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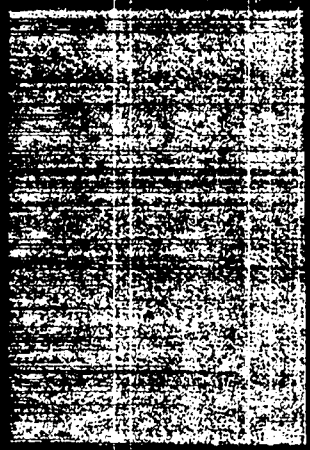

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SOME OBSERVATIONS ON THE REACTIVITY OF PLUTONIUM DIOXIDE

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TECHNOLOGY-PLUTONIUM
(M-3679, 15th edition)

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ABSTRACT

The index of refraction of PuO_2 made by thermal decomposition of $Pu(C_2O_4)_2 \cdot 6H_2O$ gradually increases from a value < 1.9 to 2.40 as the decomposition temperature is increased from 150° to 1000°C. This change in refractive index parallels a gradual change in the x-ray diffraction pattern from weak, diffuse lines for PuO_2 ignited at 150° to sharp, well-resolved lines for PuO_2 ignited at 1000°C. Similar results are observed for PuO_2 made by thermal decomposition of $Pu_2(C_2O_4)_3 \cdot 11H_2O$. The refractive index of PuO_2 made from Pu metal at 170°C is 2.40 and is not affected by further ignition at higher temperatures, although crystal growth does occur.

The rate of solution of PuO_2 in an 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 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 PuO_2.

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INTRODUCTION

It has been observed by many investigators that the rate of reaction of PuO_2 with HF gas is affected materially by the history of the particular sample of oxide used.[1,2,3,4]

As part of a study of this effect, the index of refraction of PuO_2 made at different temperatures from several starting materials was measured. The rate of dissolution of the 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.

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EXPERIMENTAL PROCEDURE

PREPARATION OF OXIDE SAMPLES

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

Thermal Decomposition of $Pu_2(C_2O_4)_3 \cdot 11H_2O$ - 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 PuO_2 at 600°C in an electric muffle. A small portion of this material was ignited longer at 600°C; a sample was removed, and the remainder was ignited at 950 - 1000°C. The experimental conditions were as follows:

Sample	Ignition Conditions
1	18 hours at temperatures < 300°C 4 hours 300 → 600°C: 1/2 hour at 600 ± 30°C
2	Additional ignition of 2.4 grams of sample 1: 8-1/4 hours at 600 ± 30°C
3	Additional ignition of sample 2: 2-1/4 hours at 600 ± 30°C 1 hour 600 → 950°C 1-3/4 hours at 950 - 1000°C

Thermal Decomposition of $Pu(C_2O_4)_2 \cdot 6H_2O$ - 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.

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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° at 1000°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° intervals between 100° and 1000°C.

A small sample of the 400° material subsequently was heated for an additional 257 hours at 400 ± 15°C, and a portion of the 600° material was heated for an additional 162 hours at 600 ± 15°C.

PuO_2 from Plutonium Metal - Approximately 19 grams of PuO_2 were made by the reaction of α metal turnings with water vapor in a slow stream of oxygen at 160 - 170°C. (The oxygen was saturated with water vapor at 25°C.) Precautions were taken to prevent the temperature of the oxide from ever exceeding 170°C.

Two 5.5 gram portions of this material were ignited to constant weight at 535 ± 10°C and 950 ± 15°C, respectively.

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HCl-KI DISSOLVING TEST

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

$$PuO_2 + KI + 4\ HCl = PuCl_3 + 1/2\ I_2 + KCl + 2\ H_2O$$

The fractions of different samples of 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 ± 0.5°C. 1.3 - 1.5 grams of 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°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_5N. The other conditions were unchanged.

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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 $Pu(C_2O_4)_2 \cdot 6H_2O$ 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 PuO_2 made from $Pu_2(C_2O_4)_3 \cdot 11H_2O$ and $Pu(C_2O_4)_2 \cdot 6H_2O$ 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 PuO_2 prepared from α 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 PuO_2 from $Pu_2(C_2O_4)_3 \cdot 11H_2O$

Sample Number	Maximum Ignition Temperature (°C)	Microscopic Examination	X-ray Diffraction
1	600°C (1/2 hour)	Homogeneous, anisotropic, refractive index $2.23_5 \pm 0.01$	PuO_2 pattern. Fuzzy lines typical of fine grain size.
2	600°C (8-3/4 hours)	Similar to (1). Portions have indices considerably in excess of 2.3	---
3	950 - 1000°C	Bulk of sample isotropic. Refractive index 2.34. A few anisotropic grains.	PuO_2 pattern. Sharp lines.

Table 2

Optical and X-ray Data for PuO_2 from $Pu(C_2O_4)_2 \cdot 6H_2O$

Sample Number	Ignition Temperature (°C)	Ignition Time (hours)	Microscope Examination Index of Refraction	X-ray Diffraction
1	Room Temp.	33 (days)	1.65-1.70*	Very weak, diffuse PuO_2 lines. A few extra lines.
2	150	8.5	1.83-1.91	Weak, diffuse PuO_2 lines becoming progressively stronger and less diffuse. No other lines. Crystal grain size < 0.1 μ .
3	150	35.5	1.89-1.93	
4	200	49	1.94-1.98	
5	300	21	2.06-2.10	
6	400	50	2.15-2.21	
7	400	307	2.20-2.24	
8	500	40	2.30_5	Lines still less diffuse. Grain size still < 0.1 μ.
9	600	40	2.34	
10	600	202	2.38_5	Similar to 40 hour 600° sample.
11	700	24.5	2.37	End doublets partly resolved. Grain size ~ 0.1 μ .
12	800	10.5	2.39	Lines sharply resolved. Good PuO_2 pattern.
13	900	5	2.40	
14	1000	2.5	2.40	

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

Table 3

Optical and X-ray Data for PuO_2 from α 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 μ.
2	535	Homogeneous, isotropic, index 2.40	Somewhat less diffuse than (1).
3	950	Homogeneous, isotropic, index 2.40	Lines sharply resolved. Good PuO_2 pattern. Grain size slightly greater than 0.1 μ.

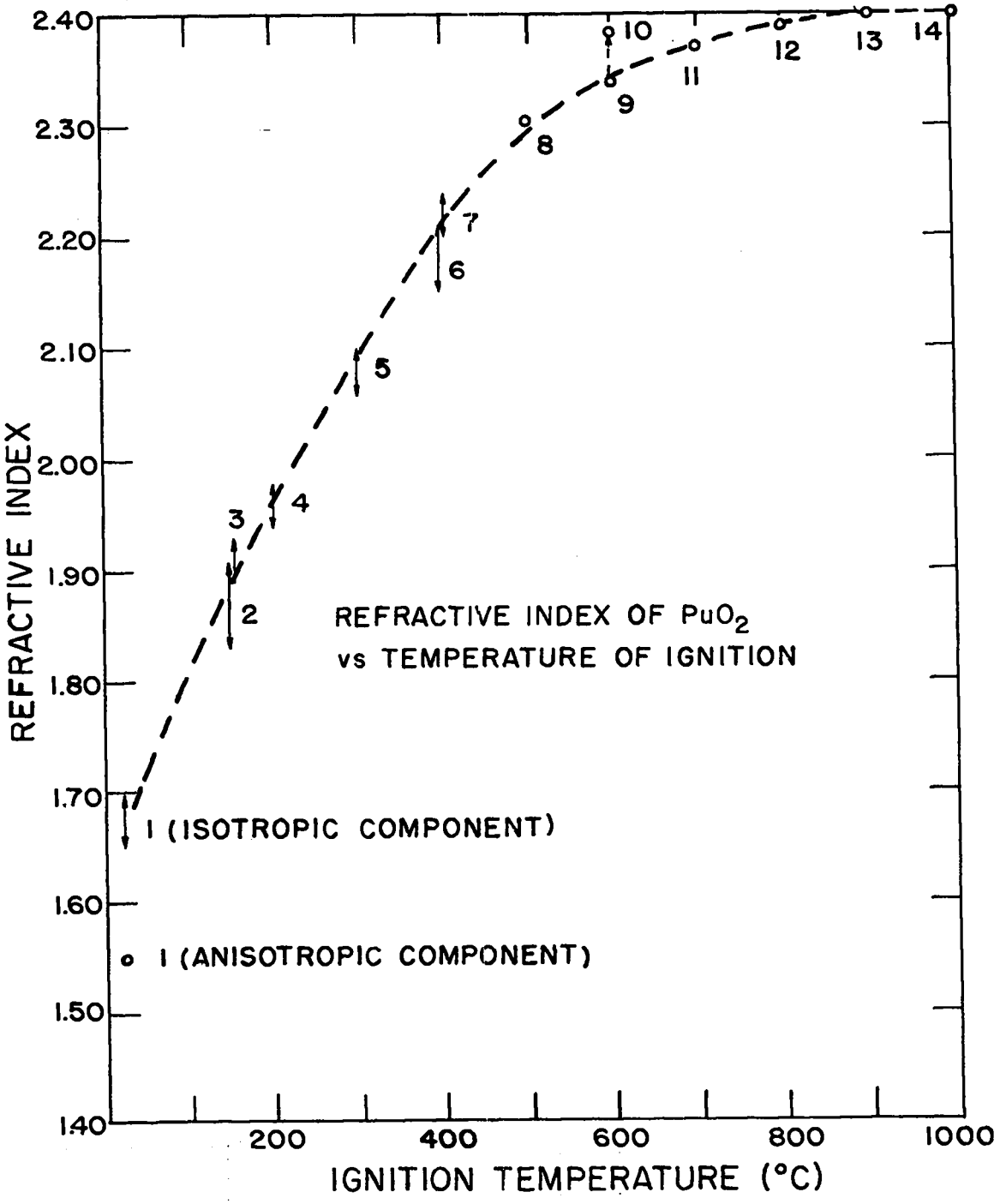

Figure 1

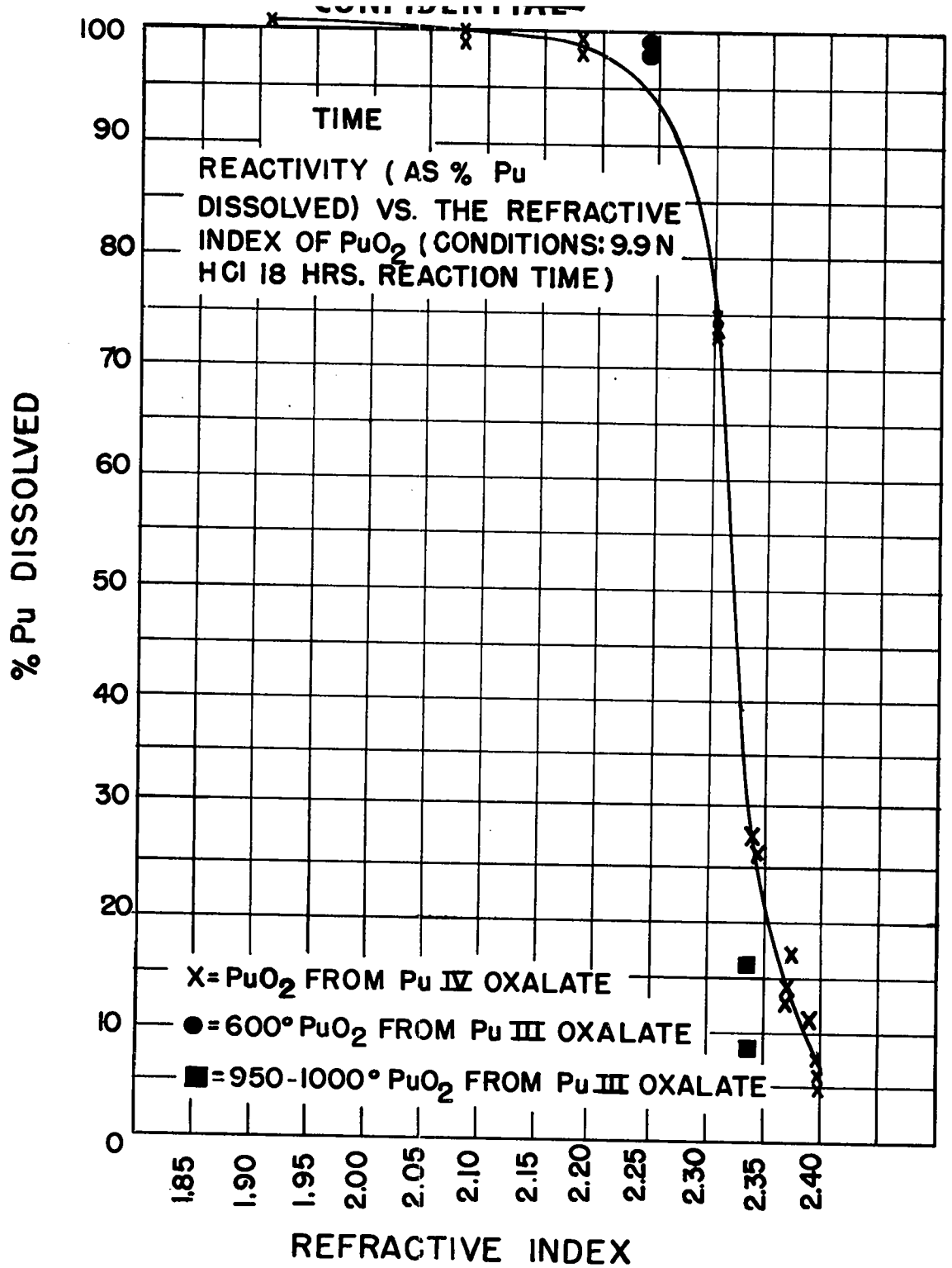

Figure 2

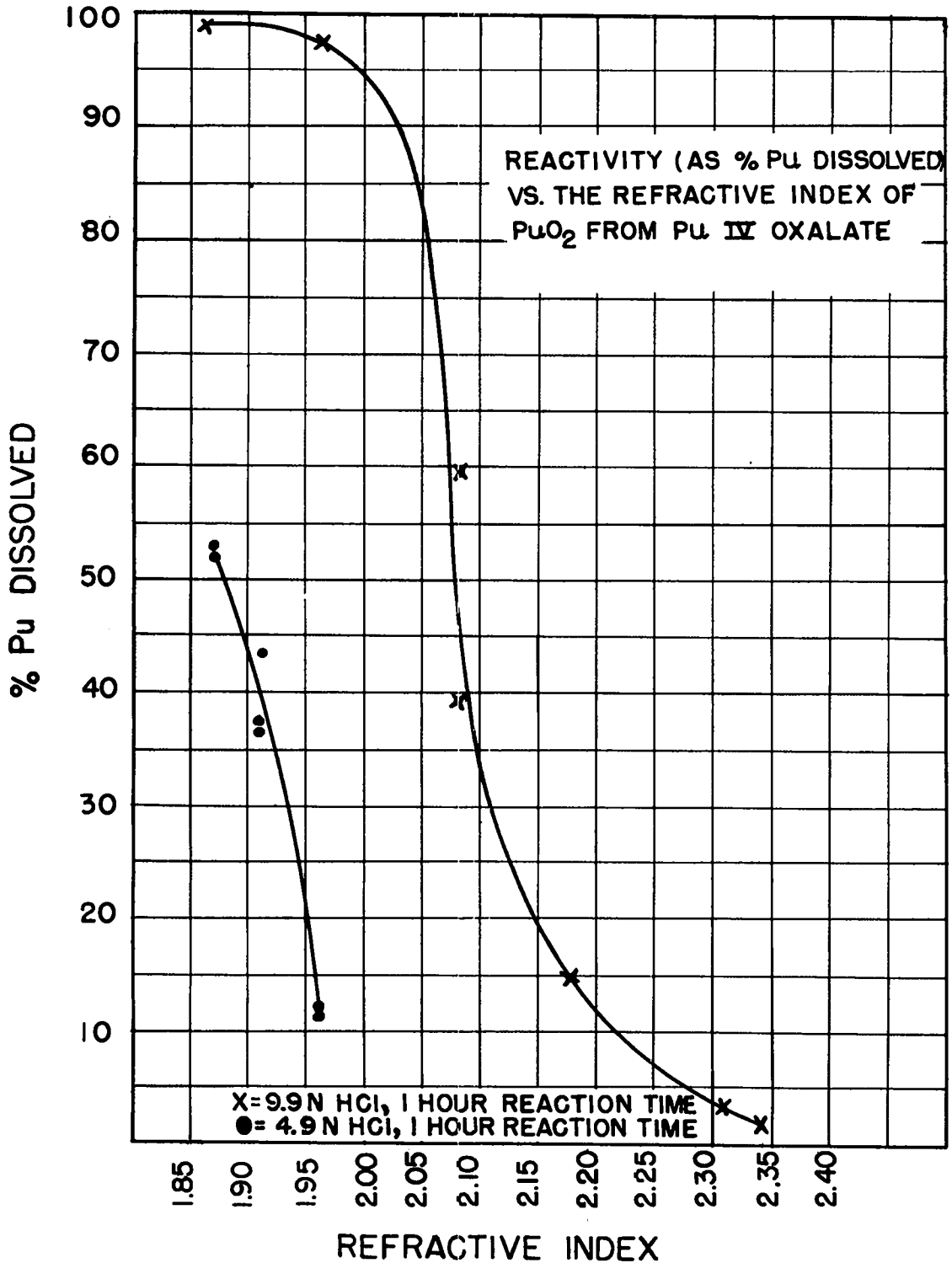

Figure 3

Table 4

Reactivity of PuO_2 Made from α Metal

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

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DISCUSSION

On the basis of the observed optical properties, x-ray diffraction patterns, and dissolution experiments the samples of PuO_2 can be divided into three major groups:

Group I - Oxides with low refractive index and grain size < 0.1 μ .

Samples in this group are characterized by a high reactivity. They include all samples of PuO_2 prepared by ignition of Pu III and IV oxalates at temperatures below 700°C. These samples are composed for the most part of tiny crystallites of PuO_2, in some regular arrangement, embedded in a matrix consisting of a disordered 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 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.

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Group II - Oxides with high refractive index and grain size < 0.1 μ .

Samples in this group also are characterized by a relatively high reactivity. The 170° and 535° samples of 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 μ .

Samples in this group are typical of the "refractory" oxides with a low reactivity. They presumably include highly ignited samples of 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 PuO_2 x-ray powder pattern.

CONCLUSIONS

From the foregoing information the following tentative conclusions have been drawn:

(1) Thermal decomposition of Pu III and IV oxalate to PuO_2 is accomplished by means of a gradual transition in degree of crystallinity from nearly amorphous material at low temperatures to well crystallized PuO_2 at high temperatures; i.e., a gradual perfection of an originally highly distorted lattice coupled with the slow growth of crystallites as the ignition temperature is increased. Decomposition of the oxalates proceeds gradually even at room temperature.

(2) The reactivity of PuO_2 from Pu III and IV oxalates and from Pu metal decreases with increasing temperature of ignition. The relative reactivity of different samples can be estimated if the refractive index and an x-ray diffraction estimate of grain size are known.

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LITERATURE REFERENCES

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(3) Bluestein, B. A., and Garner, C. S., "The Preparation of Plutonium Tribromide", LA-116, July 28, 1944.

(4) Anderson, Dumrose, Garner, Kaufman, "Preparation of Plutonium Compounds for Reduction to Metal: Production of PuF_4, Bldg. D Dry Conversion Process", LA-440, October 24, 1945.

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APPENDIX

Plutonium and Carbon Analyses of Samples of PuO_2 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_9
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_3
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

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