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Hydride-Catalyzed Corrosion of Plutonium by Air: Initiation by Plutonium Monoxide Monohydride

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ABSTRACT

Chemistry and kinetics of air reactions with plutonium monoxide monohydride (PuOH) and with mixtures of the oxide hydride and plutonium metal are defined by results of pressure-volume-temperature (PVT) measurements. Tests with specimens prepared by total and partial corrosion of plutonium in 0.05 M sodium chloride solution show that reaction of residual water continues to generate H_2 after liquid water is removed by evacuation. Rapid exposure of PuOH to air at room temperature does not produce a detectable reaction, but similar exposure of a partially corroded metal sample containing Pu and PuOH results in hydride (PuH_x)-catalyzed corrosion of the residual Pu. Kinetics of the first-order reaction resulting in formation of the PuH_x catalyst and of the indiscriminate reaction of N_2 and O_2 with plutonium metal are defined. The rate of the catalyzed Pu+air reaction is independent of temperature ($E_a = 0$), varies as the square of air pressure, and equals 0.78 ± 0.03 g Pu/cm^2 min in air at one atmosphere. The absence of pyrophoric behavior for PuOH and differences in the reactivities of PuOH and PuOH+Pu mixtures are attributed to kinetic control by gaseous reaction products. Thermodynamic properties of the oxide hydride are estimated, particle size distributions of corrosion products are presented, and potential hazards associated with products formed by aqueous corrosion of plutonium are discussed.

Introduction

Interest in the corrosion chemistry of plutonium is promoted by the need to assess dispersal hazards associated with abnormal incidents involving metal and alloys. As noted in recent reports on the reaction kinetics of plutonium in air [1-4], metallic forms are not inherently dispersible. Corrosion in air is the most likely pathway by which metal is transformed into a dispersible material. The corrosion rate and the particle-size distribution of plutonium-containing product are essential parameters because they establish the mass of metal at risk during an incident and the fraction of that material with particle sizes in the respirable (<3 μm geometric diameter) and dispersible (<10 to 30 μm geometric diameter) ranges.

Accurate risk assessment requires that conditions of the incident are specified and considered in defining the source term for dispersal. Kinetic data for oxidation of plutonium in air show that corrosion rates vary by factors of 10^6-10^8, depending on temperature, humidity, and alloying [4]. Dispersible fractions vary by as much as 10^4. The situation is further complicated because the temperature dependencies of corrosion rate and size distribution are such that their effects on the source term tend to cancel. The amount of material at risk after a given time period increases sharply with temperature, but the respirable and dispersible fractions decrease.

Kinetic results presented in a recent report [4] show that a fire or other external heat source is not necessary for rapid corrosion of plutonium by air. Plutonium hydride (PuH_x, $1.9 < x < 3.0$) is a pyrophoric compound that reacts readily with oxygen at room temperature. Exposure of hydride-coated metal to air at room temperature often results in a rapid reaction that is more than 10^{10} faster than normal corrosion in air. Hydrogen produced by that reaction is not released as H_2, but reacts with available metal to form additional PuH_x. The accompanying temperature increase is sufficient to initiate the reaction of hydride with nitrogen. Corrosion is catalyzed as hydride progressively advances into the metal ahead of the PuH_x+air reaction. O_2 and N_2 react indiscriminately during the process which eliminates all kinetic effects of alloying and humidity on the corrosion of plutonium in air. The inherent rate of the catalyzed reaction is four to five times faster than the constant rate for autothermic (self-sustained) reaction of oxygen at temperatures above the 500 ± 25°C ignition point of plutonium metal and alloys [5]. Although surface hydride is essential for catalytic reaction, the hydrogen source may be unanticipated and includes radiolysis of plastics, elastomers, oils, and other organic compounds, as well as chemical reactions involving water [6].

Rapid corrosion of plutonium in air may also be initiated by reactive materials other than hydride. The pyrophoric Pu_2O_3 layer formed by auto-reduction of PuO_2 on the metal surface is capable of driving the temperature above the ignition point. Plutonium monoxide monohydride (PuOH), the hydridic compound formed by reaction of metal with near-neutral water or salt solution [7,8,9] is identified as a potential initiator of rapid reaction with air [10]. Interest in the oxide hydride is increased because of the potential for its formation in process operations and in abnormal incidents. PuOH has recently been identified as the product formed by salt-catalyzed corrosion of plutonium in glovebox atmospheres containing hydrogen chloride and water vapors [11].

The present study was initiated in an effort to define the chemical behavior of plutonium monoxide monohydride in air and to assess its potential as an initiator of rapid plutonium corrosion. Definition of kinetics for PuOH-coated plutonium in air is augmented by results of similar measurements for PuH_x-coated metal. Thermochemical properties of the oxide hydride are estimated, pyrophoric tendencies are addressed, and safety issues are examined.

Experimental Methods

Chemical and kinetic behavior of oxide hydride+metal systems were investigated using PVT (pressure-volume-temperature) methods. The stainless steel PVT system was designed for pressure and vacuum operations and consisted of a reaction vessel (49.46 cm^3), a gas manifold (31.97 cm^3) and an auxiliary volume (162.50 cm^3). Thermocouples and absolute pressure transducers were positioned in the system to permit independent measurement of T and P in the three volumes. Tests were conducted with samples (11.2 ± 0.2 g, 47 ± 1 mmol) of weapons-grade delta-phase Ga alloy with geometric surface areas of 7.0 cm^2. Product and residual gasses were analyzed by mass spectrometry.

Test specimens of PuOH+Pu were prepared by partial corrosion of alloy samples in 0.05 M NaCl solution. Accurately weighed metal samples were placed in the reactor and submerged in salt water at 23.5 ± 1.5°C. The pressure in the sealed vessel was measured as a function of time (t) to determine the extent of corrosion from formation of oxide hydride according to Equation (1) [7,8, 9].

$$\mathrm{Pu\ (s) + H_2O\ (l) \dashrightarrow PuOH\ (s) + 1/2\ H_2\ (g)} \quad . \qquad (1)$$

Earlier work shows that the corrosion reaction is stopped by evacuation of the reactor to remove liquid water and dry the product [7]. Two evacuation procedures provided different levels of dryness. In one case, the product was exposed to dynamic vacuum for three days through the low-conductance PVT manifold. The reactor was then closed and monitored for pressure change over a period of several weeks. In the second procedure, the reaction vessel was closed, transferred to a high-conductance vacuum system with an ultimate pressure capability of 10^{-7} torr, and evacuated for 45-days prior to pressure monitoring.

Pyrophoricity of PuOH and chemical behavior of the PuOH+Pu system were investigated via PVT experiments in which samples were rapidly exposed to air. The gas manifold and auxiliary volume were appropriately pressurized with dry air so that expansion of the gas into the evacuated reaction vessel gave an initial pressure of 14.7 psia (1.01 bar) in the total system and provided sufficient air to consume available Pu. Gas pressure and temperature were measured as a function of time after the expansion. Parallel air-exposure tests conducted with hydride-coated plutonium specimens are described in a prior publication [4].

Rates of reaction were derived from the experimental P-T-t data. Ideal gas behavior was assumed and results were corrected for changes in temperature during the experiment and for thermal gradients within the system. R, the corrosion rate of plutonium by air, is reported in units of mmol air/cm_2 min or g Pu/cm^2 min.

Results and Discussion

Reaction of Plutonium with Water

Test specimens were successfully prepared by corrosion of the metal in sodium chloride solution. Reaction of the alloy according to Equation 1 occurred at a constant rate of 1.9 ± 0.1 mg Pu/cm^2 h (4.0 μm H_2/cm^2 h), a value that is in excellent agreement with the rate (2.0 mg Pu/cm^2 h) predicted by the empirical correlation of corrosion rate with salt concentration [9]. Based on Equation (1) and the amounts of hydrogen produced, approximately half of each plutonium specimen was transformed to PuOH.

Termination of the corrosion reaction by drying in dynamic vacuum was surprisingly difficult and was not achieved using the low-conductance PVT system. Evacuation readily removed liquid water from the sample, as indicated by failure of the residual pressure to immediately attain the 23 torr equilibrium vapor pressure of water after the reaction vessel was closed. However, the presence of residual moisture was shown by continued generation of hydrogen in the closed vessel. Over a period of weeks, the H_2 pressure reached 100 psia (6.9 bar), a value corresponding to complete transformation of the residual plutonium to PuOH and partial reaction of that product to form a second oxide hydride according to Equation (2) [7,8]:

$$\text{PuOH (s)} + 2/7\ H_2O\ \text{(adsorbed)} \dashrightarrow 1/7\ Pu_7O_9H_3\ \text{(s)} + 4/7\ H_2\ \text{(g)}\ . \qquad (2)$$

This result suggests that substantial moisture remained in the solid mass formed by coalescence of fine PuOH particles (66 Å average diameter) during removal of liquid water [7] and that chemical reaction of residual moisture is not a suitable method for drying the corrosion product. Although formation of PuO_2 and H_2 by reaction of Pu with water vapor offers an alternative pathway for continuing pressure generation [1], occurrence of that process is discounted because the maximum rate for that reaction at 25°C accounts for less than 3% of the observed hydrogen.

Corrosion of metal by water was stopped by evacuating the reaction vessel with a high-conductance pumping system. Successful drying of the product was demonstrated by the absence of continued H_2 generation in the closed vessel. The final product used in the subsequent pyrophoricity test was 60 mol % PuOH and 40 mol % Pu.

Reaction of PuOH with Air

The chemical behavior of the oxide hydride in air is indicated by the results of air exposure tests. The absence of reaction is evident because neither a loss of pressure nor an increase in temperature was detected upon expansion of air into the evacuated reactor. This result is consistent with earlier reports that dried PuOH samples were handled in air without indication of reaction [7] and suggests that the oxide hydride is not pyrophoric.

A measure of uncertainty about the absence of pyrophoricity arises because an electrical outage shut down the pumping system during the second day of evacuation and resulted in gradual exposure of the corrosion product to 0.3 mmol of O_2 as the PVT system slowly filled with air. Although the PuOH may have been passivated by formation of surface oxide, approximately 40% of the product formed after the outage and was active during the pyrophoricity test.

Reaction of PuOH-Coated Pu with Air

As shown by the P-T and T-t curves in Figure 1, rapid air exposure of a specimen containing 60% PuOH and 40% Pu resulted in complete reaction of the residual metal within five to six minutes. Mass spectrometric analysis of residual gases showed that N_2 and O_2 were consumed indiscriminately without formation of H_2. The time scale of the reaction and retention of hydrogen in the solid product corresponds with results for rapid exposure of PuH_x-coated plutonium to air [4]. The amount of air consumed is consistent with the following reactions of nitrogen and oxygen to form compounds of Pu(III).

$$Pu\ (s) + 1/2\ N_2\ (g) \dashrightarrow PuN\ (s)\ . \tag{3}$$

$$Pu\ (s) + 3/4\ O_2\ (g) \dashrightarrow 1/2\ Pu_2O_3\ (s)\ . \tag{4}$$

Instead of discreet oxide and nitride phases, the product may be a plutonium oxide nitride formed by concurrent reaction of nitrogen and oxygen at their ratio (3.71 N_2:1 O_2) in air. The net reaction consumes 1.86 moles of Pu per mole of air. Use of this factor and PVT data defining the moles of air consumed shows that the proposed reaction accounts for 99% of the residual Pu in the test specimen.

The shapes of the pressure-time and temperature-time curves in Figure 1 suggest that the PuOH+Pu+air reaction occurs in two stages: (1) PuH_x formation and (2) PuH_x-catalyzed reaction of air. The reaction of oxide hydride during the first stage provides a hydrogen source for forming PuH_x. Hydrogen generation is attributed to oxidation reaction shown by Equation (5).

$$2\ PuOH\ (s) + 1/2\ O_2\ (g) \dashrightarrow Pu_2O_3\ (s) + H_2\ (g)\ . \tag{5}$$

Significant reaction of nitrogen with the oxide hydride is doubtful. Hydride forms as product hydrogen reacts with residual metal according to Equation (6).

$$Pu\ (s) + x/2\ H_2\ (g) \dashrightarrow PuH_x\ (s)\ . \tag{6}$$

During the second stage of reaction, the corrosion of plutonium is catalyzed as pyrophoric hydride moves into the metal ahead of the advancing Pu+air reaction. Examination of corrosion products formed by the catalyzed reaction shows that PuH_x is concentrated in the centers of particles [4]. Formulation of hydride as a variable-composition phase implies that the reaction of air continues after depletion of the metal as additional hydrogen is accommodated by increasing x.

Experimental data are consistent with occurrence of a two-stage corrosion process for the PuOH+Pu system. Comparison of the pressure-time curve in Figure 1 with that for reaction of hydride-coated plutonium with air in Figure 2 suggests that Equations (5) and (6) constitute a distinct kinetic step in which PuH_x catalyst forms on the metal surface. As shown by the slopes of the P-t curves, the maximum rate for reaction of hydride-coated plutonium with air (Figure 2) is observed at zero time, but is delayed by about 0.5 min for the PuOH-coated metal (Figure 1) as hydride is formed. A delay is not observed for hydride-coated metal because the surface is fully active prior to air exposure.

During the initial slow stage of reaction, the rate accelerates exponentially in a manner characteristic of processes involving growth of nucleation sites [12,13]. First-order growth of sites is confirmed by the linear lnR-t relationship defined by open symbols in Figure 3 and the least-squares refinement of the data.

$$\ln R \text{ (R in mmol air/cm}^2\text{/min)} = 4.725\, t - 1.99 \quad . \qquad (7)$$

The filled symbols are included to show that R decreased sharply after reaching a maximum (1.85 mmol air/cm^2 min) at t = 0.52 min, the point at which the metal surface became fully active to catalyzed corrosion by air. The nature of the nucleation sites is uncertain. The rates in Figure 3 may be a direct measure of O_2 consumption at oxide nucleation sites on a PuOH layer covering the metal. Alternatively, the R values may indirectly reflect the growth of hydride sites on the metal surface and a proportionality between the catalytically active area and consumption of air.

Growth of hydride sites during the first-order stage is suggested because similar behavior was encountered during air exposure of specimens containing both spalled hydride particles and metal that was partially coated with PuH_x [4]. In those tests, an initial decrease in total pressure was followed by attainment of a pressure maximum as H_2 was produced by reaction of air with hydride particles. The resulting accumulation of hydrogen in the vessel restricted access of air to the sample and prevented further reaction until the H_2 reacted with residual metal. In some cases, H_2 did not react and further corrosion by air did not occur. If hydrogen reacted, a progressively accelerating pressure decrease was observed during the half-minute period after attainment of the maximum pressure. The appearance of similar kinetic behavior in the PuH_x+Pu and

PuOH+Pu systems prior to onset of rapid corrosion by air suggests that the first-order kinetics defined by Equation (7) describe the growth of catalytic hydride sites on the plutonium surface.

The absence of a pressure maximum in Figure 1 is attributed to physical differences in properties of the PuOH+Pu and PuH_x+Pu systems. Hydride forms as distinct particles that remain physically isolated from the residual metal. Hydrogen produced by reaction of those particles with air accumulates in the gas phase before reacting with residual metal. The fine oxide hydride dries as a porous layer that surrounds the unreacted plutonium. H_2 produced by reaction of oxygen within the PuOH layer is readily available for nucleation and growth of hydride sites on the metal surface and does not accumulate in the gas phase prior to reaction.

Corrosion of plutonium occurs at a rapid rate during the second stage of reaction. The progressively decreasing slope of the pressure curve in Figure 1 indicates that R is sensitive to air pressure (P_a). As P_a decreased from 0.7 to 0.2 bar (10 to 3 psia), the corrosion rate decreased from 1.3 to 0.086 mmol air/cm^2 min. The kinetics of hydride-catalyzed corrosion during the second stage of reaction are described by a general rate equation that includes dependencies on temperature and air pressure.

$$R = k\exp(E_a/R^*T)P_a^n \ . \qquad (8)$$

In addition to the proportionality constant (k), this relationship includes an Arrhenius term determined by the activation energy (E_a), the gas constant (R^*), and temperature (T). Dependence of the corrosion rate on P_a is defined by the pressure exponent (n).

As implied by the mathematical form of Equation (8), the pressure exponent is defined by the slope of lnR-lnP at constant temperature. Kinetic data in Figure 4 show that experimental values are in excellent agreement with the ideal line of $n = 2$. Linear least-squares refinement of the data for air pressures in the 0.2 to 0.7 bar range yields a value of 1.995 for n. This result and observation of a second-order pressure dependence for the hydride-catalyzed corrosion of plutonium at P_a values in the 3 to 5 bar (45 to 60 psia) range [4] imply that the same corrosion mechanism occurs over a wide range of air pressure. The value of $n = 3$ reported for air pressures of 2 to 3 bar [4] is apparently in error and possibly resulted from inadequate correction of experimental pressure data for thermal gradients in the PVT system.

A surprising result of the data evaluation is the apparent absence of a kinetic dependence on T. The gas-phase temperature in the center of the reaction vessel varied from 65 to 175°C during measurement of the data shown in Figure 4. Measurements made during tests at 25°C show temperatures in excess of 500°C near the sample [4]. Although a large change in the temperature of the solid phases occurred during the measurements, lnR-lnP relationship remained linear. Such behavior implies that the effective E_a is zero. This conclusion is consistent with prior observations that R is independent of the initial sample temperature over the 25 to 500°C range [4]. Therefore, the experimental rate equation for hydride-catalyzed corrosion of plutonium at air pressures between 0.2 and 5 bar is

$$R = kP_a^2 . \tag{9}$$

The validity of Equation 9 is established by evaluating the proportionality constant at one atmosphere pressure for all data points in Figure 4. The derived value of k is 1.75 ± 0.07 mmol air/cm^2 atm^2 min.

Occurrence of hydride-catalyzed reaction during exposure of PuOH-coated plutonium to air is verified by the experimental corrosion rate. At one atmosphere pressure, R = k = 0.78 ± 0.03 g Pu/cm^2 min, a result that is in close agreement with an average rate of 0.59 ± 0.08 g Pu/cm^2 min obtained in multiple tests at sub-atmospheric pressures and 25 to 75°C [4]. The hydride-catalyzed reaction initiates at room temperature, increases the corrosion rate of the delta-phase alloy at 25°C by a factor of 10^{10}, and proceeds at a characteristic rate that is four to five times faster than self-sustained oxidation of ignited plutonium at 1000°C [2,4].

The rate of hydride-catalyzed corrosion in air is apparently determined by the participation of nitrogen. In addition to steps involving N_2, possible rate-controlling processes include those with O_2 and those by which hydrogen advances into the metal. The limitation established by steps involving oxygen and hydrogen is indicated by the rate (78 g Pu/cm^2 min) for hydride-catalyzed reaction of O_2 [4]. If N_2 is present, the corrosion rate is reduced a hundredfold.

Thermodynamic Properties of PuOH

The enthalpy and free energy of formation of crystalline monoxide monohydride are estimated using reference data for Pu_2O_3 [14] and PuH_x [15]. Values are derived by summing the enthalpies and free energies per mole of oxygen (-132 and -126 kcal/mol O, respectively) and the corresponding data for hydrogen (-19 and -14 kcal/mol H for x = 2.5, respectively). The values of ΔH°_f and ΔG°_f obtained for PuOH are -151 ± 5 and -140 ± 6 kcal/mol, respectively. The estimated uncertainties in these values include possible errors in the reference data and the method of estimation.

Thermochemical properties of reactions involving PuOH and PuOH+Pu mixtures are estimated using reference data [14,15] and the thermodynamics values derived for the oxide hydride. The estimated enthalpy for reaction of PuOH with O_2 according to Equation (5) is -47 ± 5 kcal/mol of PuOH. ΔH° values for the catalyzed reactions of metal with O_2 and N_2 according to Equations (3) and (4) are -198 ± 3 and -72 ± 2 kcal/mol of Pu, respectively. The enthalpy derived for indiscriminate reaction of Pu with air is -93 ± 3 kcal/mol of Pu.

Thermochemical evaluation of the hydride-catalyzed corrosion process shows that PuN, Pu_2O_3, and PuH_3 are the thermodynamically favored chemical state of the products at the experimental conditions of this study. All N_2 reacts to form PuN, the only nitride phase formed by plutonium. However, on the basis of conventional wisdom, one expects the minimum-free configuration to be achieved by forming PuO_2 and H_2O, not Pu_2O_3 and PuH_3. Consideration must be given to constraints of an experimental configuration that limits access of oxygen to the sample and to the consequences of that restriction on the free energy. Reference data show that the free energies for forming PuO_2 and Pu_2O_3 are -252 and -198 kcal/mol of Pu, respectively [14]. If the supply of plutonium is limited and excess oxygen is present, the minimum energy is achieved by forming PuO_2, the oxide with the highest oxygen content. If the supply of oxygen is limited, the minimum free energy is achieved by distributing oxygen in the configuration with the highest plutonium content. ΔG°_f for PuO_2 and Pu_2O_3 are -126 and -132 kcal/mol of O, respectively, and formation of the sesquioxide is favored by a limited oxygen supply.

Thermodynamic results in Table 1 are calculated for possible reactions of PuOH+Pu mixtures with O_2 [14,15,16]. As shown by the free energy changes per mole of O, Pu_2O_3 and PuH_3 are the favored products if the supply of oxygen is limited. Pu_2O_3, PuN, and PuH_3 are reactive compounds; their exposure to excess oxygen results in formation of PuO_2 and water at rates that are strongly dependent on the specific conditions.

Table 1. Calculated Free Energy Changes for Possible Reactions of PuOH-Coated Metal with O_2.

Reaction	ΔG° (kcal/mol PuOH)	ΔG° (kcal/mol O)
$PuOH + 1/4\ O_2 + 1/3\ Pu \rightarrow 1/2\ Pu_2O_3 + 1/3\ PuH_3$	-62	-124
$PuOH + 1/2\ O_2 + 1/3\ Pu \rightarrow PuO_2 + 1/3\ PuH_3$	-111	-111
$PuOH + 3/4\ O_2 \rightarrow PuO_2 + 1/2\ H_2O$	-126	-84

Pyrophoricity of PuOH

Experimental observations during tests to define oxide hydride reactivity appear inconsistent. The absence of detectable reaction during exposure of PuOH to air indicates that the oxide hydride is unreactive. However, pyrophoric behavior is demonstrated by the initiation of hydride-catalyzed reaction when PuOH-coated plutonium is exposed to air. Accurate assessment of the hazard posed by the aqueous corrosion product is predicated on adequate understanding of these observations. Data related to parameters that determine the pyrophoricity of a material during air exposure are summarized for potentially reactive plutonium compounds in Table 2.

Table 2. Selected Properties of Plutonium Compounds with Potential for Pyrophoric Behavior.

Compound	Reaction Products Formed in Air[a]	ΔH° of Reaction with Air (kcal/mol Pu)	ΔH° of Reaction with Air (kcal/mol Air)	Qualitative Assessment
PuH_2	Pu_2O_3, PuN, PuH_x[b]	-70[c]	-135[c]	pyrophoric
Pu_2O_3	PuO_2, residual N_2	-54	-45	highly reactive
PuOH	Pu_2O_3, H_2, residual N_2	-47	-39	reactive

a. Reaction products are those expected to form if the supply of oxygen is limited.
b. H_2 is produced as x of the PuH_x phase inside a reacting hydride particle approaches 3.
c. ΔH° for PuH_2 describes the indiscriminate reaction of O_2 and N_2 and decreases progressively with decreasing x to minimum values of -56 kcal/mol of Pu and -91 kcal/mol of air.

Evaluation of possible factors related to pyrophoricity suggests that spontaneous ignition and sustained reaction of the oxide hydride in air are largely determined by chemistry and by transport kinetics of the gas phase. As shown in Table 2, gaseous residues and products differ significantly for PuH_2, Pu_2O_3, and PuOH. Reaction of PuH_2 consumes both oxygen and nitrogen and forms only solid product in a process that maintains unobstructed and continuing access of air to the hydride. The Pu_2O_3+air reaction selectively removes O_2 from the reacting air and leaves residual N_2 that restricts access of additional oxygen to the oxide surface. In addition to residual nitrogen, H_2 formed by the PuOH+air reaction further limits access of oxygen to the oxide hydride.

Heat generation must also be considered because reaction rates typically have a strong dependence on temperature. Comparison of the enthalpies of reaction shows that heating is most favorable for the reaction of dihydride. If air is in limited supply, the pyrophoricity of hydride. The PuH_2+air reaction apparently initiates by selective reaction of hydride with oxygen [4]. This reaction provides the thermal source (-159 kcal/mol Pu, -44 kcal/mol air) for heating the hydride above the 230°C point required for initiation of the $Pu+N_2$ reaction [17]. As shown in this study, the ensuing reaction of air is independent of temperature.

Thermal effects are important in assessing the behavior of sesquioxide. The facile $Pu_2O_3+O_2$ reaction is an essential step in the process by which oxide-coated metal ignites at temperatures below the 500°C auto-ignition temperature of plutonium [5]. If the metal has a high surface area to volume ratio, the reaction of surface Pu_2O_3 generates sufficient heat to drive the temperature above the ignition point of plutonium. The oxidation rate in the autothermic regime above 500°C is fixed by formation of a nitrogen boundary layer [2] and a similar limitation is expected for the reaction of Pu_2O_3 with air.

Effects of temperature on the reactivity of the oxide hydride are difficult to assess. The PuOH+air reaction rate may be suppressed by a temperature increase because heating the oxide hydride above 110°C leads to thermal decomposition and formation of H_2 [7]. However, the solid products formed by thermal decomposition are also reactive and may promote rapid reaction after hydrogen is eliminated. The absence of observable reaction upon rapid exposure of PuOH to air at room temperature suggests that autothermic behavior is unlikely.

The qualitative pyrophoricity assessments for PuH_2, Pu_2O_3, and PuOH in Table 2 are based on examination of kinetic factors and chemical behavior of the compounds in air. Pyrophoricity of the hydride is well established and consistent with a reaction that does not form a boundary layer of nitrogen or hydrogen. The cubic hydride accommodates product hydrogen as PuH_x inside the reacting particle until x approaches three [13]. Abrupt termination of the PuH_2+O_2 reaction during tests in the restricted volume of a microbalance system after 10 to 20% of completion [18] apparently occurs as the PuH_x composition in small (high surface area to volume ratio) hydride particles approaches PuH_3 and the particles rupture [13]. Oxidation ceases as product H_2 fills the volume and prevents oxygen from reaching the sample. Such behavior is not observed in unrestricted configurations that allow the hydrogen to escape.

As demonstrated by initiation of autothermic reaction of plutonium [5], Pu_2O_3 is a highly reactive material. Observation shows this oxide tends to be pyrophoric if ground, but oxidizes slowly over a period of days if left undisturbed [19]. Pyrophoric behavior is severely limited if the oxide is confined in a volume that fills with residual nitrogen. In unrestricted configurations, a kinetic limitation is imposed by formation of an oxygen-depleted boundary layer at the gas-solid interface.

The absence of pyrophoric behavior for PuOH is attributed to a combination of kinetic factors that limit access of oxygen to the solid. The sludge-like oxide hydride is unreactive to air when wet or submerged in water. The porous layer of product that deposits during evaporation of liquid water is difficult to dry and the oxide hydride continues to react as long as residual moisture remains. H_2 formed by that reaction fills the free volume in the solid and restricts access of oxygen. Pyrophoric behavior is not expected even if the oxide hydride is fully dried in vacuum and then exposed to air because the initial reaction with air fills the free volume with residual N_2 and product H_2. As shown by Equation (5), hydrogen formation is especially significant because each mole of O_2 produces two moles of H_2 and causes an outward flow of gases from the solid.

The reactivity of dry oxide hydride is markedly altered by the presence of plutonium. As shown by this study, the PuOH+Pu system reacts with air and enters the regime of hydride-catalyzed corrosion. Instead of acting as a barrier of unreactive gas, H_2 formed in the porous PuOH product reacts to form PuH_x catalyst on the underlying metal. This behavior demonstrates that the oxide hydride is inherently reactive, but exhibits pyrophoric behavior only in the presence of plutonium metal.

Although rapid reaction of the PuOH+Pu system with air is demonstrated, observations suggest that onset of the hydride-catalyzed process depends on factors other than the plutonium availability. Catalyzed reaction occurred when air was expanded into an evacuated vessel containing metal that had been partially corroded by water and thoroughly dried in vacuum. Spontaneous initiation of the catalyzed reaction is extremely doubtful if solid reactants were allowed to air dry in an unconfined configuration. H_2 produced by reaction of residual moisture with plutonium limits access of oxygen to the solid reactants until dryness is reached or until all metal has reacted. In the absence of moisture, initiation of catalyzed reaction is unlikely because O_2 diffuses to the solid at a slow rate and the accumulation of hydrogen is insufficient for PuH_x formation. Reaction of residual moisture in a closed configuration generates an overpressure of H_2, but as demonstrated in this study, formation of PuH_x is not expected even at pressures of several atmospheres.

Potential Hazards

Dimensions of the PuOH particles formed by aqueous corrosion of plutonium suggest that the entire product is potentially dispersible. X-Ray diffraction analysis of the oxide hydride gives an average particle size on the order of 70 Å (0.007 μm) [7], a value well below the 3 μm dimension of respirable PuO_2. Aerosolization of wet particles is not anticipated and the product dries as a cemented layer resembling dried silt. The risk of dispersal via the aqueous phase is high because the fine oxide hydride is suspended by physical agitation and settles at a slow rate over a period of weeks. Nuclear properties of the suspension approach those of aqueous plutonium solution. The risk of entraining particles form dried oxide hydride is considered low, and even if sandblasted by other airborne particles, only a small fraction of the product might be entrained from a high-surface-area deposit of material.

The product formed by hydride-catalyzed corrosion of plutonium by air is coarse in comparison to the product obtained by reaction of hydride with air. Size data for particles formed by oxidizing PuH_x prepared at low temperatures [13] show that mass fractions with geometric diameters less than 3, 10, and 30 µm are 0.006, 0.2, and 0.8, respectively [4]. The logarithm-normal distribution of particles formed by reacting hydride-coated metal with air is shown by filled triangles in Figure 5. Data for PuO_2 formed by self-sustained reaction of ignited plutonium in air [20,21] and by reaction of hydride-coated metal with O_2 [4] are defined by open circles and filled circles, respectively. The distributions for oxides formed by ignited and hydride-coated metal have two slopes characteristic of bimodal distributions. A distribution of small fragments apparently forms during spallation of large oxide particles from the metal surface [21]. The additional fragmentation process suggested by a trimodal distribution of product from hydride-catalyzed corrosion in air is identified as oxidation of PuN to PuO_2. For the product of this complex process, the mass fractions of particles with geometric diameters less than 3, 10, and 30 µm are 0.005, 0.01 and 0.02, respectively.

Potential hazards are also associated with aqueous corrosion of plutonium and subsequent exposure of the product to air. H_2 generation during corrosion of metal by liquid water may pressurize and rupture a closed system or form an explosive mixture with air. The rate of hydrogen generation is strongly dependent on the salt concentration and pH of the water and on temperature [9]. Results of this study demonstrate that accumulated hydrogen does not react with residual plutonium if moisture is present, even though the metal is not submerged in water and the H_2 pressure exceeds several atmospheres.

As with the $Pu+H_2O$ reaction, hydrogen generation is the primary hazard posed by the PuOH product. After corrosion of the metal is complete, the oxide hydride continues to react with water and form H_2 according to Equation (2), albeit at a slower rate. Hydrogen production is expected to continue for years at progressively slower rates as reaction of water forms a series of oxides [7]. Although continued generation of H_2 after attainment of the dioxide composition was not understood during the original study, that behavior is explained by recent definition of the PuO_2+H_2O reaction at 25 to 350°C [22,23,24].

$$PuO_2\,(s) + x\,H_2O\,(l, g) \dashrightarrow PuO_{2+x}\,(s) + x\,H_2\ . \qquad (10)$$

The high-surface-area dioxide formed by reaction of PuOH with water generates H_2 at a rate of 8.9 µmol H_2/g d at 23°C. Use of an estimated specific surface area (800 m^2/g) for the dioxide gives a generation rate (approximately 10 nmol H_2/m^2 d) that is in surprisingly good agreement with the value of 3.2 ± 1.3 nmol H_2/m^2 d measured for reaction of water vapor at 25°C. The oxide stoichiometry approached $PuO_{2.3}$ during the reaction with liquid water. As discussed in the preceding section, dry PuOH is reactive, but not pyrophoric.

The PuOH+Pu system holds potential for entering the regime of hydride-catalyzed reaction. The catalyzed process rapidly transforms metal into a dispersible form, generates high temperatures, and ruptures containment vessels by expansion of the solid. However, the potential for occurrence of the catalyzed reaction is limited, and the dry condition required for the process is difficult to achieve. The likelihood of a hydride-catalyzed reaction is further reduced by the apparent need for rapid exposure of the PuOH+Pu system to air.

Conclusions

This evaluation of PuOH reactivity provides a technical basis for safe handling and storage of plutonium metal that has been partially or completely corroded by water. Placement of the material in a durable sealed container is recommended [25], but complicated by the possibility of rupture from buildup of hydrogen pressure or from expansion of the solid during continued reaction of residual water. Storage of dry material is desirable, but not easily achieved. A safe configuration is most easily attained by using a storage container with the closure sealed by a metal gasket and an evacuation port fitted with high-efficiency stainless steel particle filters and closure valves, as well as a mechanical gauge for monitoring the accumulation of gas pressure in the container. Dry storage conditions are achieved by sealing the corrosion product in the container, dynamically evacuating the vessel for a period of days, and determining the dryness by measuring the rate of pressure rise in the closed vessel.

Chemical behavior of the black solid formed by aqueous corrosion of plutonium metal is consistent with results of earlier studies that identify the product as plutonium nonoxide monohydride. Observations demonstrate that the product is a hydridic material, not an hydroxide. Reaction of PuOH with liquid or adsorbed water generates H_2. Although reactive, PuOH is not pyrophoric. Rapid exposure of dry PuOH+Pu mixtures to air may result in PuH_x formation and catalyzed corrosion of the metal. The greatest hazard posed by PuOH and PuOH+Pu mixtures is generation of hydrogen by reaction of residual moisture.

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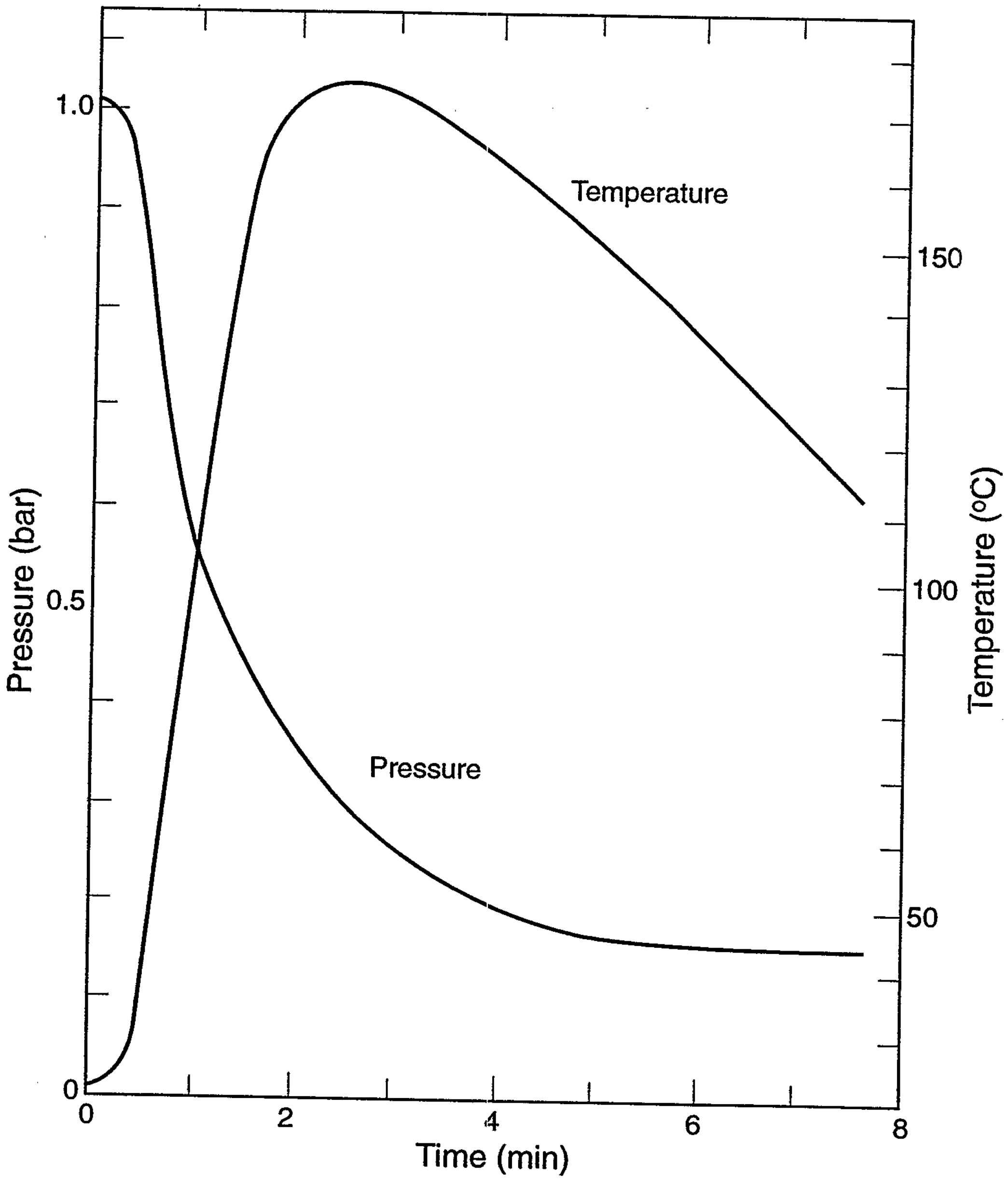

Figure 1. Time dependence of pressure and gas temperature for reaction of air with a mixture of 60% PuOH and 40% Pu in a closed system.

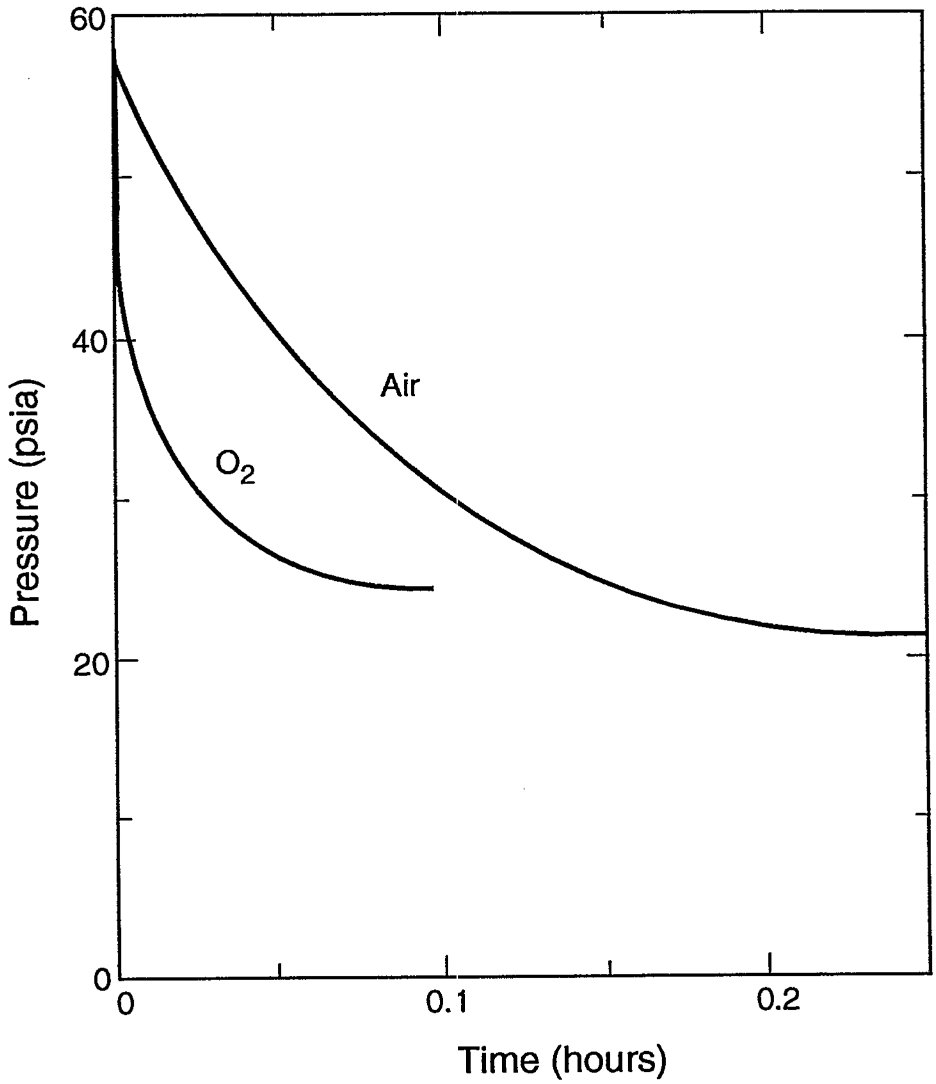

Figure 2. Time dependence of pressures for the reactions of air and oxygen with hydride-coated plutonium in a closed system [4].

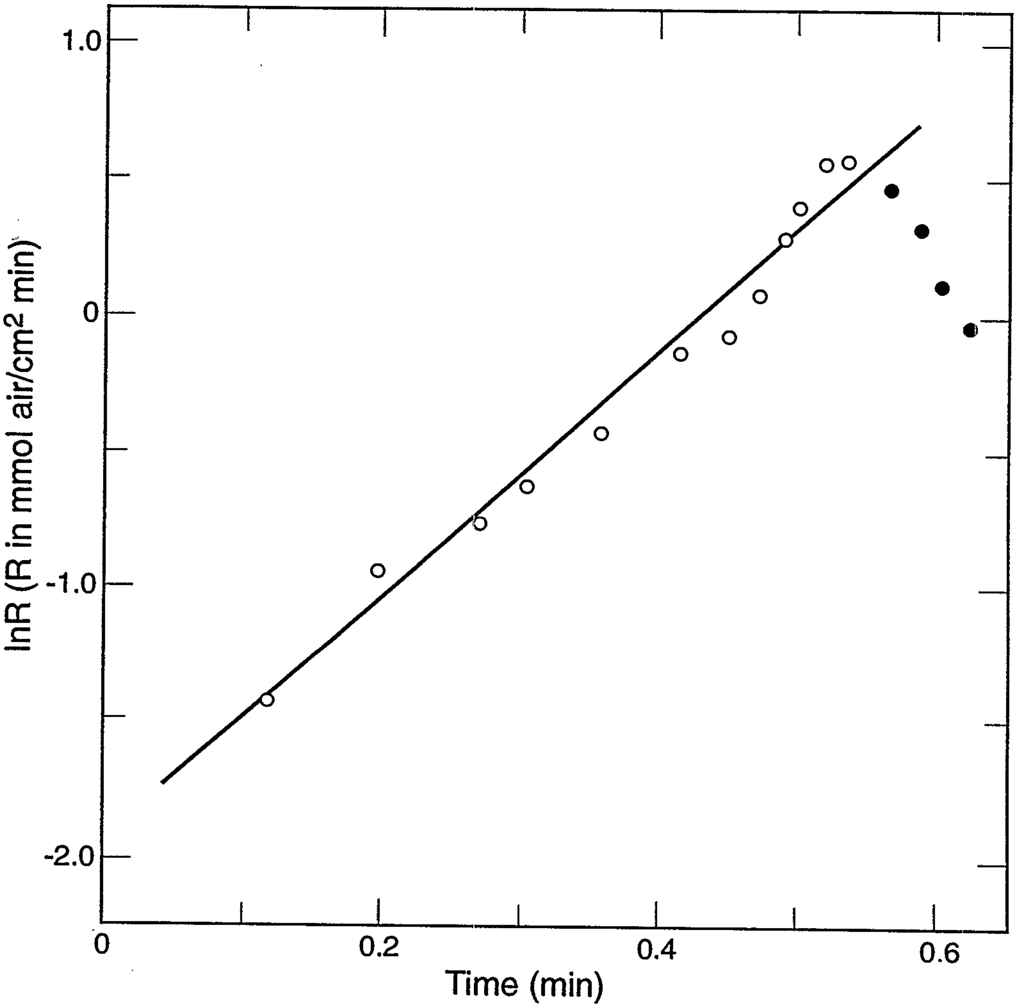

Figure 3. Time dependence lnR for reaction of air with a mixture of 60% PuOH and 40% Pu in closed system. Corrosion rates measured during the initial first-order stage of reaction are indicated by open symbols; corrosion rates measured during the second stage of reaction are indicated by filled symbols.

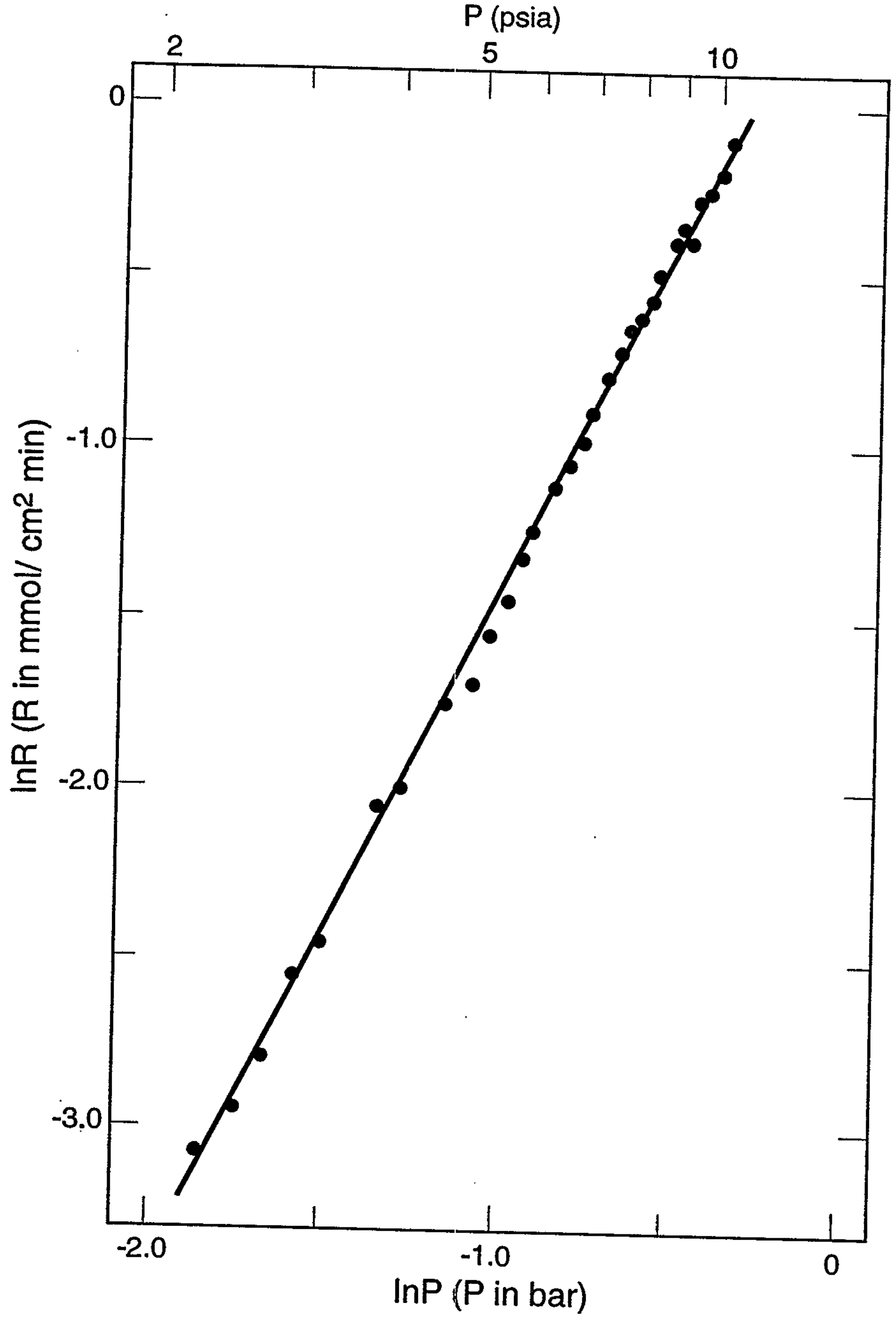

Figure 4. Dependence of lnR on lnP for reaction of air with a mixture of 60% PuOH and 40% Pu in a closed system.

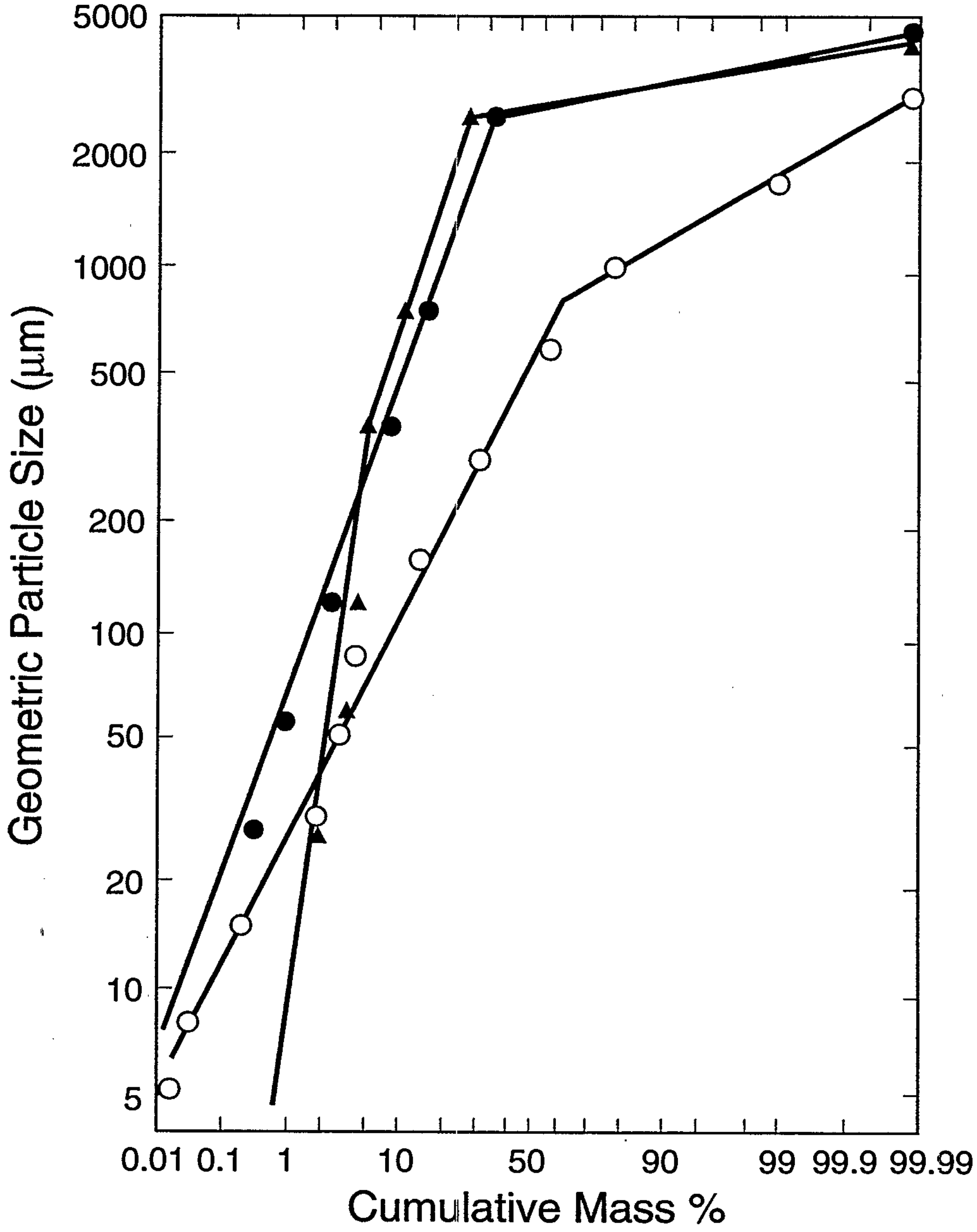

Figure 5. Cumulative mass-size distributions for products formed by corrosion of plutonium metal. Data for products of the Pu+O_2 reaction at temperatures above the 500°C ignition point of the metal [21], the hydride-catalyzed oxidation of Pu by O_2 [4], and the hydride-catalyzed corrosion of Pu by air [4] are indicated by open circles, filled circles, and triangles, respectively.

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