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PROCESS DEVELOPMENT QUARTERLY REPORT, PART I

by

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GENERAL INTRODUCTION

During the second quarter of 1953 laboratory work was divided among raw material processing, plant assistance, and metal quality projects. Evaluation studies of the metal produced in pilot plant experiments were included. A comparative study of the defects found in ingots and in slugs was started. Significant progress has been made in the development of processes for the recovery of uranium from plant waste streams.

Battelle Institute continued to collaborate with us and was able to contribute materially to our program.

Pilot plant work for this quarter is reported in Process Development Quarterly Report, Part II, NYO 1356.

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CONCLUSIONS

1. The Waxco process is adaptable to fixed bed column operation with clear liquors, and to suspended bed countercurrent batch operation with slurries. With TBP-wax the stripping step is slower than extraction, but this might be rectified using warmer strip solutions. Equilibrium studies of the stripping operation are in progress.
2. Emulsions difficulties with Rand ion exchange precipitates may be at least partially alleviated by calcination at 450°C. Further study of these materials is in progress.
3. The rate of hydrofluorination of UO_2 to UF_4 is affected by the rate of heating during the denitration of uranyl nitrate to UO_2 . There is preliminary evidence that the thermal history is important at a much earlier stage in the denitration process than was previously thought.
4. Carbonate leaching of U from slag falls short of removal to 0.05% U_2O_5 or less. Acid leach processes are successful, but exact details for most economical operation are not yet determined. Prior recovery of HF can be accomplished, but the reactivity of MgF_2 slag with H_2SO_4 is lower than that of fluorspar.
5. More favorable mold geometry results in greatly improved ingot soundness, as shown by porosity and inclusion studies of larger diameter ingots cast in the pilot plant. Defect studies of slugs indicate that slag inclusions are not the cause of striations, since slag does not conform to the rolling. Oxide inclusions and/or impurities segregated at shrinkage cavities in ingots are more suspect as being responsible for striations found in slugs. "Good crop" metal has been found to contain numerous inclusions, including MgO (probably from crucible dressing).

Battelle has obtained direct X-ray evidence that "carbide" inclusions are indeed UC. They have also started application of microradiography techniques to the study of derby, ingot, and slug metal.

6. X-ray equipment has been installed at St. Louis and has already proven useful in identification of inclusions in crop metal. Vacuum fusion equipment for determination of oxygen in metal has been built and put into operation.
7. A modification of the method of determination of nitrogen in metal has been studied. U_2N_3 and UN are not decomposed by HCl used in the present method. Perchloric acid decomposition results in much higher values in derby metal, while ingot metal values in the normal range are unchanged.

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8. Spectrographic method developments for improved sensitivity of the boron determination, and for improved sample preparation have been studied.

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THE WAXCO PROCESS

by

D. E. Rhodes

Introduction

The primary emphasis of this project has been to obtain a workable process for the recovery of uranium from the raffinate of the ether extraction system at the St. Louis Refinery. At present two processes indicate considerable promise. One process involves filtering the raffinate and passing it over wax flakes packed in a column. The other process is a batchwise process using wax flakes directly with the raffinate slurry. A coarse screen, capable of letting the solids through, can be used to separate the wax from the raffinate.

At present both processes are being investigated by the laboratory and the pilot plant.

Tributyl phosphate is the only complexing agent investigated since it appears to be quite satisfactory for the present purpose. It is hoped that other complexing agents can be investigated for use with wax in the near future.

Conclusions

Tributyl phosphate as high as 50% by weight can be used with certain waxes.

High melting point microcrystalline waxes (75-95°C) appear to be satisfactory for use with tributyl phosphate at room temperature.

Capacities as high as 56mg U/g wax have been obtained using batchwise extraction, with indications that even high capacities may be realized.

Equilibrium data indicate advantages for countercurrent stripping of uranium from the wax.

Procedures

I. Preparation of TBP-wax

The wax mixtures were prepared by melting the wax, adding the TBP, mixing, and pouring into rapidly agitated cold water. This results in flakes of wax which were air-dried prior to use.

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II. Column Operation

The use of wax flakes in glass columns has been described in NYO 1354.

III. Batchwise Operation

Wax flakes were contacted with raffinate slurry in a twelve liter bucket. A Lightnin mixer with a three-bladed agitator near the bottom of the bucket was used to bring fresh solution into contact with the floating wax bed. There was no direct contact between the wax particles and the agitator. Earlier work (NYO 1354) indicated direct contact of the wax with an agitator would tend to break the wax into particles too small for separation from raffinate.

IV. Wax-TBP Equilibrium Studies

Each run involved 200ml of uranyl nitrate solution of various concentrations, and 20g of wax. The solution and wax were stirred twenty-four hours in a 500ml Erlenmeyer using a glass agitator. In the present work equilibrium was approached only from one direction, no uranyl nitrate in the wax initially. Eventual study will be from both directions to ascertain that equilibrium is being reached in the specified time.

V. Analytical

Uranium analyses were made using an extraction procedure using ten percent tributyl phosphate in ether and a $\text{LiNO}_3\text{-HNO}_3$ acid solution wash followed by carbonate re-extraction and a carbonate - peroxide reading on a Beckmann Model B spectrophotometer.

Experimental Data and Discussion

I. Column Study

The column using 30% TBP in wax as described in NYO 1354 was used to make a single run with a pitchblende raffinate from the Plant. The results are given in Table I.

Table I

The Column Extraction of Uranium from Pitchblende
Raffinate Using Tributyl Phosphate in Wax

Conditions:

Flow rate = 0.15ml/g wax/min.
Grams of wax used = 100 (dry basis)
Composition of wax (by weight)

30% Tributyl Phosphate
35% Shell MX-170 Wax
35% Glyco Acrawax C

Inside diameter of column = 22mm
Volume in column occupied by wax = 235cm³
Original U in raffinate: Series I - 1.5g U/l
Series II - 1.1g U/l

No regeneration of wax between Series I and II

<u>Total Volume Through Column ml</u>	<u>Series I U g/l In Effluent</u>	<u>Total Volume Through Column ml</u>	<u>Series II U g/l in Effluent</u>
700	0.06	2800	0.23
1200	0.11	3300	0.59
1400	0.18	3700	0.74
1700	0.41	4200	0.84
2300	0.68	4500	0.86

There was a twenty-four hour lag between Series I and Series II raffinate flow which appeared to increase the uranium capacity of the wax slightly. The capacities for this run are as follows:

Capacity to 12% leakage = 20mg U/g wax
Capacity to 78% leakage = 43mg U/g wax

No further work using a column has been done in the laboratory, however, pilot plant work has been started along this line.

II. Batchwise Process

Since it would be desirable to be able to handle raffinate without filtration, it was decided to work on a process which could be used with slurries. A batchwise contact was tried previously (NYO 1352 and NYO 1354) without too much success. However, with agitation such that the agitator does not come in direct contact with the wax, satisfactory operation has been obtained. Also a modification in the wax composition produced a product which tends to ball slightly rather than break down.

In the first batchwise experiment raffinate slurry was contacted with 30% TBP in wax. Results are given in Table II.

Table II

Extraction of Uranium from Raffinate Slurry Using 30% TBP in Wax

Conditions:

550g wax used (dry basis)

Wax composition (weight basis)

30% Tributyl phosphate

27% Glyco Acrawax C

43% Glyco S-1167 wax

Nine liters raffinate each run

No regeneration between runs

Room temperature

Time of Stirring minutes	Run I U g/l	Run II U g/l
0	1.75	2.20
15	0.31	0.86
30	0.24	0.62
45	0.22	0.77
60	0.16	0.56
90	0.03	0.50

The capacity of the wax for these two runs was 28mg U/g wax at the end of the first run, and 56mg U/g wax at the end of the second run. These results were somewhat encouraging, but the wax was apparently too brittle and had a tendency to break down. Also a greater ratio of wax to volume of raffinate appeared to be needed to extract the uranium more quickly and completely.

Another composition of wax was then tried with better results, as are indicated in Table III.

Table III

Conditions:

2200g wax used (dry basis)

Wax composition (by weight)

50% Tributyl phosphate

50% Shell MX-170 wax

Nine liters raffinate each run

No regeneration of wax between runs

<u>Time of</u> <u>Stirring</u>	<u>Run I</u> <u>U g/l</u>	<u>Run II</u> <u>U g/l</u>	<u>Run III</u> <u>U g/l</u>	<u>Run IV</u> <u>U g/l</u>
0	2.2	1.2	5.0	5.3
15	0.10	0.17	0.14	1.3
30	0.09	0.04	0.05	0.38
60	0.009*			0.23
90	0.006*			0.15

* Fluorimetric analysis

During Run IV the wax was held in place using a stainless steel basket, 8 mesh, and largely explains the slower rate of uranium recovery during this run.

This particular wax composition behaved very well, actually rolling into distinct balls approximately 1mm in diameter. No small particles of wax were noted.

The capacity of the wax to the end of Run IV was 52mg U/g wax. How much higher the limiting practical capacity is will have to be determined by future experiments.

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In this process using the above ratio of wax to raffinate, the uranium from at least four batches of raffinate could be recovered before regeneration of the wax would be necessary. If more than one stage of contact is used, the number of batches treated prior to regeneration would undoubtedly be greatly increased.

The wax used in the last experiment was washed with 1500ml of 2M $Mg(NO_3)_2$ to remove most of the raffinate left on the wax particles. The uranium was then stripped from the wax using distilled water. The results are given in Table IV.

Table IV

Cocurrent Stripping of Uranium from Wax-TBP

Strip solution I - 5.5 liters of distilled water

Strip solution II - 9.0 liters of distilled water

Total uranium on wax - 115.3g

<u>Length of Stirring min.</u>	<u>Strip I U g/l</u>	<u>Strip II U g/l</u>
0	0.0	0.0
15	5.6	-
30	6.6	4.1
60	7.3	4.6
120	8.7	5.5
180	8.8	-
24 hours	10.0	6.2

Uranium recovered after two cocurrent stripping stages = $\frac{111}{115} \times 100 = 97\%$

By using countercurrent stripping with several stages a higher concentration of uranium could be obtained. Pilot plant work is being planned to investigate this, and more fully evaluate the whole process.

III. Equilibrium Data

Some data on the equilibrium between TBP-wax and uranyl nitrate solution has been obtained. Results are given in Table V.

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Table V

~~CONFIDENTIAL~~Equilibrium Data for TBP-Wax and Uranyl Nitrate Solution

Conditions:

UO₂(NO₃)₂·6H₂O used to make up solution

200 ml of solution

20g wax containing no uranium

Temperature 30-35°C

Stirred 24 hours

Wax composition (by weight)

50% TBP

50% Shell MX-170 wax

Run	Conc. U in Wax mg U/g Wax	Conc. U In Solution mg U/g sol	$K_d = \frac{\text{mg U/g wax}}{\text{mg U/g sol}}$
1	62	45	1.38
2	11	19	0.58
3	6.9	9.6	0.72
4	3.4	4.9	0.69
5	0.7	0.96	0.73
6	77	42.0	1.83
7	47	37	1.27
8	41	33	1.24
9	30	28	1.07
10	19	23	0.83

The results of Table V are given graphically in Figure 1, as well as the operating curve for determining countercurrent stages of stripping at a ratio of 1000g solution to 250g wax.

It may be seen that if the wax initially contains 100mg U/g wax, three countercurrent stages of stripping will theoretically remove almost all the uranium with stripping solution containing 25g U/l. Other waxes are to be tested to determine their influence on the distribution uranium between aqueous solutions and wax.

This equilibrium study is to be continued not only for TBP in waxes under different conditions, but also for evaluating new complexing agents and different waxes as they become available.

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Equilibrium Data For 50% TBP In Wax And Uranyl Nitrate Solution

I-Equilibrium Curve
II-Operating Line For 250 g Wax / 1000 g Solution
(Countercurrent Multiple-Contact Extraction)

FIGURE I

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STUDIES OF NEW RAW MATERIALS

by

G. W. Lewis, Jr.

Introduction and Summary

Previous work on this problem has been reported on pages 22 and 23 of NYO 1354. The present report is concerned with further laboratory studies on the Rand Precipitate, samples 21-1, 21-2 and 21-3.

Three techniques for the treatment of undesirable silicious material present in digest liquors of calcined Rand material have been tried. Filtration did not avoid emulsion formation during extraction. Boiling the digest liquors for one hour prevented emulsion formation for properly calcined material but was not very effective for poorly calcined material. The addition of HF avoided emulsions but inhibited the extraction leading to high uranium content raffinates.

Filtration of Digested Rand Precipitate

Since previous work indicated the presence of considerable silica gel in the digest liquors of Rand Precipitate, some experiments were conducted to study whether emulsification during extraction could be avoided if the silica were removed by filtration. A vinyon cloth filter leaf was the first filtering technique attempted.

Samples of 21-2, calcined in a pot furnace at 450°C for six hours, were subjected to a cold digestion with 45% HNO₃ and filtered through the vinyon leaf. The filtration was quite rapid but not complete, for the filtrates were turbid. These filtrates were adjusted to be 0.88 molar with respect to Ca(NO₃)₂ and Mg(NO₃)₂, 0.44 molar to Al(NO₃)₃, and 70g HNO₃ per liter. One volume of the adjusted filtrates were shaken with two volumes of neutral diethyl ether; a heavy emulsion resulted in each extraction. A sample of 21-3 was also tried and heavy emulsification also occurred.

The next filtration techniques attempted were one-fourth inch and one inch cakes of John's Manville "HYFLOW" on a Buchner plate. Samples of 21-2 were calcined and digested as previously described. Filtration was quite slow but good clear filtrates were obtained. These filtrates were treated with Ca(NO₃)₂, Mg(NO₃)₂, Al(NO₃)₃, and excess HNO₃, and extracted as before. Emulsions were formed during these shakeouts but they did not appear to be as heavy as those obtained with the vinyon leaf filtrates.

Coagulation of Silica through Boiling

A 50 gram sample of 21-2 was calcined at 450°C for six hours and allowed to cool overnight in the pot furnace. Twenty-three ml of 71% HNO₃ and 70ml of water were added to the calcined material in a 250ml beaker. The beaker was set upon a hot plate and stirred with a stainless steel stirrer while the digest liquor was heated to boiling and maintained at boiling for one hour. The sample was removed from the hot plate; 25.0 grams of Ca(NO₃)₂·4H₂O, 27.3 grams of Mg(NO₃)₂·6H₂O and 20.0 grams Al(NO₃)₃·9H₂O were added and the volume adjusted to 90ml. Then the system was adjusted to 70g HNO₃ per liter excess. Fifty ml of the adjusted liquor was shaken successively with four 100ml volumes of neutral diethyl ether. The ether layers were added to 50ml of distilled water and evaporated. The samples were submitted to the analytical laboratory for analysis. The data are given in Table I.

Table I

Extraction of Western Reef's Rand Material

<u>Stage</u>	<u>Volume of Aqueous Layer</u>	<u>Uranium g/l</u>	<u>Remarks</u>
Feed	50	241	in feed
1st	63	118	in ether layer*
2nd	68	52	" " " *
3rd	69	17.6	" " " *
4th	68	.71	" " " *
--	--	.52	raffinate

* Analytical result for 50ml aqueous solution containing uranium originally present in 100ml ether.

These data indicate some emulsification occurred but extractions yielded a low uranium content raffinate.

Attempts were made to repeat this experiment using the pelleted Western Reefs material (21-3). Heavy emulsions resulted during the first shakeout. These results indicated that the conditions of calcining apparently have a marked influence upon the behavior of Rand Raw Material. The six hour calcining at 450°C apparently was sufficient for the powdered Western Reefs (21-2) material but not sufficient for the pelleted Western Reefs material.

Use of HF as Emulsion Inhibitor

Previous experience in this laboratory has indicated that digest slurries containing silicious sols may be occasionally treated with small amounts of HF to avoid emulsion formation during the

ether extraction. Two experiments involving the treatment of digest liquors of pelleted Western Reefs (21-3) with HF were performed. In both experiments the conditions for calcining, digestion and extraction were like those described above. In Table II are the extraction data from a slurry to which was added 1.0ml of 48% HF before the addition of salting agents. In Table III are the extraction data from a slurry to which was added 1.0ml of 48% HF with the salting agents already present; the addition of HF caused the instantaneous formation of a precipitate. Both extractions took place without emulsion formation.

Table II

HF Added Before Salting Agents

<u>Stage</u>	<u>Uranium g/l</u>	<u>Remarks</u>
Feed	211	in feed
1st	129	in ether layer*
2nd	62	" " " *
3rd	22	" " " *
4th	4.4	" " " *
--	2.1	raffinate

* Analytical result for 50ml aqueous solution containing the uranium originally present in 100ml ether layer.

Table III

HF Added After Salting Agents

<u>Stage</u>	<u>Uranium g/l</u>	<u>Remarks</u>
Feed	188	in feed
1st	104	in ether layer*
2nd	32.8	" " " *
3rd	14	" " " *
4th	7	" " " *
	21.6	raffinate

* Analytical result for 50ml aqueous solution containing the uranium originally present in 100ml ether layer.

The addition of HF appears to condition the silicious sols to avoid emulsions during extraction. However, the concentrations of HF used here appear to seriously inhibit the extraction judging from the raffinate assays. It is possible that a lower amount of HF might avoid emulsification and still permit good extraction. This latter possibility will be investigated on more typical Rand Raw Material when such material becomes available.

Conclusions

Tentatively the results of the experiments described indicate that filtration does not avoid emulsification during the extraction step.

Coagulation of the silicious sols in certain digest slurries may be accomplished through boiling. The extraction of this coagulated material appears to be normal and raffinate uranium assays are low. However, coagulation through boiling does not appear to be very effective with improperly calcined material.

The use of HF avoided emulsions but appeared to inhibit the extraction of uranium.

HIGH AMMONIUM OXALATE INSOLUBLE IN UF_4

by

R. M. Paine

J. A. Rode

Introduction

The problem of high A.O.I. in MCW UF_4 continues to be studied. Current investigations are being directed toward the UO_3 from which UF_4 is made. The reactivity studies of UO_3 , reported in NYO 1354, pp27ff, are being continued and additional results are reported here. Some surface area measurements and tap densities are also reported. Preliminary X-ray diffraction data on UO_3 are discussed briefly.

Conclusions

The results of this series of investigations are inconclusive, but the work is being continued. Definite conclusions will be presented in a later report.

Recent Reactivity Studies of UO_3

The results reported here were obtained from samples reduced and hydrofluorinated with the apparatus described in NYO 1354, pp27ff, and using an identical procedure. The existing equipment, however, is now being modified in an attempt to provide more consistent results from run to run. The modifications now in progress include the addition of an HF flowmeter and changes in the inlet and outlet gas connections to the furnace in order to provide a more even flow of gas over the twelve samples.

Data obtained from some of the recent runs are shown in Table I. Previous results had indicated that heating the UO_3 caused the A.O.I. to increase, and this effect was substantiated by Runs A15 through A18. The temperature to which the UO_3 was heated appeared to be more important than the length of time of heating. Runs A17 and A18 were made with samples withdrawn from two different pots at various times after the batch was done.* All samples in each run were taken from the same batch. Although the effect of the additional heating time after done was to increase the A.O.I. of the green salt produced, differences greater than those produced by additional heating were noticed, in these and in subsequent runs, between various batches of UO_3 ,

* In this report the term done refers to that point at which the powder becomes dry. At this point burners are shut off. Cooling is a slow process, however, and the oxide is still fairly hot two hours later at which time the pot is unloaded.

Table I

**Results of the Reduction and Hydrofluorination of Various
Samples of UO_3**

<u>Run</u>	<u>g HF Used</u>	<u>Sample¹</u>	<u>% A.O.I. in UF_4</u>
A15	-	Batch 222, Pot 10, as is	0.12
		Batch 222, Pot 10, heated 250°C, 1 hr.	0.20
		Batch 222, Pot 10, heated 350°C, 1 hr.	0.14
		Batch 222, Pot 10, heated 450°C, 1 hr.	0.14
		Batch 222, Pot 10, heated 600°C, 1 hr.	0.46
		Batch 222, Pot 10, heated 750°C, 1 hr.	0.82
A16	258	Batch 222, Pot 10, as is	0.18
		Batch 222, Pot 10, heated 250°C, 1 hr.	0.34
		Batch 222, Pot 10, heated 250°C, 2 hr.	0.41
		Batch 222, Pot 10, heated 350°C, 1 hr.	0.44
		Batch 222, Pot 10, heated 350°C, 2 hr.	0.37
		Batch 222, Pot 10, heated 350°C, 3 hr.	0.22
A17	401	Standard UO_3 ²	0.16
		Sample immediately after done	0.45
		Sample 7 min. after done	0.70
		Sample 12 min. after done	0.73
		Sample 22 min. after done	0.91
		Sample 60 min. after done	1.00
A18	460	Sample immediately after done	0.02
		Sample 10 min. after done	0.12
		Sample 20 min. after done	0.07
		Sample 40 min. after done	0.41
		Sample 90 min. after done	0.15
		Sample 120 min. after done	0.33

Continued

Table I (cont'd.)

Run	g HF Used	Sample	% A.O.I. in UF ₄
A25	397	Standard UO ₃	0.19
		Continuous U ₃ O ₈ ³ , on 60 mesh fraction	4.93
		Continuous U ₃ O ₈ , on 200 mesh fraction	3.15
		Continuous U ₃ O ₈ , on 325 mesh fraction	2.40
		Continuous U ₃ O ₈ , through 325 mesh fraction	1.02

¹ All samples, except where stated otherwise, were first screened through a 30 mesh sieve to remove the very large particles.

² One lot of UO₃ was arbitrarily chosen as a standard. This lot was from normal plant production in August, 1952, when A.O.I. analyses were averaging about 1%.

³ This was recently produced in the Pilot Plant Continuous Denitration Furnace.

all sampled at approximately the same time after done. Fluctuations in the A.O.I. of the resulting UF₄ were noticed in samples taken from various pots immediately after done.

Comparison of the A.O.I.'s between Runs A17 and A18 indicated in general that the two oxides differed considerably at the time the first sample was withdrawn, i.e., immediately after done.

The original sample used in Runs A15 and A16 was taken from a slow* pot 10 minutes after done. This sample gave a fairly low A.O.I. except when heated to a very high temperature before the reactivity test. A sample taken from a very fast pot 5 minutes after done and treated as in Run A15 gave A.O.I.'s ranging from 1.0% to 4.2% (Run A13, NYO 1354; p 32) depending upon the temperature to which it was heated.

The results of Run A25 indicated that U₃O₈ produced in early experiments by the continuous process is not very reactive even when ground to a very fine powder. The decomposition cycle in the production of continuous U₃O₈ and UO₃ may not have been favorable to the production of a reactive product.

* Pots which have relatively short heating cycles are generally referred to as fast pots, while those with long heating cycles are referred to as slow pots.

Additional samples taken from plant pots indicated that the UO_3 which produced the UF_4 with high A.O.I. generally came from fast pots, while only occasionally did a slow pot produce UO_3 which gave high A.O.I. UF_4 . However, the fast pots also produced good UO_3 much of the time. The samples used in these runs were obtained from regular plant production batches. Some difficulty was encountered in making accurate correlations between the heating cycle of a particular batch and the A.O.I. of the resulting UF_4 for several reasons. The pot cycles varied over a wide range and it was sometimes difficult to say that a pot was either fast or slow.

In many instances when a pot was running slow, one or more extra burners were turned on for the remainder of the cycle. This caused overheating of the final UO_3 and could possibly have offset any advantages of a slow cycle. To complicate matters still further, it is difficult for the pot room operators to keep records of the accuracy required for a controlled experiment.

In view of these circumstances the decision was made to run closely controlled experiments in the plant. For this purpose permission was obtained to use two plant pots for research purposes during the day shift. An experienced operator was also provided to give full time attention to these two pots.

Although the processing of these plant samples is as yet incomplete, several rather interesting observations have been made. Preliminary tests indicated that the orange oxide cake formed on the pot walls (mill cake) produced high A.O.I. UF_4 . Since the oxide appeared to cake extensively on cool pot surfaces, i.e., those surfaces which did not get the direct heat of the gas flame, uniform heating on the pot surfaces from light dough stage* to done might improve the product noticeably. The elimination of caking problems would simplify unloading of the pots. Experiments indicated that uniform, low-temperature heating of the pot from dough to done does indeed reduce the magnitude of the caking problem, though the plough clearance is undoubtedly a major factor influencing the caking tendency. Further work along these lines is in progress.

Several runs were made in which the oxide powder was heated for 30 minutes after done. No serious change in the appearance of the product resulted. Some black oxide apparently did form on the outer surface of the UO_3 cake, but no change in the luster of the powder was observed**.

* Light dough stage is that stage at which bubbling liquid can no longer be observed in the pot.

** The presence of U_2O_5 in the UO_3 generally reduces the luster of the powder; sometimes to such an extent that the product is hardly recognizable as orange oxide.

X-ray Diffraction Studies of UO_2

Preliminary studies of UO_2 and its hydrates using the Norelco Diffractometer agreed quite well with the work done at Battelle¹ where the usual film technique had been used. However, there has as yet been no comparison of actual patterns between MCW and Battelle. In the future it is hoped that the various phases will be fully characterized, and definite patterns established for each phase. At the moment, concern is centered about differences in phases, and how these differences might affect reactivity.

A recent sample of good MCW UO_2 (Batch 330), Hanford Lot HL061, and a sample of continuously produced UO_2 all gave the same X-ray pattern, although the Hanford and the continuous UO_2 also gave a weak hydrate pattern (arbitrarily called Hydrate I).

The Hanford UO_2 and the continuous UO_2 were hydrated by slurrying hot for one hour and drying at 110°C overnight. The hydrated Hanford oxide gave a very clear pattern, indicative of good crystal growth. This pattern was designated as Hydrate I and is presumed to correspond to Battelle's type "A" hydrate. The continuous UO_2 gave the Hydrate I pattern plus an additional hydrate pattern (designated Hydrate II); the two hydrates were estimated to be in a 1:1 ratio. The continuous UO_2 hydrate also contained a small amount of the original anhydrous phase, indicating that hydration of continuous UO_2 was more difficult than hydration of Hanford UO_2 .

The Hanford UO_2 hydrate and the continuous UO_2 hydrates were then heated at 350°C for an extended period (more than 20 hours), both giving a very dark orange product. The X-ray patterns obtained with both of these materials consisted of only a few short, broad lines. The major portion of both samples was either composed of extremely small crystals or of amorphous material. That fraction of Hanford oxide which did give an identifiable pattern was the original anhydrous UO_2 phase, while the crystalline fraction which was converted from the hydrated continuous UO_2 was mainly an entirely new phase containing only a very small amount of the original anhydrous phase.

Data was presented in NYO 1354 (p33) which indicated that hydration (or hydration with subsequent heating) of Hanford oxide greatly improved the reactivity, while similar treatment of the continuously produced oxide did not affect the reactivity.

Surface Area of UO_2 vs Reactivity

Some surface area measurements of UO_2 were made by J. W. Stevenson using a methane adsorption

¹ Private communication from Dr. C. M. Schwartz.

procedure at liquid nitrogen temperatures. Surface areas from 0.7 to 1.8 square meters/gram were obtained, but they indicated no correlation with A.O.L. of the resultant UF_4 . The A.O.L.'s decreased with increasing surface area in some instances, but the reverse was also noticed.

The hydrated UO_3 and the hydrated UO_3 which had been reconverted to anhydrous oxide by heating had only average surface areas.

Some Tap Densities of UO_3 and UO_3 Hydrate

The improved reactivity of UO_3 resulting from hydration stimulated interest in the effect of hydration on tap density. Results shown below are typical of oxides and their hydrates as prepared in this laboratory. Preparation of hydrates with higher densities may be possible, and work along this line is anticipated.

<u>Sample</u>	<u>Tap Density, g/cc</u>
MCW UO_3	4.2
MCW UO_3 hydrated (monohydrate)	2.5
MCW UO_3 hydrate reconverted to anhydrous	2.6
Continuously produced UO_3	4.1
Cont. UO_3 hydrated (monohydrate)	2.7
Cont. UO_3 hydrate reconverted to anhydrous	2.9

THE RECOVERY OF HF AND URANIUM FROM MgF_2 BOMB SLAG

by

J. W. Stevenson

Introduction

This work concerns the recovery of uranium and HF from bomb slag, MgF_2 . Previous reports on this problem were presented in NYO 1349, NYO 1352, and NYO 1354.

Aim

The aims of this study continue to be:

1. To establish a process that will reduce the uranium content of slag to less than 0.05% and at the same time permit recovery of most of the fluoride.
2. To investigate various processes in order to gain as much economy and flexibility in slag handling as possible.

Summary

Slag is definitely not as reactive as fluor spar toward sulfuric acid. It appears that only a plant test will establish the magnitude of this difficulty.

Sodium carbonate leaching and washing of very finely ground slag does not consistently remove uranium to less than 0.05% in the treated slag. Because of the potential advantages of this process it may be reconsidered from time to time but at present no further work is planned.

Even dilute acid, 1%, dissolves appreciable amounts of slag. This is objectionable because it leads to fluoride contamination of the uranium concentrate. It has not been established that an excess of 1% acid will result in satisfactory uranium removal although it is known that 10% acid is satisfactory. Because a dilute H_2SO_4 leach process seems to offer the best method of uranium recovery, future work will be directed toward gathering pre-pilot plant data for this process.

Experimental Data and Discussion

Most of the effort on these problems, during the past quarter, has been directed toward examining literature and experimental data in order to narrow the field of study to one or possibly two of the most promising methods. The limited amount of experimental work which has been done has served to solidify the conclusions which evolved from this consideration of past work.

Two additional samples of fluorspar were tested by reacting with H_2SO_4 in platinum at 190° to $215^\circ C$. The percent reacted versus time of reaction is shown in Table I.

Table I

Reaction of Fluorspar with H_2SO_4 (B120P108)

Time (min.)	% Reacted	
	Sample I	Sample II
10	59	52
20	69	61
30	75	65
40	77	69
50	80	71
60	86	73
70	91	74

Screen analyses for these samples are given in Table II (B114P32) .

Table II

Screen Analyses of Fluorspar Samples

Sample	Screen Size		
	+ 200	- 200 +325	- 325
I	7.8%	38.9%	53.4%
II	31.0%	40.0%	26.8%

When compared with previous work, this experiment confirms the belief that fluorspar is much more reactive toward H_2SO_4 than is slag. It appears that only a plant scale test of slag will provide the quantitative data required to judge the seriousness of this difference in reactivity.

At Prof. Shreve's suggestion a sample of slag was heated to $700^\circ C$ then water quenched. The thought was that such a procedure might make the slag more reactive toward H_2SO_4 . However, the slag still appeared to be quite coarse. When reacted with a two-fold excess of H_2SO_4 at 200 to $250^\circ C$ for 1 hour, 48% of the slag reacted compared to 45% reaction for untreated slag (B131P26).

The screen analysis of this slag before treatment is given in Table III (B120P113).

Table III

Screen Analysis of Slag

<u>Screen</u>	<u>%</u>
on 100	23.1
- 100 + 200	22.8
- 200 + 325	14.0
- 325	40.1

This experiment showed that the heating and quenching did not improve the reactivity of the slag.

An experiment involving hot ball milling of a slag- Na_2CO_3 slurry was mentioned briefly in last quarter's report as offering promise. This experiment will be described, not because it was successful, but because it was almost successful and because a carbonate process would have a number of advantages.

Four hundred fifty four grams of slag was milled in a 1 gallon porcelain jar closed with a brass lid bearing a pressure relief device. One quart of flint pebbles was used. The mill also contained 473ml of a solution containing 108 gm Na_2CO_3 per liter and 12gm NaHCO_3 per liter. Five g $\text{Ca}(\text{OCl})_2$ was added as an oxidant. The temperature was maintained at 70 to 80°C. As each sample was taken it was filtered and slurry washed with water for ½ hour at 80 - 90°C.

As will be shown below the uranium was still undersirably high in the residue. Therefore, the samples were reslurried for 1 hour at 80 - 90°C in a dilute Na_2CO_3 liquor at 3 lbs. dry solids/gal. The Na_2CO_3 liquor contained 27g Na_2CO_3 and 3g NaHCO_3 per liter. This filtrate gave a qualitative test for uranium, therefore, the cake was washed twice more with dilute carbonate liquor. The final filtrate did not give a qualitative test for uranium. Two different samples of slag were tested. The results appear in Table IV.

Table IV

Hot Carbonate-Slurry Milling of Slag

<u>Sample</u>	<u>Initial % U</u>	<u>% U after 6 hours</u>	<u>% U after 12 hours</u>	<u>% U after 12 hours and 3. dilute Na_2CO_3 washes</u>
1	1.13	0.13	0.15	0.05
2	1.60	0.20	0.11*	0.09

* Two dilute Na_2CO_3 washes. B114P33

In another series of experiments much the same sort of test was made except that the slags were ground to -325 mesh to start with and the digestion was in beakers rather than the mill. The slurries were more dilute but the carbonate concentration was unchanged. The digestions were made at 90 to 100°C and H_2O_2 was maintained in excess. Digestion and washing were continued until the final digest filtrate did not give a qualitative test for uranium (B131P16). The results are given in Table V.

Table VResidual Uranium In Carbonate Leached Slag

<u>Sample</u>	<u>% U</u>
1	0.07
2	0.05
3	0.08

Taken together these two sets of experiments show that the carbonate leaching process at the present stage of development will not satisfactorily remove uranium from slag. Therefore, no further work on this process is planned. However, because of the potential advantages of a carbonate leach process, some work will be done from time to time as new approaches are suggested.

A brief experiment was performed to determine the solubility of slag in dilute acid and dilute carbonate. Ten grams of slag was heated for 1 hour at 90 to 100°C with 100ml of solution. The slurries were filtered and the residues dried at 110°C and weighed. The data are shown in Table VI (B131P23).

Table VISolubility of Slag in Dilute Acids and Dilute Carbonate

<u>Solution</u>	<u>% Dissolved</u>
Water	0.0
1% H_2SO_4	6.8
2% H_2SO_4	8.1
1% Na_2CO_3	0.5

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The screen analysis of this slag has been given in Table III. The initial uranium content was 0.51%. Qualitative tests indicated that detectable amounts of uranium remained in the slag which is not surprising in view of the relative coarseness of the slag. The sample contained some constituent that was readily soluble in hot dilute acid as determined by titration of a slurry to methyl red end point. The amount of this constituent, calculated as MgO, was 1.6%. The amount of magnesium was not determined but was almost certainly less than 2.0%. This experiment provides further evidence that some slag does dissolve in acid as dilute as 1% H₂SO₄. The amount dissolved is approximately that which can be calculated from solubility products and ionization constants. This solubility of slag means that fluoride complexers and a final high temperature roast will be necessary to reduce the fluoride contamination of the uranium concentrate. Future work will be directed toward accumulating pre-pilot plant data for a dilute H₂SO₄ process.

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METALLOGRAPHIC PROGRESS REPORT FOR THE SECOND QUARTER OF 1953

by

H. C. Kloepper, Jr.

O. L. Lisot

R. M. Paine

A. E. Ruehle

R. S. Vogel

Introduction

This program concerns the examination of uranium metal with respect to metal quality. Previous work is reported in NYO 1352 and NYO 1354.

Aim

The aim of this program has been to seek out and identify the various types of inclusions found in the metal. We have also tried to help evaluate the development work of others in the light of the materials that have been identified and thereby hope to aid in their elimination from the product.

Summary of Conclusions

1. Superheating of the melt has very little effect on slag removal as determined in the cast ingot.
2. All mold design factors have not been evaluated but larger diameter molds are indicated as being better.
3. Egg cups painted with mold wash are slightly better than unpainted cups as far as ingot quality is concerned.
4. All "good crop" ingots are of very poor quality.
5. Some progress is being made in developing new techniques that can be applied to the identification of inclusions in uranium metal.

Discussion of Results

I. Examination of Pilot Plant Ingots

a. Heats 202 and 203.

The purpose of this experiment was to see if a high holding temperature would volatilize more slag and produce a cleaner ingot. This idea was suggested by Mr. Kaulbach of the New York A.E.C. Office. The heats were cast in production type molds with 45" of zircon insulation, and having 0.1% slag added to the crucible charge. Heat 202 was held at 2550°F

and poured while heat 203 was held at 2800°F and poured. Samples were taken 5", 25", and 40" from the bottom of each ingot.

A porosity examination of the samples from the two heats showed no difference in the number of slag inclusions.

b. Miscellaneous Mold Designs

The following pilot plant heats have been examined and have been ranked in the order of increasing porosity, the last heat being the most porous.

1. Heat 197 - 6 $\frac{1}{4}$ " diameter production mold, tapered insulation, top reflector.
2. Heat 196 - Self casting in crucible, cooled from 2200°F to 1800°F in 4 hours.
3. Heat 198 - 4 $\frac{1}{4}$ " diameter production mold, tapered insulation, top reflector.
4. Heat 204 - Heat tapered step tapered type A mold, tapered insulation, top reflector.
5. Heat 195 - Copper mold, water cooled, $\frac{1}{4}$ " pourhole.

As far as pin point porosity and inclusions is concerned they are all much better than regular production ingots. Heat 195, which is the most porous, is about 3 times less porous than a regular production ingot, and heat 197 is about 10 times less porous than a regular production ingot.

II. Examination of Production Plant Ingots

a. Painted vs Unpainted Cup Molds

A series of ten ingots was cast in the production plant to determine the effect of painting the egg cups with a mold wash. Five ingots were cast using painted cups and five cast using unpainted cups.

Samples from these ingots were examined and counts made on the number of voids, and the number of slag and oxide inclusions. The voids and slag were reduced by a factor of two in the painted mold but the oxide inclusions were increased by a factor of two, the overall effect being a reduction of about $\frac{1}{2}$ in the total pin point porosity and inclusion count.

Since it is possible to reuse an egg cup mold that has been painted with a mold wash and the overall effect is a reduction in porosity and inclusions this practice has been recommended for use in the production plant.

b. All "Good Crop" Ingots

Five ingots were cast in which "good crop" made up the entire charge entering the melting crucible. The so-called "good crop" is the metal that is cropped from the top of the ingot after the top one inch or "top crop" is removed. "Good crop" is removed in one or two inch slices until density and pipe specifications are met.

Three of the five heats were examined in the laboratory and were found to be extremely porous and had a very large number of large slag and oxide type inclusions. They also had numerous inclusions of a hard dark granular material that appears to be sintered into a porous mass. When subjected to X-ray diffraction using a technique to be described later, this material gave a diffuse UO_2 pattern for its major constituent; other lines were obtained but have not yet been identified.

One of the larger shrinkage cracks was filled with a soft white material that was tinged with a reddish brown discoloration. An X-ray diffraction analysis of this material revealed its major constituent to be MgO and one of its minor constituents has been identified as UO_2 . A typical photomicrograph of the all "good crop" material is shown in Figure 1.

The sintered dark granular material was prepared for X-ray diffraction by using a replica-transfer technique. The sample was prepared for visual examination in the normal manner, then a lucite replica of the surface was made using a mounting press. The replica was broken away from the specimen revealing a plastic replica of the surface with some materials from the inclusions embedded in its surface, but projecting in relief. The plastic was sectioned in such a manner that it could be mounted in an X-ray diffraction powder camera. Figure 2 is a reproduction of the pattern obtained. This technique is in the early stages of its development here at Mallinckrodt and is included because of its novelty.

In the case of the MgO inclusion a plastic replica was not made but the material was dislodged with a needle and mounted on the end of a fine glass fiber with Canada Balsam. The sample was then mounted in an X-ray diffraction powder camera. The pattern obtained using this technique is shown in Figure 3.

III. Examination of Slugs

At the present time the examination of slugs is in the stage of method development. The methods used to identify inclusions in ingot metal of necessity have to be revised since the amount of sample obtainable from an inclusion only a few microns wide is very limited. It

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Figure 1.

All "good crop" heat No. 4663
showing numerous slag, oxide,
and carbide inclusions. Sample
was rough ground on 400 SiC
paper and photographed at 50X
under polarized light.

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A.

B.

Fig. 2

X-Ray diffraction patterns
obtained with 57.3 mm powder
camera; A. Inclusion stripped
out with Lucite. B. Standard
UO₂ pattern.

Fig. 3

X-Ray diffraction pattern
obtained with 114.6 mm powder
camera. Inclusion mounted
on glass fibre.

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has forced us to work under higher magnification while trying to dislodge samples for spectrographic analysis. A rough calculation of the amount of material removed from a slag inclusion showed that we were able to transfer about 0.5 to 2.0 micrograms of material to a spectrographic electrode.

Samples of materials found in reject slugs have been analyzed by spectrographic means, and the analysis obtained on slag and oxide type inclusions are similar to those obtained on samples removed from ingots. It must be remembered that the small amount of impurities found in spectrographic graphite is of little or no concern when dealing with normal amounts of material, but becomes extremely important when handling samples in the limited amounts described above. In order to neutralize the effect of electrode impurities such techniques as preburning of electrodes, electrode blanks, etc., have been tried with some success.

In attempting to develop new transfer methods to be used in conjunction with X-ray diffraction and spectrographic techniques, it was noted that 1 : 1 HCl attacks the striations found in slugs at a faster rate than the surrounding metal. Therefore, some etching experiments were carried out. The acid after contacting the sample was analyzed spectrographically and was found to contain U, Si, and Ca over and above the blanks run on the materials involved. More work will have to be done before conclusions can be drawn. A micro spark technique for direct excitation of inclusions in metal is also under development.

In examining a number of reject slugs it was noted that slag does not conform in the rolling operation. A slag inclusion should be distorted longitudinally to 25 times its original diameter and transversely to $\frac{1}{4}$ of its original diameter. Figure 4 shows a slag inclusion in the midst of a number of striations. It is obvious that the slag has not been elongated 25 times. This fact alone ought to eliminate slag as a probable cause of striations in slugs.

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Figure 4.

Reject slug rough ground on
400 grit SiC paper, photographed
at 50X using polarized light.
Rolling direction is in the
direction of the striations
and the white slag material
obviously does not conform in
rolling operation.

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CARBON CONTAMINATION IN CAST URANIUM

by

R. D. Piper

Introduction

Work on decreasing the amount of carbon contamination incurred on melting uranium in graphite crucibles has been described in previous quarterly reports (NYO 1352 and NYO 1354). A few additional tests have been made during this quarter and are described below.

Experimental

The apparatus and procedure previously described were used to test the effectiveness of an ethyl silicate bonded magnesia dressing. A slurry of powdered magnesia and ethyl silicate diluted with isopropyl alcohol was applied to the crucibles and partially hydrolyzed by using a crucible previously soaked in water or by storing the treated crucible in a moist atmosphere. A soft, but fairly adherent coating was produced by either method. On testing these coatings by melting uranium in the treated crucibles, ingots with 1000 - 1100ppm carbon were obtained, indicating only a slight improvement over untreated graphite and much poorer performance than the magnesia dressing now used in plant production which gives ingots with 500ppm carbon under similar conditions. ✓

Several 2 1/4" diameter sintered magnesia crucibles have been received from Norton Abrasive Co. and tested using five pound charges of derby metal. Two attempts to heat the metal directly by induction resulted in breaking the crucible, presumably from thermal strains set up on heating a piece of metal inside the crucible. One charge was melted successfully and heated to 2500°F, using a steel sleeve outside the crucible as a susceptor for the induction heating. The resulting ingot met purity specifications and contained only 29ppm carbon. These tests, however, indicate that considerable care must be exercised in using this type of crucible to prevent thermal or mechanical breakage.

VACUUM FUSION OXYGEN DETERMINATION

by

R. D. Piper

Introduction

Increased emphasis on metal quality and on the use of crucible dressings or oxide crucibles have made it necessary to study oxygen contamination more closely than has been done heretofore. The best method available for determining oxygen in uranium is the vacuum fusion method in which the uranium is melted under vacuum in an iron bath with an excess of carbon. At temperatures above 1750°C any oxygen or oxides present form carbon monoxide which is pumped off and analyzed. Nitrogen and hydrogen are also removed and can be determined from the same sample. Considerable work has been done on developing this method, and a few references are listed below.^{1,2,3,4}

Apparatus

The apparatus used in this work was originally copied from a similar apparatus at Battelle Memorial Institute, but has undergone considerable modification. A photograph of the completed apparatus is shown in Figure 1, and a schematic diagram of the system is shown in Figure 2.

The reaction takes place in a 1 1/4" O.D. x 3" long graphite crucible which is mounted in a 1 1/4" I.D. quartz tube and insulated by loose graphite powder in the annular space. This assembly is contained in a 2" I.D. vacuum tight quartz tube and is supported in the induction coil by another quartz tube which rests on the bottom of the outer container. The outer quartz tube is sealed with Apiezon "W" wax to a brass flange which is connected, by means of a flanged 1 1/2" tube sealed with rubber "O" rings, to a Leybold's Nachfolger Hg45 mercury vapor diffusion pump. This pump has a pumping speed of 45 l/second and provides rapid removal of evolved gases to minimize reabsorption of the gases by metal films formed on the walls of the apparatus.

A sample "tree" is mounted above the connection to the diffusion pump so that samples may be dropped, without opening the system, by means of iron "pushers" operated by a magnet. A glass sleeve, also mounted in the sample tree, can be moved in front of the sight glass on top of the tree to prevent the sight glass from becoming clouded with vapors from the crucible. Temperatures are measured through this sight glass using an optical pyrometer.

The crucible is heated using a 2 1/4" induction coil mounted outside the quartz tube. Power is supplied by a 10 kilocycle, 15 KW Tocco motor generator set. The maximum outgassing temperature of 2200°C can be reached using only 20% of the rated output of the unit.

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Figure 1

Vacuum Fusion Apparatus

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SCHEMATIC DIAGRAM OF VACUUM FUSION SYSTEM

Figure 2

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The rest of the system is used to analyze the evolved gases for hydrogen, carbon monoxide, and hydrogen. This part of the system is all glass and made using 18mm I.D. glass tubing and stopcocks to permit rapid pumping through the system. The stopcocks are sealed with Dow Corning silicone grease which has given satisfactory performance in keeping leaks from this part of the system to less than 0.2 liter-micron per minute. The gases are pumped into one of three known volumes using D.P.I mercury vapor pump capable of operating against a fore pressure of up to 6mm. The pressure of the trapped gas is measured with a McLeod gauge calibrated from 0.2-1200 microns. The diffusion pump is also used to circulate the gases around the system where they are passed over a CuO catalyst to oxidize the hydrogen to water and the carbon monoxide to carbon dioxide. The gases are then fractionally frozen out using dry ice-acetone and liquid nitrogen. The differences in pressure on collecting the gases in the known volume after each step are used to determine the amounts of hydrogen and carbon monoxide present. The residual gas is assumed to be nitrogen so the final pressure can be used to determine the amount of nitrogen present.

Procedure

The procedure described below has been adopted for analyzing hydrogen, nitrogen, and oxygen in uranium metal.

Two 10-15g samples of uranium metal, previously cleaned with a file and rinsed in acetone, and 50g of iron in the form of 1" pieces of $\frac{1}{4}$ " drill rod are loaded in the sample tree. The crucible is mounted in the powdered graphite insulation described above and the system is closed. The system is pumped out very slowly and left with the pump on overnight before the crucible is heated.

The crucible is then heated to 2200°C in about 1½ hours. The long pumping and slow heating are necessary to avoid blowing the graphite powder out by too rapid evolution of gas. After outgassing at 2200°C for 3 hours, the crucible is cooled to 1400° while the iron is dropped and then reheated to the operating temperature of 1750°C. The iron is outgassed for one hour and a blank is taken. If the blank is less than 6 liter-microns per minute, the gases collected in 15 minutes are analyzed by circulating over the CuO catalyst at 210°C and the dry ice-acetone trap for 10 minutes, collecting in the known volume, measuring the pressure, circulating over the liquid nitrogen trap, collecting in the same volume, and measuring the pressure again. After the system has been pumped out, a sample is dropped, the gases are collected for 15 minutes, and the same analytical procedure as described above is followed. Since each gas collection and analysis requires about 80 minutes, a crucible can be outgassed and two samples analyzed in an 8 hour day.

Preliminary Results

Difficulties with leaks and high outgassing rates have delayed operation of the apparatus on a routine basis. Several modifications of the original design have been made and leaks have been

virtually eliminated, but outgassing from the hot crucible and diffusion pump still lead to fairly high blanks (5 liter-microns per minute). The reproducibility of results obtained by this apparatus has been checked by analyzing four samples cut from the same portion of an ingot. Sampling errors were reduced by cutting a one inch cube of ingot metal into 24 pieces and selecting three of these pieces at random for each sample. In this series values of 13, 12, 12, and 15ppm oxygen were obtained in successive runs. Although this indicates only fair reproducibility, it is expected that it will improve as experience is gained in using the apparatus.

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MODIFICATIONS OF THE PYROELECTRIC CONCENTRATION METHOD FOR IMPROVING BORON SENSITIVITY

by

R. S. Vogel

Introduction

The possibility of production of uranium metal having a boron concentration less than 0.10ppm necessitates a more sensitive test than is now available.

Aim

An investigation is being made of possible ways to increase the sensitivity of the modified pyroelectric concentration method¹ used in this laboratory.

Experimental

An enhancement of the line-to-background ratio may be accomplished by an exposure period more favorable with respect to boron evolution and by the use of a carrier giving lower background density than gallium oxide in the vicinity of the boron lines. Moving plate studies show boron evolution to be strongest during the first fifteen seconds of arcing time. Longer exposures build up background, thereby diminishing boron sensitivity. Preparations of a sample containing 0.14ppm B exposed for successively longer periods between 12 and 35 seconds show a systematic decrease of line-to-background ratio.

Indium oxide as a carrier behaves similarly to gallium oxide, but its chief advantage with respect to boron is the absence of any strong lines in the vicinity of 2498 Å. Trials using In_2O_3 show considerably greater boron sensitivity than is obtained using Ga_2O_3 .

The use of a pelletized electrode charge offers promise by increasing the allowable sample weight by 50% without increasing background density.

Preliminary trials using a combination of these conditions show a possibility of lowering the limit of detection of boron to less than 0.01ppm. When the work is completed a report will be made.

¹ Scribner, B. F. and Mullin, H. R. - "A System of Methods for the Spectrochemical Analysis of Uranium-Base Material," A-2907 (Special) (1945).

GRINDING SAMPLE PREPARATIONS FOR SPECTROGRAPHIC ANALYSIS

by

R. S. Vogel

In a previous report, H. R. Mullin of NBL reported the use of a dental amalgamator (Wig-L-Bug manufactured by Crescent Dental Manufacturing Company, Chicago, Illinois) to mix previously ground samples with graphite for spectrographic analysis.

At the suggestion of Dr. J. U. Shepardson of MCW an attempt was made to apply the Wig-L-Bug to the grinding of U_3O_8 - Ga_2O_3 mixtures used in the carrier-distillation method. The Wig-L-Bug is normally supplied with a plastic capsule $\frac{1}{8}$ " x 1" (internal size) and a pestle ($\frac{3}{16}$ " x $\frac{1}{4}$ " plastic rod having a metallic core for added mass). In use, a rapid reciprocating motion of the capsule containing pestle and sample causes the pestle to strike against the ends of the capsule, thereby reducing the sample to a fine powder in a very short time.

Sample mixtures of 490mg U_3O_8 and 10mg Ga_2O_3 ground in a mullite mortar for 2-3 minutes and mixtures processed by the Wig-L-Bug for an 8-second period showed comparable fineness and uniformity under microscopic examination.

Spectrographic results on sample mixtures prepared by the two methods are listed in Table I.

Table IComparison of Results Obtained by Grinding in Mullite and in Wig-L-Bug

<u>Element</u>	<u>Preparation</u>	
	<u>Ground in Mullite 2-3 min.</u>	<u>Processed in Wig-L-Bug 10 sec.</u>
Al	<5 ppm	<5 ppm
Bi	<1	<1
B	0.14	0.12
Co	<1	<1
Cr	1	1
Cu	<1	1
Fe	15	10
In	<0.1	<0.1

Table I (cont'd.)

<u>Element</u>	<u>Preparation</u>	
	<u>Ground in Mullite 2-3 min.</u>	<u>Processed in Wig-L-Bug 10 sec.</u>
Mg	5 ppm	5 ppm
Mn	<1	<1
Mo	<5	<5
Ni	1	<1
P	<10	<10
Pb	<1	<1
Sb	1	1
Si	<5	<5
Sn	<1	<1
V	<10	<10
Zn	10	10

In addition to a considerable saving of time in the preparation of a large number of samples, the Wig-L-Bug method yields more reproducible results by elimination of variations between operators.

THE DETERMINATION OF NITROGEN IN URANIUM METAL

by

Gerhard P. Lang

Introduction

Uranium ingots recast under vacuum have been tested for nitrogen on a routine basis for many years by methods developed early in the Manhattan Project. Derbies, which are the reguluses produced in the thermite reaction which yields uranium metal, have not been tested on a routine basis. However, on occasions, when derby samples have been analyzed, nitrogen values considerably lower than the usual ingot values have been obtained. Any calculation of nitrogen pickup in the process between derby and ingot could not account for the difference actually determined. For this reason a restudy of the methods of nitrogen determinations was begun.

The literature (cf. especially reference 1 and the papers there referred to) indicates that the method now in use is considered to be adequate for ingots. However, the hydrochloric acid method of solution, which is the one being used, was questioned by J. W. Stevenson since it is reported² that the nitrides of uranium are insoluble in hydrochloric acid. For this reason, improved methods of solution were the chief aim of this investigation.

Experimental

The method in routine use in this laboratory is that described by Mundy¹ which employs Nessler's reagent and a Fisher Nesslerimeter for estimating the distilled ammonia.

Variations of this method included the spectrophotometric estimation of the Nesslerized solutions as described by Wright³ and the volumetric estimation of the ammonia as described by Mundy¹.

The methods of solution used were the following:

- A. Hydrochloric Acid Method: Ten ml of 6M hydrochloric acid are added to the cleaned sample. A vigorous reaction results leaving a black fine-grained precipitate. It has been shown that this precipitate does not prevent the distillation of ammonia from the reaction mixture.
- B. Hydrochloric Acid-Hydrogen Peroxide Method: In this method the hydrochloric acid slurry is oxidized with 39% hydrogen peroxide until complete solution is obtained. Large blanks are obtained in this method.

- C. Hydrochloric Acid-Perchloric Acid Method: In this method the hydrochloric acid slurry is oxidized by adding 3.0ml 72% perchloric acid and evaporating to fumes of perchloric acid, at which point complete solution is immediately obtained.
- D. Phosphoric Acid Method: The sample is heated with 5ml 85% phosphoric acid until complete solution results. Solution is somewhat slow unless the sample is finely divided. With gram-sized samples, the precipitation of gelatinous uranous phosphate on dilution makes the sample difficult to handle.

Determination of Nitrogen in Uranium Nitrides

In order to test the above procedures on uranium nitrides, several preparations of the nitrides were made by J. W. Stevenson and R. D. Piper of our Research Laboratory.

To prepare uranium sesquinitride (U_2N_3), 200 grams of uranium metal turnings were heated in nitrogen at 1 atmosphere in a stainless steel tube. The reaction was followed by observing the pressure of nitrogen in the reaction tube. The temperature of the tube rose to $1000^{\circ}C$ in about one hour and was held there for approximately another hour before cooling. The gain in weight of the sample corresponded approximately to a product of composition $UN_{1.5}$.

To prepare uranium mononitride, a second preparation of the sesquinitride was made. From the gain in weight it had a composition corresponding to $UN_{1.4}$. This product was then transferred to a graphite crucible and heated for four hours at $1400^{\circ}C$ in a high vacuum. The pressure at the start was less than 20 microns of mercury. This rose to 400 microns during the reaction and then slowly fell again but never to the original pressure. The change in weight of the sample during this operation could not be obtained because quantitative transfer could not be made.

It is evident that pure nitrides of a definite composition were not obtained. Since uranium nitrides are easily oxidized, the products probably contained oxides. A carbon determination on the sample called UN showed that it also contained uranium carbide (v. i.).

Even though these uranium nitride preparations were not suited to a critical test of the above nitrogen procedures, it was possible to obtain qualitative information concerning the ability of these various procedures to determine nitrogen in uranium nitrides.

It can be seen from the qualitative observations on the solubilities of these nitrides in various acids (Table I) that the hydrochloric acid method of solution is inadequate, and that, of the methods tried, those employing perchloric or phosphoric acid are the best.

Nitrogen analyses were made on these preparations using various methods of solution and estimation. The uranium analyses listed were performed by means of a ceric sulfate titration method.

On the material called UN_{1.3}, an average nitrogen analysis approximating that in UN_{1.1} was obtained (cf. Table II and III), but the uranium analysis is 2.5% lower than that contained in UN_{1.1}. These values correspond fairly closely to a product which is 82.3% in U₂N₃ and 17.7% in U₃O₈.

The sample called UN contained less than half the nitrogen theoretically in this compound. A carbon determination showed the sample to contain 10% C. This corresponds to 21% UC, if all carbon is present as UC. The rest of the sample probably consisted of uranium oxides.

Table I

Solubility of Uranium Nitride Preparations

<u>Reagent</u>	<u>UN_{1.3}</u>	<u>UN</u>
HClO ₄	Soluble	Soluble
H ₃ PO ₄	Soluble	Soluble
HCl	Insoluble	Insoluble
HNO ₃	Mostly soluble. Leaves fine black residue.	Soluble except for slight residue.
HCl-H ₂ O ₂	Partially soluble	Soluble except for slight residue

Table II

Nitrogen Determinations on Uranium Nitride Preparations

<u>Method of Solution</u>	<u>Method of Estimation</u>	<u>UN_{1.3} % N</u>	<u>UN % N</u>
H ₃ PO ₄	Volumetric	7.10	2.84
H ₃ PO ₄	Volumetric	6.11	-
H ₃ PO ₄	Volumetric	6.35	-
H ₃ PO ₄	Volumetric	6.85	-
H ₃ PO ₄	Volumetric	7.00	-
H ₃ PO ₄	Volumetric	6.94	-
H ₃ PO ₄ *	Volumetric	7.06	-
HClO ₄	Volumetric	6.51	2.85
HClO ₄	Spectrophotometric	6.25	2.30
HClO ₄ *	Spectrophotometric	-	2.80
HCl-H ₂ O ₂	Volumetric	-	2.20
		av. 6.68	av. 2.59

* Devarda's Metal (1.0g) was added during distillation.

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Table IIIComparison of Determinations with Theoretical Values

	<u>% N</u>	<u>% U</u>
Theory for UN _{1.3}	7.10	92.90
Found for UN _{1.3}	av. 6.68	90.40
Theory for UN	5.56	94.44
Found for UN	av. 2.59	93.40

The results in Table III indicate that if the nitrogen is present as uranium nitride, our routine method, which uses hydrochloric acid solution, would not be adequate, whereas the phosphoric acid and perchloric acid methods provide a more nearly correct result.

Determination of Nitrogen in Derbies

Derbies are sampled by sawing a section 3-5mm in width through a diameter of the derby and punching approximately 2g samples from this slice. In order to determine the distribution of nitrogen in a derby, punches were taken at various places in the slice, and these samples were numbered as in Figure 1.

Figure 1.

The results of the hydrochloric and perchloric acid methods are shown in Table IV. The ammonia was estimated by the spectrophotometric method. It is very evident that the hydrochloric acid method fails completely for derbies. This probably means that the nitrogen is present in derbies largely as uranium nitrides which are insoluble in hydrochloric acid. It is

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also evident that the nitrogen is very inhomogeneously distributed through the derby, and adequate sampling is a major problem.

Table IV

Nitrogen Determinations on Derbies

HClO₄ Method

<u>Derby Number</u>	<u>Nitrogen in p.p.m. from Location</u>								
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>
	<u>(Top)</u>		<u>(Center)</u>		<u>(Bottom)</u>				<u>(Side)</u>
848	1040		155		44				240
	200		175		163				30
			329		231				
			345						
			279						
			232						
609			42						
			38						
594	2700	68	32	59	30	82	75	81	99
571	330	20	-	66	50	65	34	77	81
626	2000	42	17	55	62	61	76	81	79
636	410	38	72	72	70	82	85	88	83
660	1050	25	27	66	79	34	18	85	92

HCl Method

848	31		45		25				14
594	19	<10	<10	<10	<10	<10	<10	<10	<10
571	<10	<10	<10	<10	28	<10	<10	<10	<10
626	13	<10	<10	<10	<10	<10	<10	<10	<10
636	24	<10	<10	<10	<10	<10	<10	<10	<10
660	29	<10	<10	<10	<10	<10	<10	<10	<10

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Determination of Nitrogen in Ingots

Furman, Mundy and Wolf^{4,5} have shown that the hydrochloric acid method and the hydrochloric acid-hydrogen peroxide method give the same results on ingot samples. Using a standard ingot sample, which is analyzed periodically to keep a running check on nitrogen determinations in this laboratory, it has been found that there is no difference between the hydrochloric acid and the perchloric acid methods.

Table VDetermination of Nitrogen on a Standard Ingot Sample

<u>Method</u>	<u>Number of Determinations</u>	<u>Average (ppm)</u>	<u>Precision at the 95% Confidence Level (ppm)</u>
HCl	75	39	± 7
HClO ₄	14	41	± 5

A comparison between ingots and top crops was also made. Top crops are the top one to two inches of a uranium casting which are removed before it is designated as an ingot. The first two columns of Table VI show the difference between the two methods on ingot and top crop samples taken from the same casting. The nitrogen values on top crops are generally higher. Also, the perchloric acid method gives higher results than the hydrochloric acid method on top crops. The values in the last two columns were obtained by dissolving samples in hydrochloric acid, separating the precipitate by centrifuging and determining nitrogen on the two fractions by the perchloric acid method. The separation of the precipitate was not entirely complete due to its very fine nature.

Table VIComparison of Nitrogen in Ingot and Top Crop Samples

<u>Sample No.</u>	<u>HCl Method, ppm</u>	<u>HClO₄ Method, ppm</u>	<u>HClO₄ Method</u>	
			<u>Filtrate, ppm</u>	<u>Precipitate, ppm</u>
W5182	65	58	69	0
T5182	157	>400	150	240
W5079	62	54	56	4
T5079	42	190	67	74
W5012	9.9	.8	18	8
T5012	16	10	15	5

W - indicates ingots
T - indicates top crops

Here again the hydrochloric acid method is adequate for ingot samples but not for top crop samples, because hydrochloric acid does not completely dissolve the nitrogen compounds contained in the top crop. The anomolous results of sample 5012 may be due to contamination, or to a variation of nitrogen content within sample slices.

There is a possibility that ingot samples which have a high (greater than 60ppm) nitrogen content may give falsely low values by the hydrochloric acid procedure. This possibility will be investigated.

Summary

Since uranium nitrides are insoluble in hydrochloric acid, any nitrogen analysis which is performed on materials containing nitrides and which utilizes hydrochloric acid alone as solvent will fail. Although no ideal standards have been available for checking, dissolution in perchloric or phosphoric acid was shown to yield a more nearly correct answer. Very low results with hydrochloric acid and higher results with perchloric acid on derby metal indicate the apparent presence of uranium nitrides and the impracticability of using hydrochloric acid on derbies. There is some evidence to indicate the possibility of nitride presence also in the tops of ingots.

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