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*Storage of Plutonium Extracted
from Weapons (U)*

March 12, 1993

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from Weapons (U)*

J. M. Haschke
J. C. Martz

March 12, 1993

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March 12, 1993

STORAGE OF PLUTONIUM EXTRACTED FROM WEAPONS (U)

by

John M. Haschke and Joseph C. Martz

ABSTRACT (U)

The storage form for plutonium extracted from pits is examined from the standpoints of ease of reconstitution, applicability to weapon manufacture, and technical and regulatory requirements. The impact of storage form on dismantlement and preparation for storage is considered, as is the potential impact of storage form on proliferation. In summary, plutonium stored in any reasonably concentrated form does not present a significant obstacle to reconstitution of material suitable for use in nuclear weapons. The most difficult step in preparing plutonium for weapon use is the fabrication of plutonium metal into the proper geometry.

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Demonstrated production-scale processes only exist for preparation of metal and oxide. An examination of capability shows that no facility currently exists, either operational or capable of restart, which could extract and process material from pits at even modest levels of throughput. Further, no facility with sufficient capacity will be available within a few-year time frame. Only with great difficulty and streamlining of environmental and regulatory constraints could existing facilities such as Rocky Flats or Savannah River be prepared to dismantle weapons and process material for storage. Under the best of circumstances, such facilities might be available within 5 to 10 years. Appropriate facilities for recovery and processing are included in Complex 21 development activities and should be available within a 10 to 15 year time frame.

From a material property perspective, metal is an acceptable storage form for plutonium extracted from pits. Metal prepared for storage should meet the certification and cleanliness standards for war-reserve (WR) components. Oxide is also suitable for storage if cleanliness and certification requirements are met. The lack of fundamental chemical property information for alloys of plutonium with non-nuclear metals may preclude their use as long-term storage forms. Other forms such as mixed plutonium/uranium oxides, plutonium carbides, and plutonium nitride may be suitable for long-term storage if appropriate certification procedures are defined. However, despite extensive evaluation of these materials for use as reactor fuels, large uncertainties exist about their behavior in storage environments. Plutonium carbides and nitride are reactive and are readily hydrolyzed by moisture to form potentially explosive or hazardous gases. Plutonium hydride, another candidate storage form, is pyrophoric. Typical production operations for non-metallic materials (e.g. oxide, nitride, carbide, etc.) yield high-surface-area powders. A large fraction of respirable particles may be released from these forms on exposure to air (greater than 25% mass percent). Technologies for consolidation of oxide and other powdered materials into pellets or briquettes are well established, but existing methods generate considerable quantities of radioactive waste. Since conversion of plutonium from one material form to another and any treatment of an existing form results in considerable waste generation and worker radiation exposure, advantage is gained by storing plutonium in its existing form and minimizing process operations. Complex 21 must be capable of producing the desired storage form; the present design must be altered if a form other than metal is adopted.

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I. Executive Summary

The storage form for plutonium extracted from pits is examined from the standpoints of ease of reconstitution, applicability to weapon manufacture, and technical and regulatory requirements. The impact of storage form on dismantlement and preparation for storage is considered, as is the potential impact of storage form on proliferation. A consideration of storage-form options includes examination of ES&H concerns, assessment of capability, and preservation of options for ultimate, final disposition of the stored material. When problems arise, the availability of appropriate remediation is of considerable importance. Individual sections of this chapter examine the ease of material reconstitution and the effectiveness of isotopic diluants in rendering a material less desirable for use by national or subnational proliferant groups. Subsequent sections consider technical issues associated with various concentrated material forms.

In addition to plutonium dioxide (PuO_2) and plutonium metal (Pu), possible material forms considered for storage of plutonium extracted from pits include plutonium hydride (PuH_{2+x} , $0 \leq x \leq 1$), plutonium carbide (PuC_2), plutonium nitride (PuN), and alloys of plutonium with metals such as aluminum (Al), iron (Fe), copper (Cu), uranium (U), and cobalt (Co). Long-term storage of plutonium in solution is not considered a viable option. Candidate material forms should be considered in light of readiness requirements as well as the needs for research, development, facility modification, and process implementation.

A. Reconstitution and Isotopic Dilution

The perceived difficulty in reconstitution of a particular form is often used as justification for processing to and storage of that form. Hence, it is of foremost importance to consider the ease with which plutonium can be reconstituted. Reconstitution of plutonium from a variety of forms has been addressed in several studies.

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Reconstitution of plutonium from any of the candidate forms does not present a formidable barrier to the construction of a nuclear device. Fabrication of metallic components is more difficult than recovery of the metal. Storage of plutonium in any form (including Pu metal) requires fabrication of metal components as a necessary step in device construction

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justification that plutonium be stored in a particular form because of reconstitution difficulty must be carefully examined.

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(Indeed, "the fact that Pu containing more than 8% Pu-240 (reactor grade) can be used to make nuclear weapons" is unclassified.

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b(3)**B. Technical Issues Related to Storage Form**

Knowledge of certain nuclear, chemical, and physical properties of plutonium and relevant compounds is essential for evaluating candidate storage forms, for addressing ES&H concerns, and for examining other technical issues. From a chemical perspective, Pu is an active metal that reacts with most other elements and materials. Plutonium reacts with oxygen, air, water and many oxygen-containing compounds to form Pu_2O_3 and PuO_2 . Plutonium dioxide has an active surface and strongly absorbs molecules like H_2O and CO_2 . Depending on the method of oxide preparation, large variations in surface area (from less than 0.1 to more than 60 m^2/g , typically 10 m^2/g), particle size, and bulk density are observed. Other compounds of interest include plutonium carbides and plutonium nitride. These materials are typically formed as powders and burn to PuO_2 in oxidizing environments. Plutonium metal reacts rapidly with hydrogen at room temperature to form nonstoichiometric plutonium hydride. The chemical behavior of plutonium-containing systems may be dramatically altered by radiolysis of organic or molecular compounds on or

close to the material surface. Radiolysis products frequently contain H_2 , CO, HCl, and other reactive gases.

Plutonium also reacts to varying degrees with other metals. Whereas the refractory metals such as vanadium and tantalum are slightly soluble in liquid Pu (mp = 640 °C), other metals form intermetallic phases (alloys). In addition to phase equilibria, the crystal structures and theoretical densities of many of these alloys are known, but these materials are poorly characterized and considerable difficulty is encountered in their preparation.

1. Chemical Reactivity

Plutonium oxide is a relatively unreactive material. In contrast, oxidation of plutonium metal is thermodynamically favored and highly exothermic. However, the rate is slow and does not present a reactivity hazard even at elevated temperatures. Massive plutonium is not pyrophoric and can be handled in air without risk. Spontaneous ignition occurs only when the metal is in a finely divided state (less than 0.2 mm thick) and when the temperature also exceeds 150 °C. Of greater concern is the volumetric expansion of product during reaction with oxygen. If metal is confined to a limited space, the mechanical forces accompanying oxide growth can exert pressure on the storage container. This expansion could rupture or burst the storage vessel. The chemical reactivities of intermetallic phases formed by Pu with Al, Fe, Cu, U, or Co is difficult to evaluate because fundamental information on their thermodynamic properties, kinetic behavior, corrosion processes, and pyrophoric tendencies are unknown.

Oils or other organic materials which remain on plutonium metal surfaces are decomposed by alpha-particle radiolysis to form carbon-rich residues and hydrogen. Subsequent $Pu+H_2$ reaction produces pyrophoric hydride. Since the extent of hydride formation is limited by the amount of hydrocarbon initially present on the Pu surface, cleaning procedures are effective in mitigating this phenomenon.

Plutonium hydride, nitride, and carbides react exothermically on exposure to oxidizing environments. Hydride decomposes to metal and hydrogen gas on heating above 500 °C. Plutonium carbide reacts with water to form Pu oxides and hydrocarbons. Hydrocarbons formed include gases such as methane and acetylene, as well as polymerized species which continue to reside on the Pu surface until they radiolytically decompose to hydrogen and other gaseous hydrocarbons. All finely divided Pu forms strongly absorb or react with water. The quantity of absorbed water can be considerable: as much as 10mg H₂O per gram of PuO₂. This corresponds to approximately ten monolayers of absorbed water on the oxide surface.

2. Storage Experience

Of the forms considered here, only metal and oxide have relatively extensive storage histories. Pu metal has been stored for more than forty years as weapon components in the stockpile. This experience with Pu-containing pits has been trouble free and can be directly transferred to storage of metal. Established certification procedures for pits show that the integrity of plutonium components is preserved during extended storage. Experience also exists in the storage of oxide. Preparation of oxide as an intermediate in metal production has formed an integral part of plutonium processing. Procedures for preparation of a certified WR oxide for storage are not fully developed.

Limited experience exists in the storage of plutonium hydride, carbide, or nitride. Carbide and nitride are fabricated for use in reactor fuels, usually relying on cladding materials to prevent undesired chemical corrosion. Hydride is stable at low temperatures in inert environments.

3. Container Pressurization

An important concern is the risk of container pressurization during storage. Several potential pressure sources are identified: helium from alpha decay of Pu, hydrogen and other gases from radiolytic decomposition of organic and other residues, and gases from chemical

reaction or desorption of adsorbed species. In each of these cases, the quantity of gas generated depends on the physical surface area of the stored material. Per unit of mass, the surface area of a typical powdered form is 10^4 times larger than that of massive forms such as bulk metal or alloys.

Whereas only an extremely small fraction of the He escapes from massive metal, a major fraction is released from finely divided forms due to the small particle dimensions. After 100 years in a typical unvented storage environment, less than 1 torr of He pressure build-up is expected for metallic forms, while near 1000 torr will accumulate during storage of powdered materials.

Radiolysis of compounds is prevalent for finely divided forms because of their tendencies to both absorb organic species and to disperse within storage environments. All organics, even those initially isolated from the radiolytic surface cause concern. Isolated materials such as polyethylene bags, vinyl tape, or rubber o-rings have lead to problems in past incidents. Finely divided forms are entrained by natural convection currents within the storage container and may deposit on all accessible surfaces within the storage environment. Radiolytic decay of organic materials results, often breaching container integrity and generating further corrosive gases. Variations in atmospheric pressure due to meteorological changes can "breathe" large amounts of air through a small opening in a container as well as transport gases containing entrained particles within environments sealed by flexible media. This provides a potential mechanism for moving entrained oxide from within metal storage cans to bagging material on the exterior. Exclusion of all organic materials is necessary to prevent pressure generation by radiolysis.

Other processes for pressure generation arise from chemical reaction of species on surfaces and thermal desorption of adsorbates. Both of these phenomena are strongly dependent on the surface area of the stored material.

C. Environment, Safety, and Health Concerns

1. Waste Generation

The level of waste generation is a major consideration in assessing storage options for extracted plutonium. Though advantage is gained by upgrading process technologies, the greatest benefit is achieved by avoiding all unnecessary processing. The simplest method to limit waste generation is intuitive: leave materials in their existing form. Interconversion of material forms should be minimized to avoid waste generation and other ES&H concerns associated with handling of material. However, potential problems with a particular material may require processing to an alternate form to alleviate concerns. Nearly all plutonium in US inventories is currently metal or oxide, with a minor fraction stored mostly as process wastes including ash and salts. The inventory existing as carbide, nitride, hydride, or dilute alloys is small.

Certain options might be suggested to remediate anticipated storage problems. For instance, it has been suggested to briquette oxide to prevent dispersion in storage. Though perhaps simple in design, practical and demonstrated processes to accomplish such remediation often do not exist. All processes and alternatives must be evaluated to assess their net impact on waste generation and other ES&H concerns.

2. Criticality Safety

A large body of experience exists in managing criticality safety. Primary controls include limiting the quantity of stored material in any given container, and careful control of storage vault geometry. No storage form presents an abnormal criticality risk provided well established control procedures are followed.

3. Environmental

The possibility of dispersing plutonium-containing particles during an accident is a serious environmental concern. Two situations merit examination: an accident in which the storage container is mechanically breached and one in which the intact container is exposed

to a fire with temperatures in excess of 640 °C. If risk from physical damage is measured by the quantity of material that might be dispersed during container rupture and subsequent action of air currents and other transport processes, the potential hazard posed by storage of bulk forms is small compared to that posed by finely divided material. Although the likelihood of losing containment of molten metal during a fire is considered small if remedial containment technologies are employed, the formation of dispersible oxide will be accelerated at elevated temperatures. The possibility of pressurized storage containers also poses a credible risk during a fire. The combination of rise in gas pressure and loss of steel strength at high temperatures could lead to container rupture and dispersal of respirable material.

4. Personnel Safety

Exposure to ionizing radiation is an additional risk to personnel. The levels of radiation present for bulk and finely divided forms are not the same because of differences in self-absorption behavior and an increase in neutron radiation due to alpha-n reactions. The increase in neutron radiation from PuO₂, PuC₂, and PuN (compared to Pu) is relatively small. The principle source of neutrons in these materials is ²⁴⁰Pu. Shielding of process operations and storage containers provides a potential remedy for all storage forms.

D. Summary

Plutonium stored in any reasonably concentrated form does not present a significant obstacle to reconstitution of material suitable for use in nuclear weapons. The most difficult step in preparing plutonium for weapon use is the fabrication of components into the proper geometry.

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From a material property perspective, metal is an acceptable storage form for plutonium extracted from pits. Storage in this form preserves all currently suggested disposition options. Metal prepared for storage should meet appropriate certification and cleanliness standards (such as those established for war-reserve components). Precautions should include exclusion of air, water, and organics from the storage environment.

Oxide is also suitable for storage if similarly stringent cleanliness and certification requirements are met. One of the most common problems in plutonium storage is pressurization of the primary storage container. Pressure build-up may be caused by helium release due to alpha decay, radiolytic reactions on the Pu surface, chemical reactions that create gaseous products, and elevated temperatures that volatilize components of the system. All of these phenomena are potentially significant in oxide storage. Oxide is less reactive than metal, but more easily dispersed in the event of container rupture. Technologies for consolidation of oxide and other powdered materials into pellets or briquettes are known, but existing methods generate considerable quantities of radioactive waste.

The lack of fundamental chemical property information for plutonium alloys may preclude their consideration as long-term storage forms. Other forms such as mixed plutonium/uranium oxides, plutonium carbides, and plutonium nitride may be suitable for long-term storage if appropriate certification procedures are defined. However, despite extensive evaluation of these materials for use as reactor fuels, uncertainties exist about their behavior in storage environments. Plutonium carbides and nitride are reactive and are readily hydrolyzed by moisture to form potentially explosive or hazardous gases. Plutonium hydride, another candidate storage form, is pyrophoric. Typical production operations for non-metallic materials (e.g. oxide, nitride, carbide, etc.) yield high-surface-area powders. A large fraction of respirable particles may be released from these forms on exposure to air (greater than 25% mass percent).

Conversion of plutonium from one form to another and any treatment of an existing form results in additional waste generation and worker radiation exposure. We suggest plutonium should be stored in its existing form provided this poses no abnormal safety or environmental problems. Interconversion of material forms should be avoided. Complex 21 must be capable of producing the desired storage form; the present design must be altered if a form other than metal is adopted.

II. Introduction

A consideration of storage-form options includes examination of ES&H concerns, assessment of capability, and preservation of options for ultimate, final disposition of the stored material. When problems arise, the availability of appropriate remediation is of considerable importance. Individual sections of this report examine the ease of material reconstitution and the effectiveness of isotopic diluants in rendering a material less desirable for use by national or subnational proliferant groups. Subsequent sections consider technical issues associated with various concentrated material forms.

In addition to plutonium dioxide (PuO_2) and plutonium metal (Pu), possible material forms considered for storage of plutonium extracted from pits include plutonium hydride (PuH_{2+x} , $0 \leq x \leq 1$), plutonium carbide (PuC_2), plutonium nitride (PuN), and alloys of plutonium with metals such as aluminum (Al), iron (Fe) and cobalt (Co). Long-term storage of plutonium in solution is not considered a viable option.¹ DOE facilities have production-scale process experience with oxide and metal. Storage experience for WR material resides almost exclusively with these forms. Carbides and nitride have been extensively studied for use as reactor fuels though storage experience with these forms is limited. Candidate material forms should be considered in light of readiness requirements as well as the needs for research, development, facility modification, and process implementation. Material forms can be diluted (e.g. storage of mixed uranium and plutonium oxides), but the advantage gained by storage of such materials should be considered in light of separation and recovery

¹Chemical and radiolytic compatibility, criticality safety concerns, storage volumes, configuration requirements, surveillance, and inventory activities all suggest storage of material as aqueous plutonium solutions is unacceptable. For these reasons, the authors have chosen to exclude aqueous solutions as viable candidate forms in this analysis. Detailed justification of this decision is beyond the scope of this report, but interested readers are directed to the extensive body of literature on plutonium in solution for further information. Good initial references include J.M. Cleveland, "The Chemistry of Plutonium," American Nuclear Society, La Grange Park, IL 1979, or O.J. Wick, ed., "Plutonium Handbook, A Guide to the Technology - Volumes I and II," American Nuclear Society, La Grange Park, IL 1980.

options. Storage of mixed oxides is often suggested, since one possibility for ultimate disposition is use of such materials in power reactors.²

Relatively few studies have expressly examined long-term plutonium storage. The limited literature on storage may be attributed to the plutonium shortage that existed in the US weapons complex until recently. Material was stored on an interim basis until it was used for weapon manufacture. However, specific issues related to plutonium storage have been addressed. For example, the chemical properties of plutonium metal and certain compounds have been extensively investigated. The helium-release behavior of $^{238}\text{PuO}_2$ (generated by alpha decay) has also been studied as a component of heat source development. This experience has important implications in predicting the behavior of Pu in long-term storage.

A comprehensive plutonium storage study is found in the report of a 1981 task force headed by H. H. Van Tuyl. Though never formally published, copies of this report are available.³ A recently published white paper also addresses many of the issues outlined here, though in a somewhat cursory manner.⁴ L. E. Musgrave examined plutonium metal storage in 1973.⁵

²As is discussed later in the text, conversion to this form would most appropriately occur at the time a decision is made to dispose of Pu in this manner. Premature preparation of a reactor-feed material may hinder other disposition options, and the wastes generated will remain essentially constant whether the material is prepared prior to interim storage or just before introduction into the reactor. Likewise, preparation of storage forms which fit other suggested disposition options is most appropriately delayed until a decision on ultimate disposal is made.

³H.H. Van Tuyl, "Packaging of Plutonium for Storage or Shipment," Pacific Northwest Laboratory, March 1981 (unclassified).

⁴J.C. Martz and J.M. Haschke, "Long-Term Storage of Plutonium: An Overview (U)," Los Alamos Report LA-CP 92-275, October 1992 (UCNI).

⁵L.E. Musgrave, "Storage of Unalloyed Plutonium in Metal Cans," Rocky Flats Report PRD-950461-105, July 25, 1973 (unclassified).

III. Fundamental Plutonium Properties

Knowledge of certain nuclear, chemical, and physical properties of plutonium and relevant compounds is essential for evaluating candidate storage forms, for addressing ES&H concerns, and for examining other technical issues. In addition to the ^{239}Pu isotope that simultaneously undergoes alpha decay ($t_{1/2} = 2.4 \times 10^4$ years) and spontaneous fission ($t_{1/2} = 5.5 \times 10^{15}$ years), weapons-grade material contains small amounts of other plutonium isotopes including ^{241}Pu . Beta decay of ^{241}Pu ($t_{1/2} = 13.2$ years) leads to in-growth of ^{241}Am that decays at a slower rate ($t_{1/2} = 458$ years) with emission of an energetic (60 keV) gamma ray. From a chemical perspective, Pu is an active metal that reacts with most other elements and materials.⁶ Plutonium reacts with oxygen, air, water and many oxygen-containing compounds to form Pu_2O_3 and PuO_2 . Although dioxide is the more stable of these products and is considered to be the equilibrium phase in air, recent observations for reaction of Pu with water vapor show that the most stable oxide is near $\text{PuO}_{2.2}$, a mixed-valent compound with $\text{Pu(IV)}_4\text{Pu(VI)O}_{11}$ stoichiometry.⁷ Plutonium dioxide has an active surface and strongly absorbs molecules like H_2O and CO_2 . Depending on the method of oxide preparation, large variations in surface area (from less than 0.1 to more than 60 m^2/g , typically 10 m^2/g), particle size, and bulk density are observed.^{8,9,10} Other compounds of interest include plutonium carbides (PuC , Pu_2C_3 , PuC_2) and plutonium nitride (PuN). These materials are

⁶J.M. Cleveland, "The Chemistry of Plutonium," American Nuclear Society, La Grange Park, IL 1979. See also O.J. Wick, ed., "Plutonium Handbook, A Guide to the Technology - Volumes I and II," American Nuclear Society, La Grange Park, IL 1980.

⁷J.L. Stakebake, D.T. Larson, and J.M. Haschke, "Characterization of the Plutonium-Water Reaction Part II: Formation of a Binary Oxide Containing Pu(VI)," Los Alamos Report LA-UR-93-0040, January 1993 (unclassified). Submitted for publication in J. of Metals and Alloys.

⁸J.D. Moseley and R.O. Wing, "Properties of Plutonium Dioxide," Rocky Flats Report RFP-503, August 24, 1965 (unclassified).

⁹J.M. Haschke, "Evaluation of Source-Term Data for Plutonium Aerosolization," Los Alamos Report LA-12315-MS, July 1992 (unclassified).

¹⁰J.L. Stakebake and M.R. Dringman, J. Nucl. Mat., 23 (1967) p. 349.

typically formed as powders and burn to PuO_2 in oxidizing environments. Whereas the carbides react with water to form hydrated plutonium oxide ($\text{PuO}_2 \cdot x\text{H}_2\text{O}$) and gaseous hydrocarbons (e.g., methane and acetylene), hydrolysis of the nitride produces $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ plus gaseous ammonia and hydrogen. Plutonium metal reacts rapidly with hydrogen at room temperature to form nonstoichiometric PuH_{2+x} ($0 \leq x \leq 1$) with x determined by the temperature and hydrogen pressure. The pyrophoric hydride has a moderately high surface area ($0.2 \text{ m}^2/\text{g}$ maximum) and reacts to form oxide, nitride, and hydrogen upon exposure to air.¹¹ The chemical behavior of plutonium-containing systems may be dramatically altered by radiolysis of organic or molecular compounds on or close to the material surface. Radiolysis products frequently contain H_2 , CO , HCl , and other reactive gases.

Plutonium also reacts to varying degrees with other metals. Whereas the refractory metals such as vanadium and tantalum are slightly soluble in liquid Pu ($\text{mp} = 640 \text{ }^\circ\text{C}$), other metals form intermetallic phases. Aluminum forms three compounds including PuAl_2 ($\text{mp} = 1540 \text{ }^\circ\text{C}$), PuAl_3 , and PuAl_4 that melt incongruently at 1420 and $915 \text{ }^\circ\text{C}$, respectively.¹² In addition to PuFe_2 ($\text{mp} = 1240 \text{ }^\circ\text{C}$) and PuCo_2 ($\text{mp} = 1310 \text{ }^\circ\text{C}$), iron and cobalt form Pu_6Fe and Pu_6Co near-eutectic compositions that melt at 410 and $408 \text{ }^\circ\text{C}$, respectively. The Pu-Co system is especially complex with intermetallic phases at Pu_3Co , Pu_2Co , PuCo_3 and $\text{Pu}_2\text{Co}_{17}$. In addition to phase equilibria, the crystal structures and theoretical densities of the alloys are known.¹³ Kilogram-size quantities of intermetallic compounds have been prepared,^{14,15} but these materials are poorly characterized and considerable difficulty is encountered in their preparation.

¹¹A.E. Hodges, III, and J. M. Haschke, "Reaction of the Plutonium-Plutonium Hydride System with Air (U)," Rocky Flats Report RFP-2854, July 1979 (Secret/RD).

¹²F.H. Ellinger, W.N. Miner, D.R. O'Boyle, F.W. Schonfeld, "Constitution of Plutonium Alloys," Los Alamos Report LA-3870, December 1968, p. 5 (unclassified).

¹³F.H. Ellinger, W.N. Miner, D.R. O'Boyle, F.W. Schonfeld, "Constitution of Plutonium Alloys," Los Alamos Report LA-3870, December 1968, p. 29 and p. 39 (unclassified).

IV. Ease of Reconstitution

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The perceived difficulty in reconstitution of a particular form is often used as justification for processing to and storage of that form. Hence, it is of foremost importance to consider the ease with which plutonium can be reconstituted. Reconstitution of plutonium from a variety of forms has been addressed in several studies. A joint DOE task force examined this issue in detail in 1977 and 1978.^{16,17} Our own technical assessment of reconstitution issues is in agreement with the conclusions of the DOE study.¹⁸ The purpose and scope statement from that report reveals the comprehensive nature of the study.

The purpose of this study is to assess the potential usefulness of materials in the licensed reactor industry as fissile materials for the construction of nuclear explosives. A comprehensive list of materials has been considered in order that the scope of the study not be limited by too specific constraints. The list was drawn from the present and possible future reactor industry sources and from the nuclear weapons program.

The results of the study provide an overall framework for assessing the usability of reactor materials for nuclear explosives. Broad categories have been defined which are related to the technical difficulty of using various materials, and all the materials have been placed in these categories.

¹⁴D.R. Harbur, J.W. Romero, and J.W. Anderson, "Plutonium-Cerium-Cobalt Fuel Development for Molten Reactors," AFS Meetings: Modern Castings, 48 (1965) p. 124.

¹⁵D.R. Harbur, J.W. Anderson, and W.J. Maraman, "Studies on the U-Pu-Zr Alloy System for Fast Breeder Reactor Applications," Los Alamos Report LA-4512, November 1970.

¹⁶W.J.Ogle (DOE/OMA), T.J.Hiirons (LANL), J.C.Mark (NRC), W.C.Myre (SNLA), and R.W.Selden (LLNL), "A DOE Special Study Report: Reactor Materials and Nuclear Explosives (U)," DOE Report DOE/DP-0003, February 1978 (Confidential NSI).

¹⁷A secret version of the previous reference is available: W.J.Ogle (DOE/OMA), T.J.Hiirons (LANL), J.C.Mark (NRC), W.C.Myre (SNLA), and R.W.Selden (LLNL), "A DOE Special Study Report: Reactor Materials and Nuclear Explosives (U)," DOE Report DOE/DP-0002, February 1978 (Secret/RD).

¹⁸The difficulty of reconstitution is often speculated upon by analysts unfamiliar with the details of plutonium processing. The distinguished study group which addressed this issue included experts intimately familiar with various plutonium processing operations. Considerable conjecture has occurred which is in conflict with the results of our and the study group's assessment. We consider the issue of reconstitution important enough to show detailed results from Ogle et al., and hope this examination presents the technical issues in a manner free from speculation or bias.

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As a part of the assessment, this report describes some of the technical characteristics associated with these explosives and discusses the resources and time required for the design and construction of nuclear explosives.

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The overall safeguard categories are defined as follows:

Category I. Materials which can be used directly in a nuclear explosive with a minimum of processing and handling requirements. Materials in this category must be regarded as the most usable and should be accorded the highest level of protection.

Category II. Materials which can be used directly in a nuclear explosive or converted to more usable forms, but with increasing technological and/or material requirements. These materials are less sensitive than those of category I, but still deserve a high level of protection.

Category III. Materials which must be converted before they can be used to construct a nuclear explosive. A substantial effort is required to convert these materials to a form which is directly usable. These materials require the lowest levels of protection.

Plutonium in more dilute forms was assigned to Category II. Only the most dilute plutonium forms, those with less than 0.5% plutonium content, were rated as a Category III material.

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An assessment of the time and resources needed to process material to usable weapons is addressed.

The time scale and the financial resources of the subnational program are very difficult to estimate, since they depend so much on the competence, knowledge, and motivation of the group. The design scheme chosen and the degree of sophistication the group chooses to employ also affect the estimates. In general, it is expected that the subnational designs would put a high priority on limiting complexity and cost, even at the expense of performance, safety,

¹⁹W.J.Ogle et al., "A DOE Special Study Report: Reactor Materials...", DOE-DP-0003, page 19-22.

²⁰J.W. Anderson, W.J. Maraman, "Plutonium Foundry Practices," Trans. of the Amer. Foundrymens Soc., 70 (1962) p. 1057.

²¹D.R. Harbur, "Thermal Processing of Alpha Phase Castings," Los Alamos National Laboratory Internal Presentation (1981).

²²D.R. Harbur, J.W. Romero, J.W. Anderson, and W.J. Maraman, "Preparation of Sound High Purity Plutonium Rods, Part 1: Effect of Chill Casting and Subsequent Heat Treatment on Microcracking," J. Nucl. Mat., 25 (1968) p. 160.

²³D.R. Harbur, M.C. Flemings, J.W. Anderson, and W.J. Maraman, "Preparation of Sound High Purity Plutonium Rods, Part 2: Observed Phase Transformations during Quenching from Elevated Temperatures," J. Nucl. Mat., 33 (1969) p. 195.

reliability, and probability of success. The costs could range from a few tens of thousands of dollars to a few tens of millions of dollars. The time scale could range from several months to a few years.

Under the scenario in which all weapon components except the fissile materials are prefabricated, the following time scale is suggested for final completion of the weapon assembly (this scenario might include the subnational group which has completed all planning and preparation, and has completed most of the nonfissile assembly in advance):

The minimum time scale will range from two weeks to two months (for category I materials). If ... conversion of category II to category I is involved, then the minimum time will be extended several weeks.

Recall that plutonium in any but the more dilute forms is rated as Category I, and as such, is relatively easy to purify and requires modest resources and time to complete fabrication. Though storage of highly dilute plutonium forms is possible, this option results in copious generation of waste and necessitates immense storage volumes. Monitoring and inventory of highly dilute forms is more difficult than surveillance of pure metal or oxide. A decision to store in highly dilute forms requires that reconstitution issues assume overriding importance, and must consider the penalties incurred from environmental, safety, accountability, and economic standpoints. Moreover, advances in chemical process technologies may now make even highly dilute forms easier to process than they were in 1977 when the initial evaluation was made. Indeed, the decision that plutonium forms containing concentrations less than 0.5 at. % Pu be placed in Category III (including Process Category P III, a similar designation rating the difficulty of processing) is somewhat arbitrary:

Plutonium compounds at plutonium concentrations of less than 0.5 atomic percent (at. %) were assigned to group P III. That concentration is a relatively arbitrary number chosen to represent the fact that for very low concentrations, huge quantities of material must be obtained and processed, and the scale of the operation becomes so large that it warrants a P III designation.

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does not address PuH_{2+x} , presumably because the hydride dissociates into metal and hydrogen at high temperatures, and hence, is inappropriate for consideration as a reactor fuel. It is also extremely reactive in oxidizing environments. [However, reconstitution of metal from PuH_{2+x} is trivial, requiring only the heating of the material above roughly 500 °C (in vacuum or inert atmosphere) to drive off the hydrogen gas. Dehydriding is both simple and attractive from a waste generation standpoint and is the basis of a key process operation in the recovery of plutonium from retired pits.]

In summary, the reconstitution of plutonium from any of the candidate forms does not present a formidable barrier to the construction of a nuclear device. Fabrication of metallic components is more difficult than recovery of the metal. Storage of plutonium in any form, including Pu metal in a non-weapon geometry such as a critically safe ring configuration, requires fabrication of metal components as a necessary step in device construction. Any justification that plutonium be stored in a particular form because of reconstitution difficulty must be carefully examined.

V. Isotopic Dilution of Plutonium

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²⁴J. C. Mark, "Reactor-Grade Plutonium's Explosive Properties," A publication of the Nuclear Control Institute, NPT/95, August 1990. (unclassified)

²⁵R. W. Selden, "Reactor Plutonium and Nuclear Explosives," presentation to representatives of the IAEA, November 1976. Copies available in Los Alamos National Laboratory internal memorandum IT-2(U)-92-383.

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Indeed, "the fact that Pu containing more than 8% Pu-240 (reactor grade) can be used to make nuclear weapons" is unclassified.²⁷ However, the "isotopic composition of the Pu fuel in a designated weapon" is SRD "if it contains more than 8% Pu-240." Bob Selden (ref. 25) notes

The concept of 'denatured' plutonium – plutonium which is not suitable for explosives – is fallacious. A high content of the plutonium 240 isotope is a complication, but not a preventative.

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These statements are supported by considerable background data, a summary of which is given here.²⁸

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²⁶J.C. Mark, "Use of Reactor Grade Plutonium in Weapons (U)," Los Alamos Report LA-3287-MS, April 8, 1965 (Secret/RD).

²⁷"Guide to Classification of Technical Information (U)," LA-4000, Rev. 6 (Secret/RD).

²⁸Much of this discussion taken from J.W. Gordon, Los Alamos internal memorandum IT-2(S)-92-380, "Notes of the Nonproliferation Nuclear Weapons Working Group", December 4, 1992. (Secret/RD)

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Background neutrons arise from many sources including the small flux

from cosmic rays. The major source of neutrons arises from spontaneous fission, notably ^{240}Pu . Other neutron sources include alpha-neutron (α, n) reactions in which neutrons are produced by the collision of alpha particles with light-element nuclei. The presence of excess neutrons can lead to preinitiation – the premature initiation of the neutron chain reaction before the nuclear material is fully compressed into the supercritical state. Although preinitiation can lead to an uncertainty in yield, crude nuclear designs employing high-neutron background materials can be used to achieve yields in the kiloton range.²⁹

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VI. Storage Form

A. Chemical Reactivity

Plutonium oxide is a relatively unreactive material. In contrast, oxidation of plutonium metal is thermodynamically favored and highly exothermic. However, the rate is slow and does not present a reactivity hazard even at elevated temperatures. Massive plutonium is not pyrophoric and can be handled in air without risk. Spontaneous ignition occurs only when the metal is in a finely divided state (less than 0.2 mm thick) and when the temperature also exceeds 150 °C.³⁰ Pu is normally protected by a passivating oxide surface layer and massive samples (greater than 0.5 mm thick) must be heated above 500 °C before self-sustained reaction occurs.³¹ Of greater concern is the volumetric expansion of product during reaction with oxygen. If metal is confined to a limited space, the mechanical forces accompanying oxide growth can exert pressure on the storage container. This expansion

²⁹Preinitiation is a statistical process which can lead to uncertainty in the yield. The problem for weapon designers is to insure that the maximum and minimum yields of the statistical distribution meet the expected needs of the design.

³⁰J.L. Stakebake, "Plutonium Pyrophoricity," EG&G Rocky Flats Report RFP-4517, 1992 (unclassified).

³¹ibid.

could rupture or burst the storage vessel. Expansion is not necessarily isotropic; leakage of air into a container and swelling of oxide product in the radial direction have burst a storage container even though sufficient axial volume was present to theoretically accommodate expansion.³²

[The reaction of molten Pu with steel poses a potential environmental hazard if the temperature of a steel-based storage container exceeds the melting point of plutonium (640 °C for pure Pu). Although the thermodynamically stable Pu-Fe phase at 10 at. % Fe is a eutectic melting at 410 °C, formation of the liquid alloy is not observed at this temperature because of chemical kinetic limitations. Plutonium and iron are both solids at 410 °C and the diffusivities of both metals are sufficiently low that interdiffusion (reaction) of Pu and Fe proceeds at a slow rate. Adherent oxide layers on both surfaces provide additional kinetic barriers that prevent the system from reaching equilibrium. Rapid alloying (container corrosion) only occurs when kinetic constraints are overcome by fusion of plutonium.]

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³²J. Lowe, (Sellafield, UK), Private communication with the authors, December 17, 1992.

³³J.M. Haschke and T.H. Allen, "Hydrogen Corrosion of Plutonium in Nuclear Weapons (U)," Defense Research Review (U), 4 (1992) (Secret/RD).

³⁴D.R. Horrell, G.E. Bixby, A.E. Hodges, III, and J.M. Haschke, "Parameters which Control the Reaction of Pu + PuH_x Systems with Air (U)," Rocky Flats Report RFP-3353, September 27, 1982 (Secret/RD). Under certain conditions (such as exposure to air) hydrogen can be reevolved and made available for continued

The chemical reactivities of intermetallic phases formed by Pu with Al, Fe, or Co is difficult to evaluate because fundamental information on their thermodynamic properties, kinetic behavior, corrosion processes, and pyrophoric tendencies are unknown. The high-melting intermetallic compounds such as PuAl_2 , PuFe_2 and PuCo_2 are attractive because they remain in the solid state at temperatures typically encountered in fires. However, alloys with lower melting points (e.g. Pu_6Fe , Pu_6Co) could potentially breach storage containers by mechanisms similar to pure Pu. The possibility of container failure due to alloying reactions can be reduced by employing simple measures such as container modification and/or chemical immobilization. Chemical immobilization uses a reactive metal liner such as aluminum inside the container to form high-melting intermetallic compounds that prevent molten metal from reaching the steel. Tantalum and other refractory metals could be employed as containment barriers, but these materials readily oxidize at elevated temperatures and their cost may be prohibitive.

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Plutonium hydride, nitride, and carbides react exothermically on exposure to oxidizing environments. Hydride decomposes to metal and hydrogen gas on heating above 500°C . Plutonium carbide reacts with water to form Pu oxides and hydrocarbons. Hydrocarbons formed include gases such as methane and acetylene, as well as polymerized species which continue to reside on the Pu surface until they radiolytically decompose to hydrogen and other gaseous hydrocarbons. All finely divided Pu forms strongly absorb or

reaction with plutonium. Such "recycle" reactions could potentially convert massive amounts of material to PuO_2 and PuN . In addition, the exothermic nature of this process leads to large thermal excursions.

³⁵A.E. Hodges, III and J. M. Haschke, "Reaction of the Plutonium-Plutonium Hydride System with Air (U)", Rocky Flats Report RFP-2854, July 1979 (Secret/RD).

³⁶A.G. Phillips and J.M. Haschke, "Use of Ceramic Coatings for Corrosion Protection (U)," Rocky Flats Report CD88-1910, April 1988 (Secret/RD).

react with water. The quantity of absorbed water can be considerable: as much as 10mg H₂O per gram of PuO₂ when handled under routine conditions.³⁷ This corresponds to approximately ten monolayers of absorbed water on the oxide surface.

B. Storage Experience

Experience in storage of candidate materials is an important consideration that includes the existence of technologies for preparation, certification, and packaging of forms, as well as knowledge of problems which may occur during storage. Of the forms considered here, only metal and oxide have relatively extensive storage histories. Pu metal has been stored for more than forty years as weapon components in stockpile. This experience with Pu-containing pits has been trouble-free and represents the largest degree of experience with any form of plutonium. Established certification procedures for pits show that the integrity of plutonium components is preserved during extended storage.³⁸ Experience has shown that oxidation does not occur if the pit is sealed and leak free. Metallographic changes in aged Pu-metal have been documented by several authors. Self-irradiation damage through alpha decay is well known,³⁹ as is swelling of delta-phase alloys after extended times.⁴⁰ Examination of a high purity Pu rod (99.9999% Pu) prepared in 1966 has continued on a regular basis. 200 kV transmission electron microscopy has revealed numerous aging effects in this sample.^{41,42,43}

³⁷J.L. Stakebake and M.R. Dringman, "Hygroscopicity of Plutonium Dioxide," Rocky Flats Report RFP-1056, 1968 (unclassified).

³⁸D.R. Horrell (Los Alamos National Laboratory), personal communication with the authors, January 1993. An extensive body of classified literature exists from surveillance programs on this topic. Interested readers are directed to the surveillance program offices at Los Alamos National Laboratory in the Weapons Engineering and Nuclear Materials Technology divisions.

³⁹R.O. Elliott, C.E. Olsen, and G.H. Vineyard, *Acta Met.*, 11 (1963) p. 1129.

⁴⁰G.E. Bixby, A. E. Hodges III, and V.M. Paine, "Stability Development Report (U)," Rocky Flats Report PPC 87-056, June 26, 1987 (Secret/RD).

⁴¹D.L. Rohr, K.P. Staudhammer, and K.A. Johnson, Los Alamos Report LA-9965-MS (1984).

Techniques for preventing hydride corrosion during extended storage of metal are well established.

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Experience also exists in the storage of oxide. Preparation of oxide as an intermediate in metal production has formed an integral part of plutonium processing. Procedures for preparation of a certified WR oxide for storage are not developed. Problems and uncertainties in oxide storage outlined in 1965 are still of concern today:

The effect of radiation on undecomposed anions (SO_4^{2-} , NO_3^- , $\text{C}_2\text{O}_4^{2-}$, etc. in the oxide matrix is not known. This effect is apparently negligible on well calcined materials for short periods of time, i.e. 2 to 3 months unvented storage. The effect of radiation on incompletely calcined materials during long storage periods is not known. If long storage periods are anticipated, additional information on radiolysis effects should be obtained.⁴⁷

⁴²D.L. Rohr and K.P. Staudhammer, J. Nucl. Mat 144 (1987) p. 202.

⁴³M.F. Stevens, T.G. Zocco, and J.H. Steele, "Bubble-Void Formation in Delta Phase Plutonium (U)," Los Alamos Report MST-5-88-9, August 25, 1988 (Secret/RD).

⁴⁴J.M. Haschke and T.H. Allen, "Hydrogen Corrosion of Plutonium ...", *ibid.*, p. 5.

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Oxide has been successfully stored, though problems encountered with oxide (e.g., container pressurization) contrast with the virtual absence of difficulties experienced during storage of thousands of certified stockpile pits. These problems can usually be traced to the high-surface area and ease of dispersion of the material.⁴⁸ High surface areas allow large quantities of absorbates to be introduced into the storage environment. Subsequent reaction, desorption, or decomposition of these absorbates leads to gas build-up and in some cases, container rupture. Further, on container rupture, the large mass percentage of aerosolizable particles has lead to contamination problems in past incidents. Pressurization phenomena are covered in more detail in section VI. C. 7

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⁴⁷J.D. Moseley and R.O. Wing, "Properties of Plutonium Dioxide," Rocky Flats Report RFP-503, August 24, 1965, p. 25 (unclassified).

⁴⁸H.H. Van Tuyl, "Packaging of Plutonium for Storage or Shipment," Appendix E, "Examples of Past Occurrences," Pacific Northwest Laboratory, March 1981 (unclassified). 7

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C. Container Pressurization

An important concern is the risk of container pressurization during storage. Several potential pressure sources are identified: helium from alpha decay of Pu, hydrogen and other gases from radiolytic decomposition of organic and other residues, and gases from chemical reaction or desorption of adsorbed species. In each of these cases, the quantity of gas generated depends on the physical surface area of the stored material. Per unit of mass, the surface area of a typical powdered form is 10^4 times larger than that of massive forms such as bulk metal or alloys. Experience with metal in pits and with ^{238}Pu that undergoes alpha decay at a relatively rapid rate ($t_{1/2} = 86$ years) shows that only the small amount of He formed in the near-surface ($< 1 \mu\text{m}$) region is released. Whereas only an extremely small fraction of the He escapes from massive metal, a major fraction is released from finely divided forms due to the small particle dimensions (typically on the order 50 to 100 nm).⁵⁰ Results from studies of $^{238}\text{PuO}_2$ are readily extrapolated to the storage of $^{239}\text{PuO}_2$.^{51,52} These studies provide estimates of He diffusivity in PuO_2 as well as a means of characterizing the morphological change in the material as a result of helium release. Less information on He release and metalurgical changes in metal is available, but metalographic results from 25-year-old WR metal show that helium is trapped as bubbles at grain boundaries.⁵³

Pressurization of storage containers also arises from radiolysis of compounds exposed to nuclear materials. This phenomenon is prevalent for finely divided forms because of their tendencies to both absorb organic species and to disperse within storage

⁵⁰J.L. Stakebake and M.R. Dringman, J. Nucl. Mat., 23 (1967) p. 349.

⁵¹R.N.R. Mulford and B.A. Mueller, "Measurements of Helium Release from Materials Containing $^{238}\text{PuO}_2$," Los Alamos Report LA-5215, July 1973 (unclassified).

⁵²B.A. Mueller, D.D. Rohr, and R.N.R. Mulford, "Helium Release and Microstructural Changes in $^{238}\text{PuO}_2$," Los Alamos Report LA-5524, April 1974 (unclassified).

⁵³M.F. Stevens, T.G. Zocco, and J.H. Steele, "Bubble-Void Formation in Delta Phase Plutonium (U)," Los Alamos Report MST-5-88-9, August 25, 1988 (Secret/RD).

environments.⁵⁴ Radiolysis usually creates hydrogen.⁵⁵ Certain materials (including Pu metal) can act as getters for H₂. All organics, even those initially isolated from the radiolytic surface cause concern. Isolated materials such as polyethylene bags, vinyl tape, or rubber o-rings have lead to problems in past incidents.⁵⁶ Finely divided oxide is entrained by natural convection currents within the storage container and may deposit on all accessible surfaces within the storage environment. Radiolytic decay of organic materials results, often breaching container integrity and generating further corrosive gases. Variations in atmospheric pressure due to meteorological changes can "breathe" large amounts of air through a small opening in a container as well as transport gases containing entrained particles within environments sealed by flexible media. This provides a potential mechanism for moving entrained oxide from within metal storage cans to bagging material on the exterior. Subsequent radiolytic decay of the organic bagging could result in a breach of containment. Exclusion of all organic materials is necessary to prevent pressure generation by radiolysis.

Another process for pressure generation arises from chemical reaction of species on surfaces. The existence of a higher valence oxide than PuO₂ implies that water absorbed at the oxide surface may react slowly over time to produce PuO_{2.2} and H₂.⁵⁷ Oxide is unreactive with H₂ and thus, this mechanism could result in a build-up of hydrogen pressure. In fact, analysis of past incidents involving oxide storage experience show considerable H₂

⁵⁴A.R. Kazanjian, P.M. Arnold, W.C. Simmons, and E.L. D'Amico, "Gas Generation Results and Venting Study for Transuranic Waste Drums," Rocky Flats Report RFP-3739, September 23, 1985 (unclassified).

⁵⁵D.K. Roggenthen, T.L. McFeeters, and R.G. Nieweg, "Waste Drum Gas Generation Sampling Program at Rocky Flats," Rocky Flats Report PSD88-037, March 1989 (unclassified).

⁵⁶H.H. Van Tuyl, "Packaging of Plutonium for Storage or Shipment," Appendix E, Pacific Northwest Laboratory, March 1981 (unclassified).

⁵⁷J.L. Stakebake, D.T. Larson, and J.M. Haschke, "Characterization of the Plutonium-Water Reaction Part II: Formation of a Binary Oxide Containing Pu(VI)," Los Alamos Report LA-UR-93-0040, January 1993 (unclassified). Submitted for publication in J. of Metals and Alloys. The complete reaction is more properly written $5\text{PuO}_2 + \text{H}_2\text{O} \rightarrow \text{Pu(IV)}_4\text{Pu(VI)O}_{11} + \text{H}_2$.

generation within the container.^{58,59} This has been attributed to radiolytic decomposition of organics. However, the recently suggested reaction between PuO_2 and H_2O to yield $\text{PuO}_{2.2}$ and H_2 may also contribute to hydrogen gas build-up. Careful analysis of past storage data may help distinguish between these two processes. For a typical storage configuration, a single monolayer of water on the oxide surface is capable of generating 50 psi of H_2 pressure in the container if this reaction proceeds to completion. Multiple monolayers of H_2O are known to strongly chemisorb on the PuO_2 surface. The rate of this chemical process at storage temperatures is unknown and may or may not contribute significantly to container pressurization. Use of containers with filters or filtered relief valves could potentially alleviate this problem.⁶⁰

Thermal desorption of adsorbed species can lead to pressurization at elevated temperatures. An incident of this type led to the breach of a container holding "calcined" PuO_2 and prompted the Van Tuyl investigation. In this particular occurrence, the oxide contained a larger fraction of $^{238}\text{PuO}_2$ than previously packaged.⁶¹ The heat load from this material was sufficient to desorb considerable quantities of water and light organics which eventually ruptured the storage container.

⁵⁸J. Philips, R. Zocher, and A. Drypolcher, " ^{238}Pu -Hydrogen Formation Problem," presentation at Los Alamos National Laboratory, January 21, 1993.

⁵⁹D.K. Roggenthen, T.L. McFeeters, and R.G. Nieweg, "Waste Drum Gas Generation Sampling Program at Rocky Flats," Rocky Flats Report PSD88-037, March 1989 (unclassified).

⁶⁰The impact of filters or valves on vessel integrity and material containment must be carefully considered. Historically, such devices are difficult to implement. According to one DOE official, filters or valves are not considered suitable for future storage containers (S.A. Thompson, DOE Albuquerque, Nuclear Environmental and Safety Division, personal communication with the authors, December 10, 1992).

⁶¹H.H. Van Tuyl, "Packaging of Plutonium for Storage or Shipment," Pacific Northwest Laboratory, March 1981, page E.1 (unclassified).

D. Materials Accountability

Nuclear materials accountability measurements frequently rely on chemical analysis of "representative" samples to establish a plutonium content for the material. This method assumes the plutonium concentration in the material is homogeneous. Inhomogeneity presents less of a problem for "pure" metal and binary compounds (oxide, nitride, hydride) formed by gas/solid reactions. However, compounds formed by reactions of solids and liquids (e.g. carbides, alloys, some oxides) are more difficult to homogenize. Preparation of stoichiometric-monophasic products in the Pu + C, Pu + Fe, and Pu + Co systems is further complicated by the presence of multiple binary phases that hinder equilibration by imposing a series of steps (each with kinetic limitations) on the reaction path. In these cases, the time and effort required to obtain a form suitable from a materials control and accountability standpoint may be considerable. The necessity of homogeneity is recognized as a sampling issue in the Van Tuyl report:

The value of obtaining a representative sample cannot be overemphasized. In fact, many incidents can be traced to poor sampling. One incident is a classic example wherein inadequately calcined plutonium oxide (was) combined with a nonrepresentative sample (which) resulted in a pressurization-contamination incident. *sic*

In classic sampling circles, "grab" samples are considered inadequate. But for plutonium systems and particularly heterogeneous systems—and there are many when dealing with plutonium materials—most sampling is done using the grab technique... Perhaps the most productive way to homogenize a material and render it a better candidate for packaging is to heat the sample to fairly high temperature, i.e., by calcination or incineration. This small step rids the material of water, organics, pyrophoric materials, and provides a material much easier to sample. One may even obtain a stoichiometric compound.⁶²

Results of certain non-destructive assay (NDA) methods such as neutron or gamma-ray spectroscopies are sensitive to the sample matrix.⁶³ Inhomogeneities may alter the results

⁶²J.L. Holst (Rocky Flats Plant), in H.H. Van Tuyl, "Packaging of Plutonium for Storage or Shipment," Pacific Northwest Laboratory, March 1981, page D.1 - D.3 (unclassified).

of such measurements. Heavier elements which change the self-absorption characteristics of a material are of particular concern.

VII. ES&H Issues

A. Waste Generation

The level of waste generation is a major consideration in assessing storage options for extracted plutonium. Though advantage is gained by upgrading process technologies, the greatest benefit is achieved by avoiding all unnecessary processing. Complex 21 development activities include a thorough assessment of waste generation of each individual unit operation involved in pit dismantlement and preparation for storage.⁶⁴ The simplest method to limit waste generation is intuitive: leave materials in their existing form. Interconversion of material forms should be minimized to avoid waste generation and other ES&H concerns associated with handling of material. However, potential problems with a particular material may require processing to an alternate form to alleviate concerns. Nearly all plutonium in US inventories is currently metal or oxide, with a minor fraction stored mostly as process wastes including ash and salts. The inventory existing as carbide, nitride, hydride, or dilute alloys is small.⁶⁵

Certain options might be suggested to remediate anticipated storage problems. For instance, it has been suggested to briquette oxide to prevent dispersion in storage. Though perhaps simple in design, practical and demonstrated processes to accomplish such remediation often do not exist. Further, providing a seemingly elegant solution to one

⁶³K. Thomas, J. Markin, M. Mullin, D. Close, and W. Stanbro, "Safeguards and Security," input to DOE AN-10 Study on Plutonium Storage Issues, January 1993.

⁶⁴W.R.Dworzak, W. Brown, B. Flamm, J. Haschke, D. Hays, T. Cremers, T. Sampson, T. Nelson, J. Martz, and L. Bronisz, "ARIES Development Plan," Los Alamos Report NMT-DO:(U)92-639, January 13, 1993 (unclassified).

⁶⁵Certain delta-stabilized alloys make up a large portion of the US stockpile. These alloys typically contain 0.5 to 1.0 mass% gallium.

problem frequently creates larger and more costly problems elsewhere. All processes and alternatives must be evaluated to assess their net impact on waste generation and other ES&H concerns. The value of demonstrated, proven unit operations can not be overstated in considering process modifications for Complex 21 or other dismantlement facilities.

B. Criticality Safety

A large body of experience exists in managing criticality safety. Primary controls include limiting the quantity of stored material in any given container, and careful control of storage vault geometry. Although the likelihood of a criticality incident is small, credible accident scenarios include immersion of the material in water or other hydrogenous media that moderate and reflect neutrons. Under such circumstances, the dispersion of the material in the liquid becomes an important factor. The more finely divided the material, the greater the likelihood of uniform, heterogeneous dispersion. Finely divided forms are amenable to mixing and dispersion. Metal is hydrolyzed in water by a salt-catalyzed reaction which can also yield a dispersible product.⁶⁶ The reaction rate of metal is such that a casting must remain submerged for two to three weeks in seawater for complete conversion to a fine oxide-like powder.⁶⁷ Less reactive environments such as tap- or distilled water slow the reaction considerably. However, even in the case of dispersible material, the actual risk of a criticality incident in an accident scenario is small if the quantity of material per container is limited to 3 or 4 kg.

Criticality concerns also arise from deliberate or accidental violation of procedures. Metal in bulk ingot form could readily be assembled to a critical mass by knowledgeable

⁶⁶J.M. Haschke, A.E. Hodges, III, G.E. Bixby, and R.L. Lucas, "The Reaction of Plutonium with Water. Kinetic and Equilibrium Behavior of Binary and Ternary Phases in the Pu+O+H System," Rocky Flats Report RFP-3416, February 3, 1983 (unclassified).

⁶⁷J.M. Haschke, "Hydrolysis of Plutonium: Plutonium-Oxygen Phase Diagram" in Transuranium Elements. A Half Century, L.R. Morss and J. Fuger, eds., American Chemical Society, Washington, D.C. (1992) p. 416-425.

personnel. Storage of plutonium as critically safe metal castings (such as ring geometries) reduces such concerns provided the geometric integrity of the plutonium is maintained. Dry oxide, nitride, or carbide powder can be assembled into a critical mass as well, but considerably more material is required than for denser metal systems. No storage form presents an abnormal criticality risk provided well established control procedures are followed.

C. Environmental

The possibility of dispersing plutonium-containing particles during an accident is a serious environmental concern. Contamination of the immediate area with radioactive material has a large impact, but the greatest potential hazard is from dispersal of fine particles in the aerosolizable and respirable ranges. The maximum size of a respirable particle depends on its geometry and density and remains uncertain. Measurements show that PuO_2 particles with dimensions up to $10 \mu\text{m}$ are entrained by a 12 mph draft and this size limit provides a convenient basis for assessing relative dispersal risks posed by the candidate storage forms.^{68,69} The potential for dispersal from a metal source is small until loose oxide particles are formed. Because an adherent and passivating oxide layer forms on the metal surface during the initial stage of oxidation, negligible quantities of oxide particles appear after first exposure to air. Calculations using kinetic data suggest that spallation of the product layer may begin after a week or more in air at ambient temperature.⁷⁰ In contrast, typical process oxides consist of fine particles and have bulk densities as low as 1 g/cm^3 .⁷¹

⁶⁸J. Mishima, "Plutonium Release Studies I. Release from Ignited Bulk Metallic Pieces," USAEC Report BNWL-205, Battelle Pacific Northwest Laboratory, December 1965 (unclassified).

⁶⁹J. Mishima, "Plutonium Release Studies II. Release from Ignited Bulk Metallic Pieces," USAEC Report BNWL-357, Battelle Pacific Northwest Laboratory, November 1966 (unclassified).

⁷⁰J.L. Stakebake and L.A. Lewis, J. Less. Comm. Met. 136 (1988) p. 839.

Particle sizes for hydride are larger, but hydride reacts quickly with air to form PuO_2 particles with 25 mass % in the size range less than $10 \mu\text{m}$.⁷² Oxides obtained by other processes are comprised completely of particles in the aerosolizable range.⁷³

Two situations merit examination: an accident in which the storage container is mechanically breached and one in which the intact container is exposed to a fire with temperatures in excess of 640°C . If risk from physical damage is measured by the quantity of material that might be dispersed during container rupture and subsequent action of air currents and other transport processes, the potential hazard posed by storage of bulk forms is small compared to that posed by finely divided material. Although the likelihood of losing containment of molten metal during a fire is considered small if remedial containment technologies are employed, the formation of dispersible oxide will be accelerated at elevated temperatures. Particle size data show that less than 0.1 mass % of oxide formed by metal oxidized in air at temperatures above 500°C appear in the size range below $10 \mu\text{m}$.⁷⁴ The possibility of pressurized storage containers also poses a credible risk during a fire. The combination of rise in gas pressure and loss of steel strength at high temperatures could lead to container rupture and dispersal of respirable material. The fact that finely divided material is more likely to result in container pressurization compounds the potential dispersal problem.⁷⁵

⁷¹J.D. Moseley and R.O. Wing, "Properties of Plutonium Dioxide," Rocky Flats Report RFP-503, August 24, 1965 (unclassified).

⁷²J.M. Haschke, "Evaluation of Source-Term Data for Plutonium Aerosolization," Los Alamos Report LA-12315-MS, July 1992 (unclassified).

⁷³J.L. Stakebake and M.R. Dringman, J. Nucl. Mat., 23 (1967) p. 349.

⁷⁴ibid.

⁷⁵Please see the discussion in section VI. C. concerning pressurization from thermal outgassing as well as Appendices A and E in H.H. Van Tuyl, "Packaging of Plutonium for Storage or Shipment," Pacific Northwest Laboratory, March 1981 (unclassified).

D. Personnel Safety

Exposure to ionizing radiation is an additional risk to personnel. The levels of radiation present for bulk and finely divided forms are not the same because of differences in self-absorption behavior. A larger percentage of the high energy gamma rays emitted during ^{241}Am decay escape from powdered material than from massive metal or alloys. Separation of Am from plutonium in the metallic and aqueous states is a developed technology. Techniques for removal of Am from other forms of plutonium have not been developed. The advantage of reducing radiation levels in all future process operations must be weighed against the disadvantages of waste generation and exposure during Am extraction. Shielding of process operations and storage containers provides a potential remedy for all storage forms.

Alpha-n reactions can lead to increased neutron radiation when Pu is combined with light elements such as O, C, B, or F. Effective shielding is constructed from these same light elements to moderate and absorb neutrons. Neutron shielding is different from gamma and x-ray shielding (the later relying primarily on heavy elements). As such, shielding requirements for Pu must address penetrating radiation from both sources. The increase in neutron radiation from PuO_2 , PuC_2 , and PuN is relatively small. The principle source of neutrons in these materials is ^{240}Pu .

IX. Facility Requirements and Capabilities

The technologies currently available and the ES&H impact of these processes must be considered in evaluating capabilities and options. These issues were addressed by the complex-wide Plutonium Technology Assessment and Selection Panel (Pu-TASP) that evaluated and ranked proven technologies for use in designing Complex 21.⁷⁶ After

extensive evaluation, the TASP panel recommended a process flowsheet based on pyrochemistry. In pyrochemical processing, plutonium remains as a metal throughout the recovery and certification processes, while aqueous chloride and nitrate recovery technologies are employed on a limited scale to handle process residues.⁷⁷ An aqueous-based method was not selected because such multi-step processes (metal dissolution, separation, precipitation, calcination, reduction back to metal) are inefficient and generate large waste quantities.⁷⁸ Aqueous processing through the calcination step is the only developed production-scale technology available for preparing oxide. Direct oxidation of metal is slow and difficult; use of a hydride intermediate to accelerate direct reaction appears promising but requires development.

Considerable effort has been expended in Complex 21 design activities. Currently, March 1995 is established as the cutoff date for inclusion of new technologies into Complex 21. Any decision regarding plutonium storage form will significantly impact the configuration of the dismantlement and storage facilities. Likewise, Complex 21 capabilities will influence the selection of forms for long-term storage. Considerable benefit is gained by the expeditious selection of a desired storage form so that necessary modifications to the design can be made in a timely manner. Under an optimistic scenario, Complex 21 will be available in 2003. An examination of other facilities and capabilities provides an estimate of interim options for dismantlement and storage. A complete review is not given here; a summary of extensive input to a DOE-AN study of these options is provided.⁷⁹

⁷⁶D.C. Christensen, "Weapons Complex Reconfiguration: The Future of Plutonium Technology," in 1992 Nuclear Materials Technology: Weapons Complex 21 Reconfiguration, Los Alamos Report LALP 92-41, p. 8, June 1992 (unclassified).

⁷⁷J.C. Martz, J.M. Haschke, T.J. Beugelsdijk, and L.R. Bronisz, "Automation and Integration of Site-Return Processing," in 1992 Nuclear Materials Technology: Weapons Complex 21 Reconfiguration, Los Alamos Report LALP 92-41, p. 18, June 1992 (unclassified).

⁷⁸J.M. Haschke, "Site-Return Processing Overview," in 1992 Nuclear Materials Technology: Weapons Complex 21 Reconfiguration, Los Alamos Report LALP 92-41, p. 13, June 1992 (unclassified).

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A. Reference Capabilities

Pantex. Pantex is the only currently operating facility for the dismantlement of weapons. Pantex is capable of storing only intact pits. Current capacity is roughly 4500 pits, though an approval to stack units in the storage igloos will increase that capacity to 16,500. After dismantlement, pits were historically shipped to Rocky Flats for removal and recovery of plutonium.

Rocky Flats. The maximum dismantlement throughput at Rocky Flats (RFP) was 450 pits/year. At this rate, nearly 40 years would be required to dismantle the expected number of site returns. Pits were bisected with a cutting tool and plutonium was subsequently recovered by both aqueous and pyrochemical techniques. Rocky Flats maintained a substantial storage capability for separated metal, oxide, and scrap. Currently, this storage space is occupied by approximately 100 metric tons (MT) of material containing roughly 3 MT of Pu. The volume of waste produced in dismantlement activities was large, nearly 140 liters of mixed hazardous waste per pit disassembled. Reuse of facilities at RFP would require a substantial upgrade of chemical processing capability to meet requirements of DOE order 6430.1A.⁸⁰

B. Other Current Capabilities

Los Alamos (TA-55). TA-55 is a plutonium research and development facility. As an R&D facility, it was not designed for production-scale operations such as those conducted at RFP. Pit disassembly has occurred at TA-55 as part of normal development activities and surveillance programs. The magnitude of this disassembly has been small, however, never exceeding more than 20 or 30 pits per year. A new program at TA-55 is intended to demonstrate an advanced technology for dismantlement of pits and recovery of plutonium.

⁷⁹S. Kinkead and C. Olinger, "Storage of Material Extracted from Pits: Facility Requirements," input to DOE AN study for plutonium disposition (Secret/RD). Most of the comments which follow are based on this work.

⁸⁰This order governs facility environmental, safety, and health requirements. Substantial capital improvements would be required to comply with this order.

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The ARIES (Automated Retirement and Integrated Extraction System) project is a pyrochemical-based technique intended to support Complex 21 development activities.⁸¹ When operational, ARIES might be capable of processing 250 pits per year with minimal waste generation. ARIES produces cast, americium-free Pu metal as its final product. Under optimistic scenarios, this capability will be available in 1995.⁸² A substantial storage vault has been constructed at Los Alamos (the Special Nuclear Materials Storage Facility, SNMSF), but certain modifications are necessary to meet DOE order 6430.1A standards and other security and safeguards concerns. When operational in two to three years, SNMSF has the capacity for roughly 11,000 items (intact pits, Pu metal, oxide, stable residues, etc.). A separate area has been established at the SNMSF for storage of Strategic Asset Material.

Livermore. The primary plutonium handling facility at LLNL is Building 332. Operations have been suspended there for some time, and closure is expected in the near future. Under an emergency order, facilities for processing roughly 100 to 150 pits per year could be established. No substantial storage space exists at LLNL.

Savannah River. Plutonium processing capability is available in the F Canyon plant. In addition, the new special recovery line (NSRL) has been modified to dissolve Pu metal for feed to F-Canyon. Throughput is limited by NSRL capacity to approximately 100 pits/year. Savannah River (SRL) does not have a current capability to bisect pits. Processes at SRL are aqueous based and generate large quantities of waste similar to previous RFP operations. Sulfamic acid is used to dissolve Pu, while mixer/settler technology provides purification of plutonium. F-Canyon is not currently operational, and some modifications may be necessary to assure compliance with DOE orders. Final product from F-Canyon is plutonium oxide.

⁸¹W.R. Dworzak, Q. Appert, B. Bowden, L. Bronisz, W. Brown, T. Cremers, D. Hays, J. Martz, B. Flamm, and J. Haschke, "ARIES Preconceptual Design Report," Los Alamos Report NMT-DO:(U)92-318, May 26, 1992 (unclassified).

⁸²W.R. Dworzak, J. Martz, and B. Bowden, "ARIES Program Plan," Los Alamos Report NMT-DO 92-286, April 30, 1992 (unclassified).

Other Facilities. No other substantial Pu processing capability is currently operating within the weapons complex. Storage facilities for intact pits could become available at the Hanford Z-plant or the Mound facility with some modification and upgrade. Assembly facilities at the Nevada Test Site (NTS) might be converted for dismantlement and storage of intact pits.

C. Summary of Capability and Facilities

A small capability to extract plutonium from pits and process material to a form suitable for storage currently exists within the complex. However, capacity is small compared to that previously existent at Rocky Flats. Even if RFP were operating at its peak throughput, the sum capability in the complex would require decades to disassemble and process the 17,000 expected site returns. Even under near war time conditions, it required 40 years to build the stockpile to this level; dismantlement and disassembly of this same stockpile now requires a heightened sensitivity to environmental, safety, health, and nonproliferation concerns. Table 1 summarizes the current and expected near-term capabilities as outlined in the discussion above.⁸³ The design basis for Complex 21 is currently set at a dismantlement throughput of 1500 pits/year.⁸⁴

X. Summary and Conclusions

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The most difficult step in preparing plutonium for weapon use is the fabrication of components into the proper

⁸³taken from S. Kinkead and C. Olinger, "Storage of Material Extracted from Pits: Facility Requirements," input to DOE AN study for plutonium disposition, p. 6 (Secret/RD).

⁸⁴This number changes frequently. The recent trend has been an increase in the dismantlement rate with a commensurate decrease in manufacturing throughput to 150 pits/year. This latter figure may be revised downward in future design calculations.

Facility	Reference	Present-1995	1995-2003	Storage [‡]
Pantex	-	-	-	2500-7500
RFP	450	0	0	1000
SRL		100	100	100-500
LANL		100	100	50-11,000*
With ARIES			250	
LLNL		100	100 [†]	50-100
Other	-	-	-	2000-5000 [§]
Totals	450	300	550	5,700-25,000

Table 1. Near-term Plutonium Processing and Storage Capability (pits/year)

- ‡ Storage: Equivalent to number of intact pits.
- * With commissioning of the SNMSF
- † Assumes continued operation of bldg. 332
- § Upgraded facilities to meet DOE 6430.1A

geometry.

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Demonstrated production-scale processes only exist for preparation of metal and oxide. An examination of capability shows that no facility currently exists, either operational or capable of restart, which could extract and process material from pits at even modest levels of throughput. Further, no facility with sufficient capacity will be available within a few-year time frame. Only with great difficulty and streamlining of environmental and regulatory constraints could existing facilities such as Rocky Flats or Savannah River be prepared to dismantle weapons and process material for storage. Under the best of circumstances, such facilities might be available within 5 to 10 years. Appropriate facilities for recovery and processing are included in Complex 21 development activities and should be available within a 10 to 15 year time frame.

From a material property perspective, metal is an acceptable storage form for plutonium extracted from pits. This conclusion is amplified in the Van Tuyl study of

plutonium storage: "Metal is the best characterized, best understood, and easiest to store physical form of plutonium."⁸⁵ Storage in this form preserves all currently suggested disposition options. Metal prepared for storage should meet appropriate certification and cleanliness standards (such as those established for war-reserve components). Precautions should include exclusion of air, water, and organics from the storage environment.

Oxide is also suitable for storage if similarly stringent cleanliness and certification requirements are met. One of the most common problems in plutonium storage is pressurization of the primary storage container. Pressure build-up may be caused by helium release due to alpha decay, radiolytic reactions on the Pu surface, chemical reactions that create gaseous products, and elevated temperatures that volatilize components of the system. All of these phenomena are potentially significant in oxide storage. Oxide is less reactive than metal, but more easily dispersed in the event of container rupture. Technologies for consolidation of oxide and other powdered materials into pellets or briquettes are known, but existing methods generate considerable quantities of radioactive waste.

The lack of fundamental chemical property information for plutonium alloys may preclude their consideration as long-term storage forms. Other forms such as mixed plutonium/uranium oxides, plutonium carbides, and plutonium nitride may be suitable for long-term storage if appropriate certification procedures are defined. However, despite extensive evaluation of these materials for use as reactor fuels, uncertainties exist about their behavior in storage environments. Plutonium carbides and nitride are reactive and are readily hydrolyzed by moisture to form potentially explosive or hazardous gases. Plutonium hydride, another candidate storage form, is pyrophoric. Typical production operations for non-metallic materials (e.g. oxide, nitride, carbide, etc.) yield high-surface area powders. A

⁸⁵H.H. Van Tuyl, "Packaging of Plutonium for Storage or Shipment," Pacific Northwest Laboratory, March 1981, p. 26 (unclassified).

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large fraction of respirable particles may be released from these forms on exposure to air (greater than 25% mass percent).

Conversion of plutonium from one form to another and any treatment of an existing form results in additional waste generation and worker radiation exposure. We suggest plutonium should be stored in its existing form provided this poses no abnormal safety or environmental problems. Interconversion of material forms should be avoided. Complex 21 must be capable of producing the desired storage form; the present design must be altered if a form other than metal is adopted. The value of demonstrated, proven unit operations can not be overstated in considering process modifications for Complex 21 or other dismantlement facilities.

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