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Oxidation kinetics of plutonium in air: consequences for environmental dispersal

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Abstract

Kinetic studies show that plutonium corrosion in air is catalyzed by plutonium hydride on the metal surface and causes storage containers to fail. The reaction initiates at 25°C, indiscriminately consumes both O_2 and N_2, and transforms Pu into a dispersible product at a 10^7–10^{10} faster rate (0.6 ± 0.1 g Pu/cm^2 min) than normal air oxidation. The catalyzed reaction of O_2 advances into the metal at a linear rate of 2.9 m/h. Rate equations and particle size data for atmospheric and catalyzed corrosion at temperatures up to 3500°C provide a technical basis for assessing the dispersal hazard posed by plutonium metal. © 1998 Published by Elsevier Science S.A.

Keywords: Plutonium; Oxidation; Kinetics; Dispersal

1. Introduction

Environmental dispersal of plutonium is a worldwide concern with possibilities of release from military and civilian sources. Most of the plutonium inventory exists as metal or oxide, two material forms with inherently different potentials for entrainment. Unlike oxide that often includes a large mass fraction of potentially dispersible particles, metal is not readily dispersed and presents a relatively low environmental hazard. However, the risk may be significantly enhanced by corrosion processes that transform the metal into plutonium-containing particles.

Corrosion rates of plutonium metal and alloys in dry and humid air are defined by early studies [1] and several recent investigations [2–6]. Kinetic behavior is strongly dependent on alloying and humidity below 400°C [6], but is independent of these factors at the 500 ± 25°C ignition point of the metal [7]. The oxidation rate of ignited Pu is constant under static conditions that produce an oxygen-depleted boundary layer of nitrogen, but has a 40 kJ/mol activation energy for the dynamic conditions of free fall [8]. Free fall eliminates the oxygen-depleted layer and self-heating drives the droplet temperature above 3300°C, the point above which Pu vapor ‘explosively’ vents through a layer of molten oxide and leaves a hollow spherule of PuO_2 [9].

This report describes experimental results that account for cases in which rapid corrosion of plutonium in storage vessels led to containment failure and release of plutonium [10–12]. In separate incidents, Pu castings (2.2–2.5 kg) were contained in unsealed metal vessels, a sealed plastic contamination barrier, and an outer unsealed can. In one case, solid expansion during corrosion ruptured all barriers. In a second incident, contamination was found during handling of a package after 14 years in storage. Subsequent inspection revealed that the plastic barrier had failed and one end of the inner welded, but unsealed, steel container had ruptured. During unpacking in a reduced oxygen ($<3\%$) atmosphere, the container became warm and its diameter increased by about 50% in 3 h.

A proposed explanation for these observations is hydride-catalyzed reaction of plutonium with air. Even when pumped by atmospheric pressure, insufficient O_2 reaches the metal through a small opening to rupture a container [12]. Unrestricted oxidation of a kg-size casting by moist air at 25°C is expected to consume only 5–10 g Pu/year [6]. According to the proposed mechanism, fine oxide particles are transported out of the inner container by atmospheric pumping; radiolytic decomposition of the plastic degrades the barrier and produces H_2, which forms pyrophoric hydride, PuH_x ($2<x<3$) [13]. Exposure of the system to air upon failure of the plastic barrier results in rapid reaction.

By examining the reactivity and kinetics of the Pu–PuH_x system, the present study investigates hydride enhancement of Pu corrosion in air, evaluates the proposed

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mechanism, and defines properties relevant to environmental dispersal.

2. Experimental methods

A series of PVT (pressure-volume-temperature) experiments was conducted to define the chemistry and kinetics of the Pu–PuH_2 system upon exposure to air. The stainless steel PVT system consisted of heatable reaction, air/hydrogen source, and water source volumes that were interconnected by a vacuum-pressure manifold for handling and sampling of gases. For each test, a weighed specimen (25–50 g) of Pu-1 wt.% Ga alloy was placed in the reaction vessel that was first evacuated and then backfilled with a desired amount of H_2. After hydriding was complete, the air reservoir was filled with the required partial pressures of water and air, temperatures of the reactants were fixed, and the air was expanded into the evacuated vessel at 1.01 bar initial pressure. Reaction was monitored by measuring the time (t) dependence of pressure (P) and temperature (T). Reaction and air vessels were isolated and sampled for mass spectrometric (MS) analysis. Size distributions of solids were measured by sieving and light scattering methods.

The matrix of 25 experiments included three test configurations and several variables. In one configuration, 25-g samples of Pu were converted to PuH_x powder by slow addition of H_2 at a low temperature [13]. In configuration two, half of a 50-g Pu sample was hydrided using the same procedure. In certain tests, 25 g of PuH_x and 25 g of Pu were placed in the reactor under inert conditions. In configuration three, Pu was heated to 400°C and enough H_2 was added to form a 250-μm-thick layer of adherent hydride on the metal [13]. During tests with the first and second configurations, initial temperatures of the solid and the air were varied from 22 to 78°C and from 25 to 55°C, respectively. Partial pressures of H_2O in the air varied from 0 to 30 mbar. Samples coated with adherent hydride were heated to 500°C and exposed to air or O_2 at 3.5 bar.

Results are derived from PVT-t and MS data. Reaction rates (R) are based on gas analyses, geometric metal area, and ideal reactions for formation of Pu_2O_3 and PuN. Pu readily forms a PuH_x ($2<x<3$) solid solution [13]; PuH_2 is assumed to coexist with the metal if x is undefined. Reaction of nitrogen is defined by the N_2:O_2 ratio, which equals 3.71 if the two components of air react indiscriminately.

3. Results and discussion

Both O_2 and N_2 react when PuH_x is exposed to air. The time dependencies of P and gas-phase T of a typical PuH_x+air test are shown in Fig. 1. The heat product causes thermal excursions of 100–125°C; the H_2 product generates pressures in excess of the initial value over a period of 30 s. The negative pressure spike near 0.1 min results from equipment design. Analysis of residual gases in the reactor (0.040 l) and air reservoir (2.78 l) shows 50–75 mol.% H_2 plus N_2 and 2–7 mol.% H_2 plus air, respectively. Calculated fractions of PuH_x ($x\sim2.7$), PuN, and Pu_2O_3 products are 0.80–0.95, 0.03–0.15, and 0.02–0.05, respectively. An average N_2:O_2 ratio of 1.6 ± 0.5 suggests that PuH_x+air reaction is somewhat unpredictable, but demonstrates that nitrogen is the primary reactant. Behavior was not altered by varying initial temperature or humidity.

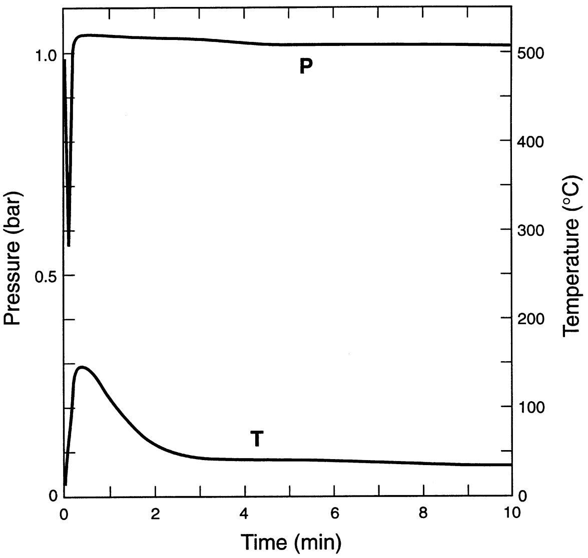

Fig. 1. Time dependence of pressure and gas temperature for reaction of air with plutonium hydride in a closed system.

Though spontaneous reaction of PuH_x with O_2 is expected, involvement of N_2 is somewhat surprising. Early studies show that PuN is formed by the PuH_x+N_2 reaction above 230°C [14]. Hydride temperatures probably exceed this value as a result of the PuH_x+O_2 reaction. Each N_2 reacts with PuH_2 to form two H_2, but observed amounts of hydrogen are much less than expected because the product is accommodated within the reacting particles by increasing x of the remaining hydride. The composition increase continues until x approaches three [13]. Particle fracture and H_2 release occur first for small particles with large surface area to volume ratios. The gradual pressurization seen in Fig. 1 terminates the reaction by preventing entry of additional air.

Further reaction of air is possible if Pu metal and hydride coexist. Fig. 2 shows P–t and T–t curves for reaction of a Pu+PuH_x mixture with air. For the first 30 s, the behavior closely parallels that for the PuH_x+air reaction, except that P never reaches 1 bar. Corrosion of Pu is evidenced by decreasing P and increasing T after 1 min. Analysis of residual gases shows air in the reservoir, an equimolar mixture of H_2 and N_2 in the reactor, and more than 95% of the initial hydrogen as PuH_x. The

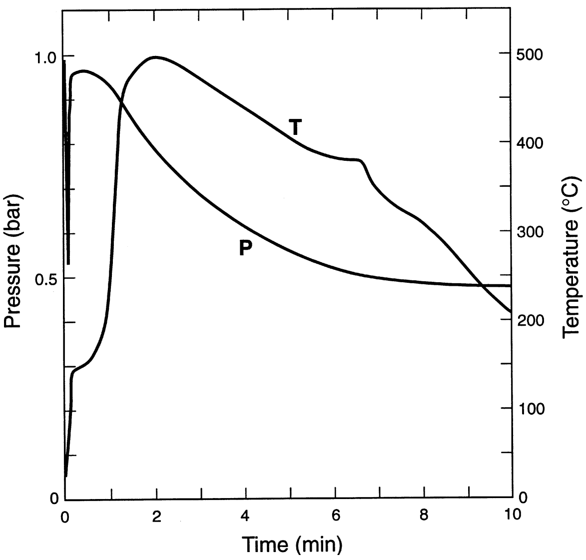

Fig. 2. Time dependence of pressure and gas temperature for reaction of air with an equimolar mixture of plutonium metal and hydride in a closed system.

average N_2:O_2 consumption ratio (3.4±0.1) indicates indiscriminate reaction of metal to form PuN and Pu_2O_3 in a ratio of 5.2:1. Initial and average values of R (0.75±0.09 and 0.59±0.08 g Pu/cm^2 min, respectively) show effects of P, but are insensitive to initial T and humidity.

Results suggest that corrosion of Pu by O_2 and N_2 is catalyzed by surface hydride. Hydrogen formed by rapid reaction of the PuH_x layer with air advances into the metal at a rate accelerated by rapid transport of H in PuH_x [13]. H_2, which was released from PuH_x particles and apparently stopped the reaction in several tests by filling the gas volume around the metal, must react before catalyzed corrosion can occur. Nucleation of the Pu+H_2 reaction is temperature dependent, and though important, heat flow is an undefined factor. The uniqueness of surface hydride is shown by the absence of catalytic corrosion in all tests in which separate pieces of metal were combined with hydride.

Effects of PuH_x particles and temperature are demonstrated by results of tests with hydride-coated metal. Observed P–t and T–t behavior parallels that for t greater than 1 min in Fig. 2. Analytical data yield an N_2:O_2 ratio of 3.7:1 and show that H_2 did not form during the reaction or while products were heated at 500°C for 15 h. Initial and average R values are 1.6±0.4 and 0.6±0.1 g Pu/cm^2 min, respectively. As defined by the slope of ln$R$–ln$P$, the exponents relating rate to air pressure at 475±25°C are 2.0 and 3.0 for P greater and less than 2.0 bar, respectively, suggesting that the reaction mechanism is complex. Except for a change in solid volume, reacted specimens remained largely intact and consisted of a silver gray product shell around a hydride core.

Reaction of hydride-coated Pu with O_2 is violent and complete in less than 1 s. Gas phase temperatures exceed 1000°C. H_2 was not observed during reaction or over several hours in O_2 at 500°C. Appearance of H_2O after cooling to room temperature is consistent with catalytic properties of oxide [6]. The solid product resembled that obtained in air and contained a core of PuH_x. P and T data taken after 1 s give an R of 78.1 g Pu/cm^2 min, or a linear rate of 2.93 m/h.

The estimated R (0.3 g Pu/cm^2 min) encountered during unpacking of the storage vessel is derived from approximate metal area, volume expansion during a 3-h period, and measured product density (6.5±0.5 g/cm^3). Agreement of this R for unalloyed Pu with the average test result (0.6 g Pu/cm^2 min) suggests that hydride-catalyzed corrosion is independent of alloying and responsible for observed failures of Pu storage containers.

Comparison of hydride-catalyzed reaction with normal air oxidation assists in defining hazards posed by Pu corrosion. Important considerations are the rate of corrosion and the particle size distribution of the product. The kinetics of uncatalyzed oxidation in air are described by Arrhenius relationships presented in Fig. 3 and Table 1. Effects of alloying and moisture are seen below 400°C, a point at which all rates converge. Curves a–d for unalloyed Pu define the envelope of humidity effects between −25 and 200°C. Moisture dependencies of curve c for the transition region and of R within the envelope are given in a prior report [6]. Curves e and f indicate effects of moist and dry air on the Ga alloy, respectively. The somewhat uncertain transition to the ignition point at 500°C is

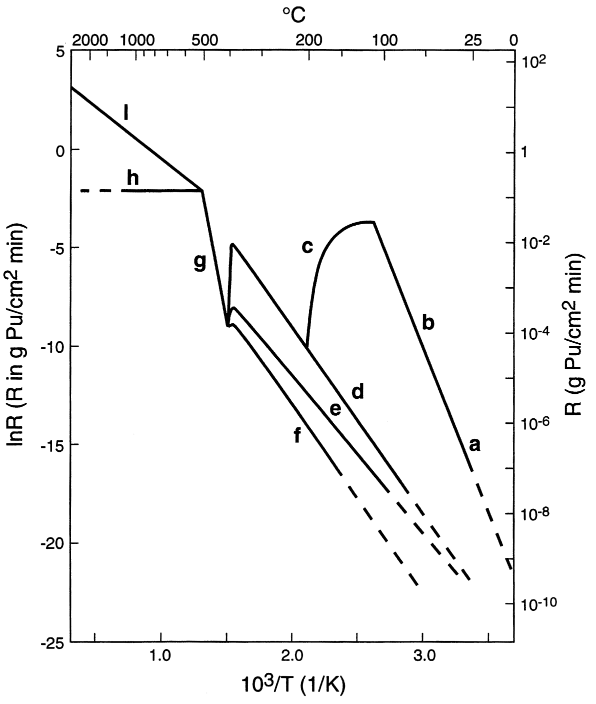

Fig. 3. Arrhenius curves for the reactions of unalloyed and alloyed (1 wt.% Ga) plutonium with dry and moist air or water. Curves a–g are derived from [6] and [8] and are identified in the text and in Table 1.

Table 1
Arrhenius equations[a] for oxidation of unalloyed and alloyed Pu in air and in water vapor

Curve	Reaction	Temperature range (K)	A	B	Reference
a	Unalloyed $Pu+H_2O$ at P_e[b]	248–334	41.46	17 120	[6]
b	Unalloyed $Pu+H_2O$[c]	334–383	40.74	16 880	[6]
d	Unalloyed Pu+dry air[d]	<673	8.78	9010	[6]
e	Alloyed $Pu+H_2O$[c]	334–673	9.18	7850	[2,3,6]
f	Alloyed Pu+dry air	<673	6.40	9560	[4,6]
g	Pu+air[d] or H_2O[c]	673–773	44.51	35 940	[6]
h	Static Pu+air	>773	−1.97	0	[9]
i	Dynamic Pu+air	773–3773	4.21	4830	[9]

[a] Equations are for the linear stage of oxidation [6], and with the exception of curve c for the transition region between 110 and 200°C have the form $\ln R$ (in g Pu/cm^2 min)$=A-B/T$.

[b] P_e is the equilibrium pressure of condensed water at T.

[c] The H_2O pressure is 160 torr, the partial pressure of O_2 in air.

[d] Dry air contains less than 0.5 ppm H_2O.

described by curve g. Self-sustained reaction of ignited metal at a T-independent rate under static conditions is shown by curve h, and the autothermic reaction of an ignited Pu droplet during free fall is described by curve i [8,9]. As shown by the right-hand ordinate of Fig. 3, measured oxidation rates span a range of about 10^9.

Catalytic enhancement of plutonium corrosion by hydride significantly increases the risk associated with metal. The amount of oxide formed per day by exposing a kg-sized casting to air at 25°C varies from a few μg to a few mg depending on alloying and humidity. If hydride is present, the N_2 boundary layer is absent and R increases by 10^7–10^{10} to a value that is four times greater than the rate of self-sustained oxidation in static air. A kg-size casting reacts completely in 15–30 min. R for $Pu+O_2$ increases by as much as 10^{13}, implying that catalyzed corrosion in air is also throttled by slow reaction of nitrogen. In addition to causing solid expansion and thermal excursion, catalyzed corrosion markedly increases the amount of plutonium at risk.

Table 2
Size distribution data for plutonium oxide[a] particles formed by corrosion of Pu metal

Corrosion reaction	Cumulative mass fraction at specified size[b]		
	3 μm	10 μm	30 μm
Unalloyed Pu+room air at 25°C	0.03	0.05	>0.95
Pu+air at 500°C	6×10^{-6}	5×10^{-4}	0.01
$Pu–PuH_x$+room air at 25°C[c]	6×10^{-3}	0.2	0.8
$Pu–PuH_x$+air at 500°C	5×10^{-3}	0.01	0.02
$Pu–PuH_x+O_2$ at 500°C	5×10^{-5}	2×10^{-4}	0.002
Pu droplet explosion at 3300°C	0.7	0.8	0.8

[a] Though residual PuH_x and PuN may remain in products formed by hydride catalysis, particles with sizes less than 30 μm probably oxidized to PuO_2 during handling in air.

[b] Particle sizes are geometric; the aerodynamic equivalent diameter of a dioxide particle is about a factor of three larger than the geometric diameter.

[c] Data are for a product formed without a large thermal excursion by slow reaction in a storage container.

Particle-size data for different corrosion processes in Table 2 (T.E. Ricketts, personal communication) show that the airborne release fraction is strongly dependent on the conditions of reaction. The mass fraction of small particles correlates strongly with reaction temperature, but the true correlation is apparently with reaction rate. Unlike rapid corrosion, slow reaction promotes formation of small particles by allowing time for extensive nucleation and propagation of cracks in the density-stressed product layer on the metal.

Though the bounding particle size for oxide entrainment varies from 10 to 30 μm geometric diameter depending on air velocity, the mass fractions of dispersible particles vary by more than 10^5 depending on product history. Reliable assessment of the dispersal hazard is unlikely if the origin of the oxide is not considered.

4. Conclusions

Along with static and dynamic (explosive) oxidation of ignited plutonium, hydride-catalyzed corrosion of metal by air occurs within the time span of a credible incident and may substantially increase the dispersal hazard posed by metal. Unique features of catalyzed reactions are spontaneous initiation at low temperature and a large thermal excursion. Catalyzed reaction of oxygen is unusually rapid for a gas-solid process and merits further study to define transport processes, characterize products, and investigate potential application in the direct recovery of metal as oxide.

Acknowledgements

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