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ASSESMENT OF THE BASIS FOR MODELING RELEASES FROM PLUTONIUM OXIDATION

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SUMMARY

This report responds to the request of Westinghouse Idaho Nuclear Company for an assessment of the data available to support an analysis of plutonium oxide release from a bulk plutonium metal fire. Such fires are among the accidents to be considered in plant design efforts as well as future safety studies for the Special Isotope Separation (SIS) facility.

Because neither data nor theory can currently support a theoretical model for aerosol release, empirical models have been derived from the existing experimental database (after collating it using a consistent set of assumptions and definitions of aerosol properties). The simplest level of empirical model, upper-limit values for all cases of combustion, was derived by examining the maximum release rates in the existing data set. It appears that a value on the order of 10^{-3}/h (expressed as a fraction of the original plutonium) may be an upper limit for the aerosol release rate. This value must be used with an estimated oxidation rate, and an accident description, to determine how long the oxidation could continue.

A more detailed, condition-specific empirical model was also derived by performing a multiple linear regression (least-squares fit) on the experimental database. The result is a set of correlations between the aerosol release rate (the predicted variable) and the peak temperature of the metal and relative humidity (the predictors). More than 70% of the variation in the release rate is explained by the variation in the two predictors. Similar correlations were found for the respirable release rates (the release of aerosol with aerodynamic diameter below 10 μm). Despite the good correlation statistics, the correlations underpredicted the maximum release rates for the database. The size distribution exhibited considerable scatter and could not be expressed in a meaningful correlation, although it was possible to devise conservative (i.e., minimum mass-median diameter) closed-form size distribution estimates for different ranges of temperature and humidity conditions. These can be used readily in release prediction models.

The statistical correlations of aerosol release show that relatively few variables are needed to describe a plutonium oxidation accident well enough to allow prediction of aerosol releases. However, some methods of predicting

peak temperature (including self-heating) and duration of oxidation were also needed. Linear regression was therefore used to provide a correlation of the peak temperature reached by the plutonium under accident conditions. This correlation was successful for pure metal, explaining 86% of the variation in peak temperature, but less so for the delta (δ)-stabilized alloy, explaining only 44% of the variation. The available data were not comprehensive enough to permit oxidation time to be correlated; however, the literature (Felt 1967) does provide some basis for recommending an oxidation rate of 180 g/h to be used in estimating the oxidation time.

Briefly, our recommendations for further study include the following:

- Embed the statistical correlations for aerosol release and peak temperature, as well as the closed-form size distributions and the oxidation rate estimate, in an existing computer code capable of calculating the room conditions and airborne radioactive releases during a fire. FIRIN (Andrae et al. 1978) is one such code.
- Run a set of plutonium oxidation experiments under conditions that should produce maximum aerosol releases, to verify that those maximum releases can be predicted by the model.
- Survey the literature for information on the corrosion of plutonium (and its surrogate, uranium) by water vapor at low temperatures to improve the knowledge of releases that occur under normal operating and storage conditions.

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INTRODUCTION

Ideally, a model of the release of plutonium aerosols from plutonium during oxidation or combustion should begin from a description of the plutonium material and its surroundings and proceed unequivocally to a situation-dependent estimate of the amount of oxide released and its size distribution. Such a model would need to provide a description of the heat- and mass-transfer processes involved and link them directly to the rate of aerosol production. The first step, the description of heat and mass transfer, is more easily achieved from current information than the second, the aerosol release.

The release of aerosols from the oxidation of plutonium depends partly on the forces acting on the particles while they remain attached to the bulk material and partly on the ability of the airstream around the plutonium to transport the particles once they become detached. The forces that attach or detach the plutonium oxide particles can be roughly described as (on the attachment side) binding of the particle to the oxide or metal around it and (on the detachment side) expansion and contraction stresses, sparking and sputtering, and external jarring and vibration. The ability of the atmosphere to support and carry the particles comes from externally driven convection, such as wind or ventilation, and from the natural convection that arises around the hot plutonium.

Much of the pertinent literature has been reviewed to determine what information is available to permit modeling of the effects of the forces or processes just listed. The documents that are cited in this report are listed in the references; other related, but uncited, documents are listed in the bibliography. The reviewed documents are marked with either a "*" or a "U". Those marked with a "*" contain data or commentary directly pertinent to aerosol releases from plutonium oxidation, while those marked with a "U" do not contain immediately pertinent information. (The unmarked documents are believed to contain some related information but have not been reviewed.)

The sections of the report titled "Physical Fundamentals" and "Available Theoretical Information" describe the approach that would be required for theoretical modeling. The "Experimental Results" section describes the information on aerosol releases, size distributions, peak temperatures, oxidation rates, and experimental conditions that we have gleaned from the existing experimental literature. (Brief summaries of the experiments are given in Appendix A.) Table 1 summarizes the data, and the bibliography lists the relevant literature that has and has not been reviewed. The trends in the data, and the apparent "holes" in the existing experiments and documentation, are described in the "Interpretation of Experimental Data" section. Empirical upper-limit and statistical correlation models of aerosol release were derived, as discussed in the "Statistical Analysis" section. Our descriptions of the work needed for the development of a model for estimating the aerosol releases are given under the heading of "Recommended Activities." The conditions that should be met by the experimental design for any new experiments are described in Appendix B, "Experimental Technique."

PHYSICAL FUNDAMENTALS

The creation of plutonium oxide particulate material and the size distribution of the material are the result of three processes: fragmentation of the bulk material into relatively coarse particles because of bulk internal stresses, comminution of the coarse fragments into fine particles because of friction at the edges of the coarse particles, and condensation and oxidation of vaporized plutonium (Stewart 1964; Carter and Stewart 1970). This last process plays little part in the oxidation of massive plutonium (Hilliard 1963), because the heat loss to the surface supporting the plutonium typically prevents the metal from approaching the boiling point of 3230°C; in fact, the vapor pressure of molten plutonium at 1200°C is less than 10^{-4} mm Hg (Miner and Schonfeld 1967). However, dripping molten plutonium may produce fume aerosols typical of oxidized condensed vapor (Carter and Stewart 1970). The combination of the different processes often produces bimodal or multimodal size distributions (Stewart 1963).

The first of the processes that cause the oxidation and release of plutonium oxide is the oxidation process itself. During the initial stages of a high-temperature oxidation reaction, the oxidation kinetics are believed to control the rate of reaction. Later, when the oxide layer has become relatively thick and begun to crack and spall (because of the much higher molar volume of the oxide), the reaction rate may be controlled by oxygen diffusion through cracks in the oxide. Finally, near the end of the reaction, the amount of unreacted metal becomes the rate-controlling factor.

Near the beginning of the plutonium oxidation reaction, parabolic behavior is observed:

$$x = A(b + k\sqrt{t}) \qquad (1)$$

Here x is the fractional conversion, b a constant, k the kinetic rate constant, A the exposed area, and t the elapsed time. The kinetic behavior

becomes linear at later times, apparently depending on the thickness of the oxide covering the active metal surface. The functional dependence is as follows:

$$x = A(b + kT) \tag{2}$$

According to one theory, this "paralinear" behavior results from the presence of two layers of oxide. An inner layer grows parabolically, consistent with diffusion. An interfacial reaction causes constant attrition of this inner layer, so that the inner layer grows to a limiting thickness and the outer layer grows at a constant rate (Waber 1967). The outer layer is subject to cracking, while the inner layer tends to be relatively unbroken and adherent.

The later linear phase of plutonium oxidation can also be explained by the extensive oxide cracking that occurs; when sufficient "short-circuit" paths develop, the rate-limiting step may become O_2 diffusion. When this is the case, the rate dependence is

$$x = kT \tag{3}$$

This equation describes a situation in which a shrinking core of metal in a constant-size metal/oxide specimen is reacting with a gas, with gas-layer diffusion controlling the rate of oxidation (Levenspiel 1972). Here k is a "rate constant" that is proportional to the gas-film mass-transfer coefficient and inversely proportional to the specimen radius. The reaction rate is linear in these circumstances, as observed for the later stages of plutonium oxidation.

The reaction rate can display yet a third type of dependence when diffusion through the oxide itself is limiting:

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = kT \tag{4}$$

This more complicated dependence describes a situation in which a shrinking core of metal in a constant-size metal/oxide specimen is reacting with a gas, with diffusion through the growing layer of oxide controlling the oxidation

rate (Levenspiel 1972). Here k is a "rate constant" that is proportional to the diffusivity of oxygen and inversely proportional to the square of the specimen radius. The actual behavior of plutonium oxidation rates during the latter part of the reaction may be a mixture of gas-layer and oxide-layer controlled diffusion.

It is assumed in the preceding discussion that the oxidation process is isothermal. This is seldom the case, because of the strongly exothermic character of oxidation and the exponential increase of the kinetic reaction rate with temperature. Frequently, the heat-transfer capability of the surroundings is high enough to prevent plutonium oxidation self-heating from occurring. For example, combustion was not self-sustaining when massive plutonium specimens were ignited on plates of stainless steel or aluminum (high thermal conductivity) instead of on insulating surfaces (Felt 1967). If the surface area of the plutonium is high (increasing the area available for reaction), or if some outside event contributes heat to the metal, a point may be reached at which heat production outruns the losses. At the "ignition temperature" the heat losses fall far behind the heat generation, allowing a sharp increase of temperature. Ignition has been observed at temperatures from 110°C to 520°C (Stewart 1963), depending partly on the heat-transfer properties of the shape of the metal; for comparison, the melting point is 640°C. At some later time, the heat losses and generation become equal, permitting a peak temperature to be attained.

The heat generated by reaction is proportional to the rate of reaction. The temperature dependence is exponential, resulting from the Arrhenius dependence of the kinetic rate constant k:

$$k \propto e^{-E/T} \qquad (5)$$

where T is the temperature and E an activation energy characteristic of the reaction. A diffusion-controlled reaction exhibits a lower activation energy and temperature dependence, which comes from the temperature dependence of the diffusivity in air and the concentration of oxygen. This smaller temperature dependence probably contributes to decrease the heat generation, which in turn

allows heat losses to "catch up" with heat generation. This might not be possible during the exponentially dependent part of the reaction.

Heat is lost from the material through conduction to the support and through radiation and convection from its exposed surface. Although the growing oxide crust provides thermal insulation from the surroundings, the fourth-power dependence of radiative heat transfer on temperature can at high temperatures more than make up for this hindrance. The convective and conductive heat transfer are approximately linearly dependent on temperature. However, if oxide growth is limited on the area in contact with the support, conductive heat loss can be substantial.

The stresses that affect the bulk material and cause aerosol to be detached occur because of the expansion and contraction of the metal and its oxide crust. Some of the expansion is purely thermal in nature, or results from temperature-dependent phase changes in the metal, and can be reversed in the course of any temperature oscillations that occur. (Both the expansion and the contraction probably contribute to detachment of particulate material.) The remainder of the expansion is due to the conversion of metal to oxide at higher molar volume and cannot be reversed.

Once the particle has reached its final size and become detached from the oxide mass, it must be transported as an aerosol. Transport is a function of the aerodynamic diameter of the particle, its effective density, and the vertical and horizontal airflow to which the particle is subjected. Forced convection is described by the pressure gradients in the room, which depend on the ventilation design. The temperature gradients produced by the hot plutonium augment the airflow through natural convection. It is possible to describe the resulting natural airflow in terms of the pressure and temperature gradients.

A theoretical model to describe the heat transfer, mass transfer, and reaction processes occurring in the material would have to consider 1) the movement of the oxide and the metal phases, 2) the net heat transfer between the material and its surroundings (atmosphere, support, and other surfaces),

3) the rate of heat generation through reaction, and 4) the thermal diffusivities of the oxide and the metal phases. The information available on each of these four topics is summarized in the following section.

AVAILABLE THEORETICAL INFORMATION

MOVEMENT OF THE OXIDE AND METAL PHASES

The information that is available on this topic includes the densities and molar volumes of the oxide and metal phases, the temperatures at which phase changes occur, and the thermal expansion coefficients of the oxide and metal phases (Skavdahl and Chikalla 1967). This information can be used to develop a numerical description of phase motion as a function of extent of oxidation and temperature and include it in a solution of the heat- and mass-transfer equations.

NET HEAT TRANSFER

The heat transfer that occurs can be subdivided into conduction into the supporting surface, convection (both forced and natural) into the atmosphere, and radiation to the atmosphere and surrounding objects. It should be possible to estimate all three of these forms of heat transfer using already developed algorithms together with information as to the nature of the supporting surface and the characteristics of the ambient atmosphere. Any uncertainty arises in characterizing the roughness of the oxide surface, which is of some importance in convection, greater importance in conduction, and the greatest importance in radiation. Photomicrographs have been used to examine the morphology of the particles, but not the bulk oxide surface.

RATE OF REACTIVE HEAT GENERATION

The heat of reaction for oxidation and the heats of phase transformation are available in the literature (Mishima 1969; Miner and Schonfeld 1967), and the kinetics of plutonium oxidation have been the subject of numerous experiments. Some of the most recent work has been performed by Stakebake and Lewis (1987, 1988) and Stakebake (1986). Much of the earlier work was listed and reviewed by Mishima (1964) and Stewart (1963). The reaction rate is known to depend on the temperature, the availability of oxygen, the humidity (at temperatures below about 350°C), and the phase of the metal. For the pure metal, the past treatment of the metal in terms of mechanical working and phase (thermal) cycling may also be important (Stewart 1963; Chatfield 1968).

Some important issues are the characterization of the inward diffusion rate of oxygen (and perhaps water) and possibly the migration of plutonium metal vapor outward through the oxide shell. The unknown quantities include the diffusivities of these vapors in solid oxide, the surface area of unreacted metal that is available for the reaction, and the amount of cracks, pores, and sintering in the oxide crust. Cracking models or photomicrographs of large fragments of the crust might help to describe this material.

THERMAL DIFFUSIVITIES

The thermal diffusivity (thermal conductivity divided by the product of heat capacity and density) is the parameter that defines heat transfer. It is also necessary to determine transient temperature behavior. Data are available to permit calculation of the thermal diffusivity of the metal and the oxide in all phases (Miner and Schonfeld 1967; Skavdahl and Chikalla 1967; Cleveland 1967). However, the thermal diffusivity is affected by porosity, cracking, and sintering in the oxide crust.

From the point of view of modeling heat transfer, mass transfer, and reaction behavior, data are needed to describe the morphology of the bulk oxide crust. From the point of view of aerosol release modeling, the qualitative relationship between the aerosol generation rate and the conditions that produce the aerosol needs to be better understood.

To theoretically relate oxidation to particulate release, it is necessary to calculate the time dependence of the stress in the oxide and to find the energy required to detach particles from the bulk. It is also necessary to determine how the energy of detachment determines the distribution of sizes. The contributions of very fine particles produced by comminution (caused by friction between larger particles) and condensation from vapor are also needed. (However, for typical bulk metal oxidation the contribution from these latter processes would be minor.) Such a model is probably not possible at present.

The information to link particulate release to bulk material behavior can be provided by experimental data. The experiments, to be useful, must be well defined in terms of what particulate material is produced (amount and size

distribution) and what regimes of bulk behavior exist in the plutonium material. For the sake of helping to evaluate the usefulness of the experiments that we review in this report, an "ideal" experiment for studying plutonium oxidation is described in Appendix B. This appendix can also be taken as a summary of the recommended protocol for any future experiments.

EXPERIMENTAL RESULTS

Table 1 is intended as a summary of the plutonium oxidation aerosol experiments that have been reviewed to date, their experimental techniques, the variables that were considered, and their results. Each experiment is compared to the "ideal experiment" criteria in Appendix B. The tabulation also includes the total aerosol release rate, the fraction of the released aerosol that is respirable (aerodynamic diameter below 10 μm), and the particle mass median geometric diameter for each of the experiments. In determining the geometric diameter from measured aerodynamic diameter, the material is assumed to have the density of PuO_2. A glossary that explains the "Experimental Criteria" section of Table 1 is located at the end of the table.

Table 1 also contains the data on experimental conditions that are needed to make a meaningful comparison of results. The first column of Table 1 describes the metal specimens and some special conditions such as rate of heating and non-air atmospheres. The metal phase, the relative humidity and flow rate of the air, and the peak temperature reached by the plutonium material are the parameters and variables that have the most bearing on determining the oxidation regime in which release occurs. The remaining parameters are less important: the initial temperature, the ignition temperature (where applicable), the extent of oxidation, and the length of time over which sampling occurred. The "Experimental Criteria" column gives a qualitative idea of the completeness of the experimental writeup and of data gathering. (Appendix B contains more detail on the rationale for the criteria.) The number of asterisks is a rough assessment of the ease with which this experiment can be compared with others and the ease with which the experimental conditions could be reproduced. The greater the number of asterisks, the more complete the writeup is.

In most cases, the release rates in Table 1 are the results of single experiments. In other cases they are the maximum values measured by a series of experiments that were all performed under the same conditions. In a few cases, a series of experiments was used to provide release estimates at the 95% confidence limit. These variations in the reported data are marked by footnotes (g).

TABLE 1. Summary of the Conditions and Measurements from Experiments Concerning Particulate Release from Oxidation and Combustion of Plutonium

Reference/Experiment	Experimental Criteria ABCDEFGHIJKLMNOPQ	Metal Phase	Relative Humidity (%)	Airflow Speed (cm/s)	Init Temp (°C)	Peak Temp (°C)	Ignition Temp. (°C)	Percent Oxidized (%)	Sampling Duration (h)	Aerosol Release Rate[a]	Respirable Release Fraction	Geom. MMD (μm)
Andersen 1963												
Room air sample	* *	?	?	?	?	?	?					1.5
Stewart 1963												
7 g cylinders[b]	**X? ?? *? ** ?	α	0	?	22	22	n/a	?	168	9.6E-13	1.00	0.2
7 g cylinders	**X? ?? *? ** ?	α	100	?	22	22	n/a	?	168	2.9E-09	0.30	3.5
7 g cylinders	**X? ?* *? ** ?	δ	0	?	22	22	n/a	?	168	3.3E-14		
7 g cylinders	**X? ?* *? ** ?	δ	100	?	22	22	n/a	?	168	3.3E-10	0.20	3.5
7-11 g specimen	**** *** ***** ?	β	< 1	5	123	123	n/a	76	70	3.0E-08[c]	0.80	0.5
7-11 g spc, 5 cycles	**** *** ***** ?	β	1	5	123	123	n/a	65	18	3.0E-08	0.80	0.5
7-11 g specimen	**** *** ***** ?	α	1	5	113	113	n/a	21	210	1.1E-09	0.80	0.5
7-11 g specimen	**** *** ***** ?	δ	< 1	5	123	123	n/a	3	570	7.3E-08[c]	0.50	3
7-11 g specimen	**** *** ***** ?	δ	0	5	113	113	n/a	5	525	2.8E-09	0.50	3
10-15 g spc, <10°C/min	??? ?* *??**X*?	δ	?	?	room	900	490	100	?	1.5E-05		2
10-15 g spc, <10°C/min	??? ?? *??**X*?	pure	?	?	room	950	520	100	?	1.6E-05		2
10-15 g spc, 15°C/min	??? ?? *??**X*?	pure	?	?	room	630	350	67	?	2.4E-03		3
10-15 g spc, 150°C/min	??? ?* *??**X*?	δ	?	?	room	800	515	< 20	?	1.3E-04		1.3
1-2 g swarf	.? ?* *??**X*?	δ	?	?	room	780	110	100	?	1.0E-04[c]		0.6
5-7 g spc, O_2	??? ?* * ??**X*?	δ	?	?	room	>1000	340	?	?	2.1E-02		6.1
5-7 g spc, 30% O_2	??? ?* * ??**X*?	δ	?	?	room	970	500	25	?	1.8E-04		8.5
5-7 g spc, 40% O_2	??? ?* * ??**X*?	δ	?	?	room	1200	245	100	?	1.9E-04		5
5-7 g spc[d], 15°C/min	***? ?* * ? ** ?	δ	0	?	room	?	515	0.94	?	1.0E-07	0.85	0.7
5-7 g spc, 15°C/min	***? ?* * ? ** ?	δ	100	?	room	?	505	0.57	?	2.3E-07	0.85	2
5-7 g spc[e], 15°C/min	***? ?* * ? ** ?	δ	0	?	room	?	500	0.90	?	1.5E-07	0.85	1.0
5-7 g spc[d], 15°C/min	***? ?* * ? ** ?	pure	100	?	room	?	394	0.68	?	3.0E-07	0.98	0.6
5-7 g spc, 15°C/min	***? ?* * ? ** ?	pure	100	?	room	?	382	0.90	?	7.2E-06	0.98	0.7
5-7 g spc[e], 15°C/min	***? ?* * ? ** ?	pure	0	?	room	?	404	0.98	?	4.0E-06	0.98	0.7
5-7 g spc, 20% O_2	*?? ?* ??? **?	δ	0	?	624	690	n/a	53	0.75	8.5E-05	0.90	0.9
5-7 g spc, 10% O_2	*?? ?* ??? **?	δ	0	?	525	625	n/a	17	0.05	1.5E-06	0.90	0.9
5-7 g spc, 17% O_2	*?? ?* ??? **?	pure	0	?	500	620	n/a	12	0.17	7.5E-05	0.90	0.9
5-7 g spc, 17% O_2	*?? ?* ??? **?	pure	100	?	560	630	n/a	5.6	0.12	1.8E-05	0.90	0.9

TABLE 1. (contd)

Reference/Experiment	Experimental Criteria ABCDEFGHIJKLMNOPQ	Metal Phase	Relative Humidity (%)	Airflow Speed (cm/s)	Init Temp (°C)	Peak Temp (°C)	Ignition Temp. (°C)	Percent Oxidized (%)	Sampling Duration (h)	Aerosol Release Rate[a]	Respirable Release Fraction	Geom. MMD (μm)
Mishima 1966a												
10-11 g rods, ignited	**** ?* **** **?	pure	0	50	room	650	495	97	1.25	4.2E-07[c]	1.00	<0.2
10-11g oxide, entrain	**** ?* **** **?	oxide	0	7	room	room	n/a	n/a	0.33	4.5E-07[c]	1.00	<0.1
10-11g oxide, rapped	**** ?* **** **?	oxide	0	7	room	room	n/a	n/a	1.33	2.3E-04[c]	1.00	<0.1
Mishima 1966b												
570 g low-density	??** *	pure	?	525	room	960	375	100?	1.5	3.2E-04		
1770 g high-purity	??** * * *	pure	?	525	room	950	510	100?	0.75	1.9E-04	0.20	4.2
997 g specimen	??** *	δ	?	525	room	930	?	100?	0.37	4.5E-05		
Mishima et al. 1968												
1 g oxide, entrained	?** * ?* *	oxide	?	10	room	room	n/a	n/a	?	6.1E-08		
1 g oxide, entrained	?** * ?* *	oxide	?	117	room	room	n/a	n/a	?	5.6E-03[f]		
1 g oxide, entrained	?** * ?* *	oxide	?	10	800+	800+	n/a	n/a	?	6.3E-08		
1 g oxide, entrained	?** * ?* *	oxide	?	117	800+	800+	n/a	n/a	?	2.5E-04		
Chatfield 1968												
7 g pellets	**X* ? ?? * ?	pure	100	10-80	20	20	n/a	?	?	7E-09[c]	0.15	>10
7 g pellets	**X* ? ?? * ?	pure	100	10-80	120	120	n/a	?	?	4E-08[c]	0.70	1
7 g pellets	**X* ? ?? * ?	pure	100	10-80	350	?	?	?	?	4E-06	0.15	8
7 g pellets	**X* ? ?? * ?	pure	100	10-80	600+	?	?	?	?	8E-05[c]	0.70	2
7 g pellets	**X* ? ?? * ?	δ	100	10-80	20	20	n/a	?	?	8E-10[c]	0.10	>10
7 g pellets	**X* ? ?? * ?	δ	100	10-80	120	120	n/a	?	?	1E-09	0.30	6
7 g pellets	**X* ? ?? * ?	δ	100	10-80	350	?	?	?	?	2E-06[c]	0.30	6
7 g pellets	**X* ? ?? * ?	δ	100	10-80	600+	?	?	?	?	5E-06	0.70	2
7 g pellets	**X* ? ?? * ?	pure	0	10-80	20	20	n/a	?	?	2E-12[c]	0.995	0.4
7 g pellets	**X* ? ?? * ?	pure	0	10-80	120	120	n/a	?	?	9E-99	[illegible]	1
7 g pellets	**X* ? ?? * ?	pure	0	10-80	350	?	?	?	?	8E-07[c]	0.15	8
7 g pellets	**X* ? ?? * ?	pure	0	10-80	600+	?	?	?	?	4E-05[c]	0.70	2
7 g pellets	**X* ? ?? * ?	δ	0	10-80	20	20	n/a	?	?	5E-14[c]	0.85	1.4
7 g pellets	**X* ? ?? * ?	δ	0	10-80	120	120	n/a	?	?	8E-08[c]	0.30	6
7 g pellets	**X* ? ?? * ?	δ	0	10-80	350	?	?	?	?	1E-07[c]	0.30	6
7 g pellets	**X* ? ?? * ?	δ	0	10-80	600+	?	?	?	?	7E-05[c]	0.70	2

TABLE 1. (contd)

Reference/Experiment	Experimental Criteria ABCDEFGHIJKLMNOPQ	Metal Phase	Relative Humidity (%)	Airflow Speed (cm/s)	Init Temp (°C)	Peak Temp (°C)	Ignition Temp. (°C)	Percent Oxidized (%)	Sampling Duration (h)	Aerosol Release Rate[a]	Respirable Release Fraction	Geom. MMD (μm)
Chatfield 1969b												
<0.1 g foil ignition	?** ? *? ?*	?	?	80	300	1100	?	100	?	4.5E-05[c]	0.41	> 3
Carter and Stewart 1970[g,h]												
Exploding wire	??? ** * ?	?	?	?	room	?	?	?	n/a	0.5		< 1
Static foil oxidation	???* ?* ??*** *??	δ	?	?	?	?	?	?	n/a	1E-04		3
Falling droplet	???* ?* X *** *??	δ	?	?	600	?	?	?	n/a	0.01		0.2
Burning droplet	???* ?* X *** *??	δ	?	?	2000	?	?	?	n/a	0.01		0.2
Eidson and Kanapilly 1983												
0.5-1 g pellet	****? * ??* ***	δ	0	75	room	200+	?	100?	?	5.0E-05[g]	0.90	1.5
Eidson et al. 1988[h,i]												
1 g specimen, H_2	*?***?* ??* ****	δ	0	40	450	700?	?	100?	1+	2.8E-04		1-3
1 g specimen, H_2	*?***?* ??* ****	δ	0	500	450	700?	?	100?	1+	3.7E-03[c]		1-3
1 g specimen, H_2	*?***?* ??* ****	δ	0	1000	450	700?	?	100?	1+	4.6E-03[c]		1-3
10 g specimen, H_2	*?***?* ??* ****	δ	0	40	450	700?	?	100?	1+	4.2E-04[c]		1-3
1 g spc, H_2+N_2	*?***?* ??* ****	δ	0	40	450	?	?	100?	1+	9.2E-05		1-3
1 g spc, H_2+N_2	*?***?* ??* ****	δ	0	500	450	?	?	100?	1+	3.0E-04		1-3
1 g spc, H_2+N_2	*?***?* ??* ****	δ	0	1000	450	?	?	100?	1+	4.5E-04[c]		1-3
10 g spc, H_2+N_2	*?***?* ??* ****	δ	0	40	450	?	?	100?	1+	1.2E-05[c]		1-3

(a) The aerosol release rate is the fraction/hour of the original metal released as aerosol; the respirable release rate is the aerosol release of <10 μm aerodynamic diameter (for unit density spheres). If the value is underlined, it is not a time rate of release but the released fraction over the entire duration of sampling.
(b) These billets were 0.7 cm in diameter and 1 cm long.
(c) These are maximum values for more than one run made under equivalent conditions.
(d) These samples had already been oxidized at 123°C.
(e) These samples had already undergone one ignition and quenching.
(f) This measurement is believed to be anomalously high because of experimental error.
(g) In these experiments, the releases are at the 95% confidence limit.
(h) In these experiments, the values given under "aerosol release" are respirable, not total, release rates.
(i) In these experiments, the 1-g cylinders were 0.63 cm in diameter and 0.2 cm long; the 10-g cylinders were 1 cm in diameter and 0.8 cm long. 1- and 10-g foil specimens were also used; there was no statistical difference between the results for the foil and the pellet specimens.

Glossary for Table 1

The meaning of the "Experimental Criteria" categories

A -- The air humidity and dust content are controlled.
B -- The temperature of and around the specimen is controlled.
C -- The airflow linear speed and overall direction are controlled.
D -- Constraints on aerosol size caused by transport are stated.
E -- All aerosol sinks (including the walls and floor of the apparatus) are sampled.
F -- Abrupt changes in airflow direction between the specimen and the impactors are avoided.
G -- The past cycling and oxidation history of the specimen is known.
H -- The weight change of the specimen is measured.
I -- The core temperature of the specimen is measured.
J -- The surface temperature of the specimen is measured.
K -- The entire duration of the oxidation event is included in sampling and time histories.
L -- The morphology of the aerosol is examined.
M -- The morphology of the residue is examined.
N -- The cascade impactor size distribution is checked (or calibrated) as part of the experiment.
O -- The size distribution of the aerosol is examined.
P -- The size distribution of the residue is examined.
Q -- The lognormality of the size distribution was confirmed before variance-based statistical techniques were used.

The meaning of the notations in the "Experimental Criteria" categories

* -- This criterion is met by the experiment and described well enough to be included as a value in a database.

X -- This criterion is met by the experiment but the reader is not informed of enough of the details to allow quantification.

(blank) -- This criterion was definitely not met by the experiment.

? -- This criterion may have been met by the experiment but it is not clear from the description, and quantification is not possible.

The major uncertainty in the aerosol release rate, or the aerosol release fraction, is whether all of the aerosol was measured. In some experiments there is doubt as to whether measurements covered the entire duration of combustion (Mishima 1966b), or whether rates from rapidly quenched ignition are representative of complete combustion (Stewart 1963). In most experiments, there was an upper limit on the particle size that could be transported by the airflow, and this limit was often not clearly documented. Finally, there were uncertainties (of roughly plus or minus 25%) that were imposed by the difficulty of accurately reading release rates from small logarithmic graphs, when the values were only available in that form (Chatfield 1968).

Size distribution data were usually available only as size distribution graphs. It was unusual to be able to extract mass median diameters (MMDs) and respirable fractions to more than one significant figure accuracy. Another source of uncertainty in the work done by Stewart (1963) is the ambiguity as to whether the diameters reported are geometric or aerodynamic diameters. For the MMD and respirable fraction values in Table 1, it is assumed that aerodynamic diameters were used. If in fact geometric diameters were intended, the MMDs in Table 1 would be multiplied by a factor of 3.4 and the respirable fractions divided by a roughly equal amount. Thus, the assumption of aerodynamic diameters is conservative because it gives the larger of the two possible values of respirable release and the higher transportability.

INTERPRETATION OF EXPERIMENTAL DATA

One way to evaluate the applicability of the existing data is to devise a model of particulate release f om plutonium combustion that might be used as part of an existing accidental release model. The factors tha would have to be considered in such a model are the following:

- the moisture and oxygen content of the air
- the phase of the metal
- the mechanical disruption to which the oxide is subjected
- the highest temperature attained by the metal
- the rate of heating to which the material is subjected
- the airflow speed and direction.

The release trends that are associated with each of these factors, and the amount of experimental data available to quantify the trends, are discussed below.

ATMOSPHERIC MOISTURE AND O_2 CONTENT

At and below temperatures of about 350°C, increases in humidity act to increase the rate of release of aerosol and to increase the size of the particulate released (Stewart 1963; Chatfield 1968). At room temperature, the plutonium-water reaction is rate-determining, so that dry-air release rates can be a factor of 10,000 lower than saturated-air release rates. At higher temperatures, saturated-air rates are typically on the order of 10 times as high as dry-air rates. Under dry conditions, particles tend to break away continuously as fine particulate material, with MMDs often less than 1 μm. Under saturated conditions, particles break away as larger fragments, frequently with MMDs greater than 1 or 2 μm, with the fines apparently produced during or after breakaway. The difference in oxidation rate and particle size distribution may result from hydriding of plutonium metal by water vapor; analogously, uranium is converted to uranium hydride when exposed to water vapor in the absence of air (Waber 1967).

As was the case for increased humidity, an increase in atmospheric oxygen content increases the rate of aerosol release. However, the effect of oxygen (unlike that of humidity) is to increase the fineness of particle size (Hilliard 1963; Stewart 1963). Runs made with pure oxygen have been described as producing violent reactions, reaching peak temperatures greater than 1000°C, and creating a "smoke" of very fine powder. The second highest release fraction in Table 1, 0.021 fraction of the original material released as aerosol, was for a pure O_2 atmosphere; the MMD was estimated to be 0.1 μm (geometric). Runs at above-atmospheric O_2 concentrations have also given high release rates, but have not produced fine particulate material (e.g., MMDs of 5 and 8.5 μm were measured). The small number of runs at below atmospheric O_2 concentrations have shown increased ignition temperatures, decreased release rates, and moderate particle size (MMD 0.9 μm). At oxygen content below about 0.04 atm, ignition becomes unlikely (Chatfield 1969a).

Recent kinetic studies of the effect of O_2 pressure on oxidation rate (measured by weight gain) in the pre-ignition temperature range show two different regimes (Stakebake and Lewis 1987, 1988; Stakebake 1986). At O_2 pressures below 10 to 60 torr (depending on the temperature), there is no measurable dependence of oxidation rate on O_2. At higher O_2 pressures, the oxidation rate varies with a power of the O_2 pressure; this exponent varies from 1/7 to 1, increasing together with the temperature. It seems reasonable to surmise that this dependence on O_2 is shared to some extent by the aerosol release rate.

The references cited above contain data from more than a dozen tests that show the effect of humidity on sub-ignition oxidation of plutonium. These experiments, however, lack detailed information on the airflow speeds; and (in Chatfield's 1968 experiment) there is a low cutoff (20 μm, presumably geometric) on the particle size that could be transported to the sampling device. These omissions make it difficult to estimate the effect of humidity at higher airflows, capable of picking up larger particles.

METAL PHASE

Aerosol release and kinetic studies have been carried out both for pure plutonium metal and for plutonium alloyed with a metal that holds the plutonium in delta (δ) phase below its unalloyed temperature range (310 to 452°C). The nature and quantity of the alloying material added to plutonium to retain it in δ phase are typically not documented in the aerosol release studies. Thus, this is a source of some possible inconsistency in the measured releases from δ alloy. [Note that the behavior of δ-stabilized alloy is not of concern in the Special Isotope Separation (SIS) project, which uses only pure metal.]

The oxidation rate and the particulate release rate for pure plutonium are higher than for δ-stabilized alloy (Stewart 1963). Typically, the particulate release for the pure metal is 10 to 100 times as high as for δ alloy, and the particle size (as expressed by MMD) can be 5 to 10 times smaller. This difference between the two phases can be found at all temperatures and humidities, though above ignition temperature the differences between pure metal and δ alloy decrease. Another difference that can be seen in Table 1 is that the ignition temperature of the pure metal, under a given set of conditions, tends to be about 100°C lower than that of δ alloy.

These differences appear to result from the fact that the oxide layer covers the unreacted metal more closely and completely for δ alloy, for which it is often described as an adherent scale, than for the pure metal, in which the oxide layer is a crumbling friable powder. Thus the δ-alloy oxide layer hinders diffusion of oxygen to the metal more severely than the oxide on pure metal. Because of the adherency of the oxide on δ alloy, oxidation may proceed in a stepwise manner, proceeding when a layer of oxide has recently cracked and fallen off, and being retarded while the layer is relatively intact (Stewart 1963). By contrast, oxidation of the pure metal is continuous.

The lower oxidation rate that is characteristic of δ alloy, and of the δ phase in the pure metal, has received extensive experimental attention. Much of this kinetic information has been reviewed by Stewart (1963), Mishima (1964), and Waber (1967). More recent work (with δ alloy only) has been done

by Stakebake and Lewis (1987, 1988) and Stakebake (1986). The effects of phase on particulate release have been studied by Stewart (1963), Chatfield (1968), and Mishima (1966b). These experiments compose an extensive, and probably adequate, description of particulate release at sub-ignition temperatures. The effect of phase on ignition-related particulate releases is less clear because the occurrence of ignition was not documented in Chatfield (1968), the releases from the ignition experiments in Stewart (1963) were not given as time rates, and only one δ specimen was tested by Mishima (1966b). There is some indication in Table 1 that at temperatures above the melting point the distinction between the phases is smaller than the range of experimental repeatability.

MECHANICAL DISRUPTION

In general, particulate release is lower for experimental designs in which the plutonium material is well supported and undisturbed than for those in which some mechanical disruption (e.g., rapping) is applied. Some of the factors that may contribute to mechanical disruption are rapping, sieving, elutriation, crumbling of the material under its own weight, rupture of the oxide shell by liquid plutonium, and temperature oscillations or rapid quenching. This variable is inherently difficult to quantify, and usually not well documented, but it is intuitively reasonable that jostled material gives off more aerosol, and tends to fragment into smaller sizes, than undisturbed material.

Mishima (1966a) noted the increase in the fine particulate fraction that was produced by sieving the oxide residue; he also attributed the greater friability of the oxide in some runs to increased thermal stress (large temperature oscillations and rapid cooling). During this same experiment, agitating ("rapping") the residual oxide while it was being elutriated produced much higher releases than were observed for unagitated elutriation. (The difference was a factor of between 10 and 100.) Of the several ignition-in-air experiments described by Stewart (1963), the one that yielded the highest release fraction (0.0024) was the one that experienced the most temperature oscillations. The relatively high release rates seen by Mishima

(1966b), in which the large plutonium specimens underwent substantial crumbling and rupture by plutonium melt, may also reflect the effect of mechanical disruption.

Mechanical disruption is probably not a practical modeling variable. None of the experiments to date have attempted to treat stress as a separate experimental variable, so it is not possible to rigorously separate the effect of stress from the effects of other variables. In an accident situation, it would probably not be possible to predict whether temperature oscillations or disturbance of the specimen would occur or guarantee that they could be prevented.

PEAK TEMPERATURE

Most of the data indicates an increase of particulate release rate with increasing temperature. There is no clear effect of temperature on the size distribution, which shows considerable scatter with temperature. Mishima (1966a), in an experiment in which pellets of plutonium were heated to ignition in air, commented that the run that had the highest peak temperature and the shortest oxidation time also produced the largest particle size and the oxide with the lowest friability. He theorized that the higher temperature might have produced some sintering of the oxide particles. Eidson and Kanapilly (1983) noted that plutonium metal tended to produce less powder when heated at 1000°C than when heated at 450°C or 650°C. However, the data collected by Chatfield (1968) by heating plutonium pellets in air show a clear trend of release increasing with temperature in the 600°C to 1000°C range.

The main ambiguity in the temperature data is the possible noncomparability of the temperature measurements in different experiments. In many experiments [Mishima (1966a), Stewart (1963), Stakebake and Lewis (1987, 1988), and Stakebake (1986)] the temperature of the air near the specimen was measured. This approach represents surface temperature if oxidation occurs well below the ignition point (at which self-heating is significant) or if the amount of difference between the measured temperature and the true metal surface temperature has been tested and found to be small. In some other experiments with small specimens at and above ignition temperature, the specimen surface temperature was measured with a contact thermocouple (Stewart

1963; Chatfield 1969b). In a third group of experiments with larger specimens above the ignition temperature, a thermocouple was inserted into the specimen to obtain internal temperatures (Stewart 1963; Mishima 1966b). Finally, there is a large and important set of experiments (Chatfield 1968) whose description gives no clue as to how metal temperature was measured or whether in fact air temperature rather than metal temperature might have been used. The difference between air and metal temperatures for small specimens might have been on the order of 30 to 40°C in the pre-ignition temperature range, as in the oxidation experiments carried out by Stakebake (1986). Higher temperature differences would have been possible if ignition occurred.

RATE OF (EXTERNAL) HEATING

The heating rate (i.e., the externally applied rate of specimen heating) has been a measured experimental variable in several experiments. Stewart (1963) used heating rates varying from less than 10°C/min to 150°C/min. Mishima used a uniform heating rate, 30°C/min, for all the runs in the first series of tests (Mishima 1966a). In a second series of runs, he used an arc welder to apply a heating rate that was probably substantially greater (Mishima 1966b). In the tests in which heating was supplied by a furnace, it appears that external heating applied at rates greater than about 15°C or 20°C/min frequently initiates combustion that is not self-sustaining when the external heating is removed. In some of the tests at higher heating rates, some particulate material sintering was observed or deduced to have occurred. High heating rates may cause lower releases if the external heating is not reapplied or higher releases if the heat source is reapplied and several temperature oscillations occur.

The effect that heating rate has on release from ignited plutonium has not been approached systematically to the same extent as have the effects of humidity, for example, or phase. This effect cannot be distinguished from the effect of temperature with the data available. In the event of an accidental fire involving plutonium and other combustibles, however, the external heating of the plutonium could be significant.

AIRFLOW SPEED

The significance of airflow speed comes from its effect both on the amount and the size distribution of the material that can be suspended. Secondarily, it also affects the heat transfer and, therefore, the temperature-related aspects of oxidation and release. Most plutonium oxidation experiments to date have been carried out at airflow rates below 100 cm/s, a range of speeds that Stewart puts in the category of "static" plutonium oxidation (i.e., oxidation in which the residue is not disturbed enough to release any trapped fine material). The exceptions are Mishima (1966b) with ignition and combustion at 525 cm/s, Mishima et al. (1968) with entrainment of oxide powder at 117 cm/s, and Eidson et al. (1988) with oxidation at speeds including 500 and 1000 cm/s. These experiments, in general, produce release rates or release fractions that are among the highest that have been measured.

It is difficult to use these experiments to predict the ratio between low-speed and high-speed releases, because there are not many sets of experiments that include both low-speed and high-speed tests under conditions that are otherwise the same. Airflow speeds of 10 and 117 cm/s were both used in Mishima et al. (1968), but one of the two measurements at 117 cm/s was regarded as an anomaly or an experimental error. Eidson et al. (1988) found no statistically significant differences between releases at airflow speeds of 40, 500, and 1000 cm/s. Consistent trends of increase of release with increase of speed appear to be visible in their 95% confidence limit results, given in Table 1, but the statistical significance of these apparent trends is doubtful.

OTHER VARIABLES

There are other variables that may affect the rates of oxidation and particulate release. These include (but may not be limited to) the mass and specific area (cm^2/g) of the specimen, the thickness of the oxide layer that may exist before the experimentally controlled oxidation begins, and the amount of working the metal has undergone.

Only one set of experiments has systematically addressed the effects of the specimen size and geometry. Eidson et al. (1988) studied the aerosol releases from δ-alloy foils and pellets of 1- and 10-g mass. They found that the respirable aerosol release fraction showed a statistically significant dependence on mass (being higher for the 1-g than for the 10-g specimens). However, there was no significant difference between the releases or the size distributions for the high-specific-area foil and the lower-area pellets, at the same specimen mass. The applicability of these results to oxidation of plutonium is somewhat unclear, however, because this set of experiments was carried in atmospheres containing hydrogen, so that the oxide was produced either after or during a hydriding step. Since the metal temperatures were not documented, it is also not clear what part temperature dependence may have played in the results. Thus, the effect of specimen mass and area are not clear at this time.

The volume changes caused by phase cycling may produce the effects of working in the pure metal (Stewart 1963), as does mechanical working (such as rolling the metal into foil or cutting it into swarf) for both pure and alloyed plutonium. Phase cycling has been observed to produce microvoids (Stewart 1963), which may increase the area available for oxidation. In this context, it is interesting to note that the highest release rate in the literature data came from a low-density plutonium sample (Mishima 1966b), which presumably contained internal void space. Phase cycling is believed not to be a concern for the plutonium used in the SIS project.

The existing experiments have in general not defined the working history, or the pre-experimental degree of oxidation, of the specimens; therefore, no definite conclusions can be reached. Stewart (1963) tested a specimen of pure metal that had been put through five α-β phase cycles; its aerosol release rate was equal to the maximum rate for several specimens that had only been cycled once. Some of the differences in plutonium oxidation release results that appears in the literature may come from differences in the metal history.

STATISTICAL ANALYSIS

The simplest statistical model of aerosol releases and size distributions uses a value that is the maximum of all the observations that fit in some physically significant category. A more accident-specific model requires some form of statistical correlation of existing data to quantify the upper-limit effects of the variables that have already been listed.

MODEL 1 -- MAXIMUM VALUES OF RELEASE

The advantages of a maximum-value "model" are simplicity and conservatism. The disadvantages are that the extreme values of aerosol release may not represent accident conditions and may severely overestimate the release. Another possibility is that the existing database may have omitted a possible combination of conditions that tend to produce high releases; this would lead to underestimation.

Consider the existing experimental database as it is described in Table 1. These 66 release values represent a database that contains more than 66 points because some of the values are maxima or upper limits for multiple measurements. [The 66 values exclude Andersen (1963), the work of Eidson et al. (1988) with reducing and oxidizing atmospheres, and the falling droplet and exploding wire tests of Carter and Stewart (1970) as being not generally applicable.] The release data for the highest three release fractions and the highest three release rates, together with the experimental conditions that produced them, are given below. No experimental durations were given for the experiments giving release fractions.

- Highest release fraction: 0.021, from Stewart (1963), oxidation of a 5- to 7-g pellet of δ alloy in pure oxygen.
- Second-highest release fraction: 0.0024, from Stewart (1963), oxidation of a 10- to 15-g pellet of pure metal in air.
- Third-highest release fraction: 1.9×10^{-4}, from Stewart (1963), oxidation of a 5- to 7-g pellet of δ alloy in 40% O_2.
- Highest release rate: 3.2×10^{-4}/h, from Mishima (1966b), the ignition and combustion to complete oxidation in a 525-cm/s airflow of a 570-g specimen of low-density pure metal ignited by an arc-welder.

- Second highest release rate: 2.5×10^{-4}/h, from Mishima et al. (1968), the entrainment at 117 cm/s of the 15- to 44-μm fraction of a plutonium oxide powder sample which was residue from combustion.
- Third highest release rate: 2.3×10^{-4}/h, from Mishima (1966a), the agitation and elutriation at 7 cm/s of the residual plutonium oxide powder from combustion.

On the basis of this information, and the rest of the data in Table 1, it appears that unusual atmospheres are needed to produce release fractions greater than or equal to 0.01 (as a fraction of original material). However, the highest release rates, which are on the order of 10^{-4}/h, as well as those release fractions that are on the order of 10^{-3}, appear to be produced by circumstances that are not so unusual. These circumstances include high external heating rates, large plutonium samples, airflows of 100 to 500 cm/s, and repeated agitation and jarring, all of which might occur in the course of accidental fires.

Table 2 lists the three highest release rates (or fractions) for pure metal and δ alloy under experimental conditions that excluded the "extraordinary conditions" of oxygen-enriched atmospheres. The sets of maxima are separated into groups according to whether the temperature was above or below the ignition temperature. The release fractions in Table 2 are calculated on the basis of complete conversion of metal to oxide. That is, if the experiment did not produce complete conversion, the observed release fraction was divided by the fractional conversion to obtain the release fraction at complete conversion.

The maximum release rates above ignition are consistently higher than those below ignition. In the sub-ignition temperature range, the maximum release rates for δ alloy and pure metal are of the same order of magnitude. However, above the ignition temperature the maximum release rates for the pure metal are roughly 2 to 3 times as high as those for the δ alloy. The relation between the maximum release fractions (which are all above ignition) and the corresponding maximum release rates is somewhat surprising. The fractions have values between 2 and 10 times as high as the rates, which would appear to indicate combustion that went on for 2 to 10 h. However, actual experimental

TABLE 2. Maximum Observed Release Rates and Fractions, Excluding Extraordinary Conditions

Data Subset	Number of Points	Rank	Release Rate or Fraction(a)	Conditions of Experiment
Pure metal, no ignition, rate	21	1st	4.0E-06/h	350°C, 100% humidity (Chatfield 1968)
		2nd	8.6E-07/h	350°C, 0% humidity (Chatfield 1968)
		3rd	2.0E-07/h	350°C, 0% humidity (Chatfield 1968)
Pure metal, ignition, rate	18	1st	3.2E-04/h	massive metal, 960°C, 0% humidity (Mishima 1966b)
		2nd	1.9E-04/h	massive metal, 950°C, 0% humidity (Mishima 1966b)
		3rd	8.0E-05/h	1000°C, 100% humidity (Chatfield 1968)
Pure metal, ignition, fraction	5	1st	3.6E-03	630°C, 0% humidity (Stewart 1963)
		2nd	8.6E-04	382°C, 100% humidity, ignition quenched (Stewart 1963)
		3rd	4.1E-04	404°C, 0% humidity, ignition quenched (Stewart 1963)
Delta alloy, no ignition, rate	18	1st	2.0E-06/h	350°C, 100% humidity (Chatfield 1968)
		2nd	8.0E-07/h	350°C, 100% humidity (Chatfield 1968)
		3rd	8.0E-07/h	350°C, 100% humidity (Chatfield 1968)
Delta alloy, ignition, rate	8	1st	8.5E-05/h	690°C, 0% humidity (Stewart 1963)
		2nd	7.0E-05/h	700°C, 0% humidity (Stewart 1963)
		3rd	4.5E-05/h	massive metal, 930°C, 0% humidity (Mishima 1966b)
Delta alloy, ignition, fraction	7	1st	6.5E-04	800°C, 150°C/min heating rate, 0% humidity (Stewart 1963)
		2nd	1.0E-04	swarf, 780°C, 10°C/min, 0% humidity (Stewart 1963)
		3rd	6.0E-05	swarf, 895°C, 38°C/min, 0% humidity (Stewart 1963)

(a) The units of release rates are fraction/h of the original Pu metal released, and the units of release fractions are total fraction of the original Pu metal released.

durations were seldom longer than 1 or 2 h. The reason for this apparent discrepancy is not clear, but it does suggest that the maximum release fractions are plausible upper limits for total release.

The maximum values given in Table 2 are mostly from experiments that were not replicated. For these cases, there is no way to be certain whether the observations are really the maxima that might occur for a set of experiments run under those same conditions. However, they can probably safely be used as upper limits for releases from conditions including either sub-atmospheric oxygen pressures or lower metal temperatures than those that produced the observed releases.

MODEL 2 -- STATISTICAL CORRELATION OF RELEASE

The data that have been gathered and summarized in Table 1 fall naturally into four categories: pure metal and δ alloy, and, within those, total aerosol release and respirable aerosol release. Another subdivision of the data is also required because of differences in experimental technique and reporting. As can be seen in Table 1, aerosol releases have been reported both in terms of fractional release rates (fraction of original plutonium released per hour) and in terms of the total fraction released over the entire oxidation event. The release rate is more useful for safety or design analysis purposes because a plutonium oxidation event is likely to be terminated before its natural end. For that reason, we confined the attempts to find statistical correlations to the release rate portion of the database.

Accordingly, we broke up the data set represented by Table 1 into the following subsets:

- total aerosol release rates for pure metal
- total aerosol release rates for δ alloy
- respirable (less than 10-μm aerodynamic diameter) aerosol release rates for pure metal
- respirable aerosol release rates for δ alloy.

We performed multiple linear regression analyses on each data subset in order to find the variables that most consistently "drive" aerosol releases.

We also reviewed each data subset to see which iables were pre$ent with enough variation, independent of variation in other variables, to allow their effect on aerosol release to be judged. results of this work are discussed below.

Table 3 contains the regression equations t were obtained for each data subset together with estimates of the stard error in the aerosol release predicted by the regression and the vaice. As can be seen in Table 3, regression relationships can be formu'd, using the existing data, that explain between 74% and 84% of the variat in the logarithm of the aerosol release (rate or fraction). The standerror of prediction for the log of the release rate or fraction ranges fro042 (a factor of roughly 11 in the release) to 1.229 (a factor of roughly Figures 1 through 4 show the regressions for total aerosol release ratetted against measurements.

Table 4 compares the predictions and obse ions of aerosol releases for the maximum, median, and minimum values in eac ta subset. The predictions in Table 4 were made using both the correlatio tained directly from the least-squares regression and a "conservatively usted" correlation. The adjustment consisted of adding the standard er of prediction to the constant of the regression equation. This ess ally had the effect of raising the regression line from one that pass hrough the center of the data to one passing over mos of the data beca the predicted releases were increased by a factor of one standard error of diction.

The observations given in Table 4 show a ern of being lower than the corresponding predictions, except in the case he maximum releases. "Adjustment" of the regressions permits the mam predicted aerosol releases (total and respirable) for the δ alloy to equa exceed the maximum observation made under the same conditions. Howeve or the pure meta al even the "adjusted" maximum aerosol release predictions l below the maximum observations for the same temperature and humidity.

The adjusted pure metal correlations are ble of predicting releases that are higher than any observed, as can be s in the "Maximum Predictions" column of Table 4. However, these maximum pre ions are made for experiments (i.e., conditions of humidity and tempere) other than those that

TABLE 3. Results of Regression Analyses of the Aerosol Release Data Sets. Note: Regressions are of the log of the aerosol release rate (fraction/h).

Data Subset	Number data points		Regression coefficients and variables			Prediction Std. Error	Variance
	Total	Non-duplicate	Term	Coefficient	Variable range		
Pure metal, total rate	37	12	Constant	-3.483		1.163	0.744
			% humidity	0.01292	0%, 1%, 100%		
			(1/peak temp.)	-2123	20-1100°C		
Pure metal, respirable rate	36	12	Constant	-3.829		1.042	0.776
			% humidity	0.01232	0%, 1%, 100%		
			(1/peak temp.)	-2081	20-1100°C		
Delta alloy, total rate	26	10	Constant	-2.131		1.229	0.831
			% humidity	0.01169	0%, 1%, 100%		
			(1/peak temp.)	-2823	20-1100°C		
Delta alloy, respirable rate	24	8	Constant	-2.384		1.138	0.839
			% humidity	0.007012	0%, 1%, 100%		
			(1/peak temp.)	-2779	20-1100°C		

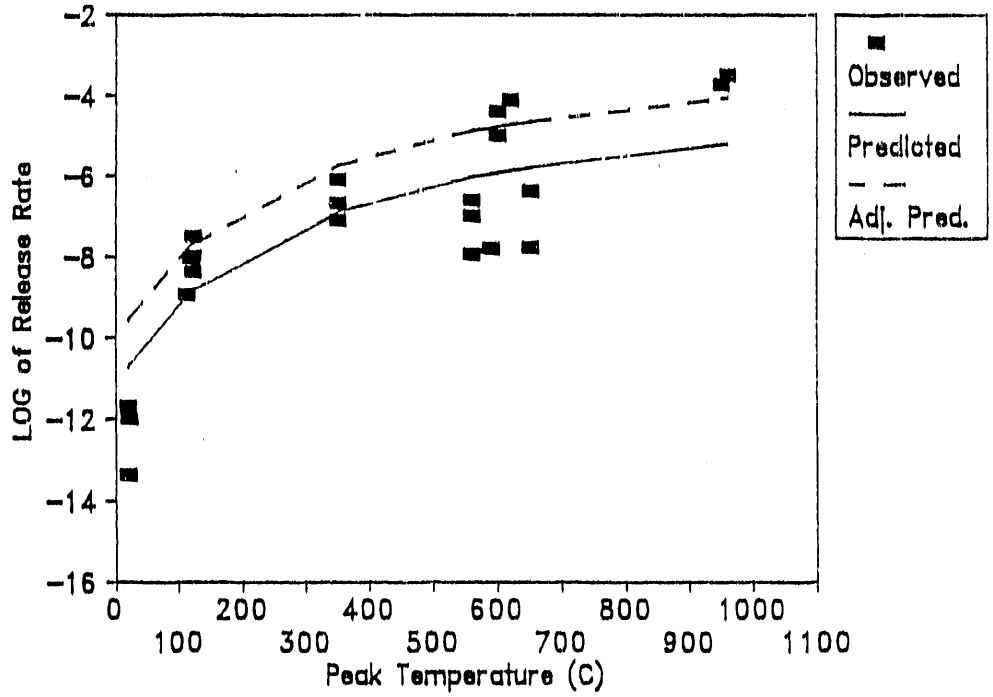

FIGURE 1. Predicted and Observed Aerosol Release from Pure Metal for 0% Humidity

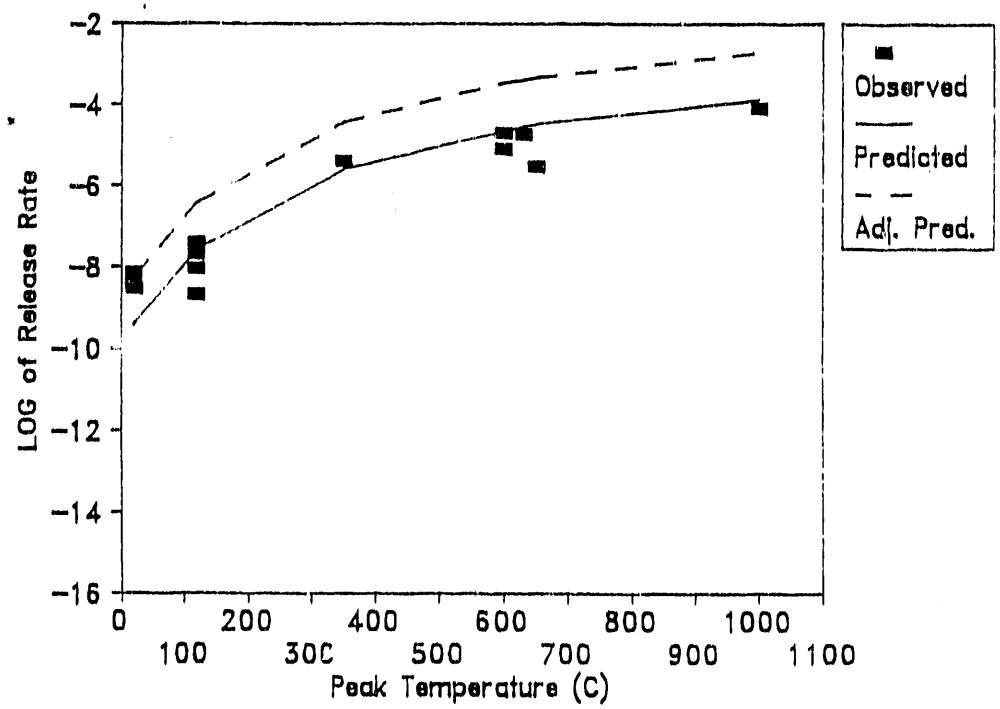

FIGURE 2. Predicted and Observed Aerosol Release from Pure Metal for 100% Humidity

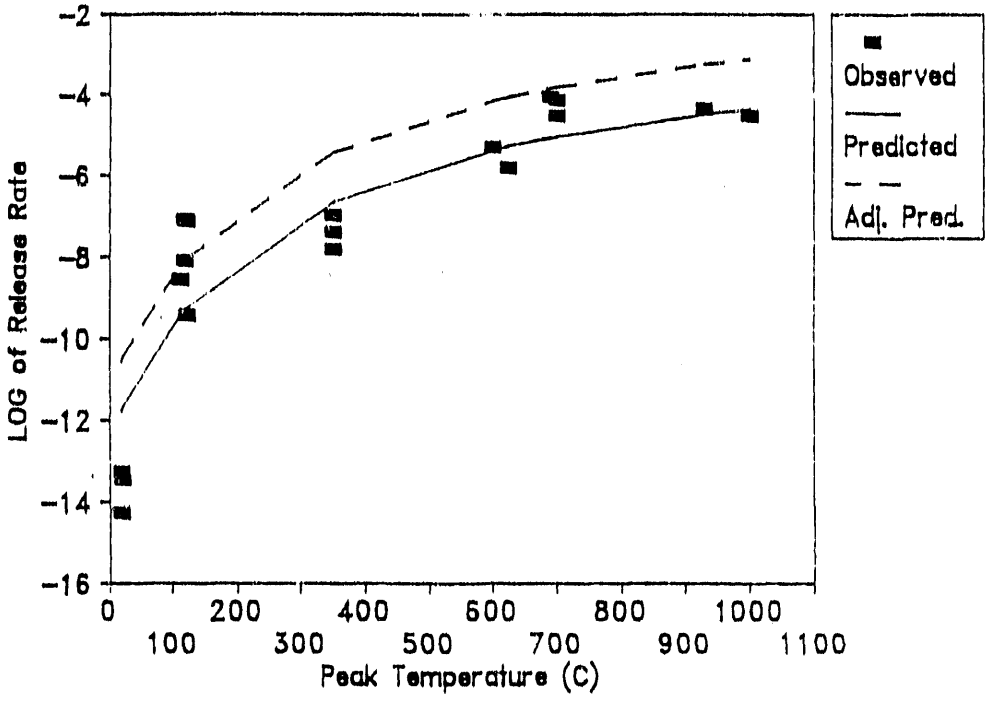

FIGURE 3. Predicted and Observed Aerosol Release from δ Alloy for 0% Humidity

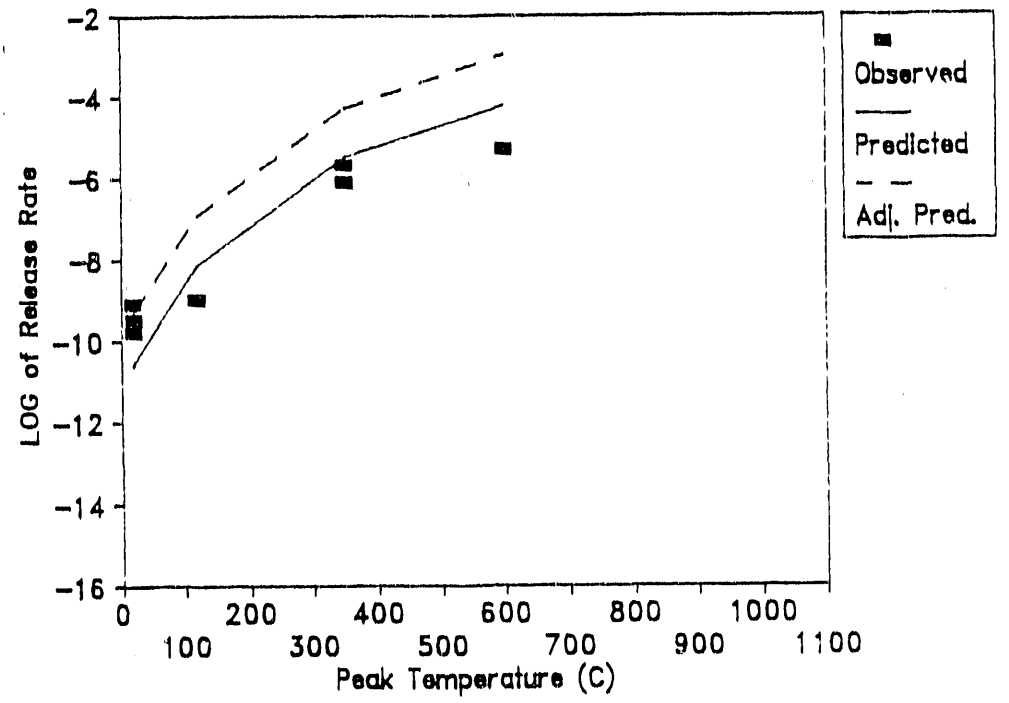

FIGURE 4. Predicted and Observed Aerosol Release from δ Alloy for 100% Humidity

TABLE 4. Predicted Versus Observed Maxima, Medians, and Minima in Aerosol Release Rates and Fractions. Note: the "corresponding prediction" is the regression prediction for the same experiment that produced the observed maximum. The "maximum prediction" is the prediction for the experiment whose conditions produced the maximum regression prediction.

Data Subset	Maximum Observation	Corresponding Prediction	Maximum Prediction	Median of		Minimum of	
				Observations	Predictions	Observations	Predictions
Pure metal, total rate							
Least-squares fit	3.2E-04(a)	6.2E-06	1.4E-04(b)	3.0E-08	1.3E-07	4.0E-14	1.9E-11
Adjusted for conservatism	3.2E-04(a)	9.1E-05	2.0E-03(b)	3.0E-08	1.9E-06	4.0E-14	2.7E-10
Pure metal, respirable rate							
Least-squares fit	6.7E-05(c)	5.9E-07	5.9E-05(d)	2.2E-08	6.8E-08	4.0E-14	1.2E-11
Adjusted for conservatism	6.7E-05(c)	7.6E-06	6.4E-04(d)	2.2E-08	7.4E-07	4.0E-14	1.3E-10
Delta alloy, total rate							
Least-squares fit	8.5E-05(e)	8.6E-06	6.4E-05(f)	7.6E-08	2.2E-07	5.0E-15	1.7E-12
Adjusted for conservatism	8.5E-05(e)	1.5E-04	1.1E-03(f)	7.6E-08	3.7E-06	5.0E-15	2.9E-11
Delta alloy, respirable rate							
Least-squares fit	7.6E-05(e)	5.4E-06	2.7E-05(g)	2.7E-08	1.4E-07	4.2E-15	1.3E-12
Adjusted for conservatism	7.6E-05(e)	7.4E-05	3.7E-04(g)	2.7E-08	2.0E-06	4.2E-15	1.8E-11

All of the maximum observations and predictions in this table were obtained from experiments that were not run in duplicate for verification.

(a) Mishima (1966b), first run.
(b) Stewart (1963), 5-7 g specimen ignited at 17% O_2 (run 4 of those conducted with sub-atmospheric O_2 pressures).
(c) Stewart (1963), 5-7 g specimen ignited at 17% O_2 (run 3 of those conducted with sub-atmospheric O_2 pressures).
(d) Chatfield (1968), 1000°C, saturated air.
(e) Stewart (1963), 5-7 g specimen ignited at 20% O_2 (run 1 of those conducted with sub-atmospheric O_2 pressures).
(f) Chatfield (1968), 600°C, saturated air.
(g) Chatfield (1968), 1000°C, dry air.

produced the maximum observations. This may indicate high experimental variability that cannot be handled by regression, or it may indicate the effect of some third parameter that is not included in the regression and probably cannot be included because the parameter does not vary enough in the database. Whichever is the case, the regression is flawed to the extent that it does not reliably predict maximum observed releases for pure metal.

On theoretical grounds, one would expect that temperature, oxygen concentration, humidity, and specimen history should have some effect on release rate, since they all affect the oxidation rate. The specific area (surface area per unit mass) and mass of the specimen might appear to correlate with aerosol release. But, theoretically, this would result only from the effect of mass and specific area on the heat balance (and so the temperature) because these variables are not fundamentally related to oxidation rate.

In general, the specimen-dependent variables such as specimen mass, specific area, and the amount of working to which the specimen had previously been subjected seemed not to be useful as release fraction predictors. This may be a false appearance, because the material history was seldom described and because the data did not systematically include a very wide range of masses or specific areas. The few massive metal tests included unusually high heating rates and airflow speeds as well as unusually high masses (and low specific areas), so that the effect of mass was not necessarily distinguishable. However, some agreement as to the lack of effect of specimen mass and area was found by Eidson et al. (1988).

The regressions for total and respirable aerosol release have very similar coefficients for the δ alloy and the pure metal. The apparent dependence on relative humidity and peak metal temperature alone may be deceptive, though, since these were the only parts of the experimental design that were varied over the entire database. The effects of airflow speed, heating rate, and oxygen content were not studied extensively. Most of the experiments that varied the heating rate and oxygen content were documented as release fractions rather than rates and so were not correlated. As a further difficulty, the sets of experiments that supplied most of the release rate data did not document the airflow speeds they used (Stewart 1963; Chatfield 1968). However, the effects that were studied seem to be well represented by

the regressions: the variance estimates show that the regression predictors explain 73% or more of the variation in aerosol release rate.

The aerosol release regressions correlate the log of the release rate with the quantity (-humidity/temperature). The (-1/T) dependence is consistent with the Arrhenius exponential dependence of the oxidation kinetic rate constant. The physical basis of the humidity dependence is less obvious; it may reflect the difference in Arrhenius activation energy for corrosion by water vapor and by oxygen. Waber (1967) cites activation energies of 17 kcal/mole for the attack on plutonium of H_2O vapor at low temperatures, 33 kcal/mole for the initial (parabolic) kinetic rate constant of oxygen oxidation, and 16 kcal/mole for the linear kinetic oxidation rate constant.

The form of the statistical relation between aerosol release and humidity also suggests, perhaps misleadingly, that the humidity produces the same factor of increase at all temperatures. The data show, however, that the release rate increase caused by humidity is much more noticeable at ambient temperature than at higher temperatures. This phenomenon has some significance for releases resulting from normal operating conditions and procedures.

The apparent good predictive ability of the ignited metal release regressions may be partly illusory (as is suggested by the difficulty of correctly predicting maximum observed release rates). Many of the experiments that "drive" the regressions were not replicated, and there is no certainty that the maximum release for the experimental design was produced. Some indication of the amount of difference in release rates produced by repeated experiments even with the same experimental design can be seen in the rather large standard error of prediction of the correlations. (The standard error of prediction is the distance between the "predicted" and "adjusted prediction" lines in Figures 3 and 4.) Furthermore, some of the basic variables (such as mechanical disruption, heating rate, O_2 content, and airflow speed) were not systematically varied or documented. To provide a reasonable certainty of avoiding underestimation of aerosol releases, we recommend using the "conservatively adjusted" regression equations together with techniques that somewhat overestimate peak temperature.

SIZE DISTRIBUTIONS

Figures 5 through 8 show the MMDs for dry and humid conditions (0% and 100% relative humidity, respectively), and pure metal and δ alloy. The amount of scatter in the data is evident in these figures. There appear to be three rough trends:

1. The MMDs below about 100°C are higher for humid than for dry conditions, for both pure metal and δ alloy.
2. MMDs seem to be somewhat higher for the δ alloy than for the pure metal; and
3. The maximum MMDs exist for a temperature range under about 400°C.

The formation of hydride by water vapor, and the subsequent conversion of that hydride to oxide, might be the cause of the variation of MMD with humidity.

Given the scatter in the MMD database, we suggest that the prediction of size distributions might best be made by choosing the minimum MMD and the maximum respirable fraction that were measured for each of several different ranges of conditions. Assuming a lognormal distribution, the geometric standard deviation can be calculated from the chosen MMD and respirable fraction. This approach should provide conservative size distributions by forcing the aerosol to have as much material below the respirable limit (10 μm aerodynamic diameter) as can be justified by the experimental data.

Table 5 gives one possible set of ranges of conditions, together with the minimum measured MMD and the maximum measured respirable fraction for each range. (In Table 5, as elsewhere in this document, "respirable fraction" refers to the fraction of the aerosol release that is respirable, and a fraction of 1.00 means that 100% of the airborne material is respirable, i.e., below 10 μm aerodynamic diameter.) Some idea of the amount of conservatism may be obtained by looking at the ratio of the maximum and minimum respirable fractions for each range of conditions. (The minimum respirable fractions are also included in the table to allow this comparison.) The table also includes σ_g, or lognormal standard deviation, that was estimated using the method described above. This σ_g and the minimum MMD can be used with the aerosol release rate correlation to provide conservative estimates of respirable release. Humidities between 0% and 100% should be interpolated.

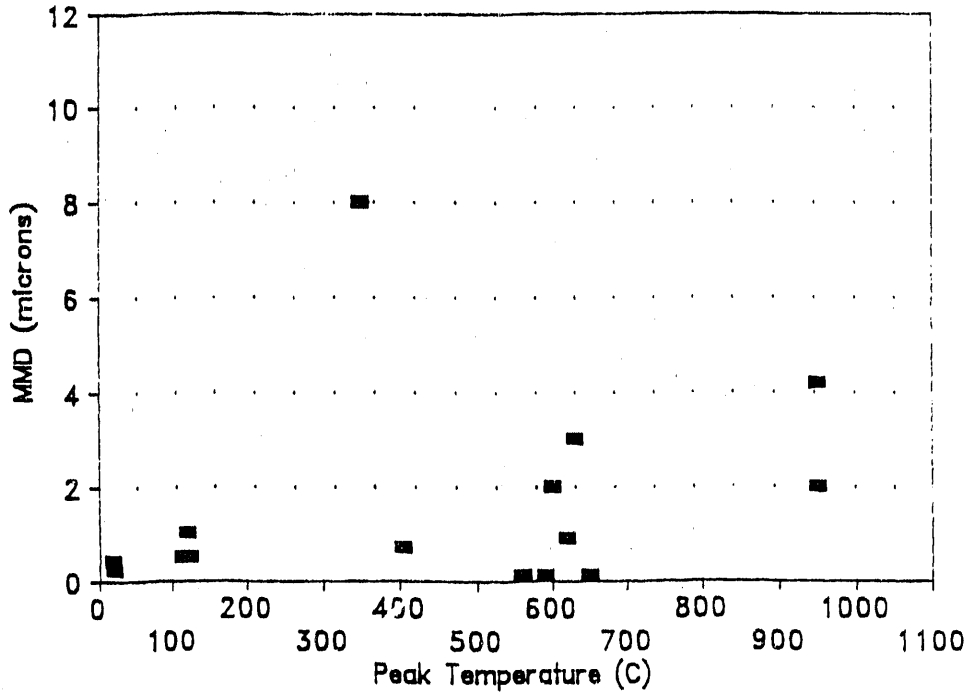

FIGURE 5. Mass Median Diameters Measured for Aerosols Released by Pure Plutonium Metals at 0% Humidity

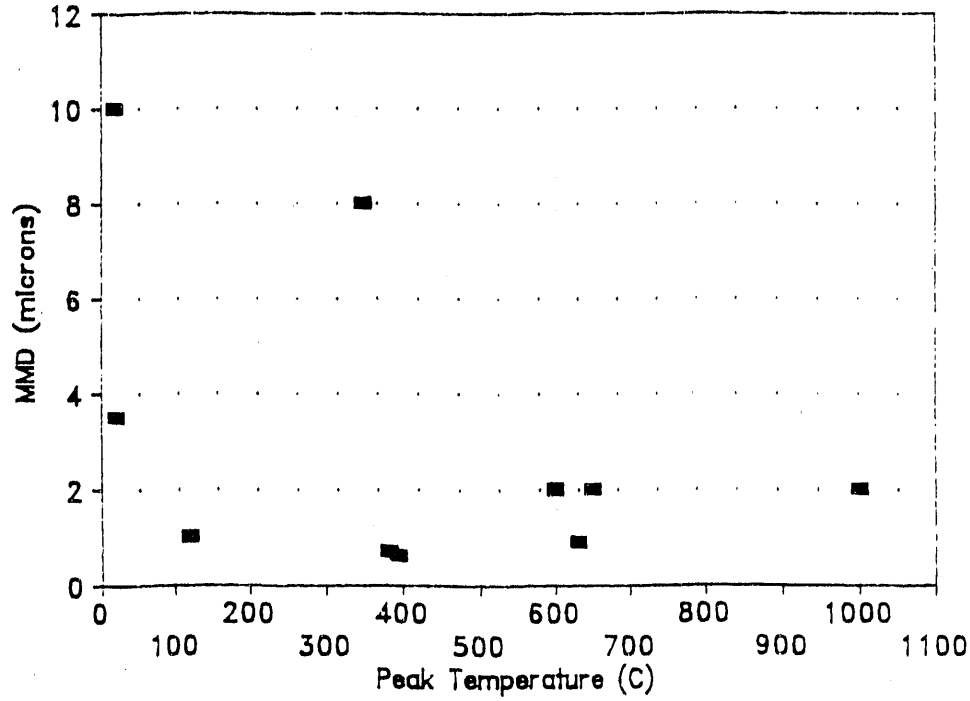

FIGURE 6. Mass Median Diameters Measured for Aerosols Released by Pure Plutonium Metals at 100% Humidity

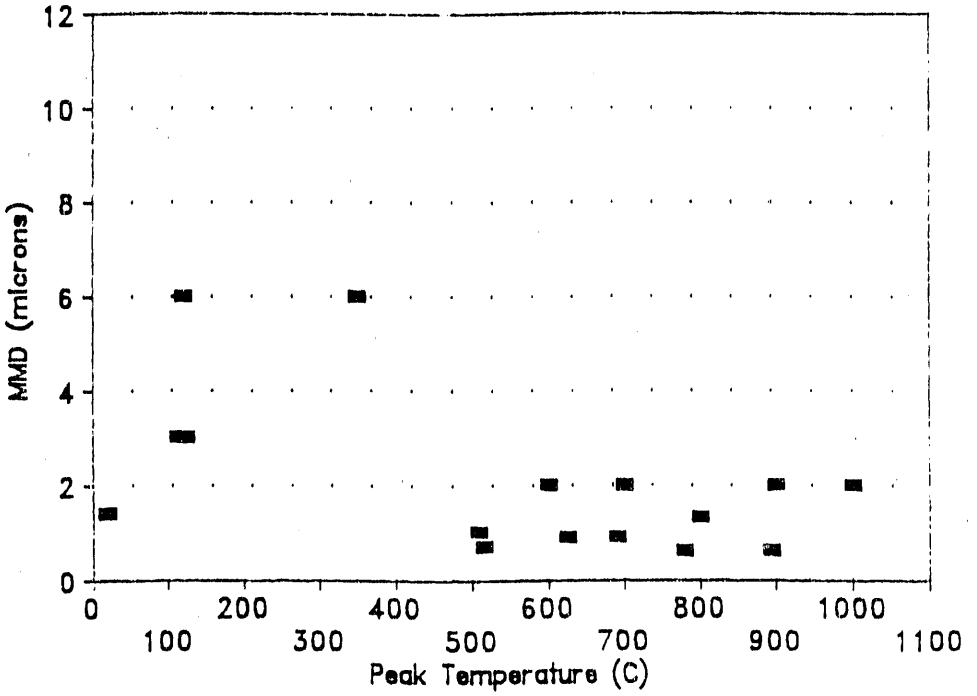

FIGURE 7. Mass Median Diameters Measured for Aerosols Released by δ-Stabilized Plutonium Alloy at 0% Humidity

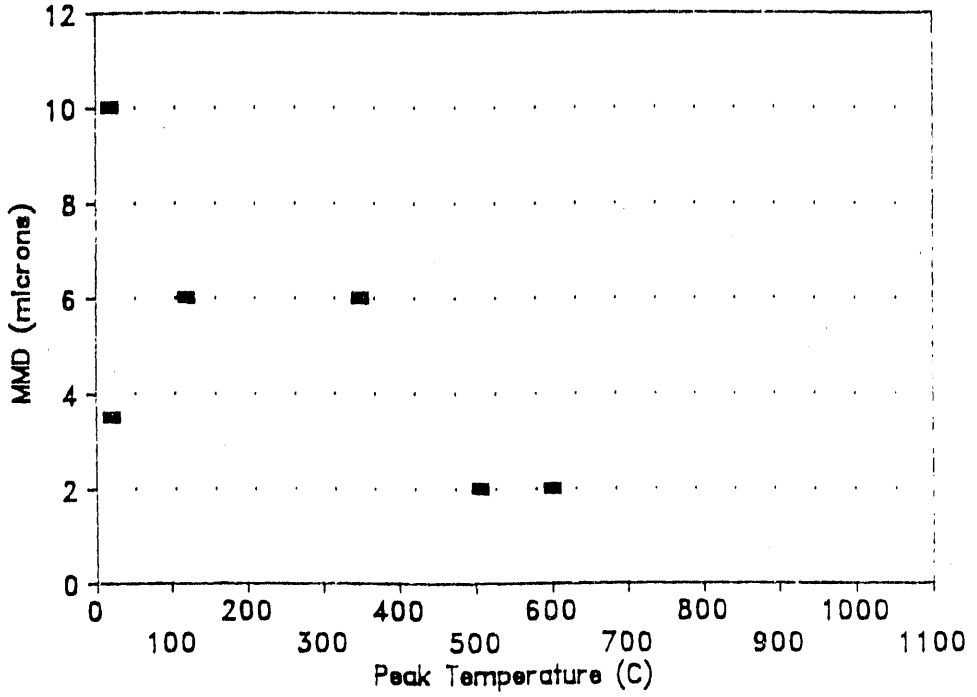

FIGURE 8. Mass Median Diameters Measured for Aerosols Released by δ-Stabilized Plutonium Alloy at 100% Humidity

TABLE 5. Conservative Mass Median Diameters and Respirable Fractions for Several Ranges of Conditions

Conditions	Number of Points	Minimum MMD[a] (μm)	Maximum Respirable Fraction	Minimum Respirable Fraction	Lognormal Standard Deviation, σ_g
Pure metal					
0% relative humidity					
< 400°C	12	0.2	1.00	0.15	2.4
> 400°C	13	0.1	1.00	0.20	3.1
100% relative humidity					
< 400°C	11	0.6	0.98	0.15	2.2
> 400°C	5	0.9	0.90	0.70	2.5
Delta alloy					
0% relative humidity					
< 400°C	10	1.4	0.85	0.30	2.0
> 400°C	12	0.6	0.90	0.70	3.5
100% relative humidity					
< 400°C	7	3.5	0.30	0.10	1.4
> 400°C	2	2	0.85	0.70	1.4

(a) The "minimum MMD" is the minimum value for the entire data subset. Similarly, the "maximum respirable fraction" and the "minimum respirable fraction" are the maximum and minimum values for the data subset.

STATISTICAL CORRELATION OF PEAK TEMPERATURE

The data of which Table 1 is a subset can be used to provide correlations of the peak temperature as well as of the aerosol release rate. Only the data for experiments carried out above the ignition temperature were of use for this purpose. Peak temperature data from Felt (1967) were also used. The correlations, which were derived using multiple linear regression analyses, help to provide a quantification of the self-heating for the pure plutonium metal and δ alloy under different experimental conditions.

A regression analysis was performed for each of two data subsets, one for pure metal and one for δ alloy. The pure metal regression predicts the natural log of the peak ΔT in terms of heating rate and airflow speed, while the δ-alloy regression predicts peak ΔT in terms of inverse percent O_2, heating rate, and airflow speed. (The peak ΔT is defined as the difference between the initial and peak temperatures.) The heating rate is the most important predictor for the pure metal, but (percent O_2)$^{-1}$ is the most important predictor for the δ alloy. (Note that the pure metal experiments included no variation in percent O_2.) Table 6 contains the regression equations that were obtained for each data subset together with estimates of the variance and the standard error in the peak ΔT predicted by the regression. As can be seen, the regression relationships explain 86% of the variation in peak ΔT for the pure metal, but only 44% for the δ alloy (in spite of the greater number of variables in that equation). The standard error of prediction is a factor of 10% for the pure metal and about 135°C for the δ alloy. Figures 9 and 10 provide a comparison of the predicted and observed peak ΔT values.

The pure-metal regression analysis employed the independent variables of external heating rate and airflow speed. Because the ΔT includes the temperature increase produced both by the external heating applied and by self-heating, the dependence on external heating rate is not surprising. The dependence on specimen mass may be related to convective heat transfer. It should be noted, though, that correlations with equally high variance could have been obtained using the specimen specific area or the mass instead of the airflow speed.

TABLE 6. Results of Regression Analyses of the Peak ΔT Data Sets

Data Subset	Number data points: Total	Number data points: Non-duplicate	Regression coefficients and variables: Term	Coefficient	Variable range	Prediction Std. Error	Variance
Pure metal	17	8					
LN (ΔT) regression:			Constant	6.659		0.0852	0.858
			LN (air speed)	0.0283	3-15, 525 cm/s		
			(heating rate)	-0.0124	0 - 30°C/min		
Delta alloy							
(ΔT) regression:	13	7	Constant	1231		135	0.441
			Air speed	0.230	3-15, 525 cm/s		
			Heating rate	-0.799	0-30, 150 °C/min		
			(1 / % O2)	-9760	20, 30, 40, 100 %		

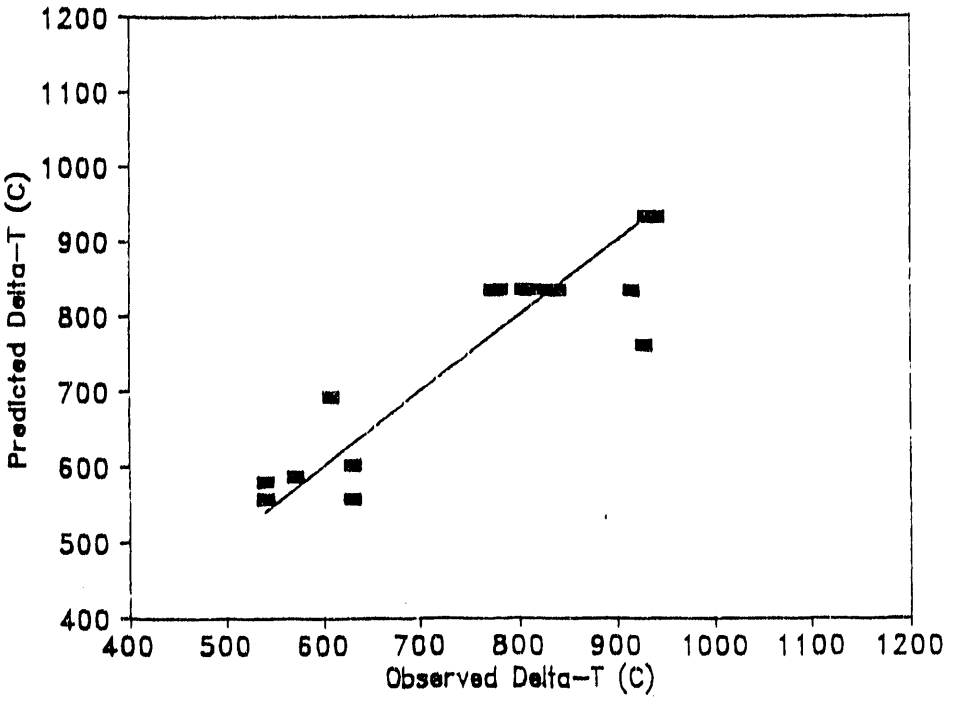

FIGURE 9. Predicted Versus Observed Peak ΔT for Oxidized Pure Metal

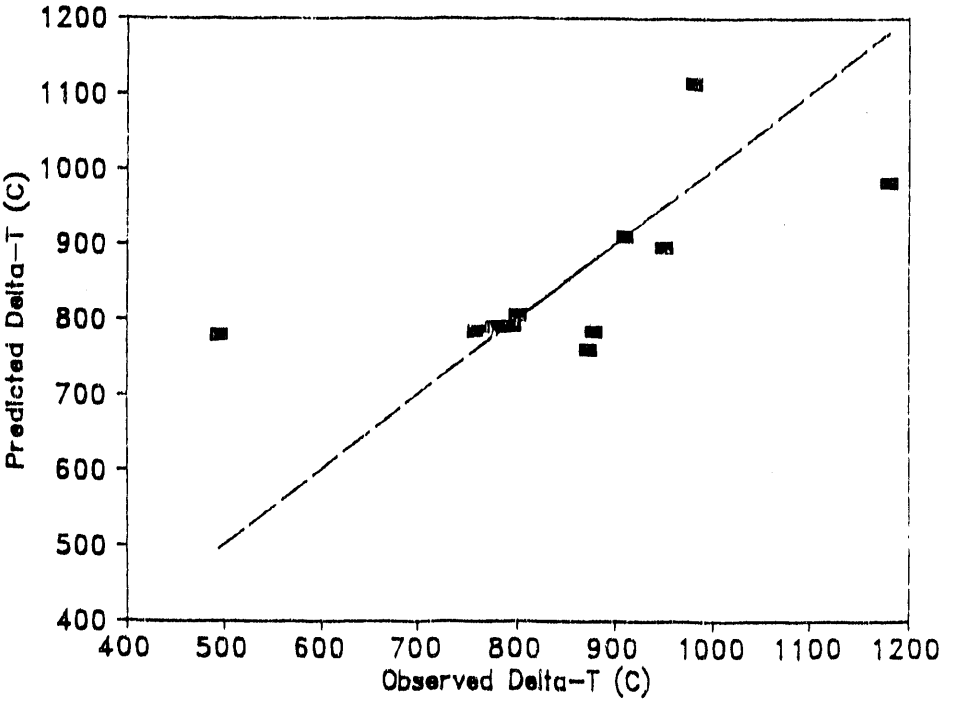

FIGURE 10. Predicted Versus Observed Peak ΔT for Oxidized δ Alloy

The difficulties with using this peak ΔT correlation are, first, that it describes the peak ΔT from both self- and external heating. It would be difficult to separate the two effects in these experiments. This is true even in those experiments in which heat input was applied only at the beginning of the experiment, not continuously (Mishima 1966; Felt 1967). Second, there is no estimate of heat loss to the surroundings in the experimental descriptions, so that this could not be included in the correlation. Experiments carried out by Felt (1967) on supports of differing thermal conductivity showed the significance of heat loss to the support. Third, the quantity predicted is the peak temperature over the entire oxidation process, not that at any particular point in time. Because the temperature rise can be quite rapid, it may be appropriate to assume the peak temperature is reached within a very short time after the ignition temperature is attained. Lastly, it may be difficult to estimate the airflow speed under accident conditions (even though the speed needed is that provided by forced convection, not the natural convection resulting from plutonium heating). This difficulty is to some degree offset by the low importance of airflow speed as a predictor, compared to heating rate or percent O_2.

RATE OF OXIDATION

Most of the oxidation rate data that have been collected by kinetics experimenters have been in the pre-ignition temperature regime; self-heating was avoided because of the complications it causes. There are few (if any) data available for temperatures above 500°C (Waber 1967; Stakebake 1986; Stakebake and Lewis 1988). Furthermore, these experiments typically employ small masses of metals, often in the shape of thin coupons, such that the oxide crust does not cause as much diffusive hindrance as it might for large chunks of material.

Post-ignition oxidation rate information can be found in Mishima (1965), Mishima (1966), and Felt (1967). In the first reference, six 10-g billets of plutonium were heated to ignition. The times required for complete oxidation ranged from 22 to 64 min. There was some indication that higher airflow (the range was 3.3 to 50 cm/s) and higher peak temperature (the range was 560 to 900°C) decreased the time. [For comparison, Stewart (1963) mentions that in

some of his post-ignition experiments 10-g masses appeared to be completely oxidized in about 10 min. However, these experiments were conducted with the specimens suspended by wires and may not be representative of "process" conditions.] In the second reference, large pieces of metal (500 to 2000 g) were burned. They required 10 min or less to come to peak temperature and 40 to 60 min to become completely oxidized. These experiments were carried out in an unusually high airflow, 525 cm/s.

Felt (1967) conducted further experiments with relatively large pieces of metal, using a low (but unspecified) airflow speed. He found that for large mass metal (1 to 3 kg) in cylinder form, an average burn rate of about 180 g/h and a time of 12 to 15 min to reach peak temperature could be expected. The rate was slightly lower for δ alloy. Smaller pieces of metal (200 to 1000 g) had similar burn characteristics, except that the typical time to peak temperature was 6 to 10 min. Casting skulls and metal turnings, with much higher surface area, further reduced the time to peak temperature, to 3 to 4 min. However, even for these high-area cases the burn rate was not above 180 g/h: for example, a 200-g sample of turnings burned in 2 h, or 100 g/h. The burn rate appeared to increase with temperature.

Based on the available information, it would probably be reasonable to use a burn rate of 180 g/h for metal masses of 100 g or more. Smaller pieces of metal, in the 10-g range, may require more time. However, it would probably be conservative to use the 180 g/h burn rate for such small pieces of metal because this would permit more oxidation in the (typically) limited time of an accident.

RECOMMENDED ACTIVITIES

Available analytical techniques still need to be compared with those required in a tool to calculate aerosol releases from plutonium oxidation and/or ignition and combustion. An accident-specific model of releases from plutonium oxidation and combustion needs to include the effects of the surroundings, which might be a general fire, upon the plutonium metal, as well as the effect of the metal's own self-heating. Ideally, it should be usable as a module of a larger model that could provide and use similar data for other combustibles, so that a general fire accident could be modeled.

One such model is FIRIN, a computer code that models accidental fire and radioactive airborne releases in nuclear fuel cycle facilities (Chan et al. 1989). The primary purpose of FIRIN is to estimate the aerosol release rate and size distribution of radioactive materials from a fire accident. FIRIN also calculates (among other items) transient conditions such as temperature, pressure, and composition (including oxygen and water content) of the atmosphere in the fire compartment. The FIRIN code is designed to provide fire compartment inputs to the Los Alamos National Laboratory code FIRAC, which analyzes fire-induced flow and thermal and material transport in a building ventilation system (Andrae et al. 1978).

The following discussion covers some of the points to be considered in replacing the current plutonium oxidation release FIRIN module with a new one. FIRIN already takes as input, or calculates, the water vapor content and oxygen content of the air and the heat flux external to the plutonium. The current plutonium oxidation release module is based on a limited review of the data and does not include self-heating calculations, or any "first principles" understanding of aerosol release from heating plutonium metal.

Bearing this existing analytical tool in mind, we recommend the following activities to provide a method for predicting accident-specific aerosol release rates from plutonium metal oxidation.

1. **Include the empirical predictions of aerosol release, temperature, and oxidation rate described in this paper in FIRIN.** The algorithm for temperature and oxidation rate, the statistical correlations for aerosol releases, and the closed-form size distributions should be incorporated as a new plutonium oxidation module in FIRIN. FIRIN

already estimates the temperature and humidity of the "hot layer," and the calculation of the heat flux reaching the plutonium should be possible using techniques that are already part of the FIRIN code. The new plutonium oxidation module should use the following methods:

(a) Use the FIRIN code's calculations of heat flux into the plutonium to estimate the plutonium temperature, until the ignition point is reached. The aerosol release correlation and the closed-form size distributions derived in this document, as well as the humidity and plutonium temperature calculated by FIRIN, can be used by the module to estimate pre-ignition releases if desired.

(b) Waber (1967) cites data that show that plutonium specimens with less than 1.5 cm^2/g specific area tend to have ignition points of about 500°C. Above that specific area limit, the ignition points are about 300°C. These area and temperature criteria can be used to determine whether or not the ignition temperature has been reached.

(c) At the ignition point, the peak ΔT can be estimated using the statistical correlation for pure metal. The input to the correlation should be the incoming heat flux and the forced-convection airflow speed near the plutonium. These quantities may change with each timestep; if so, the predicted peak ΔT should also be changed. This ΔT is added to the original (pre-accident) ambient temperature to obtain the peak temperature. The module should also calculate the duration of oxidation starting at the time of ignition, using a 180 g/h oxidation rate. The plutonium temperature should rise to the peak temperature over a 10-min period (or over the entire oxidation time, whichever is shorter) and remain at the peak temperature for the remainder of the oxidation period.

(d) The aerosol release correlation can be used to calculate the amount of plutonium released at each timestep by multiplying the fraction of the original plutonium oxidized during the timestep by the aerosol release rate (as a fraction/h) and by the estimated oxidation time. The correlation uses the temperature estimated in the module and the humidity calculated by FIRIN to provide an airborne release amount. The appropriate closed-form size distribution can then be applied to the release.

2. **Make a further study of the mechanism by which humidity increases the release rate of plutonium at low and ambient temperatures.** The factor by which the presence of moisture increases the plutonium oxidation release rate is great enough to suggest that it would be useful to further identify the mechanism of water corrosion of plutonium. Under normal operating and storage conditions, even high-humidity release rates are quite low; but such conditions exist for much longer periods of time than

do accidents. The first step in such a study should be a survey of all the literature data on humid-air and water corrosion of uranium and plutonium.

3. **Get experimental verification of the release predictions of the correlation under maximum-release conditions.** The fact that the "adjusted" correlation somewhat underpredicts some of the maximum aerosol releases suggests that it would be useful to run more release tests under conditions associated with maximum releases. These include temperatures well above the plutonium melting point (650°C), high humidity, airflow above 100 cm/s, and possibly plutonium specimen masses above about 100 g. [Note that all of these conditions, except the humidity, were met by the massive metal experiments of Mishima (1966b), whose release rates rank in the top three for the entire database, as shown in Table 2.] Size distributions should also be measured to augment the existing data, and the experimental protocol in Appendix B should be followed. Any insights gained from these experiments should be applied to improve the statistical release correlations and size distribution formulations.

CONCLUSIONS

While there are not sufficient data to allow the creation of a detailed theoretical model of the aerosol release from oxidation and combustion of plutonium metal, it appears to be possible to produce an empirical model. The simplest level of empirical model, an upper limit value for all cases of combustion, has been derived by statistical analysis from the existing data set. A value on the order of 10^{-3}/h should be an upper limit for the fractional aerosol release rate. As this is based on complete combustion, it must be multiplied by the oxidation time to obtain the release for a given mass of material. An oxidation rate of 180 g/h is recommended for this purpose.

Statistical correlations of aerosol release rates, peak metal temperature, and atmospheric humidity have been developed by analysis of the database to provide a more detailed empirical model (one with some relationship to theory). These correlations, when adjusted to make release predictions that are one "standard error" above the least-squares fit, predict or overpredict all except the maximum release rates of the database. Correlations have also been developed to estimate peak temperature during an oxidation episode, and supplemental recommendations have been made concerning size distributions, oxidation rates, and ignition temperatures.

We recommend that the algorithms discussed in this report be included in the FIRIN code. We also recommend experiments to test and improve the statistical correlations for aerosol release rates at the upper end of the range of releases that have been measured. Finally, we suggest further study of the effect of humidity on oxidation of plutonium under normal operational and storage conditions (i.e., ambient temperature).

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APPENDIX A

SUMMARIES OF EXPERIMENTAL DESIGNS

This appendix contains brief descriptions of the experiments summarized in Table 1. One related experiment [Felt (1967)] that did not include particulate material measurements is also included.

APPENDIX A

SUMMARIES OF EXPERIMENTAL DESIGNS

[Andersen 1963, p. 2, 5-6] This experiment employed the routine air samples taken at Hanford and tested the plutonium oxide found there under normal and abnormal operating conditions. These were room air samples taken at 5 to 10 CFM through asbestos-based paper filters or membrane filters of 16 to 32 $in.^2$ area. The filters were changed at periods ranging from 8 h to 1 wk. These filters were examined using autoradiography: the filter was exposed to nuclear track film for a given period of time and the number of tracks from each particle detected was counted. In this experiment, each filter was exposed for times of 12, 120, 1,200, and 12,000 min, and the tracks were counted only for those particles that produced between 5 and 50 tracks. In interpreting the results, it was assumed that the particles were spheres with the density of pure PuO_2.

[Stewart 1963, p. 545] There were four sets of experiments in the series described in this paper. In the first set, plutonium metal was oxidized at room temperature, with different levels of humidity, and the resulting aerosol was measured. The specimens were cylinders 0.7 cm in diameter and 1 cm long, of α and δ metal. They were suspended in a tube in a flow of filtered air; loose particulate material was removed from the apparatus before each experiment. The airflow was between 14 and 24 cm/s. Sampling by cascade impactor was carried out for about half of the 7-day duration of each experiment. Spherical particles larger than 10 μm were not expected to reach the impactor, because of the design of the apparatus.

[op. cit., p. 548] In a second set of experiments, plutonium metal was oxidized at 123°C with different levels of humidity, and the resulting aerosol was measured. The specimens were cylinders 0.7 cm in diameter and 1 cm long, of α and δ metal. They were weighed continuously with an electromagnetic balance, while suspended in a tube in a flow

(about 5 cm/s) of filtered, humidity-controlled air; loose particulate material was removed from the apparatus before each experiment. A small electric furnace outside the tube provided heating, and a small porcelain crucible hung below the specimen to catch falling fragments. Sampling was done by cascade impactor, and spherical particles larger than 18 μm were not expected to reach the impactor. The balance was calibrated under the temperature and flow conditions of the experiment. As another precaution, abrupt changes in airflow direction between the specimen and the impactors were avoided.

[op. cit., p. 553] In a third set of experiments, plutonium metal was oxidized under nearly static conditions, at or above the ignition temperature. Specimens consisted of plutonium metal (α metal or δ alloy) cylinders 0.7 cm in diameter and 1 cm long. The specimen was suspended in the middle of a small resistance furnace that was open at both ends. At the bottom of the furnace was a nickel crucible to catch falling oxide fragments and the cooled residue. The platinum and platinum-rhodium wires by which the specimen was suspended acted as a thermocouple. Cascade impactors were used to sample the aerosol, and micro-sieves were used to examine the residue. It was found that a small amount of the oxide became airborne outside the apparatus and was found on the floor after each experiment.

[op. cit., p. 559] In the fourth set of experiments, plutonium was oxidized under dynamic conditions. The metal sample was mounted above a tantalum metal tray in a tube through which air flowed; part of the tube was inside an electric furnace that was used to heat the sample. The gas flowing through the tube (a flow rate up to 10 cm/s) was sampled continuously by cascade impactors, and a platinum-rhodium thermocouple was axially inserted in the specimen to measure temperature. The experimental plan was to apply a heating rate of about 15°C/min until ignition occurred, then cut off the air supply, switch off the furnace, and purge with nitrogen, whereupon the specimen temperature fell rapidly. Only the fraction below about 20 μm was expected to reach the sampler.

[Mishima 1966a, p. 3-10] The aerosol from burning small pieces of plutonium was studied. The six specimens were small rods of the pure metal, 0.25 in. in diameter and 0.75 in. long, with masses between 9 and 12 g. The test assembly consisted of a plutonium specimen suspended above a quartz boat, which was centered in a horizontal quartz combustion tube. A resistance furnace was used to raise the temperature of the filtered dry air flowing around the specimen and to maintain a constant temperature once ignition occurred. The airflow ranged from 3.3 to 50 cm/s and the ignition temperatures from 410 to 650°C. The particles passing through the combustion tube were caught in filters and sampled while oxidation was occurring. No melting or collapse was documented in the reference; however, during some of the later runs, the apparatus was rapped to dislodge particles. Temperature was measured with a thermocouple positioned directly above the specimen. The amount of airborne plutonium was determined by alpha counting, and its size distribution was observed with a microscope. The residue was also examined with a microscope, and classified by means of a combination sieve-air elutriator-cascade impactor technique. The residue was classified into 1) particles that could be entrained into air equivalently to a 15-μm sphere of PuO_2, 2) particles that were larger but still small enough to pass through a 44-μm screen, and 3) particles larger than 44 μm.

[Mishima 1966b] This experiment measured the aerosol produced by burning massive plutonium. The test assembly consisted of a chimney through which air was drawn at a calibrated velocity of 525 cm/s. The plutonium ingot to be tested was placed under the chimney; there was less than 1-in. clearance between the chimney and the Transite[a] plate on which the ingot rested. The entire assembly was located in

(a) Transite is the tradename for an asbestos-cement board made by Johns-Manville.

a glove box. The particles passing through the chimney were caught in filters and sampled during the time in which the specimen was above ambient temperature. The sampling period did not consistently include the time at which melting first occurred (with accompanying rupture of the oxide coat). The amount of plutonium was determined by alpha counting of particles that reached a filter at the top of the chimney. The size distribution was obtained by classification with a particle size analyzer used on shadowed particles taken from a side-arm sampler on the chimney. In addition, core temperatures were measured using thermocouples inserted in wells drilled in the ingots. The four specimens were ingots with all dimensions in the 1- to 2.5-in. range, with masses of between 455 g and 1770 g and initial surface area of 10 to 30 $in.^2$. Of the three runs that were made with complete oxidation, one used δ-stabilized plutonium alloy and two used pure plutonium.

[Felt 1967, p. 5-6] As part of a study of methods to extinguish plutonium fires, massive plutonium metal was ignited. A carbon-arc torch (with a peak temperature of about 5000°C) was used to ignite the specimens. The specimens were of several different types: 1- to 2-kg buttons or ingots of α metal, cylinders of α metal weighing less than 1 kg, stabilized δ-alloy "pie shapes" in the 0.2- to 1-kg range, casting skulls (150 to 265 g), and metal turnings (about 200 g). Thermocouples were located in the center of each specimen, and temperature-time histories were taken. The support surface was Transite, chosen for its low thermal conductivity.

[Mishima et al. 1968, p. 6-16] The 15- to 44-μm fraction of powder resulting from oxidation of plutonium above the ignition temperature was used, and the aerosol from heating it was studied. The powder specimen was placed in a stainless-steel cap on an Alundum[(a)] thimble that was heated with induction coils. An upsweep airflow of 10 or 100 cm/s was drawn over the sample into a chimney above it.

(a) Alundum is a trademark of Norton Company, Metals Division, Newton, Massachusetts.

The nominal velocity at the mouth of the chimney was about twice that in the chimney. A thermocouple placed in a well in the cap was used to measure temperatures, which were maintained roughly constant for an hour. The aerosol deposited on the outflow filter and on the chimney liner was measured (by alpha counting) to determine the amount of airborne plutonium. Sampling was continued for an hour after the heat was turned off. Size analysis was done by microscopic examination.

[Chatfield 1968, p. 97] This experiment studied the oxidation of and formation of aerosol from plutonium surfaces. Small plutonium cylinders (0.7 cm in diameter and 1.0 cm in length) were placed in glass tubes and heated using a resistance furnace. Specimens included both the pure metal and the δ alloy. Airflows (either dry or saturated air) over the specimen were between 10 cm/s and 80 cm/s; these airflows and the containment setup were chosen such that particles larger than about 20 μm in diameter would be deposited rather than sampled. The aerosol concentration and size distribution were measured with a May type cascade impactor[(a)], and the plutonium in the samples was estimated by counting X-ray emissions or (for low-activity samples) alpha particles.

[Chatfield 1969b, p. 230] The major point of this experiment was to test the oxidation of plutonium-sodium combinations; some plutonium-only runs were included. The test assembly consisted of a specimen of plutonium foil (less than 0.1 g) in a nickel or titanium foil combustion boat, all located within a silica tube. The specimen was heated to 300°C in an 80-cm/s flow of argon, and then oxidation was begun by switching to an equal flow of air. The sampling equipment was a modified cascade impactor [the first two stages of a Casella instrument[(a)] and a terminal filter]. A thermocouple was used to measure the specimen temperature.

[Carter and Stewart 1970, p. 820-821] The experiment studied the aerosols generated by various "dynamic" and "static" types of

(a) Manufactured by C. F. Casella, London, England.

oxidation processes in two ways. First, the aerosols created by electrically exploding wires of plutonium were removed from the chamber at about 1 min after formation. The chamber was about 3.5 L in volume, and the nominal energy input was 4 kJ. Size information was obtained using cascade impactors, and membrane filters were used for microscopy. Second, aerosols were generated by dropping burning fragments or droplets of plutonium through air in a vertical column about 0.75 m tall and 0.14 m in diameter. A resistance heater at the top of the column heated the specimens, which were δ alloy, from 30 mg to 2.5 g in mass, with specific areas in the range of 2 to 4 cm^2/g. An upwards airflow in the column was used to restrict the particles sampled to those below about 30 μm. Three cases were studied in the column:

(1) "static" ignition and oxidation of a metal sample, occurring without sample movement; the cooled residue fell into the column

(2) metal droplets at about 660°C, produced by heating a fragment in argon, and then dropped into the air in the column

(3) metal droplets at about 2000°C, heated in air.

Similar experiments were also carried out for uranium.

[Eidson and Kanapilly 1983, p. 4-8] This study examined the respirable particulate oxides produced when plutonium is exposed to several different gases and then to air. Pellets of δ plutonium, weighing 0.1, 0.5, or 1 g, were heated in 3% H_2 + Ar, 3% H_2 + 5% N_2 + Ar, air, and Ar, at different humidities. The specimens were placed in crucibles of tantalum or of stainless steel coated with erbium oxide. The crucible was located in a furnace-heated quartz reaction tube, into which gases were introduced at measured flow rates. The apparatus was purged with argon before use. All of the gases were dried with a gettering furnace before they were passed over the specimen, then combined with humidified air or argon as needed. The flow rate was 15 L/min. Pyrometers were used to monitor temperatures. The aerosols were measured in a downstream sample chamber, which was lined with 1- by 2-cm segments of foil so that plutonium

on the chamber surfaces could be collected and its location noted. However, in the first set of experiments not all surfaces were covered, and there was no boat under the crucible to catch lost powder. The residue was the powder that remained in or near the crucible area after cooling. Glass fiber filters were used to measure aerosol concentrations and 7-stage cascade impactors to obtain particle-size distributions. Some samples were also collected by electrostatic precipitators to be examined by electron microscopy. The size distribution of the residue was measured using sieving and sedimentation techniques.

[Eidson et al. 1988, p. 42-45] This study examined the respirable particulate oxides produced when plutonium hydrides and nitrides were exposed to air. Pellets and foils of δ plutonium, weighing 1 or 10 g, were heated in 3% H_2 + Ar, 3% H_2 + 5% N_2 + Ar, or air. The 1-g pellets were cylinders 0.63 cm in diameter and 0.2 cm long, while the 10-g pellets were 1 cm in diameter and 0.8 cm long. The specimens were placed in crucibles of stainless steel coated with erbium oxide. The crucible was located in a furnace-heated quartz reaction tube, into which gases were introduced at measured flow rates. All of the gases were dried with a gettering furnace before they were passed over the specimen. The flow velocities upstream of the sample were 40 or 80 cm/s, depending on flow rate, but velocities at the sample were in some experiments increased to 500 or 1000 cm/s by using a tube with a constriction at the sample. Pyrometers were used to monitor temperatures. The aerosols were measured in a downstream sample chamber, which was lined with foil ruled in 3-cm squares so that plutonium on the chamber surfaces could be collected and its location noted. The tube downstream of the crucible was also lined. Glass fiber filters were used to measure aerosol concentrations and 7-stage cascade impactors to obtain particle size distributions. Some samples were also collected by electrostatic precipitators to be examined by electron microscopy. The size distribution of the residue was measured using sieving and sedimentation techniques. The system was purged with

argon and the specimen heated to 450°C before the test atmosphere was introduced; after 60 min the reaction gas flow was stopped and the tube was cooled and purged with argon. When cooling was complete, the residue and aerosol samples were taken; the tube, chamber, and impactors were washed; and the washings were analyzed for radioactivity.

APPENDIX B

EXPERIMENTAL TECHNIQUE

This appendix describes the criteria that should be met by an experiment studying the aerosol release from plutonium oxidation.

APPENDIX B

EXPERIMENTAL TECHNIQUE

1. The environmental parameters that should be controlled, varied, and quantified are the air temperature, humidity, dust content, and the airflow linear speed and direction. The air temperature, speed, and direction pertain to convective heat transfer and particle transport. The humidity is known to affect the oxidation rate. The dust content of the air may affect the agglomeration of the aerosol particles (Swain and Haberman 1961). The thermal diffusivity, temperature, and mass of the specimen support should also be stated, at least in general terms, so that the heat loss to the support can be roughly estimated. Finally, the ambient temperature of the surroundings should also be recorded, because this relates to radiative heat loss.

2. The metal temperature and (if appropriate) the heating rate applied to be metal should be measured.

3. All constraints on aerosol transport that are a result of the experimental design or the apparatus design should be identified, and all the possible aerosol sinks (all surfaces in the apparatus) should be sampled for particulate material and cleaned or purged between experiments (Eidson et al. 1988). Abrupt changes in airflow between the specimen and the impactors should be avoided (Stewart 1963).

4. The phase, purity level, alloying materials, oxidation history, and (for pure metal) the past cycling history of the plutonium specimens should be known, controlled, and varied. These material characteristics are known or surmised to affect the oxidation rate (Stewart 1963; Waber 1967). The mass, specific area, and shape of the specimen should also be recorded.

5. The non-particulate material data that are measured should include time histories of the specimen weight change, which can be measured with an electromagnetic balance (Stewart 1963), and the core and surface temperature of the specimen. The times of occurrence of any singular events

(such as liquid plutonium breaking through the oxide shell) or of application of controls (such as N_2 quenching) should also be noted. The extent of conversion to oxide in the final material should be determined.

6. Particulate material samples and other data should be taken starting at the time when the sample begins to oxidize under controlled conditions and ending when the sample cools down to the final temperature. The cooldown step has been found to contribute significantly to particulate release (Stewart 1963).

7. Aerosol sampling methods should, at minimum, allow time histories of the aerosol release rate to be measured, and preferably should also allow for time histories of the size distribution and the aerosol morphology. It should be clearly stated whether size distributions are presented in terms of geometric or aerodynamic diameters.

8. Electron microscopy should be used to examine the morphology of both the residue and the aerosol. It should also be used to spot-check the size distribution on each collector plate of the cascade impactor, as an extra calibration step (Stewart 1963).

9. Cascade impactors should be used to determine the size distribution of the aerosol, and sedimentation and sieving techniques should be used on the residue. Some particle agglomeration has been reported to occur in aerosol samples that have been left standing; particle breakup during sieving and cascade impaction has also been reported. In the usual brief procedures these artifacts have been considered to have little effect (Stewart 1963). However, the effect of comminution and fragmentation was readily measurable when the residual oxide was elutriated for an hour (Mishima 1966a). Another feature of the plutonium oxide particulate material is its non-sphericity, which can cause particles with a relatively wide range of dimensions to be deposited on each impactor stage. The extent to which this occurs should be spot-checked using optical and electron microscopy.

10. All experiments should be replicated at least once (same specimen type and experimental conditions) so that the experimental variability under those conditions can be seen. Unless this is done, the amount of "scatter" in aerosol properties may be underestimated.

11. Any statistical techniques used should not depend on the assumption that a lognormal distribution of particle sizes exists (for a particular experiment) until that distribution has been verified from the data (Eidson et al. 1988).

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