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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 59-46

EXAMINATION OF FURTHER URANIUM OXIDE SAMPLES PRODUCED BY HYDROMETALLURGICAL PROCEDURES AT THE UNIVERSITY OF BRITISH COLUMBIA

by

A. HUBERT WEBSTER AND NORMAN F. H. BRIGHT

MINERAL DRESSING AND PROCESS METALLURGY DIVISION

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A. Hubert Webster^A and Norman F. H. Bright^{AA}

SUMMARY OF RESULTS

Uranium oxide powders, produced by precipitation from a solution containing the uranyl ion by catalysed hydrogen reduction under pressure, at the University of British Columbia, have been examined and assessed for sinterability. It was found that certain samples exhibited bloating when sintered in pellet form, but that a powder which had been produced by a modified technique did not bloat on sintering.

Discrepancies have been found between the oxygen/uranium atomic ratios determined by oxidation to stoichiometric U_3O_8 and those determined by reduction to stoichiometric uranium dioxide.

Possible reasons for these behaviours have been investigated to some extent and discussed, but it was not found possible to account completely for them.

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(46 pages, 9 tables, 1 figure, 2 appendices with 8 tables and 1 figure)

INTRODUCTION

The work to be described in this report represents a continuation of the investigation on which an earlier report was written(1).

The production of reactor-grade UO_2 by a hydro-metallurgical procedure, such as the catalysed hydrogen reduction under pressure of an aqueous solution containing the uranyl ion (UO_2^{2+}), has been the subject of an extended series of investigations in the Department of Mining and Metallurgy of the University of British Columbia, under the general direction of Professor Frank A. Forward. Two progress reports on this work prepared by Dr. D. R. Wiles and Mr. J. P. Vizsolyi were included as Appendices in the earlier report(1). A further progress report (No. 3), by Dr. D. R. Wiles, dated June 15, 1958, was received subsequently to the publication of that report. This progress report dealt mainly with the use of ethylene diamine carbonate as the solvent for the uranyl ion; it was a document of considerable length and hence it has not been reproduced as an Appendix to this present report. The work on this project was then taken over by Dr. Ian H. Warren. No copy of his first progress report was received at the Mines Branch. However, a copy of his second progress report, dated August

(1) References at end of Report, see page 20.

1958, was received in September 1958. This progress report, with a copy of the covering letter, is reproduced as Appendix I to this present report.

A third progress report with covering letter was received in February 1959. This progress report, along with the Mines Branch comments thereon, is given as Appendix II to this present report.

A fourth progress report, with a covering letter, and an additional sample for investigation were sent in April 1959. This report is given as Appendix III.

Many of the samples referred to in these progress reports have been sent to the Mines Branch for investigation during the last six months. The samples of uranium oxide were produced by precipitation from aqueous solution. The uranium was reduced from uranyl carbonate solution by hydrogen under pressure using a nickel catalyst. The resultant precipitates were collected, examined at the University of British Columbia and then sent to the Mines Branch for further study. Nine samples of powder and a sintered pellet have been received; the samples, with dates of receipt, are listed below.

Samples	Date Received
D-54, D-57, D-66, D-68/69, D-72/73	3/11/58
D-91	22/12/58
D-105	21/1/59
Pellet	28/1/59
D-130	27/2/59
"UO _{2.022} "	30/4/59

EXPERIMENTAL

The powder samples were examined by the standard techniques used at the Mines Branch and described in an earlier Research Report(2). The sintering behaviour of certain of these materials was studied in some detail, since it was found that pellets made from some powders exhibited bloating on firing in hydrogen to 1700°C.

A. Results of Tests Other than Sintering

(1) Differential Thermal Analysis and Air Permeability

The details of the procedures used for differential thermal analysis and for air permeability determinations have been fully described previously(2). In the present work, six powder samples of UO₂ were examined, after the samples had been exposed to the air. A summary of the results obtained is given in Table 1.

TABLE 1

Examination of Uranium Oxide Samples by Differential Thermal
Analysis and Air Permeability

Sample No.	D. T. A.				Air Permeability Blaine Number (arbitrary units)
	1st Peak (°C)	2nd Peak (°C)	Peak Separation (deg. C)	Remarks	
D-54	227	398	171	Anomalous large exothermic peak at 479°C Smaller peaks: endothermic, 599°C exothermic 338°, exothermic 727°C	214
D-57	199	411	212	"Shoulder" on first peak	181
D-66	279	432	153	---	132
D-68/69	183	394	211	---	84
D-72/73	210	426	216	"Shoulder" on first peak	102
UO _{2.022}	218	366	148	---	68

The results of the D.T.A. tests are somewhat different from those generally obtained with powders produced by the hydrogen reduction of uranate compounds using dry methods. The 2nd peaks produced by the present samples mostly occur at higher temperatures than are usually observed (i.e. $360^{\circ} \pm 20^{\circ}\text{C}$) thus giving anomalous peak separation values. Large peak separations are generally associated with powders which will sinter to high densities. The cause of the extra peaks and "shoulders" observed in some of the D.T.A. analyses is not known; they may possibly be attributable to unspecified impurities.

The high Blaine Numbers indicate that the samples generally have quite small particle size and correspondingly high surface areas. Such materials would normally be expected to give reasonably high D.T.A. peak separation values.

(2) Chemical Analyses

Determinations of oxygen/uranium atomic ratios were made by both reduction and oxidation procedures(3). In the reduction procedure, the water produced by hydrogen reduction of the sample to $\text{UO}_{2.00}$ is collected and weighed; in the oxidation procedure, the gain in weight of the sample on oxidation to stoichiometric U_3O_8 is determined.

Since considerable quantities of CO_2 and moisture were adsorbed on the powders, determinations of these gases

were made by desorption at 500°C, followed by collection and weighing in absorption towers. In one determination (D-105), the further desorption of CO₂ and moisture on heating from 500°C to 900°C in argon was estimated.

The results of the various determinations are presented in Table 2. In general, it was found that the oxidation method gave lower oxygen/uranium atomic ratios than did the reduction method.

Determinations of nickel, carbon, and a number of other possible impurities are reported in Table 3. The total carbon content of sample D-105 was equivalent to more CO₂ than was evolved during the CO₂ desorption procedure. Furthermore, for sample D-130, the difference between the carbon content of the original sample and the carbon contents of the residues from the oxygen/uranium ratio determinations is greater than can be accounted for by the evolved CO₂. This "excess" carbon may be present as organic material or as graphite, and may be lost from the sample as CO during the oxygen/uranium ratio determination.

TABLE 2

Chemical Analyses of Uranium Oxide Samples for O/U Ratio,
Moisture, and CO₂

Sample	Ottawa Determinations					U.B.C. Determinations			
	Remarks	% Moisture	% CO ₂	O/U ratio by oxidation	O/U ratio by reduction [★]	% Moisture	% CO ₂	O/U ratio by oxidation ^{★★}	
D-54	After exposure to air	0.61	0.39	--	2.25	--	--	2.14	
D-57	" " " "	0.70	0.22	--	2.21	--	--	2.107	
D-66	" " " "	0.72	0.19	--	2.184	--	--	2.125	
D-68/69	Before exposure to air	0.64)	0.13)	--	2.175)	--	--	2.07	
		0.67)	0.10)	--	2.178)	--	--	--	
	After exposure to air	0.74	--	--	2.204	--	--	--	
D-72/73	" " " "	0.75	0.22	--	2.225	--	--	1.98	
D-91	Before exposure to air	0.43	0.06	--	2.123	0.49	0.09	2.009	
	After " " "	0.49	0.12	2.109	--	--	--	--	
D-105	Before exposure to air	0.76	0.11	--	2.159	0.95	0.195	2.067	
	" " " "	0.88	0.24	2.077	--	--	--	--	
	Special reduction cycle:								
	Heating to 500°C		0.74	0.097	--	--	--	--	--
	" from 500° to 900°C		0.02	0.052	--	--	--	--	--
	Hydrogen reduction		--	0	--	2.171	--	--	--
Totals		0.76	0.15	--	--	--	--	--	
D-130	Before exposure to air	0.53	0.23	--	2.151	0.60	0.37	2.086	
	" " " "	0.58	0.30	2.104	--	--	--	--	
UO _{2.022}	Before exposure to air	0.31	0.20	--	2.068	0.36	0.29	2.022	
	" " " "	0.39	0.21	2.065	--	--	--	--	

★ Corrected for CO₂ and H₂O losses on heating, and for Ni content.

★★ Samples not exposed to air.

-- Determination not made.

TABLE 3

Analyses of Uranium Oxide Samples for Trace Elements

Sample No.	Chemical Determinations				Spectrographic Determinations			
	% Ni (total)	% N (total)	% C	% NiO	% Si	% Mg	% Cu ⁽¹⁾	% V ⁽¹⁾
D-54	0.49	--	--	--	0.5	0.06	0.05	N.D.
D-57	0.19	--	--	--	--	--	--	--
D-66	<0.001	--	--	--	--	--	--	--
D-68/69	0.59	0.005	0.086	N.D.	0.2	0.03	0.06	0.09
D-72/73	0.56	--	--	--	0.2	0.03	0.06	0.1
D-91	0.38	0.012	--	--	--	--	--	--
D-105	0.23	--	0.085	--	--	--	--	--
D-130	<0.03	--	0.11 ⁽²⁾	--	--	--	--	--
UO _{2.022}	0.01	--	--	--	--	--	--	--

(1) Identification not positive

(2) In D-130 % C in original sample = 0.11 (0.40% as CO₂)

% C in residue of oxidation method = 0.007 (0.025% as CO₂)

% C in residue of reduction method = 0.004 (0.015% as CO₂)

N.D. = none detected

(3) X-Ray Diffraction Examinations

X-ray examination of the first five powder samples received gave the results listed in Table 4. The samples had all been exposed to the air before examination. The back-reflection lines were somewhat diffuse and, hence, the lattice parameters quoted carry a probable error of $\pm 0.005\text{\AA}$. There was no evidence of the presence of tetragonal uranium oxide (i.e. U_3O_7).

TABLE 4X-Ray Diffraction Examination of Uranium Oxide Samples

Sample	Phases Present	Cell edge for cubic (fluorite type) phase (A)
D-54	Cubic + U_3O_8 [*]	5.460
D-57	Cubic + trace U_3O_8	5.452
D-66	Cubic only	5.432
D-68/69	Cubic only	5.45 ₂
D-72/73	Cubic only	5.46 ₀

* Weak line at 2.12A. Unidentified

B. Sintering Tests

(1) Sintering tests were conducted on samples D-54, D-57, D-66, D-68/69 and D-72/73. It was found, however, that pellets made from these powders exhibited bloating on firing to 1700°C in hydrogen.

The procedure used in these tests was as follows:-

One-half inch diameter pellets weighing 5 g each were dry-pressed at 40,000 psi using kerosene as binder and alcoholic stearic acid

solution as mould lubricant. These pellets were fired to 1700°C in a hydrogen atmosphere in a molybdenum-wound furnace, soaked for 30 min at that temperature, and cooled to room temperature. The heating and cooling rates were approximately 400 degs C per hour.

(2) The pellet received on 28/1/59 had been sintered at U.B.C. in argon, with soaking at 1400°C. This pellet was examined with the following results:-

a) The pellet was fired to 1700°C for one-half hour in hydrogen, but did not bloat or change dimensions.

b) Density of pellet:

	<u>As received</u>	<u>After H₂ firing</u>
By weighing and dimensional measurement	10.13 g/cm ³	10.02 g/cm ³
By displacement of water	10.73 g/cm ³	10.60 g/cm ³
By displacement of alcohol	10.75 g/cm ³	---

c) The oxygen/uranium ratio before reduction was 2.15. This figure was calculated assuming that complete reduction to UO_{2.00} occurred on firing in hydrogen, that all the weight change was due to oxygen loss and that the effect of any impurities present could be disregarded.

d) X-ray examination of the material before firing in hydrogen indicated two fluorite-type phases with the following cell-dimensions:-

$$a_o = 5.46_3 \text{ \AA} \quad (\alpha\text{-UO}_2)$$

$$a_o = 5.45_1 \text{ \AA} \quad (\beta\text{-UO}_2 \text{ or } \text{U}_4\text{O}_9)$$

These lattice parameters are somewhat different from the usually accepted values of 5.469\AA and 5.44\AA for $\alpha\text{-UO}_2$ and U_4O_9 , respectively. The discrepancies may be due to incomplete disproportionation of the UO_{2+x} solid solution into stoichiometric $\alpha\text{-UO}_2$ and U_4O_9 on cooling.

(3) The uranium oxide sample D-130, which had been produced by a modified technique, was found to sinter without bloating when fired to 1700 °C in H_2 , and also when fired to 1400 °C in argon. The pellets were prepared by the method described in paragraph (1) above, except that no binder was used. The results of these trials are given in Table 5.

TABLE 5
Sintering Trials on UO_2 Batch No. D-130

Sintering Cycle	Sintered Density (g/cm^3)		Remarks
	By weight and dimensional measurement	By displacement of water	
H_2 : $\frac{1}{2}$ -hour soaking at 1700 °C	9.86	10.06	Mean for 2 pellets
Argon: $\frac{1}{2}$ -hour soaking at 1400 °C	8.62	8.85	Mean for 2 pellets

A few small "blisters" appeared on the surfaces of the argon-sintered pellets. The pellets spalled to some extent on firing and were subject to chipping on handling after sintering.

(4) The sample labelled " $\text{UO}_{2.022}$ " was sintered in hydrogen at 1700°C for 30 min. The pellets unfortunately spalled and "capped" on sintering, but gave good sintered densities, as determined by the displacement of water. This spalling of the compacts on firing would be a disadvantage if it occurred frequently with this type of powder and could not be overcome by some modification of fabrication procedure. There were no signs of bloating with the compacts made from this material. The results of the sintering tests on this sample are as follows:-

Pellet No.	Green Density (g/cm^3) (by weight and measurement)	Sintered Density (g/cm^3) (by displacement of water)
1	6.24	10.54
2	6.27	10.63

C. Investigation of Bloating

(1) Sintering Experiments

In an attempt to determine the nature of the bloating phenomenon and, if possible, to find the cause of the bloating, several sintering experiments were performed under various conditions. A summary of these experiments is given in Tables 6 to 9, and each series will be discussed separately.

TABLE 6

Experiments to Investigate Bloating

Series (1) - Heating Rates and Pre-treatment of Powder

UO ₂ Batch No.	Cycle	Sintered Density g/cm ³	Remarks
D72/73	H ₂ : heating rate 80 deg C/hr; ½-hr soaking at 1700°C; cooling rate 620 deg C/hr.	---	Blisters on surface; some bloating no binder used.
D72/73	H ₂ : heating rate 340 deg C/hr to 1500°C; ½-hr soaking at 1500°C; heating rate 280 deg C/hr to 1700°C; ½-hr soaking at 1700°C; cooling rate 450 deg C/hr.	---	Pellet split; bloated.
D-57	H ₂ : heating rate 300 deg C/hr; ½-hr soaking at 1700°C.	---	UO ₂ powder heated at 600°C in argon prior to forming pellet; pellet bloated.
D-72/73	H ₂ : ½-hr at 1700°C.	---	Powder pre-pressed and broken up twice before final pressing; pellet deformed.

Series (1)

It will be seen from Table 6 that neither the lowering of the heating rate and soaking at 1500°C, nor the desorption of CO₂ and moisture in an argon stream at 600°C before sintering, nor the pre-pressing of the powder, was successful in preventing the bloating. It was concluded that the bloating phenomenon was not due to the slow evolution of gas below sintering temperatures nor to the effect of strains produced by too rapid sintering.

TABLE 7Experiments to Investigate BloatingSeries (2) - Effect of Soaking Temperature

UO ₂ Batch No.	Cycle	Sintered Density ^A g/cm ³	Remarks
D-72/73	H ₂ : ½-hr soaking at 1300°C	8.87	No bloating
D-72/73	H ₂ : ½-hr soaking at 1500°C	10.03	ditto
D-72/73	H ₂ : ½-hr soaking at 1600°C	--	Split; bloated
D-72/73	H ₂ : ½-hr soaking at 1700°C	--	Bloated
D-72/73	H ₂ : 2-hr soaking at 1500°C	9.90	No bloating
D-54	H ₂ : ½-hr soaking at 1500°C	10.20	ditto
D-57	H ₂ : ½-hr soaking at 1500°C	10.15	ditto
D-68/69	H ₂ : ½-hr soaking at 1500°C	10.20	ditto

^A As determined by weighing and dimensional measurement.

Series (2)

It will be seen from Table 7 that the bloating appears to begin somewhere between 1500° and 1600°C. Pellets can be sintered at 1500°C without bloating. The densities obtained at 1500° are quite good, considering the relatively low soaking temperature.

TABLE 8Experiments to Investigate BloatingSeries (3) - Argon and CO₂ Atmospheres

UO ₂ Batch No.	Cycle	Sintered Density g/cm ³	Remarks
D-72/73	Argon: ½-hr soaking at 1400°C	8.05	No bloating
D-72/73	CO ₂ : heating to 1400°C ½-hr soaking at 1400°C H ₂ : ¼-hr soaking at 1400°C A+H ₂ : cooling to 1000°C A: cooling to room temp.	7.95	No bloating; 2 pellets used.

Series (3)

It will be seen from Table 8 that the use of argon or of CO₂ atmospheres at 1400°C for sintering did not produce as good densities as are obtained with H₂ at 1300°C. This difference between the behaviour in CO₂ or argon and that observed in hydrogen is precisely opposite from that observed with powders

produced by the hydrogen reduction of dry ammonium diuranate at 900 °C; such powders sinter to better densities in argon and CO₂ than in hydrogen at the same temperature. Sintering in the region of 1600° to 1700 °C could not be conveniently carried out using an argon atmosphere with the equipment available, hence it is uncertain whether the bloating would take place in argon in this temperature range.

TABLE 9

Experiments to Investigate Bloating

Series (4) - Impurities Added to "Normal" Powder

UO ₂ Batch No.	Cycle	Sintered Density g/cm ³	Remarks
P-14-a	H ₂ ; ½-hr soaking at 1700 °C	10.38	No additions; no bloating.
P-14-a	H ₂ ; ½-hr soaking at 1700 °C	10.40	0.5% Ni powder added; no bloating; 2 pellets used.
P-14-a	H ₂ ; ½-hr soaking at 1700 °C	9.94	Additions: (SiO ₂ 0.6% (all in the (MgCO ₃ 0.15% same (CuO 0.07% sample) (V ₂ O ₅ 0.2% (Ni 0.5% no bloating

Series (4)

It will be seen from Table 9 that the addition to a uranium oxide of normal sintering behaviour, of small quantities of certain impurities which could conceivably be present in the U.B.C. materials, produced no bloating on sintering. The

impurities were chosen on the basis of the results of the chemical analyses reported on page 8. It should be noted, however, that the state of chemical combination of the impurities could be an important factor in determining their effect insofar as bloating behaviour is concerned, and no account has been taken of this factor.

(2) Description of Bloating Phenomenon

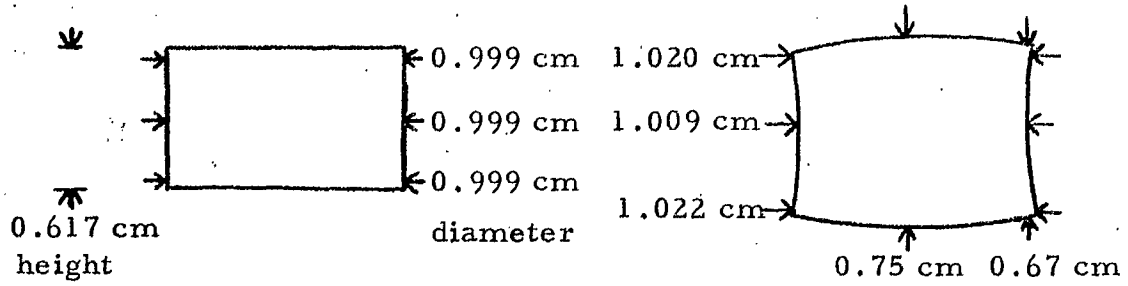
A pellet sintered at 1500°C in hydrogen (Series (2), Batch #D-57) was re-fired to 1700°C in H₂. The dimensions of the pellet before and after firing to 1700° are shown in Figure 1 (see page 18). The expansion of the pellet between 1500° and 1700°C is probably due to the decomposition of some impurity, with the production of a gas which, unable to diffuse out of the sintered or partly sintered pellet, caused the pellet to bloat.

Most of the voids in the bloated pellets appear to be lamellar in form and parallel to the end of the pellet; i.e. perpendicular to the direction of force during pressing. There was no evidence of a liquid phase having been present at the temperature of bloating.

DISCUSSION

The air permeability results given in Table 1 indicate that most of the powders probably possess small particle size and high surface area, and, hence, would be expected to sinter to good

FIGURE 1



Dimensions of pellet after
1500°C firing and before
1700°C firing

Dimensions of pellet after
1700°C firing

(UO₂ Batch No. D-57)

densities. The B.E.T. experiments performed at the University of British Columbia confirm the high surface areas (see Appendix II, page 27). The attainment of densities over 10.0 g/cm^3 on several occasions shows that good densities can be achieved using powders produced by the precipitation technique developed at U.B.C. This is particularly true of the most recent sample, "UO_{2.022}".

The bloating observed with many of these powders on sintering appears to be due to the release of some gas and not to be an inherent property of uranium dioxide as such. The nature of the impurity which gives rise to this gas remains obscure. However, it has been found possible to change the procedure used in precipitating the uranium oxide in order to overcome the difficulty of bloating (see Appendix II, page 27).

The discrepancy between the O/U atomic ratios, as determined by oxidation and as determined by reduction, could be attributed to the presence of some impurity which undergoes oxidation or reduction during the determinations. The presence of a relatively small quantity of such an impurity could make appreciable differences in the resulting O/U ratios. The presence of small amounts of foreign substances in the uranium oxide are indicated by the analyses given in Table 3; these, however, do not appear to account for the bloating or the O/U atomic ratio discrepancies.

REFERENCES

1. Bright, N.F.H., "The Investigation of Certain Uranium Oxide Samples Produced at the University of British Columbia, Vancouver, by Hydrometallurgical Techniques". Mines Branch Investigation Report IR 58-8, January 24, 1958.
2. Bright, N.F.H., K. V. Gow, and A. T. Prince, "Factors Influencing the Sintering Properties of Uranium Dioxide for Use in Nuclear Reactor Fuel Elements". Mines Branch Research Report No. MD209, September 1956.
3. Bright, N.F.H., L. G. Ripley, J. F. Rowland, and R. H. Lake, "The Determination of the Oxygen-Uranium Atomic Ratio in Non-Stoichiometric Uranium Dioxide and other Oxides of Uranium". Mines Branch Research Report No. MD207, July 1956.

(Appendices I, II, and III)
(follow on pages 21 to 46.)

AHW:NFB:CL

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APPENDIX I

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

Department of Mining
and Metallurgy

September 10th, 1958.

Mr. A. Thunaes,
Eldorado Mining and Refining Limited,
P.O. Box 379,
OTTAWA, Canada.

Dear Arvid:

I enclose two copies of Progress Report No. 2 by I. H. Warren on the Production of Reactor Grade Uranium Oxide by Pressure Reduction of Aqueous Solutions of Uranium, covering work done to the end of August.

The work has progressed rather more rapidly than we had anticipated and has, I think, provided some interesting and useful data. Possibly the most significant result is that it now appears to be possible to produce quite readily a uranium oxide having a U/O ratio of 1/1.75 using a nickel gauze catalyst. By using suitable techniques in the initial stage of the operation the resulting uranium oxide can be prepared with high purity, containing barely detectable amounts of nickel. When purified ADU is used as a starting material the only other impurity in the $UO_{1.75}$ would be H_2O and CO_2 in the order of about 1%. There is some prospect of controlling the particle size but this has not been fully established.

If you wish to have samples of the uranium oxide product for sintering or other tests, 100-gram lots can be readily and quickly prepared in the laboratory autoclave. We would like to know which U/O ratio you would prefer. It would be a simple matter to prepare a U/O of 1/2.0 and another U/O of 1/1.75 should you wish to compare them.

Also, within a few days we will have the equipment set up to produce samples of uranium oxide of as much as 1000 gm, with

controlled U/O ratio in the above range. The particle size is as yet uncertain--it may be different in the larger lots. If you wish to have amounts of this magnitude we will require a further 10 lbs. of purified ADU. Upon receipt of this material production of the uranium oxide will require a week or two but should not present any difficulties.

I gather from my associates here that the low oxygen (1.75) variety of uranium oxide might well have interesting properties in respect of sintering and, perhaps, reaction with containers, in view of the possibility that a lattice defect structure deficient in oxygen should behave differently from a stoichiometric or oxygen-rich material in that in the low oxygen material diffusion may take place by movement of oxygen atoms rather than uranium atoms.

I look forward to having your comments and advice on this matter. I expect to be in Ottawa September 22nd and hope I may see you at that time.

Sincerely,

(sgd.) F. A. FORWARD.

FAF/DC
Encl.

cc. J. Convey
W. M. Campbell
I. H. Warren

COPY

THE PRODUCTION OF REACTOR GRADE URANIUM OXIDE
BY PRESSURE REDUCTION OF AQUEOUS SOLUTIONS OF URANIUM

I. H. Warren

Report No. 2 - August, 1958

Introduction

The work described in this report is concerned with studies of the reduction of solutions (and suspensions) of uranyl carbonate with compressed hydrogen. The reasons for selecting for study the reduction of uranium in combination with carbonic acid have been stated in Report No. 1. The possibility of using such combination of uranium followed from the observation that uranium trioxide could be dissolved in carbonic acid at room temperature and atmospheric pressure.

Materials

Uranium trioxide used in the majority of these experiments was prepared from ADU supplied by Eldorado Mining and Refining Limited. Nickel powder catalyst was from Sherritt Gordon and nickel gauze catalyst from Newark Wire Cloth Company.

Procedure

Experimental technique was continuously modified during the course of the experiments as results of various experiments were analysed. The procedures outlined below are described in the sequence in which they were developed.

- (a) For initial experiments, slurries of uranium trioxide of volume 2 litres containing 6 g uranium were gassed with carbon dioxide at room temperature and pressure. To the resulting yellow solution, 5 g of 120 micron nickel powder were added and the solution treated under carbon dioxide and hydrogen pressures at various temperatures in a glass-lined autoclave. The uranium oxides produced were separated from the nickel powder by decantation, centrifuged and then dried at 60°C in a vacuum oven. The oxygen/uranium ratios of the products were then determined by the high temperature oxidation technique (1).

- (b) Similar experiments to those above were run, using a nickel gauze catalyst of 10 mesh per inch 0.025 wire, size 13" x 7".
- (c) Studies of the behaviour of uranyl carbonate under various temperatures and pressures of carbon dioxide showed that in all previous experiments uranyl carbonate must have been present primarily in the form of a slurry during the reductions. Accordingly, slurries of uranyl carbonate of concentration 25 g U/litre were made up by carbonating uranium trioxide slurries under 100 psi carbon dioxide pressure at room temperature. These slurries were then reduced using procedures as in (b) above.
- (d) Analyses for nickel in the uranium oxides produced showed that using gauze catalyst approximately 0.2% Ni was present. This nickel was found to be brought into the product during the warm-up period of the experiments. This nickel contamination was eliminated by bringing the catalyst in the presence of water to operating temperature (210°C for all these experiments) under carbon dioxide and hydrogen; on reaching operating temperature a concentrated slurry of uranyl carbonate was then added and reduction performed.
- (e) During most of the more advanced experiments samples of the oxides were withdrawn from the reaction, dissolved in hot concentrated sulphuric acid and analysed for U^{4+} and U^{6+} by titration procedure with potassium permanganate. This method could, of course, be used for production control to a specified U/O ratio.

Results

The high temperature oxidation analytical technique for the U/O ratio was checked both against a Mines Branch analysis, and for reproducibility. The results obtained are shown in Table 1.

TABLE 1

High Temperature Oxidation U/O Analysis Results

Springfields Oxide (Our analysis)				Mines Branch Analysis
Experiment 1	UO _{2.0474}	0.228% H ₂ O	0.032% CO ₂	UO _{2.048}
Experiment 2	UO _{2.0495}	0.195% H ₂ O	0.038% CO ₂	
Product Analysis				
Experiment 1	UO _{2.255}	0.73% H ₂ O	0.18% CO ₂	
Experiment 2	UO _{2.267}	0.72% H ₂ O	0.18% CO ₂	

The results obtained using nickel powder catalyst and the results of over 50 experiments using nickel gauze catalyst will be shown in a later appendix to this report. Results shown in Table 2 below are typical of those obtained by reducing 2 litres of uranyl carbonate slurry of concentration 25 g U/litre under 100 psi CO₂ pressure and 400 psi H₂ pressure. The oxides produced in these experiments were found to be particles in suspension quite free from the catalyst surface.

TABLE 2

Analyses of Uranium Oxides Produced at 210°C

using procedure (c) outlined above

Time from Start of Reduction	O/U Ratio	% H ₂ O	% CO ₂ ^A	% Ni
2 hours	2.25	0.82	(not greater)	0.14
4 hours	1.89	1.42	(than 0.5)	0.06
6 hours	1.76	1.5	1.5	0.13

^A Note: For reasons yet unknown the 6-hour material invariably had higher carbon dioxide content than the 2-hour. Improved flushing techniques at the end of the experiment are being examined with a view to reducing these carbon dioxide contents.

Using procedure (d) as already outlined, no nickel could be detected by standard chemical procedures in the oxides produced.

Powder X-ray photographs of the oxides in the range $\text{UO}_{2.0}$ to $\text{UO}_{2.2}$ confirmed their simple composition.

Conclusions

It has been shown that slurries of uranyl carbonate may be rapidly reduced at a nickel gauze catalyst to produce uranium oxides of high purity. The oxides are produced in suspensions quite free from the catalyst, and may have an oxygen/uranium ratio as low as at least 1.75 to 1. The procedure may be applied to produce, by batch operation, slurries of high concentrations of these oxides.

Future Programme

It is proposed to next examine the surface area of the uranium oxides produced by this carbonic acid/hydrogen technique and to obtain evaluations of the properties of the various oxides in the sintered states.

References

- (1) The Determination of the O/U Ratio in Uranium Oxides. Mines Branch, July 1956, N. F. H. Bright et al.

COPY

APPENDIX II
THE UNIVERSITY OF BRITISH COLUMBIA
VANCOUVER 8, CANADA

Department of Mining
and Metallurgy

February 4th, 1959.

Mr. A. Thunaes,
Eldorado Mining and Refining Ltd.,
P.O. Box 379,
OTTAWA, Canada.

Dear Arvid:

Please find enclosed a copy of Progress Report No. 3 on "The Production of Reactor Grade Uranium Oxide by Pressure Reduction of Aqueous Solutions of Uranium", covering the period ending January 31, 1959.

The results of studies of reaction mechanism, O/U ratio control and particle size control are given in the report. We are quite confident that we can produce readily and reproducibly uranium oxide with any specified O/U ratio between 2.66 and 1.75 with any specified particle size between 2.0 and 20.0 square meters per gram. Also we believe we can make reproducibly UO_2 compacts having a density, sintered in H_2 at $1700^\circ C$, of 10.6 which is 97% of theoretical density. There is some indication that a substantially similar density can be obtained by sintering at $1400^\circ C$.

We look forward to further close collaboration with Eldorado, the Mines Branch, and Chalk River in this project.

Sincerely,

(sgd.) F. A. FORWARD.

FAF/DC

Encl.

cc. W. M. Campbell

E. B. Spice

J. Convey

COPY

THE PRODUCTION OF REACTOR GRADE URANIUM OXIDE
BY PRESSURE REDUCTION OF AQUEOUS SOLUTIONS OF URANIUM

I. H. Warren

January 31, 1959

Report No. 3: A Review of the Present State of Research
with Suggestions for Future Work

Introduction

Two earlier reports have described preliminary work concerned with the production of uranium oxides by catalytic reduction with hydrogen of uranyl carbonate slurries. Over the past few months investigation of this proposed process has been continued. During this time attention has been given to the following topics:

- (a) Determination of the surface areas of uranium oxides produced by the process and investigation of possible methods of varying their surface area.
- (b) Production of uranium oxides with low nickel contents.
- (c) Examination of the kinetics of the production of the uranium oxides, with a view to determining the mechanism of the reduction and precipitation processes involved.
- (d) Determination of the sintering behaviour of some typical uranium oxides produced by the process.

During November approximately 400 gms of uranium oxide was prepared and sent to the Mines Branch, Ottawa, for comparison of analytical results and evaluation of sintering properties. Two problems arose from work on these samples. Firstly, a discrepancy of 0.1 oxygen was found to exist between U.B.C. analyses and Mines Branch analyses on the oxygen/uranium ratios of the samples. As may be seen from Table 1 it has now been established that the difference arose through employment of different methods of determination at each location. Analyses by the "oxidation" method at each location agree well. The reason for the existence of the discrepancy between results given by the two methods is being examined at the Mines Branch.

TABLE 1

Comparison of Oxygen/Uranium Ratios of Uranium Oxides at
U.B.C. and Mines Branch, Ottawa

Sample 1

U.B.C. Oxidation Method	Ottawa Reduction Method	U.B.C. Oxidation Method	Ottawa Oxidation Method	Ottawa Reduction Method
O/U 2.009	2.123	2.067	2.077	2.159
CO ₂ 0.09%	0.061%	0.195%	0.24%	0.11
H ₂ O 0.49%	0.43%	0.95%	0.88%	0.76

The second problem which arose from the Mines Branch investigation was that compacts of the uranium oxides deformed and bloated on sintering. This problem is considered further in the section (d) below on sintering investigations.

The present status of work on the four topics (a) to (d) enumerated above is now considered.

(a) Surface Area of the Uranium Oxides

To determine the surface areas of the various samples a single form of the B.E.T. apparatus has been constructed. As may be seen from Table 2 results obtained with this apparatus agree well with those obtained by other workers.

TABLE 2

Comparison of Surface Areas of Uranium Oxides as Determined at
U.B.C. and Carleton University, Ottawa

Samples	Surface Area, U.B.C.	Surface Area, Ottawa
A	0.40 sq.metre/gm	0.62 sq.metre/gm
B	5.11 " " "	5.58 " " "
C	1.78 " " "	1.97 " " "
D	0.89 " " "	1.06 " " "
E	1.27 " " "	1.09 " " "

The surface areas of uranium oxides produced by reducing slurries of uranyl carbonates of concentration 25 gms uranyl carbonate per litre at 210 °C using a nickel catalyst gauze of area 90 sq. inches, were found to be between 4 and 5 sq. metres/gm.

By the addition of small quantities of ammonia (up to 0.5 gm NH_3 per litre of slurry) at the start of the reduction, it was found that the surface area of the product could be carried over wide limits. The results of three series of experiments with such additions are shown in Table 3.

TABLE 3

Effect of Ammonia Addition on Surface Area of Uranium Oxides

Ammonia addition gms NH_3 /litre	Surface area sq.metres/gm
0	4.2
0	4.8
0	4.7
0.25	6.5
0.25	9.2
0.25	6.8
0.50	14.4
0.50	18.1

It is believed that the effect of ammonia is to limit the solubility of U^{4+} ions in solutions--with increase of ammonia concentration the solubility of U^{4+} decreases and the chances of a U^{4+} ion finding a UO_2 nuclei before precipitating decrease. Further work has shown that some change in surface area may be also effected by change in the partial pressure of carbon dioxide during reduction.

(b) Production of Uranium Oxides with Low Nickel Content!

This aspect of the problem has presented some difficulty. By the use of a polarographic method for nickel analysis it has been shown that the lowest nickel content oxide produced so far has contained 0.03% Ni (300 p.p.m.). This result is in contradiction to earlier results reported, when under certain conditions of reduction, no nickel was reported in the oxides produced. Considerable attention has been given to prevention of dissolution of the nickel gauze catalyst and it has been found that this problem is inseparable to a large degree from problems associated with the rate of production of the oxide. This will become apparent on consideration of the work outlined in section (c) below.

(c) Examination of the Kinetics of Production of the Uranium Oxides

In this work slurries of uranyl carbonate were made by carbonating nuclear pure uranium trioxide with carbon dioxide at 100 psi pressure for 1 hour at 130°C. In this way at least 95% conversion of the oxide to UO_2CO_3 was ensured. Three series of experiments were then run with these slurries.

Series I

The slurries of uranyl carbonate were placed in the autoclave with the required area of nickel gauze present, 100 psi of carbon dioxide pressure was added and the autoclave brought to 210°C. At this temperature the overpressure of hydrogen (400 psi) was added and reduction performed.

Series II

Water, sufficient to cover the catalyst gauze, was placed in the autoclave which was then brought to 210°C; again, under 100 psi carbon dioxide pressure. At this temperature hydrogen overpressure (400 psi) was added, concentrated uranyl carbonate slurry injected and reduction performed.

Series III

As for Series II, except that the water and catalyst were brought to operating temperature under 100 psi hydrogen pressure, followed by addition of carbon dioxide overpressure and injection of concentrated uranyl carbonate slurry.

The nickel contents of uranium oxides produced by using these three warm-up techniques are shown in Table 4.

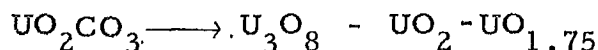
TABLE 4

Nickel Contents of Uranium Oxides. Autoclave Load 50 gm
Uranium Oxide

	Present at warm-up	% Ni
Series I	$\text{H}_2\text{O} + \text{CO}_2 + \text{UO}_2\text{CO}_3$	0.2 - 0.5
Series II	$\text{H}_2\text{O} + \text{CO}_2$	0.05 - 0.1
Series III	$\text{H}_2\text{O} + \text{H}_2$	0.03 - 0.05

In addition to the "warm-up" procedure determining nickel content of the produced oxides, it was also found that the "warm-up" procedure drastically affected the rate of reduction. This effect is clearly shown in Graph I. (See page 34)

By X-ray analysis of the solid contents of the autoclave during a reduction experiment using any of the three "warm-up" techniques, it has been shown that the reduction proceeds stepwise as below.



It appeared from this X-ray work and the nature of the plots in the Graph on page 34, that the "warm-up" procedure determined the rate of reduction of U_3O_8 to UO_2 .

It has now been shown that the increased rate of reduction U_3O_8 to UO_2 obtained by using the Series I or II "warm-up" procedures instead of Series III may be simulated by the addition of a trace of formaldehyde or better glycolaldehyde to the slurry containing U_3O_8 .

The effect of additions of formaldehyde on the rate of reduction $\text{UO}_2 \longrightarrow \text{UO}_{1.75}$ has not been investigated. This and other aspects of the formaldehyde addition are now being examined.

(d) Determination of the Sintering Behaviour of Some Typical Uranium Oxides Produced by the Process

A brief examination has been made of the sintering behaviour up to 1400°C in an atmosphere of argon, of some uranium oxides produced by reduction using Series I to III "warm-up" procedures.

In agreement with work at Ottawa "bloating" has been found with material made using Series I procedure, yielding oxides containing relatively large amounts of nickel. However, two argon atmosphere sinters on material made using Series II procedure--containing 0.05% nickel--have given unbloated and undeformed compacts with a density of 10.75 gms/cc. When one of these compacts was reduced in hydrogen at 1700°C at Ottawa the density became 10.6 gm/cc, that is, 97% of the theoretical density of $\text{UO}_{2.0}$.

Conclusions

It is now evident that the process of reducing uranyl carbonate slurries with hydrogen in the presence of compressed carbon dioxide and a catalyst will yield material having a specified O/U ratio, a specified surface area, and specified purity for sintering to dense uranium oxide.

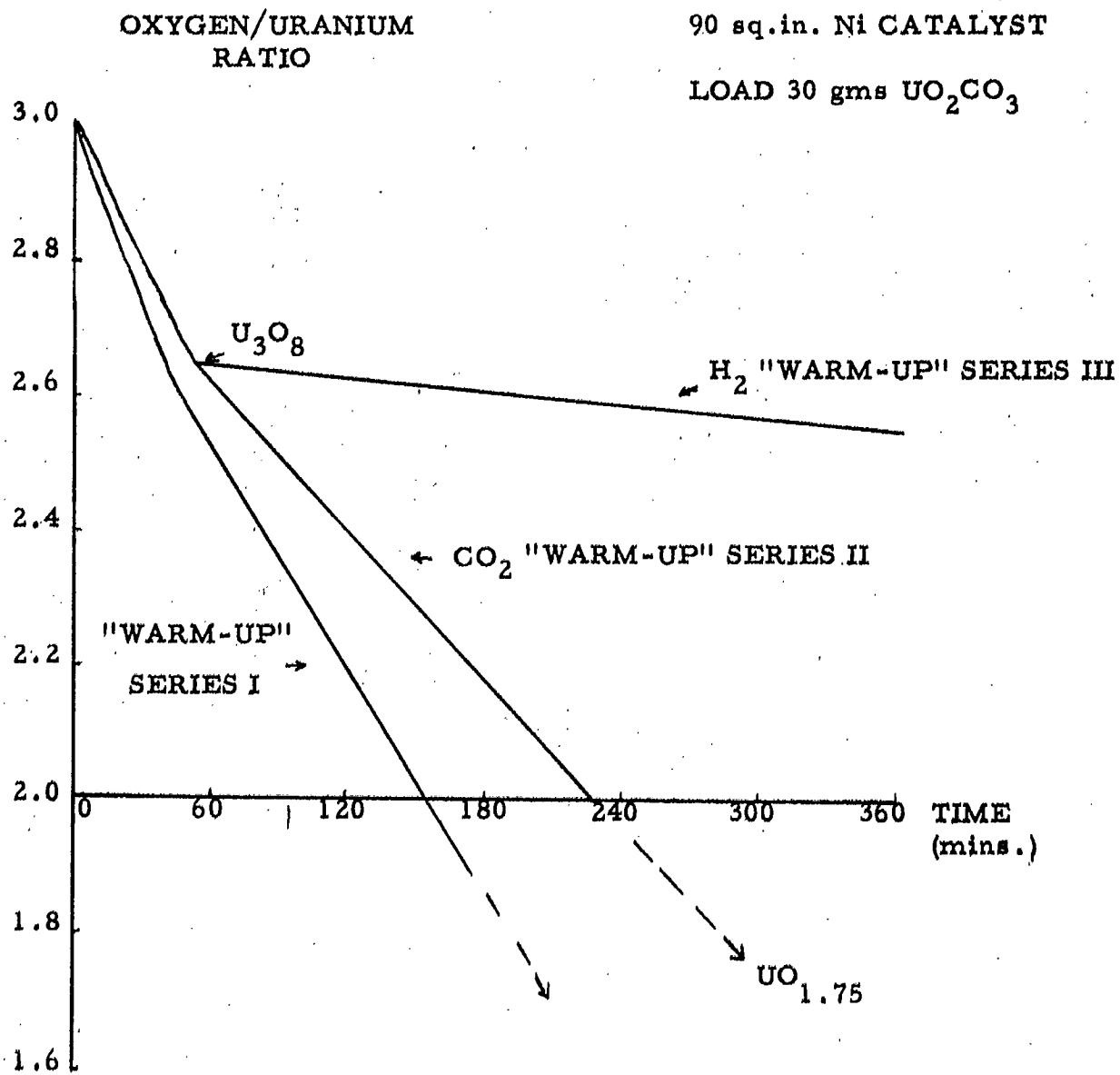
Future Work

It is proposed in the forthcoming months to investigate fully the kinetics and mechanism of this proposed uranyl carbonate process for producing uranium oxide. The effect of formaldehyde presumably on the rate of solution of U_3O_8 is of particular interest in other fields.

Also it is proposed to examine the use of platinum catalysts in the reduction process.

Considerable work on the sintering of compacts of various samples, particularly of mixed particle size, is also planned.

In the long run it is proposed to examine the feasibility of integrating the process into the present purification process for uranium. At the moment uranium trioxide is the starting material for the preparation of uranyl carbonate, but it seems possible that uranyl carbonate might be obtainable by some type of carbonate strip from the organic extraction process.



COPY

555 Booth Street,
25 February 1959.

Professor F. A. Forward,
Department of Mining and Metallurgy,
University of British Columbia,
Vancouver 8, British Columbia.

Dear Professor Forward:

I thank you for the copy of your letter to Mr. Thunaes, dated February 4th, 1959, with the accompanying Progress Report No. 3, entitled "The Production of Reactor Grade Uranium Oxide by Pressure Reduction of Aqueous Solutions of Uranium", and prepared by Dr. I. H. Warren.

This Progress Report has been passed to Dr. Norman F. H. Bright and Dr. A. H. Webster of the Crystal Chemistry Section of our Mineral Dressing and Process Metallurgy Division, who are interested in this field of activity and they will be submitting their comments to you in a separate communication.

We thank you for keeping us posted as to the progress of this very interesting research and we wish you and your colleagues every success therein.

Yours sincerely,

(sgd.) John Convey,
Director,
Mines Branch.

COPY

Division of
Mineral Dressing
and
Process Metallurgy

552 Booth Street,
2 March 1959.

Professor F. A. Forward,
Department of Mining and Metallurgy,
University of British Columbia,
Vancouver 8, B.C.

Dear Professor Forward:

The Progress Report No. 3 on "The Production of Reactor Grade Uranium Oxide by Pressure Reduction of Aqueous Solutions of Uranium", covering the period ending January 31st, 1959, and prepared by Dr. Ian H. Warren has been passed by Dr. Convey to Dr. Webster and myself for comments. We find the continued progress of this project very interesting and it certainly appears possible to produce a wide variety of UO_2 -type products by your techniques.

As you know, we have been collaborating quite closely with Dr. Warren on certain aspects of this work and, indeed, received another sample from him for examination, just at the end of last week.

Your findings given in Table 3, depicting the variation in surface area of the resultant UO_2 with the addition of ammonia to the slurry to be reduced give a nice parallel to the experience of ourselves and the people at A.E.C.L., Chalk River on the preparation of ammonium diuranate. We found that with increasing pH, the ADU that was produced gave, on reduction, a uranium dioxide which had progressively better sintering properties and thus, presumably, greater surface area. We experienced an optimum condition at $pH = 10$; I wonder whether any such optimum was obtained in Dr. Warren's work. Incidentally, it is reassuring to see the good agreement in surface area determinations between your figures and those obtained for us by Prof. J. M. Holmes at Carleton University, Ottawa.

We are intrigued by your claim of the stepwise nature of the reduction:-



We have never encountered any sub-stoichiometric uranium dioxide in our work nor have we heard of any anhydrous material containing the uranium in a substantiated net valency state lower than four. I wonder if your " $\text{UO}_{1.75}$ " contains some hydrated $\text{U}(\text{OH})_3$, which is, I believe, a compound known to exist under certain conditions, but which has, to the best of my knowledge, never been dehydrated to give U_2O_3 or $\text{UO}_{1.5}$. You claim that the presence of $\text{UO}_{1.75}$ has been confirmed by X-ray analysis. This interests us greatly, as, in our experience, most of your earlier samples submitted to us for examination were insufficiently well crystallized for any precise determination of the U:O atomic ratio from the X-ray diffraction pattern to be obtainable. If you have obtained such a material with a sharply defined X-ray diffraction pattern, this represents a real and very interesting advance in our knowledge of the crystallography of " UO_2 ". We would be most interested to receive a sample of this highly sub-stoichiometric material for examination ourselves, and to augment our library of standard X-ray diffraction patterns.

The problem of bloating of the compacts on sintering is certainly a difficult one, and, in spite of a considerable amount of work, we have not, as yet, succeeded in pin-pointing the cause of the trouble. The presence of nickel in the compact is not, of itself, the root of the trouble, as we have incorporated quite high proportions of fine nickel metal (about 0.5%) in the compacts without obtaining any bloating on sintering.

We are in process of writing up the work that we have been doing on this and other problems on Dr. Warren's behalf and hope to submit copies to you in the not too far distant future.

Dr. Webster and I send sincere personal regards to Dr. Warren, Dr. Wiles and yourself, and we look forward to seeing you during your next visit to Ottawa.

Yours very sincerely,

(sgd.) Norman F. H. Bright,
Head,
Physical and Crystal
Chemistry Section.

COPY

APPENDIX III

THE UNIVERSITY OF BRITISH COLUMBIA
VANCOUVER 8, CANADA

Department of Mining
and Metallurgy

April 28th, 1959.

Dr. N. F. H. Bright,
Mineral Dressing and
Process Metallurgy Division,
Mines Branch,
Department of Mines and
Technical Surveys,
552 Booth Street,
OTTAWA, Canada.

Dear Norman:

I must apologize for being so tardy in replying to your last letter and, also, to your comments on my last report to Professor Forward.

We have been very actively looking into the problem of the organic material synthesized in our "CO₂ warm ups" and, although we have not identified this, we have found a material which functions about as well--it is anthraquinone. Using this material, we can produce at high speed, UO₂ with very low nickel content. I am enclosing a copy of our latest report (No. 4), and under separate cover sending you a sample of UO₂ produced by this method of using anthraquinone as a "promoter". I shall be very interested to receive your comments on this material.

I am now looking fully into this business of O/U ratios below 2.0 and will be in touch with you again as soon as I have some more information and samples.

I don't think we have much to worry about with our UO_{2.0} material now, apart from a bit of surface area control with small ammonia additions to increase the surface area a bit.

Many thanks for your comments and help, and looking forward to hearing your evaluation of this new material.

Best regards,

(sgd.) I. H. Warren.

IHW/DC
Encl.

COPY

THE PRODUCTION OF REACTOR GRADE URANIUM OXIDE
BY PRESSURE REDUCTION OF AQUEOUS SOLUTIONS OF URANIUM

I. H. Warren

April 28, 1959

Report No. 4Introduction

The last report on this work described the finding of differences in the rate of reduction of uranyl carbonate slurries, depending on which one of three "warm up" techniques was used. Correlated with these differences were differences in nickel contents of the products--high rate of reduction yielding a high nickel content product. The differences in rate were mainly evident in the second stage of the reduction, when U_3O_8 was being reduced to UO_2 . During the past three months an extensive investigation has been made into why these differences existed. The ultimate objective of the investigation was to find a method of operation that would yield a high rate of reduction and a low nickel content product. As will be seen from this report, this objective has been achieved.

Experimental

A hypothesis advanced to explain the differences observed was that during a "carbon dioxide warm up" (Series II, Report 3), an organic material was being formed which served at a later stage in the reduction as a powerful solvent for U_3O_8 . Attempts to identify this organic material were made by concentrating by vacuum evaporation, solutions produced by heating carbonated water under pressure with nickel catalyst. The concentrated solutions thus produced gave reactions, on testing with organic spot reagents, that were characteristic of a carbohydrate or hydroxy-carboxylic acid. Glycollic acid and possibly glyoxilic acid were identified in the concentrate by paper chromatography. The concentrate, freed from any nickel, was also found to decolourise permanganate and bromine water. Preparation of a benzimidazole derivative from a portion of the concentrate gave an infra-red spectra which showed the possible presence of a furane ring.

With these results in mind, a series of experiments was run in which Series III warm up procedure was followed--water and nickel catalyst were brought to operating temperature (210°C) under 100 psi

hydrogen pressure, 100 psi of carbon dioxide pressure was then added, followed by injection of a uranyl carbonate slurry, and "topping up" with hydrogen to 950 psi total pressure. When the rate of reduction had slowed down (U_3O_8 stage), solutions containing small amounts of various organic materials were added and the rate of reduction again checked. The additions made, with the results obtained, are shown in Table 1. In each case additions were made to two litres of slurry containing 25 gm. "uranyl" uranium.

TABLE 1

Effect of Additions of 0.05 gm. of Organic Materials
on Rate of Reduction of U_3O_8 Slurries to UO_2

<u>Addition</u>	<u>Effect</u>
Formic acid)	Increased rate same amount but not as much as CO_2 "warm up"
Oxalic acid)	
Acetic acid	Very slight increase in rate
Glycollic acid	No effect
Glyoxilic acid	No effect
Glyceric acid	No effect
Gluconic acid	No effect, but produced excellent settling in final slurry
Sachàric acid	No effect
Tartaric acid	Increase same as for formic acid, also with excellent settling
Furoic acid	No effect
Tartronic acid	No effect
Hydroxy-tartaric acid	Slight increase in rate
Salicylic acid	No effect
Citric acid	No effect
Formaldehyde	First experiment increased rate, but not reproducible
Glycolaldehyde	Increased same as for formic acid
Methanol	No effect
Glycol	No effect
Glycerol	No effect

The only obvious deduction to be made from these experiments was that many of the materials which were known complexing agents for uranium had no effect on the rate of reduction.

At this point in the investigation, information was received that Sherritt Gordon were using anthraquinone as a catalyst in the reduction of nickel. It also seemed feasible, since it now appeared unlikely that uranium could be dissolved from U_3O_8 , reduced at the nickel gauze, and then reprecipitated as UO_2 , that the material being produced in the CO_2 "warm up" might be a hydrogen "carrier" and was reducing U_3O_8 to UO_2 in situ. With this in mind, firstly hydroquinone, and then anthraquinone were added to a partially reduced uranyl carbonate slurry. Hydroquinone was without effect--as would be expected since quinone is a better oxidizing agent than the uranyl ion; anthraquinone, however, dramatically increased the rate of reduction--giving a rate eight times as fast as with no anthraquinone, and also yielded a low nickel product which settled readily. The effect of additions of other hydrogen carriers has been briefly examined--alizarin, anthraquinone-sulphonic acid, and ascorbic acid. All of these increase the rate, although not quite so effectively as anthraquinone itself. The effect of ascorbic acid is interesting--it could lend support to a theory that the material produced in the CO_2 warm up was an unsaturated diketone, possibly with some type of sugar structure.

When the effect of anthraquinone had been established, the production of a bulk quantity of UO_2 was started. For this task 210 sq. in. of nickel gauze were used, with an autoclave loading of 3 litres. The autoclave was brought to operating temperature ($210^\circ C$) under hydrogen, and 60 gms. uranyl uranium added as uranyl carbonate, together with 0.05 gm. anthraquinone. At five-hour intervals after this, 500 mls. of slurry were withdrawn and further uranyl carbonate added, together with further anthraquinone at the rate of 0.05 gm. anthraquinone per 100 gms. uranyl uranium. Two experiments were performed in this way, in the first 240 gm. of UO_2 were produced, and in the second 360 gms. For the first experiment the autoclave was run continuously for 24 hours, and in the second 36 hours, thus giving a rate of production of 10 gm. UO_2 per hour. At the end of both experiments the nickel gauzes were as clean and bright as at the start of the experiments.

The analysis of the bulked product of the two runs is shown in Table 2.

TABLE 2Analysis of Bulk Uranium Dioxide

O/U Ratio	2.022
% CO ₂	0.29
% H ₂ O	0.36
% Ni	0.02
Surface Area	2.22 square metres per gm.

Material from a single precipitation experiment with 60 gms. uranyl uranium had a nickel content of 0.014% and a surface area of 2.86 square metres per gm. Material from the bulk experiment and the single experiment, when compressed into pellets and sintered for two hours at 1700 °C in hydrogen, yielded pellets having densities of 10.42 and 10.46 grams per cc. respectively.

Conclusions

It has been shown that the addition of small quantities of a hydrogen carrier such as anthraquinone to slurries of uranyl carbonate greatly increases their rate of reduction at high temperatures in the presence of a nickel catalyst. The product from such a reduction has a nickel content of 0.02% or below, and sinters to high density uranium dioxide.

Future Work

It is proposed in the next three months to investigate more fully the effects of anthraquinone and its derivatives (such as amino anthraquinone) on the reduction process. The effect of these reagents on possible reduction below an O/U ratio of 2.0 will also be investigated, together with the sintering behaviour of the products. After this work, attention will be given to experiments with carbon dioxide stripping of uranium from organic solvents.

COPY

Division of
Mineral Dressing
and
Process Metallurgy

552 Booth Street,
12 May 1959.

Dr. I. H. Warren,
Department of Mining and Metallurgy,
University of British Columbia,
Vancouver 8, B.C.

Dear Ian:

We have examined your sample labelled "UO_{2.022}" which we received on April 30th along with a copy of your Progress Report No. 4. The pellets unfortunately spalled and "capped" on sintering, but gave good sintered densities as determined by the displacement of water. This spalling of the compacts on firing would be a disadvantage if it occurred frequently with this new type of powder, and could not be overcome by some modification of fabrication procedure. There were no signs of bloating with the compacts made from this material.

The detailed results obtained in tests on the present sample were as follows:-

A. Sintering

Pellet No.	Green Density - g/cm ³ (by weight and measurement)	Sintered Density - g/cm ³ (by displacement of water)
1	6.24	10.54
2	6.27	10.63

Pellets fired to 1700°C with soaking for 30 minutes in H₂.

Pellets spalled and capped on firing.

B. Chemical Analyses

	Ottawa Results		U.B.C. Results
	By H ₂ reduction	By oxidation	
Moisture	0.31%	0.39%	0.36%
CO ₂	0.20%	0.21%	0.29%
O/U ratio	2.068	2.065	2.022
Ni		0.01%	0.02%

Our results for the O/U ratio are, as usual, rather higher than yours. The results obtained by the oxidation and reduction methods agree well with each other. Since our O/U ratio results are always somewhat higher than yours, it may be that some traces of oxygen obtain access to the sample at some stage of handling and shipping, thereby increasing the O/U ratio.

C. Air Permeability

Blaine Number in arbitrary units = 68

D. Differential Thermal Analysis

1st exothermic peak 218°C
 2nd " " 366°C
 Peak separation 148 degs. C

The air permeability and D.T.A. results are consistent with a relatively low surface area, as indicated by your B.E.T. measurements, viz., 2.22 square metres per gram (see Mines Branch Research Report MD 209).

We thank you for your very interesting progress reports. The anthraquinone procedure seems to be a neat method of catalysing the hydrogen reduction.

We may be doing a few more tests on this material with a view to investigating the spalling, and shall be glad to examine any further samples you may send.

We have almost completed writing up a report incorporating all our recent work on your samples and copies of this should be in your hands in the near future.

With best regards.

Yours sincerely,

(sgd.) Norman F. H. Bright,
Head, Physical and Crystal
Chemistry Section.