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## ANALYSIS OF AIR OXIDATION OF PLUTONIUM METAL

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### Abstract

Rates of oxidation of plutonium metal alloys exposed to high-temperature air are analyzed. Department of Energy facilities, including the Savannah River Site, utilize direct metal oxidation in air (DMO) to convert surplus plutonium metal alloys to a stable oxide form. The plutonium oxide can be either stored or used as feed for other processes. Typically, DMO is performed in an electrically heated furnace; the furnace supplies the heat needed to raise the metal temperature to its ignition point, which is a requirement for oxidation in dry air.

Oxidation rates are calculated for oxidation of a 3.5-in. diameter by 1.25-in. thick cylinder and for a 4-in. by 4-in. by 0.125-in. piece of foil. The calculations demonstrate that the oxidation rates are not limited by the build-up of the oxide powder layer on the surface of the metal but instead are kinetically controlled. Heat transfer calculations show that the air supply to the furnace must be throttled to limit the furnace temperature after ignition.

Separate analyses are included to estimate the minimum oxygen concentration in the air and the porosity of the oxide powder generated by the oxidation. The minimum oxygen concentration is estimated from the likelihood that an oxygen molecule will diffuse to an oxidation reaction site on the metal surface. The porosity is calculated from the assumption that the oxide layer expands to a minimal extent in the direction normal to the metal surface.

### Introduction

Plutonium metal oxidation rates are analyzed for the high temperature air oxidation of plutonium metal pieces. Rates are analyzed for both alpha phase and stabilized delta phase plutonium metal. Oxidation times are calculated for two representative pieces, a 0.0889-m diameter by 0.0318-m thick cylindrical "button" and a 0.1016-m by 0.1016-m by 0.00318-m foil.

The analysis of plutonium burning rates is based on information obtained from a literature search and a review of Savannah River Site operating experience. Savannah River Site tests have shown that plutonium can be oxidized either by moist air at approximately 473 K or by dry air at or slightly above the plutonium ignition temperature, which is about 773 K.

During moist air oxidation, the hydrogen from the water vapor forms a plutonium hydride phase, which then readily oxidizes. The moist air oxidation method was used to recycle plutonium with excessive impurity levels in the Savannah River Site FB-Line. This method avoided any risk of raising the temperature past the plutonium metal melting point of 913 K.<sup>1</sup> (Molten plutonium metal alloys with stainless steel and other metals such as tantalum; the formation of such alloys was undesirable for plutonium production.) The rate for moist air oxidation was sufficient to convert a plutonium button to oxide within one day, provided that the plutonium metal was alpha phase. Delta-stabilized plutonium is not susceptible to attack from water vapor and therefore oxidizes unacceptably slowly.

High temperature oxidation (also known as direct metal oxidation or DMO) involves direct attack of the metal surface by oxygen. If the plutonium surface temperature exceeds approximately 743 K (or 773 K for delta-stabilized plutonium),<sup>2</sup> the metal ignites. After ignition, the metal surface temperature undergoes an excursion to a temperature that can exceed 1073 K, before dropping to an equilibrium level that depends on the rate of cooling of the metal piece. The oxidation reaction is highly exothermic, so no heat source is required to sustain the reaction past the ignition point, i.e., the reaction becomes autothermic. Experience has demonstrated that it is difficult or impossible to control the metal surface temperature to prevent ignition in a processing environment. Typically, instead, the air feed rate is limited to control the rate of oxidation so that heat can be removed at the rate it is generated by the reaction. In this calculation the DMO oxidation approach is evaluated.

Los Alamos National Laboratory has conducted DMO tests with the objective of converting plutonium from weapons components into oxide.<sup>3</sup> In the Los Alamos DMO process, the plutonium metal is oxidized while being tumbled in a wire basket. The tumbling removes the outer oxide layer to improve heat transfer from and mass transfer to the oxidizing surface. Tests were conducted using a 1:2 helium/oxygen mixture at temperatures ranging from 748 K to 873 K.

At temperatures below the ignition point, the oxidation rate varies with temperature as predicted by an Arrhenius curve but undergoes several step changes that generally coincide with metal phase transitions. In particular, after the plutonium metal transitions to the delta phase, at approximately 673 K, the oxidation rate drops as a protective layer of substoichiometric oxide forms at the metal surface. The oxidation rate then rapidly climbs until ignition is reached. After ignition, the intrinsic chemical oxidation reaction is limited by solid phase diffusion of negatively charged oxygen ions across the substoichiometric surface layer.<sup>4</sup> The intrinsic oxidation rate is constant with temperature up to about 1273 K.<sup>5</sup> The overall oxidation rate for a metal surface covered by a thick oxide layer may be limited by gas phase diffusion through the oxide layer.

The following two sections present analyses of the minimum oxygen concentration required for ignition of plutonium metal and the effect of the oxide layer thickness on the rate of oxidation. The latter analysis shows that the maximum effective oxide layer thicknesses for the foil and the cylindrical “button” do not reach the critical thickness at which the intrinsic oxidation rate is inhibited. Consequently, the oxidation rates for both pieces can be considered to be kinetically controlled. The last section of this paper presents a heat transfer analysis, conducted to determine the maximum reaction rate at which the temperature of the oxide inside a furnace can be limited so that it does not significantly exceed the ignition temperature.

### **Analysis of Threshold Oxygen Concentrations for Ignition of Plutonium Metal**

The calculation of the threshold volume fraction oxygen required for ignition of a plutonium metal object is based on the number of available, i.e., adjacent, molecules at each oxidation reaction site. The theory behind this calculation is that, for the oxidation reaction to propagate through the metal, the probability of an oxygen molecule contacting and reacting at a given reaction site must be greater than 0.5. If more than 50% of the available reaction sites are active, the number of active sites will crowd out the number of inactive sites and the oxidized layer will propagate through the metal. If fewer than 50% of the sites are active, the inactive sites will predominate and the oxidation will fail to proceed.

A simplifying assumption is made that the air molecules surrounding each reaction site are arranged at a uniform density as close-packed, uniform size spheres. The number of available molecules at each equivalent molecular radial distance from the reaction site is assumed to be equal to the number of tangent spheres in that shell layer within the close packed arrangement. For the first few shell layers, the number of tangent spheres contains a discretization error. To minimize this error, the equivalent number of tangent spheres is calculated for successive shells proceeding outward until this number converges. The equivalent number of tangent spheres is computed by normalizing the gross count by the square of the equivalent radius for that shell.

For the initial sphere, there are three spheres located on the plane above and six spheres in the same plane. The three spheres in the plane below are not counted because they are assumed to lie below the surface. Only half the number of spheres in the surface plane is counted, giving a total of six spheres in contact. The second shell contains 12 spheres in the same plane, nine spheres in the first layer above the plane, and either six or seven spheres in the second layer above the plane, depending on the second layer orientation with respect to the first layer. The total number of spheres in the second shell is half of 12, or six, plus nine plus 6.5, for a total of 21.5. A similar count can be performed for each succeeding shell. The following equations summarize the number of spheres in each succeeding shell:

$$n_1 = 6 \quad (1)$$

$$n_2 = 21.5 \quad (2)$$

$$n_i = 2n_{i-1} - n_{i-2} + 10.5, \quad i \geq 2 \quad (3)$$

where

$n_1$  = number of spheres in the first shell

$n_2$  = number of spheres in the second shell

$n_i$  = number of spheres in the  $i$ th shell

$n_{i-1}$  = number of spheres in the shell one layer inside the  $i$ th shell

$n_{i-2}$  = number of spheres in the shell two layers inside the  $i$ th shell

The effective number of tangent spheres is computed by multiplying the gross number of tangent spheres by the ratio of the shell radius to the radius of the first shell, which is two sphere radii:

$$n_{i,\text{eff}} = n_i \left( \frac{r_1}{r_i} \right)^2 \quad (4)$$

where

$n_{i,\text{eff}}$  = equivalent number of spheres in the  $i$ th shell, projected to the first shell

$r_i$  = radius of the  $i$ th shell

$r_1$  = radius of the first shell

The shells are not propagated uniformly, but by layer. Therefore, the effective radius in the plane tangent to the reacting surface is greater than the effective radius in the normal plane. The average radius is calculated as a weighted geometric mean of the tangential and normal radii. The tangential radius is weighted twice as heavily as the normal radius to account for the fact that the tangential radius expands in two directions, compared to one direction for the normal radius. The average radius is given by:

$$r_i = (r_{i,\text{tan}})^{2/3} (r_{i,\text{norm}})^{1/3} \quad (5)$$

where

$r_{i,\text{tan}}$  = average radius of the  $i$ th shell, tangent to the plane of the reacting surface

$r_{i,\text{norm}}$  = average radius of the  $i$ th shell, normal to the plane of the reacting surface

The ratio of the tangential radius to the nominal radius is equal to the square root of the ratio of the areas of a circle and a hexagon inscribed in that circle. Thus,

$$r_{i,\text{tan}} = ir_1 \left( \frac{3(3)^{0.5}}{2\pi} \right)^{0.5} = 0.9094ir_1 \quad (6)$$

The ratio of the normal radius to the nominal radius equals the ratio of the close packed sphere layer height to the sphere radius. Therefore,

$$r_{i,\text{norm}} = ir_1 \left( \frac{(6)^{0.5}}{3} \right) = 0.8165ir_1 \quad (7)$$

The number of molecules adjacent to each reaction site is evaluated as the limiting number of tangent spheres as the number of shell layers expands:

$$n_{\text{eff}} = \lim_{i \rightarrow \infty} (n_{i,\text{eff}}) = 6.82 \quad (8)$$

where

$n_{\text{eff}}$  = limiting equivalent number of adjacent spheres, projected to the first shell

The limiting number of adjacent molecules converges on 6.82.

The probability that an adjacent molecule will react is assumed to be the probability that that molecule is an oxygen molecule; in other words, it is assumed that an adjacent oxygen molecule always will react. The probability is computed under the assumption that movement of air toward the surface occurs much faster than the rate of reaction, so that oxygen molecules are replaced by air molecules as they react. It is convenient to visualize the probability as the sum of this oxygen likelihood with replacement for each adjacent molecule. Viewed this way, the overall probability for an oxygen molecule reacting is given by:

$$p(x_s) = n_{\text{eff}} \sum_{j=1}^{\infty} x_s^j \quad (9)$$

where

$x_s$  = oxygen concentration at the surface

$p(x_s)$  = probability of reaction at a reaction site

The series  $\sum_{j=1}^{\infty} x_s^j$  is equal to  $\frac{x_s}{1-x_s}$ . Thus,

$$p(x_s) = \frac{n_{\text{eff}} x_s}{1-x_s} \quad (10)$$

For the oxidation reaction to propagate downward from the surface, the probability of reaction at any given site must be greater than 50%. For the limiting oxygen concentration required for ignition, then,

$$p(x_{s,\text{min}}) = 0.5 \quad (11)$$

where

$x_{s,min}$  = limiting oxygen concentration at the surface

$p(x_{s,min})$  = limiting probability of reaction at a reaction site

The preceding two equations combine to yield:

$$x_{s,min} = \frac{1}{2n_{eff} + 1} \quad (12)$$

The effective number of adjacent molecules is 6.82. For this value,

$$x_{s,min} = 0.0683 \quad (13)$$

The limiting surface concentration is the threshold concentration for ignition for bare plutonium metal in the absence of an oxide layer. If an oxide layer has formed, the minimum oxygen concentration increases due to diffusion through this layer. The minimum bulk oxygen concentration outside the oxide layer can be estimated as a function of the minimum surface concentration through an analysis of the diffusion equation.

Diffusion of oxygen through the oxide layer involves countercurrent diffusion of the nitrogen in air. Customarily, as in evaporation from a liquid surface, this is analyzed by adding a bulk flow term and setting the total mass flux of the noncondensable gas, comprised of diffusive and bulk flow, to zero. Diffusion to a reacting surface differs from evaporation in that the surface reaction rate contains local variations, whereas the evaporation rate from a liquid is nearly uniform. The variations in the local reaction rate can be pictured as setting up recirculation patterns within the oxide layer, where air flows toward the surface and oxygen diffuses to the surface over active reaction zones, and there is a counterbalancing flow of air away from the surface over inactive portions of the surface. The air circulation within the oxide layer is modeled using a dispersion term. With the addition of this dispersion term, the steady state mass transfer equation for flow of air and diffusion of oxygen toward the surface takes the form:

$$v \frac{dx}{dz} = D_{eff} \frac{d^2x}{dz^2} \quad (14)$$

where

$z$  = distance from the oxidizing surface

$v$  = convection velocity in the porous oxide layer

$x$  = mole fraction oxygen

$D_{eff}$  = effective dispersion coefficient for oxygen flow through the oxide layer

The rate of diffusion can be assumed to be sufficiently slow that the convection velocity remains constant throughout the oxide layer. For a constant velocity, the mass transfer equation becomes linear and can readily be solved with the appropriate boundary conditions.

The boundary conditions for the mass transfer equation are:

$$x = x_s \text{ at } z = 0 \quad (15)$$

and

$$x = x_b \text{ at } z = L \quad (16)$$

where

$x_b$  = bulk concentration of oxygen in the gas outside the oxide layer

$L$  = oxide layer thickness

For these boundary conditions, the solution of the mass transfer equation is:

$$x = \frac{\left( \exp\left(\frac{vL}{D_{\text{eff}}}\right) - \exp\left(\frac{vz}{D_{\text{eff}}}\right) \right) x_s + \left( \exp\left(\frac{vz}{D_{\text{eff}}}\right) - 1 \right) x_b}{\exp\left(\frac{vL}{D_{\text{eff}}}\right) - 1} \quad (17)$$

The fact that the surface oxidation reaction is heterogeneous allows the mass transfer equation to be integrated without the addition of any constants of integration. Because the surface reaction drives the diffusion, the integral mass transfer equation is applied at the metal surface. The surface integral mass transfer equation is:

$$vx_s = D_{\text{eff}} \left. \frac{dx}{dz} \right|_{z=0} \quad (18)$$

The solution to this integral equation gives the surface oxygen concentration as a function of the bulk concentration:

$$x_s = \frac{x_b}{2 - \exp\left(\frac{vL}{D_{\text{eff}}}\right)} \quad (19)$$

For the remainder of this analysis, it is convenient to introduce a dimensionless Péclet number defined by:

$$Pe = \frac{(-v)L}{D_{\text{eff}}} \quad (20)$$

and a concentration ratio defined by:

$$y = \frac{x_s}{x_b} \quad (21)$$

where

Pe = Péclet number for diffusion of oxygen through the oxide layer

y = ratio of the oxygen concentration at the metal surface to the oxygen concentration at the top of the oxide layer

The solution to the integral equation in terms of these dimensionless quantities becomes:

$$y = \frac{1}{2 - \exp(-Pe)} \quad (22)$$

The value of the Peclet number and the solution for the bulk oxygen concentration as a function of the surface concentration is obtained by analyzing the local rate of surface oxidation. The total local rate of reaction  $f_R R_{\text{diff}}$  equals the sum of the contributions from diffusion and convection:

$$f_R R_{\text{diff}} = -vx_s - D_{\text{eff}} \left. \frac{dx}{dz} \right|_{z=0} \quad (23)$$

where

R = nominal rate of surface oxidation

$f_R$  = multiplier to account for variations in the rate of surface oxidation

From the integral mass balance, the diffusive and convective mass fluxes at the metal surface are equal. Thus, from this mass balance:

$$f_R R_{\text{diff}} = \frac{2Pe}{2 - \exp(-Pe)} \left( \frac{D_{\text{eff}} x_b}{L} \right) \quad (24)$$

It may be noted that no restrictions have been placed on the surface rate of reaction other than those for diffusion through the oxide layer. In the absence of any such restrictions, the local oxidation rate scales proportionally as the rate of oxide layer diffusion. Linear scaling implies that:

$$\frac{d(f_R R_{\text{diff}})}{d\left(\frac{D_{\text{eff}} x_b}{L}\right)} = 1 \quad (25)$$

This scaling relationship is satisfied if:

$$\frac{2Pe}{2 - \exp(-Pe)} = 1 \quad (26)$$

The iterative solution to this equation takes the form:

$$Pe = Pe + \frac{2 - 2Pe - \exp(-Pe)}{2 - \exp(-Pe)} \quad (27)$$

The solution for the Péclet number and the concentration ratio  $y$  is

$$Pe = 0.7680 \quad (28)$$

and

$$y = 0.6510 \quad (29)$$

If an oxide layer has formed, the minimum bulk concentration required for ignition, i.e., the minimum concentration at the top of the oxide layer, is given as a function of the minimum surface concentration by:

$$x_{b,\text{min}} = \frac{x_{s,\text{min}}}{y} \quad (30)$$

where

$x_{b,\text{min}}$  = limiting oxygen concentration at the top of the oxide layer

The solution for the minimum bulk concentration is:

$$x_{b,\text{min}} = 0.1049 \quad (31)$$

The calculated minimum surface concentration of 6.8 vol % is in approximate agreement with the measured minimum concentration for ignition of 6 vol %, and the calculated minimum bulk concentration of 10.5 vol % is consistent with the observed concentration of 10 vol % for the onset of accelerated quenching.<sup>2</sup>

### **Analysis of Limiting Oxide Layer Thickness for Reduction of the Plutonium Oxidation Rate**

The minimum oxide layer thickness at which the plutonium metal surface oxidation rate begins to decrease can be estimated by comparing the pressure drop for flow across the oxide layer to the pressure change generated by the oxidation reaction at the limiting condition for ignition. The pressure change created by the reaction is equal to the product of the ambient pressure and the oxygen concentration change across the oxide layer, expressed as a volume

fraction. When the oxide layer thickness begins to affect the oxidation rate, this pressure change equals the pressure drop for flow:

$$\Delta P = P_a (x_{b,min} - x_{s,min}) \quad (32)$$

where

$\Delta P$  = pressure drop for flow of oxygen associated with plutonium oxidation across the oxide layer

The pressure drop for flow is given by the Ergun equation, which takes the form:<sup>6</sup>

$$\frac{\Delta P}{L} = \frac{150\mu v(1-\varepsilon_{ox})^2}{\varepsilon_{ox}^3 d_p^2} + \frac{1.75\rho v^2(1-\varepsilon_{ox})}{\varepsilon_{ox}^3 d_p} \quad (33)$$

where

$\mu$  = air viscosity

$d_p$  = average oxide layer particle diameter

$\rho$  = air density

The preceding two equations combine to give an expression for the limiting oxide layer thickness required for a reduction in the rate of oxidation:

$$L_{min} = \frac{P_a (x_{b,min} - x_{s,min})}{\frac{150\mu v(1-\varepsilon_{ox})^2}{\varepsilon_{ox}^3 d_p^2} + \frac{1.75\rho v^2(1-\varepsilon_{ox})}{\varepsilon_{ox}^3 d_p}} \quad (34)$$

where

$L_{min}$  = minimum oxide layer thickness resulting in a reduction in the rate of plutonium oxidation

For oxide layers thicker than this minimum thickness, the time-average oxidation rate decreases proportionally as the thickness increases.

It is assumed that the bulk flow rate equals the rate of consumption of oxygen at the metal surface. Therefore, the velocity is given by:

$$v = \frac{R_{rxn}}{M_{Pu}\rho_{g,m}} \quad (35)$$

where

$M_{Pu}$  = atomic mass of plutonium, 0.239 kg/mol

$\rho_{g,m}$  = molar gas density

The molar gas density is calculated using the ideal gas relation:

$$\rho_{g,m} = \frac{P_a}{R_g T} \quad (36)$$

where

$R_g$  = gas law constant

The evaluation of the oxide layer porosity is based on the assumption that the volumetric expansion that accompanies the metal oxidation is confined to the direction perpendicular to the oxidizing surface. Moreover, the expansion in this direction is limited to the direction outward from the metal surface. Mathematically, this implies that the ratio of the void volume to the

solid volume within the oxide equals the fraction of the volumetric expansion prevented by this steric hindrance,  $1 - f$ , divided by the total oxide volume associated with the fractional expansion allowed,  $f$ . In other words:

$$\frac{\varepsilon_{ox}}{1 - \varepsilon_{ox}} = \frac{(1 - f)(V_{PuO_2} - V_{Pu})}{fV_{PuO_2}} \quad (37)$$

where

$\varepsilon_{ox}$  = the oxide layer porosity

$V_{PuO_2}$  = the molar volume of  $PuO_2$

$V_{Pu}$  = the molar volume of Pu metal

To calculate the porosity, the fraction  $f$  and the molar volumes must be evaluated. The ratio of the two molar volumes is given by:

$$\frac{V_{PuO_2}}{V_{Pu}} = \frac{M_{PuO_2}\rho_{Pu}}{M_{Pu}\rho_{PuO_2}} \quad (38)$$

where

$M_{PuO_2}$  = molecular mass of  $PuO_2$ , 0.271 kg/mol

The fraction of the expansion that is not prevented by steric hindrance can be calculated by integrating the outward normal from the oxidizing surface over a uniform distribution of vectors, which takes the shape of a sphere. Thus, if  $\theta$  is the angle between a random vector and the outward normal vector, then:

$$f = \frac{\int_{-\pi}^0 r^2 \sin^2(\theta) \cos(\theta) dr \cos(\theta)}{\int_{-\pi}^0 \pi r^2 \sin^2(\theta) dr \cos(\theta)} \quad (39)$$

where

$r$  = radial distance from the center of a sphere

$\theta$  = angle between random vector and outward normal vector from the center of a sphere

Integration of this equation gives:

$$f = \frac{3}{16} \quad (40)$$

Substitution of Equations 38 and 40 in Equation 37 yields:

$$\varepsilon_{ox} = \frac{13 \left( \frac{M_{PuO_2}\rho_{Pu}}{M_{Pu}\rho_{PuO_2}} \right) - 13}{16 \left( \frac{M_{PuO_2}\rho_{Pu}}{M_{Pu}\rho_{PuO_2}} \right) - 13} \quad (41)$$

The oxide layer porosity is computed to be 0.627.

From the preceding analysis, the minimum oxide layer thickness required for a reduction in the rate of oxidation after ignition is 0.0891 m for an oxidation rate of 1.0 kg Pu/m<sup>2</sup>/min, 0.0677

m for an oxidation rate of 1.4 kg Pu/m<sup>2</sup>/min, and 0.0424 m for an oxidation rate of 2.1 kg Pu/m<sup>2</sup>/min.

The oxide layer thickness is calculated from the following volume balance, which equates the ratio of the oxide layer volume for the oxidizing specimen to the theoretical ratio of oxide to metal volumes from Equation 41:

$$\frac{V_{\text{tot}} - V_{\text{Pu}}}{V_{\text{Pu},0} - V_{\text{Pu}}} = \frac{\rho_{\text{Pu}} M_{\text{PuO}_2}}{\rho_{\text{PuO}_2} M_{\text{Pu}} (1 - \varepsilon_{\text{ox}})} \quad (42)$$

where

$V_{\text{tot}}$  = total volume of the remaining plutonium metal and oxide layer

$V_{\text{Pu}}$  = volume of the remaining plutonium metal

$V_{\text{Pu},0}$  = initial volume of the plutonium metal piece prior to oxidation

The oxide layer thickness is evaluated for the two pieces considered in this report, the 0.0889-m diameter by 0.0318-m high cylinder and the 0.1016-m by 0.1016-m by 0.00318-m square foil. If the top and side surfaces of the cylinder are assumed to oxidize at a uniform rate, then the volumes of the remaining metal, the original metal cylinder, and the total volume including the metal and the oxide layer are given by:

$$V_{\text{Pu}} = \frac{\pi (d_{m,0} - 2\Delta t_m)^2 (t_{m,0} - \Delta t_m)}{4} \quad (43)$$

$$V_{\text{Pu},0} = \frac{\pi d_{m,0}^2 t_{m,0}}{4} \quad (44)$$

and

$$V_{\text{tot}} = \frac{\pi (d_{m,0} + 2\Delta t_{\text{tot}})^2 (t_{m,0} + \Delta t_{\text{tot}})}{4} \quad (45)$$

where

$\Delta t_m$  = change from the original thickness of the plutonium metal piece

For the square foil, the corresponding volumes are:

$$V_{\text{Pu}} = (s_{m,0} - 2\Delta t_m)^2 (t_{m,0} - \Delta t_m) \quad (46)$$

$$V_{\text{Pu},0} = s_{m,0}^2 t_{m,0} \quad (47)$$

and

$$V_{\text{tot}} = (s_{m,0} + 2\Delta t_{\text{tot}})^2 (t_{m,0} + \Delta t_{\text{tot}}) \quad (48)$$

For both the cylinder and the foil, the oxide layer thickness is equal to the sum of the changes in the metal piece and the total thicknesses:

$$L = \Delta t_m + \Delta t_{\text{tot}} \quad (49)$$

A corrected oxide layer thickness can be estimated by accounting for dispersion of the oxygen flow across the layer. The dispersion follows the same pattern as the dispersion of the heat flux across an insulating layer, for which the effective thickness is proportional to the actual thickness times the square root of the ratio of the inner and outer surface areas. Thus,

$$L_{\text{corr}} = \left( \frac{A_m}{A_{\text{tot}}} \right)^{0.5} (\Delta t_m + \Delta t_{\text{tot}}) \quad (50)$$

where

$L_{\text{corr}}$  = oxide layer thickness, corrected for the effect of gas dispersion due to the change in cross-sectional area as the oxide layer grows

$A_m$  = surface area of the remaining metal piece available for oxidation

$A_{\text{tot}}$  = outer surface area of the oxide layer

The metal piece and total surface areas for the cylinder are:

$$A_m = \frac{\pi(d_{m,0} - 2\Delta t_m)^2}{4} + \pi(d_{m,0} - 2\Delta t_m)(t_{m,0} - \Delta t_m) \quad (51)$$

and

$$A_{\text{tot}} = \frac{\pi(d_{m,0} + 2\Delta t_{\text{tot}})^2}{4} + \pi(d_{m,0} + 2\Delta t_{\text{tot}})(t_{m,0} + \Delta t_{\text{tot}}) \quad (52)$$

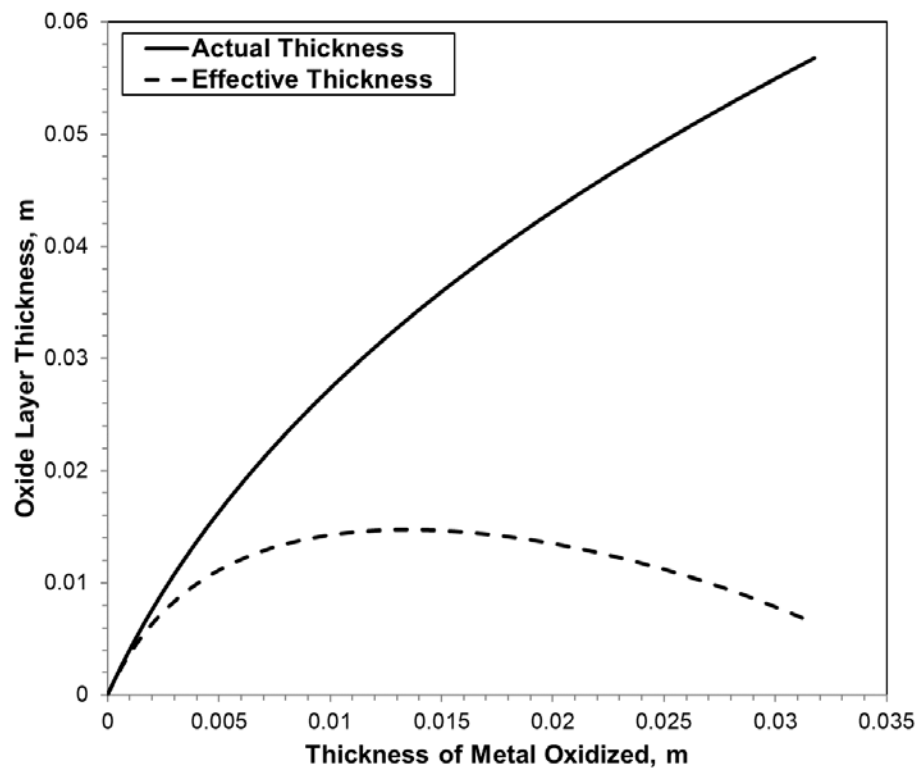
For the foil,

$$A_m = (s_{m,0} - 2\Delta t_m)^2 + 4(s_{m,0} - 2\Delta t_m)(t_{m,0} - \Delta t_m) \quad (53)$$

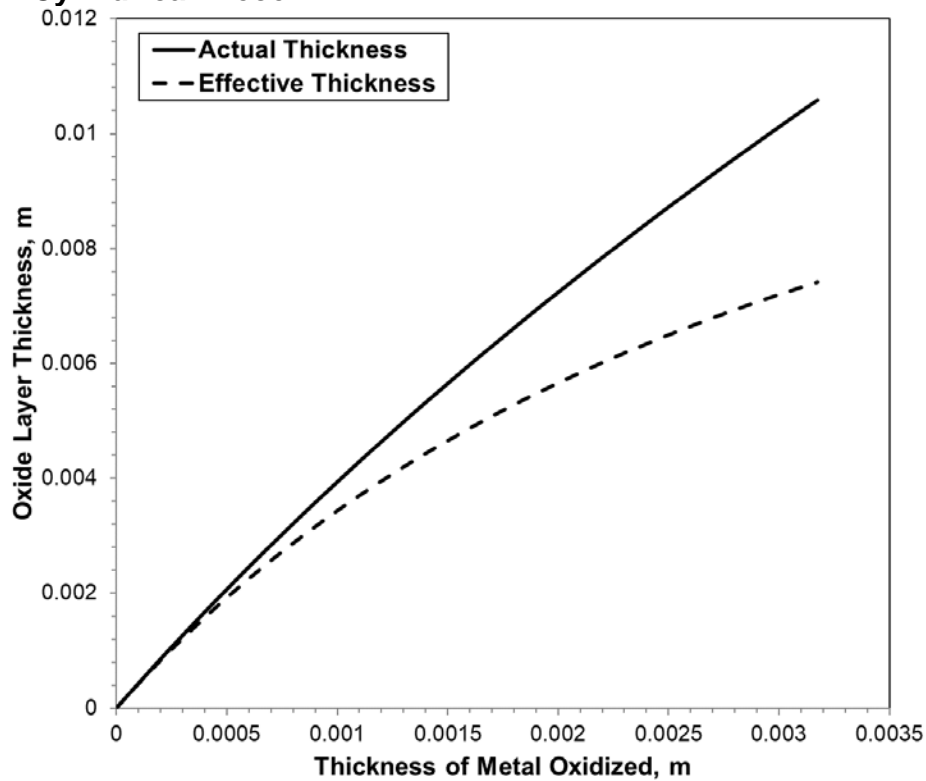
and

$$A_{\text{tot}} = (s_{m,0} + 2\Delta t_{\text{tot}})^2 + 4(s_{m,0} + 2\Delta t_{\text{tot}})(t_{m,0} + \Delta t_{\text{tot}}) \quad (54)$$

Figure 1 depicts the variation of the oxide layer thickness during oxidation of the 0.0889-m diameter by 0.0318-m high cylinder. Without any correction for dispersion of the oxygen flow, the maximum oxide layer thickness is 0.0568 m, at the end of the oxidation transient. With the dispersion correction, the effective oxide layer thickness peaks at 0.0147 m, when approximately half of the piece has oxidized. Figure 2 portrays the variation of the oxide layer thickness for oxidation of the 0.1016-m square by 0.00318-m thick rectangular prism. The maximum oxide layer thickness for this piece is 0.0106 m without the correction for dispersion and 0.0075 m with this correction. The maximum effective oxide layer thicknesses are significantly less than the minimum thickness at which the oxidation rate is reduced. Therefore, it may be stated that the oxide layer does not inhibit oxidation for the two metal pieces that are analyzed and that the appropriate rate for calculation of the total oxidation time is the intrinsic chemical rate reported by Los Alamos National Laboratory, which ranges from 1.0 to 2.1 kg Pu/m<sup>2</sup>/min.<sup>5,7,8,9</sup>



**Figure 1. Variation of Oxide Layer Thickness during Oxidation of a 0.0889-m Diameter by 0.0318-m Thick Cylindrical Piece**

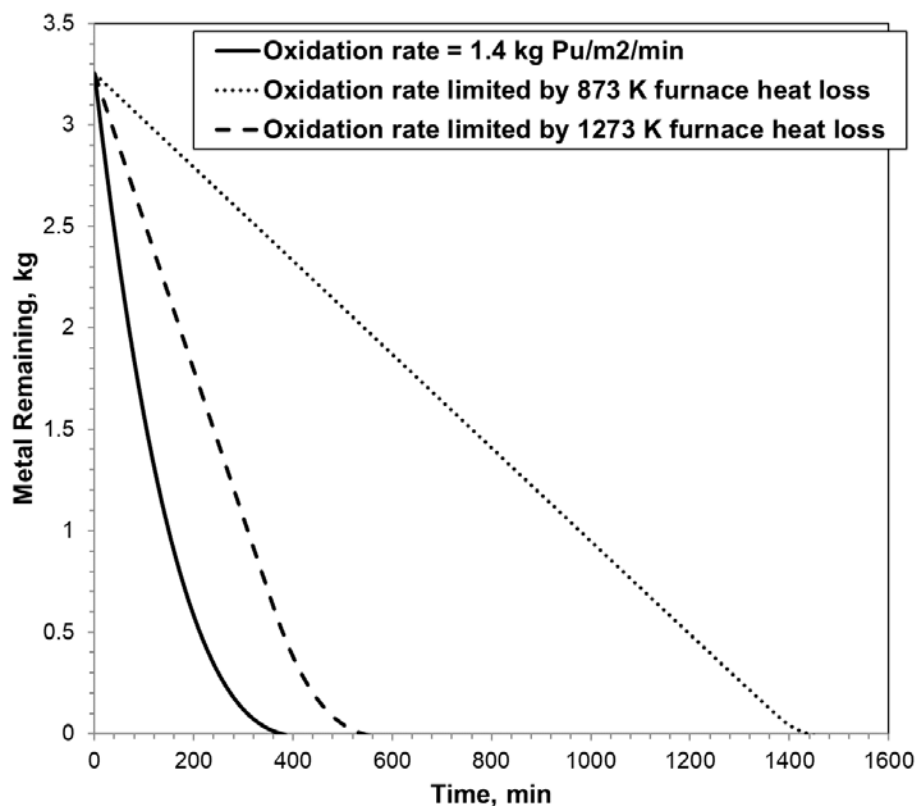


**Figure 2. Variation of Oxide Layer Thickness during Oxidation of a 0.1016-m Square by 0.00318-m Thick Foil**

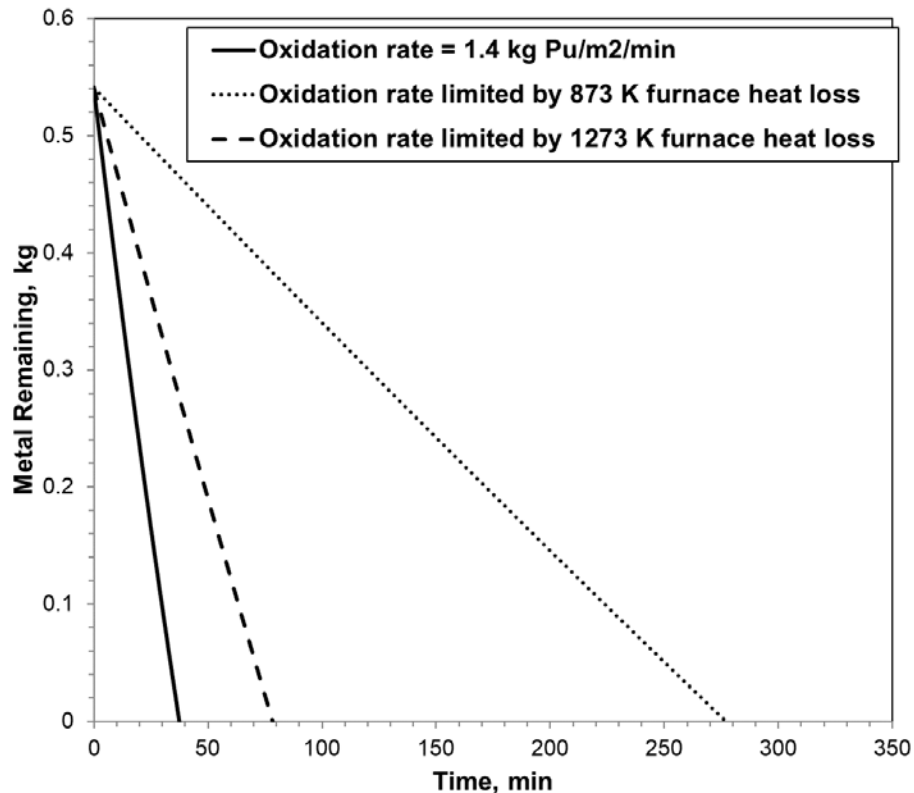
### Results of Oxidation Rate Calculations

Heat transfer calculations were performed to determine the limiting oxidation rates at varying maximum oxide temperatures inside a typical Savannah River Site muffle furnace, which has the dimensions of a 0.305-m cube, with 0.076-m thick alumina fiber walls. The heat transfer calculations assume that heat losses from the oxide to the furnace walls occur primarily by thermal radiation; the emissivity of the plutonium oxide was set at 0.9, and the emissivity of the alumina furnace walls was set at 0.42. The alumina fiber walls have a thermal conductivity of 0.10 W/m/K. A typical lower bound heat transfer coefficient of 5.0 W/m<sup>2</sup>/K was used to estimate external heat losses. Heat transfer to the air entering the furnace was modeled using natural convection correlations for enclosures.<sup>10</sup> The heat of combustion of the plutonium metal was set equal to the heat of formation for PuO<sub>2</sub>, which is -1056 kJ/mol.<sup>11</sup>

The heat transfer calculations show that, for the average reported oxidation of 1.4 kg Pu/m<sup>2</sup>/min, the furnace is too well insulated to allow for oxidation without triggering a temperature excursion. Figures 3 and 4 compare intrinsic rates of oxidation of the cylindrical “button” and the foil with the rates that can be achieved when the furnace is limited to 873 K and 1273 K. The results of the heat transfer calculations demonstrate that the oxidation reaction must be throttled by limiting the air flow into the furnace. The temperature-limited oxidation rate is about half the intrinsic rate at an oxide temperature of 1273 K and less than one-fifth of the intrinsic rate at an oxide temperature of 873 K.



**Figure 3. Comparison of Intrinsic Oxidation Rate for 0.0889-m Diameter by 0.0318-m Thick Cylindrical Piece with Rates Limited by Air Supply Rate**



**Figure 4. Comparison of Intrinsic Oxidation Rate for 0.1016-m Square by 0.00318-m Thick Foil with Rates Limited by Air Supply Rate**

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