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PLUTONIUM RELEASE STUDIES

I. Release From The Ignited Metal

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PLUTONIUM RELEASE STUDIES
I. Release From The Ignited Metal

A B S T R A C T

Six plutonium rods, 1/4-inch in diameter and 3/4-inch in length, were ignited in dry air at temperatures ranging from 410 to 650 C. Air drawn over the specimens at velocities ranging from 3.3 to 50 cm/sec was examined for particulate plutonium oxide. Plutonium oxide entrained ranged from 3×10^{-6} to 5×10^{-5} w/o. The entire oxide produced was subsequently sized using an elutriation-sieving technique. The quantity of particulate material less than 15 microns was found to depend upon the mechanical work used in sizing the particles. Particles equivalent to less than 15 microns in diameter represented as much as 0.03 w/o of the total oxide and 70 - 80 per cent of this material was less than 0.1 micron in size. Oxidation conditions producing internal stresses in the oxide increase friability. Less friable oxides are produced by high oxidation temperatures. Increasing particle size is found with increasing oxidation temperatures. The amount and rate of release under any stated conditions is dependent on friability and the forces to which the oxide mass is subjected. Results of this study are compared with other data available relating to particle size and fractional release from ignited plutonium. Reasonable agreement is noted.

INTRODUCTION

If subjected to the proper conditions of temperature and atmosphere, plutonium metal may ignite and oxidize completely. The fine particulate plutonium oxide formed will be airborne to a greater or lesser degree depending upon oxidation rate, airflow, mechanical working, and several other variables. When considered in terms of a fire involving plutonium the degree to which the oxide is released to the atmosphere and the nature of the particles airborne is of great importance in the evaluation of the accident consequences.

A review of available data on the oxidation rate and fractional release of plutonium during overheating was previously reported.^[1] This review also noted the need for further study of the behavior of plutonium and its compounds in overheating situations. The experiments in the current study were undertaken as the first of a series planned to provide additional information useful in the evaluation of the hazards from plutonium and its compounds when involved in fires.

To evaluate the inhalation hazard from the irregular particles released during oxidation of metallic plutonium, one must know the aerodynamically equivalent size distribution of the oxide since this will dictate the behavior of the airborne particles produced. Particle size distribution data coupled with fractional release for a given situation permits the potential hazard to be estimated.

Experiments undertaken to establish fractional release and size distributions of airborne particles must be designed to give realistic values, hence size distributions are best determined by methods which utilize the aerodynamic properties of the particles. For example, air elutriation may be used to collect sizes of particles of interest. With a material as friable as plutonium oxide, one must be concerned with the potential for breaking the sample down to an unrealistic size distribution in screening or sizing the particles.

Further complicating the design of an experiment to produce data applicable to practical situations is the myriad of systems and forms in which plutonium is found. Plutonium metal is generally handled in dry air or inert atmospheres but in accidents it may be exposed to air of various humidities or other gases. It is found in a variety of shapes from turnings to massive metal. It can be enclosed in stainless steel or be stored adjacent to flammable materials. Each of the conditions can affect the behavior of the metal and its products. A factual, objective analysis of the fate of plutonium in a postulated serious accident involving overheating plutonium is difficult to achieve because of the peculiarities and general complexity of each situation, and the lack of experimentally determined data.

A maximum or "reasonable" maximum hazard is estimated for a given situation. Data are extrapolated from experiments performed under similar or more severe conditions. Since it is impossible to duplicate every set of conditions, either the most common or severe conditions are tested.

K. Stewart^[2] has reported the size distributions of oxide produced by the oxidation of plutonium metal and **delta** alloy under various conditions of temperature and humidity. The initial experiments herein **reported** were designed to establish the nature and quantity of plutonium released when plutonium is heated in dry air or inert gases. Results are to be compared with available data.

PURPOSE

The objective of this study was to determine the nature and amount of the particles formed during the oxidation of plutonium metal upon ignition in dry air. Several temperature ranges and air velocities were used to determine associated changes in size distribution of resultant particles.

SUMMARY

Six unalloyed plutonium rods with area to mass ratios ranging from 0.36 to 0.39 were ignited and allowed to oxidize to completion in dry air. Temperatures during oxidation ranged from 410 to 650 C. Air was drawn over the oxidizing specimens at velocities ranging from 3.3 to 50 cm/sec. From 2.8×10^{-6} to 5.2×10^{-5} w/o of particulate oxide was collected on membrane filters from the effluent air during oxidation and cooling. The residual oxide* was initially separated into three fractions by a combination air washing-screening technique.

The three fractions were:

- a. Particles which could be entrained in air at the terminal velocity of a 15μ sphere of PuO_2 .
- b. Particles aerodynamically equivalent to plutonium dioxide spheres greater than 15μ in diameter but small enough to fall through an NBS 325 mesh screen (~ 44 microns).
- c. Particle retained by a NBS 325 mesh screen (greater than 44 microns).

The fraction aerodynamically equivalent to plutonium dioxide spheres less than 15 microns was a greater as 0.031 per cent with 70 to 80 w/o of this material less than 0.1 micron in diameter. The fraction **greater** than 44 microns in diameter was further classified by sieving. During this operation, an additional amount of material less than 44 microns in diameter was separated. The amounts produced ranged from 0.33 to 1.83 w/o and was primarily composed of fragments from larger particles.

The amount of oxide entrained during **oxidation** and cooling under the conditions of these experiments was small -- up to 5×10^{-5} w/o. Disturbing the oxide mass may increase the amount released. Undisturbed, the residual oxide released an amount of material less than 15 microns comparable to that entrained

* The oxide produced was composed of two types of particles -- an elongated, dark, crystalline material, and a yellowish-brown, submicron particle.

during oxidation and cooling -- up to 5×10^{-5} w/o per hour. Under moderate agitation, periodic rapping, the release rate of material less than 15 micron in size increased up to 0.03 w/o per hour. The size distribution and release rate are dependent upon the conditions of oxidation and the forces to which the oxide mass are subjected.

EXPERIMENTAL METHODS

In order to obtain a size distribution which would be representative of the material available for entrainment from the oxidation of metallic plutonium, an average sized metal specimen and atmosphere were chosen. The air velocity and oxidation temperature were varied to determine their effect upon the particle size distribution produced. It appeared desirable to aerodynamically separate those particles in the region of inhalation hazard* before disturbing the size distribution of the oxide produced under the stated conditions of oxidation. Initial samples indicated that fractionation was incomplete under these conditions and some disturbance of the size distribution was necessary to allow the air passing through the sample to pick up particles trapped inside the oxide mass.

Unalloyed, metallic plutonium was melted, cast and machined into rods 1/4" in diameter and 3/4" in length. The composition as the metal was:

TABLE I
COMPOSITION OF PLUTONIUM METAL
(SRP41FE-35)

Plutonium	99.9
Iron	12 ppm
Nickel	15 ppm
Chromium	25 ppm
Aluminum	Not Detectable
Silicon	Not Detectable
Tin	Not Detectable
Carbon	Not Detectable

* Normally, particles aerodynamically equivalent to 20 micron diameter spheres of unit density or less are considered to penetrate the nose to some degree and deposit in the lungs.[2] For particles with the density of plutonium dioxide, these would be equivalent to ~6 micron spheres. In this study, particles equivalent to or less than 15 micron spheres were included to allow for any future adjustments required in the lung deposition model.

All combustions were performed in the all quartz combustion system shown schematically in Figure 1. Specimens to be oxidized were placed on the supports welded near the top edge of a quartz combustion boat, ~ 1 inch in diameter and 3 inches long. The boat and specimen were centered in a quartz combustion tube 1 inch in diameter and 18 inches long. The combustion tube was held in a 720 watt, 13-inch long clam shell resistance furnace.* The downstream end of the combustion tube was sealed with a cap containing a quartz thermowell used to position the Pt-Pt 13% Rh thermocouple directly over the ignited sample. No more than a 10 C temperature difference was found for temperature taken directly and through the thermowell. Temperatures were recorded outside the glovebox on a modified Micromax Recorder.**

Air was drawn into the combustion tube via a 10 cm O.D. side arm located approximately 1-1/2 inches from the downstream end. The air entering the ignition tube was filtered through a 47 mm, 0.8 micron pore size membrane filter.† The air exited the combustion tube through an 18/9 ball socket joint into a 6-inch water cooled condenser. Cooling of the air was provided to prevent damage to the membrane filter used to collect entrained particulate oxide. The air was again filtered by an assault mask particle filter before passing out of the glovebox. Flow was manually regulated by a 1/4-inch needle valve and a 0-0.8 cfm flowmeter.

Initial size separation was performed using the combination screen-air washing apparatus shown schematically in Figure 2. The entire recovered oxide sample was transferred after weighing and examination to the NBS 3-inch, 325 mesh screen of the apparatus. The lower portion of the 3-inch screen was firmly held in a 2-15/16 inch orifice in the stainless steel cylinder. A neoprene gasket between these two pieces assured an air tight seal. The orifice tapered to 1-5/8 inch at the bottom of the cylinder and was sealed by a membrane filter supported by a fritted glass retaining ring.

The elutriation section was a thin wall, stainless steel cylinder 2-29/32 inches I.D., 6 inches long. An additional 1 inch section was used to taper to the 7/8 inch rectangular opening at the top of the section. Either a Casella Mark II cascade impactor[∞] or a membrane filter was fitted to the elutriator by means of a rubber adapter. All joints were sealed with plastic tape prior to

* Hevi-Duty Model 123, manufactured by the Hevi-Duty Elec. Co., Milwaukee, Wis.

** Leeds & Northrup, Philadelphia, Pennsylvania.

† Type AA manufactured by the Millipore Filter Corp., Bedford, Mass.

[∞] Manufactured by C.F. Casella & Co., Ltd., London, England.

Figure 1 SCHEMATIC DIAGRAM - 2 IGNITION APPARATUS

Figure 2.

SCHEMATIC DIAGRAM-COMBINATION ELUTRIATION SCREENING APPARATUS

initiation of air flow. The diameter of the elutriator section was calculated to lift a particle aerodynamically equal to a plutonium dioxide (density 11.5) sphere of 15 microns in diameter using an airflow of 17.5 liters/min. This was the design airflow for the cascade impactor.

Particles aerodynamically equivalent to 15 micron diameter plutonium dioxide spheres but less than 44 microns remained between the screen and filter but were caught by the lower filter when airflow ceased. Particles larger than 44 microns were retained on the screen. This fraction was subsequently reclassified into five fractions using NBS 3-inch screens.

All fractions were microscopically examined to check separation efficiency. The amount of material in the less than 15 micron fraction was determined by chemical dissolution and α -particle counting. The remaining fractions were weighed directly on the analytical balance located in the glovebox.

DISCUSSION AND RESULTS

Six oxidation runs using unalloyed plutonium metal rods were performed. The individual runs are designated as A through F. Experimental condition and physical measurements of the metal specimen used in these runs are listed in Table II.

Specimen Examination

The six metal specimens used in these experiments were physically uniform. They ranged from 0.594 to 0.625 cm in diameter, from 1.78 to 1.89 cm in length, and from 9.8964 to 11.3423 grams in weight. Area to weight ratios for the rods varied from 0.36 to 0.39 cm²/g.

Each of the rods was examined under X100 magnification. All bore surface machining marks 10 to 20 microns wide around their circumferences at approximately 90 micron intervals. In addition to the machining marks, the specimens used in runs A and B showed some surface pits ranging in size from 25 microns in diameter to 75 × 450 microns. Random surface scratches were visible on most of the rods up to 30 microns in width and several millimeter in length. All rods also exhibited some degree of surface oxidation which varied the appearance from metallic silver to bronze. The oxide particles observed were amorphous, yellowish brown masses with an uneven intensity of color giving them a mottled appearance. The particles appeared to be loosely held to the surface of the rod.

TABLE II

PHYSICAL DIMENSIONS OF SAMPLES AND EXPERIMENTAL DURING
Pu RELEASE STUDIES -- I. Release from Ignited Metal

<u>Run Designation</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Length of Sample, cm	1.73	1.89	1.85	1.89	1.89	1.89
Diameter of Sample, cm	0.602	0.594	0.625	0.625	0.625	0.625
Weight of Sample, grams	9.8944	10.5398	10.9014	11.2030	11.2796	11.3423
Temperature at Ignition	490 C	490 C	495 C	495 C	500 C	480 C
Temperature Range During Oxidation	480 to 560 C	410 to 560 C	630 to 650 C	630 to 650 C	535 to 560 C	520 to 590 C
Air Velocity, cm/sec	3.3	13.5	50.	3.3	3.3	20.
Time of Oxidation, Min.	22	38	30	62	61	64
Time of Cooling, Min.	122	25	129	73	80	40

Ignition Behavior

After the metal specimen was positioned in the combustion tube and the airflow begun, the plutonium was heated to ignition at the maximum heating rate possible with the apparatus, approximately 30 C/minute. After the specimen ignited, the heat supplied was reduced to a level sufficient to maintain the desired temperature. In runs A through D the temperature dropped and the metal stopped glowing. All these runs required reignition by increasing the temperature to approximately 580 C. Once reignited, the metal continued to glow upon reduction of heat supplied. In run B, the temperature was allowed to drop to a much lower temperature (approximately 395 C) than in the other three runs. Much larger temperature variations were experienced in Runs A and B, 130 to 150 C, than in the other four runs. Run A also had the highest maximum temperature (approximately 900 C) and the shortest oxidation period (22 minutes).

The appearance of the metal during oxidation was similar in all six runs. Upon heating, the metal darkens, expands greatly in size and layers of oxide peel off. Ignition was indicated by glowing at the site at which the reaction was initiated. As the oxidation progressed, the volume expansion of the material caused layers of oxide to separate from the main mass. These layers were often held onto the main oxide mass at a single point. The individual layers continued to swell and produce additional small layers which separated and gave the material a herringbone pattern.

Fractional Release During Oxidation and Cooling

The per cent of oxide entrained during oxidation and cooling in the air experiments described ranged from 2.8×10^{-6} to 5.2×10^{-5} . Results are summarized in Table III.

The amount of particulate oxides entrained during the oxidation and cooling periods was very small and was near the lower detection limits of the analytical procedures used. During runs A, B and D, a single sample was taken combining the release during both oxidation and cooling periods. The sampling times varied from 24 minutes in Run B to 155 minutes in Run A. During runs C, E, and F, separate samples were taken of material released during oxidation and cooling. Total sampling periods for these runs range from 75 minutes in Run C to 153 minutes in Run E. The lowest release was found in Run A with 2.8×10^{-6} w/o. The highest release was found in Run C

TABLE III

FRACTIONAL RELEASE FROM UNALLOYED PLUTONIUM RODS DURING OXIDATION AND COOLING

<u>Run</u>		<u>Time (Min)</u>	<u>Temperature Range (°C)</u>	<u>Air Velocity (cm/sec)</u>	<u>Airborne w/o</u>	<u>Cumulative w/o</u>
A	Oxidation & Cooling	155	Ambient-900	3.3	2.8×10^{-6}	2.8×10^{-6}
B	Oxidation & Cooling	74	Ambient-560	13.5	3.1×10^{-5}	3.1×10^{-5}
C	Oxidation	46	Ambient-650	50	3.8×10^{-5}	5.3×10^{-5}
	Cooling	29	Ambient-610	50	1.5×10^{-5}	
D	Oxidation & Cooling	146	Ambient-650	3.3	4.1×10^{-6}	4.1×10^{-6}
E	Oxidation	73	Ambient-560	3.3	7.8×10^{-6}	2.6×10^{-5}
	Cooling	80	Ambient-550	3.3	1.8×10^{-5}	
F	Oxidation	77	Ambient-560	20	2.6×10^{-6}	3.1×10^{-6}
	Cooling	40	Ambient-540	20	5.2×10^{-7}	

with 5.2×10^{-5} w/o. No particles were visible by microscopic examination, showing that the oxide collected was smaller than a few tenths of microns.

The amount of oxide released did not indicate any trend due to air velocity or temperature used during the experiments. Although the highest and lowest releases were found in the runs with the highest and lowest air velocities, the second highest release is found for a velocity of 13.5 cm/sec (the next lowest velocity used) and the second lowest release is found with the second highest velocity used (20 cm/sec). Even normalizing the releases for air-volume or sampling times, does not indicate correlation. The same lack of correlation can be noted with temperature.

Residual Oxide

Nature of Oxide

After cooling, the residual material in the ignition boat and tube was collected and weighed. Weight per cent oxide recovered ranged from 97.37 to 99.97, based upon the weight of plutonium dioxide possible.

In five of the six runs the residual oxide was allowed to cool to ambient temperatures in the insulated furnace. Cooling times for these two runs ranged from 40 to 120 minutes. In run B, the furnace was opened and the oxide allowed to cool more rapidly (25 minutes).

Due to the large volume increase in the conversion of metal to oxide, as well as fragmentation due to thermal stress, some material was found outside the combustion boat in all runs. This material was carefully collected and added to the material in the boat prior to weighing. The oxide recovered was weighed in the tared combustion boat on the analytical balance located in the glovebox. The apparent low oxide recovery may be partially due to the incomplete conversion of metal to the dioxide. Schnizlein and Fisher have also reported less than theoretical weight gain from the ignition of metallic plutonium in air.^[3]

The particulate oxide formed in all six runs was similar in physical appearance. When first removed from the furnace, the oxide is a dark brown, loosely-joined mass with patches bearing a greenish hue. The outline of the mass vaguely resembles the shape of the starting material but greatly expanded in size. The oxide was primarily an aggregate of loosely-joined, elongated, rectangular particles in a herringbone pattern.

A large size range of particles which had broken away from the main mass was found in the bottom of the combustion boat. The loosely-joined mass was quite fragile and was easily broken during recovery into pieces less than 1/2 inch in size.

Under magnification, two distinct types of particles were discernible. The most prevalent type consisted of dark brown, elongated particles up to 200 microns in width and up to 3 millimeters in length. The material was opaque with a hard, crystalline appearance. The second type of particles was a yellowish-brown, finely divided material present as fine individual particles, and as shapeless agglomerates in which the individual particles were not discernible. This material was found separately or adhering to the surfaces of the elongated particle.

Classification of Residual Oxide

The particle size distribution of the oxides remaining in the combustion apparatus was determined by a combination air elutriation-screening technique, using the apparatus described earlier. During the initial separation particles aerodynamically equivalent to spheres less than 15 micron in diameter were collected in either a membrane filter or in a cascade impactor whose final stage was a membrane filter. During the first two runs (A and B), classification was incomplete due to the short sampling period and entrapment of fine particles within the oxide mass. Subsequent oxide samples were elutriated for longer periods of time and the sample agitated by rapping the elutriator and screen. Although the degree of classification improved in these runs, additional fines were produced by deagglomeration and fragmentation. Complete separation into size fractions was not accomplished. Under these conditions, up to 0.031 w/o of the oxide was found to be less than 15 microns in diameter. Further classification of this fraction with a cascade impactor indicated that 70 - 80 per cent of this material is less than 0.1 micron. Results of the elutriations is shown in Table IV.

The oxide not carried through the elutriator was further classified. The particles falling through the NBS 325 mesh screen but not carried out of the elutriator were considered as greater than 15 but less than 44 microns in size. This fraction was composed of agglomerates and fragments of larger particles. The fraction remaining on the 325 mesh screen was further fractionated using a series of four screens (40, 120, 200 and

TABLE IV

FRACTIONAL RELEASE FROM RESIDUAL OXIDE DURING ELUTRIATION

(Particles < 15 μ Equivalent Diameter)

	<u>w/o</u>	<u>Cumulative w/o</u>
<u>RUN A</u>		
20 min. impactor sample ^(a) , no agitation	8.1×10^{-6}	8.1×10^{-6}
<u>RUN B</u>		
20 Min. Impactor Sample ^(a) , agitation	2.3×10^{-4}	2.3×10^{-4}
<u>RUN C</u>		
20 min. Membrane Filter ^(b) , no agitation	1.5×10^{-5}	1.5×10^{-5}
Additional 10 min. filter ^(b) sample, agitated	2.3×10^{-4}	2.5×10^{-4}
" " " " "	2.9×10^{-4}	5.4×10^{-4}
" " " " "	9.1×10^{-5}	6.3×10^{-4}
" " " " "	6.3×10^{-5}	6.9×10^{-4}
" " " " "	3.2×10^{-5}	7.4×10^{-4}
" " " " "	1.5×10^{-4}	8.9×10^{-4}
<u>RUN D</u>		
60 min. Impactor Sample ^(a) , agitated	2.4×10^{-4}	2.4×10^{-4}
Additional 30 min. filter ^(b) sample, agitated	6.1×10^{-4}	8.5×10^{-4}
<u>RUN E</u>		
60 min. Filter ^(b) Sample, agitated	0.03	0.03
Additional 10 min. Filter ^(b) Sample, agitated	0.0011	0.0311
Additional 10 min. Filter ^(b) Sample, agitated	2.5×10^{-4}	0.0311
<u>RUN F</u>		
60 Min. Filter ^(b) Sample, agitated	0.016	0.016
Additional 10 min Filter ^(b) Sample, agitated	2.4×10^{-5}	0.016
Additional 10 Min Filter ^(b) Sample, agitated	4.9×10^{-4}	0.016

(a) Mark II Casella Cascade Impactor, C.F. Casella & Co. Lt., London

(b) Type AA Millipore Membrane Filter, Millipore Filter Corp.
Bedford, Mass.

and 325 mesh). During the screening operation, additional material less than 325 mesh (approx. 44 micron) was produced and was primarily fragments. The amount produced varied from 0.35 w/o in Run A to 1.82 w/o in Run B, and was indicative of the friability of the material produced. Results for the six runs are shown in Table VI.

Observations and information covering individual runs are given below.

RUN A -- The amount released during the air elutriation was 8.1×10^{-6} w/o. In the classification of the oxide from this run, air was simply drawn through the oxide mass on the elutriator screen in an attempt to eliminate any contribution to this fraction by sample handling. Air was drawn through the sample at the rate of 17.5 liters/min. (velocity of 6.7 cm/sec) for 20 minutes. Only a small amount of material was carried out of the apparatus. The rate of release (2.4×10^{-5} w/o per hour) is comparable to those found for release during oxidation and cooling (7.8×10^{-7} to 5.0×10^{-5} w/o per hour). Microscopic examination of the 15-44 micron fraction revealed many particles and agglomerates less than 15 microns in diameter. Apparently many of the smaller particles were trapped in the elutriator by larger particles and could not be made airborne at the velocity used. Analysis of the cascade impactor stages showed that **seventy** w/o of the material which does become airborne under these conditions is less than 0.1 micron in diameter. Cascade impactor results for the three runs during which the impactor was used are given in Table V.

TABLE V

SIZE DISTRIBUTION OF AIRBORNE OXIDE DURING
ELUTRIATION WITH AIR AT 6.7 cm/sec

	<u>Run A</u>	<u>Run B</u>	<u>Run D</u>
w/o Airborne < 3.5 μ	96.2	99.1	99.1
w/o Airborne < 1.4 μ	95.5	82.7	94.6
w/o Airborne < 0.4	80.3	75.1	87.8
w/o Airborne < 0.1	69.7	70.6	83.7

TABLE VI
PARTICLE SIZE DISTRIBUTION OF OXIDE FROM
IGNITION OF UNALLOYED PLUTONIUM RODS BY SIEVING

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
w/o Calculated Oxide Recovered	98.8	99.8	97.4	100	99.4	100
w/o Oxide < 250 μ	7.72	18.23	8.04	10.25	12.47	12.22
" " < 125 μ	3.57	7.66	3.05	4.27	5.03	4.95
" " < 74 μ	2.39	3.75	1.76	2.64	2.96	2.84
" " < 44 μ *	0.99	2.63	1.17	1.76	1.89	1.81
w/o Oxide < 44 μ produced by sieving	0.33	1.83	0.49	1.13	1.23	1.03
w/o 15-44 μ **	0.66	0.80	0.68	0.63	0.60	0.76

* Oxide passing 325 mesh during elutriation plus
< 44 during sieving.

** Oxide passing through 325 mesh screen during air
elutriation.

The oxide produced in Run A had the largest particle size of all materials during these experiments.

The amount of oxide less than 250 and 44 micron for Run A is less than found in any other run. Also this run produced the smallest amount of less than 44 micron particles during sieving. Since the smallest amount of material was removed from this sample by air washing, and the oxide was not subjected to agitation, a large amount of material should be produced during sieving if the friability of all samples was the same. Obviously, the oxide produced in Run A is not as friable as found in subsequent runs. Run A had both the highest maximum temperature and the shortest oxidation time (indicative of high metal temperatures). Apparently some sintering occurred producing harder particles.

RUN B -- The w/o oxide airborne during the air elutriation of the oxide produced in Run B was 2.4×10^{-4} . The walls of the screen in the combination elutriation-screening apparatus were periodically rapped during elutriation in order to improve the fractionation of particles. The same airflow and classification time were used as in the classification of Run A. The weight per cent oxide airborne increased but microscopic examination of the 15 - 44 micron fraction still indicated incomplete separation. Cascade impactor results of the airborne material indicated some rearrangement in the larger size fractions. The w/o of the airborne fraction less than 0.1 micron remained at approximately 70 w/o.

Results from sieving the oxide greater than 44 micron show that Run B was more friable and produced the smallest particle size material found in these experiments. Table VI shows Run B produced significantly more material in all size fractions as well as more particles less than 44 during sieving than any other run. The temperatures during oxidation in Run B are somewhat lower than those in the other five runs. The metal temperature also was allowed to drop to a lower value (approximately 395 C) than in the other three runs (A, C, and D) where reignition was required. Additional stress was also likely created by the short cooling period (approximately 25 minutes). All these factors may have contributed in producing a more friable material.

RUN C -- The w/o oxide airborne during the air elutriation of the oxide produced in Run C was increased to 8.9×10^{-4} by increasing the sampling

time to 80 minutes. The same airflow (17.5 liters/min) was used but all material was collected on membrane filters. Seven successive samples were taken. The initial sample was for 20 minutes with no agitation of the oxide. Six additional 10-minute samples with agitation were then taken. The amounts collected on each filter are listed in Table IV and range from 1.5×10^{-5} w/o for the initial 20 minute sample with no agitation, to 2.9×10^{-4} w/o. The initial sample elutriated with no oxide agitation is comparable to the release in Run A (8.1×10^{-6}) collected in a cascade impactor under the same conditions. The release rates for the six 10-minute samples (1.9×10^{-4} to 1.7×10^{-3} w/o per hour) are comparable to those found in Run B (6.9×10^{-3} w/o per hour). The average release rate on the six samples with agitation is 8.9×10^{-4} w/o per hour. The release rate appeared to decrease after the initial 20 minutes of agitation but rose again to nearly its initial value on the last sample.

The size distribution of the particles produced by the conditions in Run C was similar to that produced by Run A. The values for each size fraction found for Run C by sieving are comparable to those found for Run A but slightly higher. The oxidation and cooling periods are similar for both runs, indicative of similar oxidation rates and temperatures.

The oxide formed was stable and did not change physically with additional heating. Aliquots of the oxide were heated in the combustion apparatus at temperatures of 600, 750 and 900 C for periods of 1, 4 and 1 hour, respectively. The aliquots were microscopically examined before and after each heating. No significant change in physical appearance or size range was observed.

RUN D -- The w/o oxide airborne, 8.5×10^{-4} , during the air elutriation of the material formed in Run D is comparable to that in Run C. Two samples were taken during the elutriation. An initial 60-minute impactor sample with oxide agitation was taken to find if a longer sampling period would alter the size distribution of the fraction airborne. The size distribution found is given in Table V. The fraction less than 0.1 micron increased to approximately 84 w/o. The amount airborne during this period was 2.4×10^{-4} w/o. An additional 30-minute membrane filter was then taken to determine the completeness of fractionation. The w/o airborne during this period was 6.1×10^{-4} indicating considerable material still

remained which could be made airborne under these conditions. Microscopic examination of the 15 - 44 micron fraction showed fragments of larger particles and some agglomerates of very fine particles (probably < 0.1 micron in diameter).

The size distribution determined by sieving the greater than 44 micron fraction from Run D indicates a particle size finer than in Runs A and C, and a material more friable than in Runs A and C. The w/o from 15 - 44 micron upwards for Runs C and D are comparable for comparable conditions during elutriation. The fraction less than 44 microns produced during sieving is greater than twice that produced in either Runs A or C. The oxidation time for Run D is twice as long as that found in Runs A and C, with much shorter cooling times indicative of lower oxidation rates and temperature.

RUN E -- The greatest amount of material airborne, 0.031 w/o, was found during the air elutriation of the oxide produced in Run E. Three membrane filter samples -- an initial 60 minute sample followed by two successive 10 minute samples -- for a total sampling time of 80 minutes, all with oxide agitation. Greater than 95 per cent of the material airborne, 0.03 w/o, was collected on the initial filter. The release rate decreased to approximately 5 per cent of the initial rate (1.5×10^{-3} and 3.0×10^{-2} w/o per hour). Microscopic examination of the 15 - 44 micron fraction showed primarily particle fragments with very few moderate sized agglomerates.

The size distribution determined by sieving of the greater than 44 micron fraction in Run E indicates a finer particle size than in any run except B. The amount of oxide in the 15 - 44 and less than 44 micron fractions are comparable to those found in Run D. The amount of material less than 44 micron produced by sieving is comparable to that found in Run D indicative of similar friability.

RUN F -- The w/o oxide airborne during the air elutriation of Run F was 0.016 under similar sampling conditions as used in analyzing Run E. The initial 60 minute sample contained greater than 97 per cent of the material airborne. The release rates of the subsequent 10 minute samples were 1 and 20 per cent of the initial rate (1.4×10^{-4} and 2.9×10^{-3} w/o per hour respectively). Microscopic examination of the 15 - 44 micron frac-

tion showed a composition similar to that found in Run E -- primarily fragments of larger particles.

Sieving results indicate a particle size distribution similar to that of the oxides from Run E. The distribution is slightly more coarse in all sieve fractions. Although a higher percentage of material is found in the 15 - 44 micron fraction in this run than in Run E, less material under 44 microns was produced during sieving indicating the oxide from Run E may have been subjected to harsher conditions during elutriation.

Thus, the size distribution obtained for the oxides produced by the air oxidation of metallic plutonium depends upon the conditions of oxidation, the friability of the oxide produced and the amount of agitation to which the oxide mass is subjected during classification. The greatest amount of oxide in the region of inhalation hazard was produced in oxidations at low temperatures (Runs E and F). Increasing the temperatures, as in Runs C and D, decreased this fraction approximately an order of magnitude. The oxidation conditions may also affect the size distribution by altering the proportions of the two types of particles observed. The most friable material was produced in Run B which was thermally cycled and force cooled. Runs D, E and F produced the next most friable oxide. All three had the same approximate oxidation periods indicative of similar oxidation rates and temperatures. The least friable oxide was produced in Runs A and C, both of which had short oxidation periods, indicative of higher oxidation rates and temperature. Run A also had the highest recorded maximum temperature -- 900 C. Increasing the abrasive grinding force to which the oxide is subjected can influence the rate and amount of finer particles produced. Even a moderate increase in force such as rapping increases the release and release rate orders of magnitude. There is undoubtedly some limiting size distribution for each set of conditions but none were determined in these studies.

The size distribution curves of particles obtained by sieving in three of these runs (B, D and E) are shown in Figure 3. The size distributions proposed by Stewart^[2] and one determined by Plutonium Fuel Engineering, BNW^[4], for the moist air oxidation of 2 kg buttons are also shown for comparative purposes. Stewart's curve is a composite obtained from the combustion of unalloyed and δ plutonium above the ignition temperature in various atmospheres. The curves for Runs B, D and E straddle the

FIGURE 3

Size Distributions Produced by Oxidation of Metallic Plutonium

size distribution proposed by Stewart. The removal of very fine particles (< 0.1 micron) in Run D appear fairly complete. Considering the friable nature of the oxide produced by these runs, additional working of the oxide could easily produce particles in the intermediate size range. If a smooth curve is drawn between the sieving data and the material < 0.1 micron, the curves would almost mesh with Stewart's proposed distribution. The dissimilar size distribution obtained from the moist air oxidation of massive metal in a graphite crucible does converge with the distribution proposed by Stewart at approximately 6 microns giving the same approximate concentration of material in the respirable range (~ 0.2 w/o).

CONCLUSIONS

The fraction of plutonium metal released as oxide to dry air sweeping over a specimen during oxidation and cooling ranged from 2×10^{-6} w/o to 5×10^{-5} w/o. Air velocity ranged from about 3 cm/sec (6 fpm) to 50 cm/sec (100 fpm). Times up to about 2-1/2 hours were employed for the cycle. Fractional release of plutonium during ignition under the conditions chosen may be considered reasonably typical of ignition, burning and cooling of plutonium pieces in a glovebox or other enclosure in which relatively low air currents exist. Particles airborne under these conditions of ignition and cooling were almost wholly submicron in size as judged from microscopic examination of the filter on which the particles were collected.

Fraction released and size distribution of the airborne oxide in any but the simple case of ignition and low flow of air will be influenced markedly by the mechanical disturbance to which the oxide is subjected subsequent to ignition. Passing air through the oxide at the free fall velocity of a 15μ PuO_2 particle was chosen as a lower minimum of disturbance which might cause particles to be airborne from the mass. Air at 6.7 cm/sec passed through the oxide on a 325 mesh screen entrained 8×10^{-6} to 1.5×10^{-5} w/o. Virtually all the particles air washed out of the oxide were less than 3.5 micron in diameter; a large fraction was less than 0.1 micron in diameter.

Air washing as above, coupled with mechanical rapping and shaking of the sieve support, removed a considerably large fraction of the oxide. In the maximum case 3×10^{-2} weight per cent was airborne as particles with an equivalent diameter $< 15\mu$. Of the order of 84 per cent of this material was 0.1 μ or smaller in diameter.

The mechanical work to free this 0.03 per cent was considered to be a more severe disturbance than would ordinarily be encountered in plutonium ignition incidents. This is a subjective appraisal requiring experimental verification in further studies, but is believed to be realistic.

The further sieve classification of the gross oxide identified a fraction of sizes $< 44\mu$ ranging up to 2.6 per cent for one case, but generally nearer to 2 per cent. The significance of this observation is that first it sets what is certainly a "high" maximum fraction which can be considered as a potential airborne hazard. To separate these $< 44\mu$ particles from the gross oxide required significant mechanical working capable of breaking some of the larger friable particles down to micron size. The size distribution of this $< 44\mu$ size fraction was not determined because of the doubtful value to be realized for the considerable effort in making size distributions measurements. It is almost certain, however, that no more than a few tenths of the mass of this fraction would be associated with particles of concern from an inhalation hazard point of view ($< 6\mu$). These considerations support a conclusion that the fraction which can become airborne and constitute an inhalation hazard, even under rather drastic mechanical working of the oxide is of the order of a few tenths of one per cent.

The size distribution curve suggested by Stewart^[2], shown in Figure 3, for airborne oxide from plutonium places the weight of particles less than 6μ in size at 0.2 per cent. The potential for release of inhalable particles from oxidation of metallic plutonium ranges from a low of around 1×10^{-5} w/o to less than 1 per cent. Consequences of accidents involving ignition and complete oxidation of plutonium metal must be estimated by selecting a release fraction after a more or less subjective appraisal of the potential for the oxide to be broken down into the smaller size particles and the availability of forces to make the particles airborne.

This work to date has yielded additional understanding of some of the parameters affecting airborne plutonium releases from oxidized metallic plutonium; however, additional data are required on the fractional release following simulated or actual incidents involving ignition and oxidation of plutonium.

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