Title: Plutonium Oxalate Calcination at Los Alamos National Laboratory

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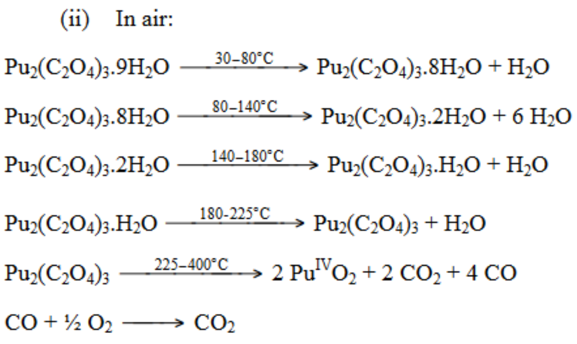
Plutonium oxalate cakes produced by both the aqueous chloride and nitrate separation processes at Los Alamos National Laboratory are calcined for conversion to plutonium dioxide. Calcination refers to the use of high temperatures to drive off a solid's volatile molecular components as well as the oxidation of that solid via a reaction with air. Both processes start with solid formation from a precipitation reaction between an aqueous plutonium mixture, oxalic acid and hydroxylamine. Hydroxylamine is used for reducing plutonium (IV) ions found in solution to plutonium (III) (1). The result for both the aqueous chloride and nitrate line is a hydrated solid plutonium (III) oxalate cake with the texture of wet sand. The cake is placed under vacuum for up to two hours in order to dry it as much as possible prior to its calcination. Although decomposition occurs spontaneously as a result of alpha radiation in plutonium oxalate, this only has an impact after several weeks (2). Since the plutonium (III) oxalate cake produced in the aqueous processes at Los Alamos National Laboratory only has a lifetime of a day the effects of alpha radiation are negligible.

The calcination step in the aqueous chloride process uses the following equipment: a fiber craft tube furnace, a Watlow Furnace Controller, and a magnesium oxide crucible. The furnace controller is connected to two thermocouples placed in either side of the tube furnace at its diameter which send feedback to the controller on the furnace's ambient temperature. These thermocouples effectively measure the airspace around the crucibles and give feedback to the controller. The airspace on all sides of the crucible and on top of the crucible is expected to be less than a quarter of an inch. The nitrate line uses a Lindberg/54S-MK6014LA Furnace with the same temperature control system, a tantalum crucible and an Inconel pull can. Both calcination steps are performed under vacuum conditions in a glovebox with a dry air environment. The furnaces are located underneath the glovebox with the top open to the glovebox environment when in a configuration to receive the crucible. Operators have noted that when the furnace is closed it often does not close fully and has an opening for gas to escape into the glovebox. The glovebox walls are not considered to be reflective. None of the crucible types can be assumed to be blackbody materials.

The first step in both aqueous process' calcination procedure is to load the plutonium oxalate into the crucible. The plutonium is packed into the walls of the crucible. For the nitrate line the tantalum crucible and Inconel can are stacked within each other. Next the crucible is placed into the furnace and the furnace is shut. Then the correct temperature profile is programmed into the furnace controller and allowed to run. The temperature profile for the nitric acid process involves ramping the temperature of the furnace to 600 degrees Celsius for four hours and a soaking time period of six hours at this temperature. Meanwhile the aqueous chloride process temperature profile includes intermediary steps. It begins with a two hour ramp to 200 degrees Celsius followed by a three hour soak at the same temperature. The next step is a two hour ramp to 400 degrees Celsius followed by a three hour soak at the same temperature. Finally a two hour ramp to 650 degrees Celsius is performed followed by a four hour soak at the same temperature. The furnaces are left running unattended until the temperature profile concludes and the contents of each furnace cool to 50 degrees Celsius. Finally, the plutonium dioxide is removed from the furnace and crucible to a tared container on a mass balance to determine the product's mass.

Thermogravimetric analysis of plutonium (III) oxalate have determined that the hydration of the freshly produced oxalate compound is in the range of 10 (3) to 6 water molecules (4). The largest consensus of studies concerning the mechanism for thermal decomposition of plutonium (III) oxalate have proposed complete endothermic dehydration followed by exothermic decomposition of anhydrous plutonium (III) oxalate (4) (5) (6) (7). However there is not a universally agreed upon reaction pathway. Figure one shows the reaction mechanism for the thermal decomposition of plutonium (III) oxalate as proposed by Almeida (6). Other authors have composed their own unique pathways including different solid intermediate plutonium compounds. As a result these other studies have different temperature profiles at which the gaseous products, water, carbon dioxide and carbon monoxide, are released (7). These temperature profiles are summarized in Table 1. These studies also produced contradicting thermodynamic data summarized in Table 2. Almeida gave an explanation for the differences in enthalpy of reaction as a result of differing calculation methods and the use of plutonium oxalate compounds at different levels of hydration (6).



(ii) In air:

$$Pu_2(C_2O_4)_3.9H_2O \xrightarrow{30-80^\circ C} Pu_2(C_2O_4)_3.8H_2O + H_2O$$

$$Pu_2(C_2O_4)_3.8H_2O \xrightarrow{80-140^\circ C} Pu_2(C_2O_4)_3.2H_2O + 6\ H_2O$$

$$Pu_2(C_2O_4)_3.2H_2O \xrightarrow{140-180^\circ C} Pu_2(C_2O_4)_3.H_2O + H_2O$$

$$Pu_2(C_2O_4)_3.H_2O \xrightarrow{180-225^\circ C} Pu_2(C_2O_4)_3 + H_2O$$

$$Pu_2(C_2O_4)_3 \xrightarrow{225-400^\circ C} 2\ Pu^{IV}O_2 + 2\ CO_2 + 4\ CO$$

$$CO + ½\ O_2 \longrightarrow CO_2$$

Figure 1. Proposed Reaction Mechanism.

Table 1. Temperature Profiles of Reaction in Air from Various Sources.

Reaction Step	Temperature Range of Stability (°C)
$Pu(C_2O_4)_3 \cdot 10\ H_2O \xrightarrow{yields} Pu(C_2O_4)_3 \cdot 9H_2O$	Up to 40 (8)
$Pu(C_2O_4)_3 \cdot 9\ H_2O \xrightarrow{yields} Pu(C_2O_4)_3 \cdot 8H_2O$	30-80 (6), 55-75 (8)
$Pu(C_2O_4)_3 \cdot 8\ H_2O \xrightarrow{yields} Pu(C_2O_4)_3 \cdot 2H_2O$	80-140 (6)
$Pu(C_2O_4)_3 \cdot 2H_2O \xrightarrow{yields} Pu(C_2O_4)_3 \cdot H_2O$	140-180 (6), 125-150 (8), Up to 100 (5)
$Pu(C_2O_4)_3 \cdot H_2O \xrightarrow{yields} Pu(C_2O_4)_3$	180-225 (6), 175-195 (8), Up to 183 (4) Up to 149 (5)
$Pu(C_2O_4)_3 \xrightarrow{yields} 2PuO_2$	225-400 (6) Up to 331 (4) Up to 450 (5)

The temperature range for calcination of plutonium oxalate to plutonium oxide is in alignment with industry standards. Around 300 degrees Celsius the decomposition is considered appreciable and by 400 degrees Celsius it is considered complete (9). Experimentally it has been shown that plutonium dioxide loses around 2% of its weight up until 800 degrees Celsius, therefore it is standard practice to continue heating the plutonium oxalate up to this bound (9).

Table 2. Thermodynamic Properties of Plutonium (III) Oxalate Thermal Decomposition

Reaction Step	Enthalpy of Reaction ΔH (kJ/mol)	Energy of Activation (kJ/mol)
Complete Dehydration	323.6 (6), 180.0 (4)	108.8 (4)
Decomposition	-454.0 (6), -293.0 (4)	146.4 (4)

Information regarding the specific heat capacity, heat transfer coefficient and thermal conductivity of plutonium (III) oxalate could not be found. Although the thermogravimetric devices used to calculate the enthalpy of reaction could also gather data necessary to determine the specific heat capacity more information regarding the reference material used is required to perform that calculation. Los Alamos National Laboratory has a Differential Scanning Calorimeter that can gather new data to determine the specific heat capacity. It also could be modified to measure thermal diffusivity. Equation 1 shows the equation used to calculate thermal conductivity from a known thermal diffusivity.

$$k = \alpha * C * \rho \tag{1}$$

Where k=Thermal Conductivity
α=Thermal Diffusivity
C=Specific Heat Capacity
P= Density

Actual density of hydrated plutonium (III) oxalate could not be found. The parameters necessary for determining the theoretical density at two stages of hydration are available. Additional XRD analysis for other stages of hydration may be done at Los Alamos National Laboratory's facilities. Since theoretical density represents the density of a substance with no open or closed pores it would be the maximum density value possible for a porous material. Equation 2 is used to calculate theoretical density. Equation 3 is used to calculate the unit cell volume necessary for the density calculation. Table 3 summarizes the unit cell dimensions for different hydrated plutonium (III) oxalate molecules from various experiments.

$$\rho_{theoretical} = \frac{N*A}{V*n_{avogadro}} \tag{2}$$

Where $\rho_{theoretical}$=Theoretical Density
N=Number of Atoms per Cell

A=Atomic Mass
V= Unit Cell Volume
$n_{avogadro}$=Avogadro’s Number

$$V = a * b * c * \sin(\beta) \tag{2}$$

Where a, b, c, and β are the dimensions of a monoclinic crystal structure

Table 3. Summary of known dimensions of Plutonium (III) oxalate at different hydration levels.

Molecule	a (angstrom)	b (angstrom)	c (angstrom)	β (degrees)	Source
$Pu(C_2O_4)_3 \cdot 9\ H_2O$	11.246	9.610	10.315	114.477	(10)
$Pu(C_2O_4)_3 \cdot 10\ H_2O$	11.595	9.599	10.171	118.94	(11)

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