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Materials Identification and Surveillance Project Item Evaluation

Item: Rocky Flats Plutonium Oxide Sample 011589

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by

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ABSTRACT

In this report, we characterize properties relevant to storage of a plutonium oxide item 011589 (77.26 mass % plutonium) in accordance with the Department of Energy (DOE) standard DOE-STD-3013-96.[1]

Methods used to characterize the oxide include mass loss-on-calcination (LOC) measurements, mass loss-on-ignition (LOI) measurements, water uptake adsorption measurements, elemental analysis, plutonium isotopic analysis, particle analyses measurements, tap and bulk density measurements , surface-area analyses, and x-ray powder diffraction. Methods used to characterize the container include x-ray radiography and photography.

Loss-on-ignition values are high. The material does not satisfy DOE-STD-3013-96 criteria for LOI after calcination for 2 h at 950°C.

1.0 INTRODUCTION

Stabilization of pure and impure oxide materials destined for DOE-STD-3013 containment throughout the complex is being evaluated by the Materials Identification and Surveillance (MIS) project. The MIS project evaluates pure and impure plutonium metal and oxide legacy materials in existence, primarily at Rocky Flats, Savannah River, Hanford, and Los Alamos. The MIS project sponsors materials stabilization and packaging studies to confirm the suitability of material processing methods and packaging for long-term storage using DOE-STD-3013. Studies include characterization of plutonium oxide and assessment of stabilization processing at 950°C for two hours. Experimental tasks and surveillance monitoring are carried out to evaluate the behavior of the oxide and packaging materials under storage conditions. The project sponsors additional activities to develop alternate methods for measuring volatiles on the oxide, determine the thermal conditions during storage, and model the pressure generation in sealed containers.

Rocky Flats has sent 24 items to Los Alamos for evaluation and verification that these materials can be stored safely for 50 years after thermal treatment. Material from all six categories discussed below were shipped; however, not all IDCs were represented in the samples.

A. Oxide Source and Characterization Data

The plutonium oxide inventory at Rocky Flats has been divided into the following source categories:

(1) Plutonium oxidation [IDCs 057, 060, 061, 083, 319, 653]

This category consists of oxide obtained from metal brushing, chip burning, hydride oxidation, and certain pyrochemical operations. All oxide is believed to have been stabilized at temperatures above 500°C. The plutonium content will vary, but the impurities are expected to be metal oxides.

(2) Aqueous processing [IDCs 060, 061, 080, 081, 082, Y61]

The aqueous processes involve dissolution of plutonium oxide followed by precipitation of peroxide, oxalate, or hydroxide salts. These salts are then calcined to form plutonium oxide. This category also includes oxide from the OY Leach process that will contain uranium as well as plutonium oxide. The efficiency of the process usually results in

plutonium contents ranging from 75-88%. Individual items with lower plutonium content are also included. Material may contain residual salts such as sulfates resulting from an incomplete calcination process. Impurities present may impact stabilization and LOI measurements.

(3) Plutonium-uranium metal and hydride oxidation [IDCs U61, Y61]

Plutonium oxide in this category contain uranium oxide and was prepared by a hydride process to separate plutonium and uranium. Oxide was formed by oxidation of the hydride at about 500°C. Uranium concentration in Y61 varies widely and ranges from 1- 100%. Stabilization of this material should not be a problem. However, accurate measurement of an LOI using gravimetric methods may be a problem and must be demonstrated.

(4) Pyrochemical cell cleanout material [IDCs 067, 086]

This material was generated during the cleaning of pyrochemical cells. The material is expected to contain Na, K, and Mg chloride salts along with plutonium oxide. **This material has not been previously stabilized.** Problems should be expected during stabilization because of the volatile nature of the inorganic salts.

(5) Dissolution residuals [IDCs 062, 065, 289]

This category consists of material that could not be dissolved when foundry and scrap oxide went through the oxide dissolution process. This material contains high fired plutonium oxide and other difficult to dissolve materials. Plutonium content varies widely. Stabilization of this material may be unpredictable because of the nature of impurities. Likewise, gravimetric LOI measurements may be inconsistent because of oxidation of material during heating.

(6) Impure calcined oxide [IDCs 159, 145, 146 , oxide from residue processing]

This category is a catch-all for material with a questionable origin or composition. One type of material consists of screenings removed from metal-generated oxide stabilized above 500°C. Impurities either oxidize slowly or are resistant to oxidation. Plutonium content varies from 1-88%. The second type of material in this category are oxides that have failed 500°C LOI tests at the 1% level. This oxide is not pure and the source is unknown. A third type of oxide is expected to be produced by solution stabilization, pyrochemical salt processing, and other residue processing activities.

B. Oxide Sample Selection

Category 1:	IDC-057	1 sample
	IDC-060	2 samples
	IDC-061	4 samples
	IDC-653	1 sample
Category 2:	IDC-061	1 sample
	IDC-080	1 sample
	IDC-081	1 sample
Category 3:	IDC-U61	1 sample
	IDC-Y61	3 samples
Category 4:	IDC-067	1 sample
	IDC-086	1 sample
Category 5:	IDC-062	1 sample
	IDC-289	2 samples
Category 6:	IDC-159	2 samples
	IDC-146	1 sample
	IDC-054	1 sample

Table I. Rocky Flats Plutonium Oxide Legacy

IDC	Description	Source	Items	Purity %Pu	Calcination °C
057	Oxide, Awaiting Spec	Metal oxidation, 15% unknown	164	49-87	450-1000
060	Oxide	Metal oxidation, aqueous processing, 15% unknown	352	14-88	450-500
061	Non-spec Oxide	metal oxidation, 45% other and unknown	680	0-88	450-1000
Y61	Pu/eU >10,000ppm U	Oxide from hydride separation process	544	0-55	500
U61	Pu/eU <10,000ppm U	Oxide from hydride separation process	45	75-85	500
062	High Purity Oxide Heel	Undissolved material from oxide dissolution	69	3-86	200-250
065	Oxide Heel, small stacker can	Undissolved material from oxide dissolution	20	6-86	200-250
067	Chlorinated Oxide	ER scrape out, may contain reactive metals	12	63-78	NONE
080	Peroxide Cake	Oxide from calcined peroxide	73	63-88	450
081	Impure Peroxide Cake	Oxide from calcined peroxide	36	29-83	450
082	Green Cake in small can (371)	Oxide from calcined peroxide	2	79	450
083	High Fired Oxide DOR	Probably metal oxidation	15	34-88	~800
086	Oxide ER Scrape Out	Same as 067, may contain reactive metals	22	53-76	NONE
145	Oxide - Failed 1 LOI	Unknown source	5	56-76	450
146	Oxide - Failed 2 LOI	Unknown source	22	53-73	450
159	Screenings from Oxide	Material left after screening during oxide stabilization	165	0-88	500
289	Low Purity Oxide Heel	Undissolved material from oxide dissolution	108	3-69	250-300
319	Oxide from Ta Crucibles	Oxide from crucible burnout	2	72 & 78	500
653	Oxide, Pu/Np	Oxide with Np impurity	86	78-88	500

Item 011589 is from IDC 060, Category 1. Los Alamos records indicate the following for item 011589:

Total Plutonium: 779.534 g
Power: 0.36 W

Isotopes are as follows:

Pu-239: 93.65 mass %
Pu-240: 6.09 mass %
Am-241: 0.15 mass %

2.0 EXPERIMENTAL METHODS

2.1 Material

Item 011589, the subject of this report, was taken from IDC 060, which is part of the category 1.

2.2 Procedure

The can was radiographed prior to opening, see Fig. 1. In Fig. 2, the as-received can is shown and the material can be seen in the inner container. The sequence of sampling and testing is presented in Fig. 3. After samples were taken from the as-received material, sample S, a portion of the powder was calcined at 950°C to produce sample S″.

Interstitial Gas Analysis Method

Water evolved at 400°C from mixed oxides is measured by sweeping it with a stream of dry argon through an NDIR detector and the voltage-time response is integrated electronically. The area measured is compared to the response obtained for injections of known amounts of hydrogen gas. The nominal sample size is 100 mg, but this must be adjusted to keep the amount of water released within the limits of the detector. The detector limits are from 1 to 630 μg of water.

3.0 RESULTS AND DISCUSSION

Affinity for water was measured for both powders, as-received and calcined at 950°C. We report only for the as-received powder in Table II and Fig.4. For the calcined powder at 950°C, some material was lost during the experiment.

Table II. Water Uptake Adsorption Measurements for the As-Received Impure Oxide 011589

Weight of sample (gr)	Test Time (days)	Weight Gain (%)	Weight Change from previous measurement (%)	Relative Humidity (%)	Temper. (F)
108.329	0.00	0	0	0.8	74
108.339	0.23	0.0208	0.0208	0.4	85.3
108.348	0.87	0.0372	0.0164	0.3	75.1
108.348	1.01	0.0376	0.0004	0.6	74.7
108.347	1.11	0.0352	-0.0024	0.9	74.1
108.343	1.89	0.0274	-0.0078	0.9	73.8
108.345	2.02	0.033	0.0056	0.2	73.9
108.350	2.11	0.0422	0.0092	0.1	74.1
108.357	2.26	0.056	0.0138	0.9	73.9
108.347	2.85	0.0364	-0.0196	1	73.6
108.349	3.12	0.0404	0.004	0.8	76.5
108.357	6.86	0.056	0.0156	0.4	73.8

Table III. Percent Mass Loss During Calcination of Sample 011589

Sample	Calcination Temperature (°C)	Heating Time (h)	Mass Before Calcination (g)	Mass After Calcination (g)	Mass Loss (%)
S	950	2	930.5	903.1	2.94

Table IV. Supercritical, Interstitial, and LOI Analyses Results of the Impure Oxide 011589

Method	Powder S[a] LOI (mass %)	Powder S″[b] LOI (mass %)
Supercritical CO_2 3000 psi, 140°C	0.48	0.26
Interstitial Gas Analysis at 400°C	0.22	<0.001
Interstitial Gas Analysis at 950°C	0.50	Not reported
LOI at 1000°C for 2 h	4.32	1.87

[a]Powder S is the impure oxide as received.
[b] Powder S″ is obtained after impure oxide S is calcined at 950°C for 2 h.

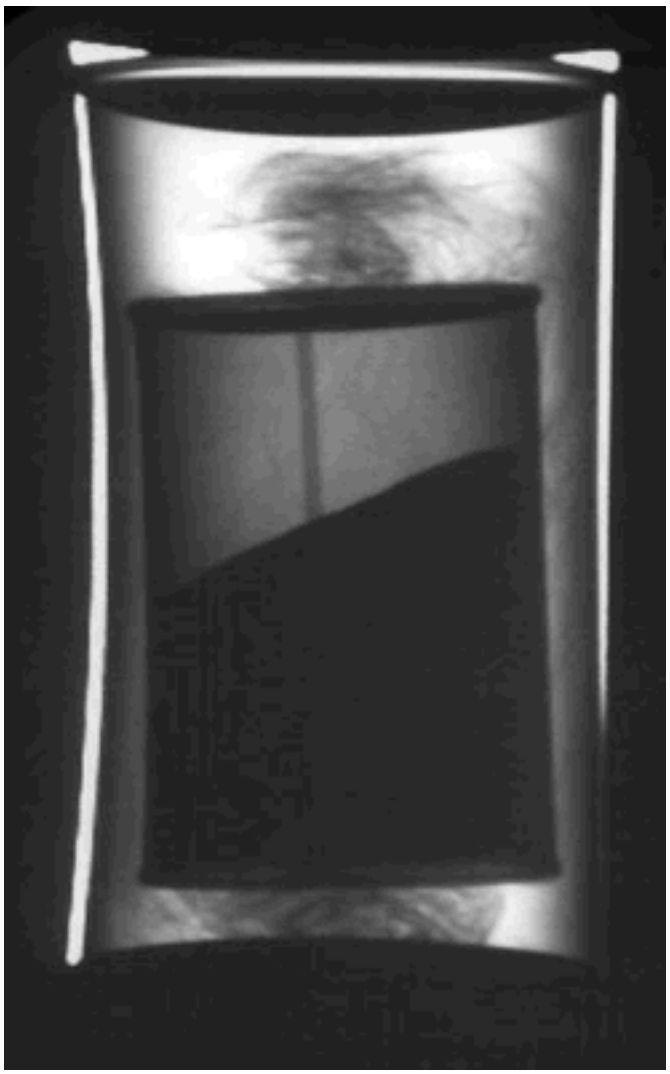


Fig. 1. Radiograph of the canister at 0 degrees.

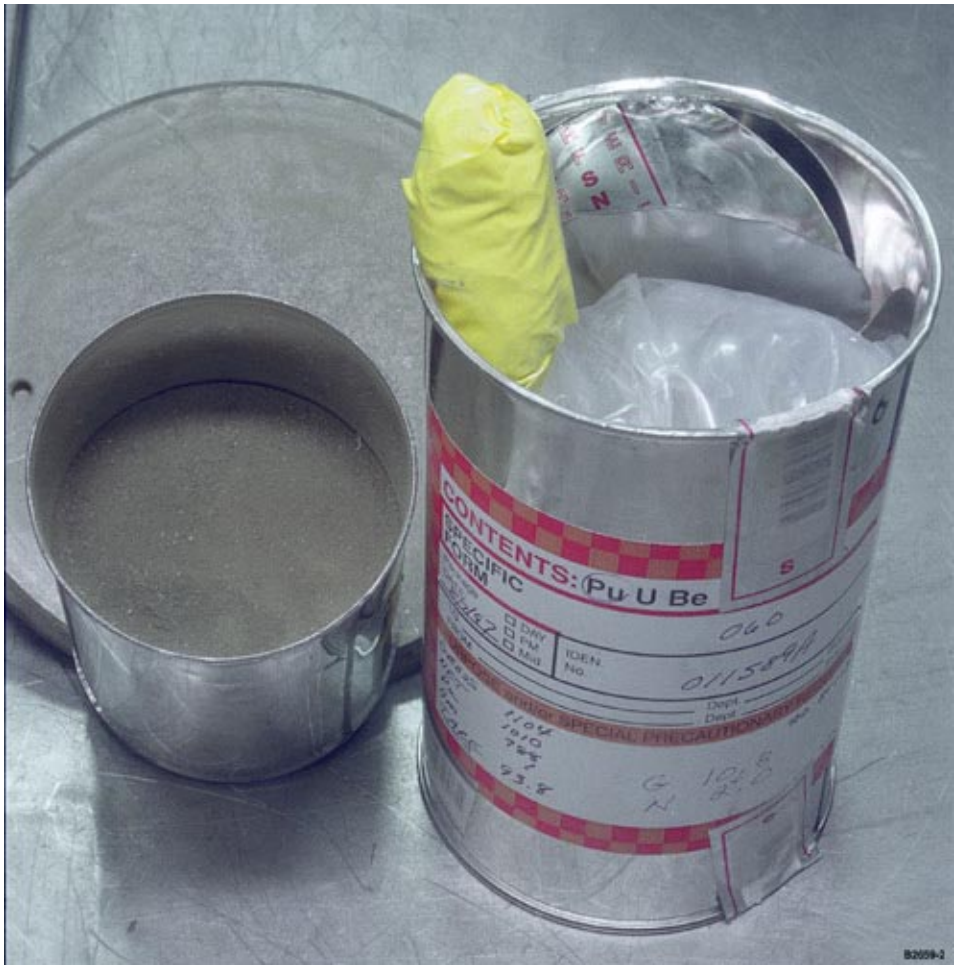


Fig. 2. The as-received can and inner can opened.

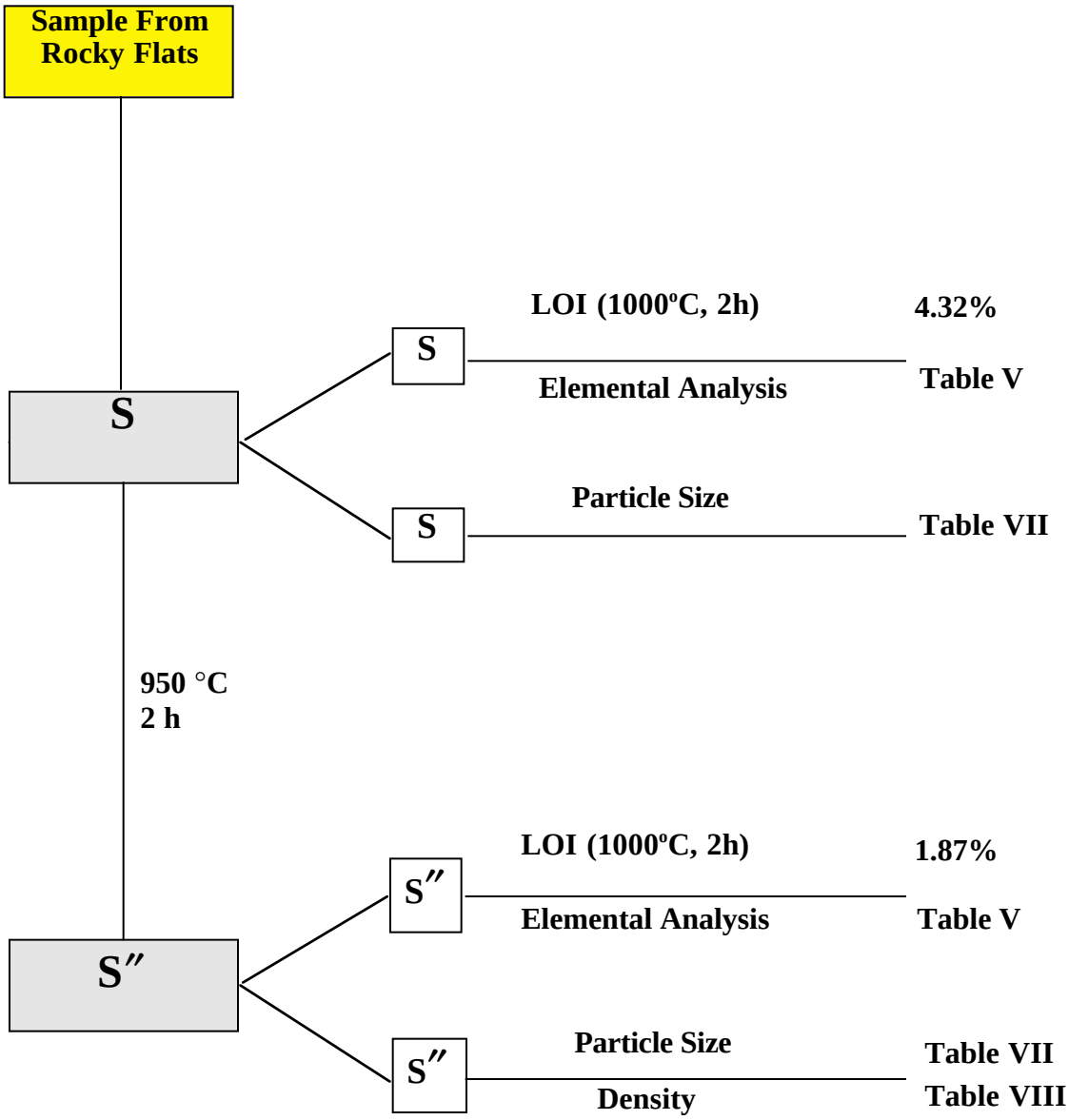


Fig. 3. Characterization of the impure plutonium oxide 011589.

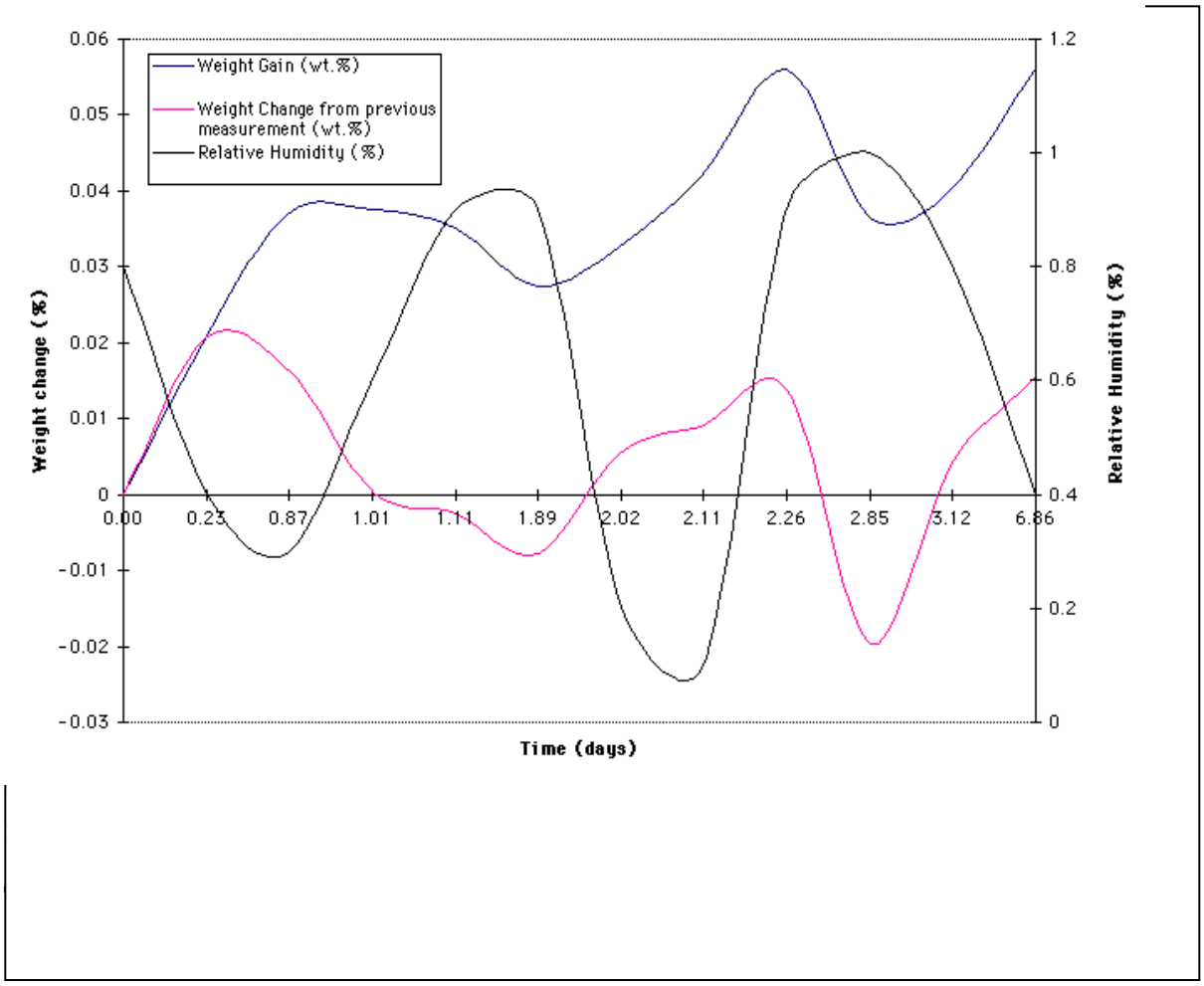


Fig. 4. Water uptake adsorption measurements for the as-received impure oxide 011589

Table V. Elemental Analysis of As-Received Powder S[a] and Calcined Powder S″[b]

Atomic Number	Symbol	Element	Powder S[a] (μg/g)	Powder S″ [b] (μg/g)
3	Li	LITHIUM	<10	<10
4	Be	BERYLLIUM	13	78
5	B	BORON	35	39
6	C	CARBON	7400	210
11	Na	SODIUM	3691	2583
12	Mg	MAGNESIUM	22688	22586
13	Al	ALUMINUM	4657	4673
14	Si	SILICON	7918	7849
15	P	PHOSPHORUS	< 84	< 84
16	S	SULFUR	205	442
19	K	POTASSIUM	6995	3097
20	Ca	CALCIUM	3856	3779
21	Sc	SCANDIUM	<10	<10
22	Ti	TITANIUM	43	48
23	V	VANADIUM	16	21
24	Cr	CHROMIUM	386	140
25	Mn	MANGANESE	70	52
26	Fe	IRON	3655	3622
27	Co	COBALT	<10	<10
28	Ni	NICKEL	195	165
29	Cu	COPPER	1274	491
30	Zn	ZINC	169	13
31	Ga	GALLIUM	3490	3569
32	Ge	GERMANIUM	<10	<10

33	As	ARSENIC	<10	<10
34	Se	SELENIUM	<10	<10
37	Rb	RUBIDIUM	<10	<10
38	Sr	STRONTIUM	<10	121
39	Y	YTTRIUM	<10	<10
40	Zr	ZIRCONIUM	117	130
41	Nb	NIOBIUM	<10	<10
42	Mo	MOLYBDENUM	16	13
44	Ru	RUTHENIUM	<10	<10
45	Rh	RHODIUM	<10	<10
46	Pd	PALLADIUM	<10	<10
47	Ag	SILVER	<10	<10
48	Cd	CADMIUM	<10	<10
49	In	INDIUM	<10	<10
50	Sn	TIN	20	17
51	Sb	ANTIMONY	<10	<10
52	Te	TELLURIUM	<10	<10
55	Cs	CESIUM	655	161
56	Ba	BARIUM	<10	14
57	La	LANTHANUM	<10	<10
58	Ce	CERIUM	22	19
59	Pr	PRAESEODYMIUM	<10	<10
60	Nd	NEODYMIUM	<10	<10
62	Sm	SAMARIUM	<10	<10
63	Eu	EUROPIUM	<10	<10
64	Gd	GADOLINIUM	<10	<10
65	Tb	TERBIUM	<10	<10

66	Dy	DYSPROSIUM	<10	<10
67	Ho	HOLMIUM	<10	<10
68	Er	ERBIUM	108	120
69	Tm	THULIUM	<10	<10
70	Yb	YTTERBIUM	<10	<10
71	Lu	LUTETIUM	<10	<10
72	Hf	HAFNIUM	<10	<10
73	Ta	TANTALUM	627	896
74	W	TUNGSTEN	60	42
75	Re	RHENIUM	<10	<10
76	Os	OSMIUM	<10	<10
77	Ir	IRIDIUM	<10	<10
78	Pt	PLATINUM	<10	<10
79	Au	GOLD	<10	13
80	Hg	MERCURY	<10	<10
81	Tl	THALLIUM	<10	<10
82	Pb	LEAD	170	22
83	Bi	BISMUTH	<10	<10
90	Th	THORIUM	<10	<10
92	U	URANIUM	< 84	< 84
94	Pu	PLUTONIUM	845830	840354

[a]Powder S is the impure oxide as received.
[b]Powder S″ is obtained after impure oxide, S, is calcined at 950°C for 2 h.

Table VI. Specific Surface Area Results for the Impure Oxide 011589 (m^2/g)

As-received	Calcined at 950°C
7.38	2.54

Table VII. Particle Analysis Results of Precalcined Powder S[a] and Calcined Powder S″[b]

Property	Powder S	Powder S″
Mean Spherical Equivalent by Particle Number (μm)	9.9	19.05
Mean Spherical Equivalent by Volume (μm)	32.9	68.1

[a]Powder S is the impure oxide as received.

[b]Powder S″ is obtained after impure oxide, S, is calcined at 950°C for 2 h.

Table VIII. Tap Density and Bulk Density of Powders S[a] and S″[b]

Property	Powder S	Powder S″
Tap Density (g/cc)	3.9	4.5
Bulk Density (g/cc)	2.7	4.1

[a]Powder S is the impure oxide as received.
[b]Powder S″ is obtained after impure oxide S is calcined at 950°C for 2 h.

Table IX. Particle Size Distribution

Particle Size (μm)	As-Received	Calcined at 950°C
<0.7	143292	74451
0.7	31561	14852
1	36208	17459
1.3	33583	16974
1.8	34739	17629
2.3	43135	23193
3	47724	27220
4	46540	28733
5	49356	31580
6.5	52104	36001
8	52684	38564
10	48787	37558
13	44258	34384
17	42693	35604
20	40140	36460
25	34186	35379
31	25261	30798
37	17916	28365
44	11838	25474
53	6880	20932
63	3630	16653
75	1692	13072
88	761	9481
105	320	6449
125	134	4166
149	49	2299
177	20	845
210	3	346
>250	5	181
Particles Measured	849499	665102

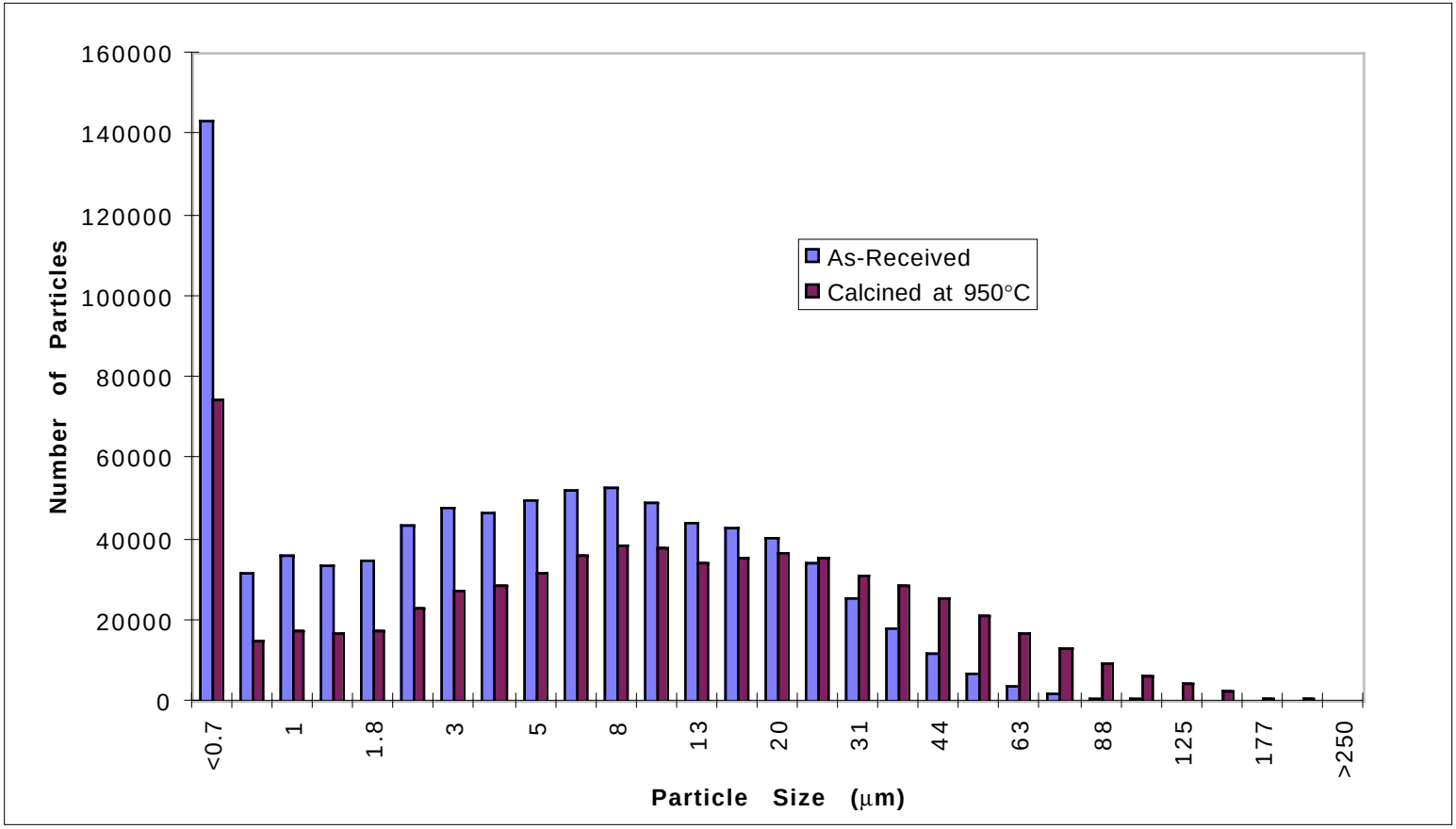


Fig. 5. Particle Size Distribution for 011589

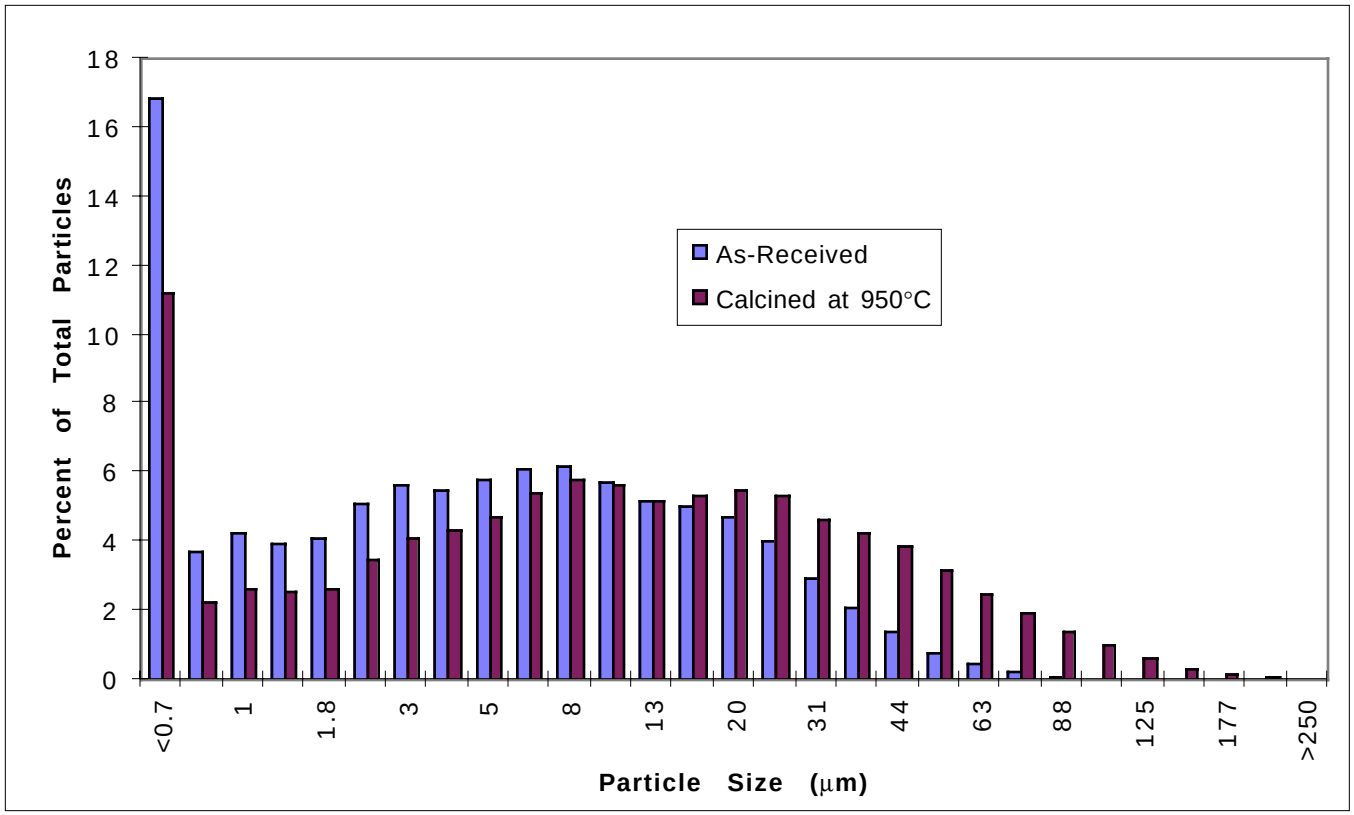


Fig. 6. Normalized Particle Size Distribution for 011589.

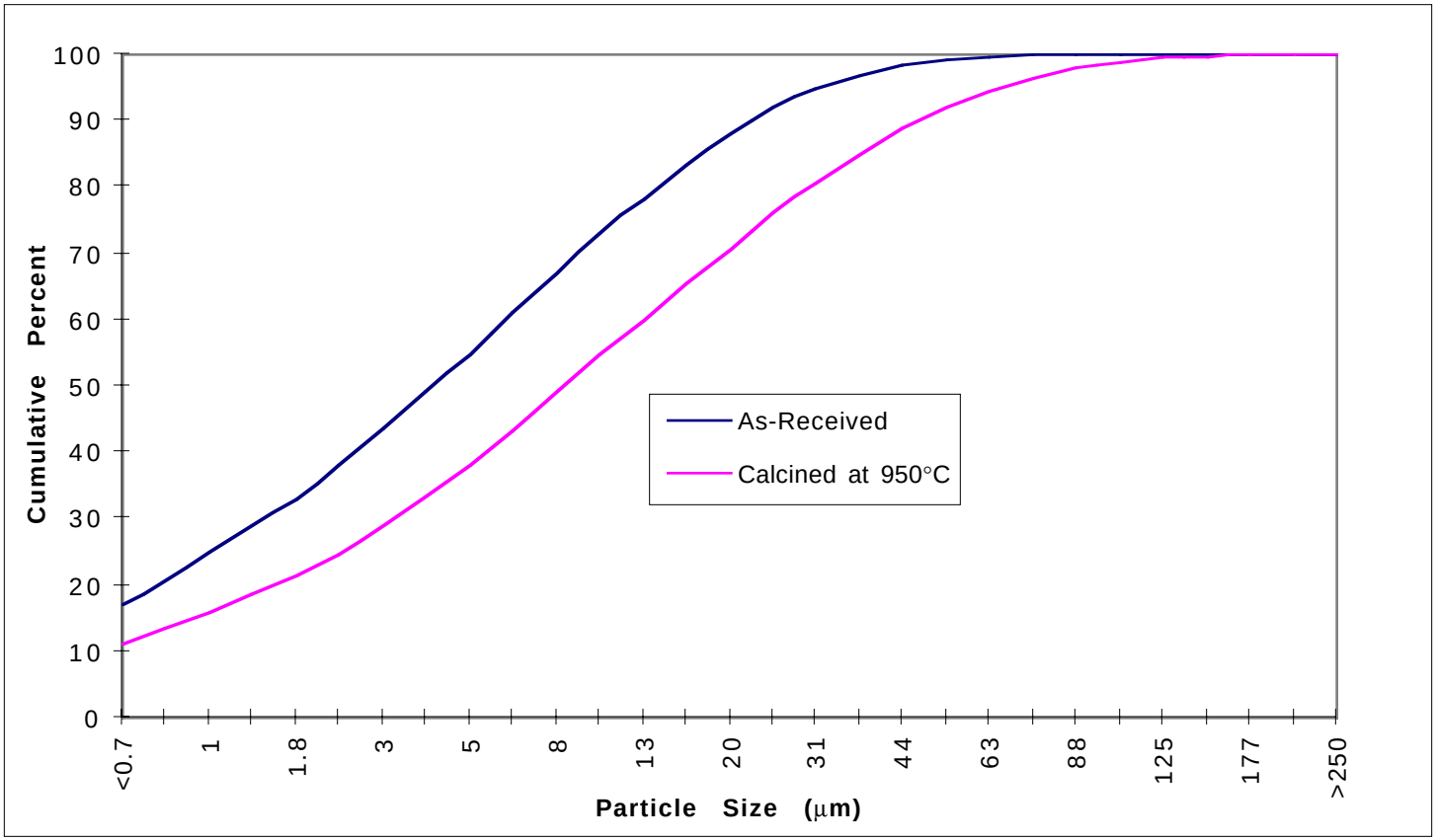


Fig. 7. Cumulative Particle Size Distribution for 011589.

The X-ray results are given in Appendix 1 and Appendix 2.

In Appendix 1 the X-ray crystallographic analysis results are given for the as-received material, S. This sample has a single component of plutonium dioxide with a face centered cubic (FCC) structure with a lattice constant of 5.4119 Angstroms. No other phases were observed. The X-ray crystallographic spectrum is with background removed. The lines near 20.6 and 20.8° are from the aluminum sample holder.

In Appendix 2 the X-ray crystallographic analysis results are given for the calcined material, S″. This sample has a single component of plutonium dioxide with a face centered cubic (FCC) structure with a lattice constant of 5.3941 Angstroms. No other phases were observed. Magnesium was not seen, even though by ICP-MS it was found to be about 2.2%. It would have to be above 5% in order to be seen by x-ray diffraction.

4.0 CONCLUSION

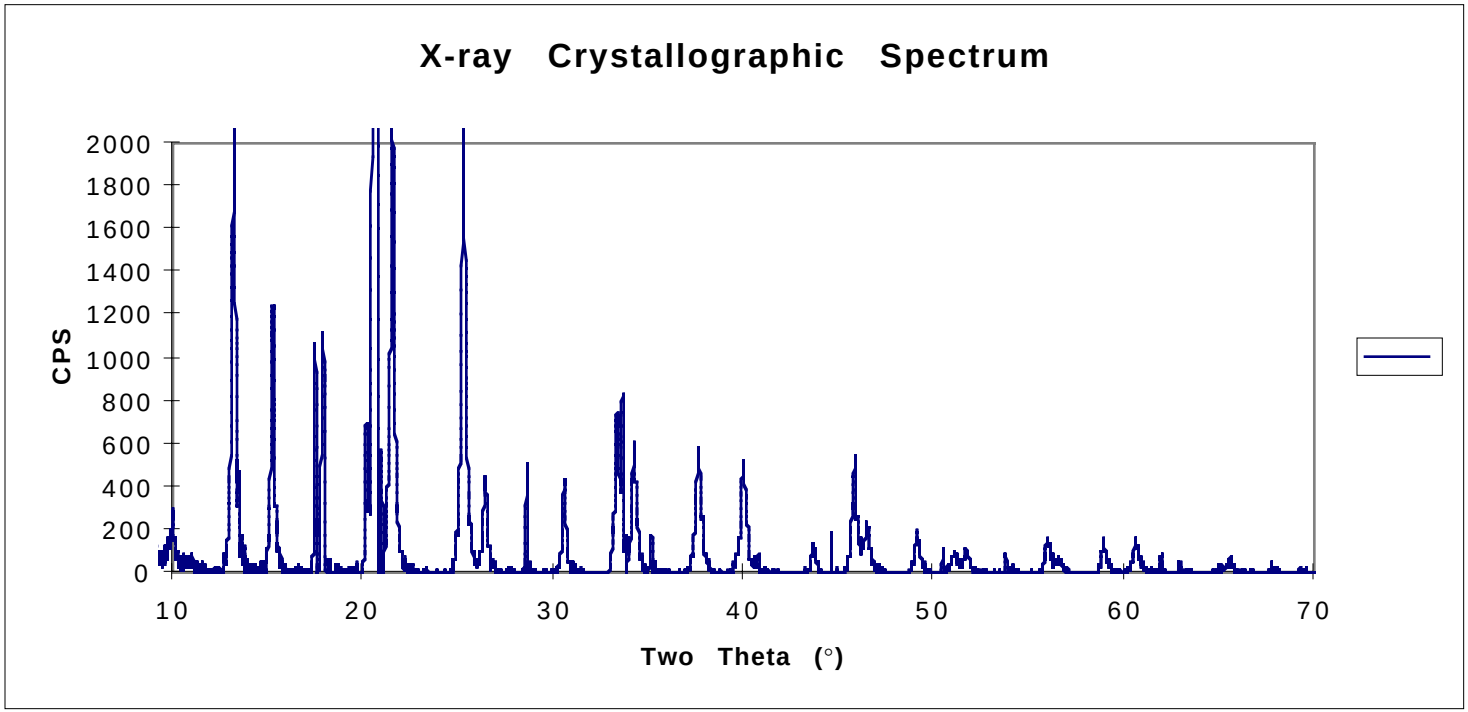
Loss-on-ignition values are high. The material does not satisfy DOE-STD-3013-96 criteria for LOI after calcination for 2 h at 950°C.

REFERENCES

1. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," Department of Energy document DOE-STD-3013-96 (September 1996).

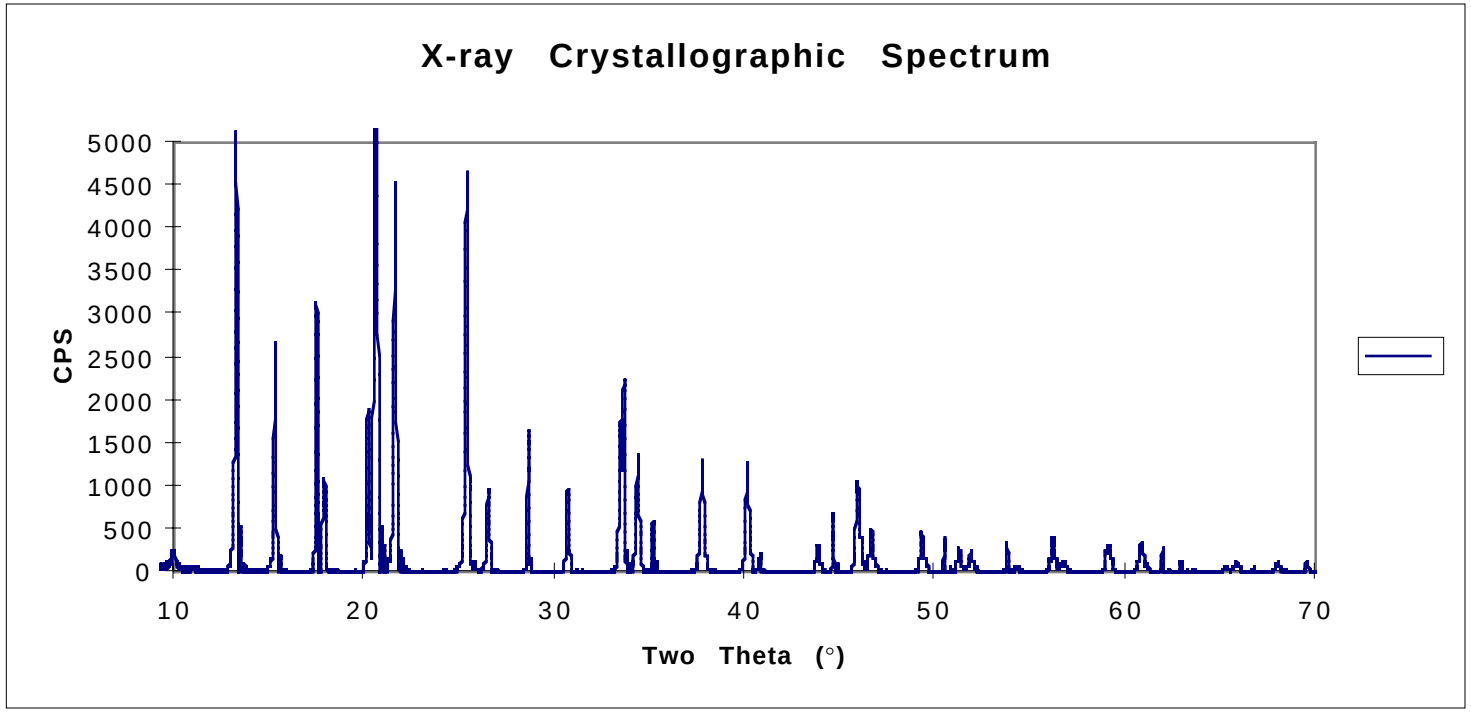
APPENDIX 1. X-ray results for the as-received powder 011589.

Scan Type: Normal	Ave Displacement	-.166
Start Angle: 5 deg.	Max Displacement	.034
Stop Angle: 70 deg.	Min Displacement	-.366
Num. Points: 3251	Wavelength	0.7093
Step Size: 0.02 deg.		



APPENDIX 2. X-ray results for the calcined at 950ºC powder 011589.

Scan Type: Normal	Ave Displacement	-.180
Start Angle: 5 deg.	Max Displacement	.020
Stop Angle: 70 deg.	Min Displacement	-.380
Num. Points: 3251	Wavelength	0.7093
Step Size: 0.02 deg.		



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