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EXAMINATION OF AMMONIUM DIURANATE (YELLOW CAKE)
SAMPLES PRODUCED BY THE EXTRACTION METALLURGY DIVISION,
MINES BRANCH, OCTOBER 1959 TO JANUARY 1960

by
NORMAN F. H. BRIGHT, A. HUBERT WEBSTER
AND RICHARD H. LAKE

MINERAL SCIENCES DIVISION

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SUMMARY OF RESULTS

Thirteen samples of "yellow cake" produced by ammonia precipitation from a sulphuric acid leach of Elliott Lake uranium ore, by the Extraction Metallurgy Division of the Mines Branch, Ottawa, have been assessed as to their potentialities as possible source materials for the production of reactor-grade uranium dioxide. The materials consist of ammonium diuranate of variable $\text{NH}_3:\text{UO}_3:\text{H}_2\text{O}$ molar proportions, with significant amounts of uranyl sulphate and other materials as impurities.

Reduction in hydrogen at 900-925°C yields a very fine pyrophoric uranium dioxide. The pyrophoricity can be controlled to some extent by special handling procedures.

Pellets made by the cold-pressing and sintering technique were, in general, unsatisfactory owing to cracking, bloating and distortion. High densities were, however, obtainable with some samples.

The unsatisfactory physical characteristics of the pellets could not be attributed solely and directly to the sulphur contamination.

Certain samples gave quite reasonable behaviour and might be considered as a basis for further work towards the production of reactor-grade uranium dioxide.

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INTRODUCTION

During recent months, the Extraction Metallurgy Division of the Mines Branch, Ottawa, has been engaged on a programme of work on Elliott Lake uranium ore. This programme, conducted on a pilot-plant scale, involved an acid leaching with sulphuric acid and subsequent precipitation with ammonia with the intention of recovering an ammonium diuranate (or "yellow cake") precipitate. It was hoped that this ammonium diuranate (ADU) would be of such a quality that, after hydrogen-reduction to yield uranium dioxide powder, it could be fabricated into uranium dioxide compacts by the cold-pressing and sintering technique. It was further hoped that this uranium dioxide powder would be of reactor-grade quality, that is, that the sintered compacts made from it would have a high sintered density (10.3 g/cc or higher) and would be of satisfactory physical form, viz., free from cracks, bloating, distortion and other defects, and also would contain no impurities that would be exceptionable from a thermal neutron capture point of view.

During the period October 1959 to January 1960, thirteen such samples of yellow cake, were submitted to the Mineral Sciences Division by Mr. H.W. Parsons and Mr. R. Simard of the Solution Metallurgy Section of the Extraction Metallurgy Division, with a request for their evaluation as possible sources of UO_2

for reactor fuel elements and also for spectrographic analyses of the UO_2 obtained, for significant impurities. This request was contained in a Memorandum dated October 9, 1959, from Dr. K.W. Downes, Chief, Extraction Metallurgy Division, to Dr. A.T. Prince, Chief, Mineral Sciences Division.

The samples have been evaluated as to their suitability as sources for reactor-grade UO_2 in the Physical Chemistry Section and examined spectrographically in the laboratories of the Analytical Chemistry Section.

The code numbers of the thirteen samples are listed in Table 1, which also gives certain analytical results which were supplied by the Extraction Metallurgy Division. The various samples had been precipitated under widely differing conditions of temperature, pH, settling times, and additions of flocculating agents.

TABLE 1
Assays of Yellow Cake Samples

Sample No.	Assay (Wt. %)		
	Uranium as U_3O_8	$SO_4^{=}$	NH_3
# 453	84.97	4.08	2.91
# 455	81.88	9.15	3.64
# 456	91.11	0.75	1.48
# 458	88.42	2.11	2.17
# 461	85.05	4.65	2.96
# 462	89.25	1.28	2.31
# 466	89.27	0.75	2.01
# 467	88.95	1.02	2.29
# 468	86.95	1.92	2.62
# 469	88.37	1.77	2.40
# 470	88.88	2.64	2.45
# 471	87.89	1.89	2.38
# 472	89.50	0.63	2.00

The work done on these powders is described under the following headings: Examination of the samples, as received; Reduction to uranium dioxide powder; Examination of the UO_2 powder; Sintering tests; Effects of the presence of sulphur compounds on the sintering behaviour.

EXPERIMENTAL

A - Examination of the Samples, as Received

(i) Qualitative Spectrographic Analyses

The results of qualitative spectrographic analysis on six of the yellow cake samples are shown in Table 2. It appears that there are a number of impurities present in the yellow cake, in addition to sulphate, which is not detected spectrographically. The principal impurity detected was sodium; also present was arsenic, copper, magnesium and possibly, zinc, which were recorded in "strong trace" quantities. The cadmium and boron are possibly present in concentrations which would be objectionable from the standpoint of neutron capture.

TABLE 2
Qualitative Spectrographic Analyses

Sample No.	Impurity Elements															
	Na	As	Zn(?)	Cu	Mg	Pb	Cd	Fe	Si	Al(?)	P(?)	Ni	B	Ag	Mo	Mn
# 453	2	3	3	3	4	4	4	4	4	4	4	5	5	5	5	ND
# 455	2	3	3	3	3	4	4	4	4	4	4	5(?)	5	5	5	5(?)
# 456	2	3	3	3	3	4	4	4	4	4	4	4	5	5	5	5
# 458	2	3	3	3	3	3	4	4	4	4	4	5	5	5	ND	5
# 461	2	3	3	3	3	4	4	4	4	4	4	5	5	5	5	5(?)
# 462	2	3	3	4	4	4	4	4	4	4	5	5	5	5	ND	ND

1 - Major Constituent

3 - Strong Trace

5 - Faint Trace

2 - Minor Constituent

4 - Trace

ND- None Detected

(ii) Differential Thermal Analyses (DTA)

The experimental technique of differential thermal analysis has been adequately described in several earlier reports, and will not be detailed here. It will suffice to say that the tests were conducted in air, using a heating rate of 12 deg C per min. A high-fired alumina sample block was employed for this work. Pure alumina was used as the standard material and Pt: 13% Rh thermocouples were used to measure the sample and differential temperatures. The tests were conducted from room temperature up to 950-1000°C. The experimental observations made for the various samples are detailed in Table 3.

TABLE 3

Differential Thermal Analysis Results on Yellow Cake Samples

Temperature Range Sample No.	Observations in various Temperature Ranges				
	Room temperature-200°C	200°C-400°C	400°C-600°C	600°C-800°C	800°C-1000°C
# 453	Moderate, broad continuous endothermic reaction, with ill-defined peaks at 137°C and 199°C	Moderate endothermic peak at 332°C	Moderately small exothermic peak at 444°C	Moderate endothermic peak at 670°C	Large endothermic peak at 789°C. Nothing significant in range 830-950°C
# 455	Small broad endothermic peak at 173°C	Large endothermic peak at 333°C, with shoulder at 405°C	Small exothermic peak at 499°C	Moderately small endothermic peak at 642°C	Very large endothermic peak at 833°C. Nothing significant in range 860-1000°C
# 456	Moderate broad endothermic peak at 160°C	Moderately small endothermic peak at 345°C, possibly another at 289°C	Large exothermic peak at 419°C	Large endothermic peak at 644°C. Very small endothermic peak at 720°C	No significant feature in range 750°C-950°C
# 458	Small broad endothermic peak at 160°C	Moderate broad endothermic peak at 338°C	Moderately small exothermic peak at 435°C	Moderately large endothermic peak at 680°C. Moderate endothermic peak at 772°C	No significant feature in range 800°C-1000°C
# 461	Moderate broad endothermic peak at about 200°C with shoulder at 148°C	Moderately large broad endothermic peak at 345°C with shoulder at about 309°C	Moderate exothermic peak at 436°C	Moderate endothermic peak at 670°C	Large endothermic peak at 798°C. Slight endothermic indications in range 850°C-1000°C
# 462	Moderate broad endothermic peak at 189°C	Moderate endothermic peak at 335°C	Moderate sharp exothermic peak at 422°C	Fairly large endothermic peak at 680°C. Small endothermic peak at 752°C	Very small endothermic indication at 881°C. No further peak up to 1015°C
# 466	Moderate broad endothermic peak at 170°C	Rather small broad endothermic peak at 325°C	Large exothermic peak at 389°C	Moderately small endothermic peak at 663°C. Very small endothermic peak at 721°C	Slight endothermic indication at 880°C. No other peak up to 1025°C
# 467	Moderate broad endothermic peak at 188°C	Moderate broad endothermic peak at 329°C	Moderate exothermic peak at 423°C	Moderate endothermic peak at 660°C. Small endothermic peak at 747°C	Very small broad endothermic peak at 876°C. No further indication up to 1015°C
# 468	Moderate broad endothermic peak at 197°C	Fairly large broad endothermic peak at 333°C	Moderate exothermic peak at 427°C	Moderate endothermic peaks at 672°C and 771°C	Slight endothermic indication at 860-880°C. No further peak up to 1020°C
# 469	Moderate broad endothermic peak at 190°C	Fairly large broad endothermic peak at 335°C	Moderate exothermic peak at 432°C	Moderate endothermic peaks at 670°C and 768°C	Very slight endothermic indication at 880°C. No further peak up to 1015°C
# 470	Moderate very broad endothermic peak at 194°C	Large endothermic peak at 340°C	Moderate exothermic peak at 431°C	Moderate endothermic peak at 664°C. Fairly large endothermic peak at 780°C	No indication in the range 800°C-1015°C
# 471	Moderate broad endothermic peak at 196°C	Large endothermic peak at 333°C	Moderate exothermic peak at 425°C	Moderate endothermic peaks at 648°C and 770°C, the lower quite broad.	No indication in the range 800°C-1015°C
# 472	Moderate broad endothermic peak at 177°C	Small endothermic peak at 338°C	Fairly large exothermic peak at 418°C	Moderate endothermic peak at 663°C	Slight endothermic indication at about 880°C. No other peak up to 1020°C

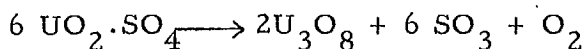
Since the samples were known to contain sulphate impurity in variable amounts, it was decided to conduct differential thermal analysis tests on uranyl sulphate, which is one likely form in which this impurity could be present. The material available for test was uranyl sulphate trihydrate, $\text{UO}_2 \cdot \text{SO}_4 \cdot 3\text{H}_2\text{O}$. When subjected to DTA in air under the same conditions as for the ADU samples, the following results were obtained:-

- a) Small endothermic peak at 98-105°C
- b) Large endothermic peak at 239-243°C
- c) Very sharp, moderate-sized endothermic peak at 307-309°C
- d) Small endothermic peak at 769°C
- e) Small endothermic peak at 804-809°C
- f) Very large endothermic peak at 840-890°C

The first three peaks are due to loss of water of crystallization.

The fourth peak is due to a crystallographic rearrangement in the anhydrous uranyl sulphate molecule. This fact is demonstrated by cooling the material immediately after this peak has been registered. An exothermic peak of the same magnitude and at the same location is observed. On re-heating the endothermic peak is again registered. On cooling the sample after registering peak f, peak d is not observed in reverse.

The final peak(s) are caused by the loss of SO_3 and oxygen from the uranyl sulphate according to the overall equation:-



The final product is U_3O_8 . These findings are in good accord with work recently published by Notz and Jaffé (1).

(iii) Thermogravimetric Analyses (TGA)

These were conducted at atmospheric pressure of air using a Stanton Thermobalance with a linear heating rate of about 375 deg C per hour. Sample weights of approximately 1.3 to 1.7 g were taken and the tests were conducted up to temperatures of about 1100-1150°C. All the observed weight changes were losses, which varied in relative magnitudes in the various samples and, in some cases, were more sharply resolved into discrete stages than in others. In all cases, there was a large loss of weight occurring in the temperature range R.T. to about 470 \pm 10°C. This loss was seen to be composite in nature in most cases, but the variations of gradient on the traces were insufficient to be able accurately to resolve the losses into sharply defined stages. However, there was generally a slight change in gradient at a temperature of about 250 \pm 10°C, and the weight loss at this stage was noted.

Over the temperature range 480°C to about 600°C, little, if any, weight change occurred. Thereafter, there was a moderate weight loss up to a temperature of about 700°C, followed

(1) For references, see page 38.

by a further loss occurring in the temperature range 700-850°C.

These last two stages were not perfectly resolved, but they were sufficiently so to permit a reasonable estimate of the weight losses involved in the two stages to be made. There was generally a very slight additional loss in the range 850-950°C, after which the weight remained sensibly constant up to the maximum temperature of observation.

The following table gives the detailed weight losses and temperatures for all the samples tested.

TABLE 4

Thermogravimetric Results on ADU Samples

Sample No.	Temperature Range	% Weight Loss Occurring in Given Temperature Range					Accumulated Weight Loss (%)	Direct Weight Loss by gravimetric data (%)
		R.T. to 250°C	250°C to 480°C	480°C to 700°C	700°C to 850°C	Above 850°C		
# 453		4.1	5.3	1.5	3.4	0.2	14.5	14.53
# 455		3.2	6.3	0.9	8.0	0.1	18.5	18.55
# 456		4.0	2.9	1.9	0.4	0.1	9.3	9.43
# 458		2.3	4.5	1.6	1.8	0.1	10.3	10.27
# 461		3.9	5.5	1.4	3.9	0.2	14.9	14.90
# 462		5.2	3.9	1.8	0.9	0.1	11.9	12.08
# 466		4.8	3.6	1.9	0.5	0.1	10.9	11.08
# 467		5.0	4.1	1.7	0.9	0.1	11.8	12.01
# 468		4.6	4.5	1.6	1.8	0.1	12.6	12.84
# 469		3.8	4.3	1.7	1.6	0.1	11.5	11.74
# 470		3.0	4.7	1.5	2.1	0.1	11.4	11.66
# 471		4.0	4.5	1.6	1.8	0.1	12.0	12.23
# 472		4.7	3.6	1.7	0.4	0.2	10.6	10.87

Thermogravimetric data were also obtained for uranyl sulphate trihydrate, in order to compare with the DTA data mentioned earlier. The results obtained were as follows:-

- a) a loss in weight, corresponding to approximately 0.5 mol. H_2O , occurring at a temperature below 130°C ; this was virtually complete before the next stage of dehydration occurred;
- b) an additional loss in weight, corresponding to approximately 2.5 mol. H_2O , occurring in the temperature range 130°C to 320°C ; there was an indication of complexity in this reaction, as there was a slight change in gradient at about $250\text{-}260^\circ\text{C}$, corresponding to a total water loss of 2 mol. H_2O from the original material;
- c) no further change until a temperature of about 730°C was reached;
- d) a large weight loss, not resolvable into separate stages, occurring in the range 730°C to 910°C , at which temperature it ceased abruptly.

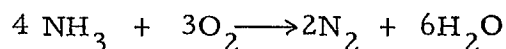
The magnitude of this final weight loss is in accord with the equation for SO_3 and O_2 evolution quoted on page 9.

(iv) Discussion of DTA and TGA Results

Ammonium diuranate is a material of somewhat ill-defined composition and may be represented by the formula $x \text{NH}_3 \cdot y \text{UO}_3 \cdot z \text{H}_2\text{O}$.

Its decomposition occurs in several stages:

- a) the loss of water and of ammonia, probably to some extent simultaneously, yielding a substantially anhydrous UO_3 ; this stage is endothermic.
- b) the ammonia may undergo oxidation in the gaseous phase to yield nitrogen and water, thus:-



This reaction is exothermic.

- c) the UO_3 produced by stage a, above, may undergo a crystallization from an amorphous to a crystalline form; this would be an exothermic process, and has been observed to occur in the course of earlier work on ADU and on the hydrates of UO_3 .
- d) the UO_3 loses oxygen to yield U_3O_8 as a final product; this is also an endothermic process.

The stages of decomposition of uranyl sulphate have already been detailed.

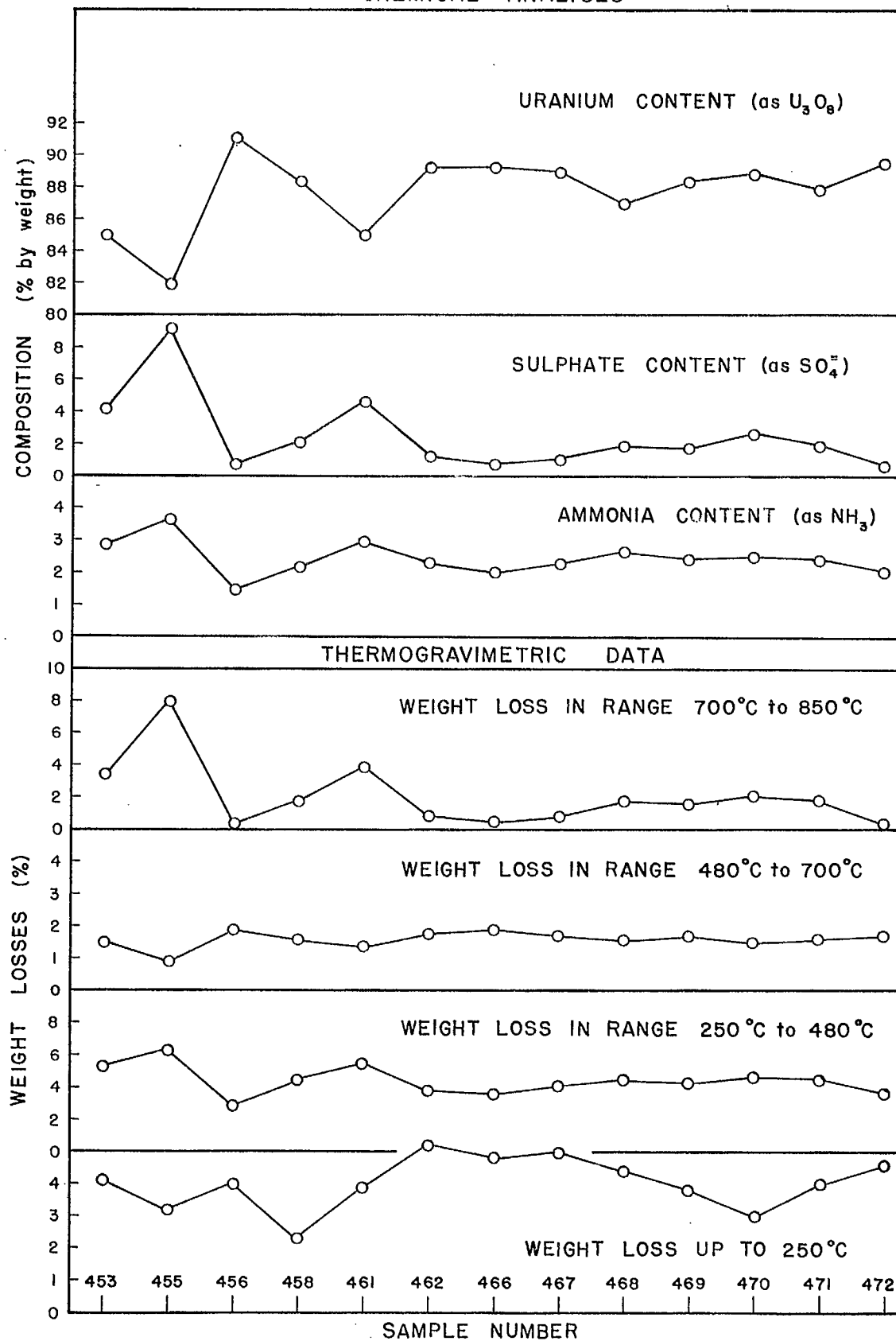
It is profitable now to consider the various stages of decomposition as observed in DTA and detailed in Table 3, and the

various stages of weight loss as observed in TGA and detailed in Table 4, along with the chemical analyses for uranium, sulphate and ammonia content as detailed in Table 1.

The various stages of weight loss, as recorded by TGA, for the various samples are plotted on Figure 1. On this figure are also plotted the analytical data given in Table 1. The correlations between the weight losses and the composition of the materials as supplied, can readily be observed by a study of these graphs.

FIGURE 1

CHEMICAL ANALYSES



It will be seen from Figure 1 that the variations in weight loss from one sample to another, occurring in the temperature range up to 250°C, follow the variations in uranium content (as U_3O_8) qualitatively to a large extent, though not perfectly. This will imply a somewhat variable degree of hydration of those materials which can lose water at temperatures below 250°C. This will include ADU particularly, as the degree of hydration of the uranyl sulphate is reasonably well defined.

Considering now the reactions occurring in the temperature range 250°C to 480°C, it will be seen that the weight losses follow quantitatively the sulphate content given in Table 1, and that there is good qualitative agreement between this sulphate content and the magnitude of the endothermic DTA peak(s) occurring at approximately 330°C. This is a strong indication that this peak is due to the dehydration of the uranyl sulphate impurity; it is observed at approximately the appropriate temperature.

Considering now the small exothermic peaks which occur in the range 420-440°C, it will be seen that there is no corresponding observable effect on the thermogravimetric charts. Such a behaviour could be obtained from the occurrence of a crystallization phenomenon from an amorphous condition in the specimen. A study of the magnitude of these exothermic peaks shows that there is a good qualitative correlation between this magnitude and the uranium content of the samples. It is known

from earlier work that uranium trioxide does exhibit such a recrystallization phenomenon in just this temperature range. It is, therefore, considered that the ADU will have decomposed to substantially anhydrous UO_3 at this stage, and that the UO_3 inverts from an amorphous to a crystalline condition, giving rise to this exothermic peak.

Considering now the reaction observed as an endothermic phenomenon occurring at $660 \pm 20^\circ\text{C}$ by DTA, and as a weight loss in the range 480°C to 800°C by TGA, it will be seen that the weight losses for the various samples follow the U_3O_8 content quite closely qualitatively. The magnitude of the DTA peaks behave somewhat similarly, though less obviously so.

This peak, and the weight loss, are attributed to the loss of oxygen from the UO_3 produced from the ADU, yielding U_3O_8 . This phenomenon, however, is complicated by the occurrence, at the same temperature range, of the crystal inversion in the now anhydrous uranyl sulphate, which will, of course, not be accompanied by any weight change. It is thus, not surprising that the correlations should be somewhat imperfect in the case of these reactions.

Considering now the endothermic peaks occurring in the temperature range 720 - 830°C , and the weight losses occurring in the range 700 - 850°C , it will be seen that there is an accurate quantitative correlation between the size of these peaks, the magnitude of the weight losses, and the sulphate content of the samples. This is

considered to be good proof that this reaction is due to the breakdown of the uranyl sulphate to U_3O_8 . Again, the phenomena are observed at the appropriate temperature.

The indication of a small endothermic reaction occurring at temperatures in the region of $880^{\circ}C$, and an accompanying very small weight loss, are thought to be due possibly to the breakdown of some additional impurity, perhaps, sodium sulphate. It will be recalled that the qualitative spectrographic analysis has indicated that sodium is a significant minor constituent in these yellow cake samples. Sodium sulphate melts at $884^{\circ}C$ and is stated to volatilize with some decomposition at somewhat higher temperatures. In the presence of much other material, the decomposition temperature may well be lowered to the range observed here.

Thus, the DTA and TGA results can be all logically explained on the basis of the samples consisting of ammonium diuranate of variable $NH_3:UO_3:H_2O$ molar proportions, and contaminated with a variable proportion of uranyl sulphate trihydrate, and also a small amount of other impurity, perhaps sodium sulphate.

B - Reduction to Uranium Dioxide Powder

A portion of each yellow cake was reduced to uranium dioxide by heating in hydrogen to 925°C, soaking for 30 min, and cooling in hydrogen. All reductions were done in a steel retort, except those of Samples #471 and #472, which were placed in copper boats held in a ceramic tube heated to the above temperature in a muffle furnace. This deviation in procedure was rendered necessary by the failure of the steel retort, after most of the samples had been reduced.

It was found, in general, that the freshly reduced samples were pyrophoric; that is, they oxidized rapidly and spontaneously, probably to U_3O_8 , on exposure to air at room temperature. This oxidation was manifested by a blackening of the sample and a marked rise in temperature. In order to inhibit the oxidation, the samples, immediately after removal from the retort, were placed on dry ice (solid carbon dioxide at -78°C) in a Dewar flask, and slowly warmed to room temperature with brief exposures to the air. In some cases, the oxidation was not arrested even by this procedure, and the sample had to be re-reduced. Table 5 indicates the stability of the samples, as determined on a small portion exposed to the air without having been previously placed on dry ice. The number of reductions to which each sample was subjected is also indicated.

TABLE 5

Reduction of Yellow Cake Samples to Uranium Dioxide Powder

Sample No.	Stability in Air after Reduction	Number of Reductions
# 453	Pyrophoric	3
# 453 (X) [★]	Pyrophoric	1
# 455	Not pyrophoric	1
# 456	Pyrophoric	1
# 458	Not pyrophoric	1
# 461	Not pyrophoric	1
# 462	Pyrophoric	1
# 466	Pyrophoric	2
# 467	Pyrophoric	2
# 468	Pyrophoric	1
# 469	Slightly pyrophoric	1
# 470	Not pyrophoric	1
# 471	Not pyrophoric	1
# 472	Pyrophoric	2

[★] Second portion of yellow cake sample #453 reduced.

The presence of sulphur oxides in the effluent gases from the retort was demonstrated by passing these gases through a lead acetate solution. The formation of a white precipitate during the heating period, which was, presumably, either lead sulphite and/or lead sulphate, indicated the presence of either SO_2 and/or SO_3 , respectively, in the gases. At higher temperatures, a black precipitate was formed; this was presumably lead sulphide, formed by the reduction of the sulphate to H_2S .

Small growths appeared on the inside surfaces of the retort during the reductions. Qualitative chemical analysis of these protrusions showed the presence of sulphide and of iron. X-ray diffraction analysis indicated a mixture of α -iron and pyrrhotite. It thus appears that sulphur from the samples was attacking the retort, possibly when in the form of moist H_2S .

C - Examination of the Uranium Dioxide Powder

Selected uranium dioxide samples, produced in the manner described in the previous section, were examined by differential thermal analysis, by X-ray diffraction, and were subjected to chemical analysis for sulphur. The results of these tests are summarized in Table 6.

TABLE 6

Results of Examination of UO_3 Powder Samples

Sample No.	DTA Results			% Sulphur in UO_2 powder	% Sulphur calculated as per page 23	Lattice Parameter a_o (in A) (± 0.005 A)
	Temperature of Lower Peak ($^{\circ}\text{C}$)	Temperature of Upper Peak ($^{\circ}\text{C}$)	Peak Separation (degrees C)			
# 453	173	398	225	0.15	1.65	5.46_2
# 453 (X)	-	-	-	0.35	1.65	-
# 455	171	413	242	0.21	3.75	5.46_4
# 456	177	407	230	0.25	0.28	5.46_6
# 458	171	409	238	0.20	0.82	-
# 461	-	-	-	0.20	1.87	-
# 462	-	-	-	0.20	0.50	-

In the DTA examination, the lower-temperature oxidation peaks occurred at temperatures considerably lower than is usual and the higher-temperature peaks at rather higher temperatures than usual, resulting in very large peak separations. This result is not unexpected in view of the observed tendency of these samples to oxidize rapidly in air. Large peak separations are, in general, associated with materials of large specific surface area which sinter to high densities (2).

The sulphur analyses in Table 6 are accompanied, for comparison, by calculated figures representing the sulphur contents which would have been obtained if no sulphur had been lost during the reduction process. These figures were deduced by use of the relationship:-

$$\frac{\% S \text{ (calc.)} \times 100}{100 - \% S \text{ (calc.)}} = \frac{\% SO_4 \text{ in yellow cake}}{\% U_3O_8 \text{ in yellow cake}} \times \frac{32}{96} \times \frac{281}{270} \times 100$$

It will be noted that, in most samples, a substantial proportion of the sulphur has been lost, and that the sulphur contents appear to approach a uniform level of about 0.2%, regardless of the initial sulphur content of the yellow cake.

The lattice parameters observed for the uranium oxide (fluorite-type structure) were very slightly lower than the lattice parameter for stoichiometric α - UO_2 , viz., $a_0 = 5.469 \text{ \AA}$. The smaller lattice parameters were, undoubtedly, the result of the presence of small amounts of non-stoichiometric oxygen,

although it is rather unusual for these departures from the value for the stoichiometric material to be observed in a material that has not been annealed at moderately elevated temperatures. There was no evidence of the presence of tetragonal U_3O_7 or of U_3O_8 .

Oxygen:uranium atomic ratios were not determined since the presence of impurities vitiates both the oxidation and the reduction methods for determining this ratio (3).

D - Sintering Tests

Since the yellow cake samples were being examined principally to assess their suitability for the production of uranium dioxide which could be cold-pressed and sintered to yield compacts satisfactory for nuclear fuel elements, an extensive series of sintering tests was undertaken, using the UO_2 samples produced as described in Section B of this report.

(i) Procedures

The "green" pellets were formed by pressing 5 g samples of uranium dioxide powder in a 0.5 inch mould, using 0.2 ml kerosene as binder and an alcoholic solution of stearic acid as mould lubricant. The forming pressure normally used was 40,000 psi, and pellets from samples #453 to #462 were formed at this pressure, even though the pellets made from sample #462 showed some tendency to chip on extrusion from the mould. Green pellets made from samples #466 to #472 were very prone to

chipping when pressed at 40,000 psi. It was found, however, that pellets from these materials, when pressed at 20,000 psi, did not chip excessively.

The pellets were sintered in a hydrogen atmosphere by either of two sintering cycles:-

- (a) the "Regular Cycle", which is the one used routinely for sintering tests previously conducted in the Physical Chemistry Section (2, 4, 5), or
- (b) the "Slow Cycle", which was adopted in an attempt to improve the quality of the sintered pellets.

The details of these cycles are as follows:-

- (a) Regular Cycle - The pellets were heated at about 350 deg C per hour to 1700°C, soaked for 30 minutes, and cooled at about 900 deg C per hour.
- (b) Slow Cycle - The pellets were heated slowly to about 1020°C, soaked at this temperature overnight, heated at 150 deg C per hour to 1700°C, soaked for 30 minutes and cooled at about 250 deg C per hour.

All sintering tests were done in a molybdenum-wound, alumina-tube furnace. Temperatures were measured using a Leeds and Northrup optical pyrometer.

Densities were determined on all sintered pellets by displacement of water, and by weighing and dimensional measurement

in the case of those pellets which were not too severely deformed.

(ii) Densities and General Appearance of Pellets

Most of the pellets were cracked and, in some cases, bloated after sintering. Such pellets would be quite unacceptable for use as nuclear fuel elements. Table 7 presents a summary of sintered densities as determined by displacement of water:

TABLE 7

Sintered Densities of UO_2 Pellets as
Determined by Displacement of Water

Conditions of Preparation								
Forming pressure	40,000 psi				20,000 psi			
Cycle	Regular		Slow		Regular		Slow	
Sample No.	Density g/cc	No. of pellets tested	Density g/cc	No. of pellets tested	Density g/cc	No. of pellets tested	Density g/cc	No. of pellets tested
# 453	10.01	7	9.95	1	-	-	-	-
# 453 (X)	-	-	9.95	1	-	-	-	-
# 455	10.17	4	10.49	3	-	-	-	-
# 456	10.41	4	10.18	4	10.35	1	-	-
# 458	10.56	2	10.68	3	-	-	-	-
# 461	10.09	2	9.89	1	-	-	-	-
# 462	10.37	3	10.61	3	-	-	-	-
# 466	10.28	1	-	-	10.22	1	10.54	1
# 467	10.05	1	-	-	9.96	1	10.32	1
# 468	10.24	1	-	-	10.11	1	10.33	1
# 469	10.23	1	-	-	10.14	1	10.42	1
# 470	10.15	1	-	-	9.75	1	10.41	1
# 471	10.68	1	-	-	10.67	1	10.77	1
# 472	10.74	1	-	-	10.74	1	10.80	1

If the density reported in this table is a mean value, then the number of pellets on which the mean was determined is indicated. In Table 8 a more qualitative evaluation of the results is presented, the samples being ranked in Classes I to VII on the basis of density and appearance (i.e., freedom from cracks and bloating) of the sintered pellets. The detailed results of all sintering tests are tabulated in the Appendix to this report. (See pages 39 to 41).

TABLE 8

Qualitative Evaluation of Sintered Pellets

Legend: Density:- A - above 10.5 g/cc
 B - 10.2 to 10.5 g/cc
 C - below 10.2 g/cc

Appearance:-
 A - good, - no superficially noticeable cracks
 B - few cracks
 C - many cracks and/or bloating

Sample Nos.	Classification	Density		Appearance	
		Reg. Cycle	Slow Cycle	Reg. Cycle	Slow Cycle
# 458	I	A	A	B	A
# 471, # 472	II	A	A	B	B
# 462, # 466	III	B	A	B	B
# 455	IV	C	A	C	B
# 456	V	B	C	B	C
# 467, # 468, # 469, # 470	VI	C	B	C	C
# 461, # 453	VII	C	C	C	C

It appears from these results that only samples #458, #471 and #472 give uranium dioxide which even approached acceptable quality.

The sintered densities obtained in some cases are, however, very good, and in agreement with expectations based on the DTA results quoted in Table 3. The poor densities exhibited by many of the pellets are due principally to internal cracking, which could be readily observed in pellets after sectioning with a diamond saw.

The effect of changing the sintering cycle from "regular" to "slow" varied from sample to sample. In certain cases, however (for example, Samples #455, #458, #462, #466), there were definite improvements in sintered density and/or appearance on changing to the "slow" cycle.

It was noted that the sintered pellets were generally tapered, having a greater diameter at one end than at the other. The difference was generally about 1% of the diameter. This effect has not been generally exhibited by material produced by precipitation of ADU from nitrate solution, insofar as the Mines Branch experience is concerned.

(iii) Further Examination of Sintered Pellets

(a) Examination of Polished Sections

Diametral sections of some of the sintered pellets were examined microscopically, after polishing and etching with 9:1 $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$. The interior portions of the pellets sintered by the

"regular" cycle showed a structure with striated grains, illustrated in Figures 2 and 4. The regions closer to the surface of these pellets did not exhibit this structure (see Figure 3). Very little or no striation was observed in pellets sintered by the "slow" cycle. This striated structure resembles the structures found in material in which twinning or slip has occurred under stress. The nature and cause of this microstructure was not determined, but it does not appear to be directly related to the deformation of the pellets, since slowly-sintered pellets showed deformation but not this unusual microstructure. Samples of pellets exhibiting this microstructure have been given to the Ceramic Fuels Section of the Metallurgy Branch of AECL, Chalk River, for their comments, but, as yet, nothing has been received concerning them.

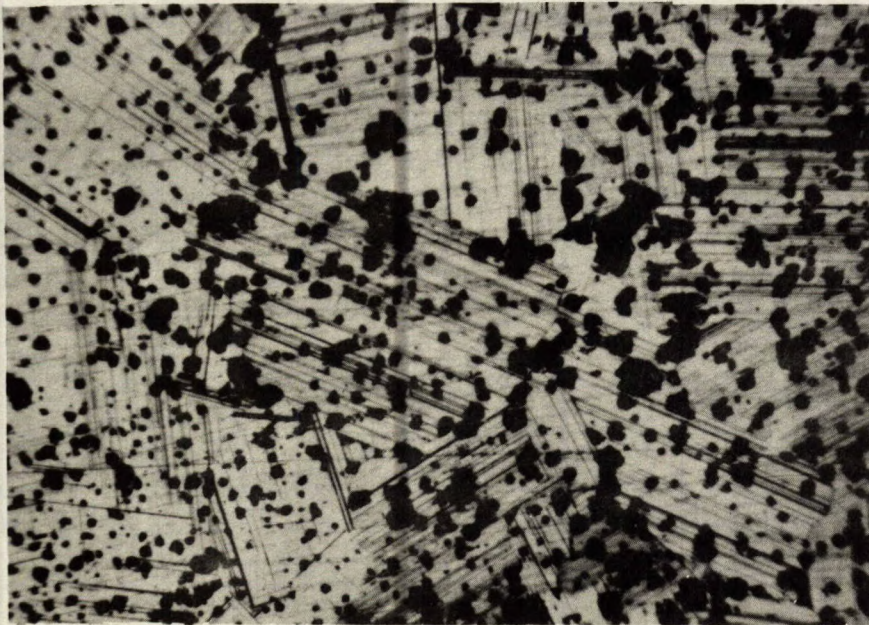


Figure 2. - Pellet 1A (Sample # 453)
Interior region, showing striated grains.
 $\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4$ etch.

Magnification: 270X

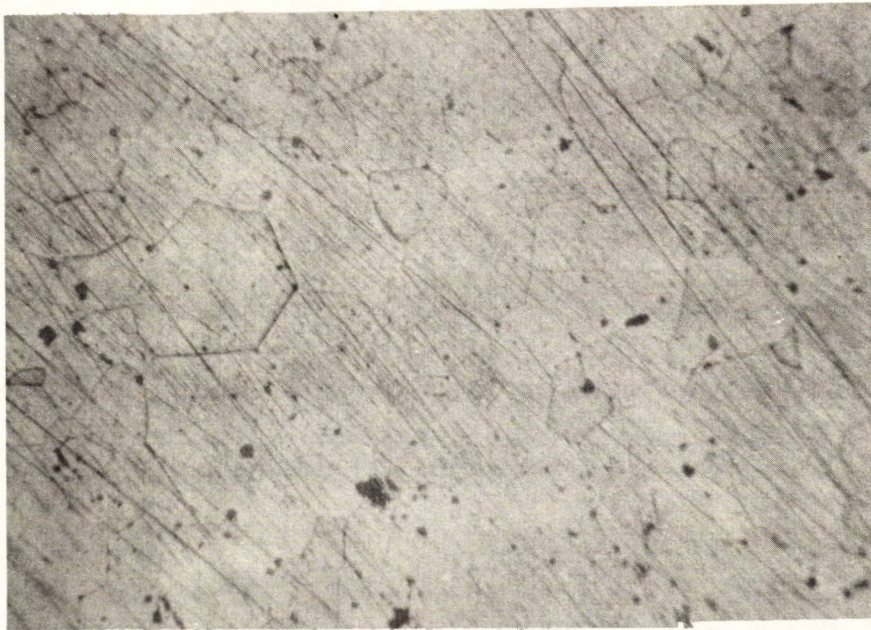


Figure 3. - Pellet 1A (Sample # 453)

Region near surface; no striated grains evident. The straight lines crossing the section are polishing scratches.

$\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4$ etch.

Magnification: 270X

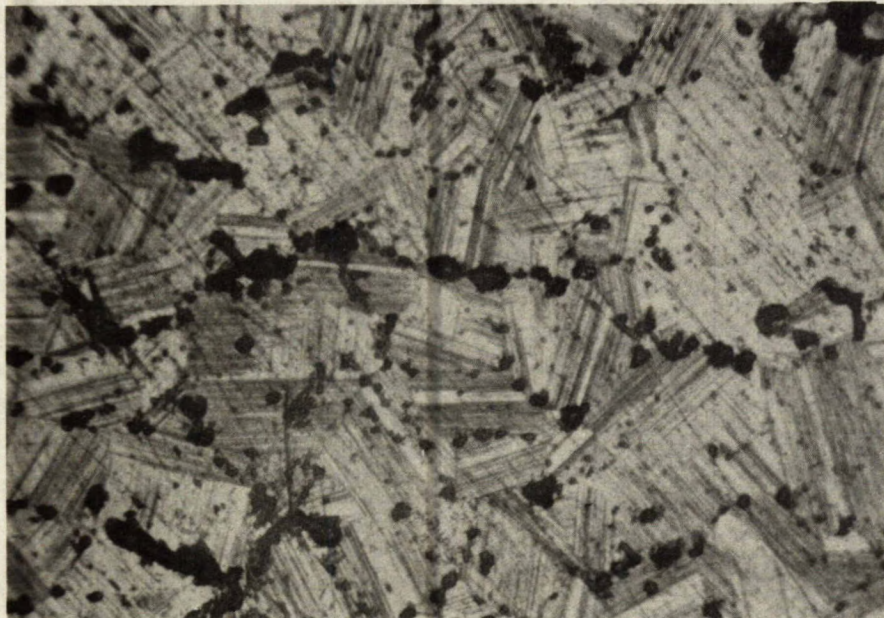


Figure 4. - Pellet 3A (Sample # 456)
Interior region, showing striated grains.
 $\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4$ etch.

Magnification: 270X

(b) X-ray Examination

X-ray examination, by the powder diffraction method, of material from one pellet (pellet 6A from Sample #462) showed the presence of only the cubic α - UO_2 (fluorite-type) phase with $a_0 = 5.473 \pm 0.003 \text{ \AA}$; this value is slightly larger than the accepted value of 5.469 \AA for stoichiometric α - UO_2 . No second phase was detectable.

E - Effects of the Presence of Sulphur Compounds on Sintering Behaviour

Considerable sulphate impurity was present in the original yellow cake samples, and the sulphur was not completely removed during the reduction to UO_2 powder. In an attempt to determine the effect of the presence of sulphur compounds on the sintering behaviour of UO_2 in the absence of other complicating factors, sulphur compounds were added to material which was known to give good pellets, i.e., to sinter to a reasonably high density, and to be free from distortion cracks, bloating, etc., when sintered in the absence of sulphur compounds.

(i) Addition of Potassium Pyrosulphate to UO_2

Potassium pyrosulphate was added to UO_2 which had been produced by the hydrogen reduction of Eldorado UO_3 . A pellet containing $\text{K}_2\text{S}_2\text{O}_7$ equivalent to 1% $\text{SO}_4^{=}$ did not crack on sintering, but gave a lower density than a similar pellet without $\text{K}_2\text{S}_2\text{O}_7$.

(ii) Addition of Uranyl Sulphate to the ADU before Reduction

Uranyl sulphate hydrate (Fisher, purified) was added to a sample of Eldorado UO_3 to give a mixture containing about 5% $\text{SO}_4^{=}$. This mixture was reduced by heating to 925°C in hydrogen according to the usual procedure; pellets from the resulting UO_2 were pressed and then sintered by the "regular" cycle.

The reduced mixture had a sulphur content of 0.13%, somewhat lower than that found in the reduced yellow cake samples. The pellets cracked and "capped" slightly on sintering, but did not show the internal cracking characteristic of the pellets made from the yellow cake samples. The "capping" may have been due to the UO_2 produced from the uranyl sulphate having poor sintering characteristics. Microscopic examination of a polished section revealed no striated grains, nor any other unusual feature.

There is thus no unequivocal evidence that the presence of sulphur compounds was the sole and direct cause of the cracking and the unusual microstructures found in pellets made from the yellow cake samples.

CONCLUSIONS

(i) The yellow cake samples, on reduction in hydrogen at 925°C, produced a pyrophoric uranium oxide. This sensitivity to oxidation can largely be overcome by special handling procedures.

(ii) Pellets made from UO_2 obtained by reduction of the yellow cake samples, were generally cracked and, in some cases, bloated on sintering in hydrogen. Changing the sintering cycle partially alleviated these effects for certain samples only.

(iii) The UO_2 powders produced from a number of the yellow cake samples were capable of giving pellets which sintered to densities greater than 10.5 g/cc.

(iv) Considerable quantities of impurities other than sulphur appear to be present in the yellow cake samples. The poor quality of the sintered pellets may possibly be associated with the presence of one or more of these impurities.

(v) As far as can be determined, the presence of compounds of sulphur is not the direct cause of the poor quality of the sintered pellets.

(vi) An unusual microstructure, consisting of striated grains, was observed in pellets sintered under certain conditions.

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NFHB:AHW:RHL/DV

Appendix follows on Pages 39 to 41 .

APPENDIX

Detailed Results of Sintering Tests

Sample No.	Pellet No.	Forming Pressure psi	Cycle	Sintered Density - g/cc		Remarks
				From weight and measurements	By displacement method	
# 453	1A	40,000	Regular	9.89	10.18	Cracked
	1B	40,000	Regular		10.32	Slight cracking and bloating
	1C	40,000	Regular	9.44	9.89	Cracked
	1D	40,000	Regular		9.90	Cracked, bloated
	1E	40,000	Regular		9.72	Cracked, bloated
	1F	40,000	Regular		10.12	Cracked, bloated
	1G	40,000	Regular		9.93	Cracked, bloated
	1C ¹	40,000	Slow		9.95	Cracked, slightly bloated
# 453(X)	1XC	40,000	Slow		9.95	Severely cracked
# 455	2A	40,000	Regular	10.46	10.06	Cracked
	2B	40,000	Regular		9.97	Broken
	2C	40,000	Slow		10.68	Good
	2D	40,000	Slow		10.35	Slightly bloated, cracked
	2E	40,000	Slow	10.11	10.45	Good
	2H	40,000	Regular	9.97	10.34	Cracked
	2I	40,000	Regular		10.28	Broken in two pieces
# 456	3A	40,000	Regular	10.32	10.60	Cracked
	3B	40,000	Regular		10.59	Slightly cracked
	3C	40,000	Slow		10.28	Cracked, slightly bloated
	3D	40,000	Slow	10.09	9.99	Bloated
	3E	40,000	Slow		10.18	Bloated
	3F	40,000	Slow		10.27	Bloated
	3F ¹	40,000	Regular		9.95	Cracked
	3G	20,000	Regular		10.35	Cracked
	3H	40,000	Regular	9.68	10.47	Cracked

(cont' d)

Appendix (cont' d)

Sample No.	Pellet No.	Forming Pressure psi	Cycle	Sintered Density - g/cc		Remarks
				From weight and measurements	By displacement method	
# 458	4A	40,000	Regular		10.49	Cracked
	4B	40,000	Regular	10.16	10.63	Slightly cracked
	4C	40,000	Slow	10.45	10.68	Good
	4D	40,000	Slow	10.34	10.72	Good
	4E	40,000	Slow	10.41	10.63	Good
# 461	5A	40,000	Regular		10.13	Cracked
	5B	40,000	Regular		10.04	Cracked
	5C	40,000	Slow		9.89	Cracked
# 462	6A	40,000	Regular		10.28	Cracked
	6B	40,000	Regular		10.38	Cracked
	6B ¹	40,000	Regular	9.97	10.45	Slightly cracked
	6C	40,000	Slow	10.29	10.57	Slightly cracked
	6D	40,000	Slow	10.37	10.64	Cracked
	6E	40,000	Slow	10.24	10.61	Cracked
# 466	7A	20,000	Regular	9.99	10.22	Slightly cracked
	7B	20,000	Slow	10.21	10.54	Slightly cracked
	7D	40,000	Regular		10.28	Cracked
# 467	8A	20,000	Regular		9.96	Cracked, slightly bloated
	8B	20,000	Slow		10.32	Cracked, bloated
	8D	40,000	Regular		10.05	Cracked, bloated
# 468	9A	20,000	Regular		10.11	Cracked
	9B	20,000	Slow		10.33	Cracked, slightly bloated
	9D	40,000	Regular		10.24	Cracked, slightly bloated

(cont' d)

Appendix (concluded)

Sample No.	Pellet No.	Forming Pressure psi	Cycle	Sintered Density, g/cc		Remarks
				From weight and measurements	By displacement method	
# 469	10A	20,000	Regular	9.74	10.14	Cracked
	10B	20,000	Slow	10.04	10.42	Cracked
	10D	40,000	Regular		10.23	Cracked
# 470	11A	20,000	Regular		9.75	Cracked, slightly bloated
	11B	20,000	Slow	10.10	10.41	Cracked
	11D	40,000	Regular		10.15	Cracked
# 471	12A	20,000	Regular	10.45	10.67	Slightly cracked
	12B	20,000	Slow	10.49	10.77	Very slightly cracked
	12D	40,000	Regular		10.68	Slightly cracked
# 472	13A	20,000	Regular	10.50	10.74	Slightly cracked
	13B	20,000	Slow	10.58	10.80	Slightly cracked
	13D	40,000	Regular		10.74	Slightly cracked