
Lu	0.17	25	150
Tb	0.7	25	36
Yb	1.7	220	130
Dy	0.9	95	105
La	14	2200	150
Pr	0.5	44	90
Nd	0.2	100	500
Sm	< 0.2	22	> 110
Er	0.9	220	240
Sc	13	2300	170
Y	3.5	710	200
Total	36.4	5800	160

6.2 Test No.3

210 grams of crude oxide was leached for one hour in one litre of 5 percent carbonate solution at room temperature. To the filtered solution, phosphate was added in slight excess (7 ml) After standing overnight, the precipitate was filtered off, washed and examined qualitatively. Calcium and magnesium were detected.

The uranium was recovered as before. Analyses of the first precipitate are given in Table 6 with the corresponding figures from Test 2 for comparison.

TABLE 6

COMPARISON OF PRODUCTS, TESTS 2 and 3

	Test 2c	Test 3
U_3O_8	95.2%	94 6%
Ca	1.20	0.86
Mg	0.24	0.24
Na	0.29	0.20
Fe	0.04	30 p.p.m.
Ti	0.02	< 2 p.p.m.
Sc	13 p.p.m.	15 "
Y	3.5 "	3 "
Total Lanthanons	18 "	10 "

6.3 Test No.4

This test was an ammonia recovery distillation. Titration of the samples (paragraph 4.4) with acid indicated that 94% of the ammonia was recovered.

6.4 Test No.5

300 grams of crude oxide were stirred for one hour at room temperature in 2 litres of 5 percent carbonate solution. The leach liquor was filtered and divided into four equal portions.

Portion A.

Phosphate in slight excess (2.5 ml) was added to this solution. After standing overnight, the solution was filtered and the product recovered as before.

Portion B.

0.25 grams of ammonium oxalate dissolved in water was used in place of phosphate.

Portion C.

0.2 grams of ammonium fluoride, dissolved in water was added to this solution but no precipitate formed.

Portion D.

To this solution 1.5 m.l. of phosphate solution and 0.1 grams of oxalate were added.

The products were recovered from these solutions and a small amount of each was taken before ignition to give a composite sample. An analysis of this material is listed in Table 7 and the calculated composition in Table 8. Most of the water was probably present as water of hydration but no information is available on the degree of hydration of the uranate.

TABLE 7

ANALYSIS OF COMPOSITE PRODUCT TEST 5

UO_3	81.98%	CaO	2.24%
CO_2	4.51	MgO	0.03
H_2O	10.80	Na_2O	0.42

Total 99.98%

TABLE 8

CALCULATED COMPOSITION OF COMPOSITE PRODUCT

$CaO.2UO_3$	(CaU_2O_7)	25.12%
$MgO.2UO_3$	(MgU_2O_7)	0.46
$Na_2O.2UO_3$	($Na_2U_2O_7$)	4.29
UO_2CO_3		33.82
H_2O		9.20
	Total	99.98%

Analyses of each of the ignited products are given in Table 9. All values other than uranium are from spectrographic analyses.

TABLE 9

ANALYSES OF PRODUCTS, TEST 5

	5A	5B	5C	5D
U_3O_8	93.2%	93.9%	93.1%	94.7%
Fe	200 p.p.m	100 p.p.m.	400 p.p.m.	100 p.p.m
Ti	10	5	40	40
Mn	15	4	10	5
Cr	50	50	120	60
V	<10	<10	20	40
B	60	40	40	60
Cd	0.4	0.6	0.4	0.6
Mo	4	3	8	10
Ni	60	60	60	60

6.5 Test No.6

Part A

60 grams of crude oxide were leached for an hour at room temperature in one litre of 2 percent carbonate solution. The product was recovered after phosphate treatment.

Part B

300 grams of crude oxide were leached for an hour at room temperature in one litre of 10 percent carbonate solution. Phosphate treatment was carried out before recovery.

Analyses of these products, after ignition, are given in Table 10 with figures for product 5A. In each of these three tests the ratio of crude oxide to carbonate was the same.

TABLE 10

COMPARISON OF PRODUCTS, TESTS 5 and 6

	5A	6A	6B
U_3O_8	93.2%	89.7%	90.8%
Fe	200 p.p.m.	300 p.p.m.	150 p.p.m
Ti	10	5	5
Mn	15	5	15
Cr	50	50	50
V	< 10	< 10	< 10
B	60	10	40
Cd	0.4	0.2	0.4
Mo	4	2	4
Ni	60	20	40

6.6 Test No.7

Four controlled leaches of crude oxide were carried out under different conditions.

Part A

25 grams of crude oxide were stirred with 500 m.l. of 5 percent carbonate solution at 20° for 6 hours. Samples were taken at intervals to determine the percentage of uranium extracted.

Part B

This test was carried out at 50° but was otherwise the same as A.

Part C

In this case 1 gram of ammonium per sulphate was added at the start of leaching. The procedure was identical with B in other respects.

Part D

This test was identical with B except that 50 grams of oxide was used.

Table 11 gives the uranium extractions as percentages at various times during each test. These figures were calculated from residue assays, assuming that the soluble material contains 90% U_3O_8.

TABLE 11

URANIUM EXTRACTIONS, TEST 7

Time	7A	7B	7C	7D
15 min	20%	59%	58%	52%
30 "	27	66	68	52
45 "	-	70	73	52
1 hour	52	71	73	52
2 "	52	73	79	60
3 "	-	77	80	58
3½ "	50	-	-	-
5 "	-	80	83	61
6 "	57	-	-	-

The weight of uranium extracted in each case was:-

7A	10.0 grams U_3O_8
B	14.0 " "
C	14.5 " "
D	21.4 " "

6.7 Test No.8

70 grams of crude oxide were dissolved and reprecipitated as in 3.2 above. The wet filter cake was halved. One part was dried at 110° overnight, while the other was kept wet. After sampling each half was leached for 5 hours at 35° in 500 ml of 5 [illegible] percent carbonate solution. Table 12 shows the results obtained.

TABLE 12

URANIUM EXTRACTIONS, TEST 8

Time	8A(undried)	8B (dried)
15 min	68%	48%
30 "	82	46
45 "	87	52
1 hour	90	53
2 "	95	57
3 "	95	57
5 "	96	65

The residue from leach 8A was releached with fresh carbonate solution. After a further 5 hours at 35°C 99% of the uranium was extracted.

6.8 General

A number of batches of oxide was prepared by the standard procedure described in paragraph 5.5. The leaching efficiency was 98 percent and the recovery of the dissolved uranium was virtually complete. The liquor after prolonged boiling (usually about 12 hours) contained less than 0.1gU_3O_8 per litre. The phosphate precipitate from one of these preparations was examined spectrographically, and found to be magnesium phosphate containing small amounts of calcium, aluminium, manganese and iron.

A further modification was the addition of 20 grams of ammonium chloride to the solution before boiling. This gave a product higher in uranium with less calcium and magnesium.

A spectrographic analysis of a typical product is given in Table 13, all figures being expressed as parts per million with respect to uranium.

TABLE 13

SPECTROGRAPHIC ANALYSIS OF PURIFIED OXIDE

Fe	100 p.p.m.	Ti	15 p.p.m.
Cr	< 2	V	10
Mg	5000	Mn	5
Pb	50	Cd	0.5
B	100	Cu	30
Be	< 0.5	Ni	35
Co	5	Au	< 0.5
Bi	< 0.5	Mo	< 1
In	< 0.1	Ge	< 1
Ga	< 2	Si	100
Al	50	Sn	< 10
Sc	32	Y	21
La	11	Ce	9
Pr	< 0.5	Nd	0.5
Sm	< 0.17	Eu	< 0.18
Gd	< 0.18	Tb	0.44
Dy	1.5	Ho	0.42
Er	2.4	Yb	4.7
Ln	1.1		

7. DISCUSSION

The first test demonstrated the feasibility of the technique and gave some idea of the sequence of precipitation of the various elements from the boiling solution. The precipitate which formed at the start of the recovery step was probably pure, the alkali and alkaline earth metals being precipitated later as uranates or di-uranates which were stable after ignition. A product of higher purity could probably be obtained by fractional precipitation.

The major impurities in the first products were calcium and magnesium and it was thought that addition of a suitable precipitant for these elements would purify the solution. Phosphate was added to solutions of product and its effect was shown by the reduction of the calcium content. Examination of a subsequent phosphate precipitate indicated the presence of more magnesium than calcium but this was probably due to the different leaching technique employed in later tests.

The economic value of the process must depend largely on the ease of recovery of the ammonium carbonate, or since carbon dioxide is relatively cheap, on the ease of recovery of the ammonia. Test 4 indicated that the ammonia is readily recoverable.

Although ammonium phosphate removed some of the impurities from the carbonate solution, other precipitants were also studied. Test 5 showed that there was little advantage in using oxalate while fluoride was ineffective, consequently all later work was done with phosphate. The presence of calcium, magnesium and sodium in the product is not a serious disadvantage, since these elements are easily removed in any metal production process. The chief objection to their presence is that they consume chlorine when used in the chlorination process as studied by Canning.

The optimum strength of the leaching solution was not determined but the use of 2 and 10 percent ammonium carbonate solution showed no advantage over the usual 5 percent. This latter strength was used in all subsequent tests.

The extraction of the uranium from the crude oxide was investigated in Tests 7 and 8. Poor results were obtained even at 50°C and in the presence of an oxidant, although there was 40 percent excess ammonium carbonate over that required to complex all the uranium as $(NH_4)_4 UO_2 (CO_3)_3$. The increased amount of uranium dissolved in part D of this experiment suggested that concentrated liquors would be obtained from a counter-current system. Test 8 established that freshly precipitated, undried oxide was leached quite readily and all subsequent preparations were from undried raw material. This is not a serious limitation since a process of this nature could be used at the site of the crude oxide production.

The releaching of the residue from test 8A resulted in 99 percent total extraction and was a further indication of the advantages of counter-current operation. This test was conducted at 35°C to minimise loss of ammonia during leaching. It is also apparent that the leaching rate is low after the first two hours and reduction of the leaching time would not seriously affect the extraction. With a leaching operation such as this, in which the major portion of the solid dissolves, the residue may be quite rich in uranium even though the extraction is high. It is interesting to note that even 99 percent extraction of the uranium from the crude oxide leaves a residue which contains about 3 percent U_3O_8.

One impurity which might be troublesom is boron which has been as high as 100 p.p.m. in some cases. Boron has a very high neutron absorption cross-section and is a most undesirable contaminant. It was at first thought that most of the boron came from Pyrex glassware, and later preparations were carried out in stainless steel equipment. The product which was analysed to give the figures in Table 13 had not been in contact with glass, and the boron content was still high. Samples of the ammonium carbonate were then analysed and although an appreciable amount of boron was found in one sample (paragraph 4.1) it was not sufficient to account for the 100 p.p.m. in the product. Apparently all the boron from both the crude oxide and the carbonate appears in the product. The results reported by Canning suggest that this impurity is removed in the electrolytic chloride process.

The addition of phosphate to the solution did not remove as many impurities as was expected and this step may not be worthwhile.

If the boron present is considered to be removable in metal production, reactor grade metal would result from reduction of the oxide product from this process. If an oxide of higher purity were required, further development of the process would be desirable.

At the time this work was commenced, no information was available relating to any similar process. Recently, however, a report has been published (Hollis, 1957) describing a similar process under development in the U.S.A. This report is not yet available in Australia.

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