Surface and Corrosion Chemistry *of* PLUTONIUM

John M. Haschke, Thomas H. Allen, and Luis A. Morales

Elemental plutonium, the form in which most of the weapons-grade material exists, is a reactive metal. When exposed to air, moisture, and common elements such as oxygen and hydrogen, the metal surface readily corrodes and forms a powder of small plutonium-containing particles. Being easily airborne and inhaled, these particles pose a much greater risk of dispersal during an accident than the original metal. The present emphasis on enhancing nuclear security through safe maintenance of the nuclear stockpile and safe recovery, handling, and storage of surplus plutonium makes it more imperative than ever that the corrosion of plutonium be understood in all its manifestations.

Metallic plutonium was first prepared at Los Alamos in 1944, during the Manhattan Project. After samples became available, scientists studied the properties of the metal, including its reactions with air, moisture, oxygen, and hydrogen. Extensive investigation of plutonium continued into the early 1970s, and the results of those studies are documented in the handbooks of chemistry, physics, and metallurgy.

In dry air—less than 0.5 part per million (ppm) of water—at room temperature, plutonium behaves much like other active metals, forming a protective layer of dioxide (PuO_2) on the surface. The PuO_2 layer limits corrosion of unalloyed plutonium to the almost imperceptible rate of 20 picometers per hour. The corrosion chemistry of plutonium is therefore assumed to be relatively simple and well understood, but that assumption is far from true. Unexplained phenomena, such as plutonium pyrophoricity (spontaneous ignition in air) and moisture-accelerated corrosion, in air were observed in the earliest plutonium studies (Cleveland 1979, Wick 1980, Katz et al. 1986). Recent Los Alamos studies confirm and add to these examples of unexpectedly rapid corrosion. Moreover, our analysis suggests that J. T. Waber, a Los Alamos pioneer in plutonium corrosion, was prescient when he wrote, “Most investigators are inclined to concentrate their attention on PuO_2, which can be well characterized, and to ignore other compounds that may contribute to the overall corrosion behavior” (Wick 1980). Indeed, we believe that plutonium oxides other than PuO_2 and compounds other than oxides play a potent role in plutonium corrosion. These compounds appear to be catalysts, causing anomalous corrosion reactions to proceed at enormous rates.

“Runaway” reactions can occur under fairly routine conditions. In one case, a failed storage package containing a plutonium casting was examined in a glove box, which had a nitrogen-rich atmosphere (less than 3 percent oxygen) normally used for handling plutonium metal. The package remained there for 3 hours after disassembly and initial inspection. Whenthe workers returned to continue their evaluation, they found that the inner container was hot to the touch and its diameter had increased by 50 percent in the region surrounding the casting (Haschke and Martz 1998b). Our subsequent investigation showed that a corrosion reaction involving both oxygen and nitrogen initiated spontaneously at room temperature and advanced into the plutonium metal at a rate of more than 1 centimeter per hour (cm/h), or a factor of 10^{10} faster than the corrosion rate in dry air. The reaction generated excessive temperatures and started under conditions that are considered safe for the routine handling of plutonium.

Further studies suggest that the course of corrosion depends very heavily on the chemical condition of the plutonium surface. A surface layer of sesquioxide (Pu_2O_3), which forms in the absence of oxygen, promotes corrosion of the metal by hydrogen. Conversely, a surface layer of hydride (PuH_x, where $1.9 < x < 3$) increases the plutonium oxidation rate in oxygen by a factor of 10^{13} to a value near 3 meters per hour (m/h). Finally, a surface layer of the previously unknown higher oxide PuO_{2+x}, which forms on the PuO_2 layer in the presence of moisture, apparently enhances the bulk corrosion of plutonium metal in moist air. The fact that PuO_2 reacts with water demonstrates that it is thermodynamically unstable in air and environmental media. Evidently, its reaction with water is responsible for both the implosion and the pressurization of sealed containers of plutonium oxide during their extended storage.

In this article, we present our observations and analysis of the chemistry and kinetic behavior of important corrosion reactions involving oxygen, nitrogen, and hydrogen. We observe that PuH_x, Pu_2O_3, and PuO_{2+x} on the metal surface catalyze anomalous corrosion reactions and that the Pu(III) and Pu(VI) oxidation states are important in addition to the predominant Pu(IV) state. We also outline the kinetics that relates specific surface compounds and conditions to anomalous reactions. Our analysis provides explanations for many puzzling phenomena, but it also leaves a multitude of unanswered questions. We conclude that the present understanding of plutonium chemistry is inadequate and that the new evidence presents an immediate technical challenge to the scientific community.

Plutonium Oxides and Atmospheric Oxidation

Plutonium corrosion and oxidation are often treated as equivalent topics because plutonium oxides are the only products normally observed during atmospheric corrosion. The metal does not react appreciably with elemental nitrogen even at elevated temperatures, although plutonium mononitride (PuN) is a stable compound. Therefore, we begin with a review of oxide chemistry and oxidation kinetics.

Diffusion-Controlled Oxidation in Dry Air. Like aluminum and other reactive metals, plutonium is passivated, or rendered unreactive, upon exposure to air because a coherent (continuous, uncracked) oxide layer rapidly forms over the entire surface. Although oxidation continues despite the protective oxide coating, its rate in dry air at room temperature is extremely low. Evidence from kinetic data demonstrates that the oxidation rate is limited by the rate at which oxygen can diffuse through the oxide surface to the oxide-metal interface.

Figures 1(a)–1(c) show the oxidation process broken down into a sequence of steps. A freshly burnished surface of plutonium is exposed to oxygen gas. Oxygen molecules (O_2) adsorb on the oxide surface at a concentration determined by temperature and the partial pressure of oxygen in the gas phase. The adsorbed molecules then dissociate on the oxide surface to form atomic oxygen, a species that either recombines or associates with electrons to form oxide ions (O^{2-}). Both adsorption and dissociation depend strongly on the electronic properties of the oxide layer and its ability to transport electrons from the metal to the gas-solid interface. After entering the oxide lattice, O^{2-} diffuses through the oxide layer and ultimately reacts with plutonium to produce oxide, electrons, and heat at the oxide-metal interface. The slowest step in this sequence is called rate limiting because the overall reaction can proceed no faster.

Kinetic data on the thickness τ of the adherent oxide layer as a function of time t demonstrate that classic oxygen diffusion is the rate-limiting step in the Pu + O_2 reaction. On a freshly burnished plutonium surface, the thickness τ reflects the extent of the reaction. This thickness exhibits parabolic growth, increasing linearly with the square root of t at a fixed temperature T. The rate of reaction, which is the time derivative of the thickness, must therefore be inversely proportional to the thickness, exactly the behavior expected if the rate of reaction is controlled by the rate at which oxygen diffuses through the oxide layer.[1] As the oxide layer gets thicker, the time to diffuse through the layer becomes longer, and thus the oxidation rate decreases with time. Figure 1(d) shows the decreasing slope of the curve describing thickness versus time during parabolic growth.

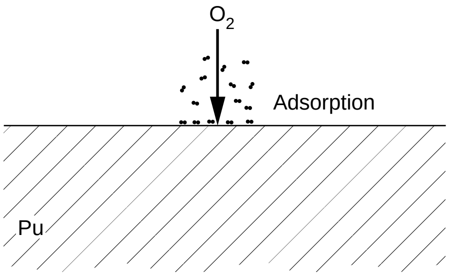
Parabolic growth tapers off to a steady-state regime when the low-density oxide—11.45 grams per cubic centimeter (g/cm^3)—on high-density plutonium (19.86 g/cm^3) begins to induce stresses that lead to the localized spallation of oxide particles from the surface. The thickness of the oxide layer then varies from point to point with regions of thin oxide in recently spalled areas, regions of thick oxide in unspalled areas, and regions of intermediate oxide thickness in between, as illustrated in Figure 1(c). During this stage, the average thickness of the oxide layer and the isothermal oxidation rate reach constant values as diffusion-controlled oxidation continues. The corrosion rate becomes constant because the continuous spallation of oxide particles and the reoxidation of the surface maintain a steady-state diffusion barrier of constant average thickness. As shown in Haschke et al. (1996), the corrosion rate of unalloyed plutonium in dry air at 25°C is approximately 0.5 nanogram of plutonium per centimeter squared a minute (ng Pu/cm^2 min), and the steady-state oxide thickness is 4 to 5 micrometers (Martz et al. 1994).

As expected, the diffusion rate through the oxide layer increases strongly with increasing temperature and produces a corresponding increase in the oxidation rate of plutonium. During both the parabolic and constant-rate stages of oxidation, the reaction rate R obeys the classical Arrhenius relationship $R = \exp(-E_a/R^*T)$, where E_a is the activation energy for the reaction and R^* is the gas constant. Activation energies for the parabolic and constant-rate stages are typically derived from the slopes of experimental curves for $\ln R$

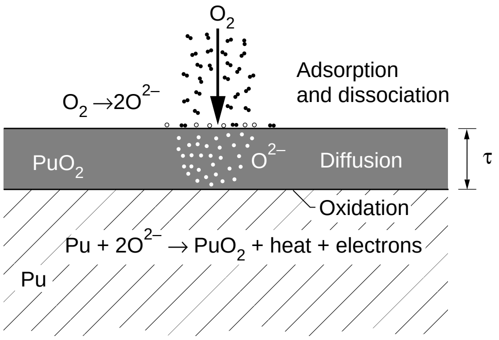
---

[1] For a diffusion-controlled reaction, the rate at which the thickness of the product layer increases is inversely proportional to that thickness, as described by the differential equation $d\tau/dt = k/\tau$. The proportionality constant k is characteristic of the reaction. We derive the parabolic rate law by rewriting this equation as $\tau d\tau = k dt$, integrating it, and applying the boundary condition $\tau = 0$ at $t = 0$. In the resulting expression of the parabolic rate law, $\tau^2 = k_p t$, k_p is the parabolic rate constant that includes the temperature-dependent coefficient for diffusion of the reactant through the product. Diffusion control of the rate is implied if a linear relationship is obtained upon graphing τ or any other experimental measure of the extent of reaction against the square root of t.

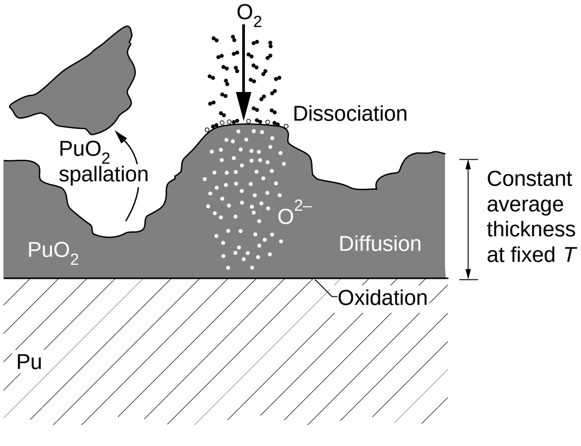
(a) Freshly Burnished Surface


O_2
Adsorption
Pu

(b) Parabolic Growth


O_2
$O_2 \rightarrow 2O^{2-}$
Adsorption and dissociation
PuO_2
O^{2-}
Diffusion
τ
Oxidation
$Pu + 2O^{2-} \rightarrow PuO_2$ + heat + electrons
Pu

(c) Steady-State Corrosion


O_2
Dissociation
PuO_2 spallation
O^{2-}
Constant average thickness at fixed T
PuO_2
Diffusion
Oxidation
Pu

(d) Oxide Thickness versus Time

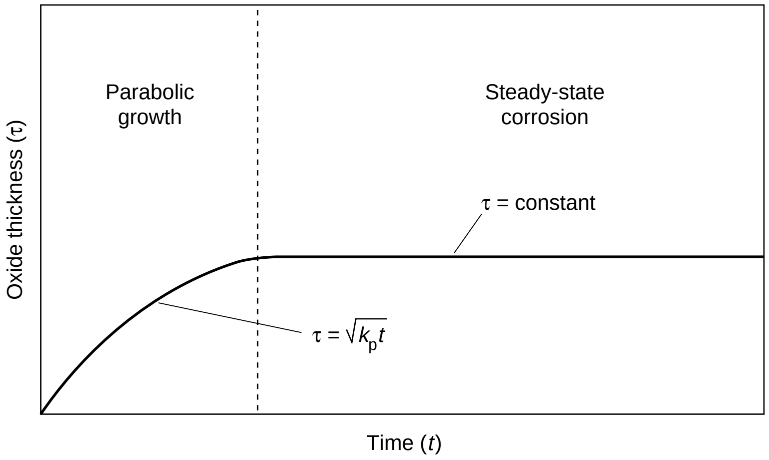


Figure 1. Standard Chemical Picture of Plutonium Oxidation in Dry Air

(a) A freshly burnished plutonium surface is exposed to molecular oxygen that readily adsorbs onto the metal surface. (b) The oxygen dissociates into atomic oxygen, and combines with plutonium to form a layer of oxide. Oxidation continues, but now the oxygen on the surface must diffuse through the oxide layer before it can react with plutonium and produce more oxide at the oxide/metal interface. The thickness of the oxide layer increases parabolically with time because its growth is limited by the rate of oxygen diffusion through the oxide layer. (c) At a certain oxide thickness (typically, 4–5 µm), at room temperature, surface stresses cause oxide particles to spall from the surface. The oxide layer reaches a steady-state thickness as further oxidation is counterbalanced by spallation. If the reaction is to occur as outlined in steps (a)–(c), the electrons must be transported from the metal to the oxide surface so that O^{2-} ions should form. (d) The plot of oxide layer thickness (τ) versus time (t) shows the two distinct oxidation stages. During parabolic growth, the reaction extent and τ grow as the square root of t, and the oxidation rate (slope of the curve) continually decreases, indicating that diffusion through the oxide layer is the rate-limiting step in the oxidation process. Later on, the extent of the reaction grows linearly with time, and the corrosion rate becomes constant as continuous spallation of oxide particles and reoxidation of the surface maintain a steady-state diffusion barrier of constant average thickness. Diffusion remains the rate-limiting step.

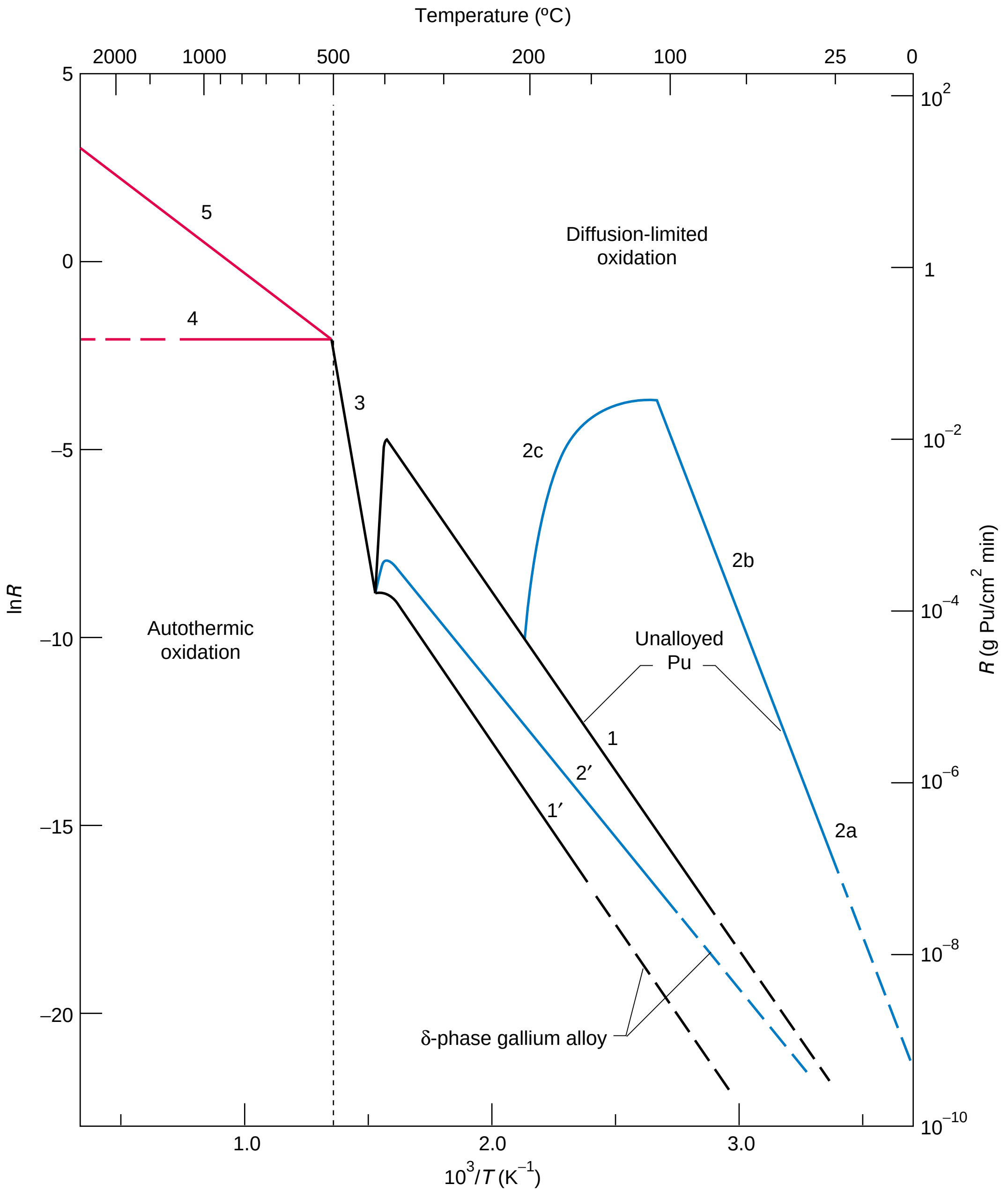


Figure 2. Arrhenius Curves for Oxidation of Unalloyed and Alloyed Plutonium in Dry Air and Water Vapor

Data on the steady-state oxidation rates of alloyed and unalloyed plutonium are summarized for a wide temperature range. Each labeled curve is an Arrhenius plot, showing the natural logarithm (ln) of the reaction rate *R* versus 1/*T* for a metal or alloy in a specific atmosphere or under a specific condition. The slope of each curve is proportional to the activation energy for the corrosion reaction. Curve 1 plots the well-known oxidation rate of unalloyed plutonium in dry air or dry O_2 at a pressure of 0.21 bar. Curve 2a shows the increase in the oxidation rate when unalloyed metal is exposed to water vapor at equilibrium pressures up to 0.21 bar (160 torr), a concentration equal to the partial pressure of oxygen in air. Curves 2b and 2c show the moisture-enhanced oxidation rate at a water vapor pressure of 0.21 bar (160 torr) in the temperature ranges of 61°C–110°C and 110°C–200°C, respectively. Curves *1’* and *2’* give the oxidation rates for the δ-phase gallium-stabilized alloy in dry air and moist air (water vapor pressure ≤ 0.21 bar), respectively. Curve 3 indicates behavior in the transition region between the convergence of rates at 400°C and the onset of the autothermic reaction at 500°C. Curve 4 defines the temperature-independent reaction rate of ignited metal or alloy under static conditions. The rate is fixed by diffusion through an O_2-depleted boundary layer of N_2 at the gas-solid interface. Curve 5 shows the temperature-dependent oxidation rate of ignited droplets of metal or alloy during free fall in air.

versus 1/T (see Figure 2). Curve 1 shows the oxidation rate of unalloyed plutonium in dry air during the constant-rate stage of the reaction, and its slope yields an E_a of 17.4 kilocalories per mole (kcal/mol).

Variations from the Standard Diffusion Picture. To get a comprehensive picture of the kinetics of plutonium oxidation, we have reviewed published data and prepared a single graph (Figure 2) of Arrhenius curves for corrosion of unalloyed metal and delta-phase gallium alloy in dry air and water vapor during the constant-rate stage of oxidation. The data are normalized to an oxidant pressure of 0.21 bar, the partial pressure of O_2 in air at 1 atmosphere.

Curve 1, the oxidation rate of unalloyed plutonium in dry air, spans a temperature range in which the metal exists in four allotropic forms: the alpha, beta, gamma, and delta phases. The variations among curves 1, 2a–2c, 1', and 2' reflect the complex effects of temperature, humidity, and alloying on the oxidation rate. The convergence of these curves near 400°C marks the onset of a region (curve 3) in which the oxidation rate depends only on temperature and oxidant pressure. The research we describe below shows that all the curves below 500°C in Figure 2 are consistent with control by classic oxygen diffusion through an oxide layer, even those enhanced by the presence of moisture.[2]

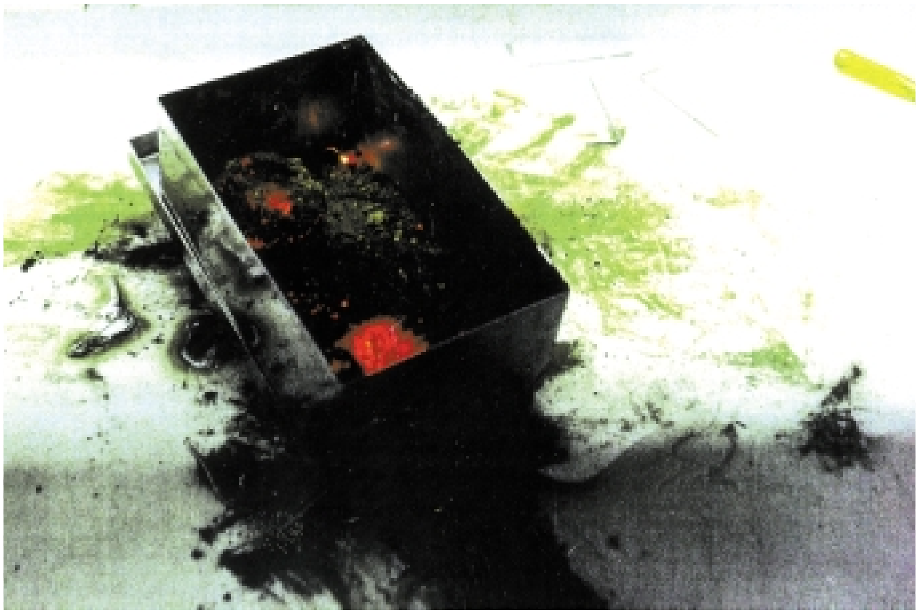


Figure 3. Plutonium Pyrophoricity

Plutonium is shown here spontaneously burning in air under static conditions. The burning metal is glowing like embers as oxidation occurs at the constant rate defined by curve 4 in Figure 2.

For completeness, we also include Arrhenius data for the very high temperature range—from the 500°C ignition point of plutonium to the boiling point of the liquid metal at 3230°C. (Haschke and Martz 1998a, Martz and Haschke 1998). Activation energies in this region are difficult to measure because the reaction temperature is determined by the rate of reaction and the accumulation of heat by the reacting metal, not by experimental control. The oxidation rate—0.14 gram (g) Pu/cm^2 min—for ignited metal droplets in static air (curve 4) is independent of temperature and fixed by the rate of O_2 transport across a boundary layer of oxygen-depleted nitrogen formed at the gas-solid interface of the burning particle. An example of this behavior is illustrated in Figure 3, in which plutonium is shown spontaneously burning in air under static conditions. The oxidation rate (E_a = 9.6 kcal/mol) for ignited metal droplets in air during free fall (curve 5) is temperature dependent because there is no longer a static nitrogen-rich boundary layer limiting the diffusion of oxygen. Self-heating by the oxidation reaction drives droplet temperatures above the boiling point of plutonium and causes an “explosion” in which unreacted metal vaporizes and burns in a flash.

Although the standard picture of diffusion-controlled oxidation given in Figure 1 seems to apply below 500°C, this model does not account either for the spontaneous ignition of metal chips and powder in air at 150°C–200°C or for the large effect of moisture on the oxidation rate (compare curves 2a and 2b with curve 1 in Figure 2). Involvement of compounds other than the dioxide and transport processes other than diffusion must be considered in addressing pyrophoricity, moisture-enhanced oxidation, and other anomalous kinetic behaviors described in subsequent sections of this article.

Pu_2O_3 and the Oxide Layer. The presence of oxide is an unavoidable feature of plutonium metal surfaces. Even if one tries to create a perfectly clean surface through repeated cycles of heating and bombardment by an energetic ion beam in ultrahigh vacuum, several atomic percent of oxygen remains on the surface, as measured by x-ray photoelectron spectroscopy (XPS). Such measurements also show that exposure of a cleaned surface to O_2 at low pressure (about 1 nanobar) immediately produces a surface layer of Pu_2O_3 (Larson and Haschke 1981). Over time, this sesquioxide oxidizes to

---

[2] This enhancement apparently results from an unanticipated increase in the oxygen gradient rather than from a proposed mechanistic change involving diffusion of hydroxide (OH^-) ions, but that story is the most surprising, and we save it for last.

PuO_2 even at these low oxygen pressures. If the surface is exposed to air at atmospheric pressure, a coherent layer of PuO_2 quickly forms over the entire metal surface. Thus, a dioxide layer is present on all plutonium metal surfaces after exposure to air unless extreme measures are exercised.

A surprising feature of the oxide layer at room temperature is the apparent absence of Pu_2O_3. Studies of the plutonium-oxygen system have shown that both Pu_2O_3 and PuO_2 are stable in the solid phase at room temperature. Moreover, above 700°C, the two oxides coexist as a solid solution in which the average composition varies between these oxides as the oxygen-to-plutonium ratio in the system increases from 1.5 to 2. (The mechanism for forming a solid compound with a continuously varying composition is described in the box "Fluorite and Fluorite-Related Structures in Plutonium Corrosion" on page 260.)

Thermodynamic data presented in the box "Thermodynamics, Kinetics, Catalysis, and the Equilibrium State in the Plutonium-Oxygen System" (page 261) verify that Pu_2O_3 is a stable oxide in the presence of plutonium metal. Thus, a thin layer of Pu_2O_3 must be present at the oxide-metal interface of the oxide layer. Because this layer is undetectable at room temperature, we deduce that Pu_2O_3 is readily oxidized to PuO_2 by oxygen and that the observed composition of the oxide layer is determined by the rapid kinetics of PuO_2 formation, not by thermodynamics. This conclusion is supported by our observations that a change in conditions, such as an increase in temperature or a decrease in the availability of oxygen, leads to an increase in the fraction of Pu_2O_3. Indeed, our recent results (Haschke et al. 1998) strongly suggest both the presence and participation of Pu_2O_3 in the corrosion chemistry of plutonium, possibilities that have not been examined by previous investigators.

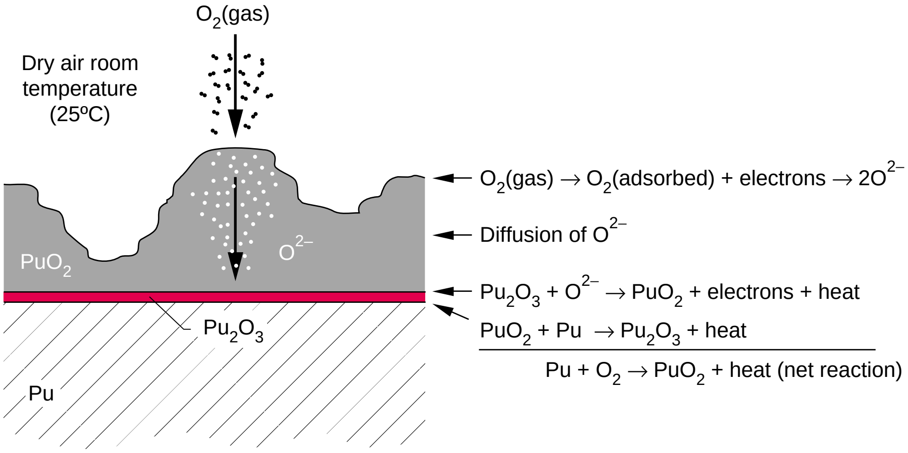

O_2(gas)
Dry air room temperature (25ºC)
PuO_2
O^{2-}
Pu_2O_3
Pu
$O_2(gas) \rightarrow O_2(adsorbed) + electrons \rightarrow 2O^{2-}$
Diffusion of O^{2-}
$Pu_2O_3 + O^{2-} \rightarrow PuO_2 + electrons + heat$
$PuO_2 + Pu \rightarrow Pu_2O_3 + heat$
$Pu + O_2 \rightarrow PuO_2 + heat$ (net reaction)

Figure 4. Kinetics of the Steady-State Oxide Layer in Dry Air at Room Temperature

In contrast to the standard picture shown in Figure 1, the oxide layer on plutonium metal in dry air at room temperature must contain a steady-state layer of Pu_2O_3 at the oxide-metal interface (red). Its thickness, however, is small compared with the constant average oxide thickness (4–5 µm) maintained by spallation. The processes producing the slow constant-rate oxidation are shown in the figure. Molecular oxygen adsorbs onto the oxide surface, it dissociates to form oxygen ions, and the ions diffuse through the oxide layer. Autoreduction of the dioxide by the metal at the oxide-metal interface continually produces Pu_2O_3. This lower oxide then reacts with the diffusing oxygen ions to produce the dioxide. The steady-state oxide layer on plutonium in dry air at room temperature (25°C) is essentially PuO_2, indicating that oxidation of Pu_2O_3 is the predominant surface reaction.

The Pyrophoricity of Plutonium. The first example of Pu_2O_3 participation is our quantitative model for the pyrophoricity of plutonium chips and powder at 150°C–200°C (Martz et al. 1994). This model grew from understanding the role of Pu_2O_3 in the kinetics of plutonium oxidation.

Figure 4 shows the revised view of the PuO_2 diffusion barrier in the presence of oxygen. By separating a region with excess oxygen from one with excess plutonium, this barrier creates a nonequilibrium condition on the metal surface, in which Pu_2O_3 is simultaneously consumed and formed by competing reactions. The dioxide is reduced to Pu_2O_3 by plutonium at the oxide-metal interface.

$$3PuO_2(s) + Pu(s) \rightarrow 2Pu_2O_3(s) \quad . \quad (1)$$

Concurrently, Pu_2O_3 is consumed by reaction with the oxygen that diffuses through the oxide layer:

$$Pu_2O_3(s) + (1/2)O_2(g) \rightarrow 2PuO_2(s) \quad . \quad (2)$$

The ultimate equilibrium state of a reaction depends on the molar ratio of oxygen to plutonium in the product. During corrosion in air, excess O_2 is present, and equilibrium is reached when all the metal is converted to dioxide. In contrast, when placed in a vacuum, an inert atmosphere, or a sealed container, plutonium consumes any residual O_2 and continues to react with the PuO_2 surface until only Pu_2O_3 is present. In the absence of excess oxygen, equilibrium is reached when the PuO_2 layer is completely reduced to Pu_2O_3 by the reaction described by

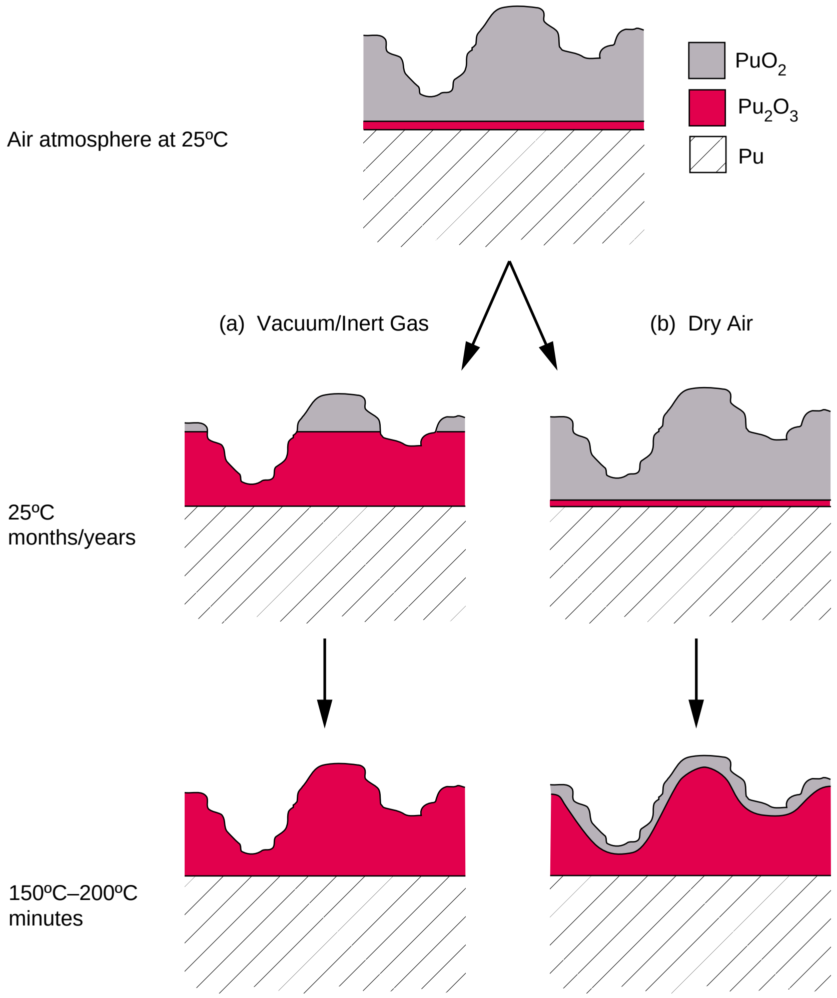


Figure 5. The Oxide Layer on Plutonium Metal under Varying Conditions

These highly idealized sketches indicate how changes in atmosphere, temperature, and time alter the surface chemistry of the oxide layer. The corrosion rate is strongly dependent on the metal temperature and varies significantly with the isotopic composition, quantity, geometry, and storage configuration of the metal. Serving as reference, the steady-state oxide layer on plutonium in dry air at room temperature (25°C) is shown at the top. (a) Over time, isolating PuO_2-coated metal from oxygen in a vacuum or an inert environment turns the surface oxide into Pu_2O_3 by the autoreduction reaction described by Equation (1). At 25°C, the transformation is slow. The time required for the complete reduction of PuO_2 depends on the initial thickness of the PuO_2 layer and is highly uncertain because the reaction kinetics is not quantified. At temperatures above 150°C, rapid autoreduction transforms a several-micrometer-thick PuO_2 layer to Pu_2O_3 within minutes. (b) Exposure of the steady-state oxide layer to air results in continued oxidation of the metal. At 25°C in dry air, the layer is essentially unaltered over time. Kinetic data indicate that a one-year exposure to dry air (<0.5 ppm H_2O at 1 bar of total pressure) at room temperature increases the oxide thickness by about 0.1 μm. At a metal temperature of 50°C in moist air (50% relative humidity), the corrosion rate increases by a factor of approximately 10^4, and the corrosion front advances into unalloyed metal at a rate of 2 mm per year. At 150°C–200°C in dry air, the rate of the autoreduction reaction increases relative to that of the oxidation reaction, and the steady-state condition in the oxide shifts toward Pu_2O_3, a phase that is simultaneously formed by Equation (1) and consumed by Equation (2).

Equation (1). Indeed, data from x-ray diffraction (XRD) and XPS measurements show that, although the surface layer of PuO_2 on a plutonium sample is not detectably altered when the sample is placed in vacuum at room temperature, the dioxide layer is immediately transformed to Pu_2O_3 when that same sample is heated to 150°C in vacuum. Evidently, the rate of Pu_2O_3 formation according to Equation (1) increases sharply with temperature as shown in Figure 5(a).

Data from XRD and XPS measurements also demonstrate that the oxide layer formed in air at 350°C is predominantly Pu_2O_3 beneath a thin layer of PuO_2 and a higher oxide. (The nature of this higher oxide is discussed later.) In other words, the ratio of Pu_2O_3 to PuO_2 at 350°C is essentially the reverse of that observed at room temperature. This observation and the rapid rate of Pu_2O_3 formation at 150°C suggest that the temperature dependence for oxide reduction, Equation (1), is stronger than for the subsequent oxidation of Pu_2O_3, Equation (2). Therefore, we conclude that the fraction of Pu_2O_3 in the oxide layer during oxidation in dry air increases significantly at elevated temperatures as illustrated in Figure 5(b). This dynamic picture of the oxide layer suggests that plutonium pyrophoricity at 150°C–200°C results from an increased fraction of Pu_2O_3 in the oxide layer at those temperatures.

With this picture in mind, we consider details of plutonium ignition studies performed earlier by numerous investigators, who determined ignition points by heating a metal specimen at a constant rate in flowing air while measuring the metal's temperature. The ignition temperature was marked by the onset of a self-sustained reaction, indicated by a sharp and sustained increase in specimen temperature above the programmed value. Temperature curves for relatively massive (greater than 0.2 millimeter in thickness) pieces of metal with low specific surface areas—less than 5 centimeters squared per gram (cm^2/g)—show small thermal spikes at 150°C–200°C, but those samples do not spontaneously

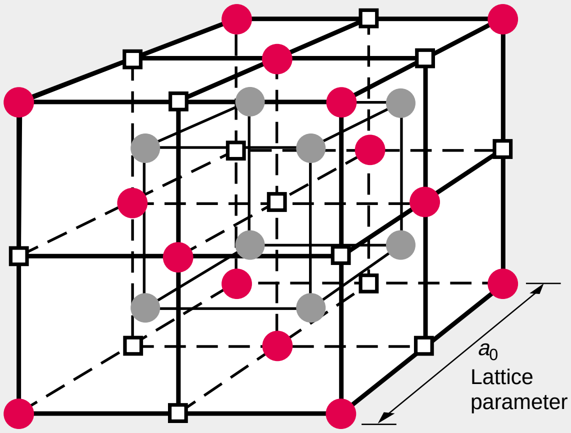
Fluorite and Fluorite-Related Structures in Plutonium Corrosion

Plutonium-oxygen compounds and many other products of plutonium corrosion form in the classic calcium fluoride (CaF_2) structure or one of its variations (see figure). As discussed below and in the main text, these particular structures seem to facilitate the remarkable catalytic properties of plutonium compounds.

Within the fluorite-type structure, plutonium cations (the red circles in the figure to the right) form a face-centered-cubic (fcc) lattice; that is, they occupy sites at the corners and centers of all the faces of a cube, where a_0 is the length of the cubic cell in angstroms. Atoms at corner sites are shared by eight cubes, and those in faces are shared by two cubes. Thus, four atoms reside within a single unit cell.

Anions such as O^{2-} and H^- occupy interstitial sites within the fcc cation lattice. The figure shows two types of interstitial sites: eight tetrahedral sites (gray circles), each surrounded by four cations, and four octahedral sites (white squares), each surrounded by six cations. The CaF_2 structure has an fcc lattice of cations with even-integer charge ($2n^+$); all tetrahedral sites are occupied by anions with charge n^-. If octahedral sites are also occupied, the resulting structure is identified as a bismuth trifluoride (BiF_3) or tri-iron aluminum (Fe_3Al) type. If anions and cations have the same charge, an ordered occupancy of all octahedral sites or half of the tetrahedral sites forms sodium chloride (NaCl) and zinc sulfide (ZnS) structures, respectively. The CaF_2-type structure is most frequently observed for hydrides, fluorides, and oxides of such electropositive metals as plutonium.

In the plutonium-oxygen system, Pu(IV) is a stable oxidation state and forms a CaF_2-type structure at the PuO_2 composition. The trivalent Pu(III) ion is also a relatively stable oxidation state. A cubic form of the oxide (α-Pu_2O_3) forms at temperatures below 1500°C. The α-Pu_2O_3 structure is obtained by ordered removal of 25 percent of the oxide ions from PuO_2. Above 700°C, a continuous solid solution (PuO_{2-x}, where $0< x <0.5$) forms between the two oxide compositions. Each decrease of x in the oxide composition of this solid solution results from the formation of anion vacancies and is accompanied by a 2x increase in the fraction of cation sites occupied by Pu(III). A homologous series (Pu_nO_{2n-2}) of oxide compositions (n = 7, 9, 10, and 12) apparently forms at low temperatures and fixed ratios of Pu(III) to Pu(IV). A hyperstoichiometric oxide, PuO_{2+x}, forms from PuO_2 by accommodating additional O^{2-} anions at octahedral sites. Charge balance is maintained because Pu(VI) cations replace the usual Pu(IV) cations in the metal lattice.



The Fluorite (CaF_2) Structure

Cationic positions occupied by plutonium are in an fcc configuration indicated by red circles. Tetrahedral and octahedral sites in the lattice are shown by gray circles and white squares, respectively. The cubic-lattice parameter is defined by a_0.

The fluorite structure also dominates the plutonium-hydrogen system. Plutonium hydride (PuH) crystallizes in a fluorite structure in the plutonium dihydride (PuH_2) composition and forms a solid solution phase, PuH_x, over the range $1.9< x <3.0$. Although formation of PuH_2 seems to imply that plutonium is present as Pu(II), a plutonium oxidation state known to be unstable, measurements show that plutonium is present as Pu(III) and that PuH_2 is metallic. These results suggest that PuH_2 may be formulated as $Pu(III)(H^-)_2(e^-)$, a phase in which charge balance is achieved by two hydride ions plus an electron in a conduction band. This description is consistent with electrical conductivity measurements showing that PuH_x progressively changes from a metallic material to a semiconductor, as x increases from 2 to 3. Electrons are apparently removed from the conduction band and bound as H^- on octahedral sites as the hydride composition increases.

Another example of a fluorite-related structure is provided by plutonium monoxide monohydride (PuOH), which is formed by the reaction of plutonium metal with liquid water at 25°C. Charge balance in this ternary compound of Pu(III) is achieved because O^{2-} and H^- occupy tetrahedral sites equally.

These fluorite and fluorite-related structures provide a stable fcc matrix of invariant, immobile plutonium cations, in which anions are surprisingly mobile. Anions move in and out of the stationary metal as chemical reactions occur and the plutonium oxidation state changes. The NaCl type of plutonium mononitride (PuN) forms from PuH_2 of the CaF_2 type because H^- is displaced from tetrahedral sites and N^{3-} is allowed to occupy all octahedral sites. The rapid rates of ionic transport and exchange are remarkably similar to those of superionic conduction, a phenomenon frequently observed in fluorite materials. Superionic conductors are solids characterized by a very rigid host lattice, light mobile ions, and high direct-current ionic conductivities. Transport in anion-deficient fluorite materials may also be enhanced because both tetrahedral and octahedral sites are vacant and able to participate in the concerted movement of anions. The impact of such factors on the surface and corrosion chemistry of plutonium has not yet been investigated.

Thermodynamics, Kinetics, Catalysis, and the Equilibrium State in the Plutonium-Oxygen System

Plutonium corrosion chemistry involves the complex interplay of thermodynamic, kinetic, and catalytic factors. Although often misunderstood and incorrectly applied, these concepts are the foundation of all chemistry and chemical processing. It is worthwhile to review those concepts and see how their careful application to the plutonium-oxygen system under varying conditions leads to some surprising results.

Thermodynamic properties quantify the fundamental driving force of chemical reactions. In particular, the drive toward thermodynamic equilibrium is due to the energy differences between atoms in different chemical configurations (or states). Energy differences between initial (reactant) and final (product) states are defined by the free energy change ($\Delta G°$) for the reaction. If a reaction releases energy ($\Delta G°$ is negative), it is thermodynamically favorable and can occur spontaneously. Conversely, if $\Delta G°$ is positive, the reaction is not spontaneous and cannot occur unless sufficient energy is added to the system.

Table I. Free-Energy Data for the Formation of Plutonium Oxides

	$\Delta G°$ of Reaction	
Reaction	**(kcal/mol Pu)**	**(kcal/mol O_2)**
$Pu(s) + O_2(g) \rightarrow PuO_2(s)$	–239	–239
$Pu(s) + 3/4\ O_2(g) \rightarrow 1/2\ Pu_2O_3(s)$	–189	–252

The reaction that occurs in a given system is not necessarily the energetically most favorable one, even though the latter would lead to the equilibrium state of that system. For example, when several reactions with negative free energies are possible, kinetics determines the reaction rate and pathway. In certain systems, energetically favorable reactions never occur at room temperature because their rates are immeasurably slow. Although such systems are not thermodynamically stable, they are kinetically stable, or "metastable." The reaction observed initially is always the one with the highest rate. If that reaction did not have the most negative $\Delta G°$, it would lead to different metastable states and to the possibility of subsequent reactions that progressively move the system toward equilibrium. A system remains in kinetic control until it reaches the equilibrium state.

Catalysts are substances that change reaction rates but not equilibrium states. By altering a reaction pathway, a catalyst increases the rate of the observed reaction or changes the chemistry of the system by enhancing the rate of a competing reaction. Typical catalysts for the reaction of gases are solids with active surfaces that promote the adsorption and dissociation of reactants and their recombination as products.

Applying these principles to the plutonium-oxygen system requires some care. Table I shows that the free energy for oxidizing 1 mole of plutonium into plutonium dioxide (PuO_2) is more negative than that for forming a half mole of plutonium sesquioxide (Pu_2O_3). However, contrary to a widely accepted view, coexistence of a PuO_2 layer and plutonium metal is not always the equilibrium configuration. If oxygen is present in excess, the most stable configuration is, indeed, achieved by reaction of the available metal with the maximum amount of oxygen. The relevant measure of stability is the energy released per mole of plutonium reactant, and PuO_2 is the equilibrium oxide. Conversely, if plutonium is present in excess, the most stable configuration is achieved by reacting the available oxygen with the maximum amount of plutonium. The relevant measure is the energy released per mole of atomic oxygen (O_2), and Pu_2O_3 is the equilibrium oxide on plutonium at room temperature. Thus, the predominance of dioxide on the metal surface at room temperature is clearly controlled by kinetic factors, not by product stability.

Figure 5 in the main text illustrates that exposure of plutonium to the abundant supply of oxygen in the atmosphere creates an inherently nonequilibrium condition. The oxide layer on the metal surface is a diffusion barrier separating an oxygen-rich region and a metal-rich region. Thus, pseudo-equilibrium conditions exist on opposite sides of that barrier. The presence of excess O_2 in the gas phase produces PuO_2 near the gas-oxide interface; the reaction of excess plutonium with the dioxide at the oxide-metal interface yields Pu_2O_3. At room temperature, the rapid formation of PuO_2 compresses the metal-rich region to the point that Pu_2O_3 is not observed, but increasing temperature promotes the formation of Pu_2O_3 , which becomes dominant above 150°C–200°C.

Although thermodynamic properties define possible reactions and equilibrium states of chemical systems, they fail to predict the strong metastable behavior of the plutonium-oxygen system. A system cannot reach equilibrium if slow kinetics prevents the most stable product from forming. Such is the case for the higher oxide, PuO_{2+x}. After early workers had failed to prepare oxides with compositions greater than PuO_2, they concluded that the dioxide is the equilibrium oxide in air. Their use of strong oxidants such as ozone (O_3) and nitrogen dioxide (NO_2) increased the free energy for reaction, making the thermodynamics favorable, but slow kinetics prevented further oxidation. Although water is energetically a less favorable oxidant than O_2, our research has shown that it both participates in and catalyzes the formation of PuO_{2+x} by altering the chemical pathway.

The need to characterize fundamental behavior in a plutonium-oxygen system and in other chemical systems is evident. We are trying not only to understand how water promotes oxidation, but also to define the phase equilibria and thermodynamic properties of PuO_{2+x}.

ignite until they reach 500°C (±25°C) during continued heating. In contrast, small pieces—turnings, chips, and powder—with maximum dimensions less than 0.07 millimeter and specific areas greater than 15 cm^2/g are pyrophoric when heated to 150°C–200°C in air. The thermal spikes observed at 150°C–200°C decrease in size with increasing specimen thickness, suggesting that pyrophoricity is driven by a surface reaction involving oxides. A surface reaction would produce a fixed amount of heat per unit of surface area, resulting in small thermal spikes for massive pieces of metal and large thermal excursions for material forms with high ratios of specific surface area to volume, exactly the pattern observed.

Our model of pyrophoricity applies the idea of surface reaction to our kinetic picture of the oxide layer. According to the model, heating the metal to 150°C–200°C in dry air transforms a large fraction of the steady-state dioxide layer (4–5 micrometers thick) to Pu_2O_3, as indicated by the lower sketch in Figure 5(b). Rapid oxidation of the Pu_2O_3 layer back to PuO_2 produces 54 kilocalories of heat per mole of dioxide, and a constant oxide thickness fixes the amount of heat produced per unit of surface area. The size of the resulting thermal spike is determined by the rate of reoxidation, the metal's ratio of surface area to volume, and the heat capacities of the oxides and metal.

We have used this model to calculate the thermal excursion of specimens with different dimensions and with geometries having the smallest (spheres) and largest (sheets) ratios of surface area to volume. We assume that the entire oxide layer is Pu_2O_3, reoxidation of Pu_2O_3 is rapid, and all heat from the reaction is instantaneously deposited in the reacting particle. If the excursion for a given metal dimension and geometry exceeds 350°C, we expect the metal temperature to reach or exceed 500°C and predict self-sustained reaction. Results show that pyrophoric behavior is not expected for metal spheres with diameters greater than 0.25 millimeter but is predicted for metal sheets with thicknesses less than 0.09 millimeter. Excellent agreement with experimental observation suggests the validity of our model.

We also propose that a likely mechanism for initiating pyrophoric reaction is exposure of the Pu_2O_3 layer to air by spallation of an oxide particle. A protective PuO_2 layer is not reestablished after ignition because rapid diffusion of oxygen and rapid reduction of PuO_2 to Pu_2O_3 are favored at the elevated temperatures reached during a self-sustained reaction. We also note that diffusion cannot account for the rapid transport of oxygen needed to initiate a self-sustained reaction at 150°C and conclude that Pu_2O_3 promotes transport of oxygen to the oxide-metal interface.

Conjecture on Oxygen Transport in Plutonium Oxide. Of the many kinetic factors introduced in this overview of corrosion in air, the mobility of the oxygen in the product layer is especially important and intriguing. One must wonder why diffusion of oxygen in PuO_2 is slow and rate limiting, whereas transport of oxygen in Pu_2O_3 is apparently very rapid. This behavior and other key properties of solid reaction products are strongly influenced by their crystal structures. All corrosion products formed by reaction with oxygen, hydrogen, and water have structures whose plutonium atoms are arranged in face-centered-cubic (fcc) configurations (see the box "Fluorite and Fluorite-Related Structures in Plutonium Corrosion" on page 260). And the chemical and kinetic behaviors described in this article suggest that the fcc plutonium lattice remains stationary whereas anions such as O^{2-} and H^- move in and out of the interstitial sites in that lattice with apparent ease. The facile transport of anions in Pu_2O_3 is neither quantified nor understood but is consistent with enhanced anionic mobility in structures with vacant lattice sites.

Reaction of Oxide-Coated Plutonium with Hydrogen

We now turn to the reaction of plutonium with hydrogen (hydriding), in which surface compounds are, once again, a determining factor. Plutonium hydride (PuH_x) is an fcc phase that forms a continuous solid solution for $1.9 < x < 3.0$ (Haschke 1991, Ward and Haschke 1994).

$$Pu(s) + (x/2)H_2(g) \rightarrow PuH_x(s) \quad . \qquad (3)$$

The observed value of x depends on hydrogen pressure and temperature. The hydride is readily oxidized by air, and it decomposes back to its component elements when heated in dynamic (continuously pumped) vacuum.

Hydriding occurs only after the ubiquitous dioxide layer on the metal is penetrated. Unlike oxidation, which proceeds evenly over the entire dioxide surface, the reaction of hydrogen initiates at a limited number of nucleation sites, and a single nucleation site typically appears only after a lengthy, but unpredictable, induction period. Once formed, these sites are the most reactive areas of the surface. They grow like bacterial colonies; that is, the hydriding rate is proportional to the active area covered by the hydride, and it increases exponentially over time to a maximum value as sites grow and ultimately cover the surface. At that point, the rate is enormous and constant because the surface is fully active. For temperatures between –55°C and 350°C and a molecular hydrogen (H_2) pressure of 1 bar, the reaction at a fully active surface consumes plutonium at a constant rate of 6–7 g/cm^2 min and advances into the metal or alloy at about 20 cm/h.

Curve b in Figure 6 shows that hydriding is 10^{11} times faster than oxidation of unalloyed metal in dry O_2 at 25°C. Moreover, the hydriding rate is independent of temperature and proportional to the square root of hydrogen pressure, indicating that the rate-controlling step involves dissociation of H_2 at the gas-hydride interface rather

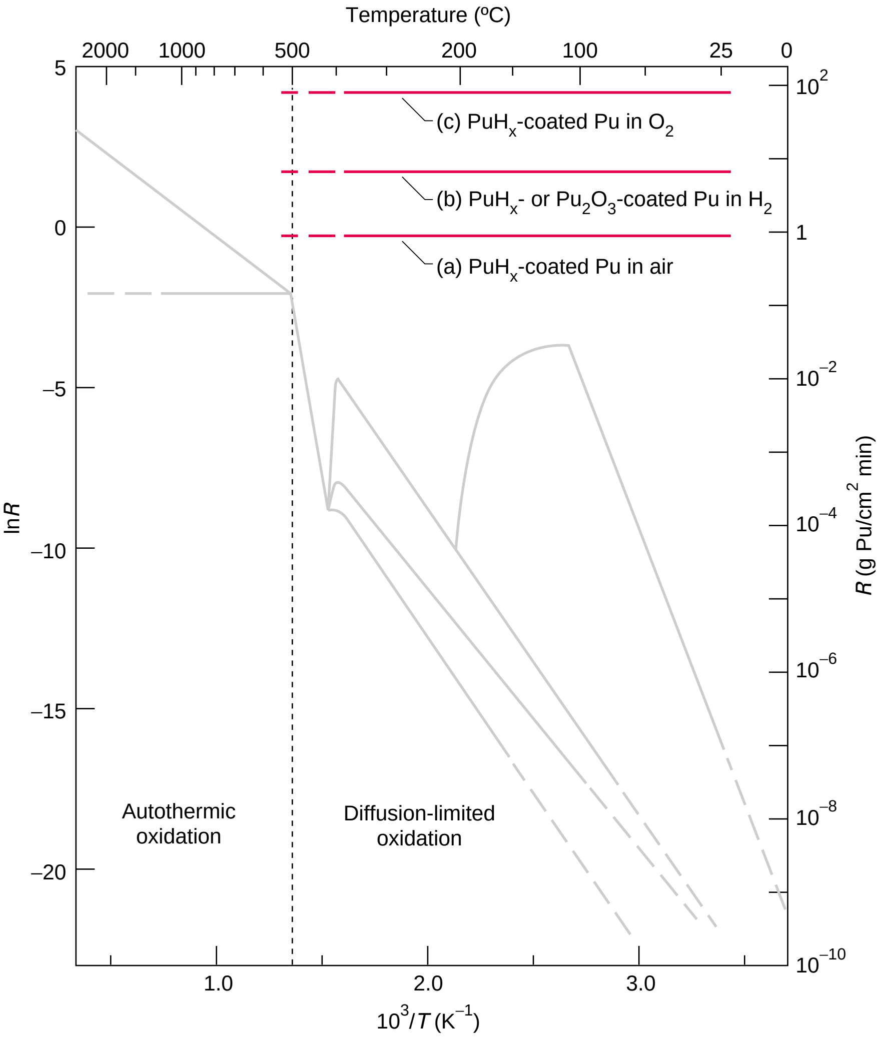


Figure 6. Rates for Catalyzed Reactions of Plutonium with Hydrogen, Oxygen, and Air

The diffusion-limited oxidation data from Figure 2 (shown here in gray) are compared with data for the rates of reactions catalyzed by surface compounds. Curves a, b, and c show the oxidation rates of PuH_x-coated metal or alloy in air, the hydriding rates of PuH_x- or Pu_2O_3-coated metal or alloy at 1 bar of pressure, and the oxidation rates of PuH_x-coated metal or alloy in oxygen, respectively, all given as a function of temperature. Notice that the rates are extremely rapid, and their values are constant regardless of the change in temperature, indicating that the surface compounds act as catalysts in promoting corrosion.

than diffusion of hydrogen through the surface layer of the hydride product. On the basis of this extremely rapid rate, we conclude that PuH_x catalyzes the dissociation of adsorbed H_2 and promotes the transport of atomic hydrogen to the hydride-metal interface.

A dramatically different kinetic behavior occurs if Pu_2O_3 replaces PuO_2 on the surface layer. Instead of forming and growing isolated nucleation sites, hydriding of Pu_2O_3-coated metal proceeds over the entire surface at once. In our studies, we heated PuO_2-coated metal to 150°C–200°C in vacuum to transform the surface to Pu_2O_3—see bottom sketch in Figure 5(a)—then cooled the sample to 25°C, and finally exposed it to H_2 at 1 bar of pressure. We found that the initial (zero time) hydriding rate equals that attained after the dioxide-coated metal is fully activated by the growth and coalescence of PuH_x sites. These results show that Pu_2O_3 is equivalent to PuH_x as a catalyst for the dissociation of H_2 and as a medium for hydrogen transport to the product-metal interface. Hydriding may nucleate at specific sites on the surface of the dioxide-coated plutonium metal because Pu_2O_3 is exposed at those locations by the autoreduction of the dioxide layer in thin areas or by the spallation of an oxide particle.

In summary, two independent surface processes catalyze the corrosion rate of oxide-coated plutonium metal by hydrogen. The surface self-activates by the nucleation and growth of PuH_x sites on the dioxide-coated metal or, before it is exposed to H_2, by the autoreduction of PuO_2 to Pu_2O_3. In both cases, the catalytic enhancements of the dissociation and transport of H_2 increase the initial corrosion rate at 25°C by a factor of 10^5.

Reaction of Hydride-Coated Plutonium with Oxygen

Suppose now that the plutonium has been coated with hydride before being exposed to O_2. We find that PuH_x and Pu_2O_3 are simultaneously involved in promoting an extreme pyrophoricity of both pure hydride particles and hydride-coated metal. We also relate the pyrophoricity of PuH_x to its variable stoichiometry, which allows the hydride to absorb additional hydrogen until x approaches 3. The stoichiometry of PuH_x varies, depending on conditions. Values of x near 2 are favored for surface layers formed on the metal at high temperatures and low H_2 pressures; higher values of x are found on isolated hydride particles at low temperatures and high pressures.

Earlier studies (Haschke 1991) show that particles of PuH_2 react spontaneously and rapidly upon controlled exposure to O_2 at 25°C, and the reaction produces an oxide layer on the exterior of the particles. The hydrogen produced by this reaction does not appear as H_2. Instead, it accumulates within the reacting particle, increasing the value of x in the residual PuH_x. Our recent work (Haschke et al. 1998) shows that self-heating from the reaction raises the temperature of the particle so that the oxide product is Pu_2O_3 instead of PuO_2. The net reaction is given by

$$xPuH_2(s) + 3(x - 2)/4O_2(g) \rightarrow [(x - 2)/2]Pu_2O_3(s) + 2PuH_x(s) \quad . \quad (4)$$

Pyrophoricity and rapid oxidation of the hydride are promoted by the absence of gaseous reaction products that would restrict access of O_2 to the surface. As the value of x within a hydride particle approaches 3, the particle raptures while the equilibrium H_2 pressure rises. The particle's extent of oxidation and ratio of surface area to volume determine the point of rupture.

In recent studies (Haschke et al. 1998), we also focused on hydride-coated metal and alloys and found that they react violently when rapidly exposed to oxygen. We prepared specimens with PuH_2 surface layers (100 micrometers thick) by first heating dioxide-coated plutonium (1–2 millimeters thick) above 150°C in vacuum to form Pu_2O_3 on the surface and then exposing that lower oxide layer to the requisite quantity of H_2. After exposure to excess O_2, the metal in the hydride-coated specimens was completely consumed in less than 1 second, and the resulting gas-phase temperatures exceeded 1000°C. Hydrogen was not released as H_2 even though excess O_2 was present. Instead, the hydrogen appeared as a small PuH_3 core inside an expanded product shell of Pu_2O_3 that retained the shape of the starting specimen. The reaction ended so quickly, and the thermal effect was so large that the rate could not be accurately determined by pressure-time data. Based on a reaction time of 1 second, the rate is about 80 g Pu/cm^2 min, corresponding to a corrosion rate of 3 m/h.

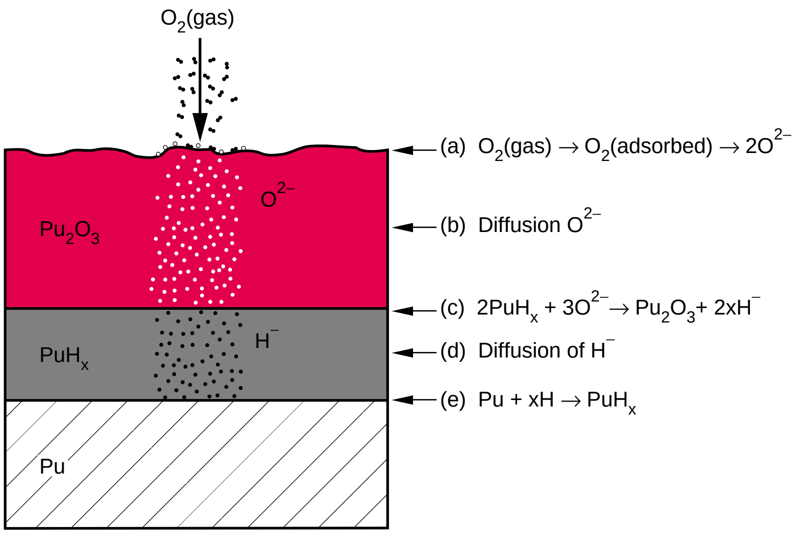

O_2(gas)
Pu_2O_3
O^{2-}
PuH_x
H^-
Pu
(a) $O_2(gas) \rightarrow O_2(adsorbed) \rightarrow 2O^{2-}$
(b) Diffusion O^{2-}
(c) $2PuH_x + 3O^{2-} \rightarrow Pu_2O_3 + 2xH^-$
(d) Diffusion of H^-
(e) $Pu + xH \rightarrow PuH_x$

Figure 7. Hydride-Catalyzed Oxidation of Plutonium

After the hydride-coated metal or alloy is exposed to O_2, oxidation of the pyrophoric PuH_x forms a surface layer of oxide and heat. Hydrogen formed by the reaction moves into and through the hydride layer to reform PuH_x at the hydride-metal interface. In the catalyzed reaction, there are five sequential processes. (a) Under the concentration gradient created by O_2 pressure, oxygen adsorbs at the gas-solid interface as O_2, dissociates, and enters the oxide lattice as an anionic species. A thin steady-state layer of PuO_2 may exist at the surface. (b) Under the oxygen concentration gradient created by the reaction of O_2 at the surface, oxide ions are transported across the oxide layer to the oxide-hydride interface. We identified the oxide as Pu_2O_3, but it might also be PuO_{2-x} ($0 < x < 0.5$), the continuous solid-solution phase formed between Pu_2O_3 and PuO_2 above 700°C. (c) Oxygen reacts with PuH_x to form heat (~160 kcal/mol of plutonium) and hydrogen. (d) The hydrogen produced at the oxide-hydride interface moves through the PuH_x layer to the hydride-metal interface under the gradient in hydrogen concentration created by oxidation. (e) The reaction of hydrogen with plutonium produces PuH_x and heat (~40 kcal/mol of plutonium).

We attribute the extraordinarily rapid oxidation of hydride-coated plutonium to catalysis by PuH_x. For both the pure hydride and hydride-coated metal, the reaction of O_2 with the hydride initiates spontaneously, produces oxide, and increases the stoichiometry of the hydride by driving the product hydrogen into the solid phase as described by Equation (4). Excess hydrogen in the hydride is continuously produced at the oxide-hydride interface and consumed at the hydride-metal interface. The reaction generates a large amount of heat (approximately 200 kcal/mol of plutonium). At elevated temperatures, the net reaction is accurately described by Equation (5).

$$2Pu(s) + 3/2\ O_2(g) \rightarrow Pu_2O_3(s) \quad . \quad (5)$$

This hydride-catalyzed oxidation of plutonium continues until all the metal is consumed and the composition of the residual hydride reaches PuH_3. Oxidation of that hydride is expected but not observed because the hydride is encased in the thick shell of the silver gray oxide.

The rate of oxidation is definitely much higher than anticipated for a gas-solid reaction. Plutonium hydride is an effective catalyst for the oxidation of plutonium because it forms at a rapid rate via the Pu + H_2 reaction and also oxidizes rapidly via the $PuH_x + O_2$ reaction. Thus, the relatively slow Pu + O_2 reaction is promoted by participation of the hydride as a reactive intermediate. As detailed in Figure 7, five major processes are involved in a hydride-catalyzed oxidation: reaction of O_2 at the gas-solid interface, transport of oxygen across the layer of product oxide, oxidation of the pyrophoric hydride at the oxide-hydride interface, transport of product hydrogen across the hydride layer, and reformation of the hydride at the hydride-metal interface. The slowest of these processes apparently determines the corrosion rate, but it has not been identified.

Other compounds also promote rapid corrosion. For example, diplutonium monoxide monocarbide (Pu_2OC), a surface phase incorrectly identified as plutonium monoxide (PuO) in early literature, forms at elevated temperatures and promotes hydriding. We have recently shown (Allen and Haschke 1998) that plutonium monoxide monohydride (PuOH) formed by the rapid corrosion of plutonium in salt water also catalyzes the Pu + O_2 reaction.

The unusual transport properties of Pu_2O_3 and PuH_x discussed in earlier examples are implied here as well. Based on the observed rate of catalyzed oxidation, the hydride advances into the metal at the rate expected for the reaction of plutonium with H_2 at a pressure of 150 bar. If transport across the hydride layer (approximately 100 micrometers thick) is rate limiting, the coefficient for the diffusion of hydrogen in PuH_x is temperature independent and on the order of 10^{-4} centimeter squared per second (cm^2/s). The corresponding value for the transport of oxygen in Pu_2O_3 must be of equal magnitude or larger. By comparison, coefficients determined for the self-diffusion of oxygen in PuO_2 at 250°C–500°C are in the range of 10^{-15} to 10^{-12} cm^2/s (Stakebake 1988). The very rapid temperature-independent transport of both oxygen in Pu_2O_3 and hydrogen in PuH_x suggests that these compounds may be superionic conductors—solids with ionic mobilities and conductivities typically observed in molten salts.

We have shown that plutonium hydride on the metal activates the surface for the catalyzed corrosion with plutonium. Often the hydride forms from unanticipated sources of hydrogen, such as α-particle radiolysis of organic materials or chemical reactions of water. Regardless of the hydrogen source, the potential consequences are enormous. A comparison of curves c and 1 in Figure 6 shows that hydride-catalyzed corrosion of δ-phase plutonium alloy by O_2 at 25°C is more than 10^{13} faster than oxidation of plutonium in dry oxygen or air.

Reaction of Hydride-Coated Plutonium with Air

When exposed to air as opposed to oxygen, plutonium hydride reacts with both oxygen and nitrogen. The $PuH_x + N_2$ reaction is slow at room temperature but occurs readily at temperatures above 200°C–250°C. According to Equation (4), the reaction of O_2 with pyrophoric hydride produces sufficient heat to promote rapid formation of PuN.

$$PuH_2(s) + [(x-2)/2]N_2(g) \rightarrow (x-2)PuN(s) + 2PuH_x(s) \quad . \qquad (6)$$

Again, the hydrogen (produced by the oxidation and nitriding reactions) remains in the solid and increases the stoichiometry of residual hydride. Thus, the pyrophoricity of PuH_x is promoted because neither product H_2 nor residual N_2 accumulates and blocks the flow of oxygen to the gas-solid interface.

Plutonium metal coated with hydride also corrodes rapidly when exposed to air, and as in the previous example, the hydride coating catalyzes the reaction. The net reactions for the corrosion of the metal by oxygen and nitrogen in air are defined by Equations (5) and (7), respectively.

$$Pu(s) + (1/2)N_2(g) \rightarrow PuN(s) \quad . \qquad (7)$$

Both reactions occur simultaneously at the gas-solid interface and indiscriminately consume nitrogen and oxygen at the molar ratio (3.71 N_2:1 O_2) of the elements in air. Hydrogen produced by these reactions is transported across the PuH_x layer and reacts at the hydride-metal interface. Each mole of air consumes 1.86 moles of plutonium and generates approximately 170 kilocalories of heat. The corrosion rate is independent of temperature and alloying, is proportional to the square of air pressure, and equals 0.7 ± 0.1 g Pu/cm^2 min in air at 1 bar of pressure. If air gains unrestricted access to surfaces of hydride-coated plutonium, a metal specimen with a thickness of 1 millimeter is completely corroded in about 1.5 minutes. We must further characterize the gray corrosion product to determine if it is an oxide-nitride mixture or a single-phase oxide nitride, but we know it reacts slowly in air at room temperature to form PuO_2.

The presence of hydride on the plutonium surface not only alters the kinetics of corrosion in air, but also changes the chemistry of corrosion. Elemental plutonium and molecular nitrogen (N_2) do not react directly to any significant extent even during their prolonged heating at temperatures above 1000°C. By contrast, nitrogen is the primary reactant during the hydride-catalyzed corrosion of plutonium in air. As a result, a nitrogen boundary layer does not form at the gas-solid interface as it does during the rapid oxidation of ignited plutonium. Thus, the observed rate for hydride-catalyzed corrosion in air is a factor of 5 faster than the rate for the self-sustained oxidation of ignited plutonium in air.

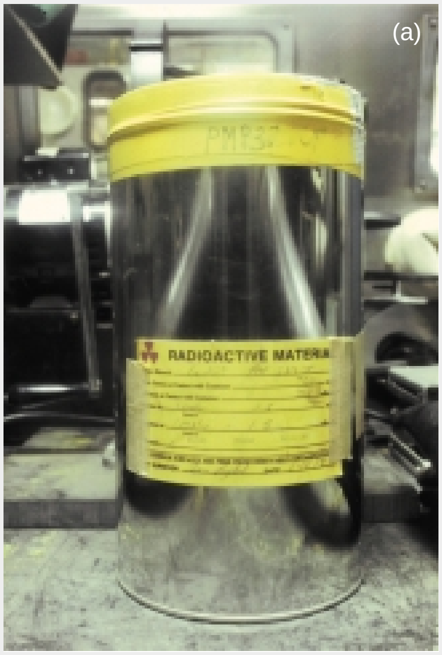
Compared with the rate for hydride-catalyzed corrosion in O_2, the rate in air is 100 times slower. This finding suggests that one or more steps involving reaction or transport of nitrogen limit the rate for air. The data in Figure 6 show that the hydride-catalyzed corrosion rate is 10^8 times faster than the oxidation rate of unalloyed metal in saturated water-vapor or moisture-saturated air at room temperature. Occurrence of this hydride-catalyzed reaction in a storage container at Los Alamos is described in the box "Catalyzed Corrosion of Plutonium: Hazards and Applications."

Catalyzed Corrosion of Plutonium: Hazards and Applications

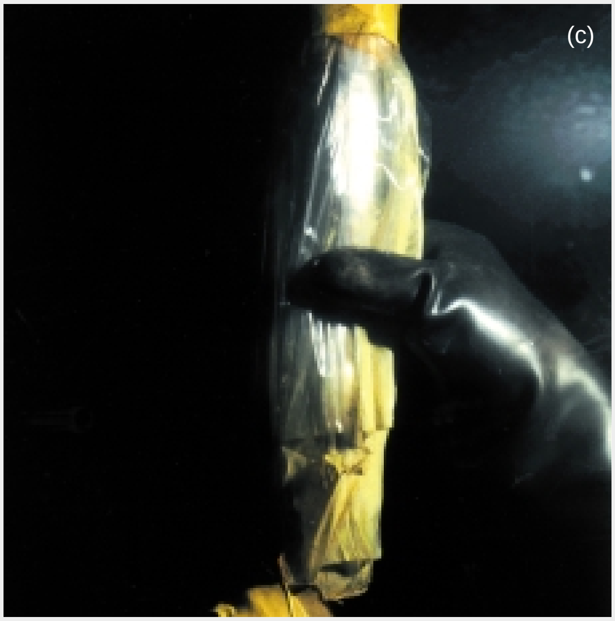
John M. Haschke and Joseph C. Martz

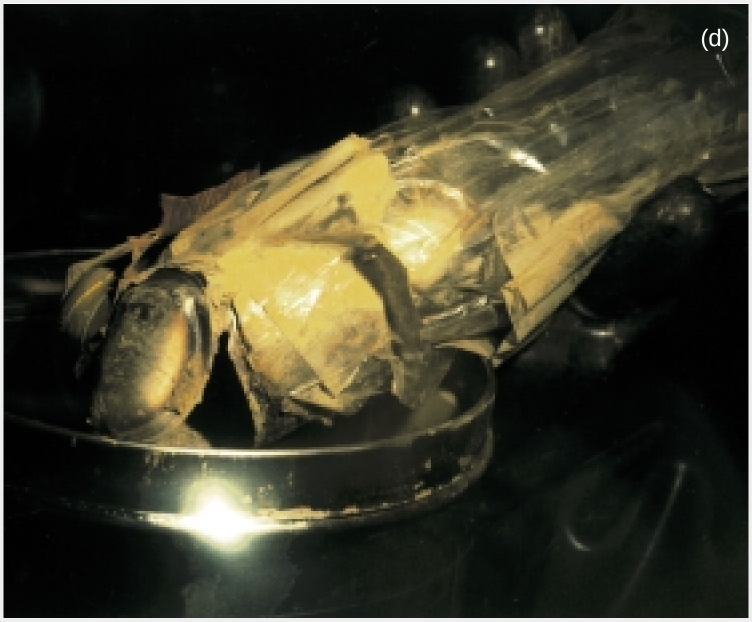
Catalyzed corrosion reactions of plutonium metal are not laboratory curiosities produced by careful manipulation of chemical reactants. Several incidents involving the corrosion of plutonium metal, failure of storage containers, and localized release of plutonium-containing particles into the work environment were attributed to catalyzed corrosion reactions (Haschke and Martz 1998b) and led to redesigning the storage package. In addition, catalyzed corrosion reactions have become the basis of efficient methods for converting plutonium metal from classified weapons configurations into simple ingots.

In 1993, a worker at the Los Alamos Plutonium Facility became contaminated with plutonium-containing particles while handling a standard storage package containing a 2.5-kilogram plutonium casting. The packaging configuration was similar to that used worldwide. It consisted of an inner cylindrical steel container to hold the casting, two layers of sealed “bag-out” plastic to contain radioactive contamination, and an outer slip-lid can. The incident occurred after the package had been stored for 11 years. As the outer can was flexed during handling, a puff of air carrying plutonium-containing particles escaped through a break in the taped seal of the can and contaminated the worker. The package was placed in a reduced-oxygen (less than 3 percent O_2) glove box, and the inner cylinder was left there for 3 hours after having been removed from the package. The accompanying photographs were taken during the disassembly. As the plastic-wrapped inner container was lifted out, its end ruptured because of pressure from the continuing rapid formation of plutonium oxides and other low-density corrosion products. A typical plutonium casting would form about 10 grams of PuO_2 per year from normal oxidation in air. Instead, the observed extent of the reaction was many orders of magnitude greater. Also, the inner vessel, which still contained unreacted metal, had become hot, and its diameter had increased by about 50 percent. The vessel was transferred to an argon-filled glove box, where the reaction ceased at once.



Evaluation of this incident shows that hydride catalysis caused by a complex set of physico-chemical processes led to rapid corrosion of





the metal casting during storage and to very rapid corrosion during the 3-hour waiting period in the reduced-oxygen glove box.

The weld at the ruptured end of the inner vessel had evidently been defective from the start, allowing gases to be continually pumped in and out of that vessel, as atmospheric pressure changes compressed and expanded the sealed plastic bagging. Plutonium oxide particles were entrained by thermal currents in the vessel, transported through openings in the weld, and deposited on the plastic over several years. During that period, the bagging isolated the metal casting from any external oxygen source, and the normal surface PuO_2 was apparently autoreduced to Pu_2O_3. Over time, the plastic bagging became discolored near the weld, as well as embrittled from the radiolytic decomposition induced by α-particles emitted from the deposited plutonium oxide particles. The molecular hydrogen produced during the radiolysis of the plastic entered the inner vessel and formed hydride on the Pu_2O_3-activated surface of the casting. During these processes, the storage package did not change its mass, and therefore the problem was not detected. When the embrittled plastic failed during storage, air reached the inner vessel, and a hydride-catalyzed reaction of the oxygen and nitrogen with the hydride-coated plutonium ensued at a throttled rate determined by access of air to the reaction zone. The resulting expansion of the solid led to the complete failure of the defective weld.

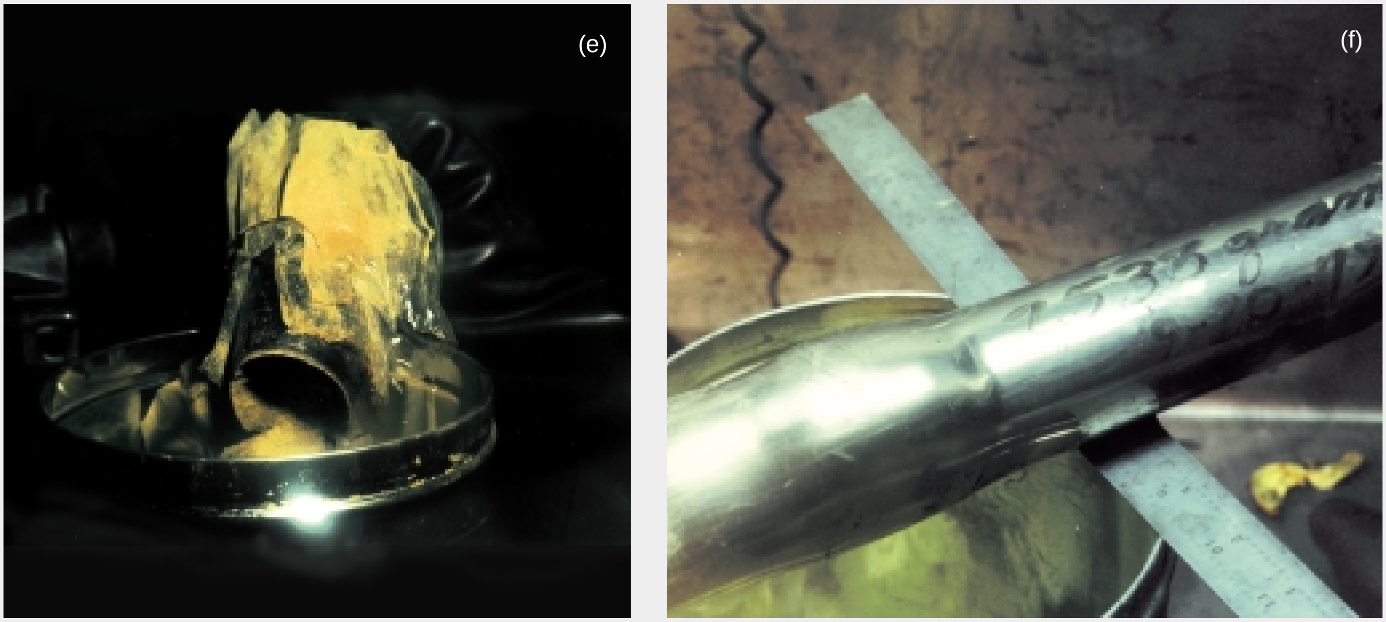
The corrosion rate became rapid during exposure to the glove box atmosphere and was estimated from the dramatic increase in the the vessel's volume during the 3-hour period, the bulk density of the corrosion product, and the approximate surface area of the metal. The result (0.3 g Pu/cm^2 min) is in excellent agreement with the value measured during studies of hydride-catalyzed corrosion (0.7 ± 0.1 g Pu/cm^2 min).

The experience and knowledge we gained from evaluating this incident and from studying catalyzed corrosion reactions find broad application in reducing the nuclear danger. The safe storage of plutonium requires using two metal containers with certified seals and ensuring that organic materials are excluded from the package. These two safety criteria are incorporated in the plutonium storage standards adopted by the U.S. Department of Energy and the International Atomic Energy Agency.

Knowledge of plutonium corrosion kinetics and particle-size distributions for a whole range of conditions enables realistic hazard assessments of plutonium dispersal during accidents. Catalyzed hydriding is also the key reaction in the hydride-dehydride recycle process for destroying weapon configurations and recovering plutonium metal—both done in a single step. Hydride-dehydride recycling generates no mixed or liquid waste of any kind. The recovered plutonium is a storage-ready ingot, and the hydrogen gas, which is both created and recycled in a uranium hydride storage system, is never released and does not present an explosion hazard. This process was recognized by the *R&D Magazine* as one of the best 100 technical innovations of the year and is the foundation technology of the Automated Retirement and Integrated Extraction System (ARIES) for separating plutonium from weapon components. The hydride-catalyzed oxidation of plutonium holds potential for development as a parallel single-step process in the rapid recovery of plutonium as oxide rather than metal.

Failed Storage Container for Plutonium Metal

Each photo shows a step in the disassembly of the container for a 2.5-kg casting of plutonium metal. (a) The outer container is placed in a glove box; (b) when the lid is removed, the plastic bagging shows; (c) when the plastic bagging and inner cylinder are lifted out of the container, discolored, embrittled plastic decomposed by radiolysis is revealed; (d) a rupture in the inner container is visible; (e) the corrosion product pours out of the ruptured end; and (f) an increase in the inner vessel's diameter near the ruptured end shows the extent of hydride-catalyzed corrosion during a 3-hour period.



Moisture-Enhanced Oxidation and the Role of Higher Oxides

The moisture-enhanced corrosion of plutonium in air was first observed during the Manhattan Project, but the mechanism of this process remained a mystery until very recently (Haschke et al. 1996, Haschke and Martz 1998b). We shall first outline that mystery.

At room temperature, the corrosion rate of plutonium by water vapor at its equilibrium vapor pressure is more than 100 times faster than the corrosion rate in dry air. At 100°C, the two rates differ by almost 10^5. Early work showed that exposure of plutonium to both molecular oxygen and water vapor results in the formation of PuO_2.

$$Pu(s) + O_2(g) \rightarrow PuO_2(s) \quad . \qquad (8)$$

$$Pu(s) + 2H_2O(g) \rightarrow PuO_2 + 2H_2(g) \quad . \qquad (9)$$

Moreover, corrosion rates for moisture-saturated air and moisture-saturated oxygen are equal to those for equilibrium water vapor, suggesting that the oxidation of plutonium metal in the presence of moisture is described by Equation (9). The situation is perplexing because O_2, not H_2O, disappears from the gas phase during corrosion, and H_2 is not observed as a gaseous product if oxygen is present. Similarly, uranium metal oxidizes faster in moist oxygen than in dry oxygen, but again O_2 disappears, the concentration of H_2O remains constant, and H_2 is not released (Baker et al. 1966). However, after O_2 is depleted from the gas phase, the H_2O concentration decreases at a rate matched by the formation of H_2.

Early attempts to explain the moisture-enhanced oxidation of plutonium metal involved changes in the mechanism of that reaction: The usual O^{2-} diffusion was eliminated as the rate-limiting step of the oxidation process. Most proposed models assumed that the increased rate was due to the relatively fast diffusion of a hydroxide ion (OH^-) through the oxide layer. Those models suggested a possible explanation for the enhanced rate but did not account for the disappearance of O_2 at the rapid rate characteristic of the Pu + H_2O reaction nor for the formation of oxide as the only corrosion product in moist air. If OH^- were the diffusing species, an equimolar mixture of PuO_2 and PuH_2 would form at the product-metal interface.

We solved the mystery by a number of discoveries. Studying the plutonium-water reaction, we observed a previously unknown product and realized it was an oxide higher than PuO_2 (Stakebake et al. 1993). In separate studies of PuO_2 (Allen and Haschke 1999, Morales et al. 1999), we defined the chemistry of the PuO_2 + H_2O reaction, in which the higher oxide PuO_{2+x} is formed. We also identified the role of this higher oxide in catalyzing the formation of H_2O from H_2 and O_2. We then realized that PuO_{2+x} would always be found on the surface of plutonium metal in the presence of moisture, increasing the oxygen gradient across the steady-state oxide layer. It then became apparent that O^{2-} is indeed the diffusing species and that the rate of plutonium oxidation increases because a higher oxygen gradient increases the flux of O^{2-} transport through the layer.

Plutonium Dioxide and Water Vapor. We gleaned the key elements of this solution while trying to define safe conditions for the extended storage of surplus plutonium oxide in sealed containers (Haschke and Allen 1995). Our initial concern was the possible radiolysis of water adsorbed on the dioxide surface. Alpha radiation produced in plutonium decay might dissociate water into hydrogen and oxygen and thereby generate unacceptably high gas pressures within the containers. In one test for radiolysis, we exposed PuO_2 to saturated water vapor (0.032 bar) at 25°C. In another test, we exposed the oxide to an O_2 + H_2 mixture in a 1:2 molar ratio at 25°C and 0.2 bar of total pressure. We measured kinetic data and identified products by chemical analysis.

These measurements demonstrated that the dioxide surface is an active template for equilibration of the oxygen-hydrogen system. When the dioxide was exposed to the O_2 + H_2 mixture, both H_2 and O_2 were consumed, and H_2O was formed as the reaction product. The reaction pathway apparently involves adsorption and dissociation of the diatomic gases on the oxide surface—Equations (10) and (11)—followed by association of the atomic species as water—Equation (12).

$$H_2(g) = H_2(ads) = 2H(ads) \quad . \qquad (10)$$

$$1/2\ O_2(g) = 1/2\ O_2(ads) = O(ads) \quad . \qquad (11)$$

$$2H(ads) + O(ads) \rightarrow H_2O(ads) = H_2O(g) \quad . \qquad (12)$$

$$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(g) \quad . \qquad (13)$$

We recently measured the rate of the net reaction defined by Equation (13). At 25°C, the production of water vapor in the presence of the oxide surface is approximately 6 micromoles per meter squared of oxide surface per day (Allen and Haschke 1999).

Molecular hydrogen appears when the dioxide is exposed to water vapor, but O_2 is not observed during these tests. Evidence for the radiolysis of water is absent. If, in fact, water is dissociated by alpha radiation, the O_2 and H_2 products are transient and immediately recombine on the catalytic oxide surface.

Our detection of hydrogen, but not oxygen, during exposure of the dioxide to water vapor is consistent with results of the earlier study (Stakebake et al. 1993), showing that an oxide with compositions substantially greater than PuO_2 forms at the gas-oxide interface during the reaction of plutonium with water vapor. The existence of the higher oxide was surprising and controversial because extensive studies by earlier workers

(Cleveland 1979, Wick 1980, Katz et al. 1986) had shown that PuO_2 does not react with oxygen, ozone, or nitrogen dioxide. The earlier workers concluded that PuO_2 is the highest oxide composition for plutonium. In contrast, our studies with the dioxide and water vapor at 25°C–350°C and a water vapor pressure of 0.025 ± 0.007 bar (20 ± 5 torr) demonstrate that water reacts with the dioxide to form a higher oxide (PuO_{2+x}) and hydrogen (Haschke and Allen 1999, Morales et al. 1999).

$$PuO_2(s) + x\,H_2O(l, g) \rightarrow PuO_{2+x}(s) + x\,H_2(g) \quad . \quad (14)$$

We readily determined the reaction rate and oxide composition by quantifying the production of hydrogen over time.

On the basis of this work, we conclude that the $PuO_2 + H_2O$ reaction in Equation (14) is a normal chemical process and is not promoted by radiolysis. The release of hydrogen from the oxide surface implies that the plutonium oxidation state in the product oxide is higher than Pu(IV). It also implies that mass increases observed by earlier workers during studies under humid conditions cannot be attributed solely to adsorption of water on the oxide surface. We measured a constant reaction rate of 6 nmol H_2/m^2 of oxide per day at room temperature and found that the rate of hydrogen production increases systematically with temperature. An Arrhenius analysis of the data yields an activation energy of 9.4 kcal/mol. Compositions in excess of $PuO_{2.25}$ are formed, but the maximum value of x is unknown. In the box "PuO_{2+x}: The Stable Oxide of Plutonium in Air and the Environment," we describe additional properties of PuO_{2+x}.

Plutonium Dioxide and Moist Air. The studies of PuO_2 in moist air unequivocally demonstrate that, relative to PuO_{2+x}, PuO_2 is thermodynamically unstable in moist air over a substantial range of temperatures. Therefore, PuO_2 must be unstable in an atmosphere of oxygen, ozone, or nitrogen dioxide. The failure of early workers to obtain PuO_{2+x} by exposing the dioxide to strong oxidants is undoubtedly a consequence of the very slow kinetics for the oxidation reaction. In contrast, according to Equation (14), the reaction of PuO_2 with H_2O occurs at a significant rate and is relatively easy to observe. Although we did not detect the formation of the higher oxide during exposure of the dioxide to dry oxygen, we did observe it when we added moisture to the system. Moreover, the behavior of the system was parallel to that encountered during the moisture-enhanced corrosion of plutonium metal: O_2 was consumed at the rate observed for the $PuO_2 + H_2O$ reaction, but H_2 was not produced until oxygen was depleted.

Defining the steps in the net reaction between PuO_2 and moist air is essential for understanding the moisture-enhanced corrosion of plutonium metal. The observed interactions of PuO_2 with water and oxygen-hydrogen mixtures in air suggest that the reaction of PuO_2 with moist air proceeds via a catalytic cycle at the gas-solid interface described below and shown in Figure 8.

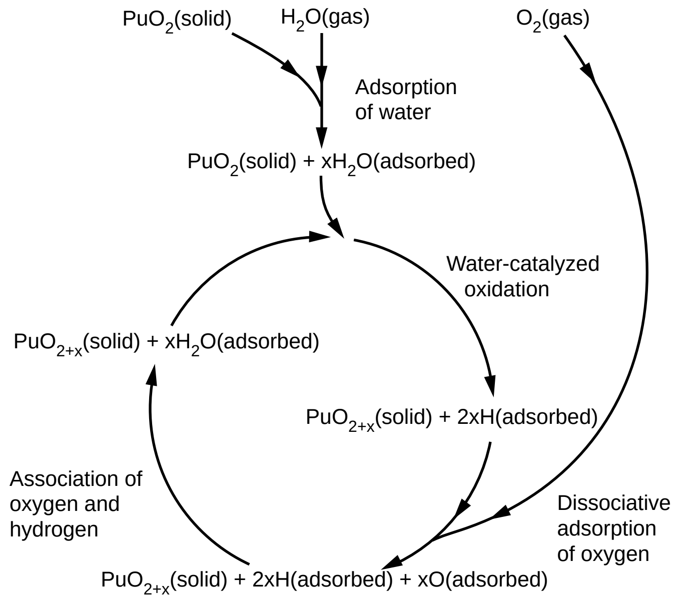
$$PuO_2(s) + xH_2O(ads) \rightarrow PuO_{2+x} + 2xH(ads) \quad . \quad (15)$$

$$(x/2)O_2(g) = xO(ads) \quad . \quad (16)$$

$$2xH(ads) + xO(ads) \rightarrow xH_2O(ads) \quad . \quad (17)$$

$$PuO_2(s) + (x/2)O_2(g) \rightarrow PuO_{2+x}(s) \quad . \quad (18)$$

The reaction of adsorbed water with PuO_2 to form PuO_{2+x} described by Equation (15) is faster than the



PuO2(solid)
H2O(gas)
O2(gas)
Adsorption of water
PuO2(solid) + xH2O(adsorbed)
Water-catalyzed oxidation
PuO2+x(solid) + xH2O(adsorbed)
PuO2+x(solid) + 2xH(adsorbed)
Association of oxygen and hydrogen
Dissociative adsorption of oxygen
PuO2+x(solid) + 2xH(adsorbed) + xO(adsorbed)

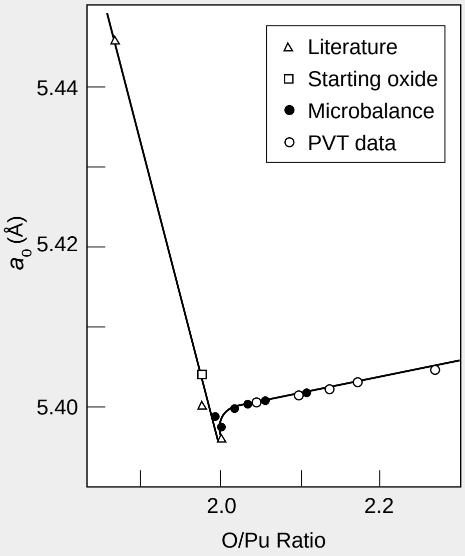
Figure 8. Moisture-Enhanced Oxidation of Plutonium Dioxide

When PuO_2 is exposed to moist air, a cyclical reaction begins, in which a higher oxide of plutonium is formed. The cycle initiates by adsorption of water on the dioxide and its subsequent reaction to form a higher oxide and adsorbed hydrogen. The cycle continues as oxygen, adsorbed and dissociated on the oxide surface, is consumed either by reacting with the adsorbed hydrogen to reform water or by reacting with the oxide to increase its oxygen content. The amount of water remains constant until all the oxygen is consumed. The reaction of water with the oxide continues in the absence of oxygen until all the water is consumed. Hydrogen formed in this reaction is released as gas.

PuO_{2+x}: The Stable Oxide of Plutonium in Air and the Environment

Thermochemical predictions and results of extensive experiments between the 1940s and 1970s led researchers to conclude that plutonium oxides with compositions greater than PuO_2 are unstable and cannot be prepared. Recent results discussed in the main article show, however, that a hyperstoichiometric oxide (PuO_{2+x}) is the thermodynamically stable plutonium phase in air at temperatures between 25°C and 350°C. The $PuO_2 + H_2O$ reaction produces the higher oxide and hydrogen, and the standard enthalpy and free energy for the formation of $PuO_{2.25}$(s) at 298 K are more negative than –270 and –253 kilocalories per mole (kcal/mol), respectively. Corresponding values for the formation of PuO_2(s) are –252.4 and –238.5 kcal/mol. Although favored thermodynamically, the reactions of O_2 and other strong oxidants with PuO_2 are not observed because they occur extremely slowly. In contrast, the reaction of the dioxide with liquid or gaseous water is kinetically favorable at low temperatures and is easily monitored by measurement of the extent to which H_2 forms. Pressure-volume-temperature methods are used for those measurements.

Data from the x-ray diffraction of PuO_{2+x} products obtained from kinetic studies reveal a fluorite-related face-centered-cubic (fcc) structure with lattice parameters near those of PuO_2. The graph plots the variation of the lattice parameter a_0 versus oxide composition. Below the dioxide stoichiometry (O/Pu = 2), a_0 decreases steeply with increasing oxygen content. Above the dioxide stoichiometry, the lattice parameter is surprisingly insensitive to composition. Evidently, the two simultaneous changes tend to have opposite effects on the lattice parameter. The proposed replacement of Pu(IV) by Pu(VI) at the cationic sites of PuO_2 tends to shrink the lattice, whereas the occupation of octahedral sites by the additional oxygen atoms tends to expand the lattice. Note that x-ray photoelectron spectroscopy data verify that Pu(VI) is present in PuO_{2+x}, and preliminary neutron-diffraction results for $^{242}PuO_{2+x}$ indicate that the additional oxygen anions in PuO_{2+x} occupy the vacant octahedral sites of the fluorite structure. The net result is that a_0 changes very slowly above the dioxide stoichiometry (an increase of 0.0018 angstrom for each increase of x by 0.10). It is also interesting that the presence of the higher oxide is easily detected by a color change. The PuO_2 and PuO_{2-x} phases are a dull yellow to khaki color, whereas PuO_{2+x} is green.



The Dependence of a_0 for $PuO_{2\pm x}$ on Composition

The lattice parameter a_0 is plotted as a function of increasing oxygen content. Below the dioxide stoichiometry, the lattice parameter decreases sharply with increasing oxygen content. Above the dioxide stoichiometry, the lattice parameter increases very slowly. The open triangles indicate reference data from literature sources. The open squares show data from the high-purity weapons-grade oxide used in our study. Filled and open circles show lattice parameters for products obtained during microbalance and pressure-volume-temperature (PVT) experiments with water vapor at 0.025 bar of pressure and temperatures in the range of 25°C to 350°C. The data point for the highest reported composition (O/Pu = 2.265) is from a literature source (Haschke 1992) describing PVT experiments of plutonium corrosion in aqueous salt solutions at 25°C. Molecular hydrogen was generated beyond the PuO_2 stoichiometry, but the experiment had been terminated before the maximum oxide composition was reached. An appropriate mass loss was observed when the $PuO_{2.265}$ product was heated at 500°C in dynamic vacuum until its mass became constant. The lattice parameter of the fired product (5.395 Å) corresponds to that of PuO_2.

The formation of PuO_{2+x} may have far-reaching consequences. In addition to promoting the corrosion rate of plutonium in moist air, the reaction of H_2O with the oxide generates hydrogen pressures capable of rupturing sealed containers during extended storage of the oxide. For this reason, plutonium oxide must be fired before it is packaged in sealed containers for extended storage. This process removes water and makes the oxide less soluble. Firing eliminates the higher oxide and thus Pu(VI). The presence of U(VI) increases the solubility of the higher uranium oxide UO_{2+x}, and the absence of Pu(VI) is expected to reduce the dissolution rate.

The PuO_{2+x} phase forms in conditions present in natural systems, implying that the higher oxide is the stable phase in the environment. Failure of x-ray diffraction measurements to identify a higher oxide is consistent with the insensitivity of a_0 to oxide composition. Recent x-ray absorption fine-structure, or XAFS, results indicate that only PuO_2 is present in the environment. Additional work is needed to resolve this discrepancy.

$PuO_2 + O_2$ reaction and determines the rate at which the higher oxide is formed. Atomic hydrogen produced by this reaction is not released as H_2 but remains on the oxide surface and recombines with O_2 to form water. According to Equation (16), adsorption and dissociation of O_2 on the dioxide surface, which we first identified in the oxygen-hydrogen-dioxide system, appear here as integral steps of the oxide-catalyzed reaction of H_2 with O_2 to form water. A water-catalyzed cycle is entered as H_2O from Equation (17) reacts with PuO_{2+x} from Equation (15) to progressively increase the x of the higher oxide. Equation (18) gives the net reaction for the process.

The catalytic cycle defined by Equations (15)–(17) accounts for the unusual behavior encountered during the reaction of PuO_2 with moist air or moist oxygen. In water vapor, the rate at which PuO_{2+x} forms is determined by the rate of Equation (14). In moist O_2, the higher oxide forms at the same rate but by following Equation (15). However, the hydrogen atoms formed by the reaction of H_2O molecules immediately recombine with oxygen atoms from O_2. Oxygen is consumed according to Equation (18) at the same rate as in the $PuO_2 + H_2O$ reaction, but H_2 is not observed. The net reaction involves two catalytic processes acting in concert: first, H_2O acts as a reactive intermediate (or catalyst) in promoting the oxidation of PuO_2 by O_2, and second, the oxide surface acts as a catalyst in promoting the regeneration of H_2O.

We can now explain the unanticipated implosion of storage vessels containing plutonium oxide. Although the reaction of the oxide with residual water shown in Equation (14) is expected to pressurize containers with H_2, negative pressures are observed in cans containing unfired oxide that was originally packaged in air. As demonstrated in laboratory tests, the pressure decreases because of the moisture-catalyzed reaction of the oxide with oxygen according to Equations (15) to (17). However, reduced pressure is a transient condition. After the O_2 in the storage atmosphere has been depleted, the pressure rises as the reaction of the residual H_2O produces H_2.

Plutonium Metal and Moist Air. Likewise, the catalytic cycle in Figure 8 can explain the moisture-enhanced corrosion of plutonium metal because that cycle creates PuO_{2+x} on the surface of the oxide-coated metal. The result is a gradient in the oxygen concentration across the oxide layer—from a higher concentration at the gas-oxide interface to a lower concentration at the oxide-metal interface. Earlier in this article, we described how the transport of oxygen from the surface to the oxide-metal interface determines the oxidation rate of plutonium in dry air. That rate of transport depends on three factors: the thickness of the coherent oxide layer, the temperature-dependent coefficient of oxygen diffusion in the oxide, and the gradient in oxygen concentration across the oxide layer. In the steady-state situation, when the temperature is fixed and the thickness of the oxide layer is constant because of continual spallation from the surface, the increase in the oxygen gradient produced by the formation of the higher oxide should increase the rate of oxygen transport to the oxide-metal interface and thereby the oxidation rate. In contrast, the higher oxide is not readily formed by dry air, and the lower rate of oxygen transport leads to a lower corrosion rate.

Thus, we find that the chemistry of plutonium corrosion in moist air or moist oxygen is consistent with a catalytic cycle similar to that proposed for the reaction of the dioxide with moist oxygen. The process is driven by the kinetically favored reaction of the metal with water as defined by Equation (19).

$$Pu(s) + H_2O(ads) \rightarrow PuO_2(s) + 2H(ads) \quad . \quad (19)$$

$$(1/2)O_2(g) = O(ads) \quad . \quad (20)$$

$$2H(ads) + O(ads) \rightarrow H_2O(ads) \quad . \quad (21)$$

$$Pu(s) + (1/2)O_2(g) \rightarrow PuO_2(s) \quad . \quad (22)$$

Instead of forming H_2 by Equation (9), as shown for water vapor, the product hydrogen from the $Pu + H_2O$ reaction combines with oxygen to regenerate water on the oxide surface. As described by the net reaction in Equation (22), O_2 and plutonium are consumed at the rapid rate characteristic of the $Pu + H_2O$ reaction. Retention of hydrogen at the surface implies that O^{2-} is the diffusing species in the oxide layer and that the rate is controlled by oxygen diffusion through the oxide layer, as it is in the reaction of plutonium with dry air.

In summary, the moisture-enhanced corrosion of plutonium in air apparently proceeds via a complex catalytic cycle in which plutonium oxide with a high stoichiometry is formed. Enhanced corrosion of plutonium would also occur if both H_2 and O_2 were present because the oxide surface would catalyze the formation of H_2O. Note that hydrogen often forms gradually through the thermal or radiolytic decomposition of organic materials. As shown in Figure 2, the effects of moisture on plutonium corrosion are evident at temperatures of up to 400°C.

Conclusions and Future Directions

Almost 60 years after it was first made in the laboratory, plutonium is still yielding surprises. We have observed unanticipated reactions and new compounds in various binary and ternary combinations of plutonium, oxygen, and hydrogen. We have also found that the reaction kinetics of those systems is extremely important in determining the reaction products. Our understanding of the chemistry of those systems seems surprisingly inadequate.

Although not reported in this article, we have also observed that the salt-catalyzed corrosion of plutonium metal by liquid water forms a rich variety of products including oxide hydrides, Pu_2O_3, mixed-valence oxides of Pu(III) and Pu(IV), and PuO_2. The higher oxide PuO_{2+x} forms as well, but it was identified only recently. Like the catalytic compounds Pu_2O_3, PuH_x, and PuO_{2+x} discussed in this article, the products obtained in aqueous media apparently have fluorite-related structures. We wonder about the importance of such materials in determining the solid-state chemistry of plutonium. More work is needed to define corrosion processes and products. We must investigate structures, thermodynamics, conductivities, transport processes, and other fundamental properties of plutonium compounds to understand how they influence the corrosion chemistry of plutonium.

We are intrigued by the consistent appearance of catalytic activity during plutonium corrosion. Although we have demonstrated the effects of surface chemistry and catalytic materials on bulk corrosion kinetics for several systems, studies are far from exhaustive. We must investigate catalytic behavior at the atomic level to augment our understanding and interpretation of kinetic results and other macroscopic observations. The following are some important research efforts in this regard: characterization of adsorption processes and adsorbates, definition of surface reactions at the atomic level, and determination of relationships between a solid's catalytic activity and electronic structure.

Of particular relevance are our continuing efforts to explore moisture-enhanced plutonium oxidation and to define the phase equilibria and thermodynamic properties of PuO_{2+x}, the higher plutonium oxide. By measuring the dissolution rates and solubilities of PuO_{2+x} in aqueous media, we hope to understand the role of PuO_{2+x} in plutonium transport. Formation of PuO_{2+x} and leaching of the hexavalent ion are consistent with the appearance of Pu(V) and Pu(VI) in aqueous media.

Another area in which the new findings on plutonium corrosion are indispensable is estimating dispersal hazards during accidents involving nuclear weapons or surplus nuclear material. Metallic plutonium is essentially nondispersible; it therefore presents very little risk of being released into the environment during an accident. In contrast, fine plutonium-containing particles (less than 10 micrometers in diameter) produced by corrosion are at much greater risk of being dispersed. When the solid expands or when gas forms during corrosion, pressures are generated that are known to rupture storage containers and release radioactive materials (Haschke and Martz 1998b). Moreover, mixtures containing hydrogen can form and explode, thus posing additional hazards. To a large extent, this potential hazard depends on the corrosion rate, size distribution of product particles, and time of corrosion, a period that may be as short as hours for accidents or as long as decades for storage.

We conclude that surface compounds are extremely important in determining the course and kinetics of plutonium corrosion and that both the chemical history and external conditions determine the chemical nature of the metal surface. We have been able to identify and characterize surface compounds and determine their effects on the reaction kinetics of plutonium metal and plutonium compounds. But the implications of our recent findings on plutonium technology have yet to be assessed. Certainly, our results are relevant to plutonium recovery, reprocessing, storage, accident assessment, and environmental migration. Continued investigation is therefore a must. ■

Further Reading

Allen, T. H., and J. M. Haschke. 1998. “Hydride-Catalyzed Corrosion of Plutonium: Initiation by Plutonium Monoxide Monohydride” (June). Los Alamos National Laboratory report LA-13462-MS.

Allen, T. H., and J. M. Haschke. 1999. “Interaction of Plutonium Dioxide with Water and Oxygen-Hydrogen Mixtures” (January). Los Alamos National Laboratory report LA-13537-M.

Baker, M. McD., L. N. Ness, and S. Orman. 1966. *Transactions Faraday Society* **62**: 2525.

Cleveland, J. M. 1979. *The Chemistry of Plutonium*. Chap. 9. La Grange Park, IL: American Nuclear Society.

Haschke, J. M. 1991. Actinide Hydrides. In *Topics in f-Element Chemistry: Synthesis of Lanthanide and Actinide Compounds.* Chap. 1, p. 1. Dordrecht, The Netherlands: Kluwer Academic Publishers.

Haschke, J. M. 1992. Hydrolysis of Plutonium: The Plutonium-Oxygen Phase Diagram. In *Transuranium Elements: A Half Century*. Edited by L. R. Morss and J. Fuger. Chap. 4. Washington, DC: American Chemical Society.

Haschke, J. M., and J. C. Martz. 1998a. *Journal of Alloys and Compounds* **266**: 81.

Haschke, J. M., and J. C. Martz. 1998b. Plutonium Storage. In *Encyclopedia of Environmental Analysis and Remediation*. Vol. 6, p. 3740. New York: John Wiley and Sons.

Haschke, J. M., T. H. Allen, and Luis A. Morales. 2000. Reaction of PuO_2 with Water: Formation and Properties of PuO_{2+x}. *Science* **287**: 285.

Haschke, J. M., T. H. Allen, and J. C. Martz. 1998. *Journal of Alloys and Compounds* **271**: 211.

Haschke, J. M., T. H. Allen, and J. L. Stakebake. 1996. *Journal of Alloys and Compounds* **243**: 23.

Katz, J. J., G. T. Seaborg, and L. R. Morss, eds. 1986. *The Chemistry of the Actinide Elements*. Vol. 1, Chap 7. New York: Chapman and Hall Ltd.

Larson, D. T., and J. M. Haschke. 1981. *Inorganic Chemistry* **20**: 1945.

Martz, J. C., and J. M. Haschke. 1998. *Journal of Alloys and Compounds* **266**: 90.

Martz, J. C., J. M. Haschke, and J. L. Stakebake. 1994. *Journal of Nuclear Materials.* **210**: 130.

Morales, L. A., J. M. Haschke, and T. H. Allen. 1999. "Kinetics of Reaction between Plutonium Dioxide and Water at 25°C to 350°C: Formation and Properties of the PuO_{2+x} Phase" (May). Los Alamos National Laboratory report LA-13597-MS.

Stakebake, J. L. 1988. "Calculation of Oxygen Diffusion in Plutonium Oxide Films during Oxidation of Plutonium 1 Weight Percent Gallium in 500 Torr Air" (May). Rocky Flats report RFP-3790.

Stakebake, J. L., D. T. Larson, and J. M. Haschke. 1993. *Journal of Alloys and Compounds* **202**: 251.

Ward, J. W., and J. M. Haschke. 1994. Comparison of 4f and 5f Element Hydride Properties. In *Handbook on the Physics and Chemistry of Rare Earths.* Vol. 18, p. 293. New York: Elsevier Science.

Wick, O. J., ed. 1980. *Plutonium Handbook.* Chaps. 6, 8, 11, and 12. La Grange Park, IL: American Nuclear Society.

John M. Haschke received his undergraduate degree from Texas Tech University, did postgraduate work as a Fulbright Fellow at Johannes Gutenberg University in Mainz, Germany, and obtained his Ph.D. degree from Michigan State University. His thesis was on the equilibrium and thermodynamic properties of lanthanide compounds at high temperatures. After working as a postdoctoral fellow at Arizona State University, Haschke joined the faculty in the Department of Chemistry at the University of Michigan. Haschke began his career in actinide chemistry as a research scientist for Rockwell International at the Rocky Flats Plant and developed his skills as a visiting scientist at the Institute for Transuranium Elements at Karlsruhe, Germany, before becoming a staff member at Los Alamos National Laboratory. His research interests have focused on fundamental aspects of plutonium corrosion chemistry and on their application to enhancing plutonium process operations, ensuring safe storage of surplus nuclear material, assessing hazards, and maintaining the nuclear stockpile. Haschke has published more than 150 technical papers and has authored several review chapters on lanthanide and actinide chemistry. He is currently working as an independent consultant on plutonium chemistry.