



# Pyrophoric potential of plutonium-containing salt residues

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## Abstract

Ignition temperatures of plutonium and the pyrophoric potential of plutonium-containing pyrochemical salt residues are determined from differential thermal analysis (DTA) data and by modeling of thermal behavior. Exotherms observed at 90–200°C for about 30% of the residues are attributed to reaction of plutonium with water from decomposition of hydrated salts. Exotherms observed near 300°C are consistent with ignition of metal particles embedded in the salt. Onset of self-sustained reaction at temperatures as low as 90°C is not precluded by these results and heat-balance models are developed and applied in predicting the static ignition point of massive metal and in evaluating salt pyrophoricity. Results show that ambient temperatures in excess of 200°C are required for ignition of salt residues and that the most reactive salts cannot ignite at low temperatures because diffusion of oxidant to embedded metal is limited by low salt porosity. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

An inventory of approximately 16 metric tons of plutonium-containing salt residues were produced during pyrochemical processing of nuclear materials at Rocky Flats over a 25-yr period [1]. These chloride salts were formed by several processes that include direct oxide reduction (DOR) of PuO<sub>2</sub> to metal, molten salt extraction (MSE) of americium from plutonium metal and molten salt electrorefining (ER) of impure plutonium metal [2]. Safe disposition of these residues is essential, but predicated on adequate assessment of their hazardous potential and verification of their compliance with acceptance criteria for disposal. The potential for pyrophoric reaction of residual metal in the pyrochemical salts is a major concern [3,4].

Although pyrophoricity is normally associated with spontaneous ignition of a material at room temperature, consideration of behavior over a broader temperature is necessary for salt residues because of possible conditions

that might be encountered during handling, transport and storage. Onset of spontaneous and self-sustained reaction at elevated temperatures is marked by the ignition point. Thermal events of concern include exposure of residues to static-temperatures as high as 150°C for extended periods of time [5].

Salt residues at Rocky Flats were formed by solidification of molten chloride phases used as solvents during pyrochemical processing [2]. Whereas CaCl<sub>2</sub> was the salt phase used for DOR, the MSE and ER solvents were typically NaCl–KCl or NaCl–CaCl<sub>2</sub> mixtures containing MgCl<sub>2</sub>. In addition to residual plutonium metal shot that did not coalesce into the product pool during processing [3], salt residues may contain magnesium metal formed during selective oxidation of Am metal by MgCl<sub>2</sub> in MSE or unreacted calcium used as the reducing agent in DOR [2]. Metallic sodium or potassium might have formed during ER processing, but the presence of those reactive metals is considered unlikely because a recent study indicates that plutonium particles embedded in salt residues are 30–40% oxidized after a decade or more in storage [6]. That characterization of ER salts by a hydrolysis method shows that metal is present at concentrations of 10 ± 5 mass percentage primarily as 1 mm diameter spheres.

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Experimental determination of ignition points for plutonium-containing salts is desirable. However, as demonstrated by variability and uncertainty in results of thermal analyses, confidence in the ability to experimentally define ignition characteristics of diverse residues is lacking. Therefore, development of thermal models for describing and predicting behavior is necessary for adequately assessing pyrophoric potential.

The present study of the pyrophoric potential posed by plutonium-containing salts involves extensive thermal analysis of residues and development of thermal models for ignition of massive plutonium and metal particles embedded in salts. Interpretation of data and formulation of the models rests on fundamental knowledge of plutonium oxidation kinetics in humid and dry atmospheres. Models are based on the principle that ignition occurs if the rate of heat generation by metal oxidation exceeds the rate of heat loss to the surroundings. Results of the complementary experimental and theoretical approaches provide a basis for assessing the reactivity and ignition potential of salt residues.

## 2. Experimental procedures

Thermal characteristics of the salt residues were determined by differential thermal analysis (DTA) measurements at temperatures between 25°C and 330°C. Samples (1–6 g) of fines and powders prepared by grinding large fragments of the salt residues were weighed and placed in a 30 mm diameter cylindrical specimen tube of borosilicate glass with a temperature well in the closed end. The tube was positioned in a vertical aluminum heating block with a thermocouple centered in the sample. Temperatures were corrected by calibration of the apparatus with melting-point standards. Samples were heated at a rate of 5°C/min with a resistance furnace driven by a programmed controller and a second thermocouple in the aluminum block. The sample tube and furnace remained open to the atmosphere during measurements to allow unrestricted access of air to the sample.

Differential curves were defined by the difference between initial and final measurements of sample temperature over time. The final curve for each sample was obtained by repetition of the heating cycle until no thermal activity remained. Data for the final cycle served as the reference for thermal inactivity. Repeated analyses of samples were frequently required to obtain stable reference curves. Thermal activity that occurred during intermediate measurements is not included in reported DTA curves because the objective of each measurement was accurate determination of thermal behavior during initial heating. Exothermal excursions observed during repeated cycles occurred at higher

temperatures and were of smaller magnitude than observed initially.

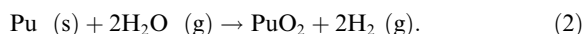
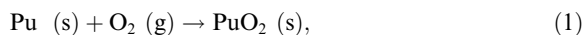
Although DTA data were obtained for representative samples of residues from different pyrochemical sources, efforts were focused on analysis of ER salts because of their comparatively high plutonium concentrations. In order to establish a high level of confidence in the results, the test matrix included samples of ER salts from 114 storage containers, the number required for 95% confidence in sampling.

Interpretation of the results was facilitated by measuring the thermal behavior of known and possible residue constituents. Reference DTA curves were obtained for hydrates of magnesium dichloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) and calcium dichloride ( $\text{CaCl}_2 \cdot \text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ), as well as for magnesium and calcium metals.

## 3. Review and evaluation of literature on plutonium reactivity

### 3.1. Oxidation kinetics

The corrosion kinetics of unalloyed plutonium and the delta-phase gallium alloy in dry and humid conditions are described in recent reports [7,8]. Plutonium dioxide is formed by the reactions of oxygen and water vapor with both metal and alloy:



Arrhenius curves presented in Fig. 1 describe the temperature dependence of these reactions during the 'linear' kinetic stage characterized by coverage of the metal surface with a steady-state thickness of oxide and by a constant oxidation rate. This linear stage of reaction results from the combined effects of a diffusion-controlled oxidation rate and continuous spallation of the oxide product.

The rate-limiting step for both Eqs. (1) and (2) is the diffusion of oxygen through the layer of product oxide [9,10]. As freshly burnished metal oxidizes, the rapid initial reaction rate decreases as the adherent layer of oxide product increases in thickness. The extent of reaction during this initial stage has a parabolic time dependence characteristic of rate control by diffusion of reactant through a product layer of progressively increasing thickness. The linear (constant rate at a fixed temperature) stage of reaction is entered as stresses induced by formation of a low-density oxide ( $11.45 \text{ g/cm}^3$ ) on high-density metal ( $19.8 \text{ g/cm}^3$ ) or alloy ( $15.8 \text{ g/cm}^3$ ) results in localized spallation of oxide particles from the surface. The thickness of the oxide layer varies from

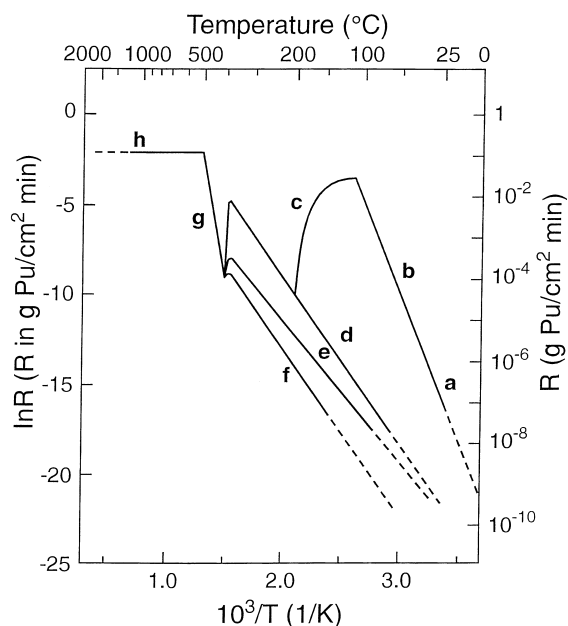


Fig. 1. Arrhenius results for oxidation of unalloyed and alloyed plutonium in dry air, moist air and water vapor at oxidant pressures of 0.21 bar. Oxidation kinetics of unalloyed Pu are described by curves a–c for moist air or water vapor, by curve d for dry air below 200°C and for the moisture-independent regime above 200°C. Oxidation kinetics of the delta-phase gallium alloy are described for moist and dry condition by curves e and f, respectively. Oxidation kinetics of both metals in dry or moist air are described by curves g and h.

point to point on the metal surface with regions of thin oxide in recently spalled areas and regions of thick oxide in unspalled areas, as well as regions of intermediate oxide thickness. A constant corrosion rate is observed as continuing oxide spallation maintains a steady-state diffusion barrier of constant average thickness. The steady-state oxide thickness is temperature dependent and equals 4–5  $\mu\text{m}$  at 25°C [11].

The Arrhenius results in Fig. 1 define the oxidation rate ( $R$ ) of unalloyed and alloyed plutonium in dry and humid air and in water vapor [8]. These curves are based on extensive experimental and literature data for oxidation of alloyed and unalloyed Pu in dry and humid air below 500°C [7], as well as in air at temperatures up to 3500°C [12]. Curves a–d are for corrosion of unalloyed metal; curves e and f are for corrosion of the delta-phase gallium alloy. Except for curve a, the oxidant pressures are 0.21 bar (160 torr), the partial pressure of  $\text{O}_2$  in air at one atmosphere. Whereas curve b describes the corrosion rate by water vapor at 0.21 bar and temperatures above 61°C, curve a defines  $R$  for equilibrium water pressures fixed at values less than 0.21 bar by the temperature. Curves a and b also describe the corrosion rate in air with equilibrium partial pressures of water and

0.21 bar water pressure, respectively. Curve c defines a transition region in which the reaction rate of water vapor decreases as the temperature increases from 110°C to 200°C. The oxidation rate of unalloyed Pu in dry (<0.5 ppm) air is shown by curve d below 200°C. Curves c and d converge near 200°C and  $R$  is independent of the water concentration at higher temperatures. As detailed in a prior report [7], the corrosion rate is proportional to the square root of water pressure within the envelope bounded by curves a–d. The relatively slow oxidation rates for delta-phase alloy in water vapor and in dry air are shown by the curves e and f, respectively. Convergence of the curves near 400°C marks the point above which the corrosion rate is independent of alloying and water concentration as defined by curve g. Curve h describes the temperature-independent oxidation of ignited metal in air at temperatures above 500°C.  $R$  is fixed by the rate of  $\text{O}_2$  diffusion through an oxygen-depleted boundary layer of nitrogen at the gas–solid interface.

Accurate evaluation and prediction of ignition behavior is contingent on selection of the appropriate kinetic data to describe oxidation of plutonium in salt residues. Use of kinetic data for the linear stage of oxidation is consistent with evidence showing that the extent of metal oxidation during residue storage far exceeds the 4–5  $\mu\text{m}$  thickness of the steady-state oxide layer [6]. Unalloyed metal is formed during pyrochemical processing and the presence of water is likely during handling and storage. Oxidation kinetics of metal in salt residues are confined to the envelope formed by curves a, b, c and d at temperatures below 200°C and are defined by curve d above 200°C. The applicable Arrhenius relationship within the low-temperature envelope depends on humidity [7].

The combined effects of moisture and temperature on the oxidation kinetics of plutonium are significant. Rates defined by curves a and b are factors of  $10^2$  and  $10^5$  faster than the respective values shown by curve d for dry air at 25°C and 100°C. However, the rate decreases by as much as  $10^4$  as the temperature increases from 110°C to 200°C. This reduction in oxidation rate is unavoidable even though the water concentration remains constant. Recognition of this behavior is essential for interpreting experimental results and formulating a thermal model to predict the ignition point.

The chemistry of plutonium oxidation in moist air at temperatures below 200°C is complex, but understanding of the process is necessary for qualitatively confirming the validity of Eq. (2) and interpreting thermal behavior of salt residues. Oxidation of metal in moist air occurs at the rapid rate characteristic of the  $\text{Pu} + \text{H}_2\text{O}$  reaction, but  $\text{O}_2$ , not  $\text{H}_2\text{O}$ , disappears from the gas phase and  $\text{H}_2$  is not observed as a gaseous product [13]. One interpretation of this behavior is that the solid

reaction product is a mixture of plutonium oxide and plutonium hydride ( $\text{PuH}_x$ ,  $1.9 < x < 3.0$ ), a compound with documented pyrophoric potential [8]. That suggestion fails to account for disappearance of oxygen and for a stable water concentration. However, all chemical and kinetic observations are consistent with a cyclic reaction based on experimental observations that  $\text{H}_2$  and  $\text{O}_2$  dissociate as  $\text{H}_2\text{O}$  on the catalytically active surface of plutonium oxide [13]. In the presence of moist air,  $\text{H}_2\text{O}$  reacts with oxide-coated Pu at the rapid rate observed for water vapor. Instead of associating to form  $\text{H}_2$ , atomic hydrogen produced by the reaction combines with atomic oxygen formed by adsorption and dissociation of  $\text{O}_2$  on the oxide surface. The  $\text{H}_2\text{O}$  product reacts with additional Pu in a net process that consumes  $\text{O}_2$  and oxidizes plutonium at the rapid rate of the  $\text{Pu} + \text{H}_2\text{O}$  reaction while the amount of water remains constant. Small quantities of moisture catalytically promote the  $\text{Pu} + \text{O}_2$  reaction via this catalytic cycle without producing  $\text{H}_2$  or  $\text{PuH}_x$ .

#### 4. Plutonium pyrophoricity and ignition

The existence of two ignition regimes for plutonium metal was first described in an early study by Schnizlein and Fisher [14]. As shown in a recent review of ignition data obtained in dynamic tests at heating rates near  $10^\circ\text{C}/\text{min}$  [15], massive plutonium metal or alloy with a thickness greater than 0.2 mm (specific surface area  $< 8 \text{ cm}^2/\text{g}$ ) ignites and oxidizes in a self-sustained reaction when heated to  $500 \pm 25^\circ\text{C}$ . Foil, chips and powder with minimum dimensions less than 0.1 mm (specific surface area  $> 15 \text{ cm}^2/\text{g}$ ) exhibit similar behavior at  $150 \pm 40^\circ\text{C}$ . Ignition temperatures ( $T_i$ ) between  $190^\circ\text{C}$  and  $475^\circ\text{C}$  are observed in a transition region for metal thicknesses of 0.1–0.2 mm. The surface area to mass ratio is identified as the major parameter affecting ignition. However, this factor alone does not adequately account for the ignition behavior of high-surface-area Pu at  $110$ – $190^\circ\text{C}$ . As shown by results in Fig. 1, the areal oxidation (heat generation) rate of plutonium is  $0.14 \text{ g Pu}/\text{cm}^2 \text{ min}$  at the  $500^\circ\text{C}$  ignition point. The highest Pu oxidation rate in low-temperature regime is  $0.012 \text{ g Pu}/\text{cm}^2 \text{ min}$  for reaction of unalloyed metal with steam at 1.01 bar and  $110^\circ\text{C}$  [7]. This rate is a factor of 10 slower than observed for ignition of 0.2 mm thick metal, but 0.1 mm thick chips ignite near  $150^\circ\text{C}$  even though the specific surface areas differ by only a factor of 2.

Factors other than surface area to mass ratio are included in conceptual and quantitative models describing the relationship between the two ignition regimes [11]. The chemical basis for these models is a non-equilibrium condition existing in the surface layer of oxide on the metal during oxidation in air. At room temperature,  $\text{PuO}_2$  is the only oxide detected on the Pu

surface, but thermodynamic relationships require the presence of a thin  $\text{Pu}_2\text{O}_3$  layer at the oxide–metal interface. Although  $\text{Pu}_2\text{O}_3$  is continually formed at this interface by the  $\text{Pu} + \text{PuO}_2$  reaction, the lower oxide readily oxidizes to dioxide at  $25^\circ\text{C}$ . As shown by the facile formation of  $\text{Pu}_2\text{O}_3$  when  $\text{PuO}_2$ -coated metal is heated to  $150^\circ\text{C}$  in vacuum [16], the temperature dependence of  $\text{Pu}_2\text{O}_3$  formation is strong and the fraction of  $\text{Pu}_2\text{O}_3$  in the oxide layer increases significantly with temperature.

According to the conceptual model, the auto-reduction reaction transforms the steady-state  $\text{PuO}_2$  layer (4–5  $\mu\text{m}$  thickness) almost completely to  $\text{Pu}_2\text{O}_3$  as the metal is heated to  $150^\circ\text{C}$ . Ignition of the  $\text{Pu}_2\text{O}_3$  layer and its rapid oxidation back to  $\text{PuO}_2$  releases heat (226 kJ/mol of  $\text{PuO}_2$ ). If the amount of heat generated is sufficient to raise the temperature of a metal particle from  $150^\circ\text{C}$  to  $500^\circ\text{C}$ , the particle ignites and oxidizes in a self-sustaining reaction. This reaction accounts for the unexplained appearance of large ( $> 100^\circ\text{C}$ ) pre-ignition exotherms during ignition tests with 1 mm thick Pu specimens that were preheated in argon at  $520 \pm 10^\circ\text{C}$  for several hours prior to testing [17]. These thermal excursions were apparently produced by oxidation of  $\text{Pu}_2\text{O}_3$  layers formed during preheating, but were insufficient for ignition.

The conceptual explanation of plutonium pyrophoricity is validated using a quantitative model [11]. In formulating the model, it was assumed that oxidation of  $\text{Pu}_2\text{O}_3$  back to  $\text{PuO}_2$  is rapid and that all heat is deposited in the reacting particle. Therefore, the dimensions of particles having thermal excursions greater than  $350^\circ\text{C}$  were readily calculated for particle geometries with the lowest (spheres) and highest (foil) surface area to volume ratios. Ignition is predicted for spheres with diameters less than 0.25 mm and sheets with thicknesses less than 0.09 mm, values that are in excellent agreement with experimental observation. A protective  $\text{PuO}_2$  layer is not reestablished after ignition because diffusion of oxygen is rapid and favored by formation of  $\text{Pu}_2\text{O}_3$  at the temperatures reached during self-sustained reaction. These results suggest that like  $\text{PuH}_x$ ,  $\text{Pu}_2\text{O}_3$  is a reactive compound capable of igniting plutonium metal upon exposure to air at low temperatures [8].

Results of ignition studies are sensitive to the experimental procedure. In a typical measurement of the ignition point, a metal specimen is heated at a constant rate in flowing air while its temperature is continuously measured. The ignition temperature is the point at which onset of self-sustained reaction is indicated by a sharp increase in specimen temperature that exceeds the programmed value and continues until the entire metal sample is consumed. Ignition experiments are dynamic and the observed ignition point is a function of the heating rate [17].  $T_i$  values for massive Pu specimens are

insensitive to the heating rate if it is greater than 5°C/min, but progressively decrease from 500°C to 355°C as the rate is reduced to a fraction of 1°/min. Other tests with massive metal show that ignition points decrease from 500°C to 375°C if specimens are held at constant temperatures for several hours. Specimens of massive metal ignite after 2 h at 375°C, but oxidized completely without igniting during 5 h tests at 350°C.

The dependence of  $T_i$  on heating rate and time demonstrate the need for exercising care in use of ignition data. Spontaneous ignition, self-sustained reaction and large thermal excursions are immediately observed if Pu is heated to 500°C in air. However, the metal also ignites at temperatures as low as 355°C if the heating rate is slow or as low as 375°C if temperature is held constant. These observations reflect the sluggishness of the ignition process at temperatures near the ignition point. Excess heat is generated by the reaction if the ignition point is exceeded by a small amount, but the rate of its accumulation is slow and strongly influence by sample size and by the heat capacity and thermal conductivity of the surroundings. The metal temperature increases significantly only after thermal momentum is gained and effects of the exponential temperature dependence of the oxidation rate are realized. Definition of the static-temperature ignition point is difficult because test specimens oxidize completely before a thermal excursion is detected.

The spontaneous ignition of plutonium fines and chips in air at room temperature is reported [15], but these reports are not documented and the conditions of the occurrences are uncertain. Reaction of clean Pu powder is rapid, but as implied by parabolic kinetics, the oxidation rate has an inverse dependence on the thickness of the product layer and slows sharply with the extent of oxidation. Run-away oxidation of clean Pu at low ambient temperatures cannot be excluded and ignition of the metal is promoted by the presence of pyrophoric  $\text{PuH}_x$  and  $\text{Pu}_2\text{O}_3$  formed in small amounts beneath the  $\text{PuO}_2$  layer during reaction of Pu with  $\text{H}_2\text{O}$  at 200–350°C [10,18]. Thermal excursions produced by rapid and unrestricted oxidation of such compounds may be sufficient for ignition of the metal. Small amounts of exposed  $\text{PuH}_x$  on the metal surface catalyze the reaction of massive Pu with air via a process that indiscriminately consumes of both  $\text{O}_2$  and  $\text{N}_2$  after the temperature exceeds 230°C [8]. The reaction initiates at room temperature and advances into the metal at more than 10 mm Pu/h, a rate that is  $10^{10}$  faster than for oxidation of unalloyed metal in dry air at 25°C. If hydride-coated metal is exposed to  $\text{O}_2$ , the oxidation rate is approximately 3 m Pu/h. Pyrophoric behavior is enhanced because the catalyzed reaction proceeds without forming a layer of oxygen-depleted  $\text{N}_2$  or a layer of  $\text{H}_2$  product at the gas–solid interface [19].

## 5. Results and discussion

### 5.1. DTA results

DTA data for plutonium-containing salt residues show that strong and reproducible exothermic reactions occurred in approximately 30% of all tests and initiate at temperatures as low as 90°C. Mass-normalized exotherms exceeding 8°C/g of salt residue were observed and resulted in sharp exothermic excursions of 150°C in some tests. Weak exothermic responses seen in about 45% of the tests and frequently preceded by mild endotherms were less than 8°C/g of salt and involved temperature increases of less than 20°C. These exotherms were typically broad and are most consistent with low plutonium concentrations in the salt residues. Endothermic activity observed in the remaining 25% of all tests is attributed to thermal decomposition of hydrated chlorides in salt samples containing negligible amounts of metal. These results establish a qualitative basis for evaluating ignition properties of salt residues and suggest that the likelihood of significant thermal excursion is very low for approximately 70% of the pyrochemical salts at Rocky Flats.

Two types of thermal behavior encountered for DTA curves with large exotherms are shown by representative results in Fig. 2. Neither corresponds with results obtained for calcium and magnesium, but the oxidation behavior of salts containing those metals is unknown. As exemplified by the upper curve observed for a third of these tests, sharp exotherms with maxima at 140–150°C often initiate as low as 90°C and frequently have well-resolved exothermic deflections at 125–130°C. Another unusual feature of these exotherms is their asymmetric shape characterized by a sharp rise to the peak and a gradual decrease approximating exponential decay as the temperature increases from 150°C to 200°C. Continuing reaction at a slow rate is indicated by a modest exothermic response beyond 200°C. A second type of behavior indicated by the lower curve in Fig. 2 and occurring in another third of the tests is characterized by an extremely small exotherm at 100–200°C, a progressively increasing thermal response over the 200–300°C range, and a sharp symmetric peak at 300–325°C. As shown by the middle curve in Fig. 2, two exotherms corresponding to those seen in the upper and lower curves were observed in the remaining third of the tests.

DTA results for hydrated dichlorides of magnesium and calcium define the temperature ranges in which these compounds decompose endothermically with loss of water. Dehydration of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  initiated with the loss of four waters of hydration at 35–50°C. The  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  product decomposed over the 90–210°C range. In a similar manner,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  decomposed at 115–255°C. Complex exothermic behavior observed for the hydrates above 150°C may result from partial

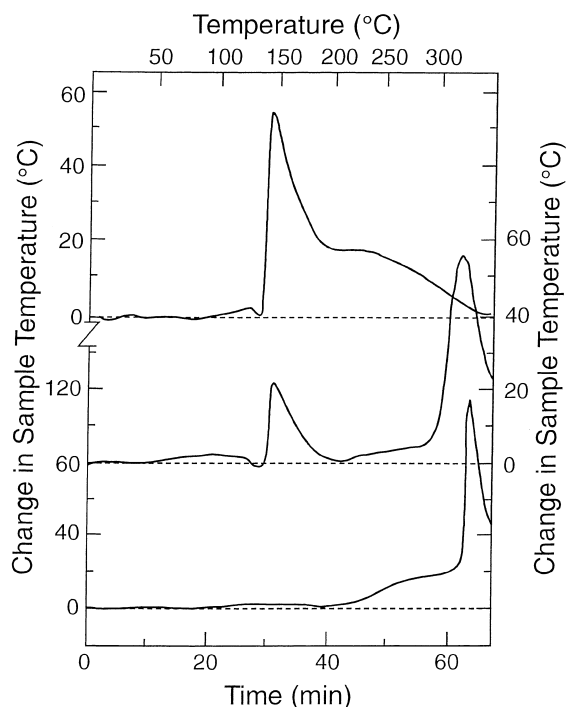


Fig. 2. Representative DTA curves for plutonium-containing salt residues.

oxidation of the chlorides during heating, a reaction indicated by incomplete solubility of the dehydration products in water. Hydration of the chloride residues during storage is suggested by similarities between these results and curves showing only endothermic behavior for 25% of the residues. The results show that release of water initiates at 90–115°C if hydrated chlorides of magnesium or calcium are present.

Hydration of the salt residues is consistent with the extent of plutonium oxidation that has occurred during storage. Results of hydrolysis measurements indicate that an average of 200–400  $\mu\text{m}$  of metal has corroded at surfaces of plutonium particles embedded in the salt during storage [6]. The linear oxidation rate of unalloyed metal is about 0.1  $\mu\text{m}/\text{yr}$  in dry air at room temperature and cannot account for the observed extent of oxidation [7]. Mixtures of  $\text{CaCl}_2$  and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  form a desiccant/buffer system that maintains an  $\text{H}_2\text{O}$  partial pressure of 0.2 mbar (0.6% relative humidity) at room temperature [20]. Linear oxidation rates derived from data for oxidation of unalloyed plutonium in air at that moisture level and temperatures of 25–35°C are 2–8  $\mu\text{m Pu}/\text{yr}$  [7]. Even with free access of air to the metal and elevated storage temperatures, the observed extent of oxidation requires a storage period of 25–50 yr. Water pressures greater than 0.2 mbar apparently exist in many storage containers and the presence of dichloride hexahydrate in the salt residues is implied.

Observations suggest that substantial quantities of water are present as hydrates in the pyrochemical salts and that moisture plays an important role in their thermal behavior. The amount of water present in a salt residue depends primarily on the extent of atmosphere exposure prior to packaging, but may also vary with the concentrations of magnesium and calcium dichlorides in the residues. If a storage container is sealed, the amount of water in the container remains constant because the water-catalyzed cycle promotes the  $\text{Pu} + \text{O}_2$  reaction without being consumed [13]. If the container is not sealed, additional water may accumulate in the salt during storage. For hydrates to form at room temperature and decompose when heated, water molecules must be able to enter, move through and leave the salt phase. Therefore, diffusion of water through the salt is a facile process for transporting reactant to embedded metal particles during storage, but the presence of fissures and cracks in the salt may also contribute to the net process. Variations in the water concentration of salt residues are likely and significantly alter thermal behavior.

Exothermic response of pyrochemical salts between 90°C and 200°C in Fig. 2 is attributed to reaction of unalloyed plutonium with water as described by curves b and c in Fig. 1. Appearance of exothermic response near 100°C coincides with onset of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  dehydration and with an increasingly rapid  $\text{Pu} + \text{H}_2\text{O}$  reaction. Dehydration increases the mobility and availability of water and coincides with frequent appearance of endothermic deflection of DTA curves at 125–130°C, as seen for this temperature range in the upper and middle curves of Fig. 2. The sharp exothermic peak at 140–150°C is attributed to increasingly rapid oxidation of metal as the concentration of available  $\text{H}_2\text{O}$  is increased by dehydration. The characteristic and reproducible decrease in exothermic response at 150–200°C coincides with the sharp exponential decline in the  $\text{Pu} + \text{H}_2\text{O}$  reaction rate with increasing temperature described by curve c in Fig. 1. Exothermic behavior above 200°C is consistent with entry into the moisture-independent kinetic regime in which the oxidation rates of  $\text{O}_2$  and  $\text{H}_2\text{O}$  are indistinguishable.

DTA results like that shown by the lower curve in Fig. 2 correspond with thermal behavior expected for oxidation of metal in salts containing low hydrate concentrations. The extremely small exothermic response observed in the 100–200°C range suggests that only a small amount of water was available. The progressive increase in exothermic response above 200°C is consistent with curve d in Fig. 1. As shown by curves b and d, the oxidation rates at 90°C and 300°C are comparable and similar exothermic responses are indicated by DTA analysis. The magnitude of the exotherm near 300°C is consistent with the ignition and self-sustained oxidation

of the metal. Appearance of exotherms near 150°C and 300°C in the middle curve of Fig. 2 suggests that a substantial hydrate concentration in the salt was exceeded by the metal concentration.

Exothermic behavior of pyrochemical salts is controlled by several factors, including the concentrations of plutonium and water, a decreasing rate of the Pu + H<sub>2</sub>O reaction between 150° and 200°C and inability of the chemical system to consistently enter a kinetic regime of self-sustained oxidation of available metal. The last factor is cited because, as indicated by appearance of exothermic behavior during repetition of the DTA test, oxidation was incomplete in about 30% of the tests with large initial exotherms. Incomplete oxidation of metal by the Pu + H<sub>2</sub>O reaction is consistent with kinetic behavior of that reaction, but failure of exothermic events near 300°C to consistently initiate self-sustained oxidation is less readily explained. Although reaction of unalloyed metal is slowed by a decrease of 10<sup>2</sup> in the oxidation rate near 400°C [21], recovery of the rate is facilitated by the steep temperature dependence of curve g in Fig. 1. Occurrence of self-sustained oxidation near 300°C is demonstrated by complete oxidation during most tests, but is apparently prevented in some cases.

Incomplete oxidation of metal during the high exothermic reaction near 300°C is consistent with fusion of the salt matrix around the metal. Transport of oxidant through fissures or via diffusion depends on the presence of a crystalline salt phase. Melting temperatures of likely salt compositions are in the order of 750–800°C. Since temperatures approaching 500°C were measured in a thermocouple well outside the glass specimen tube during DTA analyses, the fusion point was most likely exceeded near particles of reacting metal. Oxidation is expected to ceased as zones of protective molten salt form around reacting metal particles.

DTA results for salt residues show a spectrum of behavior consistent with the diverse nature of those materials. The thermal response depends on many variables and the unpredictable behavior seen in Fig. 2 is small compared to that encountered during this study. DTA results could not be consistently reproduced in duplicate analyses and are not suitable for assessing the pyrophoric potential of salt residues. However, the results establish an experimental basis for the development of the thermal model for salt residues by showing that the most reactive salts react exothermically at temperatures as low as 90°C, by suggesting participation of water during the reaction at 90–200°C and by indicating ignition of self-sustained oxidation near 300°C.

## 6. Conceptual models for plutonium ignition

Although DTA results indicate that self-sustained oxidation of plutonium in salt residues does not occur in

the temperature range of interest, the possibility of autothermic reaction cannot be excluded. The need to establish a more reliable basis for assessing the pyrophoric potential of residues is addressed by developing thermal models to describe the reactivity of massive metal and plutonium-containing salt residues.

Dependence of plutonium ignition on heating rate and the likelihood of having salt residues exposed to elevated temperatures for extended periods of time suggest that thermal behavior is best described by definition of the static ignition point. At a fixed temperature, the autothermic condition required for ignition exists only if the rate of heat generation by the oxidation of metal exceeds the rate of heat loss by convection and radiation. The temperature at which these rates become equal is mathematically tractable [22] and provides a conservative estimate of the point above which self-sustained reaction is possible.

The models for predicting ignition characteristics of massive metal and salt residues are based on important assumptions consistent with experimentally defined behavior of the salt residues. Oxidation of unalloyed plutonium metal by oxygen or water is assumed to be the only source of chemical heat generation by the residue. Although alloyed plutonium may be present in some residues, it has a significantly lower oxidation rate than unalloyed metal at temperatures below 400°C [8] and is not the most reactive metallurgical form. Since experimental data show that oxidation of the metal particles in the residues exceeds 5 μm [6], heat generation is correctly described by kinetic data for temperature-dependent oxidation during the constant-rate linear stage.

Expression of linear oxidation rates [7] in linear form facilitates the use of kinetic data in model. The area-normalized rate of oxygen consumption ( $\dot{m}$ ) is described by the general equation

$$\dot{m} = A \exp(-E_a/R_g T) = A \exp(-B/T). \quad (3)$$

The activation energy for oxidation indicated by  $E_a$ . Other symbols and the values of  $A$  and  $B$  for dry or moisture-independent regimes and for moisture-dependent condition (27 mbar or 85% relative humidity at 25°C) adopted for this study are given in Table 1. The relationships of rate equations for these conditions to the transition region characterized by decreasing oxidation rate with increasing temperature are shown in Fig. 3. As indicated by the horizontal dotted line, the rate at 90°C in moist air equals that observed at 300°C in the moisture-independent regime. This relationship is of particular interest because 90°C is the lowest point at which exothermic behavior is indicated by DTA experiments.

The potential for plutonium pyrophoricity is constrained by the rate decrease in the transition region. Oxidation rates are confined to the curve for the

Table 1

Constants and parameters used in quantitative thermal models for ignition of plutonium and plutonium-containing salt residues

Type of parameter	Definition	Symbol	Value	Units
Constants	Stefan–Boltzmann constant	$\sigma$	$5.67 \times 10^{-8}$	W/m <sup>2</sup> K <sup>4</sup>
	Emissivity of oxidized Pu surface	$\varepsilon$	0.8	–
	Gravitational constant	$g$	9.8	m/s <sup>2</sup>
	Gas constant	$R_g$	8.314	J/mol K
	Kinematic viscosity of air	$\nu$	$1.6 \times 10^{-5}$	m <sup>2</sup> /s
	Ambient thermal conductivity of air	$k$	0.024–0.046 <sup>a</sup>	W/m K
	Heat of Pu oxidation	$\Delta H^o$	$3.3 \times 10^7$	J/kg O <sub>2</sub>
	Atmospheric O <sub>2</sub> mass fraction	$Y_\infty$	0.23	–
	Density of unalloyed Pu	$\rho_m$	1900	kg/m <sup>3</sup>
	Density of atmospheric air	$\rho_g$	1.0	kg/m <sup>3</sup>
	Density of inert salt	$\rho_i$	2000	kg/m <sup>3</sup>
	Binary diffusion coeff. for atm. air	$D$	$1.8 \times 10^5$	m <sup>2</sup> /s
	Pre-exponential rate constant	$A$		kg O <sub>2</sub> /m <sup>2</sup> s
	moisture-independent/dry regime			146
	moisture-dependent regime			$3.35 \times 10^{12}$
Activation temperature		$B$		K
	moisture-independent/dry regime		9010	
	moisture-dependent regime		14 540	
Variables	Convective heat transfer coefficient	$h$	–	W/m K
	Porosity of particles or residue	$\phi$	–	–
	Rate of oxygen consumption	$\dot{m}$	–	kg O <sub>2</sub> /m <sup>2</sup> s
	Thickness of particle layer	$L$	–	m
	Diameter of Pu particle	$d_m$	–	m
	Oxidizing Pu area per unit volume	$a_m$	–	m <sup>2</sup> /m <sup>3</sup>
	Area of oxidizing Pu	$A_o$	–	m <sup>2</sup>
	Heat transfer area	$A_h$	–	m <sup>2</sup>
	Temperature of Pu	$T$	–	K
	Temperature of surroundings	$T_o$	–	K

<sup>a</sup> Values of  $k$  used in these calculations are in this range; the value used depends on specific conditions.

transition region and must decrease with increasing temperature over the 110–200°C range as shown in Fig. 3. The oxidation rate at 200°C in the moisture-independent regime equals that at 65°C in the moisture-dependent regime. The isothermal ignition temperature defined by equal rates of heat production and loss must be satisfied in both oxidation regimes. If the oxidation rate at 65°C in humid air is insufficient for ignition, then generation of heat at the same rate in dry air is also insufficient. Since exothermic behavior is not observed for salt residues below 65°C in moist conditions, auto-thermic reaction can only occur above 200°C, a temperature consistent with DTA data.

Formulation of an ignition model for massive plutonium is based on the concept that heat accumulates in a reacting chemical system if the rate of heat generation is greater than the rate of heat loss to the surroundings, the fundamental premise of the Semenov model for thermal ignition [22]. Assumptions of the model are that heat generation follows an Arrhenius dependence on temperature and that convective heat transfer to the surrounding air is proportional to the difference in temperatures of the reactant ( $T$ ) and the surroundings ( $T_o$ ). That temperature difference ( $T - T_o$ ) is a distinct

step characterized by a low Biot number, a condition that is satisfied if the reactant is metallic and surrounded by air. The model is used to calculate the temperature above which heat accumulates in the system. Use of the symbol  $T_o$  distinguishes the static ignition temperature from the dynamic ignition temperature indicated by  $T_i$ . Whereas  $T_o$  describes a condition in which heat is generated only within the system,  $T_i$  is the ignition point observed when additional heat flows into the system from an external source.

Modeling of ignition behavior in a system containing plutonium particles is inherently complex because the rate of heat generation is strongly dependent on metal surface area. For massive pieces of metal, the areas for loss of heat ( $A_h$ ) and heat generation by oxidation ( $A_o$ ) are equal. However, as shown by the sketch in Fig. 4,  $A_h$  for a collection of metal particles is determined by the confinement geometry, whereas the inherently larger value of  $A_o$  depends on the depth of confinement ( $L$ ), the particle diameter ( $d_m$ ) and the packing of the particles as defined by the porosity ( $\phi$ ).  $T_o$  for ignition of high-surface-area plutonium in air is calculated using a relationship based on the steady-state condition of the Semenov model and a value of  $A_h/A_o$  ratio derived from



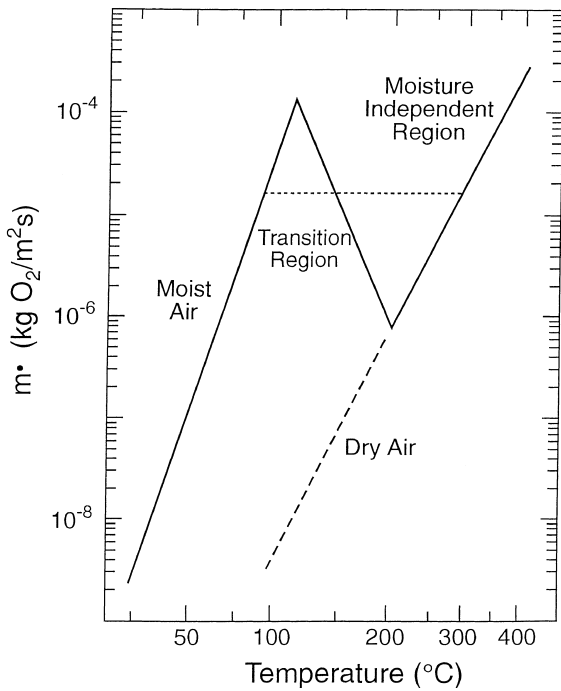


Fig. 3. Rate-temperature relationships for relevant kinetic regimes of plutonium oxidation. The partial pressure of water in moist air is 27 mbar.

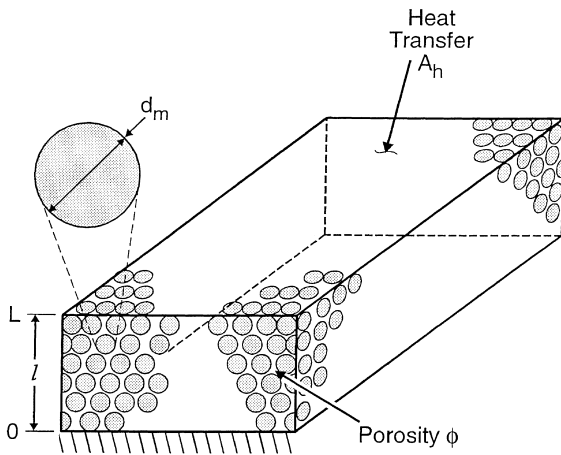


Fig. 4. Schematic representation of a layer formed by randomly packed spherical particles.

experimental data for oxidation and ignition of plutonium chips and powder.

Extension of the model to describe thermal behavior of metal particles embedded in salt is complex because  $T_o$  cannot be calculated directly. Properties required for initiation of self-sustained reaction of plutonium-containing salt in dry air at 300°C are compared with those

at the 90°C onset of thermal response in humid conditions. Characteristics of the salt are similar to those shown in Fig. 4, but metal particles are dispersed throughout a salt matrix and occupy a small volume fraction of the solid. The oxidation rate is determined by the effective porosity  $\phi$  of the salt and the active oxidation area ( $a_m$ ) of metal particles. A single relationship incorporating the heat-balance constraint of the Semenov model and diffusion of oxidant through the salt combines  $a_m$  and  $\phi$  into a single unknown parameter ( $a_m\phi$ ) that defines the minimum surface area-porosity product required for ignition. Ignition is favored by large values of  $a_m\phi$  because the rate of heat generation is increased by a high surface area and a high salt porosity. Oxidation of salt-embedded metal in the moisture-independent regime at 300°C is sufficient for ignition and the value of  $a_m\phi$  required for self-sustained reaction is calculated using kinetic data for oxidation in dry air. In the same way, the value of  $a_m\phi$  is calculated for the reaction in humid air at 90°C. Self-sustained reaction is expected at 90°C if  $a_m\phi$  equals or exceeds that for reaction at 300°C.

### 7. A quantitative ignition model for plutonium

The heat-balance condition for equal rates of heat loss and heat generation in a reacting chemical system such as oxidation of plutonium metal is given by Eq. (4):

$$A_h[h(T - T_o) + \epsilon\sigma(T^4 - T_o^4)] = A_o\Delta H^\circ A e^{B/T}. \quad (4)$$

Constants and variables used in this equation are defined in Table 1. The area-dependent expression for heat loss includes terms for heat dissipation from the surface by convection and radiation. The convective heat transfer coefficient is given by Eq. (5) [23]:

$$h = 0.15k[g(T - T_o)/T_o v^2]^{1/3}. \quad (5)$$

The area-dependent term for heat generation by oxidation of the metal surface is determined by the heat of reaction and the temperature-dependent oxidation rate.

The static ignition point of plutonium is defined by determining  $T_o$  for the steady-state condition at which the rates of heat loss and heat gain are equal. Eq. (4) is simplified for large pieces of metal because  $A_h$  and  $A_o$  are equal and cancel. Solution of the equation for  $T_o$  is also facilitated by using a relationship between the excess temperature ( $T - T_o$ ) and the activation temperature ( $B$ ) [22]:

$$T - T_o = T_o^2/B. \quad (6)$$

Use of physical constants and values of  $A$  and  $B$  for the moisture-independent regime from Table 1,  $k=0.046$  W/m K and Eqs. (4)–(6) yields a  $T_o$  of 570 K.

The predicted value of  $T_o$  of about 300°C for massive plutonium is in remarkably good agreement with results of static ignition measurements [17]. Specimens ignited at 375°C during constant-temperature experiments, but oxidized without ignition at 350°C. Ignition is impossible at  $T_o$  and is unlikely at slightly higher temperatures because the metal completely oxidizes before heat accumulation is indicated by increasing temperature.

As described in the discussion of conceptual approach, calculation of  $T_o$  for chips and powders is complex because  $A_h$  and  $A_o$  are not equal for the layer of particles in Fig. 4. The rate of heat generation increases sharply as  $d_m$  decreases because of the higher metal surface area. If the small temperature gradient existing in a shallow layer of Pu powder is ignored, the energy balance relationship is described by Eq. (4). Since the value of  $A_o$  is unknown, the  $A_h/A_o$  ratio for a typical specimen of metal particles is estimated using Eqs. (4)–(6),  $k=0.032$  W/m K, data for moisture-independent oxidation in Table 1 and  $T_o = 373$  K. This temperature is selected because it is the lowest ignition point observed during dynamic measurements with oxide coated metal fines [15]. The calculation yields an  $A_h/A_o$  ratio of  $1.6 \times 10^{-3}$ , the ratio required for ignition.

The ignition point of plutonium powder in moist air is estimated using the calculated  $A_h/A_o$  ratio. This exercise involves data from Table 1,  $k=0.024$  W/m K, and Eqs. (4)–(6). The derived  $T_o$  value of 292 K (19°C) indicates that plutonium chips and powder may spontaneously ignite at room temperature. This result is placed in perspective by remembering that  $T_o$  defines the point above which ignition is possible. Static ignition points measured for massive plutonium are 50–75°C greater than the calculated value and comparable sluggishness in the rate of heat accumulation for powdered metal suggest that the observed ignition temperature is probably near 100°C. Measurements showing ignition points somewhat greater than 100°C for high-surface-area metal [15] would have been impossible if finely divided Pu spontaneously ignites upon exposure to air at room temperature. The result emphasizes the need for appropriate caution in handling plutonium chips and powders, especially if humidity is high and the particles are not covered by oxide.

Further examination of the results for powdered metal is merited because the calculation was made with the assumption that sufficient oxygen was available to support oxidation. This issue is examined analytically by comparing the rate at which oxygen diffuses through the powder to the metal surface with the rate at which it is consumed. Sufficient oxygen is available when the rates are equal:

$$\rho_g \phi A_h D (dY/dl) = A_o A e^{-B/T}. \quad (7)$$

The quantity of material diffusing is proportional to the area and the concentration gradient in the direction of

diffusion. Constants and parameters are defined in Table 1. As shown in Fig. 4,  $l$  is the distance from the bottom of the particle layer of thickness  $L$ . At the onset of diffusion limitation, the mass fraction of oxygen ( $Y$ ) varies from zero at  $l = 0$  to  $l = Y_\infty$  at  $l = L$ . The condition for diffusion of  $O_2$  at a sufficient rate is derived by integration of Eq. (7) and evaluation at the boundary conditions:

$$\rho_g \phi A_h D Y_\infty / L A_o A e^{-B/T} \geq 1. \quad (8)$$

Evaluation of Eq (8) for  $L = 10$  mm and  $A_h/A_o = 1.6 \times 10^{-3}$  using physical constants and values of  $A$  and  $B$  for the moisture-independent regime from Table 1 yields a value of 22. Since this result is greater than 1, the oxidation rate of a typical layer of plutonium metal particles is not diffusion limited.

## 8. A quantitative ignition model for plutonium-containing salt residues

Plutonium particles are randomly distributed in a matrix of an inert porous solid that restricts access of oxidant to the metal surfaces. Consideration of oxygen diffusion to those surfaces is necessary in addition to the steady-state balance between heat generation and heat loss. Formulation of a quantitative model is facilitated by defining the surface area of spherical particles per unit volume of porous material ( $a_m$ ):

$$a_m = [6(1 - \phi)]/d_m [1 + \rho_m/\rho_i(1/Y_m - 1)]. \quad (9)$$

This area is also defined by  $a_m = A_o/LA_h$  and substitution into Eq (8) gives a relationship that describes the process of oxygen diffusion and surface reaction within an isothermal porous layer. The heat-balance constraint of the Semenov model is introduced and, for convenience, the heat transfer coefficient is replaced by a conservative linear form ( $h' = 4\epsilon\sigma T_o^3$ ) that only includes radiative losses. The resulting relationship defines the conditions necessary for ignition of reactive spheres in a porous matrix subject to a diffusion-controlled condition:

$$[B\Delta H^o e^{-B/2T}/h'T_o^2][n\rho_g a_m \phi D Y_\infty A]^{1/2} \geq 1. \quad (10)$$

Behavior of material in layer configuration is described by use of  $n = 1$  and a spherical configuration by use of  $n = 2/3$ .

Direct evaluation of Eq. (10) requires information about both the porosity of the matrix and the surface area of the metal particles. A modified approach is employed because neither  $a_m$  nor  $\phi$  is known. Rearrangement of Eq. (10) for a layer configuration, replacement of the exponent  $B/2T$  by  $1/2(B/T_o - 1)$  and substitution for  $h'$  yields a relationship that allows  $a_m \phi$  to be calculated from experimental data:

$$[B\Delta H^{\circ} e^{-1/2(B/T_0-1)}/4\varepsilon\sigma T_0^5][\rho_g D Y_{\infty} A]^{1/2} [a_m \phi]^{1/2} \geq 1. \quad (11)$$

Limiting values of  $a_m \phi$  necessary for ignition of plutonium in the salt residues are derived from kinetic data for oxidation of the metal in the moisture-independent regime. DTA results suggest that  $T_0$  is near 300°C. A limiting value of  $a_m \phi = 6$  l/m is obtained for  $T_0 = 573$  K using Eq. (11), as well as physical constants and values of  $A$  and  $B$  for the moisture-independent regime from Table 1. Parallel calculations for  $T_0 = 473$  K give a value of 24 l/m for  $a_m \phi$ .

The potential for ignition of the most reactive salt residues is assessed by calculating  $a_m \phi$  at 90°C in moist air, the lowest point at which a thermal response was observed during DTA measurements. For self-sustained reaction to occur, the value of  $a_m \phi$  must equal or exceed 6 l/m. Repetition of the calculation using Eq. (11),  $T_m = 363$  K, and values of  $A$  and  $B$  for the moisture-dependent regime from Table 1 yield an  $a_m \phi$  value of 0.053 l/m. The value is 450 times less than required for ignition and leads to the decisive conclusion that an ignition potential does not exist for the most reactive salt residues characterized by onset of exothermic reaction at 90°C.

The model is abstract, but interpretation of the results is facilitated using data from a recent characterization of plutonium-containing salts [6]. Hydrolysis measurements show that metal is present at about 10 mass percentage primarily as spherical particles with diameters near 1 mm. In combination with the derived value of  $a_m \phi$ , the calculated particle concentration (20 spheres/cm<sup>3</sup>) and  $a_m$  (65 l/m) for a typical ER residue yield effective salt porosities in the 10–40% range for the ignition condition and 0.06% for the salt at 90°C. The difference in these porosities suggests that conditions for ignition are not satisfied primarily because the diffusion rate of oxidant through the salt matrix is limited. Porosity is an intensive salt property that makes pyrophoric potential independent of salt quantity and configuration.

Identification of diffusion as the rate-limiting factor is important in considering possible effects of pyrophoric compounds and high plutonium concentrations on the ignition behavior of salt residues. Hydride is a catalyst for rapid oxidation of unalloyed and alloyed metal [8] and the lower oxide participates in self-sustained oxidation of plutonium [11]. Hydrogen is present in salt residues as water and restricted access of oxygen to dioxide-coated plutonium promotes reduction of PuO<sub>2</sub> to Pu<sub>2</sub>O<sub>3</sub>. Although the presence of pyrophoric compounds is possible, freshly ground salt residues were routinely exposed to air at room temperature without indication of exothermic reaction. The likelihood of a rapid exothermic response is not increased by presence of pyrophoric compounds in the residues because reaction rates

of metal and reactive compounds are equally limited by the rate at which oxidant is able to penetrate the salt. Since heats of reaction per mole of oxygen are lower for plutonium compounds than for metal, exotherms for salts with pyrophoric compounds cannot exceed those observed during DTA measurements. Likewise, a high Pu concentration in the salt cannot cause the temperature for onset of oxidation to decrease below 90°C because the rates of reaction and heat generation are controlled by the diffusion rate of oxidant through the salt.

## 9. Conclusions

DTA results show large variations in the thermal response of plutonium-containing pyrochemical salt residues. Results indicate that negligibly small amounts of plutonium are present in approximately 70% of the residue samples. Exotherms observed for the remaining residue fraction are of two types depending on the amount of water present as hydrates in the salt residue. A substantial exothermic response observed in the 90–200°C range is associated with oxidation of the metal by water, but runaway reaction is apparently prevented by a sharp decrease in the Pu + H<sub>2</sub>O reaction rate at 110–200°C [7]. Large exotherms observed near 300°C are consistent with ignition and self-sustained reaction of metal in the residues. Failure to observe self-sustained reaction below 300°C is an inadequate basis for concluding that pyrophoric potential is absent at low temperatures.

Utility of the heat-balance model in defining kinetic parameters and ignition behavior of metals is demonstrated by accurate prediction of a 300°C static ignition point for plutonium. Extension of the modeling capability to characterize relevant properties of the most reactive salt residues show that ignition is precluded at 90°C by the combined effect of metal surface area and salt porosity. Results conclusively show that ambient temperatures well in excess of 200°C are required for ignition and indicate that the oxidation rate is controlled by slow diffusion of oxidant in the low-porosity salt. The rates of oxidation and heat production are determined by this intensive property of the salt and the temperature for onset of exothermic reaction is independent of salt quantity.

Static ignition points derived via the heat-balance model are inherently lower than experimental values and provide a conservative estimate because heat accumulation is slow at temperatures near the point of heat-balance. Observed and calculated thermal behavior of the salt residues is consistent with the presence of metal particles having diameters on the order of 1 mm [6], a size that is expected to ignite only at temperatures above 200°C [15].

Results of this study demonstrate the effectiveness of modeling techniques in predicting ignition behavior of plutonium-containing materials. Potential exists for applying similar techniques in evaluating combustion characteristics of other residues generated by processing and fabrication of nuclear materials.

## References

- [1] Plutonium vulnerability management plan, US Department of Energy Report DOE/EM-0199, 1995.
- [2] W.S. Moser, J.D. Navatil, *J. Less-Common Met.* 100 (1984) 171.
- [3] Plutonium working group report on environmental, safety and health vulnerabilities associated with the Department's plutonium storage, US Department of Energy Report DOE/EH-0415, 1994.
- [4] Plutonium storage safety at Major Department of Energy Facilities, Defense Nuclear Facilities Safety Board, Technical Report DNFSB/TECH-1, 1994.
- [5] Transfer and Storage of Plutonium for Fire Safety, Rocky Flats Environmental Technology Site Document PRO-W89-HSP-31.11, Revision 2, 1999.
- [6] J.M. Haschke, A.G. Phillips, *J. Nucl. Mater.* 277 (1999) 175.
- [7] J.M. Haschke, T.H. Allen, J.L. Stakebake, *J. Alloys Compd.* 243 (1996) 23.
- [8] J.M. Haschke, T.H. Allen, J.C. Martz, *J. Alloys Compounds* 271–273 (1998) 211.
- [9] J.L. Stakebake, *J. Less-Common Met.* 123 (1986) 185.
- [10] J.L. Stakebake, Characterization of the plutonium–water reaction: reaction kinetics between 200°C and 350°C, in: L.R. Morss, J. Fuger (Eds.), *Transuranium Elements: A Half Century*, American Chemical Society, Washington, 1992, p. 251.
- [11] J.C. Martz, J.M. Haschke, J.L. Stakebake, *J. Nucl. Mater.* 210 (1994) 130.
- [12] J.M. Haschke, J.C. Martz, *J. Alloys Compounds* 266 (1998) 81.
- [13] J.M. Haschke, L.A. Morales, T.H. Allen, *Science* 287 (2000) 285.
- [14] J.G. Schnizlein, D.K. Fischer, *J. Electrochem. Soc.* 115 (1968) 462.
- [15] J.L. Stakebake, Plutonium pyrophoricity, Report RFP-4517, EG&G Rocky Flats, Inc., Golden, CO, June 1992.
- [16] K. Terada, R.L. Meisle, M.R. Dringman, *J. Nucl. Mater.* 30 (1969) 340.
- [17] S.H. Pitts Jr., *Nucl. Safety* 9 (1968) 112.
- [18] J.L. Stakebake, D.T. Larson, J.M. Haschke, *J. Alloys Compd.* 202 (1993) 251.
- [19] T.H. Allen, J.M. Haschke, Hydride-catalyzed corrosion of plutonium by air: initiation by plutonium nonoxide monohydride, Los Alamos National Laboratory Report LA-13462-MS, 1998.
- [20] F. Trusell, H. Diehl, *Anal. Chem.* 35 (1963) 674.
- [21] J.G. Schnizlein, D.K. Fischer, *J. Electrochem. Soc.* 114 (1967) 23.
- [22] J.C. Jones, *Combustion Science: Principles and Practice*, Millennium Books, Sydney, 1993.
- [23] M. El-Rabi, M.K. El-Redi, *Int. J. Heat Mass Transfer* 19 (1996) 1399.