

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.

~~FOR OFFICIAL USE ONLY~~

W. A. H. Webster

**Declassified
Déclassifié**

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION IR 58-8

THE INVESTIGATION OF CERTAIN URANIUM OXIDE SAMPLES
PRODUCED AT THE UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER, BY HYDROMETALLURGICAL TECHNIQUES

by

NORMAN. F. H. BRIGHT

MINERAL DRESSING AND PROCESS METALLURGY DIVISION

COPY NO. 5

JANUARY 24, 1958

IR 58-8

Declassified
Déclassifié

~~For Official Use Only~~

Mines Branch Investigation Report IR 58-8

THE INVESTIGATION OF CERTAIN URANIUM OXIDE SAMPLES
PRODUCED AT THE UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER, BY HYDROMETALLURGICAL TECHNIQUES

by

Norman F. H. Bright*

SUMMARY OF RESULTS

Two batches of uranium oxide prepared in the Department of Mining and Metallurgy of the University of British Columbia by hydrogen reduction of an aqueous solution of a uranyl salt under pressure using fine nickel as catalyst, have been shown to have the composition $UO_{2.5}$ to $UO_{2.6}$ and to contain numerous impurities in various levels of concentration.

The samples, when compressed and sintered in hydrogen at $1700^{\circ}C$, gave compacts of density approximately 9.6 g/cm^3 .

*

Head, Physical and Crystal Chemistry Section, Mineral Dressing and Process Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa.

Table of Contents

	<u>Page</u>
Summary of Results	i
Introduction	1
Experimental	3
Techniques	3
Results	4
a) Differential Thermal Analysis	4
b) X-Ray Diffraction Examination	9
c) Spectrographic Examination	10
d) Determination of Green and Sintered Densities	11
e) Chemical Analysis for Selected Elements	13
f) Determination of the Oxygen/Uranium Atomic Ratio	15
Discussion	22
References	24
Appendices I to VII	25-48

Declassified
Déclassifié

~~For Official Use Only~~

INTRODUCTION

While the author of the present report was in Western Canada during the summer of 1957, he had the opportunity of visiting the Department of Mining and Metallurgy of the University of British Columbia, Vancouver, B. C., and discussing with Professor F. A. Forward, Head of that Department, and Dr. D. R. Wiles, Lecturer, a programme of work in progress there on the production of uranium dioxide by hydrometallurgical techniques ⁽¹⁾.

The method used is the direct hydrogen reduction under pressure of a suitable aqueous solution containing the uranyl ion, $(\text{UO}_2)^{2+}$; it is based on that developed in recent years for the production of nickel and other metals in powder form, which is in commercial operation for these metals at the Sherritt-Gordon Mines, Limited, plant at Fort Saskatchewan, Alberta. The facilities of the Physical and Crystal Chemistry Section of the Mines Branch for evaluating their uranium oxide samples were offered to Professor Forward and his co-workers. Several Mines Branch Reports

(1) For References see end of Report, page 24.

dealing with uranium dioxide were supplied to the University of British Columbia during the late summer of 1957.

In August 1957, a copy of their first Progress Report was received. This is given as Appendix I to this report (see pages 25 to 31). Our comments on this Progress Report, sent out in September 1957, are given as Appendix II (see pages 32 to 34). During September 1957, also, further correspondence concerning the technique passed between the Mines Branch and the University of British Columbia; this correspondence is given in Appendices III to V inclusive (see pages 35 to 39). No samples, however, were forthcoming as an outcome of either the Progress Report or the subsequent correspondence.

Late in November 1957, two samples of products made by the hydrometallurgical technique were submitted direct to the laboratories of Eldorado Mining and Refining Limited in Ottawa, accompanied by a letter, a copy of which is given as Appendix VI, (see pages 40 to 43); a copy of this correspondence came to the Mines Branch. As a result of this correspondence, 10-gram samples of each of the two batches of product, designated as Lot 23 and Lot 24, were sent by Eldorado to the Mines Branch for examination. Later, at the request of the Mines Branch, additional 10-gram

samples were provided for test.

In January 1958, a second Progress Report was submitted from the University of British Columbia and a copy of this report appears as Appendix VII (see pages 44 to 48).

This present report gives details of the results of tests made on Lots 23 and 24 at the Mines Branch, although use is made, in the interpretation of these results, of data obtained by Eldorado Mining and Refining Limited.

Additional tests on these materials have been made in the laboratories of Eldorado Mining and Refining Limited, Tunney's Pasture, Ottawa, and will be reported separately.

EXPERIMENTAL

Techniques

The techniques employed in the examination of the samples which form the subject of this report have all been described in earlier Mines Branch Reports ⁽²⁾ to ⁽⁶⁾, and will not be described in detail here. They included:-

- a) Differential thermal analysis
- b) X-ray diffraction examination
- c) Spectrographic examination
- d) Determination of green and sintered densities under
standard pressing and firing conditions
- e) Chemical analysis for selected elements
- f) Determination of O/U atomic ratio by both oxidation and

reduction techniques.

Results

a) Differential Thermal Analysis

The samples were heated in air in an alumina block at 12 deg. C per minute and the significant responses obtained are listed in Table 1. The D.T.A. charts are given in Figure 1 (Lot 23) and Figure 2 (Lot 24).

TABLE 1
Differential Thermal Analysis of UO₂ Samples in Air
Lots 23 and 24

Temperature Range	Observations with Lot 23	Observations with Lot 24
Room temp. to 250°C	Broad, flat, <u>endothermic</u> peak of moderate size, with summit at approximately 140°C	Broad, flat, <u>endothermic</u> peak of moderate size, with summit at approximately 130-150°C
250°C to 550°C	Large, single, broad, <u>exothermic</u> peak with summit at 420°C	Large, single, broad, <u>exothermic</u> peak with summit at 420°C
550°C to 750°C	Moderately small, broad, <u>endothermic</u> peak, with multiple summits at 620°C, 650°C and 700°C	Moderately small, broad, <u>endothermic</u> peak, with main summit at 635°C
750°C to 950°C	Very small <u>endothermic</u> peak at 890°C	Very small <u>endothermic</u> peak at 895°C
950°C to 1050°C	Very small, sharp, <u>endothermic</u> peak at 980°C	Moderate, very sharp <u>endothermic</u> peak at 990°C
1050°C to 1100°C	Run discontinued at 1060°C	Run discontinued at 1075°C

FIGURE 1

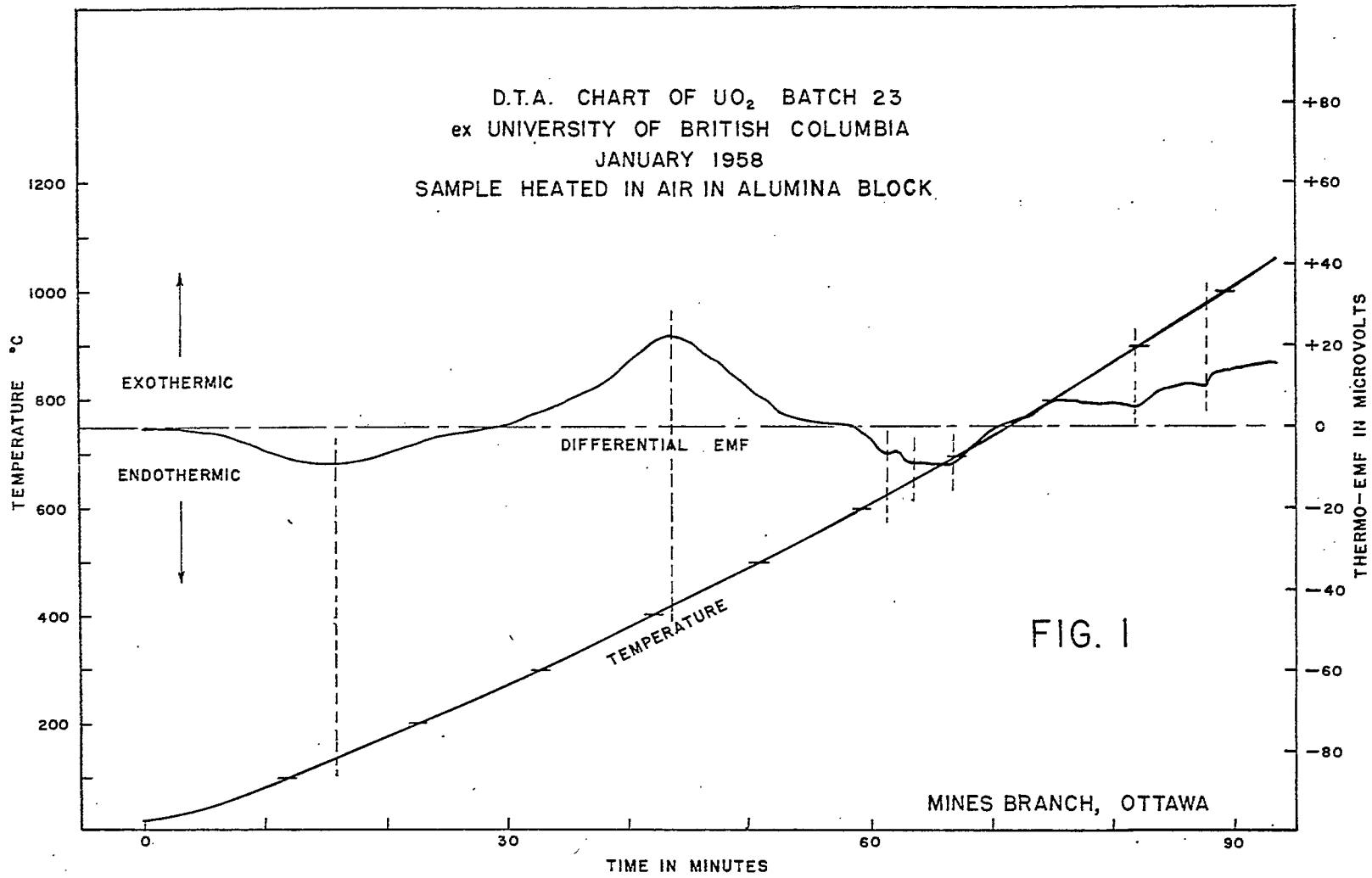
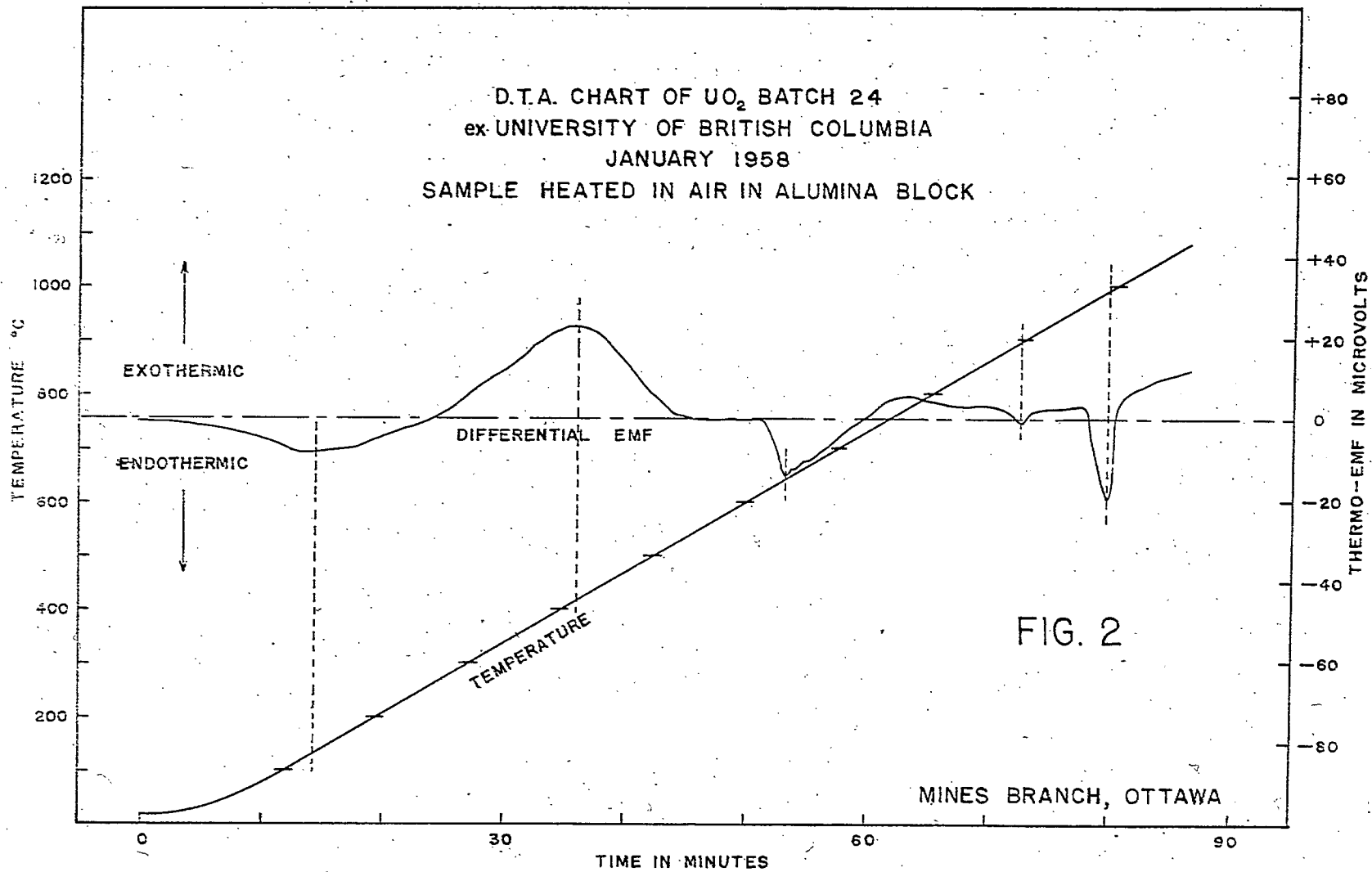


FIGURE 2



It was observed that the products, after the D.T.A. examinations were completed, were almost black in colour, considerably shrunken in size, and compacted; this is in marked contrast to the behaviour usually observed under these conditions with uranium dioxide, which becomes dark olive-green in colour and considerably swollen. However, X-ray diffraction examination of the products revealed the presence of U_3O_8 as the only detectable crystalline phase, which is normal.

The form of the D.T.A. curves is entirely abnormal for uranium dioxide. The low-temperature endothermic peak is not normally obtained at all. It is attributable to the loss of surface or adsorbed moisture from the samples and/or to the endothermic decomposition of any volatile constituents. Such a material would be ammonium carbonate. The presence of this compound in small amount is not entirely unexpected, as it was used at one stage in the preparation (see Appendix VII, page 47).

The oxidation of uranium dioxide to U_3O_8 , as observed by the D.T.A. technique, normally occurs in two well-resolved stages, the first being temperature-sensitive, depending on the nature of the sample, and occurring within the temperature range 160°C to 280°C with most of the samples tested in these laboratories ⁽²⁾, the second occurring always at a temperature within the much narrower range 350°C to 380°C , being almost independent of the nature of the starting material. Even in the

D.T.A. examination of sintered uranium dioxide, two stages of oxidation are readily observable, though less well resolved than with unsintered material. In no case of a material which was essentially UO_2 chemically was a single stage of oxidation only observed.

If, however, the sample under investigation were already in a state of oxidation higher than that produced in the first D.T.A. peak of normal material, then subsequent examination by D.T.A. in air would result in only the second, or higher temperature, peak being observed. Such a behaviour has actually been observed in these Laboratories with a material that had been subjected to controlled pre-oxidation to a formula of approximately U_3O_7 . This suggests the possibility that the present material may be quite far removed from the stoichiometric UO_2 composition.

The small endothermic peaks observed at temperatures in the range 600°C to 1000°C must be associated with the presence of various impurities, since when a pure UO_2 is subjected to this treatment, the U_3O_8 formed at the conclusion of the second oxidation stage undergoes no significant decomposition in the range 600°C to 1000°C . It does gradually lose oxygen endothermally on prolonged heating at 800°C or higher temperatures, but this reaction does not occur at sharply defined temperatures in the way shown by these small peaks. No more precise explanation can be given for the cause of these peaks.

b) X-Ray Diffraction Examination

The two materials were examined by the normal procedures of X-ray powder diffraction examination, using CuK_α radiation and a 57.3 mm Debye-Scherrer camera. The two samples gave very similar X-ray patterns of the general face-centred, cubic, fluorite type normally associated with UO_2 . However, in both cases, the lines were diffuse indicating either very fine crystallite size or imperfect crystallization. It was nevertheless possible to measure the patterns and derive reasonable values for the corresponding cubic cell edges. In both cases, values of 5.40 - 5.41 Å were obtained. These figures are rather surprising in that they are far removed from the value of 5.470 Å corresponding to stoichiometric UO_2 ; they are even lower than the value of 5.44 Å associated with U_4O_9 (i.e. cubic " $\beta\text{-UO}_2$ ").

According to the data of Brooker and Nuffield⁽⁷⁾, a cell edge of 5.40 - 5.41 Å corresponds to a composition of approximately $\text{UO}_{2.5}$. It is most unusual to obtain such a cell edge, corresponding to such a composition, with any laboratory product. As mentioned by Brooker and Nuffield, such data have been obtained with materials that have had geological time in which to come to an equilibrium state of oxidation, or which have been subjected to annealing at quite elevated temperatures. Neither condition applies in the present case, however. Hence, such a cell edge and composition from a synthetic product must be regarded as highly

unusual.

However, this suggested formula of approximately $\text{UO}_{2.5}$ for the present materials is in good accord with the indication, obtained from the D.T.A. work, that the state of oxidation of the samples was higher than that represented by the formula U_3O_7 (i.e., $\text{UO}_{2.33}$) and lower than that represented by the formula U_3O_8 (i.e., $\text{UO}_{2.67}$).

c) Spectrographic Examination

The two samples were subjected to semi-quantitative spectrographic examination in the Laboratories of the Mines Branch, Ottawa, with the following results:-

<u>Element</u>	<u>Batch No. 23</u>	<u>Batch No. 24</u>
U	Principal constituent	Principal constituent
Si	0.5%	0.5%
V	0.5	0.7
Zr	0.15	0.07
Ni	0.2	0.8
Mg	0.05	0.05

The presence of the large proportion of uranium rendered the detection or estimation of all other elements difficult by the techniques available at the Mines Branch.

It will be observed that the percentages of nickel found are in reasonable accord with those quoted in the chemical analyses supplied from the University of British Columbia (see Appendix VII, page 47) viz 0.37% for Lot No. 23 and 1.3% for Lot No. 24. Also given in this Appendix (see page 48) is a quantitative spectrographic analysis for trace elements obtained for these

materials in the Laboratories of Eldorado Mining and Refining Limited, Port Hope, Ontario. There is no significant conflict between these results and the Mines Branch data given above, although each set of results includes data not given in the other.

d) Determination of Green and Sintered Densities

Sufficient of each sample was available to prepare two 5 g compacts of each. Compacts of half-inch diameter were pressed at 40,000 psi using kerosene as binder and stearic acid as mould lubricant in accordance with the standard procedure developed at the Mines Branch⁽²⁾. The compacts were sintered in a flowing hydrogen atmosphere in a molybdenum-wound alumina tube furnace, for half-an-hour at 1700°C. Heating and cooling rates of approximately 300 deg. C and 600 deg. C respectively were used. The green and sintered densities were computed from the dimensional measurements and the weights of the compacts. The following results were obtained.

TABLE 2

Green and Sintered Densities of UO₂ Compacts

Lot No.	Compact	Green Density, in g/cm ³	Sintered Density, in g/cm ³
23	A	5.03)	9.61)
	B	5.00)	9.62)
		Mean = 5.02	Mean = 9.62
24	C	5.08)	9.64)
	D	5.09)	9.66)
		Mean = 5.09	Mean = 9.65

These figures represent materials of a relatively poor degree of sinterability.

On the basis of earlier work⁽²⁾, a sintered density of about 9.6 g/cm³ would normally be associated with a green density of about 6.0 g/cm³; a green density of about 5.0 g/cm³ would be associated with a sintered density approaching the theoretical figure of 10.97 g/cm³. Thus, these materials are much less sinterable than one is entitled to expect from their green densities. This behaviour is probably due to the presence of certain impurities, which are having a deleterious effect on the sintering process.

It must be borne in mind, however, that the above considerations are based on data obtained with materials which do not depart from the stoichiometric composition, UO_{2.0}, to anything like the same extent as is considered to be likely with the present samples. It is known that compressed U₃O₈ does not make a good starting material to yield a high-density sintered UO₂ body. It is quite possible that the considerable degree of non-stoichiometry of

the present materials as well as the presence of impurities may be contributing to the unsatisfactory sintering behaviour. As seen later in the report (see page 17), such a highly non-stoichiometric material can disproportionate on heating to temperatures well below those at which sintering in hydrogen occurs, yielding U_3O_8 and a lower non-stoichiometric oxide. It may be that this production of U_3O_8 on heating is a contributory factor to the poor sintering behaviour.

A small degree of non-stoichiometry is not harmful to the sintering behaviour, and may indeed be beneficial⁽²⁾, but the large departure from stoichiometry in the present samples is definitely not beneficial.

e) Chemical Analysis for Selected Elements

The total uranium content was determined in the Laboratories of Eldorado Mining and Refining Limited, Tunney's Pasture, Ottawa; the following results were obtained:-

Lot 23 79.7% uranium (as U)

Lot 24 79.5% uranium (as U)

The nickel metal content was determined at the University of British Columbia before the samples were submitted (see Appendix VII, page 47); the following results were obtained:-

Lot 23 0.37% nickel (as Ni)

Lot 24 1.30% nickel (as Ni)

The total carbon in the form of either free graphite or

carbides, but not including any carbon as either volatile or in-volatile carbonates was determined in the Chemical Laboratories of the Mines Branch; the following results were obtained:-

Lot 23 Less than 0.01%

Lot 24 Less than 0.01%

This is an insignificantly low figure and shows that the presence of either graphitic or carbide carbon is not responsible for the low sintered densities referred to above. Amounts in excess of 0.02% are required to produce detectable deleterious effects on the sintered density⁽⁶⁾.

Addition of dilute acid to the materials resulted in a little mild effervescence, suggesting the possibility of the presence of carbonate. Addition of hot, dilute caustic soda to the materials gave a detectable, though slight, odour of ammonia, indicating the presence of a small amount of ammonium compound(s). In the Laboratories of Eldorado Mining and Refining Limited a direct estimation of the amount of ammonium carbonate present was made; figures in the range 0.5 to 1.0% were obtained. This is in accord with the above chemical observations and also in accord with the D.T.A. findings (see page 7).

In case the high-temperature D.T.A. endothermic peaks obtained at 980-990°C were associated with the decomposition of a small amount of calcium carbonate, the proportion of calcium in the samples was estimated by flame photometry; the results obtained

were as follows:-

Lot 23 0.01% calcium (as Ca)

Lot 24 0.04% calcium (as Ca)

These amounts are insignificant and are not considered to correspond to sufficient calcium carbonate to have given rise to the quite marked D.T.A. peaks in the above temperature range. The cause for these peaks must thus be sought elsewhere.

f) Determination of the Oxygen/Uranium Atomic Ratio

There are two chemical methods available for the determination of the oxygen/uranium atomic ratio in uranium oxides, namely, a) reduction of the material to stoichiometric uranium dioxide with hydrogen and determination of the non-stoichiometric oxygen from the weight of water produced from it, and b) oxidation of the material to stoichiometric U_3O_8 , and determination of the composition from the weight increase obtained. These two methods have been described in detail in an earlier report⁽³⁾. Both methods have been applied to the two present samples.

When the attempt was made to apply the oxidation technique, a loss in weight was actually obtained with both samples, instead of the gain which should normally be recorded, thus:-

	<u>Lot 23</u>	<u>Lot 24</u>
Starting weight	5.0396 g	5.0390 g
Final weight	4.8670 g	4.9063 g

From these figures it is obvious that some process is occurring

giving a loss in weight which more than overcomes the increase due to the oxidation of the uranium oxide to U_3O_8 . X-ray diffraction examination confirmed that the products were U_3O_8 in both cases, however. The processes which might lead to this weight loss would be the loss of any surface or adsorbed moisture, and/or the volatilization of such materials as ammonium carbonate.

It thus became desirable to determine the amount of moisture and of ammonium carbonate in the sample. This was done by heating the material to $1000^\circ C$ in a dry argon stream and absorbing the H_2O and CO_2 obtained in weighed Anhydrone and Ascarite towers respectively. This ensured that any heavy metal, magnesium or calcium carbonates would also be decomposed. The non-stoichiometric oxygen is not removed by this treatment. This was verified by subjecting a known oxide of composition approximately $UO_{2.25}$, containing a known small added amount of calcium carbonate, to the same treatment. The CO_2 was recoverable quantitatively and no significant non-stoichiometric oxygen was lost.

The increase in weight of the Anhydrone tower gave the amount of water formed from the ammonium carbonate plus the amount of surface and adsorbed moisture in the sample. The increase in weight of the Ascarite tower gave the amount of CO_2 formed from carbonate present in the sample and could be used as a measure of its amount. The difference between the combined

increases in the two towers and the loss in weight of the sample gave the amount of ammonia from the ammonium carbonate present in the sample. It was found that the amount of ammonium carbonate based on the weight of CO_2 produced agreed very well with that based on the weight of NH_3 produced, indicating that there was no significant amount of other carbonates present. The results obtained up to this stage of the analysis were as follows:-

	<u>Lot 23</u>	<u>Lot 24</u>
Initial weight of sample	5.5954 g	5.5414 g
% Ni present (U.B.C. data)	0.37%	1.30%
Weight of Ni present	0.0207 g	0.0720 g
Weight of remaining material	5.5747 g	5.4694 g
Weight of CO_2 produced	0.0194 g	0.0157 g
Corresponding weight of $\text{NH}_4)_2\text{CO}_3$	0.0424 g	0.0343 g
% of $\text{NH}_4)_2\text{CO}_3$ in sample	0.76%	0.62%
Weight of water from $\text{NH}_4)_2\text{CO}_3$	0.0079 g	0.0064 g
Total weight of water produced	0.1919 g	0.1377 g
∴ Weight of free water in sample	0.1840 g	0.1313 g
% Free water in sample	3.29%	2.37%
Total loss of weight in Argon (Amm. carb. + free H_2O)	0.2264 g	0.1656 g
Experimental figure for loss in weight of sample	0.2260 g	0.1639 g

At this stage in the investigation, small samples were removed from each sample for identification by X-ray diffraction. These showed the presence of U_3O_8 and of a highly non-stoichiometric UO_2 -type phase; the diffuseness of the pattern did not permit of any reasonable measurements and calculation of the

composition from the cell-edge being made. The remaining sample was then submitted to the normal oxygen/uranium atomic ratio determination by the reduction technique. The samples were stored and weighed throughout this series of tests in an argon atmosphere in order to prevent alteration of the oxygen/uranium ratio by contact with atmospheric oxygen. A small amount of moisture was obtained in the oxygen/uranium ratio determination before the reduction stage occurred. This was presumably a residuum from the considerable amount of moisture originally present in the samples. Good agreement was obtained between the loss in weight of the sample during this determination and the combined weights of the moisture referred to above and of the oxygen in the water obtained by the reduction of the non-stoichiometric oxide.

In order to calculate the true oxygen/uranium atomic ratio of the uranium oxide of the original sample, allowance must also be made for the other impurities present. The nickel, free moisture, and ammonium carbonate have already been dealt with. From the semi-quantitative spectrographic data given on page 10, it can be seen that there are significant amounts of Si, V, and Zr present and from the data given on page 48, it can be seen that the proportion of trace elements, when combined, is also significant. It may reasonably be assumed that the Si is present as SiO_2 , or some compound involving it; similarly the V may be considered as V_2O_5 and the Zr as ZrO_2 . The trace elements total about 1000

ppm i.e. 0.1% of the total; as these trace elements are probably present as either single or combined oxides, they may be considered as making up about 0.13% of the total sample when calculated as oxides. For the purpose of allowing for the presence of Si, V, and Zr, it will be assumed that the semi-quantitative spectrographic data can be accepted as quantitatively accurate. The detailed results obtained were calculated to an oxygen/uranium atomic ratio as follows:-

	<u>Lot 23</u>	<u>Lot 24</u>
Initial weight of sample	5.5954 g	5.5414 g
Weight of Ni present	0.0207 g	0.0720 g
Weight loss in argon heating (experimental)	0.2260 g	0.1639 g
Weight removed for X-ray examination	0.0562 g	0.0626 g
Moisture obtained before reduction in H ₂	0.0072 g	0.0022 g
% SiO ₂ present)	1.07%)	1.07%)
% V ₂ O ₅ present)	0.89%)	1.25%)
% ZrO ₂ present)	0.20%)	0.09%)
% trace oxides present)	0.13%)	0.13%)
Total impurities present	2.29%	2.54%
% of UO _{2+x} in dry oxide before reduction	97.71%	97.46%
Weight of impure dry oxide before reduction	5.2853 g	5.2407 g
Weight of dry UO _{2+x} present	5.1643 g	5.1076 g
Weight of oxygen obtained as water by reduction of oxide	0.1704 g	0.1810 g

The reaction which occurs in the reduction stage is as follows:-



Whence the formula of the non-stoichiometric oxide can be calculated. The results obtained were as follows:-

Lot 23	$\text{UO}_{2.576}$
Lot 24	$\text{UO}_{2.620}$

It is possible, also, to get an estimate of the formulae of these materials from the figures for total uranium content obtained by Eldorado Mining and Refining Limited, Tunney's Pasture, see page 13, in the following manner

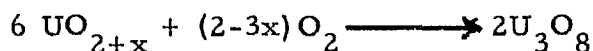
	<u>Lot 23</u>	<u>Lot 24</u>
% Nickel (ex U.B.C.)	0.37%	1.30%
% $\text{NH}_4)_2\text{CO}_3$ (from CO_2 determination)	0.76%	0.62%
% Free H_2O (direct determination)	3.29%	2.37%
% SiO_2 (semi-quantitative spec.)	1.07%	1.07%
% V_2O_5 (ditto)	0.89%	1.25%
% ZrO_2 (ditto)	0.20%	0.09%
% Trace oxides (quantitative spec.)	0.13%	approx 0.13% approx
% Total U (ex Eldorado)	<u>79.7%</u>	<u>79.5%</u>
Total Estimated quantity	86.41%	86.33%
Unestimated material, assumed to be oxygen in combination with uranium	13.59%	13.67%
Oxygen/uranium atomic ratio, obtained from these data	$\text{UO}_{2.54}$	$\text{UO}_{2.56}$

These figures are in quite reasonable accord with those obtained in the reduction technique.

Consider now the results obtained by the oxidation technique. In this method, the moisture and ammonium carbonate will be lost during the heating, and the Ni, SiO₂, V₂O₅, ZrO₂ and trace oxides will be present throughout as inert materials; the UO_{2+x} will become U₃O₈. The value of x can be obtained thus:-

	<u>Lot 23</u>	<u>Lot 24</u>
Initial weight of sample	5.0396 g	5.0390 g
Combined % of Ni + (NH ₄) ₂ CO ₃ + H ₂ O + SiO ₂ + V ₂ O ₅ + ZrO ₂ + trace oxides	6.71%	6.83%
∴ Weight of initial dry UO _{2+x} present	4.7014 g	4.6948 g
Weight of Ni + SiO ₂ + V ₂ O ₅ + ZrO ₂ + trace oxides	0.1341 g	0.1935 g
Weight of U ₃ O ₈ + Ni + SiO ₂ + U ₂ O ₅ + ZrO ₂ + trace oxides obtained	4.8670 g	4.9063 g
Weight of U ₃ O ₈	4.7329 g	4.7128 g

The reaction which occurs is



whence the following values are obtained for the oxygen/uranium

ratios	Lot 23	UO _{2.55}
	Lot 24	UO _{2.60}

DISCUSSION

The most important fact which emerges from the results obtained by the various techniques employed in this investigation is that the materials which form the subject of this report are quite far from being the uranium dioxide which they were intended to be. This applies both to their purity and to their stoichiometry.

Chemical and spectrographic analysis has shown the presence of a number of impurities in sufficient amount to have a deleterious effect on the sintering behaviour of the oxide⁽⁸⁾, notably silica and vanadium pentoxide.

The oxygen/uranium atomic ratio has been shown by various techniques to be far removed from stoichiometric UO_2 , namely:-

Differential Thermal Analysis :- O/U = greater than 2.33 for both samples

X-ray Diffraction :- O/U = 2.5 approx. for both samples

Oxidation Method :- Lot 23 O/U = 2.55

Lot 24 O/U = 2.60

Reduction Method :- Lot 23 O/U = 2.576

Lot 24 O/U = 2.620

From % Total Uranium :- Lot 23 O/U = 2.54

Lot 24 O/U = 2.56

On the basis of these figures, we may say that a reasonable mean value for the composition of the uranium oxide component of these samples is as follows:-

Lot 23 $\text{UO}_{2.56}$

Lot 24 $\text{UO}_{2.59}$

The presence of the various impurities and the high degree of non-stoichiometry of the oxides will both contribute to the somewhat unsatisfactory sintering behaviour of the oxides.

It would appear that more extensive purification will be necessary before materials produced by the hydrometallurgical technique would be acceptable as a potential source of reactor-grade UO_2 . It would also appear desirable to adapt the pressure reduction cycle in such a way as to produce, if possible, an oxide having an oxygen/uranium atomic ratio much nearer to 2.0.

Of greatest scientific interest in the current materials is the fact that they have the fluorite-type UO_2 structure with a composition so very far removed from stoichiometric UO_2 and that this structure is obtained without having subjected the materials to any high-temperature annealing stage.

Norman F. H. Bright,

Physical and Crystal
Chemistry Section.

REFERENCES

1. Bright, Norman F.H., "Visits to Certain Canadian and U.S. Establishments to Discuss Uranium Dioxide Fuel Element Technology". Mines Branch Visit Memorandum No. MDV686; June 18, 1957. (For Official Use Only).
2. Bright, Norman F.H., Gow, Kenelm V., and Prince, A.T., "Factors Influencing the Sintering Properties of Uranium Dioxide for Use in Nuclear Reactor Fuel Elements". Mines Branch Research Report No. MD209; September 18, 1956. (For Official Use Only).
3. Bright, Norman F.H., Ripley, Leonard G., Rowland, John F., and Lake, Richard H., "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 5, 1956.
4. Bright, Norman F.H., "A Study of Two Samples of Uranium Trioxide from Eldorado Mining and Refining, Limited, Port Hope, Ontario". Mines Branch Report of Investigation No. MD3113; March 12, 1956. (For Official Use Only).
5. Bright, Norman F.H., "The X-Ray, D.T.A., and Thermogravimetric Examination of Certain Uranium Oxide and Uranyl Nitrate Samples Submitted by Eldorado Mining and Refining Limited, Port Hope, Ontario". Mines Branch Report of Investigation No. MD3150; October 2, 1956. (For Official Use Only).
6. Bright, Norman F.H., Gow, Kenelm V., and Webster, A. Hubert, "The Effect of Carbon on the Sintering Behaviour of Uranium Dioxide". Mines Branch Research Report No. MD213; November 7, 1957. (For Official Use Only).
7. Brooker, E.J., and Nuffield, E.W., "Studies of Radioactive Compounds: IV - Pitchblende from Lake Athabasca, Canada". Amer. Mineralogist, 1952, Vol. 37, pp. 363-385 (particularly p. 373).
8. Webster, A. Hubert, and Bright, Norman F.H., "The Effects of Additives on the Sintering of Uranium Dioxide". Mines Branch Research Report No. MD223; November 7, 1957. (For Official Use Only).

COPY/cl

APPENDIX I

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

August 29th, 1957.

Dr. J. Convey,
Director,
Mines Branch,
Department of Mines and
Technical Surveys,
568 Booth Street,
OTTAWA, Canada.

Dear Dr. Convey:

I enclose a copy of Progress Report (No. 1) that Dr. Wiles has prepared on the production of UO_2 powder by hydrogen reduction. The uranium solutions used were produced from sodium diuranate supplied by Eldorado Mining and Refining.

The UO_2 powder can be produced using nickel powder catalyst but the product consists of agglomerates which appear to have formed on the surface of the nickel powder and subsequently, to have been detached by abrasion. These agglomerates can be readily ground to give a UO_2 product in which the particles are less than one micron diameter.

Dr. Wiles is preparing a sample lot of the fine UO_2 powder for shipment to the Mines Branch for examination.

I hope you will find the enclosed report of some interest. We look forward to keeping in touch with you in connection with this project.

Sincerely,

(sgd) F. A. FORWARD.

FAF/DC
Encl.

cc. Dr. J. B. Marshall
Mr. A. Thunaes

HYDROMETALLURGICAL PRODUCTION OF FINE UO₂ POWDER

PROGRESS REPORT NO. 1

D. R. Wiles and J. P. Vizsolyi

August 20th, 1957.

OBJECT:

The object of this work is to determine whether a uranium dioxide powder suitable for use as a nuclear reactor fuel can be produced by the hydrogen reduction of Uranium solutions.

MATERIALS:

The Uranium solutions used in this work are made from UO₃ which is, in turn, made by careful heating of Uranium peroxide, as precipitated from sulphate solutions. The Uranyl carbonate solutions are made up such as to approximate carbonate leach solutions. Other materials used are reagent grade.

The catalyst used is Sherritt-Gordon Nickel powder. Various sizes of powder were used in the initial phases of the work, but 30 μ was found most convenient and therefore was used exclusively in the later stages.

SUMMARY:

The majority of the work to date has been of an exploratory nature, attempting to find conditions such as will produce very fine ($\leq 1\mu$) UO₂ particles directly. (It is this size of particle found most satisfactory by the Mines Branch in Ottawa.) Methods investigated to date are: recycling of the precipitate, using a Nickel stirrer instead of Nickel powder catalyst, and the use of various soluble salts of Copper in an attempt to produce homogeneous catalysis. Although hope is not finally abandoned, especially for homogeneous catalysis, none of these has proved successful.

In more recent work, the emphasis has been on the production of a powder which, although seriously agglomerated, can be ground to the required fineness. This work, although still in its initial stages, has shown some promise. Particle sizes after grinding seem to be of the proper order of magnitude. A sample is being prepared to be sent to the Mines Branch for their comments and, if these are encouraging, a more exhaustive study will be continued.

The purity of the product has not yet been investigated. Likely impurities are sodium, carbonate, and Nickel. Sodium and carbonate can be removed by proper washing, and Nickel can be removed magnetically.

RESULTS:

- (a) In preliminary tests it was shown that UO_2 forms a coating on the surface of the Ni catalyst, and is removed by abrasion only in large chunks.
- (b) Recycling of the precipitate does not significantly reduce the particle size. Addition of Sodium Stearate did not appear to affect the plastering of UO_2 on the catalyst.
- (c) Use of a nickel stirrer as catalyst instead of Nickel powder gives no reduction, because of the greatly reduced surface area.
- (d) Attempts at homogeneous catalysis, using various soluble cupric salts, were unsuccessful.
- (e) Simple grinding of the UO_2 -Ni composite powder leads to an effective separation of Ni and UO_2 , and to the ultimate production of very fine powders.
- (f) Work in the near future is to be largely an investigation of the purity of the product, and of its particle size after grinding.

CONCLUSIONS:

No method has yet been found which will yield a powder as simply as that using Nickel powder catalyst. Grinding of the product of this process gives a UO_2 powder which probably can be made fine enough to meet the object of this work.

DETAILS AND DISCUSSIONS:

Experiments are in general carried out in a conventional manner, using a 1 1/2 liter charge in a glass or stainless steel beaker inside a high pressure autoclave. The nature of the charge varies considerably, but in most cases consists of UO_2^{++} ; NaHCO_3 , and Na_2CO_3 in such proportions as to approximate a carbonate leach solution. The nickel catalyst is in the form of powder, usually $\sim 30\mu$ diameter particles, but on occasion up to 100μ .

- (a) A number of experiments were done at the beginning of this work to gain familiarity with the pressure precipitation techniques. Essentially nothing new found during this phase. It was noted that at very high carbonate concentrations--120 g/L Na_2CO_3 , 60 g/L NaHCO_3 --no reduction was observed, probably because the silica leached from the glass fouled the catalyst. This experiment has not been repeated in a steel beaker, although all subsequent have been done using a steel beaker.
- (b) Recycling of the precipitated UO_2 was tried briefly, following the lead of Halpern, et al., who found this to be possible. The results were, in agreement with those of the earlier workers, that the rate of reduction decreases as the catalyst surface becomes coated with UO_2 . With 65-100 μ Nickel powder there was no evidence for significant abrading of UO_2 off the Nickel surface up to the point when the reaction rate had decreased by a factor of 3, and the UO_2 was thus not magnetically separable from the Nickel. With $\sim 30\mu$ Nickel powder as catalyst, an appreciable fraction of the UO_2 was removed from the Nickel, but its size was not diminished to the point of this being a useful method for direct production of 1 μ UO_2 powder. These experiments were therefore discontinued.

A small amount of stearic acid was added in one of these experiments in the hope of reducing the plastering of UO_2 on the Nickel catalyst. No effect was observed.

During the course of this work it was observed that precipitation runs closely following the previous run had higher rates than those done after standing for several hours. It had been observed in earlier work by Wiles and Zogović that an oxide film on the catalyst surface was detrimental, and required to be reduced before the Nickel was fully effective as a catalyst. It appears, then, that a film of oxide forms on the catalyst surface, even when the catalyst is submerged in a hydrogen-saturated solution at room temperature and pressure.

- (c) Several experiments were done using a Nickel stirrer instead of Nickel powder as catalyst, in the hope that the greater agitation at the surface of the stirrer blades might cause the newly-formed UO_2 crystals to be swept into the solution. No reduction was observed at temperatures up to 220°C and hydrogen pressures of 195 psi. Some reduction undoubtedly occurs, but due to the relatively small surface area of the stirrer blades, the reduction is so slow as not to have been observable within the space of several hours.

- (d) Several experiments were performed in an attempt to reduce Uranium homogeneously, using soluble cupric salts as catalyst. Cupric ion was complexed, respectively, by acetate ion, ethylene diamine, ammonia, and ethylene diamine tetra-acetic acid. Various temperatures and concentrations were used, but no reduction was observed. All of these experiments were conducted at about pH 10.

In several cases hydrolysis of the uranium was observed, and the hydrolysis products were shown by X-ray diffraction to be unreduced. In some cases, notably with ethylene diamine, copper metal appeared to have been produced. In other cases, hydrolysed cupric oxides and basic carbonates were formed.

- (e) After the apparent failure of all attempts to produce fine UO_2 powders directly, tests were done to determine whether the UO_2 as prepared using Nickel powder catalyst could be pulverized by standard grinding techniques.

Several grams of UO_2 -coated Nickel powder were ground by hand for one hour in a mortar. The resultant powder was found to be readily separable into magnetic and non-magnetic fractions. The non-magnetic fraction--the UO_2 --was separated according to particle size, using the Roller analyser. The results are as follows:

0 - 5 μ fraction	37.7%	- see Figure 3a (page 30)
5 - 10 μ fraction	19.9	- see Figure 3b
10 - 15 μ fraction	<u>42.3</u>	- see Figure 3c
	99.9%	

Microscopic examination of these fractions and of the unseparated material showed the following:

- i) The oxide as precipitated on the surface of the Nickel catalyst is composed of very small crystals, but is very much agglomerated.
- ii) These agglomerates can fairly readily be broken down by simple grinding.
- iii) The resultant fine powder is composed of simple crystals, whose shape and size is quite within the range of the desired end product.

FIGURE 3

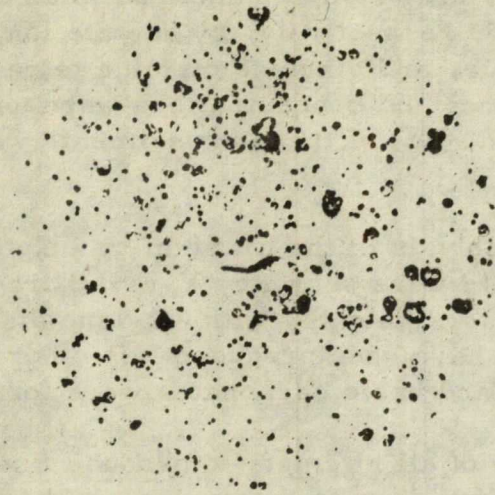


Figure 3a

0 - 5 μ

(X 750)

┌───┐
10 μ

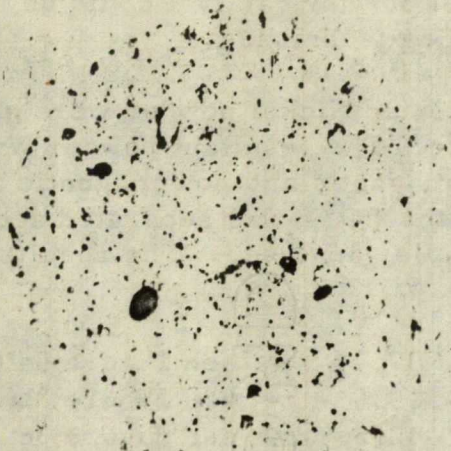


Figure 3b

5 - 10 μ

(X 750)



Figure 3c

10 - 15 μ

(X 750)

Microphotographs of the UO_2 powder produced using 30 μ Ni powder as catalyst. The product was ground by hand and the Nickel was separated magnetically.

iv) All fractions were largely composed of particles of $\sim 1\mu$ diameter, presumably formed by breaking up of the agglomerates during the analysis itself. Other samples, separated by sedimentation in water did not show this type of size distribution, but did confirm that the larger particles are large agglomerates of small crystals.

(f) Work in progress at present is directed toward:

- i) preparing a large amount of fine ($\sim 5\mu$) UO_2 powder, to be sent to the Mines Branch in Ottawa for their inspection;
- ii) obtaining an analysis of the UO_2 precipitate, to determine U:O ratio, water content, and contamination by Ni, Na^+ , and $CO_3^{=}$.

APPENDIX II

568 Booth Street,
6 September 1957.

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

Dear Professor Forward:

I thank you for your letter of August 29, 1957 with the attached Progress Report No. 1 by D. R. Wiles and J. P. Vizsolyi, dealing with the "Hydrometallurgical Production of Fine UO_2 Powder".

The investigation reported therein appears to be a creditable piece of work and the materials obtained, on the face of things at least, seem to exhibit considerable promise and to merit further study. Final evaluation of the quality of the product must, of course, await the results of the examination of the samples which Dr. Wiles proposes to send to Ottawa.

I have passed this Report to Dr. Norman F. H. Bright of our Mineral Dressing and Process Metallurgy Division, who has charge of our UO_2 work and his comments are attached to this letter.

We are very interested in this work and will examine whatever samples Dr. Wiles sends to Dr. Bright with considerable interest.

Yours sincerely,

(sgd) K. W. Downes,
for John Convey,
Director,
Mines Branch.

Comments on Progress Report No. 1 on the "Hydrometallurgical Production of Fine UO_2 Powder" by D.R. Wiles and J.P. Vizsolyi

There are a few comments and suggestions which we can make at the present stage in the investigation.

- (1) Dr. Wiles will, no doubt, realize that the milling of UO_2 to reduce its particle size is quite an established procedure, particularly in the case of materials such as the normal Mallinckrodt oxide which has a quite coarse particle size (up to 100μ).
- (2) Another method of comminution which might, perhaps, merit consideration at a later stage when larger samples are available is the "Micronizing" technique which is currently under investigation as applied to Eldorado UO_3 . Eldorado, A.E.C.L. Chalk River, and ourselves are all engaged in this particular problem at the moment and it is quite true to say that the UO_3 which, before micronizing, possesses too coarse a particle size and does not reduce to a very satisfactory UO_2 , after micronizing shows considerable signs of promise on reduction to UO_2 .
- (3) It is possible that the aggregated powder which the hydro-metallurgical process at present produces might be usable in its present condition, at its present particle size and without the removal of the nickel, by one or other of the techniques at present under experimental investigation at Chalk River. I refer to their work on fuel elements fabricated by vibratory compacting and also fabricated by swaging zirconium alloy tubes filled with uncompact powder. For this latter technique, a coarse, dense grain appears to be desirable and this seems to be what the technique is producing at present. The desirability of this technique as applied to the products would, of course, be contingent upon the acceptability from a neutron capture point of view of a material containing a small proportion of nickel.
- (4) The screen analysis quoted at the top of page 4 of Dr. Wiles' report represents a material which, as it stands, is too coarse to be very satisfactory, if a production of UO_2 fuel elements by conventional ceramic techniques is envisaged. It contains 62% of oxide coarser than 5μ particle size. I would imagine that you should aim to produce a material which contains very little coarser than 5μ , and as much as possible less than 1μ .

- (5) It would also be interesting to know the rate of atmospheric oxidation of the material and to have data on the O:U atomic ratio immediately after reduction and also after standing exposed to air for several days. It might be quite a good idea to send us samples which have been sealed up, preferably under argon or other inert atmosphere, as soon as possible after reduction, and of the same material after free exposure to air for several days, so that it could approximate to its equilibrium oxygen content. This difference in O:U ratio may well affect the sintering behaviour of the oxide.
- (6) We will be very interested to hear of the chemical analyses of the precipitates and, when the samples arrive in Ottawa, we will certainly examine them as thoroughly and as critically as the size of the samples will permit. The sample should preferably be not less than 25 g in total weight and should desirably be about twice this amount.

We trust these comments will be of interest and we take this opportunity of wishing you and your colleagues every success in this very interesting and promising investigation.

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

APPENDIX III

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

Department of Mining
and Metallurgy

September 12th, 1957.

Dr. J. Convey,
Director,
Mines Branch,
Department of Mines and
Technical Surveys,
568 Booth Street,
OTTAWA, Canada.

Dear John:

Re: UO₂ Powder Precipitation

Thank you for your letter of September 6th and the attached comments by Dr. Bright. I appreciate very much the detailed examination that Dr. Bright has given the report by Dr. Wiles.

During recent weeks we have made some modifications in the procedure that look most promising. Chiefly the change is concerned with the use of ammonium carbonate complexes, instead of sodium carbonate, as starting materials. This appears to permit the production of very fine UO₂ with considerable ease, and, of course, to give a product free of sodium.

Dr. Wiles will be writing more fully to Dr. Bright about the work and will keep in touch with him concerning the tests that you have kindly agreed to carry out on material supplied by Dr. Wiles.

Sincerely,

(sgd) F. A. FORWARD.

FAF/DC

cc. Dr. D. R. Wiles

Dr. N.F.H. Bright

APPENDIX IV

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

Department of Mining
and Metallurgy

September 13th, 1957.

Dr. N.F.H. Bright,
Head, Physical and Crystal
Chemistry Section,
Mines Branch,
568 Booth Street,
OTTAWA, Canada.

Dear Norm:

Thank you for your comments on my recent report on UO_2 powder.

Since that report was written, a number of developments have occurred, the chief of which was the switch to the ammonium carbonate system in preference to the sodium carbonate system. The reason for this is that sodium was found to be present to the extent of 3 - 4%, and was not readily removed by washing. Ammonium carbonate on the other hand is removed quite simply by gentle heating.

I was very interested in your suggestion that some nickel might be allowable in the UO_2 . We could, I am sure, use a very fine nickel powder, and leave it in the final precipitate. This nickel would remain very fine, and would be well dispersed. It is also probable that the presence of small amounts of nickel would improve the thermal conductivity of the final product. Our present product contains about 0.3% nickel but I feel that this figure can easily be reduced significantly.

Regarding the particles size of our product--I meant to imply, in the report, that the size analysis was not true, and represented only a limitation of the method. In reality, the 5 - 10 μ and 10 - 15 μ fractions were composed largely of (a) very fine ($\sim 1\mu$) particles, and (b) agglomerates of very fine particles which could easily be reduced in size. Thus, I feel that without much trouble we could obtain a powder of $\sim 2\mu$ particles.

In this same vein, can you please tell me where to obtain literature on the Micronizer. I tried some weeks ago to find out about it but was unsuccessful.

I am sorry to be so slow in sending you samples of UO_2 . We are limited by the size of our autoclaves and by the crudity of some of our techniques. I do hope to send you 50 grams of oxide in two or three weeks.

Kind personal regards to yourself and your staff.

Yours truly,

(sgd) D. R. Wiles.

DRW/DC

cc. J. Convey

F. A. Forward

APPENDIX V

Division of
Mineral Dressing
and
Process Metallurgy

552 Booth Street,
17 September 1957.

Dr. D. R. Wiles,
Department of Mining and Metallurgy,
University of British Columbia,
Vancouver 8, B.C.

Dear Don:

Many thanks for your letter of September 12, 1957. We are glad you found our comments on your Progress Report No. 1 of interest. We certainly feel that this is a project well worth while pursuing further.

We note that you have substituted ammonium carbonate for sodium carbonate, with promising results. This would appear to fall into line with the fact that ammonium diuranate is the best starting material for a fine particle size UO_2 produced by conventional reduction procedures.

The small amount of fine nickel powder left in the material (0.3% or less) would, in my opinion, probably not improve the thermal conductivity to any appreciable extent; on the other hand, it is highly unlikely that it would have any deleterious effect from this point of view.

You enquired about information concerning the Micronizer. The address of the manufacturer is as follows:-

The Sturtevant Mill Company,
Park and Clayton Streets,
Dorchester,
Boston 22,
Massachusetts, U.S.A.

So far as I know, they make three sizes of Micronizer, having 2 inch, 8 inch and 24 inch diameter comminution chambers, to handle varying quantities of material. In each case, there is a quite stringent requirement for dry, high-pressure, compressed air, but doubtless, the manufacturers will supply you with any information you request.

We shall be very pleased to examine your samples whenever you care to send them.

Wishing you all the best in your researches, with kindest personal regards from Dr. Webster and myself,

Yours very sincerely,

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

APPENDIX VI

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

Department of Mining
and Metallurgy

November 23rd, 1957.

Mr. E. B. Spice,
Eldorado Mining and Refining Ltd.,
P.O. Box 379,
OTTAWA, Canada.

Dear Ted:

Under separate cover I am sending you the following two lots of UO_2 that have been prepared in the Department laboratories:

Lot 23 - 50 grams
Lot 24 - 150 grams

The two lots should be substantially the same, having been prepared by the same procedures, and should therefore give some indication of the reproducibility of the product.

The starting material was a Beaverlodge precipitate containing significant amounts of Fe and SiO_2 as well as other impurities. To prepare the UO_2 the Beaverlodge precipitate was dissolved in boiling concentrated HNO_3 , diluted with distilled water to about 5% free HNO_3 , neutralized with NH_4OH , and H_2O_2 added to precipitate UO_4 . The product was washed and ignited at 130-150°C to produce UO_3 . The UO_3 was dissolved in a 2% $(\text{NH}_4)_2\text{CO}_3$ - 1% NH_4HCO_3 solution and the solution clarified by filtration.

The clarified solution containing 3.0 g/l UO_3 was treated in an autoclave at 150°C using H_2 at 195 psi, in the presence of nickel powder (100-micron diameter particles) which served as a hydrogen catalyst. Before use, the powder was abraded by vigorous agitation in water, then screened, to remove any small excrescences. Using nickel catalyst in an amount of about 10 g/l, the uranium content of the solution was reduced from 3.0 g/l to less than 0.01 g/l in less than 10 minutes.

When reduction was complete the resulting pulp was cooled in the autoclave to room temperature and filtered under pressure using a nitrogen atmosphere. The filtered UO_2 and nickel was

repulped in boiled distilled water (low in O_2 content) and the nickel powder (mixed with some mechanically attached UO_2) separated from the UO_2 product in a single pass through a crude magnetic tube separator. Further separation was not carried out as this would have involved using much more extensive equipment and exposing the UO_2 to possible oxygen contamination. (Lot 23 was passed through the magnet three or four times).

The UO_2 product was again filtered under nitrogen pressure and then dried at $105^\circ C$ in a stream of nitrogen. The dried UO_2 is the product we are sending to you in two small glass containers.

Our examination by X-ray diffraction indicates that this product is in fact UO_2 ; oxygen determinations show the product to be $UO_{2.07}$; photomicrographs indicate that the UO_2 is present in single particles or loose agglomerates in which particle size is about 1 micron. The nickel content we find to be as follows: Lot 23 - 0.24%; Lot 24 - 1.4-1.5% according to determinations made on separate samples. Due to presence of nickel particles samples were not exact duplicates.

We realize that the techniques used for producing UO_2 by this method can be further refined, as, for example, by removing nickel more efficiently, but we would like to have some preliminary information on the present samples. It would be most helpful if, by utilizing the facilities at your disposal, you could undertake the following:

1. Check the U:O ratio.
2. Determine the content of impurities such as Gd, Dy, B, Cd, V, Cr, Fe, Si, etc.
3. Determine $(NH_4)_2CO_3$ content.
4. Determine behaviour of this UO_2 in sintering.
5. Check behaviour of sintered product in pile.
6. Determine slip-casting properties.
7. Disregarding nickel content, comment on the desirable and undesirable characteristics of this product.

The work is continuing in the laboratory to study the solubility of UO_3 in different amine carbonate solutions and, when this is completed, the precipitation of UO_2 from amine solutions.

I look forward very much to hearing from you and to having the results of your examination of the products we are sending. It would be helpful if you could arrange to send us a second 5-lb sample of Beaverlodge precipitate.

Yours very truly,

(sgd) F. A. FORWARD.

FAF/DC

cc. A. Thunaes
W. J. Bennett
J. Convey
D. R. Wiles

November 25, 1957.

Prof. F. A. Forward,
Department of Mining and Metallurgy,
The University of British Columbia,
Vancouver 8, Canada.

Dear Professor Forward:

This will acknowledge your letter of November 23rd. We will start to work on the samples as soon as they arrive. We can probably carry out the work outlined on page 2 of your letter under items 1, 2, 3, 4 and 7.

The work suggested under 5 and 6 would be very difficult to carry out and in any event would require more material. We can investigate the possibility of irradiations but as you can guess this may be very difficult or seriously delayed.

I have asked Mr. Burger to send you the second five pound sample you requested.

Yours very truly,

(sgd) E. B. Spice.

EBS/vbf.

W. J. Bennett,
A. Thunaes,
Dr. J. Convey.

APPENDIX VII

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

Department of Mining
and Metallurgy

January 17th, 1958.

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

Dear Arvid:

I enclose a copy of Progress Report No. 2 on Preparation of UO_2 Powder by Hydrogen Precipitation.

This report outlines the procedure and results obtained using solutions of uranium in sodium and ammonium carbonates. Also included are the analyses of two lots of UO_2 made by precipitation from ammonium carbonate solutions and examined by Eldorado Mining and Refining Ltd. at Port Hope.

Some further tests are now under way to study the production of UO_2 by hydrogen reduction of the ethylene diamine complex. Results will be reported as soon as the work is complete. Also, it is proposed to make additional samples of UO_2 for spectrographic analysis and testing.

Would it be possible to obtain about 100 lbs. of representative Beaverlodge ore to make a series of ethylene diamine leaching tests? We have already done a considerable amount of work along this line on one or two other ores that happened to be on hand, but would like to see how the Beaverlodge ore behaves.

Sincerely,

(sgd) F. A. FORWARD.

FAF/DC
Encl.

cc. E. B. Spice
J. Convey
D. R. Wiles

Hydrometallurgical Production of Fine UO₂ Powder

Progress Report No. 2

D. R. Wiles and J. P. Vizsolyi

January 10, 1958.

- Object: To investigate hydrometallurgical production of UO₂ powder for possible use in producing reactor fuels.
- Method: The method used is the precipitation of UO₂ from uranyl carbonate solutions by hydrogen under pressure.
- Materials: Uranium oxide used as starting material was UO₃ prepared from Beaverlodge chemical precipitate by the peroxide method. The Nickel catalyst used is of the same nature as described in Report No. 1, but a variety of sizes have been used up to about 200 μ . Other materials used are reagent grade.
- Summary: Stress has been shifted from production of a very fine powder to production of a very pure powder, which might be reduced in size at a later stage. The use of Ammonium carbonate instead of Sodium carbonate solutions, coupled with use of larger particles of Ni catalyst have led to conditions under which rapid production of high-purity UO₂ is possible. Spectrographic analyses have shown many impurities to be below tolerance levels. The presence of other impurities in significant quantities can largely be explained by lack of awareness of their presence, and it is felt that with care the purity of the oxide may well be made to conform to specifications for most elements. Nickel still remains a problem.
- Results: Two batches of UO₂ powder were shipped to Eldorado Mining and Refining (1944) Ltd. for further testing. Results of analyses were very encouraging. Sintering and in-pile tests have not yet been done.
- Conclusions: It appears that this may prove to be a feasible method for commercial production of Reactor-Grade UO₂.
- Discussion:
- The work done since the previous Report (20 August, 1957) can be divided into several stages, which will be described

separately.

1. Production of a large amount of UO_2 powder using Sodium Carbonate

Solutions:

This work was done under various conditions, but the results showed no useful trends. It was found that several successive precipitations could be made using the same batch of catalyst. In all experiments at this stage the results indicated that only up to a maximum amount of UO_2 could this procedure be followed, and the rates were progressively slower. That this was a case of coating the catalyst with product is shown by the complete absence of a non-magnetic (i.e. Ni free) UO_2 fraction in many cases. These results, however, appear to be true only for the fine nickel powder (see below for further results).

A batch of UO_2 was ultimately produced by this tedious single-batch process. Analysis showed the following impurities:

Ni 0.39%
Na 3.81%

It was felt that a more efficient magnetic separation could remove all or nearly all of the nickel. The sodium, however, was more difficult, and washing attempts caused serious hydrolysis, and reduction of the sodium content only to 2.62%. It was therefore decided that the most immediate problem was not the direct preparation of a very fine powder, but above all the direct production of a very pure powder which, if necessary, could be pulverized further at a later stage. Subsequent work was directed toward attaining the required purity.

2. Tests of the applicability of ammonium carbonate solutions

Because of the volatility of solid ammonium carbonate, it was considered possible that ammonium carbonate solutions might lead to a higher-purity oxide. The first tests, exactly analogous to previous ones using sodium carbonate, showed that reduction in this system is, indeed, as fast as in the sodium system. Analyses of the first products showed, after magnetic separation:

Ni 0.39%

which is comparable to results obtained using sodium carbonate.

Subsequent tests showed that if larger Ni powder was used (e.g. 100 - 200 μ) the reduction was fast, and remained fast for subsequent runs. For example, in one experiment using 30 g/l 100 μ Ni powder, 45 g/l $(\text{NH}_4)_2\text{CO}_3$ plus NH_4OH to pH 8.5, the reduction of 4 g/l UO_2^{++} was complete within 10 minutes in each of ten successive precipitations. The product of this series of precipitations was identified by X-ray diffraction as UO_2 . Chemical analysis of this product showed the following impurities:

Ni	0.22%
H_2O	2.30%
N^2	trace

These results seem to indicate the usefulness of the ammonium carbonate solutions for precipitation. It should be pointed out that some nickel dissolves when fresh UO_2^{++} is added, but is apparently reprecipitated by the hydrogen.

3. Production of UO_2 using ammonium carbonate solutions

It was found uranium could be precipitated in less than 10 minutes, and that recharging and reprecipitation could be completed in 15 to 20 minutes.

Two 'production runs' were done by this method, the first of which involved 25 precipitations and the second 37 successive precipitations with no noticeable decrease in rate. The only fault with such runs is that after a large amount of UO_2 accumulates, it was found difficult to keep the sampling valve clean and pressure tight. This is not a serious problem.

The products from these two series were magnetically freed of nickel, and sent to Eldorado Mining and Refining Co. for further analysis and testing.

Analyses made in this laboratory gave the following results:

	<u>Lot 23</u>	<u>Lot 24</u>
Ni	0.37%	1.3%
Insol.	none detectable	0.04%
U:O ratio	-	1:2.071
UO_2	92%	92.8%
Volatile at 150°C	1.7%	

The following are results of spectrographic analysis kindly performed by Eldorado Mining and Refining Co.

	<u>Lot 23</u>	<u>Lot 24</u>
Ag	0.3 ppm U	1.5 ppm U
Al	> 600	600
As	9	5
B	2	> 2
Bi	< 0.2	< 0.2
Cd	0.1	< 0.1
Co	9	9
Cu	150	300
Fe	40	30
Mg	35	75
Mn	9	9
P	50	35
Pb	30	45
Si	> 2000	> 2000
Sn	5	< 1

'none detected' in either batch were Be, Mo, and Zn.

Some comment might be made on these analytical results:

The very high content of Al, Fe, and Si is likely attributable to small quantities of iron and aluminum silicates which passed through from the original A.D.U. (Beaverlodge chemical precipitate). While this original A.D.U. was purified (peroxide method), small amounts of these materials might well have passed the filters. If so, then these elements can easily be removed by more careful filtration.

The high content of copper in both batches can be traced to the fact that some of the uranium used in these experiments had previously been recovered from earlier experiments in which copper was being investigated as a possible catalyst. This impurity, too, can easily be eliminated.

Tests of the sinterability, reactor characteristics, and so on are being done by Eldorado, by the Mines Branch, and by A.E.C.L. No results have been reported yet.
