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Department of Energy / Rocky Flats Office  
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Los Alamos Technology Office  
Rocky Flats Plant  
Golden, Colorado

**PYROPHORIC POTENTIAL OF FINELY DIVIDED PLUTONIUM  
METAL IN SOIL AT THE 913 DRUM STORAGE SITE,  
ROCKY FLATS PLANT GOLDEN, COLORADO**

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IN SOIL AT THE 903 DRUM STORAGE SITE,  
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## Table of Contents

Executive Summary.....	iii
Primary Factors.....	iii
Additional Mitigating Factors.....	iv
Conclusions.....	iv
1.0 Introduction.....	1
2.0 Terminology.....	2
3.0 History of Rocky Flats Plant's 903 Drum Storage Site.....	2
3.1 Use of 903 Drum Storage Site.....	3
3.2 Leakage.....	3
3.3 Capping of 903 Site.....	4
3.4 Soil Characterization.....	4
4.0 Factors Affecting the Pyrophoricity of Plutonium.....	5
4.1 Autoignition and Oxidation Behavior.....	6
4.2 Particle Size and Activity.....	7
4.3 Effect of Moisture.....	9
4.4 Effect of Hydrogen.....	9
4.5 Purity, Composition, and Concentration of Plutonium in Soils.....	10
4.6 Amount of Protective Surface Oxide.....	11
4.7 Kinetic and Thermodynamic Considerations.....	12
5.0 Conclusions on the Pyrophoric Potential of Plutonium Metal at the 903 Drum Storage Site.....	15
6.0 Acknowledgments.....	17
7.0 Glossary.....	18
7.1 Pyrophorus and Pyrophoric.....	18
7.2 Ignition, Piloted Ignition, and Autoignition.....	18
7.3 Ignition Temperature.....	19
7.4 Combustion and Spontaneous Combustion.....	19
8.0 References.....	20

## Executive Summary

The Department of Energy's DOE's Rocky Flats Plant, near Denver, Colorado, is currently addressing the question of plutonium pyrophoricity in regard to environmental restoration activities at the 903 Drum Storage Site. Plutonium metal has been known to ignite spontaneously, and the possibility of a plutonium fire is a concern.

In the early 1960s, oils containing plutonium leaked from drums stored at the 903 Drum Storage Site; the estimated release was about 5,000 gal. The distribution of plutonium in soil under the 903 Pad is inhomogeneous, making it difficult to estimate exact concentrations. A study performed a few years after the site was capped in 1969 found both  $^{239}\text{Pu}$  (in concentrations ranging from 427 pCi/g to 20,455 pCi/g) and  $^{241}\text{Am}$  (in concentrations ranging from 282 pCi/g to 2,273 pCi/g) in the soil beneath the cap.

This report examines the pyrophoric potential of finely divided plutonium at the 903 Site by summarizing literature data and analyzing the probability and extent to which plutonium is pyrophoric in its present state in the 903 Site soil.

### **Primary Factors \*\***

Calculations show that particles of  $\delta$ -stabilized plutonium have a critical particle size of approximately 5  $\mu\text{m}$ ; that is, only particles smaller than this size would be expected to show pyrophoric behavior on exposure to air. Oils were sieved before they were placed in the drums, so plutonium particles that entered the soil were no more than 100  $\mu\text{m}$  in diameter. Dilution of these particles with large amounts of soil reduces their pyrophoricity because heat produced in oxidation processes is absorbed by the surrounding material. Additionally, oxidation of plutonium by gaseous agents such as oxygen or water vapor generates an adherent

oxide film on the surface of the plutonium particles. This oxide surface further reduces the potential of pyrophoricity. Thus, the combination of factors—the requirement for a very small particle, the presence of the protective oxide surface, and the dilution of particles in soil—should render the plutonium in the 903 Pad soil highly inert with respect to pyrophoricity.

#### **Additional Mitigating Factors**

During the intervening years, however, other mechanisms have further reduced the possibility of pyrophoricity of plutonium in the soils. It is probable that reactions between the plutonium and aqueous groundwater mixtures of chlorinated solvents known to be present in the soil beneath the 903 Pad have rendered the plutonium non-pyrophoric under the conditions presented. The plutonium oxidation kinetics shows that the lifetime of a 100- $\mu\text{m}$  plutonium particle is only 8.4 days in liquid water, and 4 minutes in a carbon tetrachloride-methanol mixture

#### **Conclusions**

It is concluded from the discussions and data presented that the plutonium in the 903 Pad soil is inert with respect to pyrophoricity. This conclusion is supported by the fact that no pyrophoricity was found during the November 1968 remedial action at the 903 Drum Storage Site, which involved scraping plutonium-contaminated soil into a smaller area. The reactions of plutonium metal or oxide phases with the potentially corrosive organic mixtures in the soil under the 903 Pad are expected to be numerous and complex. Thus, without exact data on the chemical form and speciation of plutonium under these conditions, it is impossible to predict with absolute accuracy the ultimate fate and transport of plutonium contaminants in the 903 Site soil.

**Pyrophoric Potential of Finely Divided Plutonium Metal  
in Soil at the 903 Drum Storage Site  
at Rocky Flats Plant, Golden, Colorado**

By

David L. Clark

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**1.0 Introduction**

The DOE's Rocky Flats Plant, near Denver, Colorado, is addressing the question of plutonium pyrophoricity at the 903 Drum Storage Site. Because plutonium metal has been known to ignite spontaneously, concern about the pyrophoricity of plutonium is appropriate.<sup>1-4</sup> The possibility of a plutonium fire is a serious matter because of public, worker, and environmental health and safety.

This issue is timely because the DOE is planning remedial activity at the 903 Drum Storage Site, which has been contaminated with plutonium.<sup>5</sup> From October 1958 to January 1967, drums containing waste machine cutting oil that was radioactively contaminated were stored at the 903 Site.<sup>6</sup> As a result of leakage of about 5,000 gal. of waste oil that occurred from drums while they were stored at the site, approximately 86 g (5.3 Ci) of plutonium was released into soils at the 903 Drum Storage Site.<sup>7,8</sup>

An asphalt containment pad was applied at the site in October 1969. Several years after the asphalt cover was applied, a study of the soil beneath the 903 Pad indicated that the soil was contaminated with both plutonium and americium.<sup>9</sup>

The purpose of this report is to examine the pyrophoric potential of finely

divided plutonium at the 903 Site. The report summarizes literature data on factors influencing pyrophoricity and, using this information, analyzes the probability and extent to which plutonium is pyrophoric in the soil at the 903 Drum Storage Site

## 2.0 Terminology

To provide a common basis for discussing pyrophoricity, definitions for technical terms used in this report are included in the Glossary. For a comprehensive and authoritative review of pyrophoricity, readers are referred to the Fire Protection Handbook;<sup>10</sup> many of the definitions used were taken verbatim from this source.

The adjective "pyrophoric" is defined as having the property of taking fire on exposure to air.<sup>11</sup> A distinction is often made between those elements and compounds that burst into flame on exposure to air because of their intrinsic chemical behavior and those that do so only because of their special method of preparation (such as finely divided powders). In this report, the term "pyrophoric" is used in its broadest sense; that is, it applies to all characteristics affecting pyrophoricity of metals.

## 3.0 History of Rocky Flats Plant's 903 Drum Storage Site

The following information, which was drawn from historical records, aerial photography, and interviews with plant personnel, is an abridged version of data presented in the Final Phase II RCRA Facility Investigation/Feasibility Study Work Plan.<sup>5</sup>

### 3.1 Use of 903 Drum Storage Site

From October 1958 to January 1967, the 903 Site was used to store drums containing waste machine cutting oil that was radioactively contaminated.<sup>5</sup> Most of the drums were 55 gal. in size, but some 30-gal. drums were also present, and not all of the drums were full.<sup>6</sup> About 75% of the drums at the storage site were contaminated with plutonium; the majority of the remaining drums contained uranium.

Most of the plutonium-containing drums held waste lathe coolant consisting of a high-molecular-weight, straight-chain hydrocarbon oil (Shell Vitrea) and carbon tetrachloride in diverse proportions. Other site drums contained liquid waste, such as hydraulic oils, vacuum pump oils, trichloroethylene, tetrachloroethylene, silicone oils, acetone, still bottoms, etc. The drum contents were originally indicated on the outside, but weathering and lack of other supporting records has made detailed identification difficult.

Shipment of drums to the 903 Site ended in January 1967, when drum removal efforts began. By June 1968, all drums had been removed. Frieberg describes more extensively the chronology of the 903 Site cleanup.<sup>7</sup>

### 3.2 Leakage

Leakage of oil from the drums was first noted early during the site's use, and in 1959, ethanolamine was added to the oil to reduce the corrosion rate of the steel drums.

During routine drum handling operations in 1964, drum leakage was again noted at the 903 Site. The contents of leaking drums were transferred to new drums, and the entire area was fenced to restrict access.<sup>8</sup> Information provided by individuals who were involved in site operations indicates that about 420 drums leaked to some degree; of these, approximately 50 leaked their entire contents.<sup>8</sup> It is

estimated that 5,000 gal. of waste oil leaked from drums onto the ground at the 903 Site. Based on oil samples taken from drums, the average plutonium concentration was  $4.54 \times 10^{-3}$  g/L (280  $\mu$ Ci/L). Thus, approximately 86 g (5.3 Ci) of plutonium was released into soils at the 903 Drum Storage Site.<sup>7</sup>

### 3.3 Capping of 903 Site

In November 1968, grading began at the 903 Site in preparation for an asphalt cap to be placed over the contaminated area. This work included moving contaminated soil from around the fenced area to inside the fenced area.<sup>7</sup> Of primary significance is the fundamental fact that no plutonium pyrophoricity was found during this remedial action.<sup>7</sup>

In May 1969, 33 drums of radioactively contaminated soils were removed from the area. Two layers of clean fill material were placed over the site during the late summer of 1969.

The asphalt containment pad was applied in October 1969. The cap is approximately 8 cm thick and covers a rectangular area about 370 ft x 395 ft (146,150 ft<sup>2</sup>). The cap is underlain by 15 cm of loose gravel and 8 cm of fill dirt.<sup>7</sup>

In February 1970, additional coarse road base material was applied to soils east and south of the asphalt pad because of low-level plutonium contamination in the surrounding soil.<sup>7</sup>

### 3.4 Soil Characterization

Several years after the asphalt cover was applied, Navratil, Thompson, and Kochen examined soils beneath the 903 Pad to determine the level and distribution of plutonium and americium.<sup>9</sup> This study indicated that the soil beneath the 903 Pad was contaminated with both <sup>239</sup>Pu (from 427 pCi/g to 20,455 pCi/g) and <sup>241</sup>Am (from 282 pCi/g to 2,273 pCi/g). The contamination appeared to be restricted to

shallow depths below the original ground surface.<sup>9</sup> It was estimated that the asphalt pad covered 18,000 tons of contaminated soil. In addition, data from the Phase II RCRA Facility Investigation Remedial Investigation Study Work Plan<sup>5</sup> (Round One, 1989, Volume III Appendices) showed plutonium contamination in sediments for stations at Operable Unit 2.

Phase I Remedial Investigations of environmental media showed that volatile organic contamination exists in soils, surface water, and ground water in areas adjacent to the 903 Pad, as well as under the Pad itself.<sup>5</sup> Groundwater samples were found to contain carbon tetrachloride with concentrations ranging from several hundred to several thousand micrograms per liter. Wells were found to contain tetrachloroethylene in concentrations ranging from a few  $\mu\text{g}/\text{L}$  to 528,000  $\mu\text{g}/\text{L}$ , and trichloroethylene in concentrations up to 12,000  $\mu\text{g}/\text{L}$ . Samples contained significantly lower concentrations of other volatile organic compounds, including vinyl chloride, 1,1-dichloroethylene, 1,1-dichloroethane, chloroform, dichloromethane, and acetone. Groundwater samples from the 903 Pad site also contained radionuclides, although individual concentrations were below 1 pCi/L.<sup>5</sup> These data then support the reasoning that the plutonium in the 903 Pad site is well confined to the soil beneath the Pad and its immediate surrounding area.

#### 4.0 Factors Affecting the Pyrophoricity of Plutonium

Literature pertaining to the term pyrophoricity ranges from mathematical development of combustion theory<sup>12</sup> to discussions regarding unanticipated fires or explosions that have occurred in the agriculture, fuels, and metallurgy industries. Early literature presents an historical record of the state of knowledge at the time of writing, such as many reported occurrences of spontaneous combustion of

zirconium or uranium metal scraps. At least two review articles on pyrophoricity are available.<sup>13,14</sup> Many articles have been published on the pyrophoricity of zirconium and zircalloy powders<sup>15-46</sup> and metal powders in general.<sup>42,47,48</sup>

#### 4.1 Autoignition and Oxidation Behavior

When an element experiences combustion, or catches fire, it is undergoing oxidation. Chemically, all elements not in their highest stable oxidation state in air can burn; consequently, all metals that form stable oxides can oxidize in air under appropriate conditions. Many metals oxidize so slowly that the heat generated during oxidation dissipates and ignition temperature is never reached, such as iron. Under proper conditions, however, some metals oxidize rapidly in the presence of air or moisture, generating sufficient heat to reach their ignition temperature and undergo autoignition.

Generally, autoignition can occur whenever a reaction or reactions are strongly exothermic, have negative free energies of reaction at the ignition temperature, and have a greater rate of heat production than rate of heat transfer away from the reaction zone. In such instances, the surface oxidation becomes vigorous enough to make the reaction self-sustaining.

For fine powders, the oxidation behavior is similar to that of larger specimens unless the removal of heat released by the oxidation process is too slow. In this case, the temperature of the powder rises, leading to an increase in the rate of oxidation.<sup>48</sup> For pyrophoric substances, this autocatalytic process usually culminates in the powder reaching its ignition temperature and catching fire.

C. R. Schmitt has reviewed the parameters that induce the pyrophoricity of various materials and points out that they are numerous and often interrelated.<sup>13</sup> The variables Schmitt cites as affecting pyrophoricity include the following:

1. particle size and activity,

2. moisture content,
3. hydrogen content,
4. stress,
5. purity and composition,
6. amount of surface oxide, and
7. mass of material.

The more important of these factors will be briefly reviewed in light of current literature, and their potential impact on the pyrophoricity of plutonium at the 903 Drum Storage Site will be discussed.

#### 4.2 Particle Size and Activity

"Activity" refers to the propensity of a powder to react with its environment; it determines the type and rate of reaction.<sup>47</sup> The activity of a powder particle determines the rate of material transport by bulk and surface diffusion, the rate of adsorption and desorption, and the rate of oxidation reactions with the environment.<sup>47</sup> A major factor that strongly influences activity is the amount of surface area available for chemical activity. Because finely divided particles have a greater surface area available for chemical activity, they are generally more susceptible to pyrophoricity than the same quantity of metal in bulk, or massive, form would be.<sup>49</sup> Indeed, for reactive metals such as titanium, zirconium, uranium, and plutonium, ignition temperatures are markedly dependent upon particle size.<sup>39,42</sup>

In discussions of particle size characteristics, a useful quantity is the total surface area of one gram of powder, called the specific surface.<sup>47</sup> This value is usually expressed in  $m^2/g$ . Because any reaction of particles will start on the surface, the specific surface is an excellent indicator of the conditions under which the reaction will start and of the rate of reaction. For a fine powder, the large surface

area relative to the mass (or volume) of material available for absorption of the heat produced during oxidation permits a rapid rise in particle temperature. When that temperature reaches the ignition temperature, autoignition can occur.

Evans, Borland, and Mardon determined that pyrophoric powders have a critical surface area—above which they will undergo autoignition—of about  $6 \text{ m}^2/\text{g}$ .<sup>42</sup> Applying this criterion to the factors controlling the combustion of zirconium powders, Anderson and Belz discovered that a zirconium particle diameter of  $10 \text{ }\mu\text{m}$  represents approximately the threshold between hazardous and nonhazardous powder, using a 0.01- to 0.04-J spark ignition energy as a criterion.<sup>39</sup> Other metals also display their own critical particle size, which is unique to each substance. For example, metals such as iron, copper, nickel ( $0.01\text{-}0.03\text{-}\mu\text{m}$  particle size), tungsten ( $1\text{-}\mu\text{m}$  particle size), or sodium ( $10\text{-}\mu\text{m}$  particle size) spontaneously ignite in air with disturbance or light impact.<sup>45</sup>

From this discussion, it is clear that particle size must be considered in the evaluation of the pyrophoricity of plutonium particles deposited in the soils under the 903 Pad. The oil was sieved with a  $100\text{-}\mu\text{m}$  screen before it was placed in drums at the 903 Drum Storage Site; therefore, an upper size limit of  $100 \text{ }\mu\text{m}$  can be assumed for plutonium particles in the soil.<sup>50</sup> Assuming a density for  $\delta$ -stabilized plutonium<sup>51</sup> of  $15.92 \text{ g}/\text{cm}^3$  and perfectly spherical particles, a  $100\text{-}\mu\text{m}$  particle of plutonium will have a specific surface of approximately  $0.004 \text{ m}^2/\text{g}$ , whereas a  $1\text{-}\mu\text{m}$  plutonium particle would have a specific surface of about  $0.4 \text{ m}^2/\text{g}$ .

These small specific surfaces for plutonium are due to the assumption of perfectly spherical particles and the fact that plutonium metal is among the densest of all elements.<sup>52</sup> However, metal particles will not be perfect spheres; consequently, they are expected to show much higher specific surfaces than those calculated for spherical particles.

The critical particle size has been experimentally determined for zirconium.<sup>45</sup>

and this information can be used to calculate a correction factor to obtain more reliable critical particle sizes for uranium and plutonium. If one assumes a density for zirconium metal<sup>51</sup> of 6.49 g/cm<sup>3</sup> and a spherical particle, zirconium particle specific surfaces are calculated to be 0.009 m<sup>2</sup>/g (100- $\mu$ m particle) and 0.9 m<sup>2</sup>/g (1- $\mu$ m particle). Assuming a critical surface area<sup>49</sup> of 6 m<sup>2</sup>/g, one can calculate the critical particle size for a zirconium sphere to be on the order of 0.2  $\mu$ m. In comparison, Anderson and Belz<sup>39</sup> found the critical particle size for zirconium to be 10  $\mu$ m. This provides a conversion factor of 50 to obtain more reliable estimates of the actual critical particle sizes. Using this conversion factor and a critical surface area of 6 m<sup>2</sup>/g leads to an estimated critical particle size of 5  $\mu$ m for  $\delta$ -stabilized plutonium.

#### 4.3 Effect of Moisture

Many pyrophoric materials are hygroscopic and generate large quantities of heat when wetted or when they absorb water vapor. It has, therefore, been suggested that wetting might act as a triggering mechanism to raise temperature to the point at which other exothermic reactions could occur, or that the heat of wetting might raise materials to their full combustion temperatures.<sup>13</sup> Under certain conditions, the pyrophoricity or violence of combustion of metals such as zirconium, thorium, and plutonium may be markedly increased if the metal is exposed to moisture by being partially or completely submerged in water. Several incidents and fires of this nature have been reported.<sup>29,46,53,54</sup>

It is noteworthy that plutonium metal is readily oxidized by liquid or vapor-phase water, even at room temperature.<sup>55,56</sup> The oxidation properties of plutonium metal will be discussed in detail in Sections 4.6 and 4.7.

#### 4.4 Effect of Hydrogen

The effect of hydrogen is often interrelated with the effect of moisture in

causing increased pyrophoricity. For example, reaction of plutonium with water generates hydrogen gas,<sup>56-58</sup> which, under the appropriate conditions, can adsorb through cracks in the metal to form hydrides.<sup>49</sup> Hydrogen gas liberated by reaction of an active metal with liquid water may also be ignited by the heat of reaction. This represents the principal fire hazard of alkali metals such as sodium or potassium. For plutonium, however, oxidation by liquid water converts plutonium metal into a monoxide monohydride, HPuO, which does not pose a pyrophoric threat.<sup>56</sup>

#### 4.5 Purity, Composition, and Concentration of Plutonium in Soils

In some cases, impurities can cause metal powders to become more pyrophoric; in others, they can decrease the pyrophoricity of powders. NaK alloy, for example, is more pyrophoric and has a lower melting point than the pure elements.<sup>52</sup> Likewise, the pyrophoricity of some elements increases when they are alloyed with such elements as tin, lead, or gold.<sup>59</sup>

While examining ignition temperatures of pure and alloyed plutonium, Schnizlein and Fischer found that low-purity samples have the highest ignition temperatures and the highest-purity samples have the lowest ignition temperatures.<sup>60-62</sup> The susceptibility of plutonium to oxidation can therefore be reduced by alloying it with other metals, such as aluminum or gallium, which has the effect of increasing the ignition temperature.

In addition, inert material such as sand can be mixed with pyrophoric powders to damp fire and explosions. An inert material reduces the combustibility of a powder because it absorbs heat. Normally the amount of inert material necessary to prevent a fire or explosion is considerably higher than the concentration that would be tolerated for a metal powder. During work on zirconium and zircalloy pyrophoricity, Cooper observed that 90% or more inert material would damp the explosions of dust clouds of zirconium.<sup>45</sup> This obviously

has important ramifications for reducing pyrophoricity of plutonium by dilution with soil under the 903 Pad.

The preceding discussion shows that the distribution of plutonium in soils is a crucial factor in determining how much heat per unit area will be produced by oxidation reactions, whether there is enough soil to absorb the heat, and therefore whether autoignition can occur. The distribution of plutonium at the 903 Pad is inhomogeneous, and the plutonium will occur on surfaces of large aggregates. As shown by Navratil *et al.*, the contamination range for plutonium in soil ranges from 427 pCi/g to 20,455 pCi/g of soil.<sup>9</sup> This latter limit represents a plutonium concentration of approximately 0.33  $\mu\text{g Pu/g}$  of soil.

Although these simple conversions estimate the plutonium soil concentration, they do not provide information concerning the chemical form of plutonium in soil. Thus, other factors must be considered.

#### 4.6 Amount of Protective Surface Oxide

Plutonium is a very reactive metal that oxidizes readily when exposed to oxygen or water vapor. A number of studies have been conducted to characterize the oxidation of plutonium.<sup>60-62, 67-76</sup> Most of these studies were undertaken to compare the reactivity of plutonium and plutonium alloys and to obtain some quantitative oxidation data on the effects of moisture. Characterization data (obtained by x-ray diffraction, x-ray photoelectron spectroscopy, electron diffraction spectroscopy, and metallography) show that water vapor reactions with unalloyed plutonium produce a diverse mixture of products, depending on temperature. These oxidation products include  $\text{PuO}_2$ ,  $\text{Pu}_2\text{O}_3$ , and a monoxide monohydride,  $\text{HPuO}$ .<sup>77</sup>

The oxidation of a metal is preceded by dissociative adsorption, with the high heat of adsorption falling as further oxygen is adsorbed onto the initial layer.<sup>42,63</sup> At

this stage, many metals form protective oxide films; the growth of these films is governed by a parabolic rate law in which the rate of oxide growth is inversely proportional to the film thickness and can fall to zero at some limiting film thickness.<sup>39,63</sup> This limiting thickness typically lies in the 10- to 50-Å range.<sup>39,63</sup> The kinetics of the process are dependent on the diffusion of an ion or electron through lattice defects.

An adherent oxide diffusion layer forms on the surface of plutonium during gaseous oxidation,<sup>68-70</sup> this layer is critical in preventing the pyrophoricity of plutonium metal exposed to air. It then can be seen that 0.3 µg of plutonium metal will have a much greater pyrophoric potential than will 0.3 µg of plutonium dioxide. However, in reactions with liquid water, the incoming water molecule is able to diffuse through the oxide layer. In chemical reactions with liquid water, the plutonium metal can be quantitatively converted into the monoxide monohydrate, HPuO.<sup>56</sup> Thus, for plutonium metal in soil that is in contact with liquid groundwater, formation of a protective oxide layer is not significant.

#### 4.7 Kinetic and Thermodynamic Considerations

Plutonium metal is a highly reactive substance that can react with practically every element except noble gases. A detailed summary of actinide metal oxidation can be found in reviews by Colmenares.<sup>65,66</sup>

Most metal oxides have a free energy of formation that is on the order of kilocalories per mole, while actinide metal oxides have a free energy of formation on the order of hundreds of kilocalories per mole. As a consequence, the actinide metals are thermodynamically unstable in air, and in principle, one would expect complete conversion of actinide metal into the oxide that is most stable in air. In practice, this does not occur for the actinides because of the kinetics of the oxidation process in air. In liquid water, however, the reaction kinetics are very different from

those of the gaseous reactions, and a particle of plutonium immersed in liquid water will undergo complete corrosion.<sup>55,56</sup>

The kinetics of the reaction of plutonium with liquid phases are found to differ substantially from those observed for gaseous reactions. The primary difference appears to be that in liquid water and carbon tetrachloride reactions, the corrosive liquid is able to diffuse through the oxide coating, with an end result of complete oxidation. There have been several reports on the corrosion of plutonium caused by liquid water in synthetic seawater<sup>78</sup> and salt solutions.<sup>56</sup> The reactions of  $\alpha$ - and  $\delta$ -plutonium (2.9% Ga) in water and 1-M salt solutions were studied by measuring the production of hydrogen gas formed by a sequence of hydrolysis reactions.<sup>55</sup> In contrast to reactions between plutonium metal and gaseous oxygen, which form a protective oxide layer, reactions with liquid water are extremely corrosive to plutonium. In liquid water reactions, plutonium metal was found to convert quantitatively to a fine black powder, which was identified as plutonium monoxide monohydrate (HPuO) by means of thermogravimetric analysis, x-ray diffraction, and x-ray photoelectron spectroscopy. Other hydrolysis products were also identified in aqueous hydrolysis media; these included a second hydride ( $H_3Pu_7O_9$ ) and a series of oxides ( $Pu_2O_3$ ,  $Pu_7O_{12}$ ,  $Pu_9O_{16}$ ,  $Pu_{10}O_{18}$ ,  $Pu_{12}O_{22}$ , and  $PuO_2$ ). Kinetic studies on the liquid water reaction with plutonium reveal that the reaction is catalyzed by salt.<sup>56</sup> If submerged in seawater at 25°C, a 1- $\mu$ m-thick sheet of plutonium metal will be converted to HPuO powder in approximately 16 days.

In light of the thermodynamic and kinetic driving forces for oxidation of plutonium it is possible to conclude that after 23 to 33 years of exposure to dissolved oxygen, water, and halogenated organics in the immediate environment, the plutonium deposited in the 903 Drum Storage Site has oxidized into a non-pyrophoric form.

For the corrosion of  $\delta$ -stabilized plutonium in ordinary tap water, a diffusion-

controlled corrosion reaction predominates with a corrosion rate of 0.264 mg Pu/(cm<sup>2</sup> hr) for the initial stages of reaction.<sup>55</sup> During this initial process, water must diffuse through an oxide product layer before reacting with plutonium metal. After a period of time, the corrosion layer cracks and flakes, and the reaction rate is accelerated to 0.52 mg Pu/(cm<sup>2</sup> hr).<sup>55</sup>

These important kinetic data make it possible to calculate the lifetime of a 100- $\mu$ m plutonium particle in ordinary tap water. Assuming a density<sup>51</sup> for  $\delta$ -stabilized plutonium metal of 15.92 g/cm<sup>3</sup> and a spherical particle, a 100- $\mu$ m plutonium particle weighs  $6.67 \times 10^{-5}$  g and has a surface area of  $1.26 \times 10^{-3}$  cm<sup>2</sup>. At the initial corrosion rate of 0.264 mg Pu/(cm<sup>2</sup> hr) for the diffusion-controlled liquid water reaction, a 100- $\mu$ m plutonium particle will be completely consumed in 200.9 hours, or 8.37 days, in normal tap water. A larger particle surface area will greatly increase the rate of corrosion by liquid water. If the actual surface area of a 100- $\mu$ m plutonium particle is 50 times greater than that of a perfect sphere, the calculated lifetime of the plutonium particle is reduced to only 4 hours. Therefore, 200 hours can be used as an upper limit for the lifetime of a 100- $\mu$ m,  $\delta$ -stabilized plutonium particle in ordinary tap water.

The aqueous corrosion of plutonium also has been shown to be catalyzed by salt, and the corresponding rate for  $\delta$ -stabilized plutonium corrosion in a 1.0-M CaCl<sub>2</sub> solution is increased dramatically to 15.85 mg Pu/(cm<sup>2</sup> hr).<sup>55</sup> For  $\alpha$ -phase plutonium, the same corrosion conditions produce a corrosion rate of 31 mg Pu/(cm<sup>2</sup> hr).<sup>55</sup> Thus, naturally occurring salts in Rocky Flats groundwater are expected to accelerate the corrosion rate of plutonium in contact with groundwater under the 903 Pad.

Data from groundwater sampling at the 903 Pad revealed concentrations of carbon tetrachloride and other chlorinated organics.<sup>5</sup> Crisler has reported the facile oxidation and dissolution of plutonium metal by a carbon tetrachloride-methanol mixture.<sup>72</sup> The heat of

reaction for this oxidation process was found to be -205 kcal/mole with a corrosion rate of 13 mg Pu/(cm<sup>2</sup> min) at 25°C. At Crisler's corrosion rate of 13 mg Pu/(cm<sup>2</sup> min),<sup>77</sup> a spherical 100-μm plutonium particle will have a lifetime of only 4 minutes in a carbon tetrachloride-methanol mixture.

Because of the similar reactivity of methanol and water, it is highly probable that plutonium will also be oxidized by carbon tetrachloride-water mixtures in soil, or by other liquid water mixtures with chlorinated organics in the soil. Several recent articles discuss the dissolution of actinide metals with halogenated organics. Karraker has reported the dissolution of neptunium and plutonium metal with 1,2-diiodoethane in THF solutions, producing solvated actinide iodides.<sup>79</sup> Clark and Zwick have found that simple halogens will completely dissolve actinide metals thorium, uranium, neptunium, and plutonium in polar organic donor solvents, producing solvent adducts ThX<sub>4</sub>(L)<sub>4</sub>, UX<sub>3</sub>(L)<sub>4</sub> (X = Br, I), NpI<sub>3</sub>(L)<sub>4</sub>, and PuI<sub>3</sub>(L)<sub>4</sub>, where L is a wide variety of organic donor solvents.<sup>80,81</sup> In addition, Sauer *et al.* have shown that this reaction is accelerated by the use of protic solvents such as alcohols and water.<sup>82</sup>

As indicated by the above reports and the known corrosive behavior of water and halogenated organics toward plutonium, it is likely that aqueous groundwater mixtures of chlorinated solvents will be highly corrosive toward plutonium in soils at the 903 Drum Storage Site.

#### **5.0 Conclusions on the Pyrophoric Potential of Plutonium Metal at the 903 Drum Storage Site**

Calculations show that δ-stabilized plutonium particles will have critical particle sizes of approximately 5 μm; particles smaller than this size would be

expected to show pyrophoric behavior on exposure to air. As noted, however, the oils were sieved before they were placed in the drums, so plutonium particles in the soil could range in size up to 100  $\mu\text{m}$ . As discussed in Section 4.5, the distribution of plutonium in soils under the 903 Pad is inhomogeneous, making it difficult to estimate exact concentrations. It is also known, however, that dilution of these particles with large amounts of soil will reduce the pyrophoricity by absorption of heat produced in oxidation processes.

It is also well established that oxidation of plutonium by gaseous agents such as oxygen or water vapor generates an adherent oxide film on the surface of the plutonium particles. This oxide surface further reduces the potential of pyrophoricity. Additionally, other mechanisms (reactions between the plutonium and aqueous groundwater mixtures of chlorinated solvents known to be present in the soil beneath the 903 Pad) will prevent the pyrophoricity of plutonium in the soils. These liquid reactions are the ultimate barrier to pyrophoricity of the plutonium deposited in the soil. The kinetics of the oxidation of plutonium show that the lifetime of a 100- $\mu\text{m}$  plutonium particle is only 8.4 days in liquid water, and 4 minutes in a carbon tetrachloride-methanol mixture.

Therefore, from the above data and discussions, it can be concluded that the plutonium in the 903 Pad soil is inert with respect to pyrophoricity because of the low specific surface for plutonium combined with a protective oxide surface and dilution of particles in soil. Additionally, no plutonium pyrophoricity was found in the November 1968 remedial action at the 903 Drum Storage Site where soil was scraped into a smaller area.<sup>7</sup>

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## 7.0 Glossary

To provide a common basis for discussing pyrophoricity, definitions for technical terms used in this report follow. Many of the definitions were taken verbatim from the Fire Protection Handbook,<sup>10</sup> which is a comprehensive and authoritative text on this subject.

### 7.1 Pyrophorus and Pyrophoric

The word "pyrophorus" is derived from the Greek word for fire-bearing.<sup>11</sup> The Oxford English Dictionary defines pyrophorus as any substance capable (especially in a finely divided state) of taking fire spontaneously on exposure to air.<sup>11</sup> The adjective "pyrophoric" is defined as having the property of taking fire on exposure to air.<sup>11</sup> A distinction is often made between those elements and compounds that burst into flame on exposure to air because of their intrinsic chemical behavior and those that do so only because of their special method of preparation (such as finely divided powders). In this report, the term "pyrophoric" is used in its broadest sense; that is, it applies to large masses of pure metals, or alloys, carbides, hydrides, etc., rather than being restricted to finely divided metals.

### 7.2 Ignition, Piloted Ignition, and Autoignition<sup>10</sup>

**Ignition is the process of initiating combustion.** The Oxford English Dictionary defines "ignition" as heating to the point of combustion or chemical change.<sup>11</sup> Ignition is further defined depending on its cause: that resulting from the introduction of some small external flame or spark is called "piloted ignition"; that occurring spontaneously, or without the assistance of an external pilot source, is called "autoignition."

### 7.3 Ignition Temperature<sup>10</sup>

The "ignition temperature" of a substance is the minimum temperature it must attain to ignite. Usually, the piloted ignition temperature of a substance is considerably lower than its autoignition temperature.

### 7.4 Combustion and Spontaneous Combustion<sup>10</sup>

Combustion is an exothermic, self-sustaining reaction involving a fuel and an oxidant. The process is usually associated with the oxidation of a fuel by atmospheric oxygen. The Oxford English Dictionary defines "combustion" as the action or process of burning, whereas "spontaneous combustion" is defined as the act of taking fire, or burning through conditions produced within the substance itself.<sup>11</sup>

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