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SOME OBSERVATIONS ON THE REACTIVITY OF  
PLUTONIUM DIOXIDE

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TECHNOLOGY-PLUTONIUM  
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# ABSTRACT


The index of refraction of  $\text{PuO}_2$  made by thermal decomposition of  $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  gradually increases from a value  $< 1.9$  to  $2.40$  as the decomposition temperature is increased from  $150^\circ$  to  $1000^\circ\text{C}$ . This change in refractive index parallels a gradual change in the x-ray diffraction pattern from weak, diffuse lines for  $\text{PuO}_2$  ignited at  $150^\circ$  to sharp, well-resolved lines for  $\text{PuO}_2$  ignited at  $1000^\circ\text{C}$ . Similar results are observed for  $\text{PuO}_2$  made by thermal decomposition of  $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 11\text{H}_2\text{O}$ . The refractive index of  $\text{PuO}_2$  made from Pu metal at  $170^\circ\text{C}$  is  $2.40$  and is not affected by further ignition at higher temperatures, although crystal growth does occur.

The rate of solution of  $\text{PuO}_2$  in an  $\text{HCl-KI}$  solution is greatest for samples prepared at low temperatures and decreases markedly for oxides ignited at higher temperatures.

These observations have been interpreted to mean that ignition at higher temperatures causes a gradual perfection of the originally highly distorted and impurity-containing  $\text{PuO}_2$  lattice obtained by low temperature decomposition of the oxalates and promotes the slow growth of crystallites. Both factors decrease the reactivity of the  $\text{PuO}_2$ .

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## INTRODUCTION

It has been observed by many investigators that the rate of reaction of  $\text{PuO}_2$  with HF gas is affected materially by the history of the particular sample of oxide used.<sup>(1,2,3,4)</sup>

As part of a study of this effect, the index of refraction of  $\text{PuO}_2$  made at different temperatures from several starting materials was measured. The rate of dissolution of the  $\text{PuO}_2$  in an HCl-KI solution was determined, and an effort was made to correlate these measurements with optical microscope and x-ray diffraction data.

## EXPERIMENTAL PROCEDURE

### PREPARATION OF OXIDE SAMPLES

Oxides from three different starting materials were made by the following procedures:

Thermal Decomposition of  $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 11\text{H}_2\text{O}$  - Approximately 150 grams of plutonium in nitric acid solution were purified by successive peroxide and oxalate precipitations (the latter from an HI solution), after which the Pu III oxalate was ignited to  $\text{PuO}_2$  at  $600^\circ\text{C}$  in an electric muffle. A small portion of this material was ignited longer at  $600^\circ\text{C}$ ; a sample was removed, and the remainder was ignited at  $950 - 1000^\circ\text{C}$ . The experimental conditions were as follows:

<u>Sample</u>	<u>Ignition Conditions</u>
1	18 hours at temperatures $< 300^\circ\text{C}$ 4 hours $300 \rightarrow 600^\circ\text{C}$ : 1/2 hour at $600 \pm 30^\circ\text{C}$
2	Additional ignition of 2.4 grams of sample 1: 8-1/4 hours at $600 \pm 30^\circ\text{C}$
3	Additional ignition of sample 2: 2-1/4 hours at $600 \pm 30^\circ\text{C}$ 1 hour $600 \rightarrow 950^\circ\text{C}$ 1-3/4 hours at $950 - 1000^\circ\text{C}$

Thermal Decomposition of  $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  - Approximately 80 grams of plutonium in nitric acid solution were purified as before by peroxide and oxalate precipitations. Reduction with HI was omitted in the last precipitation in order to produce Pu IV oxalate.

The Pu IV oxalate was ignited in a platinum boat in a nickel combustion tube furnace. The maximum temperature variation over the full length of the boat was  $25^{\circ}$  at  $1000^{\circ}\text{C}$ . Ignition at any one temperature was continued until the weight of the material decreased less than 0.05% per hour of heating. A 5 gram sample was then removed, and the remainder was heated at the next higher temperature. In this way ignitions were carried out at  $100^{\circ}$  intervals between  $100^{\circ}$  and  $1000^{\circ}\text{C}$ .

A small sample of the  $400^{\circ}$  material subsequently was heated for an additional 257 hours at  $400 \pm 15^{\circ}\text{C}$ , and a portion of the  $600^{\circ}$  material was heated for an additional 162 hours at  $600 \pm 15^{\circ}\text{C}$ .

PuO<sub>2</sub> from Plutonium Metal - Approximately 19 grams of PuO<sub>2</sub> were made by the reaction of  $\alpha$  metal turnings with water vapor in a slow stream of oxygen at  $160 - 170^{\circ}\text{C}$ . (The oxygen was saturated with water vapor at  $25^{\circ}\text{C}$ .) Precautions were taken to prevent the temperature of the oxide from ever exceeding  $170^{\circ}\text{C}$ .

Two 5.5 gram portions of this material were ignited to constant weight at  $535 \pm 10^{\circ}\text{C}$  and  $950 \pm 15^{\circ}\text{C}$ , respectively.

#### HCl-KI DISSOLVING TEST

As an indication of the reactivity of the different oxides the following reaction was used:



The fractions of different samples of  $\text{PuO}_2$  which dissolved under standard conditions were taken as a measure of their comparative reactivities.

All experiments were carried out in 125 ml flasks at  $28.5 \pm 0.5^\circ\text{C}$ . 1.3 - 1.5 grams of  $\text{PuO}_2$ , 3.00 grams of KI, and 50.0 ml of 9.9N HCl solution were added to a flask and the mixture was stirred for 18 hours. To prevent air oxidation of iodide ion in the acid solution the reaction was carried out in an argon atmosphere. The residue was filtered and washed with 2.5N HCl solution after which it was dried for 4 hours at  $150^\circ\text{C}$  and weighed. The filtrate was diluted to 200 ml and analyzed for plutonium.

Two additional series of reactivity measurements were made with low temperature oxides in which the reaction time was reduced from 18 hours to 1 hour. In the second of these series the HCl concentration was also reduced from 9.9 to 4.9<sub>5</sub>N. The other conditions were unchanged.

## RESULTS

Microscopic examinations and x-ray diffraction analyses were made by Eugene Staritzky of CMR-1 and F. H. Ellinger of CMR-5, respectively. Their results are given in Tables 1 through 3. (Plutonium and carbon analyses for the series of oxides from  $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  are tabulated in the table in the appendix.) Refractive index vs. ignition temperature data from Table 2 are also plotted in Figure 1.

Reactivity of Oxides in HCl-KI Solution - The reactivities of samples of  $\text{PuO}_2$  made from  $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 11\text{H}_2\text{O}$  and  $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  are shown in Figures 2 and 3. The reactivity is expressed as the percentage of the available Pu which dissolved in the standard HCl-KI solution as described under Experimental Procedure.

Since the refractive index of  $\text{PuO}_2$  prepared from  $\alpha$  metal was 2.40 regardless of ignition temperature, no similar plot could be made for it. However, the reactivity did vary with ignition temperature as shown in Table 4.



Table 1

Optical and X-ray Data for  $\text{PuO}_2$  from  $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 11\text{H}_2\text{O}$

<u>Sample Number</u>	<u>Maximum Ignition Temperature (<math>^{\circ}\text{C}</math>)</u>	<u>Microscopic Examination</u>	<u>X-ray Diffraction</u>
1	600 $^{\circ}\text{C}$ (1/2 hour)	Homogeneous, an- isotropic, refractive index $2.235 \pm 0.01$	$\text{PuO}_2$ pattern. Fuzzy lines typical of fine grain size.
2	600 $^{\circ}\text{C}$ (8-3/4 hours)	Similar to (1). Portions have indices considerably in excess of 2.3	---
3	950 - 1000 $^{\circ}\text{C}$	Bulk of sample isotropic. Refractive index 2.34. A few anisotropic grains.	$\text{PuO}_2$ pattern. Sharp lines.

Optical and X-ray Data for  $\text{PuO}_2$  from  $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ 

\*Unidentified major component was birefringent with a mean index of 1.55.

### Table 3

Optical and X-ray Data for  $\text{PuO}_2$  from  $\alpha$  Phase Metal

Sample Number	Ignition Temperature (°C)	Microscopic Examination	X-ray Diffraction
1	170	Homogeneous, isotropic, index 2.40	Diffuse pattern. Grain size estimated at less than 0.1 $\mu$ .
2	535	Homogeneous, isotropic, index 2.40	Somewhat less diffuse than (1).
3	950	Homogeneous, isotropic, index 2.40	Lines sharply resolved. Good PuO <sub>2</sub> pattern. Grain size slightly greater than 0.1 $\mu$ .

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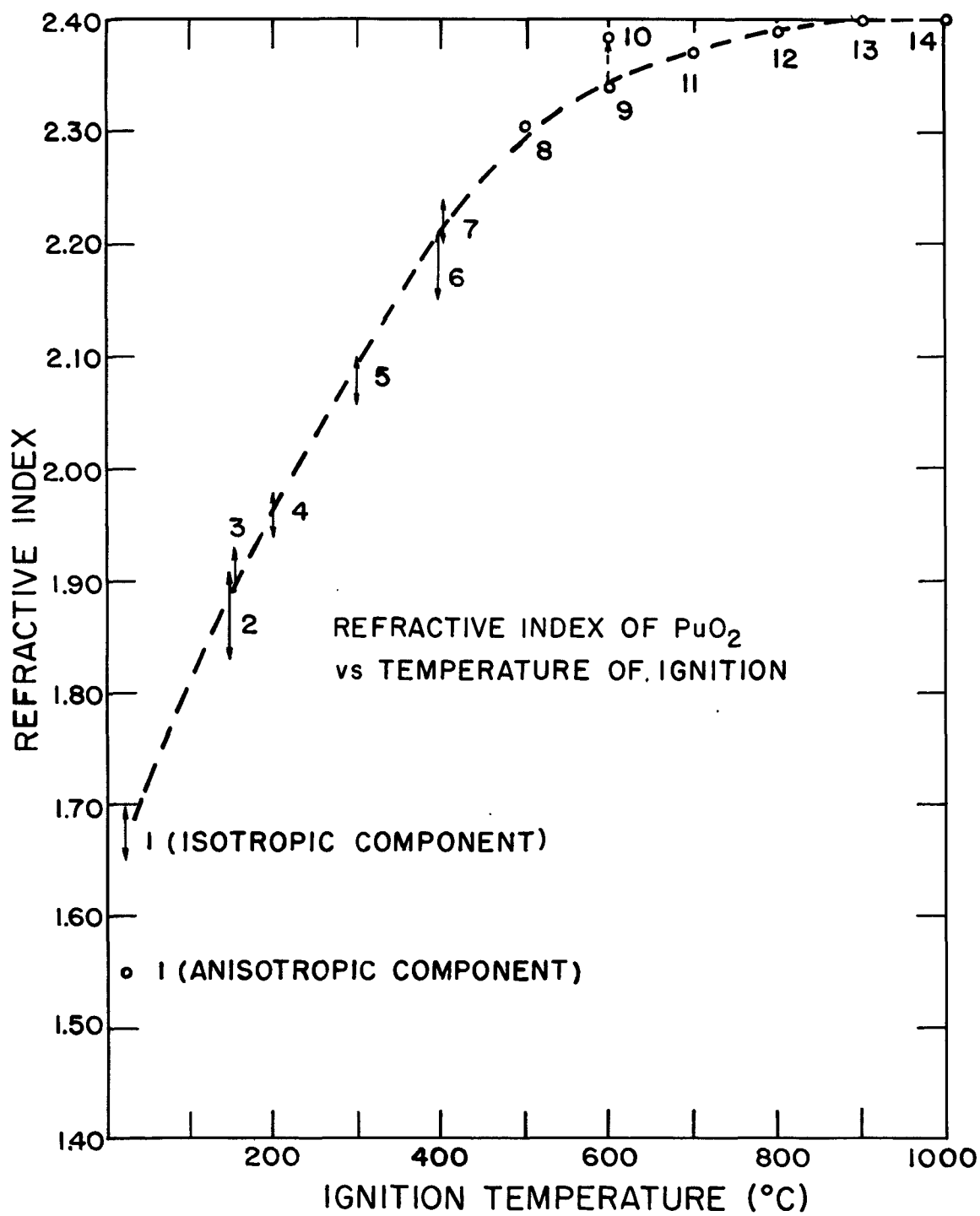


Figure 1

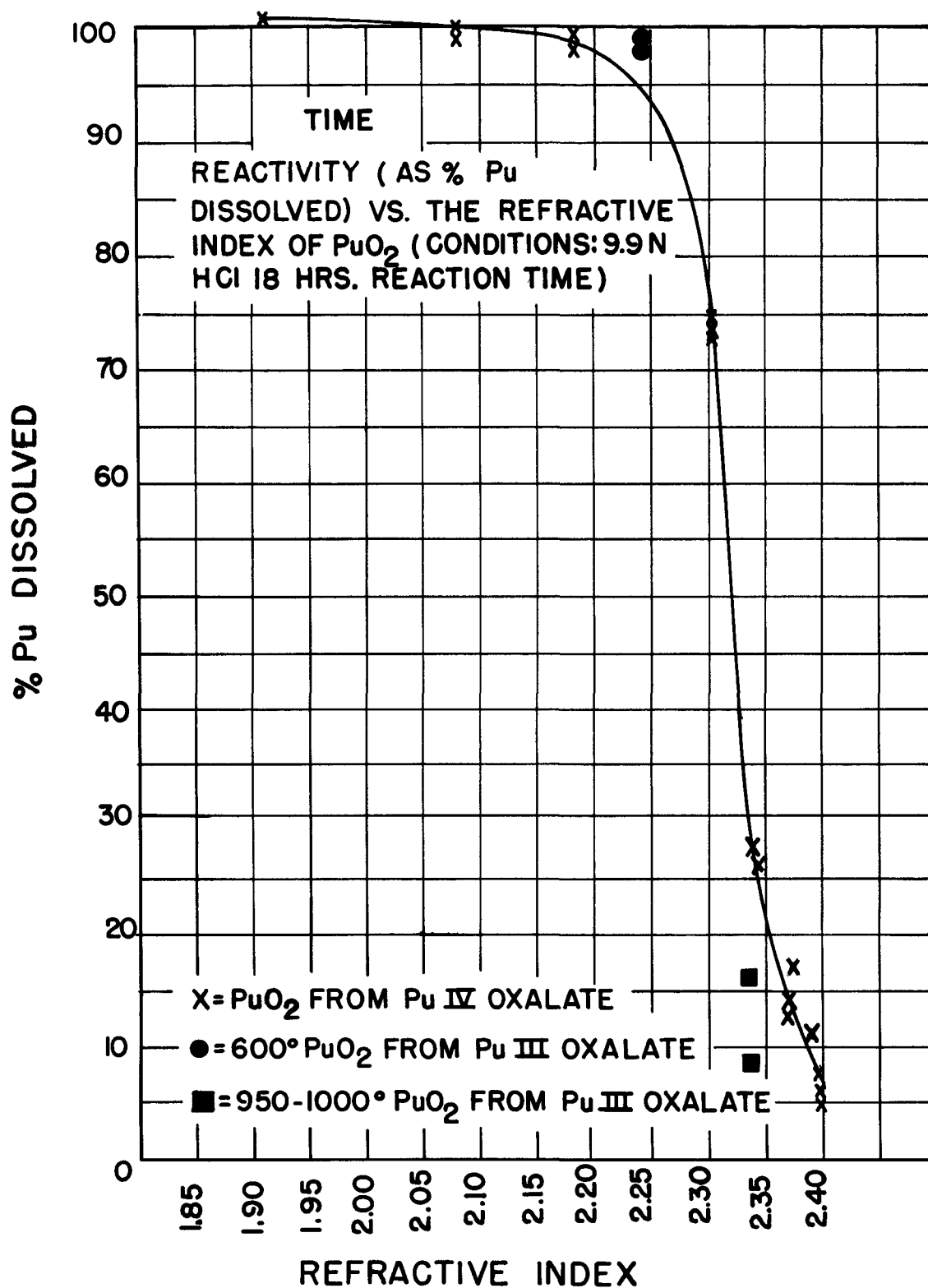


Figure 2

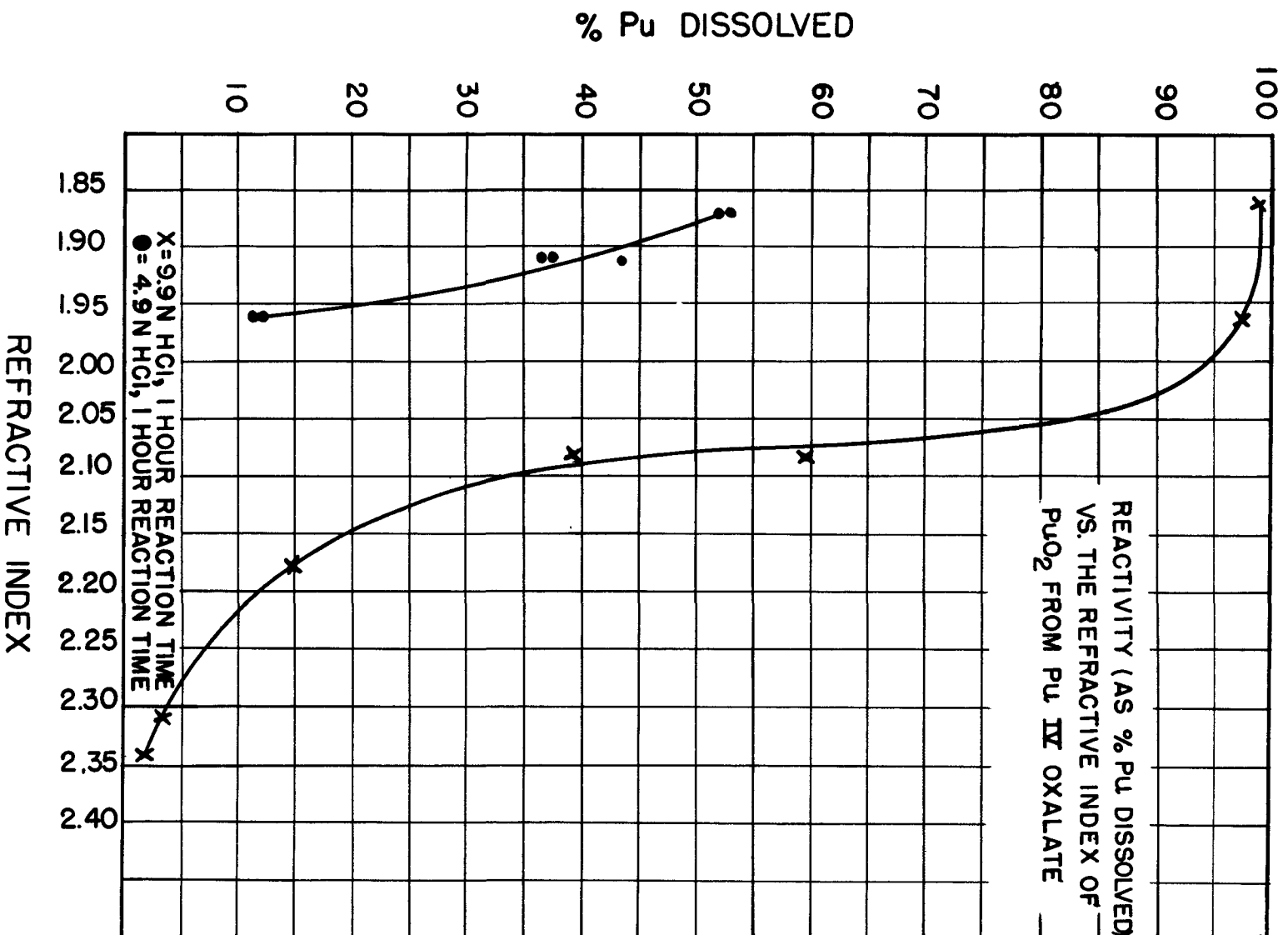
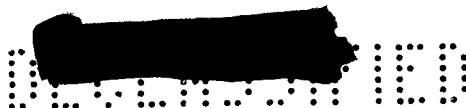


Figure 3

Table 4

Reactivity of  $\text{PuO}_2$  Made from  $\alpha$  Metal

<u>Sample Number</u>	<u>Ignition Temperature (°C)</u>	<u>% Pu Dissolved in HCl-KI Test</u>
1	170	63.6
2	535	24.5
3	950	4.2



## DISCUSSION

On the basis of the observed optical properties, x-ray diffraction patterns, and dissolution experiments the samples of  $\text{PuO}_2$  can be divided into three major groups:

Group I - Oxides with low refractive index and grain size  $< 0.1 \mu$ .

Samples in this group are characterized by a high reactivity. They include all samples of  $\text{PuO}_2$  prepared by ignition of Pu III and IV oxalates at temperatures below  $700^\circ\text{C}$ . These samples are composed for the most part of tiny crystallites of  $\text{PuO}_2$ , in some regular arrangement, embedded in a matrix consisting of a disordered  $\text{PuO}_2$  lattice. The lattice may contain intercalated carbon and excess oxygen ions as impurities. The reactivity of these samples can be attributed to the poorly crystallized, strained matrix material which probably dissolves preferentially. As the ignition temperature is increased, elimination of the impurities by diffusion becomes more complete and is accompanied by further crystallization of the  $\text{PuO}_2$  in the matrix with the result that the reactivity decreases. This explanation is corroborated by plutonium and carbon analyses reported in the table in the appendix.

The dissolution reactivity of samples in this group relative to one another would seem to be predictable from refractive index measurements alone.



Group II - Oxides with high refractive index and grain size  $< 0.1 \mu$ .

Samples in this group also are characterized by a relatively high reactivity. The 170° and 535° samples of  $\text{PuO}_2$  obtained from metal are the only members of this group which have been prepared. Their reactivity is attributed solely to the fine grain size.

Predictions of the relative reactivities of samples in this group would require both refractive index and grain size measurements.

Group III - Oxides with high refractive index and grain size  $> 0.1 \mu$ .

Samples in this group are typical of the "refractory" oxides with a low reactivity. They presumably include highly ignited samples of  $\text{PuO}_2$  prepared from any source. The low reactivity is attributed to the high degree of crystallinity and lack of impurities as evidenced by the high refractive index and well-defined  $\text{PuO}_2$  x-ray powder pattern.

CLUSIONS

From the following tentative conclusions

$\text{Pu III}$  and  $\text{IV}$  oxalate to  $\text{PuO}_2$  is a transition in degree of crystallinity from low temperatures to well crystallized oxides with gradual perfection of an originally amorphous material with the slow growth of crystallites as evidenced by x-ray. Decomposition of the oxalates occurs at low temperature.

From  $\text{Pu III}$  and  $\text{IV}$  oxalates and from the temperature of ignition. The relative reactivity can be estimated if the refractive index and grain size are known.

Preparation of the  
Series 20, 1944.  
"Plutonium Chloride", LA-112,

Production of Plutonium

Production of Plutonium  
 $\text{PuF}_4$ , Bldg. D

# APPENDIX

## Plutonium and Carbon Analyses of Samples of PuO<sub>2</sub> Prepared from Pu (IV) Oxalate

Sample Number	Ignition Temperature (°C)	Time of Ignition (hours)	Plutonium Content (%)	Carbon Content (%)
0	Air-dried	9 (days)	(35)	--
1	Room temperature	33 (days)	53.2	6.2
2	100 ± 5°C 150 ± 15°C	42.5 } 8.5 }	77.4	2.6
3	150 ± 15°C	35.5	79.8	1.7
4	200 ± 15°C	49	83.2	0.7 <sub>9</sub>
5	300 ± 15°C	21	86.3	---
6	400 ± 15°C	50	87.0	---
8	500 ± 15°C 515 - 540	25.5 } 14.5 }	87.4	0.1 <sub>3</sub>
9	600 ± 15°C	40	87.7	0.06
11	700 ± 15°C	24.5	87.9	0.04
12	800 ± 15°C	10.5	88.0	0.07
13	900 ± 20°C	5	88.0	0.06
14	825 - 980 1000 ± 20°C	1 } 2.5 }	88.1	0.05