PNNL-23468 Rev. 1
WTP-RPT-234 Rev. 1

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

Chemical Disposition of Plutonium in Hanford Site Tank Wastes

CH Delegard
SA Jones

May 2015

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract **DE-AC05-76RL01830**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed for any uses other than those related to WTP for DOE, or represents that its use would not infringe privately owned rights**. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis,osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx>

This document was printed on recycled paper.
(9/2003)

PNNL-23468 Rev. 1
WTP-RPT-234 Rev. 1

Chemical Disposition of Plutonium in Hanford Site Tank Wastes

CH Delegard
SA Jones

May 2015

Prepared for the U.S. Department of Energy
Under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

COMPLETENESS OF WORK

This report describes the results of work specified in SCN-105, "*Provision of Plutonium Chemistry Expert*." All work was performed and reviewed in accordance with the QA procedures applicable to the Waste Treatment Plant Support Program.

Approved:

5/7/15

Reid A. Peterson, Manager
WTP R&T Support Project

Date

Summary

This report examines the chemical disposition of plutonium (Pu) in Hanford Site tank wastes, by itself and in its observed and potential interactions with the neutron absorbers aluminum (Al), cadmium (Cd), chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni), and sodium (Na). Consideration also is given to the interactions of plutonium with uranium (U). No consideration of the disposition of uranium itself as an element with fissile isotopes is considered except tangentially with respect to its interaction as an absorber for plutonium.

The report begins with a brief review of Hanford Site plutonium processes, examining the various means used to recover plutonium from irradiated fuel and from scrap, and also examines the intermediate processing of plutonium to prepare useful chemical forms. The paper provides an overview of Hanford tank defined-waste–type compositions and some calculations of the ratios of plutonium to absorber elements in these waste types and in individual waste analyses. These assessments are based on Hanford tank waste inventory data derived from separately published, expert assessments of tank disposal records, process flowsheets, and chemical/radiochemical analyses.

This work also investigates the distribution and expected speciation of plutonium in tank waste solution and solid phases. For the solid phases, both pure plutonium compounds and plutonium interactions with absorber elements are considered. These assessments of plutonium chemistry are based largely on analyses of idealized or simulated tank waste or strongly alkaline systems. The very limited information available on plutonium behavior, disposition, and speciation in genuine tank waste also is discussed.

The assessments show that plutonium coprecipitates strongly with chromium, iron, manganese and uranium absorbers. Plutonium's chemical interactions with aluminum, nickel, and sodium are minimal to non-existent. Credit for neutronic interaction of plutonium with these absorbers occurs only if they are physically proximal in solution or the plutonium present in the solid phase is intimately mixed with compounds or solutions of these absorbers. No information on the potential chemical interaction of plutonium with cadmium was found in the technical literature. Definitive evidence of sorption or adsorption of plutonium onto various solid phases from strongly alkaline media is less clear-cut, perhaps owing to fewer studies and to some well-attributed tests run under conditions exceeding the very low solubility of plutonium. The several studies that are well-founded show that only about half of the plutonium is adsorbed from waste solutions onto sludge solid phases. The organic complexants found in many Hanford tank waste solutions seem to decrease plutonium uptake onto solids. A number of studies show plutonium sorbs effectively onto sodium titanate. Finally, this report presents findings describing the behavior of plutonium vis-à-vis other elements during sludge dissolution in nitric acid based on Hanford tank waste experience gained by lab-scale tests, chemical and radiochemical sample characterization, and full-scale processing in preparation for strontium-90 recovery from PUREX sludges.

S.1 Objective

The objective of this report is to summarize and evaluate the large amount of experimental and theoretical work and literature reports relating to the disposition of plutonium in tank waste, especially with respect to its interactions with compounds of the neutron-absorbing elements aluminum, cadmium, chromium, iron, manganese, nickel, sodium, and uranium.

Table S - 1 summarizes the objectives that apply to this task.

Table S - 1: Summary of Work Objectives and Results

Work Objective	Objective Met?	Discussion
Review the known technical literature related to the disposition of plutonium in alkaline Hanford tank waste, including plutonium's interactions with compounds of the neutron-absorbing elements aluminum, cadmium, chromium, iron, manganese, nickel, sodium, and uranium.	Yes	The report provides an overview of Hanford Site plutonium processes, describes the Hanford Defined Waste properties with respect to plutonium and neutron absorber relative concentrations, and lists absorber element compounds observed and postulated to be present in Hanford tank waste sludges, the primary locus of plutonium in the tank waste. It then presents an extensive review of plutonium chemistry in Hanford tank waste and in alkaline systems as gleaned from the technical literature dating from the time of the Manhattan Project. The report further describes the disposition of plutonium sent to the tank waste as both solution and as solids. A discussion of plutonium's interactions with compounds of the neutron absorber elements aluminum, cadmium, chromium, iron, manganese, nickel, and uranium through coprecipitation and sorption follows. Because of the high solubilities of most sodium salts, chemical interactions of plutonium are expected to be minimal except in the event of precipitation of lower-solubility salts such as sodium diuranate and that of the co-location of soluble sodium salts with less soluble sludge phases. Finally, the report summarizes the behavior of plutonium in the dissolution of genuine Hanford tank waste sludges by treatment with nitric acid.

S.2 Work Exceptions

No work exceptions are applicable to this report.

S.3 Results and Performance against Success Criteria

Table S - 2 presents research and technology (R&T) success criterion for achieving the work objective.

Table S - 2: The Success Criterion for the Plutonium Disposition Review Task

Success Criterion	How Work Did or Did Not Meet the Success Criterion
Review the known technical literature related to the disposition of plutonium in alkaline Hanford tank waste including plutonium's interactions with compounds of neutron absorber elements aluminum, cadmium, chromium, iron, manganese, nickel, sodium, and uranium.	This success criterion was met. The report summarizes over 100 technical publications found in journals, from the Hanford, Savannah River, and other US-DOE Sites, and international sources related to the chemistry of plutonium, absorber elements, and their joint interactions in Hanford tank waste and in related alkaline systems akin to Hanford tank waste.

S.4 Quality Requirements

The PNNL Quality Assurance (QA) Program is based upon the requirements defined in DOE Order 414.1D, *Quality Assurance*, and Title 10 of the Code of Federal Regulations Part 830, *Energy/Nuclear Safety Management*, and Subpart A—*Quality Assurance Requirements* (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, Requirements for Quality Assurance Programs for Nuclear Facilities.
- ASME NQA-1-2000, Part II, Subpart 2.7, *Quality Assurance Requirements for Computer Software for Nuclear Facility Applications*.
- ASME NQA-1-2000, Part IV, Subpart 4.2, *Graded Approach Application of Quality Assurance Requirements for Research and Development*.

The procedures necessary to implement the requirements are documented through PNNL's "How Do I…?" (HDI[1]).

The Waste Treatment Plant Support Project (WTPSP) implements an NQA-1-2000 QA Program, graded on the approach presented in NQA-1-2000, Part IV, Subpart 4.2. The WTPSP Quality Assurance Manual (QA-WTPSP-0002) describes the technology life cycle stages under the WTPSP Quality Assurance Plan (QA-WTPSP-0001). The technology life cycle includes the progression of technology development, commercialization, and retirement in process phases of basic and applied research and development (R&D), engineering and production, and operation until process completion. The life cycle is characterized by flexible and informal QA activities in basic research, which become more structured and formalized through the applied R&D stages.

The work described in this report has been completed under the QA technology level of basic research. WTPSP addresses internal verification and validation activities by conducting an independent technical review of the final data report in accordance with WTPSP procedure QA-WTPSP-601, *Document Preparation and Change*. This review verifies that the reported results are traceable, that inferences and conclusions are soundly based, and that the reported work satisfies the test plan objectives.

---

[1] System for managing the delivery of PNNL policies, requirements, and procedures

S.5 R&T Test Conditions

This report summarizes historical literature and government-sponsored reports that describe the chemistry of Hanford Site tank waste and plutonium and neutron absorber elements. No experimental testing was required to complete this review. Accordingly, the fields for summary of R&T Test Conditions, Table S - 3, are N/A for “not applicable.”

Table S - 3: Summary of R&T Test Conditions

R&T Test Condition	Discussion
N/A	N/A

S.6 Simulant Use

No simulants were used in this literature review.

S.7 Discrepancies and Follow-on Tests

This report only summarizes historical literature and government-sponsored reports that describe the chemistry of Hanford Site tank waste and plutonium and neutron absorber elements. No laboratory testing was performed in pursuit of this review. Accordingly, no discrepancies were found and no follow-on tests are required.

Acknowledgments

The authors thank Richard Freer, Theresa Campbell, Dan Herting, Robert Miles, and David Losey, in their support of the Waste Treatment Plant, for their technical guidance and review of the draft document and Sergey Sinkov of Pacific Northwest National Laboratory (PNNL) for his detailed review and insights into plutonium and absorber element behavior under alkaline and plant process conditions. Three external reviewers, Scott Barney, independent consultant, and David Hobbs and Tracy Rudisill of the Savannah River National Laboratory examined the near-complete document and provided insightful, germane, and complementary comments. We thank Reid Peterson (PNNL) for project oversight and Lisa Staudinger (PNNL) for her attention and care in formatting and technically editing this manuscript. Finally, we gratefully acknowledge the fundamental and applied research into the chemistry of plutonium and other transuranic elements in alkaline media conducted by scientists and technicians of the Institute of Physical Chemistry of the Russian Academy of Sciences. In particular we note the scientific leadership of Professors Nikolai Krot, Vladimir Peretrukhin, Vladimir Shilov, and Alexei Pikaev in teams including, among many others, LN Astafurova, Alexei Bessonov, Nina Budantseva, Iraida Charushnikova, Alexander Fedoseev, Alexander Garnov, Artem Gelis, Mikhail Grigoriev, Vladimir Perminov, Ivan Tananaev, and Alexander Yusov.

Acronyms and Abbreviations

1C	First decontamination cycle
BBI	Best Basis Inventory
CA	Column A (for primary extraction)
CAW	Column A waste
CAX	Column A extractant
CO	Column O (for organic wash)
CSER	Criticality Safety Evaluation Report
CSL	Criticality Safety Limit
CX	Column X (for solvent clean-up)
DBP	Dibutyl phosphate
DMO	Direct metal oxidation
DOE	U.S. Department of Energy
EDS	Energy dispersive spectroscopy
EDTA	Ethylenediaminetetraacetate
ER	Electroreduction
ERDA	U.S. Energy Research and Development Administration
ESP	Environmental Simulation Program (OLI Systems, Inc.)
GOI	Gains on ignition
HA	Hazards analysis
HDW	Hanford Defined Waste
HEDTA	N-2-hydroxyethyl ethylenediaminetriacetate
HLW	High-level waste
IPC(E)	Institute of Physical Chemistry (and Electrochemistry)
IR	Infrared
ITS	In-tank solidification
MIBK	Methyl isobutyl ketone, also known as hexone
MIS	Materials Identification and Surveillance
MOX	(plutonium-uranium) mixed-oxide
MSMPR	Mixed-suspension, mixed product removal
MST	Monosodium titanate
MW	Metal waste
NCAW	Neutralized current acid waste
NHE	Normal hydrogen electrode
NPH	Normal paraffin hydrocarbon
PFP	Plutonium Finishing Plant
PRF	Plutonium Reclamation Facility
PRTR	Plutonium Recycle Test Reactor
R&D	Research and development
R&T	Research and testing
RMC	Remote Mechanical Line C

RSD	Relative standard deviation
SEM	Scanning electron microscopy
SRS	Savannah River Site
SS&C	Sand, slag and crucible
TEM	Transmission electron microscopy
TFCOUP	Tank Farm Contractor Operation and Utilization Plan
TWINS	Tank Waste Information Network System
WAC	Waste acceptance criteria
WTP	Waste Treatment and Immobilization Plant
WTPSP	Waste Treatment Plant Support Project
XRD	X-ray diffractometry

Contents

Figures

Tables

1.0 Introduction

This chemistry report has been written to provide information to support development of the Waste Treatment and Immobilization Plant (WTP) process chemistry criticality safety evaluations, hazards analysis (HA), and other nuclear safety studies. This study was specifically designed to support the next update of the WTP Criticality Safety Evaluation Report (CSER) and provide background information to support upcoming HA meetings. Understanding of the form, size and density of plutonium that exists in the waste located at the Hanford Tank Farms is needed to ensure that the WTP is properly designed to handle isotopes of concern to criticality safety. Information in this report will be used to support evaluations of plutonium disposition for WTP operations during normal and upset conditions. The authors reviewed Hanford process histories, literature of relevant plutonium chemistry and Hanford tank inventories for this purpose. This study was requested in part to address an “opportunity for improvement” that was identified by the U.S. Department of Energy (DOE) Criticality Safety Group (CCN 193547).

The Waste Treatment Plant Support Project (WTPSP) implements an NQA-1-2000, Part I, QA Program, graded on the approach presented in NQA-1-2000, Part IV, Subpart 4.2. The WTPSP Quality Assurance Manual (QA-WTPSP-0002) describes the technology life cycle stages under the WTPSP Quality Assurance Plan (QA-WTPSP-0001). The technology life cycle includes the progression of technology development, commercialization, and retirement in process phases of basic and applied research and development (R&D), engineering and production, and operation until process completion. The life cycle is characterized by flexible and informal QA activities in basic research, which become more structured and formalized through the applied R&D stages.

The work described in this report has been completed under the QA technology level of basic research.

2.0 Chemistry Primer

The audience for this report comes from a wide variety of technical disciplines. This short chemistry primer is provided to aid in understanding the language and terms used in this report, as the same terms may have other meanings in different fields of expertise. Issues related to plutonium chemistry are emphasized with a few additional examples given to illustrate phenomena that relate to criticality safety controls.

The Hanford nuclear reactors and processing plants were built to produce plutonium for nuclear weapons. Uranium was used as fuel in the reactors and about 0.025% of the ^{238}U was converted to plutonium during irradiation. The processes used to separate plutonium from the irradiated nuclear fuel and convert it into forms suitable for weapons produced most of the waste in the Hanford Tank Farm system. This report discusses the separation chemistry that produced the waste and the plutonium chemistry related to criticality safety in the WTP.

There are 15 known isotopes of plutonium. The most abundant isotope in the Hanford waste is ^{239}Pu. The plutonium isotopic composition is about 93 wt% ^{239}Pu and 6 wt% ^{240}Pu relative to the total plutonium mass present. The different isotopes have different radioactive decay characteristics, but the chemistry of the element is independent of the isotope. While plutonium has some very specific nuclear properties, it is also a metallic element having chemical properties.

The last naturally occurring element in the periodic table of the elements is uranium. All elements of higher atomic number are created through human manipulation and are called *transuranic* elements. Plutonium is element 94 and uranium is element 92; both are in the actinide series of elements. The actinides are a family of chemically similar elements with atomic numbers 90 to 103.

The chemistry of plutonium is complicated. Its complex chemistry allowed early researchers to devise schemes to separate pure plutonium from a plethora of other elements in the irradiated fuel. The separation is accomplished by changing the oxidation state of plutonium, resulting in changes in solubility and other chemical properties that could be exploited in the chemical process. By taking advantage of the ability to selectively precipitate, dissolve, or extract plutonium relative to the uranium and fission products in the spent fuel, plutonium could be purified.

Part of the reason plutonium's chemistry is complicated is because it can exist in several oxidation states. The oxidation state is the difference between the number of electrons in the element and the number found in a compound or complex that includes that element. The oxidation state is indicated with Roman numerals. Plutonium in the +6 oxidation state indicated as Pu(VI) ("hexavalent plutonium") and indicates the plutonium has lost 6 electrons relative to plutonium metal. In aqueous solution, Pu(VI) is often present as the ionic species PuO_2^{2+}, Pu(V) is PuO_2^{+}, Pu(IV) is Pu^{4+}, and Pu(III) is Pu^{3+}. Oxidation state affects many properties of elements. Clark (2000) highlights the changes in color and optical spectra for five solutions containing plutonium in the +3, +4, +5, +6 and +7 oxidation states. Pu(VII) is rarely observed, but the other four oxidation states are relatively stable under conditions available in Hanford chemical processing and tank waste.

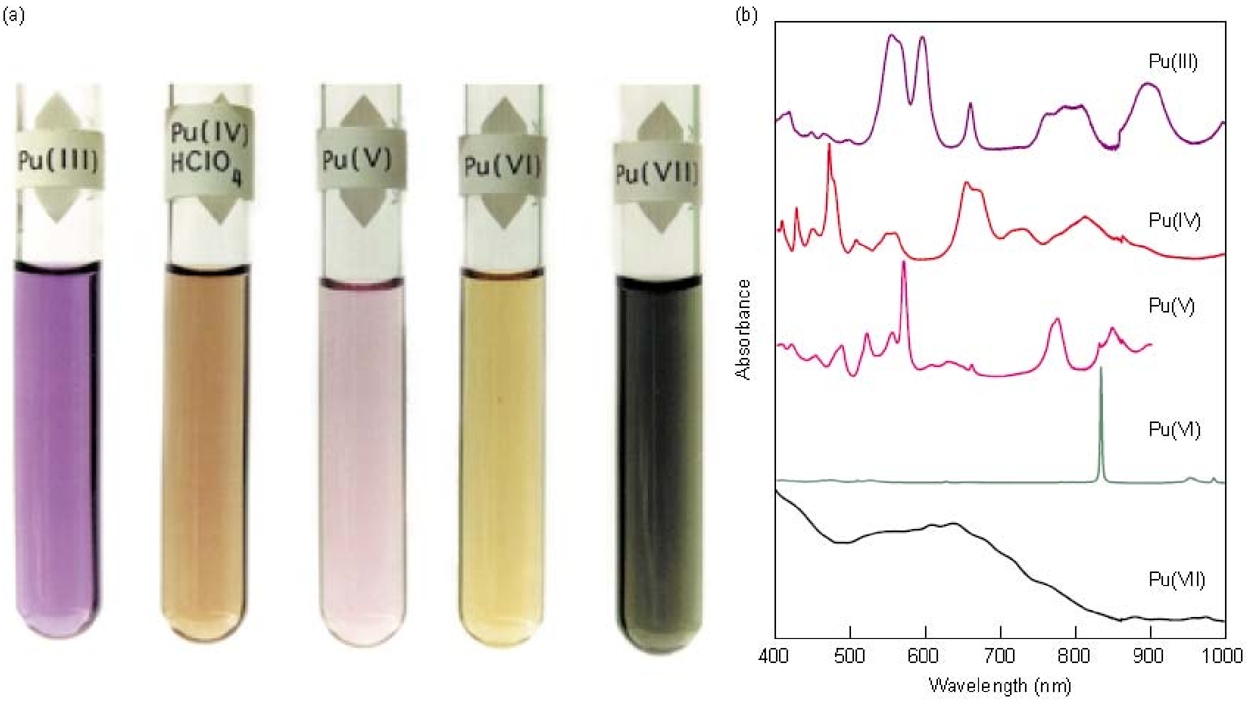

Figure 2-1. Colors (a) and Spectra (b) for Aqueous Plutonium Solutions with Various Oxidation States (Clark 2000)

The solubility of plutonium is affected by its oxidation state. In the alkaline waste matrix, Pu(V) and Pu(VI) are generally more soluble than Pu(III) and Pu(IV). For the tank waste and the WTP, this effect may be significant if a waste process has the potential to change the valence (or oxidation state) of the plutonium, because then it is possible for that process to change to amount of plutonium in the supernatant liquid (the liquid lying above a solid residue after crystallization, precipitation, centrifugation, or other process).

Hydrolysis—the interaction of the plutonium ions with water—is another important reaction in the Hanford waste and WTP processes. In the separations plants, plutonium and other metals were mostly ionic species dissolved in acidic solutions. Before being routed to the waste tanks, the acidic solutions were treated with sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3) and neutralized and made alkaline. Plutonium and many other metals hydrolyze in low-acid to alkaline or caustic solution. Some examples of hydrolysis reactions for Pu(IV) and Fe(III) can be written as

$$Pu^{4+} + 4OH^{-} \rightleftharpoons Pu(OH)_4 \text{ or } PuO(OH)_2{\cdot}H_2O \text{ or } PuO_2{\cdot}2H_2O$$

$$2Fe^{3+} + 6OH^{-} \rightleftharpoons 2Fe(OH)_3 \text{ or } Fe_2O_3 + 3H_2O$$

If the iron and plutonium are in the same solution that is made alkaline, they will coprecipitate. Coprecipitation is distinct from simultaneous precipitation. In this example with coprecipitation, the final plutonium concentration in solution will be lower largely due to its interaction with iron compared to the plutonium concentration that would have resulted from neutralization without iron present. Plutonium also may adsorb on pre-formed iron solids.

The oxide of aluminum has the formula Al_2O_3 and is amphoteric. Al(III) is soluble in low-pH acid solution, precipitates when the solution is neutralized to intermediate pH, and will dissolve again by forming a negatively charged hydroxide complex at higher pH. Amphoteric species act as either acids or bases depending upon conditions.

This primer has provided a very brief general overview of the chemistry of plutonium and other elements in the tank waste. The following sections will provide more detailed and specific descriptions.

3.0 Hanford Waste Process History

The Hanford Site, also called the Hanford Engineering Works (1943-1946) and Hanford Works (1947-1973), is located in Washington State, and was operated from 1943 until 1990 to produce and process plutonium for nuclear weapons and for nuclear fuels. The Site has been operated under the aegis of the Manhattan Project of the U.S. Army Corps of Engineers (1943-1945), the U.S. Atomic Energy Commission (1946-1975), the U.S. Energy Research and Development Administration (ERDA; 1975-1977), and the U.S. Department of Energy (DOE; 1977-present).

Most of the plutonium processed at the Hanford Site was produced on-Site by the irradiation of aluminum-clad metallic uranium fuel in eight production reactors (the B, D, F, H, DR, C, KE, and KW Reactors, in chronological order) and irradiation of Zircaloy-clad metallic uranium fuel in one dual-use production/power reactor (the N Reactor). Plutonium was separated at Hanford from the irradiated uranium fuel by reprocessing using the Bismuth Phosphate Process (B and T Plants; 1944-1956), the REDOX Process (REDOX Plant; 1952-1967), and the PUREX Process (PUREX Plant; 1956-1990). All three processes relied on changing the plutonium's oxidation state to achieve the desired separation and decontamination from the uranium and fission products, from the fuel, and from the process chemicals and corrosion products from plant operations. All processes operated with nitric acid, HNO_3, aqueous solution matrices. Because the Bismuth Phosphate Process did not recover uranium, the uranium-rich acidic waste initially was made alkaline and then discharged to selected underground storage tanks. Later, the uranium was reclaimed by sluicing and acidification of the waste, followed by tributyl phosphate solvent extraction in the Uranium Recovery Process (1952-1958).

Each process generated radioactive wastes whose compositions were largely dominated by the spent process chemicals, solvents and solvent decomposition products, and aluminum- or zirconium-based cladding residues. The radioactive constituents, including the fission products, uranium and plutonium process losses, and discharge or losses of americium and neptunium, comprised little of the waste volume aside from the uranium-rich stream from the Bismuth Phosphate Process. The wastes were made alkaline by adjustment to at least pH 8, and often much higher, using sodium hydroxide, NaOH, and sodium carbonate, Na_2CO_3, solutions. The wastes then were discharged to storage into 177 mild-steel–lined reinforced concrete underground tanks with individual capacities ranging from ~0.19 million to 4 million liters. The tank storage costs and engineering economies drove each evolving process to optimize the use of process chemicals with the result that tank waste volumes of 64 liters/kg of irradiated uranium metal fuel in the Bismuth Phosphate Process initially incurred in 1945 decreased to 1.3 liters/kg of uranium in the PUREX Process (Barney and Delegard 1999).

To augment the marked decreases in disposed tank waste volumes earned by process evolutions, further means were devised to minimize tank waste volumes. In 1954-1958, the Waste Scavenging Process was implemented to remove the radioactive and heat-producing isotopes $^{134,137}Cs$, ^{90}Sr, and ^{60}Co from raffinates of the Uranium Recovery Process and from the radiolytically dilute Bismuth Phosphate Process waste solutions using carrier precipitation by nickel ferrocyanide, calcium/strontium phosphate, and nickel sulfide, respectively. The resulting ~140 million liters of decontaminated solutions then were discharged to the ground, freeing a like volume of tank waste capacity.

Further waste volume decreases were achieved by water evaporation through self-boiling (in the 241-S, 241-SX, 241-A, and 241-AX tank farms) and atmospheric breathing of the vapor space above the wastes. Waste volume was also reduced by boiling the waste solutions using in-plant (242-B and 242-T) and in-tank (241-BY-101 and 241-BY-102) atmospheric evaporators and the 242-A (1977 to present) and 242-S vacuum evaporators (1973-1980). The collected condensates were disposed to the ground and the volume-reduced salt solutions disposed to the tanks. Water removal caused many of the dissolved salts to exceed their solubilities and crystallize as saltcakes within the tanks. Neutralization of the HNO_3 process raffinates using NaOH caused the dominant crystallized salt to be sodium nitrate, $NaNO_3$. However, other salts (e.g., $Na_2C_2O_4$, $Na_2CO_3 \cdot H_2O$, $NaAl(OH)_4$) and double salts (e.g., $Na_7F(PO_4)_2 \cdot 19H_2O$, Na_3FSO_4, $NaAlCO_3(OH)_2$) also can be found in the tank wastes (Reynolds et al. 2013 and references therein; Felmy and MacLean 2001).

The Waste Fractionization Process, operating from 1967 until 1985, addressed the practical limits in waste volume reduction imposed by fission product isotope heat loading on the tanks. It did this by removing the abundant heat-producing isotopes $^{134,137}Cs$ and $^{89,90}Sr$ using ion exchange and solvent extraction, respectively. The collected isotopes were separately double-encapsulated in the forms of cesium chloride (CsCl) and strontium fluoride (SrF_2) salts. The waste capsules remain stored underwater for radiolytic shielding and heat-dissipation. Organic complexing agents were used in the Waste Fractionization Process to sequester iron and thus aid in waste dissolution. The complexing agents included citrate, glycolate, ethylenediaminetetraacetate (EDTA), and N-2-hydroxyethyl ethylenediaminetriacetate (HEDTA) (Buckingham 1967).

At Hanford, plutonium finishing processes—operations to purify and process plutonium beyond the acidic plutonium nitrate solution product of the reprocessing plants—were also used. The plutonium finishing processes were conducted in the 231-Z Building, which housed the process to purify the plutonium nitrate solution product produced in the Bismuth Phosphate Process and initial REDOX Process using plutonium peroxide precipitation. The plutonium peroxide was re-dissolved in HNO_3 and then concentrated to a plutonium nitrate paste for shipment to Los Alamos. In subsequent operations, the 231-Z Building also produced $Pu(NO_3)_4$ solution and Pu(III) and (IV) oxalates, $Pu_2(C_2O_4)_3 \cdot 10H_2O$ and $Pu(C_2O_4)_2 \cdot 6H_2O$, respectively, for immediate processing in the 234-5 Building, later called the Plutonium Finishing Plant (PFP). The PFP produced purified $Pu(NO_3)_4$ solution, $Pu_2(C_2O_4)_3 \cdot 10H_2O$, $Pu(C_2O_4)_2 \cdot 6H_2O$, plutonium dioxide (PuO_2) and plutonium tetrafluoride (PuF_4) as process intermediates on the way to producing plutonium metal and plutonium shapes for defense. In later years, the PFP also produced PuO_2 for both defense and reactor purposes. Plutonium scrap from Hanford and off-site sources was also processed to recover the plutonium values at the 234-5 Building. Aqueous raffinates in HNO_3 media from the PFP solvent extraction purification of plutonium initially were discharged, both with and without prior neutralization, to underground disposal cribs. From 1973 onward, however, the neutral-to-alkaline wastes were disposed to the tank farms.

Laboratory and equipment decontamination wastes, ion exchange resins, and diatomaceous earth and Portland cement liquid sorbents also have been added to some tanks. The origins and general compositions of the wastes from the various processes are examined in more detail in the following discussions.

3.1 Bismuth Phosphate Process

The Bismuth Phosphate Process used cyclic batch-wise carrier precipitation with two different carriers: first, bismuth phosphate, $BiPO_4$, and then lanthanum fluoride, LaF_3, both of which carry Pu(IV) but not Pu(VI). Plutonium oxidation was accomplished using sodium bismuthate, $NaBiO_3$, and sodium dichromate, $Na_2Cr_2O_7$; while reduction was accomplished using sodium nitrite ($NaNO_2$) for the initial dissolved fuel and ferrous sulfate ($FeSO_4$) in subsequent steps (Katz and Seaborg 1957; Schneider 1951; Higley et al. 2001).

All the uranium metal fuel feeding the Bismuth Phosphate Process was aluminum-clad. As was the case for nearly all Hanford processing, the cladding was removed chemically before fuel dissolution. The cladding removal step was accomplished using sodium hydroxide to dissolve the aluminum. Sodium nitrate ($NaNO_3$) was added to the solution to scavenge the hydrogen, which otherwise would have been released and pose a flammability and explosion hazard, to produce dissolved $NaNO_2$ and ammonia (NH_3). The chemically balanced equation for the dissolution of the aluminum cladding, shown below, is based on the observation that half of the $NaNO_3$ reduction equivalents result in $NaNO_2$, and half in NH_3 (Schneider 1951):

$$Al + 0.8125\ NaOH + 0.9375\ NaNO_3 + 1.875\ H_2O \rightarrow NaAl(OH)_4 + 0.75\ NaNO_2 + 0.1875\ NH_3$$

Dissolution of silicon from the aluminum-silicon (AlSi) bonding agent used between the cladding and uranium metal fuel also occurred in this step to consume $NaNO_3$ and produce $NaNO_2$, NH_3, and sodium silicate (Na_2SiO_3). The silicon was about 3.4 mole% of the total aluminum (Schneider 1951). The cladding waste was discarded to underground storage tanks.

The de-clad irradiated fuel was dissolved in hot concentrated HNO_3. The chemically balanced reaction for uranium metal dissolution in HNO_3, below, is based on flowsheet values for uranium metal and HNO_3 charges to the dissolver and the residual amount of HNO_3 remaining in solution (Schneider 1951). It assumes that the gaseous nitrate reduction products are solely nitric oxide (NO) and nitrogen dioxide (NO_2). In practice, small amounts of nitrous oxide (N_2O) also are produced.

$$U + 4.81\ HNO_3 \rightarrow UO_2(NO_3)_2 + 1.215\ NO_2 + 1.595\ NO + 2.405\ H_2O$$

Irradiated uranium metal fuel dissolution occurred in all reprocessing plants. Refinements in the dissolver design allowed capture and oxidation of the NO_x (NO_2 and NO) gases by atmospheric oxygen, which already occurred to a limited extent, to recover HNO_3, thus saving material and waste disposal costs by decreasing HNO_3 consumption in the plant.

The oxidation states of plutonium were alternated within three cycles each of two $BiPO_4$ precipitation steps from HNO_3 solution. Thus, in the first $BiPO_4$ precipitation steps within each cycle, the plutonium was in the tetravalent state and was carried by the $BiPO_4$ solids while the uranium and much of the fission product remained in solution. The bismuth was added to the acidic dissolver solution as bismuth subnitrate, $BiONO_3$, dissolved in strong HNO_3. Two equal doses of strong H_3PO_4 solution in dilute HNO_3, the second at a slower flow rate, then were added before a treatment with $NaNO_2$ to ensure plutonium reduction to the tetravalent (IV) state, and a second dose of $BiONO_3$ in HNO_3. The $BiPO_4$ that formed carried the plutonium with the bismuth-to-plutonium weight ratio dosing adjusted to 37:1 (Schneider 1951). The U(VI), which remained in solution from the first $BiPO_4$ precipitation by sulfate complexation using added sulfuric acid (H_2SO_4), was made alkaline using NaOH solution and discarded as Metal Waste (MW). The MW also contained about 90% of the fission products. The valuable and minimally depleted uranium in the MW was subsequently recovered in the Uranium Recovery Process (1952-1958). The $BiPO_4$ precipitate cake with the carried plutonium then was dissolved in strong HNO_3, the plutonium oxidized to the hexavalent state using sodium dichromate, $Na_2Cr_2O_7$, and sodium bismuthate, $NaBiO_3$, and $BiPO_4$ precipitated again. This time, the plutonium remained in solution while much of the remaining fission products and contaminants were carried by the $BiPO_4$ and were discarded to waste.

Two similar subsequent $BiPO_4$ precipitation cycles (the first and second decontamination cycles; 1C and 2C, respectively) followed with first Pu(IV) (carried) and then Pu(VI) (remaining in solution), to achieve further decontamination from uranium, fission products, process chemicals, and corrosion products while plutonium concentration increased within the $BiPO_4$ carrier. The steps to this point took place in the 221 (canyon) Buildings of B and T Plant; i.e., 221-B and -T. The plutonium-bearing solution was transferred to the adjacent respective 224-B or -T Buildings, the contained plutonium oxidized to Pu(VI), and treated again with $BiPO_4$ to remove contaminants. After this, the Pu(VI) solution was treated with potassium permanganate, $KMnO_4$, to ensure full plutonium oxidation to the hexavalent state, and the solution treated with hydrofluoric acid (HF) followed by addition of a lanthanum (La^{3+}), salt and LaF_3 precipitated in HNO_3 to carry much of the remaining contaminants, especially lanthanide fission products, while the plutonium stayed in solution. The LaF_3 was discarded. The plutonium in solution then was chemically reduced to the (IV) state, more La^{3+} and fluoride added to precipitate LaF_3 to carry the Pu(IV), and the solution was discarded. The LaF_3 then was metathesized in alkaline solution to make lanthanum hydroxide ($La(OH)_3$) solids, which still retained the plutonium but eliminated the corrosive fluoride from further processing of the plutonium-rich concentrate (Schneider 1951).

The $La(OH)_3$ from the 224-B and -T Buildings then was transferred to the 231-Z Building where it was dissolved in HNO_3 and a nearly pure plutonium compound, tetravalent plutonium peroxide (PuO_4) precipitated by solution treatment with hydrogen peroxide, leaving the lanthanum in solution for discard. A second purification by dissolution and re-precipitation of PuO_4 then was performed before the PuO_4 was decomposed in HNO_3 by heating and the resulting plutonium nitrate product solution made ready for subsequent processing to metal.

Waste generation rates beginning in 1945 were measured at 64 liters/kg of irradiated uranium metal. Process improvements occurred such that the Bismuth Phosphate Process over its history generated, on average, 8000 gallons of tank waste per metric ton of irradiated uranium metal (~30 liters/kg uranium). About 8% of the 96,900 metric tons of the Hanford Site-irradiated uranium metal reprocessed at Hanford, or 8100 metric tons, went through the Bismuth Phosphate Process (Gephart 2003).

3.2 Uranium Recovery / Tributyl Phosphate Process and Scavenging Process

The Bismuth Phosphate Process did not recover uranium but instead reserved it within specific tanks as MW for later processing. Because the MW arose from the first step in the Bismuth Phosphate Process, this waste also contained about 90 percent of the irradiated fuel fission products. The Uranium Recovery Process, also known as the Tributyl Phosphate Process or TBP Process, was used to recover the valuable uranium, only slightly depleted by net ^{235}U fission and ^{238}U transmutation from its natural enrichment, from the MW. The TBP Process operated from 1954 until 1958.

About 89 to 94 percent of the uranium contained in MW was recovered by sluicing for feed to the TBP Process (MacCready 1957). The initial retrieval of the MW used supernatant liquor to liquify the uranium-bearing solids into stainless steel vessels located near each tank farm. Nitric acid then was added to dissolve the solids and the partially dissolved slurry was transferred to the U Plant where centrifuges clarified the liquids for treatment by the Uranium Recovery Process.

The acidic uranium-bearing solution was contacted with a solution of TBP in kerosene to extract and purify the uranium through a series of three pulse columns. The acidified MW solution entered the first column midway on the length of the column with a countercurrent of aqueous scrub solution entering the top and the less dense organic TBP solution entering the bottom. The scrub solution separated fission products and plutonium from the uranium, which remained dissolved in the organic TBP. Plutonium separation from uranium was enhanced by chemical reduction to Pu(III) using ferrous ammonium sulfate [$(NH_4)_2Fe(SO_4)_2$] and sulfamic acid [H_2NSO_3H]. At the top of the column, an aqueous stream containing HNO_3 was introduced to scrub residual fission products and plutonium from the rising uranium-bearing TBP stream. The fission products and plutonium were scrubbed from the organic and retained in the dense aqueous phase, draining the bottom of the first solvent extraction column. The uranium-bearing organic phase entered the bottom of the second solvent extraction column, where water transferred the uranium to the dense descending aqueous phase. The purified aqueous uranium solution exiting the second column was concentrated and the uranium product dried and heated to ~400° C at the UO3 Plant to produce uranium trioxide (UO_3) for recycle to enrichment plants. The HNO_3 also was recovered for use at Hanford (Gerber 1993). The third solvent extraction column treated the organic kerosene-TBP phase with a sodium sulfate (Na_2SO_4) solution to remove impurities (e.g., residual fission products and bulk chemicals) arising from both the treated MW and from the solvent degradation (e.g., dibutyl phosphate from TBP hydrolysis and radiolysis). After being made alkaline, the waste aqueous phases from the first and third columns initially were discharged to the tank farms as TBP wastes (Higley et al. 2001).

Concurrently with the Uranium Recovery Process, Scavenging Processes (1954-1958) were implemented to remove fission products from the Uranium Recovery Process waste solutions stored in the tanks. The Scavenging Processes also were applied to the waste solutions continuing to be generated from the Uranium Recovery Process and to the waste supernatant solutions from the Bismuth Phosphate Process first decontamination cycle (1C). The scavenger, sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$] was selected to precipitate and then carry ^{137}Cs from the solution. Supernatant solutions subsequently were found to contain high ^{90}Sr concentrations. To address this, calcium nitrate ($Ca(NO_3)_2$) and non-radioactive strontium nitrate ($Sr(NO_3)_2$) were added to precipitate in the alkaline solution to carry the ^{90}Sr by way of in-plant processing. Nickel sulfide was used in some tanks to carry ^{60}Co. The sulfide was introduced as sodium sulfide and the nickel as nickel sulfate (Cash et al. 1992). The supernatant solutions from the Scavenging Processes were disposed to the ground, freeing the associated tank waste volume. Aside from the increased nickel and iron, the in-plant ferrocyanide-scavenged wastes had compositions similar to those of the Uranium Recovery Process wastes. Four different solid waste types were derived from the Uranium Recovery and Scavenging Processes (Higley et al. 2001).

3.3 REDOX Process

Like the Bismuth Phosphate Process, the REDOX Process relied on oxidation state changes to effect the separation of plutonium from uranium, fission products, process chemicals, and corrosion products. The separation was achieved using a continuous solvent extraction process. The process removed uranium and plutonium from the dissolved irradiated fuel and then separated them into acidic hexavalent uranium and plutonium (i.e., U(VI) and Pu(VI)) nitrate solution streams. The solvent used in continuous solvent extraction was methyl isobutyl ketone (MIBK, also known as hexone). With hexone, the Pu(VI) is extractable but trivalent plutonium, Pu(III), is not. High ionic strengths are needed to force the Pu(VI) and U(VI) into the organic phase. Because HNO_3 is relatively soluble in hexone, which is unstable in contact with high-HNO_3 concentrations, low- or even zero-HNO_3 concentrations were used in the REDOX Process and aluminum nitrate, $Al(NO_3)_3$, was used instead as the salting agent to increase the aqueous phase ionic strength and drive the uranium and plutonium into the organic phase (Katz and Seaborg 1957; Granquist 1955; Higley et al. 2001).[1]

The aluminum cladding removal steps in the REDOX Process were similar to those used for the Bismuth Phosphate Process. However, the REDOX Plant also processed N Reactor uranium metal fuel that was clad in Zircaloy. The Zirflex Process to dissolve the Zircaloy used ammonium fluoride, NH_4F, as the dissolving agent and, like the aluminum cladding removal step, used nitrate, but in the form of ammonium nitrate (NH_4NO_3) instead of $NaNO_3$, to scavenge hydrogen radicals and inhibit flammable H_2 gas evolution. The Zirflex Process reaction stoichiometry under PUREX Plant conditions using boiling 5.5 M NH_4F / 0.5 M NH_4NO_3 solution was found to be

$$Zr + 6\ NH_4F + 0.47\ NH_4NO_3 \rightarrow (NH_4)_2ZrF_6 + 4.94\ NH_3 + 1.41\ H_2O + 0.12\ H_2$$

Hydrogen gas (H_2) still was evolved but the yield was about 6 percent of what it would have been in solution containing no added nitrate. The hydrogen attenuation factor thus was 1/0.06 or ~17. The cladding dissolver solution was added to NaOH solution before discharge to the waste storage tanks. This action formed ZrO_2 and NH_3 while any excess NH_4NO_3 and NH_4F formed $NaNO_3$, NaF, and NH_3 Some PuF_4 with UF_4 also formed during decladding. However, these salts are insoluble and remained within the dissolver. After cladding dissolver solution discharge, a metathesis step using NaOH solution was used to convert the UF_4 and PuF_4 to their respective hydrated oxides (Moore et al. 1980).

The irradiated uranium metal fuel, whether aluminum- or zirconium-clad, was dissolved in hot HNO_3 solution in a manner similar to that used in the Bismuth Phosphate Process.

The U(VI) and plutonium from the dissolver solution in the REDOX Plant were treated with $Na_2Cr_2O_7$ to oxidize the plutonium to the hexavalent (VI) state. Once the dichromate was added, the dissolver solution was boiled to remove fission product ruthenium that had proved to be difficult to separate from uranium and plutonium by the REDOX Process. The dichromate oxidized the ruthenium to volatile ruthenium tetroxide (RuO_4) and boiling served to steam-strip the ruthenium from solution and into the offgas where it could be captured. In a later refinement, ozone gas, O_3, was used rather than dichromate to produce the volatile RuO_4.

---

[1] To further decrease the deleterious effects of HNO_3 on hexone, part of the nitrate in the dissolved aluminum nitrate salt could be replaced by hydroxide through hydrolysis. For example, if one liter of a 1 M $Al(NO_3)_3$ solution were treated with 0.01 liters of 10 M NaOH, the resulting solution formally would be about 0.99 M $Al(OH)_{0.1}(NO_3)_{2.9}$ and 0.099 M $NaNO_3$. Alternatively, the $Al(NO_3)_3$ solution could be boiled to distill off HNO_3 and leave partially hydrolyzed species such as $Al(OH)_x(NO_3)_{3-x}$. Such solutions were called "acid deficient" in Hanford Site process documentation as they contained hydrolyzable cations, such as Al^{3+} or UO_2^{2+}, having pH greater than that of the corresponding solution prepared from the pure nitrate salt(s) [i.e., $Al(NO_3)_3$ or $UO_2(NO_3)_2$]. Furthermore, the extent of acid deficiency was designated as (the physically impossible) negative HNO_3 concentration (-[HNO_3]) in process documentation and was defined as the concentration of HNO_3 required to adjust the solution pH to that of the solution of the respective pure nitrate salt or salts (Schulz 1962).

The dissolver solution was treated with $Al(NO_3)_3$ to act as salting agent. The $Al(NO_3)_3$-treated dissolver solution was made low in acid (<0.1 M HNO_3) or acid deficient and contacted with the hexone solvent. The hexavalent uranium and plutonium were jointly separated from the fission products. The plutonium and uranium were then partitioned (i.e., separated from each other) by stripping of the organic phase. A solution of ferrous sulfamate ($Fe(SO_3NH_2)_2$) a chemical reductant for plutonium, was used to reduce the extracted Pu(VI) to the non-extractable Pu(III). Dilute acid was used to strip uranium from the hexone. The individual streams then underwent further purification by similar extraction and stripping steps. In the extraction steps, acid-deficient aluminum nitrate again was used as the salting agent to drive the Pu(VI)—oxidized from Pu(III) using $Na_2Cr_2O_7$—into the organic phase. The countercurrent contacts occurred in tall non-agitated columns packed with Raschig or Pall rings to improve the aqueous-organic contacting surface. The dense aqueous phase passed from the top downward in opposition to the immiscible, rising, and less-dense hexone through the tortuous paths created by the packing rings.

In later development, it was recognized that the less contaminated aluminum-rich raffinates from plutonium and uranium purification could be back-cycled to provide salting agent to the primary extraction cycles. By sending the low-activity raffinates to the primary extraction columns, economies were realized both in aluminum nitrate that otherwise would have been consigned directly to the waste and in the sodium hydroxide needed to make the aluminum solution pH-neutral. The NaOH addition precipitated $Al(OH)_3$, or if made more alkaline, converted part of the aluminum to soluble sodium aluminate, $NaAl(OH)_4$, for disposal to the underground storage tanks as shown in the following neutralization reactions:

$$Al(NO_3)_{3,\ \mathrm{solution}} + 3\ NaOH_{\mathrm{solution}} \rightarrow Al(OH)_{3,\ \mathrm{solid}} + 3\ NaNO_{3,\ \mathrm{solution}}$$

$$Al(OH)_{3,\ \mathrm{solid}} + NaOH_{\mathrm{solution}} \rightarrow NaAl(OH)_{4,\ \mathrm{solution}}.$$

In later years, an anion exchange process was used to purify the plutonium nitrate product. The plutonium product was sent to the 234-5 Building for finishing operations. The uranium nitrate product was sent to the UO3 Plant for thermal denitration conversion to solid UO_3 powder and then shipped offsite for isotopic enrichment.

Mixed uranium-plutonium oxide (MOX) fuel from Hanford's Plutonium Recycle Test Reactor (PRTR) and uranium dioxide (UO_2) fuels from the Shippingport, Pennsylvania, reactor also were processed at the REDOX Plant. This occurred from 1963 until 1967 (Gerber 1996).

The REDOX Process initially generated 4000 gallons of tank waste per metric ton of irradiated uranium metal (~15 liters/kg uranium) but process improvements such as the $Al(NO_3)_3$ back-cycling decreased the waste generation rate to ~500 gallons per metric ton (~1.9 liters/kg uranium). About 23% of the irradiated uranium metal reprocessed at Hanford, or 22,400 metric tons, went through the REDOX Process (Gephart 2003).

3.4 PUREX Process

The PUREX Process operated from 1956 until 1972 and then again from 1983 until 1988, followed by a 1990 stabilization run. The final shut-down order occurred in 1992 (Section 4.3 of Gerber (1996)). Like the REDOX Process, the PUREX Process was based on solvent extraction. However, the PUREX Process used 30 volume% tributyl phosphate (TBP) as the extractant, with normal paraffin hydrocarbon

(NPH, similar to kerosene) being the diluent. For the PUREX Process, the Pu(IV) is extracted by the organic solvent and the plutonium made to be inextractable by adjustment to Pu(III) using ferrous sulfamate. Like in the Uranium Recovery Process, the uranium in the PUREX Process was extracted as U(VI) in HNO_3 (Higley et al. 2001).

Decladding of both aluminum and Zircaloy-clad uranium metal fuels followed by dissolution of the uranium metal in HNO_3 were performed in the same manners as described for the REDOX Plant.

The solvent extraction steps in the PUREX Process occurred in mechanical pulse columns in which the denser aqueous phases flowed downward, countercurrent to the upwardly moving, lighter organic phase. The contact between the phases was improved by causing the solutions to pass through a series of perforated plates along the length of the columns. The first column achieved most of the separation, extracting U(VI), Pu(IV), and, if present, Pu(VI) into the organic phase. The fission products remained in the aqueous phase raffinate. The uranium- and plutonium-loaded organic phase then passed to a second column where the organic phase flowed upward to encounter the downward flowing aqueous phase containing ferrous sulfamate. The ferrous sulfamate chemically reduced the plutonium to the inextractable Pu(III) and effected the partitioning of uranium, which remained in the organic phase, from plutonium, which passed into the aqueous phase. The uranium remaining with the organic phase was passed to a third solvent extraction column, where the uranium was stripped using dilute HNO_3. Both plutonium and uranium separately underwent further solvent extraction processing to improve their individual purities. For process efficiency, the organic solvent from less contaminated streams could be cycled for use in the more contaminated streams. The organic solutions, stripped of their uranium and plutonium, were treated with an alkaline wash (sodium carbonate, Na_2CO_3) solution to remove acidic organic degradation products, then returned to the solvent extraction processes.

The purified uranium product in HNO_3 solution was sent to the UO3 Plant where it was converted to UO_3 powder. Most plutonium left the plant in concentrated HNO_3 solution for processing to metal or oxide in the PFP. Near the end of the PUREX Plant operations in the 1980s, some of the plutonium was processed via Pu(IV) oxalate precipitation and calcination in the PUREX Plant N Cell to form plutonium dioxide (PuO_2) product.

The PUREX Process used HNO_3 as the salting agent to drive the U(VI) and Pu(IV) into the organic TBP phase. Because the HNO_3 readily could be recovered by distillation from the wastes for reuse, the PUREX Process was chemically more efficient than the REDOX Process for which only limited back-cycling of aluminum nitrate salting agent was possible. What HNO_3 remained with the waste could largely be destroyed by denitration using reaction with sugar. This had the effect of further decreasing the waste by diminishing the sodium hydroxide needed to make the waste alkaline before its discharge to tank farms. Wastes from the PUREX Process included the high-level waste from the first solvent extraction cycle as well as cladding waste, waste from organic wash, and process cell drainage.

Besides recovering uranium and plutonium arising from uranium metal fuel irradiated in the Hanford reactors, the PUREX Plant also processed small quantities of other irradiated materials. In 1962, J and Q Cells in PUREX were modified to separate ^{237}Np. During 1965 and 1966, the PUREX Plant processed 664 tons of powdered thorium oxide fuel targets that had been irradiated to produce ^{233}U. A campaign in 1970 processed 820 kilograms of irradiated thorium oxide pellet targets. Like the REDOX Plant, the PUREX Plant also reprocessed some PRTR mixed-oxide (MOX) fuel in 1969-1972 (Gerber 1996).

Because of process improvements and economies, the PUREX Process waste stream compositions evolved over the operating life of the plant such that the initial waste generation rates of 1300 gallons per metric ton of uranium metal fuel (~4.9 liters/kg U) decreased to less than 264 gallons waste per metric ton (~1.0 liter/kg). The PUREX Process handled 66,400 metric tons, or ~69%, of the total irradiated Hanford uranium metal fuel (Gephart 2003).

3.5 Waste Fractionization Process

The Waste Fractionization Process operated from 1967 until 1985 to address the practical limits in waste volume reduction imposed by fission product isotope decay heat loading on the tanks and to decrease the hazard of the storage of waste containing high concentrations of radionuclides. The Waste Fractionization Process, operating in a refurbished portion of the Bismuth Phosphate Process B Plant, did this by removing the abundant heat-producing isotopes ^{134,137}Cs using ion exchange on zeolitic media and ^{90}Sr using precipitation and solvent extraction (Buckingham 1967). Time was allowed for the 50.4-day half-life ^{89}Sr to radiolytically decay. The collected isotopes were separately double-encapsulated in the forms of cesium chloride (CsCl) and strontium fluoride (SrF_2) salts and thus were made available for beneficial uses. The waste capsules remain stored underwater for radiolytic shielding and heat-dissipation. Methods to recover ^{147}Pm and ^{144}Ce also were developed.

The Waste Fractionization Process focused on three waste types based on their relatively high concentrations of the target radionuclides: l) current acid waste and Zirflex waste from the PUREX Process, 2) stored alkaline sludge wastes from the PUREX Process, and 3) stored alkaline supernatant liquid wastes from the REDOX and PUREX Processes. Organic complexing agents were used in the Waste Fractionization Process to sequester iron in the sludge wastes and thus aid in waste dissolution to release the associated radionuclides. The complexing agents included citrate, glycolate, EDTA, and HEDTA (Buckingham 1967). As will be noted in Section 5.3.1, hydrodynamic segregation of $PuO_2 \cdot xH_2O$ from Fe(III) (hydr)oxides, even if precipitated individually, is unlikely owing to the similarly miniscule (nanometer-scale) sizes of their respective crystallites.

3.6 Plutonium Finishing Processes

Plutonium finishing processes, that is, operations to purify and to process plutonium beyond the acidic plutonium nitrate solution product of the reprocessing plants, occurred at the Hanford 231-Z Building, the 234-5 Building or PFP, and, briefly, at the PUREX Plant. The plutonium finishing processes conducted in the 231-Z Building purified the plutonium nitrate solution product produced in the Bismuth Phosphate Process and initial REDOX Process by way of plutonium peroxide precipitation. The plutonium peroxide was re-dissolved in HNO_3 and then concentrated to a plutonium nitrate paste for shipment to the Los Alamos Scientific Laboratory from 1945 until about 1949. In subsequent operations, the 231-Z Building also produced $Pu(NO_3)_4$ paste and solution and tri- and tetravalent plutonium oxalates ($Pu_2(C_2O_4)_3 \cdot 10H_2O$ and $Pu(C_2O_4)_2 \cdot 6H_2O$, respectively) for immediate processing in the PFP. The PFP produced purified $Pu(NO_3)_4$ solution, $Pu_2(C_2O_4)_3 \cdot 10H_2O$, $Pu(C_2O_4)_2 \cdot 6H_2O$, PuO_2, and PuF_4 as process intermediates on the way to producing plutonium metal and plutonium shapes for weapons. In later years, the PFP also produced PuO_2 for both defense and reactor purposes. Plutonium scrap from Hanford and off-site sources also was processed to recover the plutonium values at the PFP (Gerber 1997).

Aqueous raffinates in HNO_3 media from the PFP solvent extraction purification of plutonium initially were discharged, with and without prior neutralization, to underground disposal cribs. From 1973 onward, however, waste from PFP was transferred from tanks in 241-Z to the 242-T evaporator. Prior to transfer to the 242-T evaporator, aqueous waste was accumulated in Tanks 39, 40, D-7 and D-8 and then transferred to Tank D-5 within PFP. Procedures at PFP specified that solutions transferred to D-5 could not contain any visible solids or organics and were not to exceed 100 g of plutonium or 200 g of americium. The D-5 solutions were sampled for compliance with waste limits prior to transfer to 242-T. The waste was not neutralized at PFP. At the 242-T evaporator, PFP acidic waste was mixed with caustic supernatant liquid that had been removed from waste tanks. The evaporator was used to concentrate liquid wastes to make more tank volume available for waste.

The 242-T evaporator functions were shut down in 1976 but tank farms continued to receive waste from PFP until 1980. Large volumes of alkaline tank supernatant liquid were blended with smaller volumes of PFP acidic waste to achieve neutralization. Absorbers were not specifically added to the PFP waste during this period and indeed no records were found indicating requirement to add absorbers to wastes discharged to the tank farms during operations prior to 1980.

Beginning in 1981, PFP aqueous wastes were neutralized in 241-Z sump tanks and transferred to the 244-TX receiver tank. Tank 244-TX was constructed as a double-contained receiver tank between the 241-TX and 241-TY tank farms. Because the tank and new transfer lines were constructed of carbon steel, the acidic waste had to be neutralized at PFP prior to transfer. Waste from 244-TX was sent to 241-SY-102 except for the last transfer from 241-Z prior to its deactivation.

In 1984, iron and diatomaceous earth were evaluated as potential additives to the PFP waste to increase the solids content and ensure that the plutonium in 244-TX waste remained below the allowed criticality safety limit (CSL) of 2 g Pu/liter of solids; cadmium and samarium also were considered as additives based on their neutron-absorbing properties (Bratzel 1984). Iron was selected because it has a very low solubility in neutralized PFP waste and forms a flocculent precipitate. Cadmium, although used briefly in PFP operations as a neutron poison and introduced as cadmium nitrate, was not selected for continued use because of its toxicity and because lab studies showed its neutralized compound, cadmium hydroxide, to be slightly soluble (10^{-5} to 10^{-4} M) leading to concern that the cadmium might ultimately wash out. Samarium, to be added as its nitrate salt and precipitated as its hydroxide, was considered for use as a neutron poison but was not selected because of its expense. Diatomaceous earth was considered as a solids diluent but lab tests showed that it dissolved to an unacceptable extent and left a hard and compact residual solid (Bratzel 1984). The addition of iron to the PFP waste to provide a solid diluent for plutonium in the 241-SY-102 sludge commenced in 1984. The iron was added in the form of ferric nitrate and precipitated as ferric hydroxide (Bratzel 1984).

3.7 Waste Concentration Processes

The 177 large underground waste storage tanks are distributed into 149 single-shell tanks and 28 double shell tanks and the wastes are grouped into three chemical-physical types: low-solubility sludge, generated from polyvalent metal ions such as Fe(III), Cr(III), Ca(II), and La(III) that have precipitated from the original acidic process solutions by being made alkaline for discharge to the mild-steel-lined waste tanks; aqueous supernatant solutions; and saltcakes generated by crystallization of water-soluble salts from concentrated supernatant solutions. The solutions generally exist above the settled sludge and saltcake layers but are also contained interstitially within sludge and saltcake beds. Of the total 56.2 million gallon (213,000 m^3) tank waste volume, supernatant solutions constitute about 37 volume%, solution-bearing saltcake about 42 volume%, and the solution-bearing sludge about 21 volume% (Rodgers 2010). The tank capacity available for additional waste storage is constrained by the obligation to eliminate solutions in the single-shell tanks, many of which have leaked, thus compelling solution transfer to the double-shell tanks. Aside from constructing more double-shell tanks or easing requirements for flammable gas control such as density limits or headspace requirements, the only way to increase capacity is through Waste Concentration operations.

Waste volume continues to be decreased by water evaporation from the supernatant waste solutions and those solutions that can be drained from the sludge and saltcake layers in an effort to minimize both the need to construct additional underground waste storage tank space and the potential for loss of radioactive solution to the ground in the event of a breach in mild-steel tank liners. The volume decreases were achieved through self-boiling in the 241-S, 241-SX, 241-A, and 241-AX tank farms and atmospheric breathing to lose water by way of the vapor space above the wastes. For in-plant (242-B and 242-T) and in-tank (241-BY-101 and 241-BY-102) atmospheric evaporators, waste volume was reduced by boiling the waste solutions using supplemental heat. Finally, the 242-A (1977 to present) and 242-S vacuum evaporator/crystallizers (1973-1980) enabled water removal by boiling to occur at lower temperatures (Higley et al. 2001). The 242-A and -S evaporators are separate sole-purpose facilities. The tank contents are pumped to these evaporators, which use MSMPR (mixed-suspension, mixed-product-removal) processing to achieve the waste volume reduction. Because fresh solutions are continuously fed while crystal-bearing concentrated liquors are continuously removed, steady-state operations occur such that consistent salt particle size and liquor concentrations can be achieved over the processing campaign. The condensates collected from the heated evaporators were disposed to the ground and the volume-reduced salt solutions from the 242-B and -T evaporators and the solution-salt slurries from the 242-A and -S vacuum evaporator/crystallizers were returned to the tanks.

The solutions being evaporated are largely of sodium salts. As noted, metals that form polyvalent ions such as Fe(III), Cr(III), Ca(II), and La(III) have little solubility in the alkaline tank waste solutions and report to the sludge. Two notable exceptions exist. Trivalent aluminum precipitates as $Al(OH)_3$ at lower NaOH concentrations and is present in the sludge. However, because it is amphoteric, it becomes increasingly soluble to exist as dissolved sodium aluminate ($NaAl(OH)_4$) with increasing NaOH concentration (or chemical activity). Chromium is the other exception because, when oxidized to the hexavalent state [Cr(VI)], it can exist as the soluble sodium chromate salt, Na_2CrO_4, that remains in the solution or crystallizes with the salt cake. If trivalent, the chromium precipitates in the form of low-solubility Cr(III) compounds that reports to the sludge.

Water removal caused many of the dissolved salts to exceed their solubilities to crystallize as saltcakes within the tanks. Because Hanford Site aqueous chemical processing largely occurred in HNO_3 solution, and treatment of the wastes to make them alkaline for mild-steel tank disposal used NaOH, the dominant salt in Hanford tank waste solution is $NaNO_3$. Thus, water and $NaNO_3$ constitute about 75 wt% of the tank waste (Barney and Delegard 1999). Sodium nitrite, carbonate, phosphate, sulfate, fluoride, aluminate, and other salts also are present in solution. Potassium also is found in the tank waste solutions, but at much lower concentrations than sodium, so it remains in solution and is not found within the saltcake solids. Because of its high concentration, $NaNO_3$ dominates the crystallized salts found in the saltcakes. However, other crystallized salts [e.g., $Na_2C_2O_4$, $Na_2CO_3 \cdot H_2O$, $NaAl(OH)_4$] and double salts [e.g., $Na_7F(PO_4)_2 \cdot 19H_2O$, Na_3FSO_4, $NaAlCO_3(OH)_2$] also can be found in the tank waste saltcakes

(Reynolds et al. 2013 and references therein; Felmy and MacLean 2001). The inventory of metallic elements, anions, and water found in the Hanford tank waste—salt cake, sludge, and solution—is summarized in Figure 3-1.

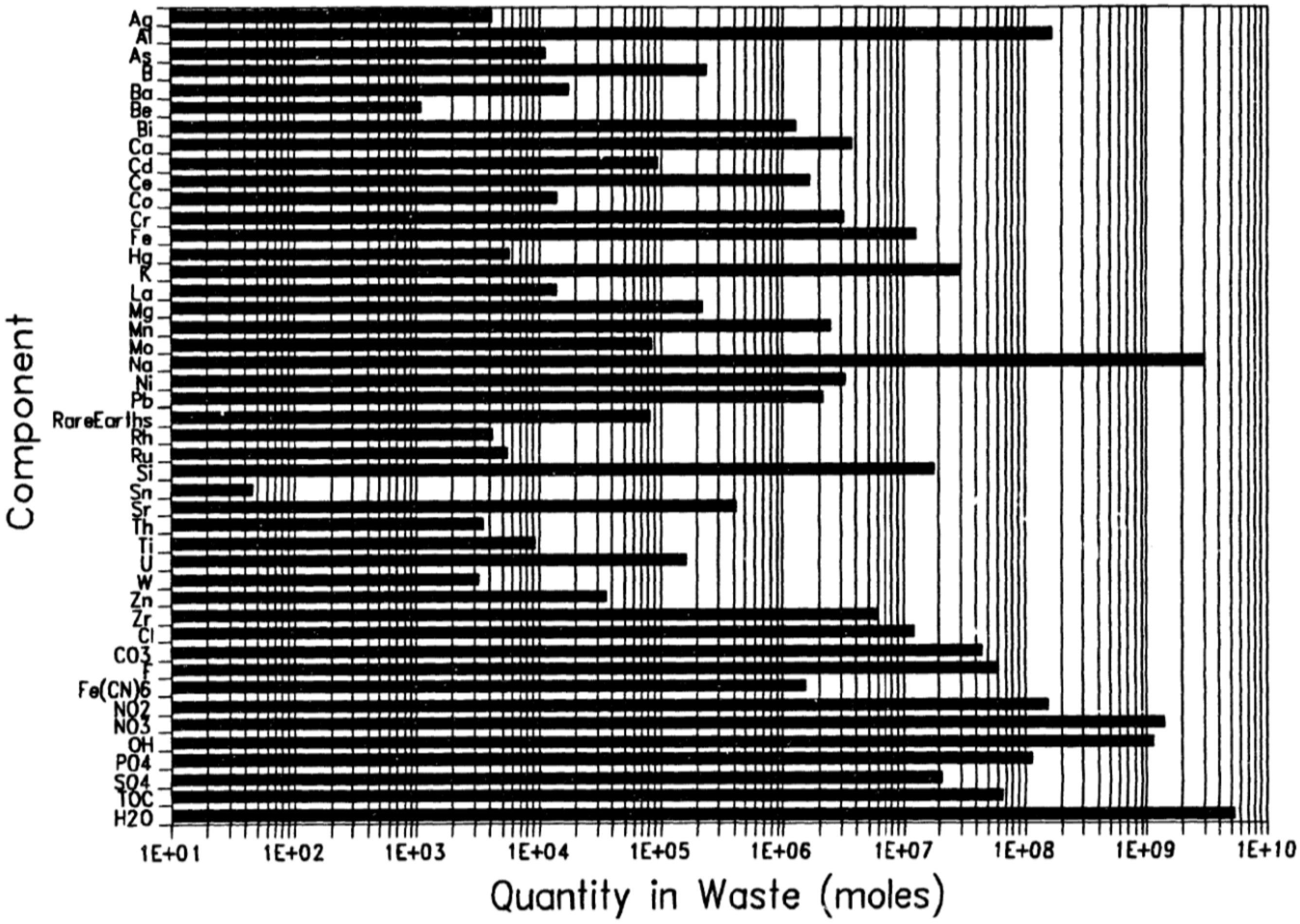

Figure 3-1. Hanford Site Tank Waste Chemical Component Inventory (Delegard et al. 1994, based on Boomer et al. 1993)

4.0 Hanford Defined Waste Compositions

Based on process evolutions and improvements in waste characterization and understanding, various waste types have been classified within the Hanford Defined Waste (HDW) Model. This model has been formulated based on process flowsheets, historical data, and the ORIGEN 2 radionuclide model to sort waste types with respect to their disposal to the waste tanks (Higley et al. 2004). The model is used to estimate the chemical and radionuclide contents within the individual waste tanks based on process knowledge, which includes reactor fuel irradiation records, separation plant dissolver charging records, separation plant and tank farm process flowsheets, and tank farm waste receipt and transfer records. The 55 waste type names and definitions are shown in Table 4-1.

Solid waste (i.e., saltcake and sludge) compositions have been developed to cover 25 of the 55 waste types listed in Table 4-1. Because the Bismuth Phosphate Process wastes MW, 1C, and 2C initially specified by Higley et al. (2001) were each later subdivided into two types (Higley et al. 2004), the MW, 1C, and 2C waste types are taken to represent, respectively, the MW1/MW2, 1C1/1C2, and 2C1/2C2 wastes listed in Table 4-1. The 25 waste types encompass 87 volume% of the saltcake and 94 volume% of the sludge within the single-shell tank waste (Higley et al. 2001). The single-shell tank waste solids inventory comprises over 84 weight% of the total tank waste solids inventory both collectively and individually in the separate saltcake and sludge strata (Rodgers 2010).

The HDW concept is useful in understanding the general outlines of waste component distribution in the individual tanks. Thus, assignment of the primary and secondary waste types present in each of the 177 individual waste tanks, as specified in the 2002 Best Basis Inventory (BBI), from the Tank Waste Information Network System (TWINS) provided in Table 3.1 of Wells et al. (2011), shows that around 80% of the tanks have at least 95% of their undissolved solids volume inventory encompassed by the first and second most prevalent waste types listed.

Table 4-1. Hanford Defined Waste Model Types and Definitions (Higley et al. 2004)

Waste Type [a]	**Definition**
1C1 [b]	$BiPO_4$ first cycle decontamination waste (1944-1949)
1C2 [b]	$BiPO_4$ first cycle decontamination waste (1950-1956)
1CFeCN [b]	Ferrocyanide sludge from in-plant scavenging of 1C supernatants; transfer to TY-Farm (1955-1956)
224-1	Lanthanum fluoride process 224 Building waste (1944-1949)
224-2	Lanthanum fluoride process 224 Building waste (1950-1956)
2C1 [b]	$BiPO_4$ second cycle decontamination waste (1944-1949)
2C2 [b]	$BiPO_4$ second cycle decontamination waste (1950-1956) and low-activity cell 5-6 drainage
A1SltCk [b]	Saltcake from first 242-A Evaporator campaign using 241-A-102 feed tank (1977-1980)
A2SltCk	Saltcake from second 242-A Evaporator campaign using 241-A-102 feed tank (1981-1988)
AR	Water-washed plutonium uranium extraction (PUREX) sludge (1967-1976)
B	B Plant HAW – rare earth FP, recovered CAW, solvent wash waste, other HAWs (1967-1972)
BL	B Plant LAW – 1AW, 1CP/OWW during PAS processing, other low active wastes (1967-1976)
BTSltCk	Saltcake from the 242-B Evaporator ops. (1951-1953) and 242-T Evaporator ops. (1951-1955)
BYSltCk	Saltcake from in-tank solidification (ITS) in BY-Farm (1965-1974)
CEM	Portland cement added to tank 241-BY-105

Waste Type [a]	Definition
CSR	Supernates from which Cs removed (1962-1967); B Plant Waste Fractionization (1967-1976)
CWP1	PUREX cladding waste, aluminum clad fuel (1956-1960)
CWP2 [b]	PUREX cladding waste, aluminum clad fuel (1961-1972)
CWR1	Reduction oxidation (REDOX) cladding waste, aluminum clad fuel (1952-1960)
CWR2	REDOX cladding waste, aluminum clad fuel (1961-1966)
CWZr1	PUREX (and REDOX) zirconium cladding waste (1968-1972)
CWZr2	PUREX zirconium cladding waste (1983-1989)
DE	Diatomaceous earth added to tanks 241-BX-102, SX-113, TX-116, TX-117, TY-106, and U-104
DW	Decontamination wastes, primarily T Plant (1967-1976)
HS	Hot semi-works ^{90}Sr purification waste (1961-1968)
MW1 [b]	$BiPO_4$ process metal waste (1944-1949)
MW2 [b]	$BiPO_4$ process metal waste (1950-1956)
N	N reactor decontamination waste (1976-1990)
NIT	Partial neutralization feed for evaporator campaigns (1977-1981)
OWW1	PUREX organic wash waste and non-boiling waste (1956-1962)
OWW2	PUREX organic wash waste and non-boiling waste (1963-1967)
OWW3	PUREX organic wash waste (1968-1972)
P1	PUREX HLW (1956-1962)
P2 [b]	PUREX HLW (1963-1967)
P2’	PUREX HLW (1964-1972)
P3 AZ1	PUREX HLW to AZ-101 (1983-March 13, 1986)
P3 AZ2	PUREX HLW to AZ-102 (March 13, 1986-1990)
PASF	PUREX ammonia scrubber feed
PFeCN1 [b]	Ferrocyanide sludge from TBP in-plant scavenged supernatant (1954-1955)
PFeCN2	Ferrocyanide sludge from TBP in-plant scavenged supernatant (1955-1958)
PL1	PUREX non-boiling waste (1968-1972)
PL2	PUREX organic wash waste and non-boiling waste (1983-1988)
RSltCk	Saltcake from self-concentration in S- and SX-Farms (1952-1966)
R1	REDOX HLW (1952-1958)
R2	REDOX HLW (1959-1966)
S1SltCk	Saltcake from the first 242-S Evaporator campaign using 241-S-102 feed tank (1973-1976)
S2SltCk	Saltcake from the second 242-S Evaporator campaign using 241-S-102 feed tank (1977-1980)
SRR	HAW from PUREX acidified sludge, solids from AR vault feed, Sr purification wastes, etc. (1969-1985)
T1SltCk	Saltcake from the first 242-T Evaporator campaign (1951-1955)
T2SltCk	Saltcake from the last 242-T Evaporator campaign (1965-1976)
TH1	Thoria process wastes (1966)
TH2	Thoria process wastes (1970)
TBP [b]	Tributyl phosphate waste (from solvent-based uranium recovery operations)
TFeCN [b]	Ferrocyanide sludge produced by in-tank or in-farm scavenging
Z	Z Plant waste (1974-1988)

a Postulated compositions of waste types in **bold** are presented by Higley et al. 2001.
b Waste types for which compositional information (Higley et al. 2001) also contains ^{239,240}Pu concentrations.

4.1 Plutonium/Absorber Ratios in HDW Compositions

Depending on the waste type, up to 23 of the chemical constituents (including the metals aluminum, bismuth, calcium, chromium, iron, potassium, lanthanum, manganese, sodium, nickel, lead , silicon, strontium, uranium, and zirconium), eight radionuclides (including ^{239,240}Pu, though not for most saltcake waste types), density, and water concentrations are reported for the 25 waste types (Higley et al. 2001). Of particular interest in the present study are concentrations of aluminum, chromium, iron, manganese, sodium, nickel, and uranium because these metals provide neutron absorption and hence could be credited in criticality control strategies. No information is reported for the remaining absorber considered in the present study, cadmium.

Of the 25 waste type compositions, only 13 (where 1C, 2C, and MW represent two waste types each) provide the ^{239,240}Pu concentrations (Higley et al. 2001). The plutonium-to-absorber mass ratios for these 10 combined waste types are compared in Table 4-2 with the target plutonium-to-absorber mass ratio that should not be exceeded. For example, the target plutonium-to-iron mass ratio is 5.18 g plutonium per kilogram of iron. Mass ratios above this value mean that there is insufficient absorption in iron alone to ensure sub-criticality under worst-case conditions. The comparisons in Table 4-2 are useful for demonstrating the neutron absorptive capabilities of individual absorber elements in the waste but do not provide indication of overall safety, which relies on analyses of individual waste feeds and which also must consider sampling and analysis variabilities. Actual criticality control strategies also credit combinations of the absorptive materials.

Table 4-2. Waste Type Compositions (from Higley et al. (2001)) and Derived Plutonium-to-Absorber Mass Ratios

Element Concentration[a]	Waste Type									
	1C	**1C FeCN**	**2C**	**A1 SltCk**	**CWP2**	**MW**	**P2**	**PFeCN**	**TBP**	**TFeCN**
Al, µg/g	15,500	8880	2010	24,100	133,000	0	39,000	31,600	2210	30,100
Cr, µg/g	830	1410	1280	4500	393	2360	2080	1790	135	275
Fe, µg/g	10,900	29,900	16,200	321	24,500	5340	145,000	30,200	21,400	22,200
Mn, µg/g	84.2	1460	88.7	54.3	1180	881	5910	545	150	214
Na, µg/g	94,400	108,000	83,000	175,000	37,500	73,500	130,000	158,000	110,000	105,000
Ni, µg/g	20.8	1550	56.4	256	1600	129	9330	8800	84.1	14,300
U, µg/g	1990	20,400	1460	794	616	75,000	1650	30,500	10,900	34,700
^{239,240}Pu, µCi/g	0.0903	0.186	0.116	0.704	1.52	0.0138	3.90	0.111	0.0235	0.231
^{239,240}Pu, µg/g[a]	1.27	2.61	1.63	9.87	21.3	0.193	54.7	1.56	0.329	3.24

Absorber Element	Pu/Absorber Mass Ratio, g/kg										
	Target[b]	**1C**	**1C FeCN**	**2C**	**A1 SltCk**	**CWP2**	**MW**	**P2**	**PFeCN**	**TBP**	**TFeCN**
Al	0.638	0.0817	0.294	0.809	0.410	0.160	NA	1.40[c]	0.0492	0.149	0.108
Cr	6.28	1.53	1.85	1.27	2.19	54.2[c]	0.082	26.3[c]	0.869	2.44	11.8[c]
Fe	5.18	0.116	0.0872	0.1	30.7[c]	0.87	0.0362	0.377	0.0515	0.0154	0.146
Mn	25.5	15	1.79	18.3	182[c]	18.1	0.220	9.25	2.86	2.20	15.1
Na	2.47	0.0134	0.0241	0.0196	0.0564	0.568	0.00263	0.421	0.00985	0.003	0.0308
Ni	9.68	60.9[c]	1.68	28.8[c]	38.6[c]	13.3[c]	1.50	5.86	0.177	3.92	0.226
U	3.70	0.638	0.128	1.12	1.24	34.6[c]	0.00257	33.2[c]	0.0511	0.0302	0.0934

a The specific activity of plutonium, 0.0713 Ci ^{239,240}Pu/g total Pu, is based on 0.93 g of ^{239}Pu and 0.06 g of ^{240}Pu per g of total Pu and the specific activities of the two isotopes – 0.06203 Ci ^{239}Pu/g ^{239}Pu and 0.2269 Ci ^{240}Pu/g ^{240}Pu (BNL 2000).
b Calculated from Table 4-2 of Miles (2009).
c In shaded cells, measured Pu:Absorber mass ratio exceeds criticality safety target.

For example, for the saltcake waste type “A1SltCk” in Table 4-2, the plutonium-to-absorber mass ratios are individually insufficient for iron, manganese, and nickel but are individually sufficient for aluminum, chromium, and sodium. Because criticality control strategies rely on not just individual absorbers but combinations of absorptive elements, criticality safety is enhanced by summing the elements’ neutron absorption contributions.

While consideration of broad tank-wide or waste type-wide compositions is of interest, phenomena that can alter the plutonium-to-absorber ratio under narrower and more specific conditions must be considered. For example, the waste type distributions within each tank over time are not guaranteed. This situation is demonstrably true for those tanks which have undergone or are scheduled to undergo sluicing and retrieval, i.e., virtually all tanks, as well as for the corresponding tanks that receive the retrieved wastes. Also, compositions for a certain waste type within a waste tank may not be spatially homogeneous due to differential particle growth or settling. The most obvious example is for sodium. Most sodium is present in the form of salts having moderate to high solubility. These salts are subject to crystal growth and ripening, and can form millimeter- to centimeter-scale particles that exclude the aqueous solution, and particularly the sludge solids that are generally richer in plutonium concentrations. Sodium salts also can form crusts at the air-waste interface because of water evaporation as well as by flotation of salt crystals by gases formed in the waste. At the other extreme, the high solubility of most sodium salts means that sluicing and its attendant dilution can partition sodium to the solution phase and decrease its concentration relative to the low-solubility plutonium. Therefore, sodium salt crystallization, salt crust formation by evaporation aided by flotation to the waste-air interface, and high sodium salt solubility challenge the utility of crediting sodium as a neutron absorber for low-solubility and finely particulate plutonium even though sodium is ubiquitous in tank waste and its concentration generally is high.

4.2 Neutron Absorber Concentrations in Tank Wastes

Neutron absorbers in the waste prevent criticality if present in sufficient concentration and proximity to the fissile material. Neutron absorbers in the Hanford tank waste originate from the processes and were introduced as chemicals, as part of the feed, or were added specifically as criticality safety controls, as well as in the fuel itself (for uranium). There are several questions related to the form of the absorbers and fissile materials.

For this discussion the fissile material is primarily ^{239}Pu, ^{241}Pu, ^{233}U, and ^{235}U. The safety and disposition of the ^{233}U and ^{235}U fissile material within the Hanford tank waste system has been addressed by the isotopic dilution afforded by the abundant ^{238}U also present in the tank waste (Miles 2009). Therefore, considerations of criticality safety in the present discussions are limited to the plutonium isotopes.

Although many elements may serve as neutron absorbers in tank waste, discussion will focus on the absorbers aluminum, cadmium, chromium, iron, manganese, nickel, and uranium. While sodium is a poorer absorber and has relatively high solubility, its very high concentration and ubiquity in the waste make it worthy of consideration in criticality safety. The form of plutonium in the waste influences how absorbers interact with it. Those associations will be addressed in subsequent sections of the present document.

Figure 4-1 shows Hanford waste streams from separations processes (Bismuth Phosphate in the B and T Plants, REDOX in the S Plant, PUREX in the PUREX Plant, and Uranium Metal Recovery in the U Plant) and the amounts of iron, uranium, aluminum, and manganese neutron absorbers present relative to the amounts considered necessary to prevent criticality (Bratzel et al. 1996). The numbers within Figure 4-1 show the absorber-to-plutonium mass ratios in the waste streams of the various plants. The ratios required to maintain sub-criticality for the considered four absorber elements are shown in the lower left corner of Figure 4-1. There is at least one absorber present at levels higher than the subcritical ratios for absorber to plutonium in each of the major streams. Depending on the mechanism producing solids in the waste, plutonium and absorbers may be simple physical mixtures or there may be a chemical association that will prevent separation even during physical processes such as pumping or settling. However, physical mixtures with similar mechanical properties such as particle size and density may not be separable by normal waste handling operations.

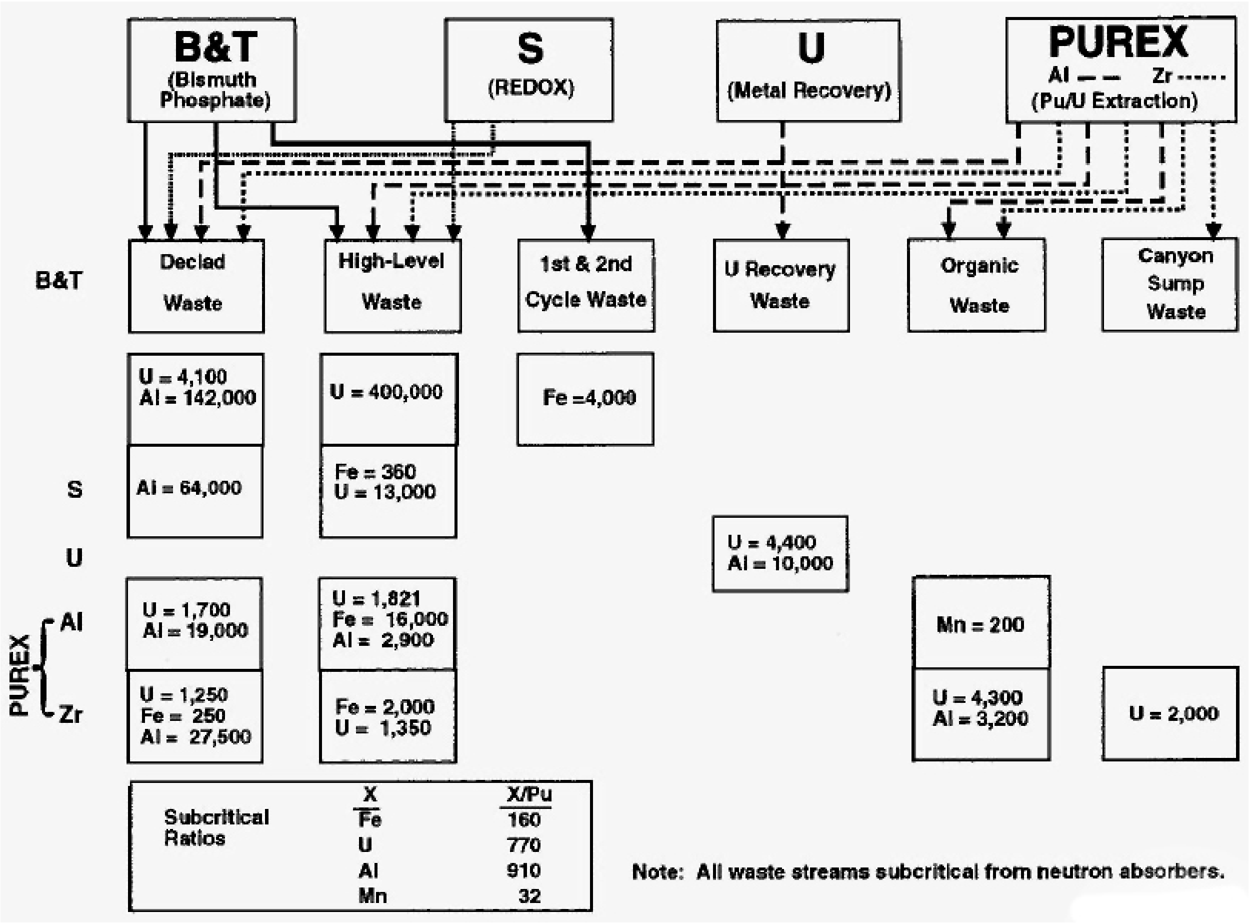

Figure 4-1. Neutron Absorber-to-Plutonium Mass Ratios Concentrations in Separation Process Waste Streams Based on the Flowsheet Compositions (Bratzel et al. 1996)

The Hanford Defined Waste (HDW) model is used to populate the BBI in TWINS. BBI values are from sample analyses (S), calculated based on another waste component (C), based on engineering information such as process knowledge or tank transfer mass balances (E), templates that may be either sample-based (TS) or model-based (TE) or any combination of these methods (Table 4-3). Tank waste volumes are based on measurements of the surface or records of tank transfers and process history.

Inventories are estimated when there are no sample data available for tank constituents. Estimates are based on the HDW model. The waste type templates in the HDW are based on sample data of what are considered representative samples and process knowledge. The analytes of concern in this document are the plutonium and uranium isotopes and the neutron absorbers aluminum, cadmium, chromium, iron, manganese, and total uranium.

Table 4-3. Bases of Tank Waste Inventory Estimates

Inventory Basis	Definition
S	Sample-based. Waste removed from tank has been analyzed and the values obtained are used as the basis for the tank inventory.
C	Calculation. Concentration of another related analyte is used to calculate the value.
E	Engineering-based values based of pre-1989 analytical results, process knowledge or estimates based on similarity to expected values in another tank.
TS or TE	Sample-based Templates (TS) or Model-based Templates (TE) are used when sample analyses and engineering values are not available.

The BBI values for tank waste contents were used to generate the waste vectors in the TFCOUP (CH2M Hill Hanford 2006) or the more recent data (Certa et al. 2011). For each of the waste streams, inventory values are assigned to a template for the composition of the waste. Templates were developed based on process flowsheets and sampling. Transfers into the tanks were assigned a source waste type and the concentrations of waste constituents were calculated as mathematical combinations of the waste. In Table 4-4, the inventory bases for several absorbers as well as fissile uranium and plutonium isotopes are tabulated. Most of the values come from tank sample results for the absorbers. The uranium and plutonium values are mostly by calculation. Often the calculation is a conversion from a sample result such as total alpha analysis to plutonium concentration based on a template.

Table 4-4. Survey of Inventory Bases for Absorbers and Fissile Material in BBI TWINS Database

Basis	**Number of Tanks**											
	Al	**Bi**	**Cd**	**Cr**	**Fe**	**Mn**	**^{233}U**	**^{235}U**	**^{238}Pu**	**^{239}Pu**	**^{240}Pu**	**^{241}Pu**
C							49	42	69	77	77	76
C/TE							57	56	42	44	44	45
C/TS									2			
C/TS/TE									1			
E	17	13	13	14	17	18	6	8	6	4	4	4
E/C							11	6	10	14	14	12
E/C/TE							4	2	2	6	6	4
E/TE	7	10		5	6	4	1	1	1	1	1	1
E/TS	5	3		4	5	8						
E/TS/TE	2	4		2	4	4			1			
S	57	21	38	61	47	41	3	7	5	3	3	3
S/C							1	4	3	1	1	3
S/E	20	14	46	21	20	20	3	7	6	1	1	2
S/E/C							1	1				
S/E/C/TE								2	2			2
S/E/TE	1	3		3		1			1			
S/E/TS	3	1		4	5	2						
S/E/TS/TE		1										
S/TE	11	24		7	7	14	1	2	1			

Basis	**Number of Tanks**											
	Al	**Bi**	**Cd**	**Cr**	**Fe**	**Mn**	**^{233}U**	**^{235}U**	**^{238}Pu**	**^{239}Pu**	**^{240}Pu**	**^{241}Pu**
S/TS	15	4		15	27	19						
S/TS/E		1				3						
S/TS/TE	3	10		2	1	2						
TE		15		3		1	40	39	24	24	24	24
TS	13	7		13	16	8						
TS/TE	23	46		23	22	32						

The ten tanks with highest plutonium inventory were selected for more detailed comparisons of the inventory basis. Iron was selected as representative of the absorbers and total plutonium for the fissile material (note that the bases listed in Table 4-4 were for isotopic plutonium and thus are more limited). In Table 4-5, the methods of arriving at inventory values of total plutonium and iron in these tanks are listed. The bases for total plutonium and iron values are mostly the same and there is some degree of estimation for all but one of the tanks (S-107).

Table 4-5. Source of Iron and Plutonium Inventory Values in the Ten Tanks with Highest Plutonium Values

Tank	**Fe Basis**	**Pu Basis**
241-SY-102	S/E/TS	E/C
241-TX-118	S/TS	S/TS
241-AN-101	S/E/TS	S/E/TS
241-C-102	E/TS/TE	E/TS/TE
241-AN-106	S/E/TS	S/E/TS
241-AY-102	S/E	S/E
241-AZ-102	E	E
241-S-107	S	S
241-AZ-101	S/E	S/E
241-A-106	E	E

For a given analyte in a specific phase of a given tank, variability may be observed due to inhomogeneity of the samples. Differences in waste may even result from sampling activities (such as collecting multiple samples and using a single riser producing liquid seepage to fill the hole or solids slumping or agitation of the waste by sampling apparatus). Additions or removals from the tanks were either through tank transfers or evaporation. Variances arise due to sample preparation in the laboratory/hot cells, analytical error, complex matrices, high dissolved solids in liquid, and high matrix concentration, primarily as NaOH, $NaNO_3$, and aluminum phases. Grab samples collected to monitor liquids for tank corrosion control show differences also can occur based on depth of sample collection indicating there is inhomogeneity even in the supernatant liquid.

How well the concentrations of plutonium and absorbers in the waste are known may be estimated by examining sampling analysis data results where duplicates of the sample were analyzed from a particular core sample or different core samples analyzed for a given sampling campaign comparing values obtained from samples collected at different times. Depending on the history of the tank and the types of waste accumulated in the tank, variability may be observed in the tank contents. Analytical variability is also observed depending on the methods used for the analyses. Variability in the distribution of plutonium and the absorber elements also will arise based on their dispositions within the primary tank waste types—supernatant solution, saltcake, and sludge. The volume inventories of these waste strata as of 2012 are shown in Table 4-6 and will change with continuing solution pumping and tank waste retrieval operations.

Table 4-6. Volumes of Waste Strata in Hanford Tank Farms

Tank	**Supernate**		**Saltcake**		**Sludge**		**Total**	
	kL	**kgal**	**kL**	**kgal**	**kL**	**kgal**	**kL**	**kgal**
A-101	0	0	878	232	11	3	889	235
A-102	12	3	106	28	0	0	118	31
A-103	17	4	1071	283	8	2	1096	290
A-104	0	0	0	0	106	28	106	28
A-105	0	0	0	0	139	37	139	37
A-106	0	0	110	29	189	50	299	79
AN-101	1414	374	90	24	1485	392	2989	790
AN-102	3483	920	584	154	0	0	4067	1074
AN-103	1769	467	1638	433	0	0	3407	900
AN-104	2298	607	1566	414	0	0	3864	1021
AN-105	2227	588	1925	509	0	0	4152	1097
AN-106	743	196	65	17	1615	427	2423	640
AN-107	3208	847	912	241	0	0	4120	1088
AP-101	4555	1203	126	33	0	0	4681	1237
AP-102	4212	1113	0	0	105	28	4317	1140
AP-103	4487	1185	198	52	0	0	4685	1238
AP-104	1546	408	378	100	0	0	1924	508
AP-105	4321	1141	396	105	0	0	4717	1246
AP-106	4291	1134	0	0	0	0	4291	1134
AP-107	4099	1083	0	0	0	0	4099	1083
AP-108	4290	1133	425	112	0	0	4715	1246
AW-101	2770	732	1403	371	0	0	4173	1102
AW-102	649	171	0	0	196	52	845	223
AW-103	2884	762	115	30	1060	280	4059	1072
AW-104	3070	811	451	119	370	98	3891	1028
AW-105	592	156	0	0	940	248	1532	405
AW-106	3304	873	1001	264	0	0	4305	1137
AX-101	0	0	1164	307	11	3	1175	310
AX-102	0	0	90	24	23	6	113	30
AX-103	0	0	298	79	30	8	328	87

Tank	Supernate		Saltcake		Sludge		Total	
	kL	kgal	kL	kgal	kL	kgal	kL	kgal
AX-104	0	0	0	0	28	7	28	7
AY-101	3224	852	0	0	398	105	3622	957
AY-102	2538	670	0	0	571	151	3109	821
AZ-101	3019	798	0	0	197	52	3216	850
AZ-102	3356	887	0	0	396	105	3752	991
B-101	0	0	232	61	106	28	338	89
B-102	15	4	81	21	0	0	96	25
B-103	0	0	157	41	4	1	161	43
B-104	0	0	192	51	1170	309	1362	360
B-105	0	0	919	243	106	28	1025	271
B-106	4	1	0	0	460	122	464	123
B-107	0	0	216	57	327	86	543	143
B-108	0	0	204	54	104	27	308	81
B-109	0	0	245	65	189	50	434	115
B-110	4	1	0	0	925	244	929	245
B-111	4	1	0	0	910	240	914	241
B-112	11	3	49	13	56	15	116	31
B-201	0	0	0	0	111	29	111	29
B-202	0	0	0	0	108	29	108	29
B-203	2	1	0	0	188	50	190	50
B-204	3	1	0	0	184	49	187	49
BX-101	0	0	0	0	180	48	180	48
BX-102	0	0	0	0	298	79	298	79
BX-103	50	13	0	0	235	62	285	75
BX-104	11	3	0	0	369	97	380	100
BX-105	18	5	94	25	160	42	272	72
BX-106	0	0	80	21	38	10	118	31
BX-107	0	0	0	0	1313	347	1313	347
BX-108	0	0	0	0	119	31	119	31
BX-109	0	0	0	0	730	193	730	193
BX-110	5	1	433	114	245	65	683	180
BX-111	0	0	538	142	121	32	659	174
BX-112	5	1	0	0	617	163	622	164
BY-101	0	0	1208	319	140	37	1348	356
BY-102	0	0	897	237	0	0	897	237
BY-103	0	0	1316	348	34	9	1350	357
BY-104	0	0	1208	319	172	45	1380	365

Tank	Supernate		Saltcake		Sludge		Total	
	kL	kgal	kL	kgal	kL	kgal	kL	kgal
BY-105	0	0	1481	391	181	48	1662	439
BY-106	0	0	1365	361	120	32	1485	392
BY-107	0	0	835	221	58	15	893	236
BY-108	0	0	587	155	151	40	738	195
BY-109	0	0	851	225	89	24	940	248
BY-110	0	0	1123	297	162	43	1285	339
BY-111	0	0	1378	364	0	0	1378	364
BY-112	0	0	996	263	8	2	1004	265
C-101	0	0	0	0	44	12	44	12
C-102	0	0	0	0	1196	316	1196	316
C-103	1	0	0	0	9	2	10	3
C-104	2	1	0	0	4	1	6	2
C-105	0	0	0	0	500	132	500	132
C-106	0	0	0	0	10	3	10	3
C-107	0	0	0	0	105	28	105	28
C-108	1	0	0	0	11	3	11	3
C-109	0	0	0	0	5	1	5	1
C-110	0	0	65	17	0	0	65	17
C-111	0	0	0	0	132	35	132	35
C-112	0	0	0	0	127	34	127	34
C-201	0	0	0	0	1	0	1	0
C-202	0	0	0	0	1	0	1	0
C-203	0	0	0	0	0	0	1	0
C-204	0	0	0	0	1	0	1	0
S-101	0	0	415	110	890	235	1305	345
S-102	9	2	219	58	71	19	299	79
S-103	4	1	647	171	34	9	685	181
S-104	0	0	451	119	500	132	951	251
S-105	0	0	1371	362	8	2	1379	364
S-106	0	0	1624	429	0	0	1624	429
S-107	0	0	145	38	1211	320	1356	358
S-108	0	0	2032	537	19	5	2051	542
S-109	0	0	1905	503	49	13	1954	516
S-110	0	0	994	263	364	96	1358	359
S-111	0	0	1028	272	245	65	1273	336
S-112	0	0	0	0	9	2	9	2
SX-101	0	0	959	253	545	144	1504	397

Tank	Supernate		Saltcake		Sludge		Total	
	kL	kgal	kL	kgal	kL	kgal	kL	kgal
SX-102	0	0	967	255	209	55	1176	311
SX-103	0	0	1516	400	294	78	1810	478
SX-104	0	0	1045	276	515	136	1560	412
SX-105	0	0	1061	280	238	63	1299	343
SX-106	0	0	1352	357	0	0	1352	357
SX-107	0	0	0	0	356	94	356	94
SX-108	0	0	0	0	280	74	280	74
SX-109	0	0	662	175	251	66	913	241
SX-110	0	0	28	7	184	49	212	56
SX-111	0	0	67	18	369	97	436	115
SX-112	0	0	0	0	283	75	283	75
SX-113	0	0	0	0	72	19	72	19
SX-114	0	0	84	22	478	126	562	148
SX-115	0	0	0	0	16	4	16	4
SY-101	3246	858	878	232	0	0	4124	1089
SY-102	1382	365	0	0	752	199	2134	564
SY-103	1444	381	1258	332	0	0	2702	714
T-101	0	0	179	47	140	37	319	84
T-102	48	13	0	0	72	19	120	32
T-103	15	4	0	0	87	23	102	27
T-104	0	0	0	0	1199	317	1199	317
T-105	0	0	0	0	371	98	371	98
T-106	0	0	0	0	82	22	82	22
T-107	0	0	0	0	655	173	655	173
T-108	0	0	30	8	20	5	50	13
T-109	0	0	197	52	0	0	197	52
T-110	3	1	0	0	1397	369	1400	370
T-111	0	0	0	0	1691	447	1691	447
T-112	27	7	0	0	226	60	253	67
T-201	8	2	0	0	107	28	115	30
T-202	0	0	0	0	77	20	77	20
T-203	0	0	0	0	136	36	136	36
T-204	0	0	0	0	136	36	136	36
TX-101	0	0	39	10	277	73	316	83
TX-102	0	0	692	183	8	2	700	185
TX-103	0	0	463	122	0	0	463	122
TX-104	9	2	93	25	130	34	232	61

Tank	Supernate		Saltcake		Sludge		Total	
	kL	kgal	kL	kgal	kL	kgal	kL	kgal
TX-105	0	0	2020	534	42	11	2062	545
TX-106	0	0	1147	303	19	5	1166	308
TX-107	0	0	86	23	0	0	86	23
TX-108	0	0	415	110	23	6	438	116
TX-109	0	0	0	0	1358	359	1358	359
TX-110	0	0	1580	417	140	37	1720	454
TX-111	0	0	1194	315	163	43	1357	358
TX-112	0	0	2290	605	0	0	2290	605
TX-113	0	0	2045	540	351	93	2396	633
TX-114	0	0	1923	508	15	4	1938	512
TX-115	0	0	1960	518	30	8	1990	526
TX-116	0	0	1903	503	248	66	2151	568
TX-117	0	0	2211	584	110	29	2321	613
TX-118	0	0	796	210	0	0	796	210
TY-101	0	0	159	42	273	72	432	114
TY-102	0	0	199	53	0	0	199	53
TY-103	0	0	150	40	390	103	540	143
TY-104	5	1	0	0	163	43	168	44
TY-105	0	0	0	0	874	231	874	231
TY-106	0	0	0	0	62	16	62	16
U-101	0	0	0	0	87	23	87	23
U-102	4	1	954	252	163	43	1121	296
U-103	2	1	1247	329	42	11	1291	341
U-104	0	0	0	0	205	54	205	54
U-105	0	0	1050	277	121	32	1171	309
U-106	6	2	484	128	0	0	490	129
U-107	0	0	946	250	57	15	1003	265
U-108	0	0	1376	364	110	29	1486	393
U-109	0	0	1112	294	103	27	1215	321
U-110	0	0	0	0	665	176	665	176
U-111	0	0	629	166	98	26	727	192
U-112	0	0	0	0	172	45	172	45
U-201	4	1	0	0	11	3	15	4
U-202	4	1	0	0	10	3	14	4
U-203	4	1	0	0	9	2	13	3
U-204	4	1	0	0	7	2	11	3

To evaluate the homogeneity of the distribution of plutonium within Hanford tank waste, an assessment of that distribution within tank 241-AN-101 was performed. Tank AN-101 has the third highest inventory of plutonium of all the tanks at Hanford. Approximately 60 kg of plutonium is distributed in waste that is described as saltcake, sludge, and the interstitial liquid within the saltcake and sludge layers; these wastes arise from 12 different processes or sources (Rasmussen 2013). See Table 4-1 for waste type definitions and process sources. Figure 4-2 graphs the liquid portion of the waste for the contributing four waste sources and Figure 4-3 shows the relative amounts of plutonium and iron in the solid waste for the twelve contributing waste sources. Most of the plutonium and iron is found in sludge and saltcake solids. The bases for these values are mostly engineering estimates and templates. The relative standard deviation (RSD) for iron determinations are about 0.07 to 1.4 percent. The highest ratio of ^{239}Pu to iron is 1.92 g/kg. Taking into consideration the other isotopes of plutonium, the plutonium-to-iron ratio is slightly higher than 2 and still well below the plutonium/metals criticality safety limit value of 6.2 for iron. If washing the waste dissolves saltcake, the plutonium and iron could remain with the sludge in the tank with an increase in plutonium concentration per unit volume of waste, but the ratio of plutonium to iron is not expected to change significantly.

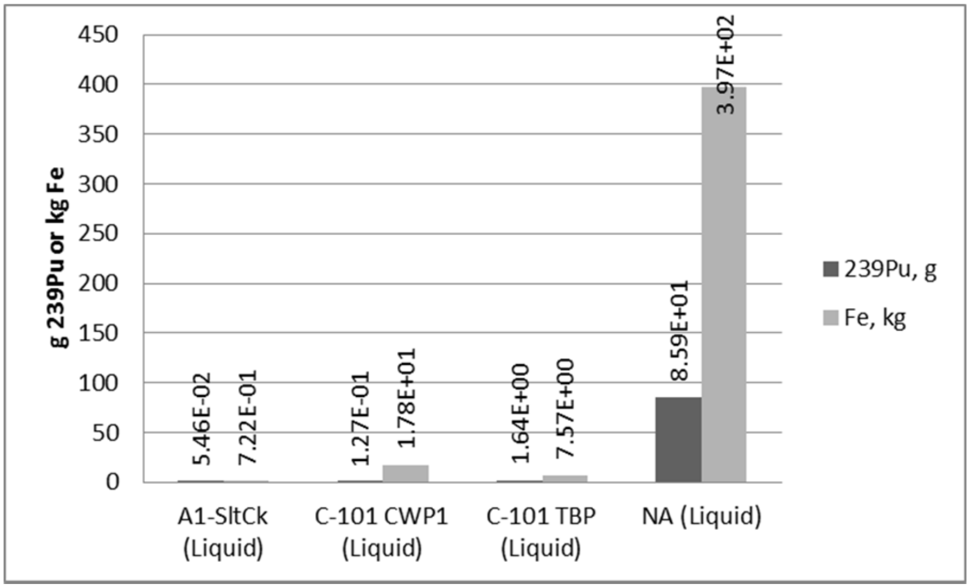

Figure 4-2. Distribution of Plutonium and Iron in Tank 241-AN-101 Liquids

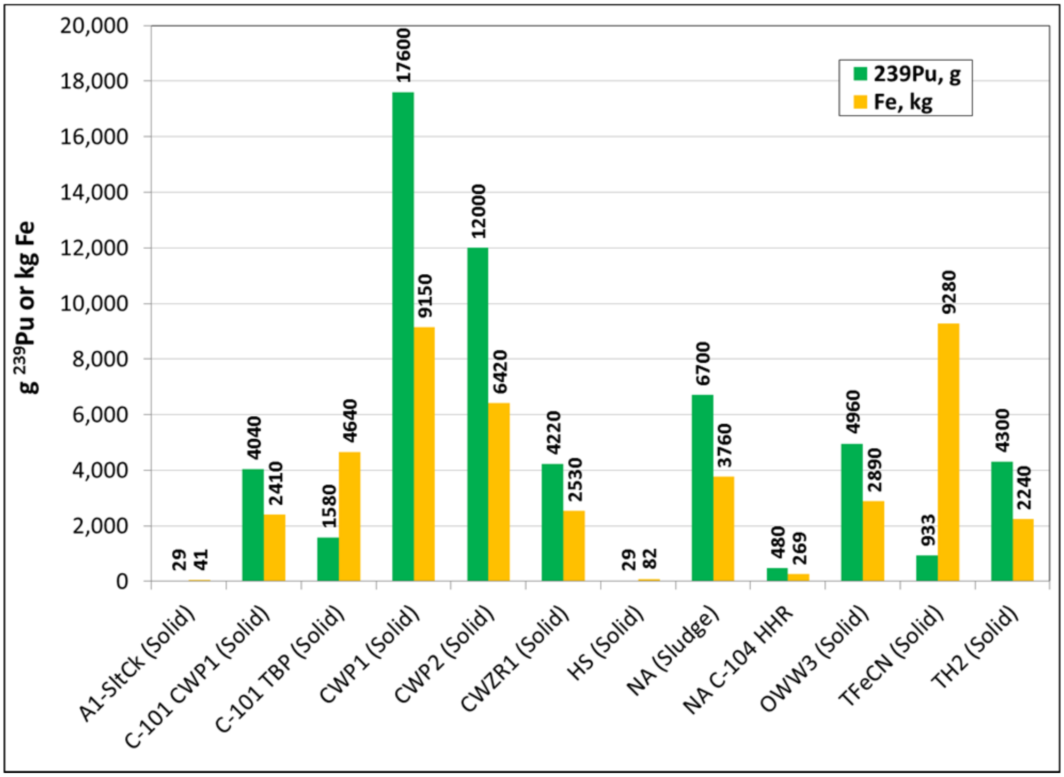

Figure 4-3. Distribution of Plutonium and Iron in Tank 241-AN-101 Solids

Tank 241-AN-101 contents have multiple phases and the tank has received waste from more than one process. The inventory basis varies for the waste phase and inventory constituent. The relative ^{239}Pu and iron inventories in the twelve waste types that constitute the tank 241-AN-101 contents, summarized in Table 4-7, show the variability of the ^{239}Pu/Fe ratios for these various waste contributors.

Table 4-7. Tank 241-AN-101 Inventory for Plutonium and Iron in Solids and Liquids

Waste Phase	Waste Type [a]	^{239}Pu, g	Fe, kg	Inventory RSD, %	Pu Basis [b]	Fe Basis [b]	^{239}Pu/Fe, g/kg
Saltcake Solid	A1-SltCk (Solid)	2.93E+01	4.14E+01	1.39	TE	TS	0.71
Sludge Interstitial Liquid	C-101 CWP1 (Liquid)	1.27E-01	1.78E+01	0.16	C	S	0.01
Sludge Solid	C-101 CWP1 (Solid)	4.04E+03	2.41E+03		C	E	1.68
Sludge Interstitial Liquid	C-101 TBP (Liquid)	1.64E+00	7.57E+00	0.067	C	S	0.22
Sludge Solid	C-101 TBP (Solid)	1.58E+03	4.64E+03		C	E	0.34
Sludge (Liquid & Solid)	CWP1 (Solid)	1.76E+04	9.15E+03		E	E	1.92
Sludge (Liquid & Solid)	CWP2 (Solid)	1.20E+04	6.42E+03		E	E	1.87

Waste Phase	Waste Type [a]	^{239}Pu, g	Fe, kg	Inventory RSD, %	Pu Basis [b]	Fe Basis [b]	^{239}Pu/Fe, g/kg
Sludge (Liquid & Solid)	CWZR1 (Solid)	4.22E+03	2.53E+03		E	E	1.67
Sludge (Liquid & Solid)	HS (Solid)	2.93E+01	8.22E+01		E	E	0.36
Supernatant	NA (Liquid)	8.59E+01	3.97E+02	0.049	C	S	0.22
Sludge (Liquid & Solid)	NA (Sludge)	6.70E+03	3.76E+03		E	E	1.78
Sludge (Liquid & Solid)	NA C-104 HHR	4.80E+02	2.69E+02		E	E	1.78
Sludge (Liquid & Solid)	OWW3 (Solid)	4.96E+03	2.89E+03		E	E	1.72
Sludge (Liquid & Solid)	TFeCN (Solid)	9.33E+02	9.28E+03		E	E	0.10
Sludge (Liquid & Solid)	TH2 (Solid)	4.30E+03	2.24E+03		E	E	1.92
Saltcake Interstitial Liquid	A1-SltCk (Liquid)	5.46E-02	7.22E-01	1.30	TE	TS	0.08
Total		5.70E+04	4.41E+04		E/C/TE	S/E/TS	1.29

a See Table 4-1 for Hanford Defined Waste Type definitions.
b See Table 4-3 for inventory estimate bases descriptions.
AN-101 Tank 241-AN-101
C-101 Tank 241-C-101
HHR Hard-to-remove Heel Retrieval
NA No available waste type
RSD Relative standard deviation

4.3 Fissile Uranium

From the BBI in TWINS (PNNL n.d.), the uranium in the waste tanks ranges from a slightly enriched 0.87% to a slightly depleted 0.67% ^{235}U compared with natural enrichment of 0.71%. Most of the uranium in the tanks is ^{238}U, but there is an inventory of the fissile isotopes ^{233}U and ^{235}U. The CSL for uranium mandates that the ratio of $U_{fissile}$ to U_{total} must be less than 8.4 g/kg. All but four of the tanks are below this limit. The ratios of $U_{fissile}$ to U_{total} for tanks 241-AW-102, 241-AW-103, 241-AW-105 and 241-AZ-101 of 8.43, 8.50, 8.58 and 8.68 g/kg respectively, exceed the 8.4 g/kg CSL. Initial consideration of fissile uranium is included here for completeness, but further consideration is beyond the scope of the present study.

4.4 Absorber Compounds Observed and Postulated in Tank Wastes

To understand the potential behaviors of the absorber elements in waste processing, it is useful to know the compositions and properties of their compounds as present in the tank wastes. In Section 3.2.3 of their report, Wells et al. (2011) critically examined tank waste characterization data to identify elemental combinations and compounds present in the tank wastes. A more detailed critical review of the solid phases found in tank wastes also was prepared (Harrington 2011); however, no information on cadmium phases was gathered in either review. In addition to materials and compounds containing just one of the absorber elements, mixed absorber metal materials also have been observed in Hanford tank wastes including the following combinations: aluminum-chromium, iron-chromium-nickel-manganese, iron-lead, iron-bismuth-phosphorus, iron-zirconium, and others—that include one or more of the absorber elements.

The following synopsis of analyses of various washed tank waste solid types done using scanning and transmission electron microscopies (SEM and TEM) and energy dispersive spectroscopy (EDS) are illustrative (Wells et al. 2011 and citations therein; Harrington 2011). It is seen that while some crystalline materials are identified, many of the solids are amorphous.

- High-bismuth bismuth phosphate sludge: iron was a major part of the washed solids but no crystalline iron phases identified. Hydrous Fe(III) phosphate, $BiFeO_3$, and small amounts of $BiPO_4$ were found.
- High-phosphate bismuth phosphate saltcake: sodium, aluminum, silicon, and phosphorus association attributed to cancrinite (a sodium aluminosilicate) with entrained sodium hydrogen phosphate.[1] Some aluminosilicates incorporated chromium and iron. Chromium, calcium, uranium, and iron were widely dispersed, suggesting their presence as oxides or hydroxides while separate iron and uranium particles also were observed.
- High-aluminum PUREX cladding sludge: Minimal amorphous material present in the washed solid; most elements were found in separate particles, not mixed. Zirconium was an exception and found associated with uranium and iron with variable zirconium-to-uranium ratio.
- High-aluminum REDOX cladding sludge: Washed solids were primarily gibbsite, $Al(OH)_3$. Some agglomerate particles contained phase mixtures. One particle was mixture of an amorphous iron compound, Ca-U oxide, and cancrinite. Another material showed aluminum, silicon, lead, iron, calcium, uranium, chromium, manganese, and phosphorus. It is unclear whether the uranium-bearing phases also contained other elements.
- High-aluminum REDOX sludge: Mixed phases not discussed but ~60% of the chromium phase was apparently entrained in boehmite, AlOOH, based on parallel aluminum and chromium leach behavior.
- High-chromium REDOX saltcake: Washed solids described as mixed amorphous aluminum-chromium agglomerate with small particle chromium scattered throughout the matrix. Iron and manganese often present at the same discrete locations as chromium.
- TBP sludge: Many washed solid particles formed agglomerates of oxygen, sodium, aluminum, phosphorus, calcium and iron. Gibbsite, $Al(OH)_3$, found in separate particles. A fine iron-calcium phosphate found attached to larger crystals rich in iron and uranium. Iron and uranium phosphates separate in some cases and mixed in others.
- FeCN (ferrocyanide) sludge: Washed solid particles formed multi-component agglomerates with a range of particle densities, sizes, and morphologies. Major elements were oxygen, aluminum, and iron, with calcium, sodium, silicon, phosphorus, uranium, nickel, and sometimes strontium and bismuth present in smaller proportions. iron oxide, uranium oxide, strontium phosphate, and iron-nickel phases found.

---

[1] Cancrinite and the related sodalite are tectosilicates of nominal formula $M_8[AlSiO_4]_6(X)_2$ in which M represents an alkali metal ion such as sodium and X represents an anion such as nitrate. Cancrinite and sodalite have framework three-dimensional open cage and/or channel structures akin to zeolites. These open structures accommodate salts such as sodium nitrate and thus direct sodium, ordinarily present in solution as a soluble salt, to low-solubility aluminosilicate phases both as contained enclathrated salt MX and as a charge-balancing counterion in the aluminosilicate framework. Salts of alkaline earth (e.g., calcium) metal ions also may be enclathrated.

Wells et al. (2011); see their Table 3.6 also listed non-salt crystalline solid phases expected based on tank waste compositions and interpreted the thermodynamic software program ESP[1] and compared them with phases, both crystalline and amorphous, actually observed in tank characterization using x-ray diffractometry (XRD, for crystalline phases) and elemental analyses by EDS. Table 4-8 shows the crystalline phases predicted by ESP (Wells et al. 2011) and the solids, both crystalline and amorphous, observed for the absorber elements aluminum, chromium, iron, manganese, nickel, and uranium (abstracted from the review by Harrington (2011) and for plutonium ((Callaway III and Cooke 2004; McCoskey and Cooke 2013); and inferences drawn from analyses of Z-9 crib sediments by Ames (1974) and Price and Ames (1975)). In general, a greater diversity of phases is observed in characterizing the washed sludge than is predicted based on ESP, and some phases predicted by ESP have not been observed. These differences can have several sources, including inadequacies of the model, difficulties in attaining thermodynamic equilibrium in the wastes, artificially introducing phases during preparation of samples for characterization, and the limited cross-section of tank wastes that have been subject to characterization efforts. Sodium is not listed because most sodium compounds in tank wastes, except cancrinite and other alkali aluminosilicates, are water soluble salts and thus would separate themselves from the low-solubility plutonium phases by simple washing. Wells et al. (2011) and Harrington (2011) provided no phase information for cadmium, but potential phases include $Cd(OH)_2$, CdO, and $CdCO_3$ (Dirkse 1986; Rai et al. 1991b; Rai et al. 1991a). Additional phases expected for plutonium are discussed in the following section of the present report.

---

[1] Environmental Simulation Program, OLI Systems, Inc.

Table 4-8. ESP-Predicted and Observed Non-Salt Compounds (Wells et al. 2011; Harrington 2011)

Element	ESP-Predicted Phases (Wells et al. 2011)	Phases Observed by XRD (Table 2-1 of Harrington 2011)	Element Combinations Observed by SEM/EDS (Table 5-1 of Harrington 2011)
Al	$Al(OH)_3$ $(NaAlO_2)_2 \cdot 2.5H_2O$ $NaAlCO_3(OH)_2$ $NaAlSiO_4$ $KAlSiO_4$	$Al(OH)_3$ $Al(OH)_3 \cdot 3H_2O$ Al(O)OH, diaspore and boehmite AlOOH $(Al_2O_3)_x \cdot (H_2O)_y$ $Al_{45}O_{45}(OH)_{45}Cl$ $NaAl(OH)_4$ $NaAlO_2$ $Ca_3Al_2(OH)_{12}$, katoite $Ca_3Al_2O_6$ $AlPO_4$ Na_3AlF_6, cryolite $Na_6Ca_2Al_6Si_6O_{24}(NO_3)_2$, cancrinite $Na_8(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O$, cancrinite $Na_{10}Al_6Si_6O_{24}(CO_3)_2$, cancrinite $Na_{96}Al_{96}Si_{96}O_{384}(H_2O)_{216}$, cancrinite $Na_6Ca_{1.5}Al_6Si_6O_{24}(CO_3)_{1.6}$, cancrinite $Na_6(Al_6Si_6O_{24})(CaCO_3)(H_2O)_2$, cancrinite $Na_7Al_5Si_7O_{24}(CO_3) \cdot 2H_2O$, cancrinite $KAl(Al,Si)_3O_8$, feldspar $KMg_3(Si_3AlO) \cdot 10H_2O$, phlogopite $Na_2Al(CO_3)(OH)_2$, dawsonite $Bi_{24}Al_2O_{39}$ Al/Cr salts $(Ca,Sr)_3(Cr,Al)_2(OH)_{12}$, hydrogarnet / hydrouvarovite $Ca_3(Cr,Al)_2(OH)_{12}$, hydrouvarovite $Na_2Fe_2Al(PO_4)_3$, ferrowyllieite	Na-Al-Zr Al-Si Na-Al-Si Al-Si-O Na-Al-F Ni-Al-O Na-Al-Fe-Mn-Bi-U Al-Na-O Al-Na-O-P Al-Na-O-P-F Cr-$Al(OH)_3$ Ca-Al-Cr-O Fe-Al-Pb-P Ni-(U)-Al-P
Cr	CrOOH	$Cr(OH)_3$ Cr(O)OH, grimaldiite $Ca_3Cr_2(OH)_{12}$ $Bi_{38}CrO_{60}$ Al/Cr salts $(Ca,Sr)_3(Cr,Al)_2(OH)_{12}$, hydrouvarovite $Ca_3(Cr,Al)_2(OH)_{12}$, hydrouvarovite $(Ca,Sr)_3(Cr,Al)_2(OH)_{12}$, hydrogarnet / hydrouvarovite $FeCr_2O_4$ $Fe(Fe,Cr)_2O_4$ Mn_2CrO_4 $Mn_{1.5}Cr_{1.5}O_4$	Ca-Cr-O Cr-PO4 Cr-Bi-O Cr-$Al(OH)_3$ Ca-Al-Cr-O Cr-$Fe(OH)_3$
Fe	FeOOH	Fe_2O_3 γ-Fe_2O_3, maghemite Fe(O)OH α-Fe(O)OH Fe(O)(OH) $Fe(OH)_3$ $FeFe_2(PO_4)_2(OH)_2$, barbosalite $FeTiO_3$, ilmenite $Fe_2Bi(SiO_4)_2(OH)$	Fe oxide Fe-Si Zr-Fe-O Bi-Fe-O Fe-Bi-Si-OH Bi, Fe phosphate Na-Bi-Fe-P Fe-Al-Pb-P Fe, Mn oxide

Element	ESP-Predicted Phases (Wells et al. 2011)	Phases Observed by XRD (Table 2-1 of Harrington 2011)	Element Combinations Observed by SEM/EDS (Table 5-1 of Harrington 2011)
		Bi/$FePO_4$ $Bi_{36}Fe_2O_{57}$ $Na_2Fe_2Al(PO_4)_3$, ferrowyllieite $FeCr_2O_4$ $Fe(Fe,Cr)_2O_4$ Fe_2MnO_4, jacobsite $(Mn,Fe)_3O_4$ Mn/Fe(O)OH $FeMnO_4$ $MnFe_2(PO_4)(OH)_2{\cdot}8H_2O$ $Fe_{1.75}Mn_{0.25}O_3$	Na-Al-Fe-Mn-Bi-U
Mn	$Mn_3(PO_4)_2$ $Mn(OH)_2$ $MnCO_3$	Mn_2MnO_4, hausmannite $MnCO_3$, rhodochrosite $MnC_2O_4{\cdot}2H_2O$, lindbergite $Na_2MnPO_4CO_3$, sidorenkite Mn_2CrO_4 $Mn_{1.5}Cr_{1.5}O_4$ Fe_2MnO_4, jacobsite $MnFe_2(PO_4)(OH)_2{\cdot}8H_2O$ Mn/Fe(O)OH $Fe_{1.75}Mn_{0.25}O_3$ $FeMnO_4$ $(Mn,Fe)_3O_4$	Fe, Mn oxide Na-Al-Fe-Mn-Bi-U
Ni	$Ni(OH)_2$ $NiC_2O_4{\cdot}2H_2O$ $Ni_3(PO_4)_2$	$Ni(OH)_2$ NiOOH $Ni_3O_2(OH)_4$	Ni-Al-O Ni-(U)-Al-P
U	$Na_2U_2O_7$	UO_3 $UO_3{\cdot}H_2O$ $UO_3(H_2O)$ UO_2 or U_3O_8; U_3O_8 may be artifact [a] β-U_3O_8; U_3O_8 may be artifact [a] $Na_2U_2O_7$ $Na_2U_2O_7{\cdot}6H_2O$ $Na_2((UO_2)O)(OH){\cdot}H_2O$ $Na_4(UO_2)(CO_3)_3$, cejkaite $Na[(UO_2)O(OH)]H_2O_{0\text{-}1}$, clarkeite CaU_2O_7 $Na(UO_2)(PO_4)_2{\cdot}6H_2O$	U-O U-PO_4-H_2O U-PO_4 Na-U-O Ni-(U)-Al-P Na-Al-Fe-Mn-Bi-U
Pu	$Pu(OH)_4$	PuO_2 [b]	Pu-O [b] Pu-Bi [b] Pu-Bi-P [b]

a - U_3O_8 may be an artifact caused by electron beam alteration from the transmission electron microscope (page 7 of Harrington 2011).

b - Plutonium phases and elemental associations for tank wastes (Callaway III and Cooke 2004; McCoskey and Cooke 2013) and inferences drawn from analyses of Z-9 crib sediments (Ames 1974; Price and Ames 1975).

4.5 Estimations of Uncertainty for Tank Waste Inventories

Estimates of the uncertainty for chemicals and radionuclides in the Hanford tank waste have been evaluated numerous times. Existing inventories provide the basis for planning, but the Waste Acceptance Criteria (WAC) and the Interface Control Document for Waste Feed (Slaathaug 2013) detail testing and criteria that must be met before the waste will enter into the WTP processes. Attempts were made to provide uncertainties for the plutonium and absorbers inventories in tank waste by examining actual samples collected and tank inventory records. However, such an assessment is far beyond the scope of the present review such that its goals would be better served by a separate investigation dedicated to that focus.

A better use of resources might be to determine what is required to minimize the uncertainties in samples that are obtained and analyzed for compliance with the WAC. A recently published report (Fountain et al. 2013) evaluated the current approach to staged feed sampling of HLW sludge to meet WAC for transfer from tank farms to the WTP. In their closing remarks they state:

"Finally, as an overall observation from this section, it must again be stressed that, as in the WAC Data Quality Objectives, decisions and confidence will all rest on actual sample results from the tank. In short, if sample means are well below action limits and variability is not too large, waste-acceptance decisions will be straightforward; however, as the sample mean approaches an action limit and/or variability is large, acceptance decisions become problematic. Hence, the ultimate outcomes and consequences associated with staged feed tank characterization and acceptance depends on actual sampling and analysis results."

Samples of actual waste will be analyzed and compliance with the WAC will be confirmed prior to any waste entering the WTP. The uncertainties in the values for species in the analyzed waste will be lower than what would be estimated from current knowledge. It is also worthwhile to note that the tank contents are still subject to change by tank-to-tank transfers, receipt of additional wastes, and chemical reactions within the tanks. Two of these chemical changes, oxidation of organics to form carbonate and absorption of atmospheric carbon dioxide, also to form carbonate, continue to occur. Both of these reactions diminish hydroxide concentrations, and in some cases, require addition of supplementary hydroxide in the form of sodium hydroxide solution to maintain corrosion control for the mild-steel–lined tanks. A cursory, and by no means critical, survey of the TWINS database of historical tank waste solution composition analyses going back to the 1980s shows sodium concentrations ranging from 0.2 to 16.2 M, hydroxide concentrations ranging from <0.02 to 8.1 M, and carbonate concentrations ranging from 0.005 to 1.4 M (PNNL n.d.). As will be seen in Section 5.0, this range of hydroxide and carbonate solution concentration has dramatic effect on plutonium solution concentrations.

5.0 Plutonium Speciation in Tank Wastes

Speciation of plutonium in alkaline media has been studied in the following contexts: early investigations within the Manhattan Project, including a study at Hanford that examined plutonium behavior in the alkaline metathesis of LaF_3 in the Bismuth Phosphate Process and in related systems (Hoekstra 1945), simulated Hanford Site tank waste and potential tank wastes, related simulated alkaline tank waste studies for the U.S. DOE's Savannah River Site, studies for nuclear waste repository alkaline systems, and investigations related to the discovery of heptavalent plutonium in alkaline solution conducted at the Institute of Physical Chemistry (IPC) of the USSR Academy of Sciences (Krot et al. 1977). In 1995, the chemistry of the transuranium elements and technetium in strongly alkaline media was reviewed by the IPC, now called the Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences (IPCE) (Peretrukhin et al. 1995). Much of the considerable work on the chemistry of the actinides in alkaline media done in the 1990s and 2000s by researchers at the IPC/IPCE was funded by the U.S. DOE and conducted to understand plutonium chemistry under conditions pertaining to the Hanford and Savannah River Site defense production tank wastes. Findings from the IPC/IPCE work and related studies of plutonium in Hanford tank waste and alkaline systems largely were captured within subsequent reviews (Barney and Delegard 1999; Clark and Delegard 2002).

The average plutonium concentration in the Hanford tank waste system is about 0.004 g/L or about 1.66×10^{-5} M based on 847 kg plutonium (PNNL n.d.) and tank waste volume of 2.13×10^{8} liters (Rodgers 2010). In an overview of tank waste analyses, Barney and Delegard (1999) showed plutonium concentrations in Hanford tank waste solutions ranging from about 10^{-9} to 10^{-5} M; i.e., much lower than the average concentration in tank waste. These values were derived from multiple analyses of the contents of 28 individual tanks of the 177 total. In the same overview, multiple analyses of sludge from 19 tanks ranged from 10^{-6} to 10^{-4} moles per kilogram for dry sludge (i.e., near or above the average tank waste concentration) while only about 10^{-6} to 10^{-7} moles of plutonium per kilogram dry saltcake was found, about a factor of 100 below the concentrations found in dry sludge. The lower plutonium concentrations in saltcake were attributed to the low expected Pu-salt interactions. It is noted, however, that the plutonium concentration projected in the A1SltCk waste type, 7×10^{-5} moles per kilogram of dry saltcake (Table 4-2), is similar to the upper plutonium concentration found in sludge (Higley et al. 2001).

Barney and Delegard (1999) authored an overview of plutonium concentration in Hanford tank waste solution and sludge, Figure 5-1, which shows the average concentrations and the concentration ranges seen for various tanks through multiple sample analyses. Surprisingly, the relative concentration scatter for the solution and sludge analyses are roughly similar despite the better homogeneity expected for the solutions. In general, the solutions are found to be less concentrated nearer the air-solution surface. This may be because of water evaporation and condensate cycling within the tank vapor space.

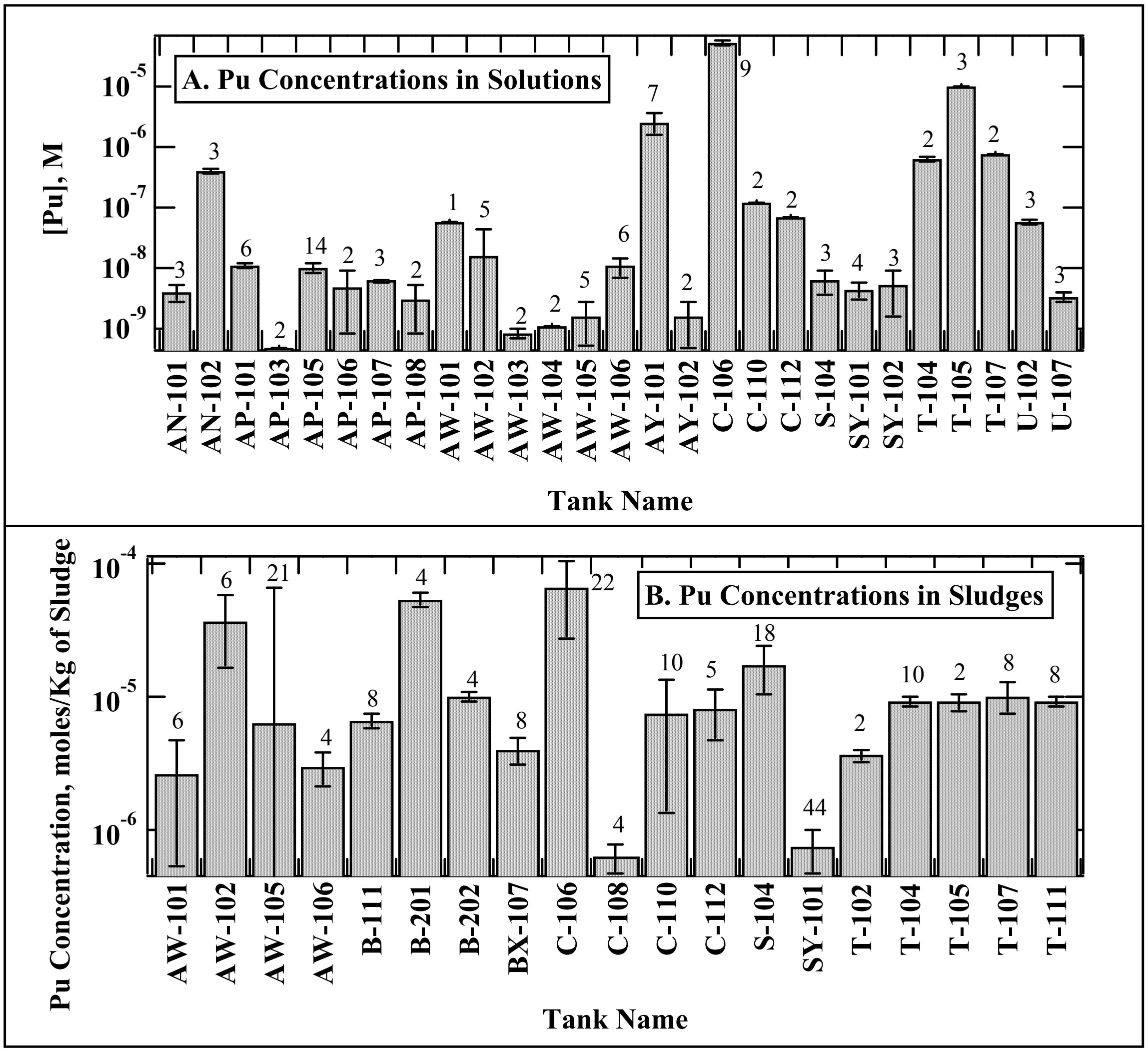

Figure 5-1. Plutonium Concentrations Measured in Tank Solutions, A, and Tank Sludges, B (Barney and Delegard 1999)

The efficiencies of the plutonium separations processes with respect to both recovery and to economy in process chemical usage, with resulting discards to waste, also affect plutonium concentrations in the tank wastes. Thus, plutonium process losses at Hanford decreased from 3% to 0.5% to 0.2% of throughput in the Bismuth Phosphate, REDOX, and PUREX processes, respectively (derived from Appendix G of Kupfer et al. (1999)). Parallel decreases in tank waste volumes for the three respective processes of ~30, 10, and 5 liters/kg uranium, as noted earlier in the report, mean that the global plutonium concentrations in the wastes over the three processes were approximately equal. The mean plutonium concentrations in Bismuth Phosphate Process waste were only about two times higher than those of the REDOX and PUREX Processes. The best-basis estimate of plutonium lost to the tank wastes is 672 kg (Kupfer et al. 1999) but conservative loss estimates range as high as 981 kg (Roetman et al. 1994). The BBI is the current standard for tank inventories. As of January 2014, the sum of plutonium in all tanks based on the BBI is 847 kg (PNNL n.d.).

Until recently, aside from concentration measurements, no definitive speciation of plutonium in Hanford tank wastes had been done, either within solid phases or in solution. However, in 2004, efforts were undertaken to determine if plutonium-rich particles existed in waste from tank SY-102 (Callaway III and Cooke 2004). In 2012, a similar investigation to find plutonium-rich particles in tank wastes re-examined wastes from tank SY-102 and also examined wastes from tanks TX-118 and AZ-101 as well as solids taken from the top layer of soil from the Z-9 crib (McCoskey and Cooke 2013). The SY-102 and TX-118 tanks are known to have received neutralized acid waste from the PFP and thus were suspected of containing particulate plutonium arising from incomplete acid digestions of plutonium-bearing scrap (e.g., refractory PuO_2 particles). The Z-9 crib likewise received pH-neutralized acid PFP wastes and was known to have received particulate PuO_2 based on prior analyses (Ames 1974; Price and Ames 1975). The wastes from AZ-101 were examined because they had high plutonium content but had not received PFP wastes. Significantly, plutonium-bearing particles were found for the tanks which received the PFP wastes and, as expected, in the previously analyzed Z-9 soils but not for the "control" solids from tank AZ-101. The findings from the recent studies will be examined further in Section 5.3 of this report, which deals with plutonium solid phases found in alkaline media and expected in Hanford tank waste.

5.1 Plutonium Oxidation States in Alkaline Media

Plutonium oxidation states from (III) to (VII) have been observed in alkaline media. Plutonium(VII) requires strong alkali and powerful oxidants to be prepared (Krot et al. 1977). The Pu(VI) and Pu(V) are more stable but less soluble in alkaline solution than they are in acid. The tetravalent (i.e., Pu(IV)) oxidation state is widely observed in the solid phase as $PuO_2{\cdot}xH_2O$, as shown in a subsequent section of this report. Trivalent plutonium is much more stable in acid than in alkali. Octavalent plutonium, Pu(VIII), with the electron configuration of radon, might be expected to exist, but attempts to prepare it in strong alkali, where it should be most stable, by chemical, electrochemical, and radiation-chemical oxidation methods were unsuccessful (Krot et al. 1972). Recent assertions of Pu(VIII) preparation in alkaline solution (e.g., Nikonov and Myasoedov (2010) and references therein) have not been universally accepted.

Plutonium(VII) is blue-green to black in solution and is identified by its distinctive electronic absorption spectrum, a broad π-f transition exhibiting fine structure with maximum absorbance (molar extinction coefficient, ε_{max}, of 595 l/mol·cm) at 635 nm in alkaline solution (Krot et al. 1977). Spectrophotometric measurements of Pu(VI) and Pu(V) are less sensitive and are completely ineffective for Pu(IV) and Pu(III) in strongly alkaline solution because of their extremely low solubilities and, for Pu(III), low stability. The Pu(VI) color reportedly changes from pale rose to lemon yellow to bright yellow as alkalinity increases above 0.1 M (Tananaev 1989) and is said to be green in NaOH solution (Bourges 1973). The spectrum of the light green Pu(VI) solution does not change between 2 and 10 M NaOH and shows broad peaks at 631 nm with ε_{max} of 15 l/mol·cm, 8 l/mol·cm at 880 nm, and 5 l/mol·cm at 925 nm (Budantseva et al. 1997). As seen in Figure 5-2, the spectra observed by Budantseva et al. (1997) at <2 M NaOH are much more intense than those found at >2 M NaOH. In similar tests but run under much more dilute plutonium conditions ($<2\times10^{-5}$ M plutonium versus $>5\times10^{-4}$ M plutonium for Budantseva et al. (1997)), it is seen that two broad peaks centered at 625 nm and 923 nm are found in 0.1 and 1 M NaOD (deuterated NaOH) with ε_{max} of ~17 l/mol·cm and ~8 l/mol·cm, respectively (Sinkov 2007). The spectra Sinkov (2007) observed in 0.1 M NaOD shown in Figure 5-2 more closely resemble the Pu(VI) spectrum for >2 M NaOH found by Budantseva et al. (1997) both in peak position and intensity. Although no distinct peak at ~870 nm was observed by Sinkov (2007), a shoulder in this region is found. The Pu(VI) spectrum found in acid solution at 800 to 1000 nm broadens, shifts to higher wavelength, and weakens in NaOH (Ray et al. 1988; Charyulu et al. 1991). Similar to the observations made by Budantseva et al. (1997), Tananaev (1989) observed a decrease in Pu(VI) peak intensity between 800 and 900 nm at >1 M NaOH and attributed the decrease to formation of the centrosymmetric $PuO_2(OH)_4^{2-}$ complex with the high symmetry of this complex hindering the *f*-*f* transitions needed to cause light absorbance to occur.

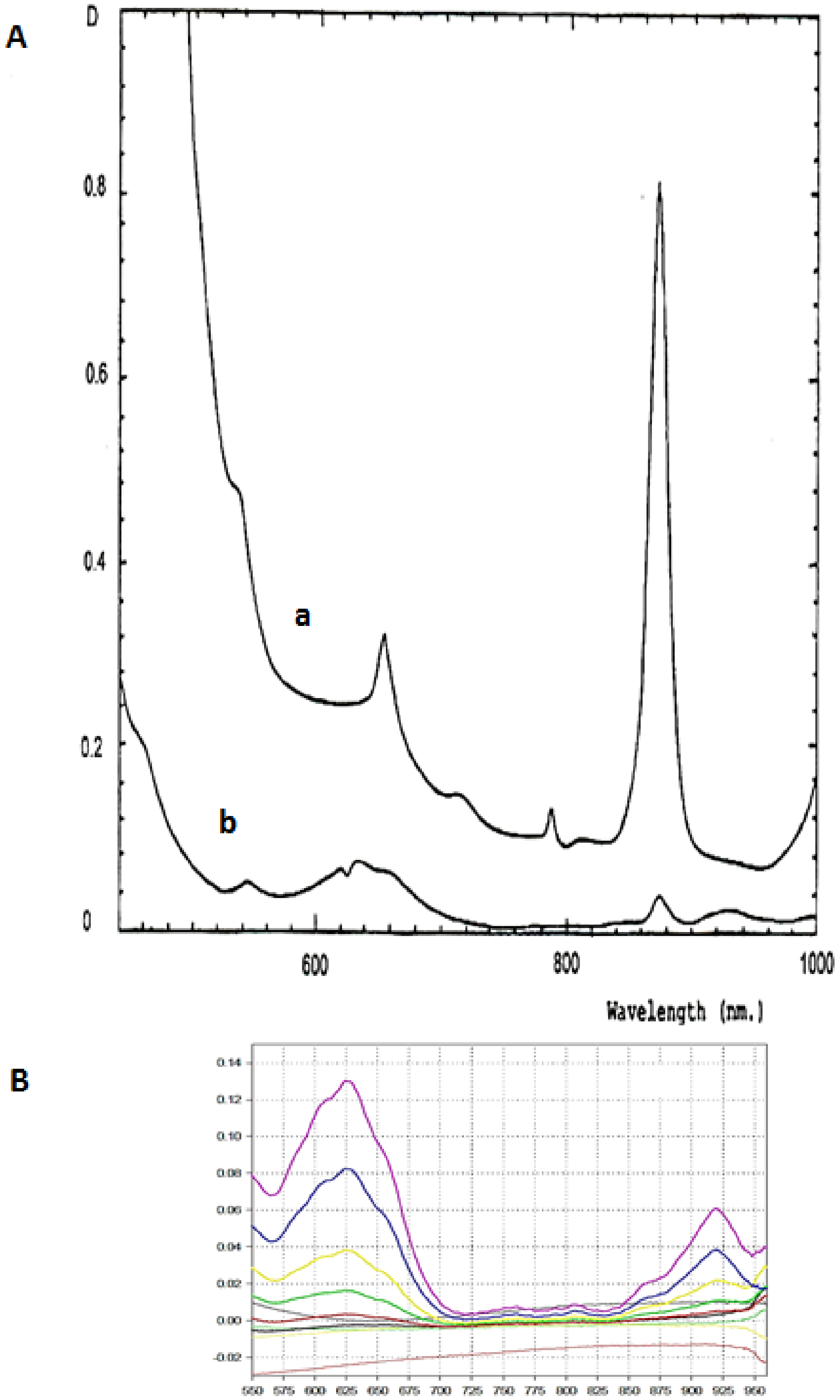

Figure 5-2. Plutonium(VI) Absorption Spectra. A: 5×10^{-3} M Pu(VI) in a: <2 M NaOH and b: >2 M NaOH (Budantseva et al. 1997). B: 0.53, 1.33, 2.66, 5.30, 10.5, and 15.6 µM Pu(VI) for black, red, green, yellow, blue, and pink spectral traces, respectively, in 0.1 M NaOD (Sinkov 2007).

Plutonium(V) in 4 M NaOH is reported to be pale yellow (Bourges 1972) or "flesh-colored" *[sic]* at higher concentrations (Budantseva et al. 1997). The Pu(V) absorbance spectrum shows a number of sharp but weak peaks related to those observed at pH 3 (Bennett et al. 1987) and 6 (Bourges 1972) with the peak observed at 568 nm practically disappearing as pH is raised to 8.89 (Bennett et al. 1987). The highly structured Pu(V) spectra observed in 4, 8, and 15 M NaOH (Bourges 1972; Budantseva et al. 1997; Delegard 1985b, respectively) and in 1 and 14 M NaOD dissolved in deuterium oxide, D_2O (as seen in Sinkov (2007) and in Figure 5-3 parts A through D, respectively), are similar. Dissolution of the plutonium in D_2O and NaOD allows long path-length optical cells to be used without the spectrum of dilute plutonium solutions being obscured by the light absorption of ordinary water. A distinctive "trident" peak pattern at 500, 530, and 550 nm (Bessonov et al. 1997) of intensity 8 to 13 l/mol·cm and similarly high peaks at 410, 450, 806, and 870 nm are observed. The small shifts in the 682- and 930-nm band locations in the 1 M NaOD when the NaOD concentration rises to 14 M indicate that the $Pu(V)O_2^+$ cation coordination sphere is practically saturated with hydroxide ligands in 1 M NaOD, with an increase to 14 M NaOD providing only a minor change in coordination (Sinkov 2007). The 0.811 mM Pu(V) in 14 M NaOD was measured with 1-cm cell (red trace). The 23.6-µM Pu(V) solution spectrum in 1 M NaOD was measured in a Liquid Waveguide Capillary Cell with 5-meter pathlength (blue trace). The latter spectrum was scaled down 35-fold to fit the vertical scale. The gray traces around red spectrum are single scans used for averaging to improve the signal-to-noise ratio in the Pu(V) stock solution spectrum.

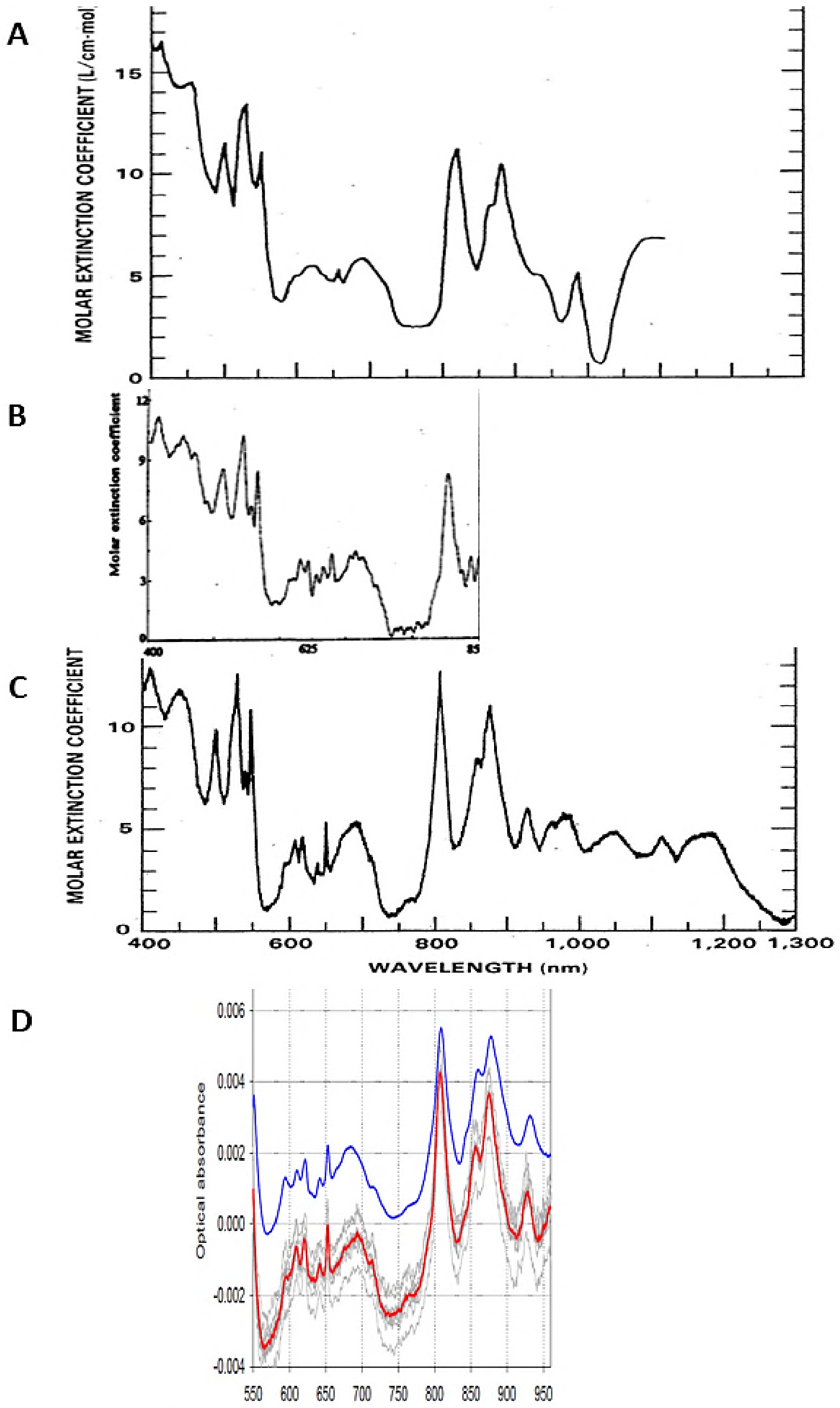

Figure 5-3. Plutonium(V) Spectra in NaOH Solutions.
A: 4 M NaOH (re-drawn from Bourges (1972)).
B: 8 M NaOH (Budantseva et al. 1997).
C: 15 M NaOH (Delegard 1985b).
D: 1 M NaOD, upper blue trace, and 14 M NaOD, lower red trace (see text for concentrations and experimental conditions) (Sinkov 2007).

Titration with oxidants or reductants can be used to identify and prepare particular plutonium oxidation states in alkaline solution. Thus, stoichiometric reduction of Pu(VII) to Pu(VI) is possible using H_2O_2 or KI (Krot et al. 1977) while ferricyanide can be used for stoichiometric titration of Pu(V) to Pu(VI) (Bourges 1973). Convenient preparation of Pu(V) can be accomplished by taking advantage of this oxidation state's great stability in alkaline solution and, likely, the effects of autoradiolysis. In parallel tests, separate aliquots of Pu(IV) and Pu(VI) in acid stock were added to 14.9 M NaOD, attaining 14 M NaOD. The solutions with precipitated plutonium solids then were sealed and stirred. After one week, Pu(V) peaks were observed; by 15 to 20 days, no further spectral changes were noted in either solution and the spectra were clearly Pu(V) for both solutions (Sinkov 2007).

Electrochemical techniques were used to study plutonium reduction potentials in 0.1 to 14 M NaOH (Peretrukhin and Alekseeva 1974; Peretrukhin and Spitsyn 1982). As shown in Figure 5-4, the 1982 findings for the Pu(VII)/Pu(VI)/Pu(V) systems generally agree with the prior findings of (Bourges (1972), 1973)). The potential of dissolved Pu(VI)/Pu(V) in 1 M NaOD, where NaOD is deuterated NaOH, is 0.145 V (Sinkov 2007). This value, ~0.088 V lower than the ~0.233 V value interpolated from the work of Peretrukhin and Spitsyn (1982), was partially attributed to neglect of liquid junction potentials in the latter tests. The Pu(VI)/Pu(V) couple is reversible, implying that the respective plutonium species have similar structures whereas the irreversible Pu(V)/Pu(IV) couple implies different structures (Bourges 1973; Peretrukhin and Spitsyn 1982). The electrochemical studies show Pu(VII) to be a sufficiently strong oxidant to convert water to oxygen gas in 0.1 to 14 M NaOH while other findings show that Pu(III) reduces water in 1 M NaOH (Cunningham 1954). Plutonium(III) certainly has little stability in 1 to 3 M KOH solution and is rapidly oxidized to Pu(IV) solids (Delegard 1987). Thus, in the absence of strong reductants or oxidants, respectively, neither Pu(III) nor Pu(VII) should be stable indefinitely in the molar NaOH solution present in most Hanford tank waste. Both dissolved chromate, CrO_4^{2-}, and precipitated $Cr(OH)_{3\ ppt}$ and other Cr(III) solid phases (Table 4-8) are observed together in Hanford tank waste while nitrate, NO_3^-, and nitrite, NO_2^-, are ubiquitous, being the third and fifth-most prevalent species in the tank waste inventory (Figure 3-1). Thus, the NO_3^-/NO_2^- and $CrO_4^{2-}/Cr(OH)_{3\ ppt}$ or $CrO_4^{2-}/CrOOH_c$ couples (potentials at 0.017, -0.12, and -0.01 volts, respectively, as in Bratsch (1989)) may control the tank waste redox potential absent supplemental perturbations (e.g., the oxidant permanganate, MnO_4^- / manganate, MnO_4^{2-} or MnO_4^{2-}/MnO_2, 0.56 and 0.51 volts, respectively, or radiolysis). If the nitrate/nitrite or chromium(VI)/chromium(III) couples, whose potentials, like those of plutonium, also decrease with increasing NaOH concentration or chemical activity, control the tank waste redox potential, Pu(IV) should be present in Hanford tank waste as shown in Figure 5-4.

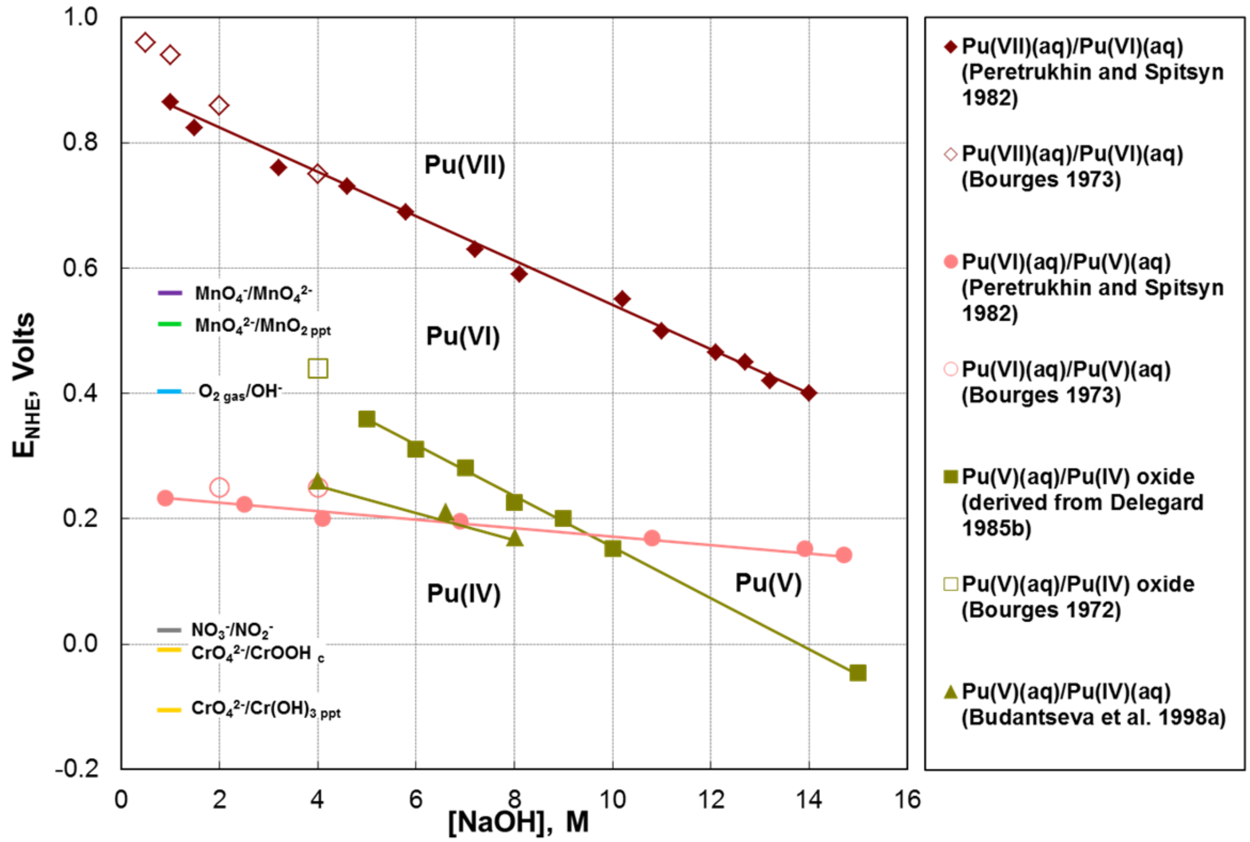

Figure 5-4. Plutonium Redox Potentials in NaOH Solution. [MnO_4^-/MnO_4^{2-}, $MnO_4^{2-}/MnO_{2\,ppt}$, $O_{2\,gas}/OH^-$, NO_3^-/NO_2^-, $CrO_4^{2-}/CrOOH_c$, and $CrO_4^{2-}/Cr(OH)_{3\,ppt}$ potentials at 1 M NaOH/pH 14 from Bratsch (1989)]

Lab tests show that chromate does not affect the redox behavior of Pu(V) in NaOD solution (Sinkov 2007). However, in 0.25 M NaOD, both manganate and permanganate rapidly oxidize dissolved Pu(IV) and Pu(V) to Pu(VI). Oxidative dissolution of $Pu(OH)_4$ [freshly precipitated plutonium(IV) hydrated oxide] solids also occurs with both manganate and permanganate in 0.25 M NaOD forming Pu(VI). Permanganate is more effective than manganate but permanganate suffers parasitic loss to water oxidation catalyzed on the plutonium solids (Sinkov 2007).

Several studies show that dissolved Pu(V) disproportionates at lower NaOH concentrations in agreement with predicted reduction potentials in 1 M hydroxide (e.g., Latimer (1952)). Thus, Pu(V) in 4 M NaOH disproportionates after three days to form a brown-green precipitate that was postulated to be hydrated Pu(IV) oxide and dissolved Pu(VI) while Pu(V) solution is stable for over a month in 12 M NaOH (Bourges 1973). Disproportionation of Pu(V) in 0.25 M NaOD also was observed (Sinkov 2007). This behavior is confirmed by reproportionation or synproportionation in which freshly precipitated hydrated Pu(IV) oxide solids were mixed with an equimolar (2×10^{-3} M) amount of Pu(VI) dissolved in NaOH solution. About 4% was converted to Pu(V) in 4 M NaOH and 12% in 6 M NaOH, confirming the increased Pu(V) stability with increasing NaOH concentration. The $Pu(V)_{(aq)}/PuO_2{\cdot}xH_2O$ formal potential [that is, the potential at ~1 M Pu(V) and ~1 M NaOH] versus the normal hydrogen electrode, NHE, was calculated to be 0.44 V at 4 M NaOH (Bourges 1972), as shown in Figure 5-4.

The solubility of $PuO_2 \cdot xH_2O$ in aerated NaOH solution has been studied and a hydroxide Pu(V) complex proposed based on measurements of plutonium and NaOH concentrations, electrode potentials, solution spectra, and confirmation of the solid phase (Delegard 1985b). The following oxidative dissolution half-reaction to form the dissolved Pu(V) complex $PuO_2(OH)_4^{3-}$ was postulated:

$$PuO_2 \cdot xH_2O + 4\ OH^- \rightleftharpoons PuO_2(OH)_4^{3-} + e^- + x\ H_2O$$

Experimental data for this half-reaction were rearranged in terms of electron activity to evaluate the $Pu(V)_{(aq)}/PuO_2 \cdot xH_2O$ couple formal potential as a function of NaOH activity. As seen in Figure 5-4, the predicted formal potentials (based on data from Delegard (1985a) at 5 to 15 M NaOH) extrapolates smoothly to the 0.44 V potential for the same reaction reported by Bourges (1972) at 4 M NaOH.

The extent of Pu(V) disproportionation to $PuO_2 \cdot xH_2O_{(s)}$ and $Pu(VI)_{(aq)}$ was studied by Pu(V) and Pu(VI) spectrophotometry. It was shown that disproportionation decreases with increasing NaOH concentration but increases with increasing temperature (Budantseva et al. 1997). The Pu(V) disproportionation rate also follows the same trends with activation energy of 88 kJ/mol (Shilov 1997). Thus, 5.4×10^{-3} M Pu(V) does not disproportionate in 8 M NaOH but disproportionates almost completely in 1 M NaOH (Budantseva et al. 1997). Higher ionic strength or hydroxide complexation apparently stabilizes Pu(V). In 5 M sodium salt solutions containing nitrate, nitrite, aluminate, and eight other anions, at compositions typical of Hanford waste, 3.5×10^{-3} M Pu(V) is stable in 4 M NaOH but unstable in 2 M NaOH; without the additional salts, incomplete disproportionation occurs quickly in 4 M NaOH (Budantseva et al. 1997).

The $Pu(V)_{(aq)}/Pu(IV)_{(aq)}$ formal potential was estimated to be 0.26 V at 4 M NaOH and 0.17 V at 8 M NaOH based on the $Pu(VI)_{(aq)}/Pu(V)_{(aq)}$ potential and the solubility-limited Pu(IV) concentration above $PuO_2 \cdot xH_2O$ in N_2H_4-bearing alkaline solution (Budantseva et al. 1998a). In response to the greater stability of $PuO_2 \cdot xH_2O$ compared with $Pu(IV)_{(aq)}$, the $Pu(V)_{(aq)}/Pu(IV)_{(aq)}$ potential at 4 M NaOH is about 0.18 V lower than the potential of the $Pu(V)_{(aq)}/PuO_2 \cdot xH_2O$ couple measured by Bourges (1972). Using another approach, the $Pu(V)_{(aq)}/Pu(IV)_{(aq)}$ potential was estimated to be 0.53 V at 1 M NaOH (Shilov 1998). This estimate was based on comparison with analogous neptunium potentials, the measured 0.51 V lower Np(V)/Np(IV) potential at 1 M NaOH versus that at pH 0, and applying this 0.51 V difference to the Pu(V)/Pu(IV) potential [i.e., 1.04 V Pu(V)/Pu(IV) at pH 0 - 0.51 V = 0.53 V at 1 M NaOH]. However, this estimate is ~0.2 V higher than the ~0.32 V predicted by straight-line extrapolation of Budantseva et al. (1998a) data to 1 M NaOH.

As shown in Figure 5-4, the $Pu(V)_{(aq)}/PuO_2 \cdot xH_2O$ and $Pu(V)_{(aq)}/Pu(IV)_{(aq)}$ potentials cross the plot of $Pu(VI)_{(aq)}/Pu(V)_{(aq)}$ potentials at ~9.5 M NaOH and ~6.5 M NaOH, respectively. These crossings indicate that Pu(V) is unstable to disproportionation to form $Pu(IV)_{(aq)}$/ $PuO_2 \cdot xH_2O$ and $Pu(VI)_{(aq)}$ at NaOH concentrations lower than the respective crossing points. However, it is known that Pu(VI) is not stable indefinitely in NaOH solution and with time, perhaps due to alpha (α) radiolysis (Peretrukhin et al. 1995), precipitates to form $PuO_2 \cdot xH_2O$ (Delegard 1985b). Therefore, with time, plutonium in NaOH solution will precipitate to form $PuO_2 \cdot xH_2O$ and $Pu(IV)_{(aq)}$ or $Pu(V)_{(aq)}$ dissolved species. Only with higher NaOH concentration, higher ionic strength (or salt effects), and at lower temperature will $Pu(V)_{(aq)}$ be favored to form in NaOH solution (Budantseva et al. 1997; Budantseva et al. 1998a).

Conclusions – Dissolved plutonium is expected to be in the (IV) state below about 6 M NaOH and in the (V) state above about 6 M NaOH. Increasing ionic strength and more oxidizing conditions will favor the (V) state.

5.2 Solubility of Plutonium Compounds in Alkaline Solution

Studies have been conducted to determine the effects of Hanford Site tank waste sodium nitrate, nitrite, aluminate, carbonate, phosphate, sulfate, fluoride, EDTA, HEDTA, citrate, and glycolate salts, over limited concentration ranges, on the solubilities of the plutonium compounds formed by their precipitation in sodium hydroxide solution (Delegard and Gallagher 1983). This study showed that increasing the hydroxide, aluminate, and nitrate concentrations increased plutonium compound solubility significantly while the organic agents (EDTA, HEDTA, citrate, and glycolate) had no discernible effect. Subsequent tests investigated the effects of systematically varying sodium hydroxide, aluminate, nitrate, nitrite, and carbonate concentrations (Delegard 1985b). More recent studies confirm that EDTA is not effective in complexing plutonium at high hydroxide concentrations (Rai et al. 2008). In all cases, the green-colored plutonium solid phase formed when Pu(IV) nitrate solution was added to sodium hydroxide solution was identified by XRD to be poorly crystalline hydrated plutonium dioxide, $PuO_2{\cdot}xH_2O$. In parallel tests, Pu(VI) nitrate solution added to NaOH solution was found to form brown solids initially that, with months of aging, also became $PuO_2{\cdot}xH_2O$. The chemical reduction of Pu(VI) was attributed to α-radiolysis (Peretrukhin et al. 1995).

These and subsequent tests (Peretrukhin et al. 1996; Shilov et al. 1996) demonstrated the influence of plutonium oxidation state and NaOH concentration on the solubility of the precipitated plutonium compounds. The solubility results, Figure 5-5, show that plutonium becomes more soluble with increase in its oxidation state from Pu(IV)→Pu(V)→Pu(VI). Solubility tests of hydrated Pu(IV) oxide in the presence of 10 M NaOH (8×10^{-6} M Pu) and 10 M NaOH containing 0.2 M $NaMnO_4$, sodium permanganate (1.4×10^{-2} M Pu), which oxidizes the plutonium to Pu(VI), are consistent with the results shown in Figure 5-5 (Rudisill and Thompson 2011). In other work, tests of oxidative dissolution of chromium(III) solid phases from genuine Hanford tank waste sludge to form soluble chromate, CrO_4^{2-}, show that enhanced plutonium dissolution also occurs. Permanganate, MnO_4^-, persulfate, $S_2O_8^{2-}$, ferrate, FeO_4^{2-}, air, oxygen gas, O_2, ozone, O_3, and peroxynitrite, $ONOO^-$, were surveyed as oxidants and run at low (~0.01, 0.1, or 0.25 M) and high (3 M) NaOH concentrations at room temperature to 85° C (Rapko et al. 1996; Rapko et al. 1997; Rapko 1998; Rapko et al. 2002; Rapko and Vienna 2002; Rapko et al. 2004). While permanganate and ferrate were the most broadly effective at Cr(III) solid phase dissolution, significant increase in collateral plutonium solid phase dissolution occurred for tests run at 3 M NaOH for all oxidants tested. With permanganate, from 0.01 to 1.5% of the plutonium dissolved at 0.1 M NaOH while at 3 M NaOH, under otherwise similar conditions, 2 to 69% of the plutonium dissolved. Overall, an average 70-fold enhancement in the amount of plutonium dissolution occurred by increasing from 0.1 M to 3 M NaOH. As shown in Figure 5-4, oxidation of plutonium to Pu(VI) probably occurred.

Other tests showed that Pu(III) has only fleeting stability in alkaline solution and quickly forms Pu(IV) (Delegard 1987), while Pu(VII), though more soluble than Pu(VI), requires extremely high NaOH concentrations and oxidizing conditions to be stable (Krot et al. 1977). The solubility-controlling solid phases formed by Pu(V) and Pu(VI) are almost certainly sodium salts such as $Na_3PuO_2(OH)_4{\cdot}xH_2O$ and $Na_2PuO_2(OH)_4{\cdot}xH_2O$, respectively, (Peretrukhin et al. (1996); salts analogous to the sodium-U(VI) salts as described in Table 4-8), and not the corresponding Pu(V) or (VI) oxides or hydroxides despite the

Pu(VI) tests of Budantseva et al. (1997) beginning with $PuO_3 \cdot H_2O$. The increasing solubilities of Pu(IV), Pu(V), and Pu(VI) with increasing NaOH concentration indicate that the dissolved plutonium species are anionic hydroxide complexes.

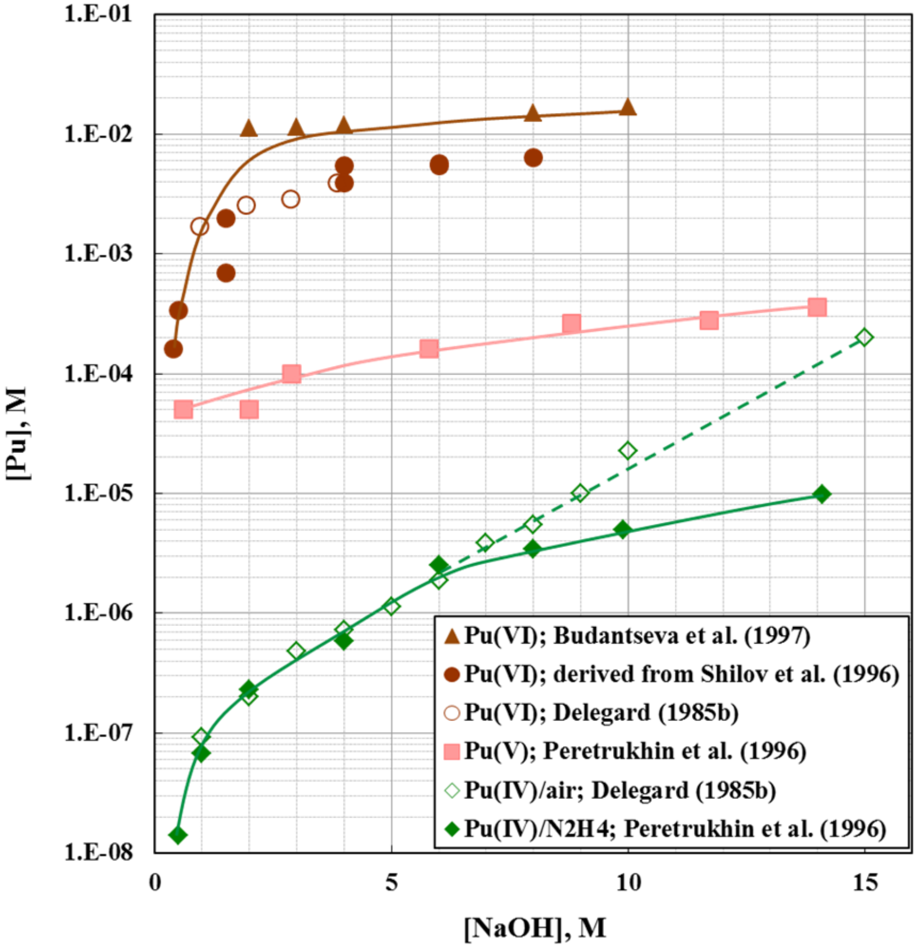

Figure 5-5. Plutonium Compound Solubilities as Functions of Oxidation State and NaOH Concentration

The divergence of the Pu(IV) solubility lines at higher NaOH concentrations in the presence of air and hydrazine, N_2H_4, respectively (Figure 5-5), indicates the change in oxidation state of the dissolved species. In the presence of air, a Pu(V) dissolved species exists in NaOH solutions at or above ~5 M as shown by absorption spectrophotometry. The rising solubility with increased NaOH concentration indicates that the dissolved species is an anionic hydroxide complex such as $PuO_2(OH)_4^{3-}$ or $PuO_2H_2O(OH)_3^{2-}$ (Delegard 1985b; Shilov 1998, respectively). Below ~6 M NaOH, the dissolved species is Pu(IV) and likely of the form $Pu(OH)_5^-$ or $Pu(OH)_6^{2-}$ (Peretrukhin et al. 1995; Peretrukhin et al. 1996; Shilov 1998). The lack of effect of the hydrazine chemical reductant, compared with aerated conditions, on the Pu(IV) solubility below about 6 M NaOH indicates that the dissolved plutonium must be tetravalent, i.e., Pu(IV).

Testing of the influence of Hanford tank waste salts showed that nitrate and nitrite had supplemental effects on plutonium compound solubilities. When sodium nitrate and nitrite were together or sodium nitrate was by itself in NaOH solutions, their salting strengths acted to increase the chemical activity of the NaOH and thus increase the plutonium solution concentration (Delegard 1985b). For example, the plutonium concentration observed at 5 M NaOH increased by a factor of ten in a 5 M NaOH solution that also contained 3 M each of $NaNO_3$ and $NaNO_2$. However, 1 to 4 M sodium nitrite without nitrate in 4 to 7 M NaOH solution was found to act as a mild chemical reductant that decreased the dissolved plutonium concentration below what would be expected for nitrite-free NaOH solution. The magnitude of the decrease was found to correspond to the solution Eh (redox potential) with a slope that indicated a one-electron change—i.e., Pu(IV)-Pu(V) – in the Pu(IV) dissolution reaction (Delegard 1985b). It is noted that sodium nitrate is ubiquitous in tank wastes and the presence of sodium nitrite in the absence of sodium nitrate is practically impossible in tank wastes except for so-called inhibited water, 0.01 M NaOH with 0.01 M $NaNO_2$, used in certain salt cake dissolution and sludge washing processes in which abundant $NaNO_3$ also would be present. Therefore, the mildly reducing conditions attained in a NaOH solution containing $NaNO_2$ but without $NaNO_3$ are practically foreclosed in actual Hanford tank waste and in waste processing operations.

Increases in plutonium concentration in aqueous solution with increasing sodium hydroxide concentration also have been observed in alkaline solutions simulating the tank wastes at the Savannah River Site (SRS) (Karraker 1993; Hobbs and Edwards 1993; Hobbs et al. 1993; Hobbs and Karraker 1996). Parametric tests quantified the effects of waste salts (sodium hydroxide, nitrate, nitrite, aluminate, carbonate, sulfate, and chloride), temperature (25° C and 60° C), and time on plutonium solution concentration, while simulated waste evaporation tests showed the effects of increasing solution concentrations even as the sodium salts crystallized with water loss. Temperature was found to have little influence on plutonium concentration. Statistical models to predict plutonium concentration as functions of solution compositions were generated based on the experimental findings and values from other studies (Hobbs et al. 1993). In these studies at somewhat limited ranges of solute concentration, increasing sulfate, aluminate, and carbonate concentrations were observed to increase solubility, while increasing nitrate and nitrite concentration decreased solubility. In contrast, the simulated waste evaporation tests showed higher plutonium concentrations than are found in pure NaOH solution of the same hydroxide concentration (Hobbs and Karraker 1996) but the plutonium concentration increase with NaOH concentration increase in the mixed solutions was not as pronounced as in pure NaOH solution.

More recent, statistically designed studies of plutonium compound solubility in alkaline solution simulating SRS wastes feature much broader ranges of solute concentrations (Rudisill et al. 2010). Solutes include NaOH, $NaAl(OH)_4$, Na_2CO_3, Na_2SO_4, $NaNO_3$, and $NaNO_2$; time and temperature also were test variables in this set of 20 experiments. Time of equilibration had no significant effect. A statistical data fit again provided an equation to predict plutonium concentration as a function of solution composition. As shown by this equation, plutonium concentration increased with increase in hydroxide, aluminate, and carbonate concentration and decreased slightly with increasing nitrite concentration.

A 1:1 Pu:aluminate complex has been surmised to exist based on enhancements in hydrated Pu(IV) oxide solubility in 5- to 10-M NaOH containing 0.3 to 2 M $NaAl(OH)_4$ (Delegard 1985b). The plutonium concentrations increased about a factor of 4 in ~6 to 7 M NaOH containing ~1 M aluminate, $Al(OH)_4^-$, compared with the concentrations found under otherwise similar conditions but in the absence of aluminate.

Complexation of Pu(IV) in moderately alkaline (pH 9 to 14) solution in the presence of silicate, SiO_3^{2-}, also has been shown to occur with 1 M silicate enhancing the Pu(IV) solubility about 40-fold at pH ~12.8 and 13.8 (Shilov and Fedoseev 2003). Analogously to aluminate, an apparent 1:1 Pu:silicate complex was formed. The enhanced solubility was also observed at pH 11 but was not seen at pH 9, probably because of silicate protonation. The Pu(IV) solid phase was not identified in this work. Complexation of neptunyl(V), NpO_2^+, by silicate as $^-O\text{-}Si(OH)_3$ is found to occur at pH levels between about 8.5 to 9.5, but the complexation is too weak to compete with carbonate at higher pHs (Yusov et al. 2005). Similarly weak silicate complexation of Pu(V) with silicate would be expected.

Aside from hydroxide, the component having greatest effect on plutonium compound solubility in Hanford tank waste solution is carbonate, CO_3^{2-}. Increasing plutonium concentrations attributed to the effects of carbonate complexation in 0.25 to 1 M sodium carbonate present in 3 to 5 M sodium hydroxide solutions were observed in laboratory tests (Delegard 1985b). As shown in Figure 5-6, these data are consistent with findings on Pu(IV) hydrated oxide solubility in potassium carbonate and potassium hydroxide media containing 5×10^{-4} M sodium nitrite holding reductant at pH 12-13 (Yamaguchi et al. 1994) and with tests in 0.25 M NaOD (deuterated NaOH) in deuterated water, D_2O, containing 0.05 to 0.25 M Na_2CO_3 (Sinkov 2007). Tests of the solubility of Pu(IV) hydrated oxide solubility in pH 9.5 solution containing 1 M sodium carbonate/bicarbonate with and without 0.2 M $NaMnO_4$ (Rudisill and Thompson 2011) are consistent with the earlier observations. With $NaMnO_4$ oxidant, the solubility is steady at $\sim7\times10^{-3}$ M and near that seen by Cunningham (1954) for 1 M Na_2CO_3. In the absence of $NaMnO_4$, the solubility is 1.2×10^{-4} M and trending upward with time. It is significant to note that solutions from genuine Hanford tank wastes having high carbonate concentrations (Bratzel 1985; Herting 1994; Castaing 1993) also are in line with the laboratory test findings as shown in Figure 5-6. These findings indicate that plutonium concentration in at least some tank waste solutions may be established by hydrated plutonium oxide, $PuO_2\cdot xH_2O$, and not by the lower concentrations expected for coprecipitation.

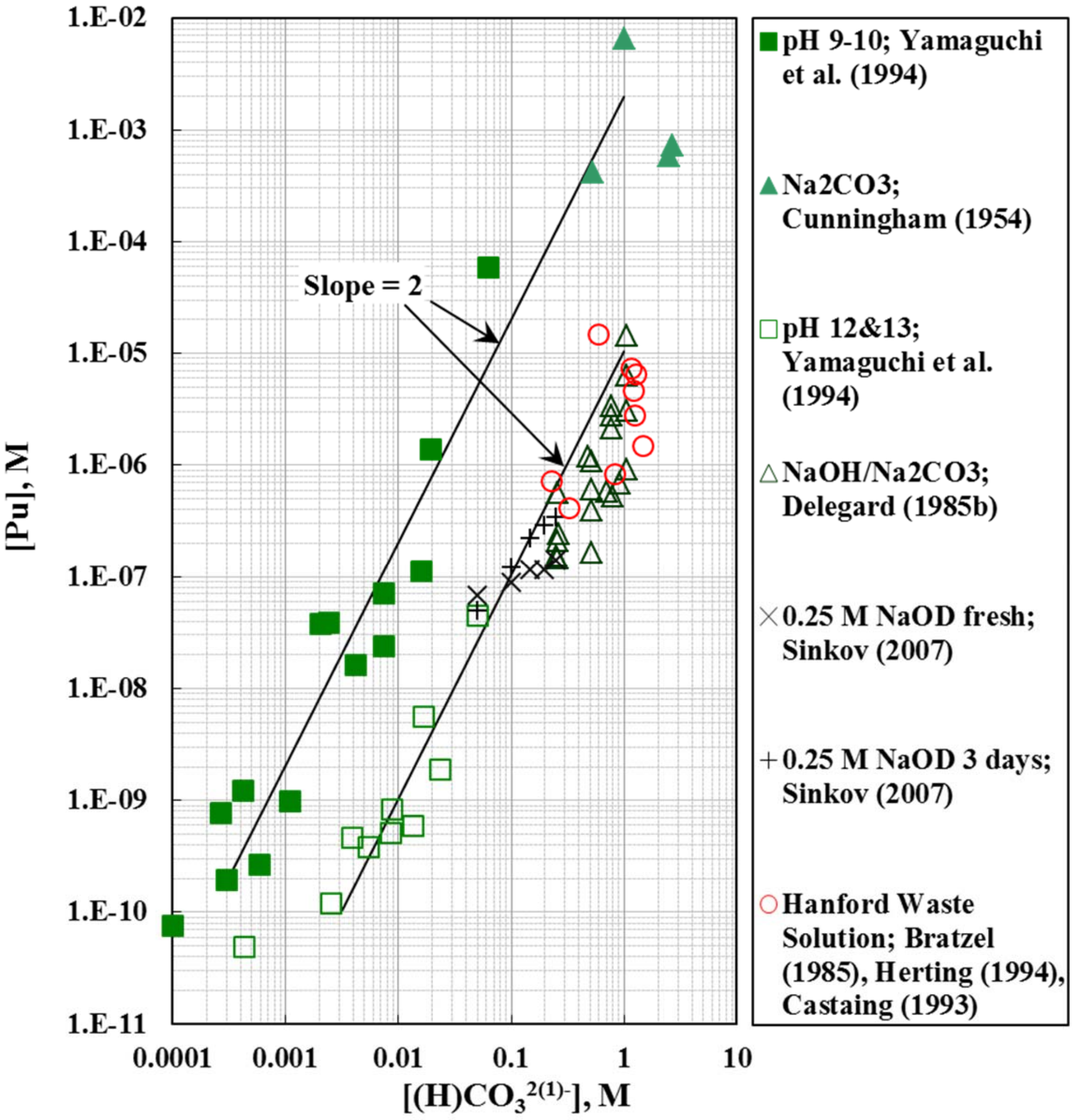

Figure 5-6. Plutonium Concentrations in Carbonate Solutions. Upper curve for bicarbonate at pH 9-10; lower curve for carbonate at pH 12 and higher.

A dissolved Pu(IV) carbonate complex, $[Pu(OH)_4(CO_3)_2]^{4-}$, was postulated by Yamaguchi et al. (1994) based on the existence of Pu(IV) in solution, as determined by extraction of Pu(IV) from the solution after acidification, and the second power dependence of the solubility on carbonate concentration. However, these oxidation state determinations are suspect because the nitrite present in the initial alkaline solution could have altered the plutonium oxidation state during the acidification. In contrast, a mix of carbonate-free and monocarbonate Pu(IV) complexes was postulated based on the half-power dependence of the solubility on carbonate concentration at 0.25 M NaOD in instantaneous measurements of tests at five carbonate concentrations (Sinkov 2007) and similar behavior found for thorium(IV) in a separate published account (Altmaier et al. 2005). For the more concentrated plutonium solutions found in 0.25 M NaOD and 0.15 to 0.25 M Na_2CO_3 in the tests after three days of equilibration (Sinkov 2007), Pu(V) spectrophotometric absorbance peaks at 653 and 825 nm wavelengths were found indicating Pu(IV) oxidation to Pu(V). The relative contributions of carbonate complexation and oxidation state changes are not known. Nevertheless, the plutonium concentration trends in carbonate-bearing 0.25 M NaOD (Sinkov 2007) are fully consistent with the plutonium concentrations in the related high alkalinity studies by Yamaguchi et al. (1994), Delegard (1985a), and the Hanford tank waste characterizations (Bratzel 1985; Castaing 1993; Herting 1994).

Around 10^{-5} M plutonium is observed in highly alkaline solution (i.e., pH 12 or higher) having 1 M Na_2CO_3 (Figure 5-6). Even at this relatively high plutonium concentration, the plutonium-to-sodium absorber mass ratio is 0.05 g plutonium per kilogram of sodium—well below the 2.79 threshold of criticality concern given in Table 4-2. In the absence of carbonate, the total plutonium solution concentration in 1 M NaOH is ~1×10^{-7} M (Figure 5-5) indicating that carbonate enhances solubility by a factor of about 100.

As Figure 5-6 illustrates, parallel ~200-fold higher plutonium compound solubilities compared with equivalent carbonate concentrations at pH ≥12 are observed in bicarbonate/carbonate (HCO_3^-/CO_3^{2-}) solutions at pH 9-10 (Yamaguchi et al. 1994; Cunningham 1954). Thus, Pu(IV) hydrated oxide solubility can be greatly enhanced if Hanford tank waste solutions are allowed to lose NaOH concentration and gain carbonate concentration, both of which are known to occur by air exposure and by organic component oxidation in the tank wastes. It is noted that the tests described by Cunningham (1954) were conducted by dissolving fresh Pu(IV) "hydroxide" in sodium carbonate solution. The decreased solubility observed at the higher 2-3 M carbonate concentrations suggests that precipitation of a sodium-plutonium carbonate double salt may have occurred.

While carbonate increases plutonium solubility, the effect is smaller at higher pH due to competition with hydrolysis. Thus, plutonium concentrations in bicarbonate-free pH 9 to 10 solution are about 10^{-10} M to 5×10^{-9} M (Figure 5-6 and 6-3) whereas if such solutions are made 1 M in bicarbonate, plutonium solubility grows to ~2×10^{-3} M (Figure 5-6), an increase in solubility by a factor of ~10^6. In highly alkaline solution (i.e., pH ≥12) containing 1 M Na_2CO_3, plutonium concentrations are 10^{-6} to 10^{-5} M (Figure 5-6) compared with ~10^{-6} M in 5 M NaOH, ~10^{-7} M in 1 M NaOH, and ~2×10^{-9} M in pH 12 solution under non-oxidizing conditions in the absence of carbonate (Figures 5-5 and 6-3 in the present report and Figure 13 of Delegard (1985b)). While the relative impact of carbonate on plutonium solubility decreases at molar hydroxide concentration, up to ten-fold increase in plutonium concentration still can be attained in 3 to 5 M NaOH in the presence of 1 M carbonate (Delegard 1985b). As seen in Figure 5-6, high plutonium concentrations in genuine Hanford tank waste solutions are consistent with the concentrations found in lab testing with simpler idealized systems. At lower pH, the impact of carbonate is much more pronounced.

> *Conclusions – Dissolved plutonium concentrations are expected to increase with increasing NaOH concentration, increasing ionic strength, increase in oxidation potential, and increase in carbonate concentration. The plutonium concentrations found in (bi)carbonate solutions at pH 9-10 are 200-fold greater than those observed for equivalent carbonate concentrations at higher pH. While the relative impact of carbonate on plutonium concentration decreases at molar hydroxide concentrations, increased plutonium concentrations still are found in actual Hanford tank waste solutions as carbonate concentration increases.*

5.3 Plutonium Solids in Alkaline Solution

Plutonium solids present in the tank farms arise from precipitation caused by acidic process solutions being made alkaline for discharge to tank farms and from already-formed plutonium solids that were lost by process actions to waste. The intrinsic preformed plutonium solids arose from process losses within plutonium scrap recovery operations at the PFP, losses of non-irradiated PuO_2 fuel or $(Pu,U)O_2$ mixed oxide (MOX) during scrap fuel recovery, or losses from reprocessing of the irradiated PuO_2 and MOX fuel (e.g., from the PRTR) in the REDOX and PUREX Plants. Most information on the forms of plutonium within the tank wastes is inferred based on experiments on the behaviors of plutonium in alkaline systems, for solutions and for the solid phases that arise from precipitation in alkaline media, or from expectations of behavior for plutonium discharged as solid phases to the tank farm wastes.

However, carefully designed and executed fractional decantation and dissolution processing of wastes from tanks SY-102, TX-118, and AZ-101 and from PFP wastes discharged to the Z-9 crib recently have been performed to reveal conclusively the existence of plutonium-bearing solids in actual wastes (Callaway III and Cooke 2004; McCoskey and Cooke 2013). The sample preparation was designed to enhance the concentrations of dense and low-solubility phases and thus improve the likelihood of detecting the suspected plutonium phases. The tests for wastes received from PFP (i.e., tanks SY-102, TX-118, and the Z-9 crib) showed three types of plutonium-bearing solids while no plutonium-bearing solids were identified in the AZ-101 wastes. The three types of plutonium-bearing solids from the PFP-origin materials were plutonium with oxygen (i.e., plutonium oxide), plutonium with bismuth, and plutonium with bismuth and phosphorus (potentially phosphate).

Further discussion of the properties and chemistry of the plutonium solids in alkaline solution are given in the following sections.

5.3.1 Plutonium Solids Arising from Precipitation in Alkaline Solution

The solid phase generally found in plutonium solubility studies in alkaline media is hydrated Pu(IV) oxide, $PuO_2 \cdot xH_2O$ (Delegard 1985b; Yamaguchi et al. 1994; Hobbs and Karraker 1996; Yusov et al. 2000b and others). The broad XRD peaks occur in locations corresponding to those of refractory PuO_2 with the broadness attributed to small crystallite size or poor crystallinity. Hydrated Pu(IV) oxide also has been described as Pu(IV) hydroxide although a discrete $Pu(OH)_4$ compound has not been identified (Lloyd and Haire 1978). The initially amorphous Pu(IV) gel dehydrates with time to form the hydrated PuO_2 crystallites; the rate of crystallization increases with temperature and with lower salt concentrations (Haire et al. 1971). As shown recently (Delegard 2013), any dissolved Pu(IV) made alkaline and discharged under tank farm conditions without a coprecipitating absorber forms 2- to 5-nm-scale $PuO_2 \cdot xH_2O$ crystallites that because of low solubility and radiolytic opposition (metamictization; i.e., internal radiolytic spallation), grow in size at exceedingly low rates even with years of aging.

It is noted that for alkaline solutions in which plutonium compounds comprise the only possible solid phase(s), hydrated Pu(IV) oxide forms in experiments begun with Pu(IV) (Westrum Jr. 1949; Rai and Ryan 1982; Delegard 1985b, 1987, 1997; Yamaguchi et al. 1994; Hobbs and Karraker 1996; Krot et al. 1998c; Yusov et al. 2000b), by air or water oxidation in tests begun with Pu(III) (Cunningham 1954; Charyulu et al. 1991; Delegard 1987), by disproportionation of Pu(V) in 0.6 to 6 M NaOH (Bourges 1972; Peretrukhin et al. 1996; Budantseva et al. 1997), and by slow radiolytic reduction of Pu(VI) in 1 to

15 M NaOH (Delegard 1985b; Peretrukhin et al. 1995). Only with strong oxidants or reductants are pure plutonium phases other than $PuO_2 \cdot xH_2O$ stable in NaOH solution, and even, as will be shown in the following paragraphs, in the presence of most tank waste anions. The tank wastes, without exception, are nitrate/nitrite mixtures subject to products from water radiolysis and thus are expected to stabilize the Pu(IV) oxidation state in the solid phase as $PuO_2 \cdot xH_2O$. Hobbs (2012b) has postulated the following behavior for plutonium in SRS tank waste sludges:

> Most of the plutonium that enters Savannah River Site (SRS) high-level waste (HLW) tanks is freshly precipitated as amorphous plutonium hydroxide, $Pu(OH)_{4(am)}$ or hydrous plutonium oxide, $PuO_{2(am,hyd)}$ and coprecipitated within a mixture of hydrous metal oxide phases containing metals such as iron, aluminum, manganese and uranium. The coprecipitated plutonium would include Pu^{4+} that has been substituted for other metal ions in crystal lattice sites, Pu^{4+} occluded within hydrous metal oxide particles and Pu^{4+} adsorbed onto the surface of hydrous metal oxide particles. The adsorbed plutonium could include both inner sphere coordination and outer sphere coordination of the plutonium. $PuO_{2(am,hyd)}$ is also likely to be present in deposits and scales that have formed on the steel surfaces of the tank. Over the operational period and after closure of Tank 18, Ostwald ripening has and will continue to transform $PuO_{2(am,hyd)}$ to a more crystalline form of plutonium dioxide, $PuO_{2(c)}$ (page v).

Further information on the nature and characteristics of the $PuO_2 \cdot xH_2O$ generated by precipitation in alkaline solution has been determined (Krot et al. 1998c; Yusov et al. 2000b). The number of water molecules, x, associated with the $PuO_2 \cdot xH_2O$ depends on humidity but found to be insensitive to the precipitation strike method (direct or reverse) or aging time and increases from 1.6 to 2.8 as water vapor pressure increases from 1.7 to 14.6 Torr (near ~100% relative humidity) at room temperature. The association of water with the PuO_2 is not thermally discrete, as a true crystalline hydrate would be, as shown by its smooth, not stepped, release from $PuO_2 \cdot xH_2O$ as the temperature is raised. Thermal analyses show that the water is evolved continuously when the oxide is heated from 50° C to 250° C with a clear endotherm at 110° C proportional to x.

The PuO_2 particles associated with water will be less dense than the theoretical density of 11.46 g/cm^3 for pure PuO_2 (Clark et al. 2006) Assuming that the water association with the underlying finely crystalline PuO_2 is only physical and that x is 2.6, the particle density of $PuO_2 \cdot xH_2O$ is 4.51 g/cm^3 assuming additive volumes [1]. For a spherical PuO_2 particle with 2.5-nm diameter, the surface water layer of $PuO_2 \cdot xH_2O$, where x is 2.3 at 35% relative humidity, is about 1.6 H_2O molecules thick. This thickness is similar to that found for PuO_2 prepared from metal oxidation in air and calcined in oxygen at 800° C in which ~2 molecules of water thickness was observed at room temperature under ~30-50% relative humidity (Haschke et al. 2001; Stakebake and Steward 1973). However, the particle density of $PuO_2 \cdot xH_2O$ in aqueous suspension may revert to that of the core PuO_2 should the surface and bulk water be indistinguishable, as suggested by the relatively weak association of water with the PuO_2.

Most tank waste anions do not affect the precipitation of the stable $PuO_2 \cdot xH_2O$ in alkaline solution (Krot et al. 1998c; Yusov et al. 2000c). In tests of Pu(IV) precipitation from its HNO_3 solution in NaOH

---

[1] $$\text{Density}\, PuO_2 \cdot 2.6H_2O = \frac{271\,\text{g PuO}_2 + 2.6\times 18\,\text{g H}_2\text{O}}{\left(271\,\text{g PuO}_2 \times \dfrac{\text{cm}^3}{11.46\,\text{g}} + 2.6\times 18\,\text{g H}_2\text{O} \times \dfrac{\text{cm}^3}{1.0\,\text{g}}\right)} = \frac{4.51\,\text{g}}{\text{cm}^3}.$$

solutions containing nitrite, carbonate, sulfate, chromate, ferrocyanide, oxalate, glycolate, citrate, EDTA, or HEDTA, the solid phases had the same compositions and hygroscopic properties as the $PuO_2 \cdot xH_2O$ formed in mixed $NaOH/NaNO_3$ solutions. Further tests of the product from the $NaOH/NaNO_3$ solution precipitation showed that sodium comprises less than 1 mole% and nitrate less than 0.03 mole% of the solid phase. Aluminate also does not affect the precipitation of $PuO_2 \cdot xH_2O$ from alkaline solution (Fedoseev et al. 1998; Yusov et al. 2000a).

Of the anions investigated, only phosphate, and particularly silicate, form at least intimate mixtures or compounds other than $PuO_2 \cdot xH_2O$ with Pu(IV) in alkaline media (Krot et al. 1998c; Yusov et al. 2000b). The phosphorus-to-plutonium mole ratio is about 0.15 for well-washed Pu-bearing solids formed by reacting Pu(IV) nitrate solution with sodium phosphate dissolved in 0.2 M NaOH. The phosphorus-to-plutonium mole ratio decreases with increasing NaOH concentration. The silicon-to-plutonium mole ratio ranges from 1.4 to 1.8 in well-washed plutonium-bearing solids formed by reacting Pu(IV) nitrate with 0.05 M Na_2SiO_3 solution dissolved in 0.2 M NaOH. Increasing the NaOH concentration to 7 M at the same silicate concentration decreases the mole ratio to about 0.3. In the reverse direction, treating freshly prepared $PuO_2 \cdot xH_2O$ with 0.05 M Na_2SiO_3 in 1 M NaOH at 120-140° C causes a metathesis reaction, forming materials with up to a 0.8:1.0 silicon-to-plutonium mole ratio. The plutonium silicate products from these tests are amorphous, potentially indicating small particle size. Under higher temperature but less alkaline hydrothermal conditions, crystalline α-$PuSiO_4$ was formed by treating thoroughly washed $PuO_2 \cdot xH_2O/SiO_2 \cdot nH_2O$ mixtures, prepared by equimolar coprecipitation in NH_4OH solution, with seven days' heating at 230° C in 1 molal $NaHCO_3$ (Keller 1963).

The above studies show that $PuO_2 \cdot xH_2O$ is the compound favored to be formed should dissolved acidic plutonium nitrate solution, of any oxidation state, be made alkaline either by direct strike treatment with added NaOH solution, by reverse strike addition to NaOH solution, or even by being made alkaline in NaOH solutions containing almost any other sodium salt. The individual $PuO_2 \cdot xH_2O$ crystallites are exceedingly small, 0.002 to 0.005 µm when produced from Pu(IV) nitrate and ~0.011 µm when produced from Pu(VI) nitrate, and crystallite growth rate is exceedingly slow (Delegard 2013 and references therein). Therefore, growth of $PuO_2 \cdot xH_2O$ crystallites to the micron-sized particles that are at risk of separation from other sludge phases by sedimentation, for example, is effectively excluded. The important iron(III) (hydr)oxide absorber particles are similarly dimensioned, with the most prominent sizes around 0.002 to 0.003 µm when prepared in alkaline solution under various conditions, while sodium diuranate ($Na_2U_2O_7$), prepared under similar conditions is 0.003 to 0.004 µm (Krot et al. 1998b). Hydrodynamic segregation of $PuO_2 \cdot xH_2O$ from the important Fe(III) (hydr)oxides, even if precipitated individually, thus is unlikely. Although it is expected that crystallite agglomerates will form though their self-association remain weak with break-up being susceptible to shearing (e.g., by pumping), it is known that smaller primary particles tend to form agglomerates of greater strength than agglomerates of larger particles (Wells et al. 2007 and references therein). Thus, the effect of shearing on $PuO_2 \cdot xH_2O$ agglomerate size is a subject for further study. Association of intrinsic $PuO_2 \cdot xH_2O$ crystallites with other small particle-size crystallites, particularly of iron(III) and other absorber elements, also is a subject for study.

> *Conclusions – Finely particulate $PuO_2 \cdot xH_2O$ is expected to be the dominant solid phase produced by introduction of dissolved plutonium, in the absence of other dissolved metal ions, into alkaline tank waste solution. However, phosphate and silicate in alkaline solution can lead to plutonium phosphate and plutonium silicate solid phases, respectively, in preference to $PuO_2 \cdot xH_2O$. The $PuO_2 \cdot xH_2O$ crystallites have sizes similar*

> *to those of Fe(III)(hydr)oxide meaning that separation of the plutonium and iron particles by hydrodynamic means is unlikely. The physical association of the plutonium and iron crystallites by agglomeration is not known.*

5.3.2 Plutonium Sent to the Tank Farms as Solids

The original "best-basis" plutonium inventory in the waste tanks is 672 kg (Kupfer et al. 1999), but conservative loss estimates range as high as 981 kg (Roetman et al. 1994). The BBI as-of January 2014 is 847 kg (PNNL n.d.). The total includes plutonium in all forms, including the disposed solutions which, when made alkaline, precipitate, and the various solids that were disposed to the tanks. Some of this solids total can be attributed to solids lost in plutonium scrap recovery campaigns in PFP and processing of PuO_2 fuels in PUREX and REDOX. Besides PuO_2, solids losses by PFP to tank farms include Pu(IV) oxalate [$Pu(C_2O_4)_2 \cdot 6H_2O$], Pu(IV) fluoride (PuF_4) from hydrofluorination of plutonium oxide as an intermediate in producing plutonium metal, plutonium fluoride salts (e.g., $PuF_4 \cdot 2.5\ H_2O$; Na_2PuF_6) from fluoride-assisted scrap dissolution, and interfacial cruds composed of plutonium-organic phosphates that formed within the PFP, REDOX, and PUREX solvent extraction operations. Plutonium(IV) oxalate process losses to tank farms from PuO_2 production at PUREX is also possible, though unlikely. Survey of the technical literature showed that, like Pu(IV) nitrate solution, the plutonium oxalate, fluoride, and crud solids are unstable in alkaline conditions and will readily hydrolyze to make $PuO_2 \cdot xH_2O$ (see Appendices A and B, respectively). Based on the known behavior of Pu(IV) nitrate under alkaline conditions, it is likely that the $PuO_2 \cdot xH_2O$ arising from hydrolysis of the oxalate, fluoride, and crud solids also will be poorly crystalline and when co-disposed to the tank wastes with added iron nitrate and made alkaline with NaOH, as was the routine practice from 1984 onward, would be coprecipitated with $Fe(OH)_3$ and other iron (hydr)oxides. These PFP-origin nitrate solution, oxalate, and fluoride solids, the solvent extraction crud solids losses, and the dissolved process losses from PUREX and REDOX constitute the hydrolyzed plutonium process losses.

Only three facilities; PFP, REDOX, and PUREX; could have sent preformed calcined or refractory plutonium material to the tank farms. These materials accounted for the remaining plutonium solids potentially discarded to the tank wastes with the PFP facility contributing most of these solids as PuO_2. The material that failed to dissolve within the PFP plutonium scrap recovery operations was sent to the solvent extraction processes and from there could have been lost with solvent extraction raffinates. The PFP-origin solids also include a small amount of plutonium metal fines. The metal fines arose from incomplete burning of scrap plutonium metal and its reporting to the tank wastes because of subsequent incomplete dissolution in the fluoride-assisted HNO_3 digestions used to prepare the solvent extraction feeds.

The PUREX and REDOX Plants processed limited amounts of PFP material but also undertook several special campaigns to recover plutonium from PuO_2 and MOX fuel (Gerber 1996).

The particle size distributions for the undissolved oxides have been determined based upon the process methods and examination of historical sources. Much of the PuO_2 arose from calcination of Pu(IV) oxalate during plant operations to make PuO_2 for fuel or as an intermediate compound on the way to plutonium metal. Process specifications give the PuO_2 particle size range of 1 to 40 µm; the PuO_2 density is ~11 g/cm^3 but lower practical densities of ~8-11 g/cm^3 would be seen because of the internal porosity of the calcined oxalate particles (Sams 2012). The PuO_2 from burnt plutonium metal that would have arrived at tank farms has a maximum particle size range of 40 to 100 µm and a density similar to that for Pu(IV) oxalate-origin oxide, 8 to 11 g/cm^3, with the lower density again due to internal porosity (Appendix C). Similarly, the unburnt plutonium metal fines arriving at tank farms from burnt scrap plutonium metal has a maximum particle size of 40 to 100 µm and density the same as that of plutonium metal itself, ~19 g/cm^3 (Appendix C). The stability of plutonium metal in tank waste is unknown. Although plutonium metal is not thermodynamically stable in aqueous solution including, presumably, tank waste, the corrosion rate of plutonium metal in strong alkaline solution is known to be very low (Appendix C and references therein). The tank wastes in SY-102 and TX-118, the primary receivers of waste from the PFP, are strongly alkaline but also contain many redox-active waste components such as nitrate and nitrite that may affect plutonium metal corrosion rates. However, because nothing is known about plutonium metal's long-term corrosion resistance in tank waste, the fate of any plutonium metal sent to the tank farms is unknown.

Of the plutonium disposed to tank farms, approximately 100 kg of particulate plutonium-bearing material was judged to have been sent from PFP, PUREX, and REDOX from plutonium oxide processing operations (Sams 2012). Of that 100 kg, approximately 30 kg was disposed as large (>10-µm and up to 40-µm) calcined PuO_2 and plutonium metal. The balance of the intrinsic plutonium-bearing material was discarded in the form of plutonium nitrate, plutonium "hydroxide," or plutonium oxalate and compounds that would readily hydrolyze in the alkaline waste solution to form fine $PuO_2 \cdot xH_2O$ solids. Of the 30 kg of 10- to 40-µm particulate, the PFP contributed ~23 kg with as much as 2.5 kg being plutonium metal from incomplete metal burning subsequent to oxide dissolution. The PUREX and REDOX facilities contributed the remaining 7 kg of 10- to 40-µm particulate and in the form of calcined PuO_2 (Sams 2012).

> *Conclusions – The plutonium solids destined for tank farm disposal either hydrolyzed to become $PuO_2 \cdot xH_2O$ [i.e., by starting as dissolved plutonium nitrate, solid Pu(IV) oxalate, Pu(IV) fluoride, plutonium fluoride salts, or interfacial cruds before hydrolysis], began as PuO_2, or were plutonium metal. Both $PuO_2 \cdot xH_2O$ and PuO_2 are expected to be stable in the tank farm wastes, as shown by the known stability of the nanometer-scale $PuO_2 \cdot xH_2O$ solids after years of aging in strong alkaline solution. Plutonium metal is highly stable to corrosion in simple metal hydroxide solution, but the stability of plutonium metal in tank waste with redox-active components such as nitrite is unknown.*

5.3.3 Plutonium Solids Discovered in Tank Farm Sludges

Until recently, no definitive identification of plutonium solid phases (e.g., by XRD; TEM; SEM/EDS) or solution species (e.g., by spectrophotometry) in Hanford tank wastes had been done. However, in careful and inventive experiments undertaken in 2004, plutonium-rich particles were found to exist in waste from tank SY-102 (Callaway III and Cooke 2004). Tank SY-102 was known to have received PFP waste that had been made alkaline. The isolation of Pu-rich particles was done using a salt dissolution and fractional decantation technique in which dense particles were enriched. The dense particle fraction then was examined by SEM/EDS techniques to map particles with high plutonium concentration and determine the associations of plutonium with other elements.

In 2012, similar investigations to find plutonium-rich particles in tank wastes were undertaken to re-examine tank SY-102 materials and also examine tank wastes from TX-118 and AZ-101 and archive samples from near the top layer of soil from the Z-9 crib (McCoskey and Cooke 2013). Samples from the top layer of Z-9, which would have been richer in Pu-bearing particles, unfortunately were not available. Like SY-102, tank TX-118 received neutralized acid waste from the PFP while AZ-101 had high plutonium content but had not received PFP wastes. The Z-9 crib had received pH-neutralized wastes from the PFP. Because the SY-102 and TX-118 tanks are known to have received PFP wastes, they were suspected of receiving particulate plutonium arising from incomplete acid digestions of Pu-bearing scrap (e.g., refractory PuO_2 particles). The Z-9 crib was known to have received particulate PuO_2 based on prior XRD analyses (Ames 1974; Price and Ames 1975).

Significantly, plutonium-bearing particles were found for the tanks which received the PFP wastes but not for the "control" analyses of wastes from tank AZ-101. The AZ-101 tank received only HDW-type P3 wastes arising from PUREX 1983-1990 HLW (Table 3.1 of Wells et al. (2011)) and thus plutonium-bearing solids only could only have arisen by coprecipitation. The tests for the wastes received from PFP (i.e., tanks SY-102, TX-118, and the Z-9 crib) found three types of Pu-bearing solids. The three types were plutonium with oxygen (i.e., plutonium oxide), plutonium with bismuth, and plutonium with bismuth and phosphorus (P; potentially phosphate).

Given the co-existence of the plutonium with bismuth and of plutonium with bismuth and phosphorus, it is tempting to conclude that the particles arose from the Bismuth Phosphate Process. However, examination of process flowsheets show that the maximum plutonium concentrations in $BiPO_4$ solids generated in a $BiPO_4$ batch is about 323 g plutonium within about 9823 g of bismuth in 1951 when the process was mature (Schneider 1951). The maximum plutonium concentration with respect to bismuth in the Bismuth Phosphate Process flowsheet implemented in mid- to late-1945, early in the process, was 292 g of plutonium per 13,410 g of bismuth (Hanford Works 1944). At these levels of plutonium in bismuth (~2-3 wt%), the plutonium would be difficult to detect by SEM/EDS techniques and certainly would not be present at the intensities observed in the EDS spectra provided in the analytical reports (Callaway III and Cooke 2004; McCoskey and Cooke 2013).

Subsequent evaluations by process experts Jacob Reynolds, James Kadinger, and Ted Venetz to examine the findings of these analytical reports for the plutonium, plutonium-bismuth, and plutonium-bismuth-phosphorus species found in tanks SY-102 and TX-118 as well as in the Z-9 crib solids and the AZ-101 wastes in light of Hanford Site process knowledge provide the following observations and conclusions:

- In the 2004 report, the plutonium-rich particles in tank SY-102 comprised <0.12% by mass of the coarse fraction particles. The plutonium-bismuth-rich or plutonium-bismuth-phosphorus-rich particles also were few, ~0.5% to 6.0%, by number, of the high atomic number population. None of the plutonium-bearing particles, including the plutonium-bismuth and plutonium-bismuth-phosphorus associated particles, had an equivalent spherical diameter greater than 10 μm.
- In the 2013 report, only trace amounts of plutonium-bismuth-rich particles were found in the coarse fraction of tank SY-102 and Z-9 crib samples.
- No discrete Pu-rich particles were detected in tank AZ-101 samples despite the relatively high plutonium concentrations in this waste. The plutonium in tank AZ-101 samples only was detected by digestion and radiochemical analyses, suggesting that plutonium coprecipitated within the bulk metal oxides or hydroxides.
- Tank characterization data evaluations for TX-118 and from BBI in TWINS data indicate that bismuth is more highly associated with the PFP waste layer than with the saltcake of other origin. Therefore, it is likely that the plutonium-bismuth and plutonium-bismuth-phosphorus originated from the PFP process chemicals or from the PFP feed sources.

- The TX-118 leach experiments reported in 2013 showed that the larger particles with plutonium-bismuth and plutonium-bismuth-phosphorus associations dissolved in concentrated organic (citric/oxalic) acid but that smaller particles did not. The present authors note that this suggests that the smaller particles were PuO_2.
- The 2013 report shows bismuth present in the Z-9 crib while process record review show that the Z-9 crib is unlikely to have received Bi from any source other than PFP.
- Because the inventories of the two tanks that received most of the PFP waste (i.e., SY-102 and TX-118) are sample-based rather than process knowledge-based, the BBI in TWINS plutonium estimates for those tanks are not affected by any inaccuracies in process knowledge.
- The exact crystal form of the plutonium-bismuth and plutonium-bismuth-phosphorus particles could not be conclusively determined. However, formation of the plutonium-bismuth-rich and plutonium-bismuth-phosphorus-rich phases under tank waste conditions is extremely unlikely because the plutonium concentration in tank waste solutions is inadequate to favor crystal growth.[1]
- The densities of the plutonium-bismuth and plutonium-bismuth-phosphorus phases is unknown but likely are limited to that of the respective pure oxides or phosphates, the highest of which is 11.46 g/cm^3 for PuO_2.

We note that many plutonium-only particles from SY-102, TX-118, and Z-9 have sharp angular splintered or petrified wood-like appearances. These features are similar to those found for an acicular (needle-shaped) Pu-bearing particle remaining in item R600885-3013 from Rocky Flats and examined by Michael Summer of the Savannah River National Laboratory in 2007. Process knowledge, EDS, and Materials Identification and Surveillance (MIS) assignment indicate that R600885-3013 arose from pure plutonium metal oxidation. As indicated by XRD, pycnometer measurements, and assay, respectively, the Rocky Flats item contained PuO_2 and $NiCr_2O_4$ calciner boat slough, had 11.56 g/cm^3 particle density, and was 86.42 wt% plutonium (Kessinger et al. 2010). Values expected for stoichiometric PuO_2 are 11.46 g/cm^3 density (Clark et al. 2006) and 88.2 wt% plutonium. The similarities between the plutonium-only Hanford samples and R600885-3013 are shown by the SEM images and EDS analyses given in Figures 5.7 and 5.8, respectively.

---

[1] It is noted that precipitation of Pu(IV) nitrate in alkaline solutions ranging from neutral to high pH, and further to molar NaOH concentrations under laboratory conditions, produces particles that range in size from ~2 to 5 nm (Delegard (2013) and references therein)—thousands of times smaller than the tens of micrometer-sized Pu-Bi and Pu-Bi-P particles found in the SY-102 and TX-118 samples. The particle growth rate in NaOH solution in laboratory tests of up to ~40 months duration was exceedingly slow and decreased with time C. H. Delegard, *Effects of Aging on $PuO_2{\cdot}xH_2O$ Particle Size in Alkaline Solution*, Radiochimica Acta 101.5 (2013). In actual tank waste, potential particle growth of plutonium-bearing solids should be further attenuated by the abundant low-solubility metal (hydr)oxide surfaces, such as those of ferric hydroxide, that can sorb plutonium, further lower plutonium's effective concentration, and provide a physical barrier to plutonium diffusion. Therefore, in-tank production of the Pu-Bi or Pu-Bi-P particles is practically foreclosed.

Figure 27. Run 45 Particle 329 (Plutonium Oxide, D_{ve} = 8.4 µm).

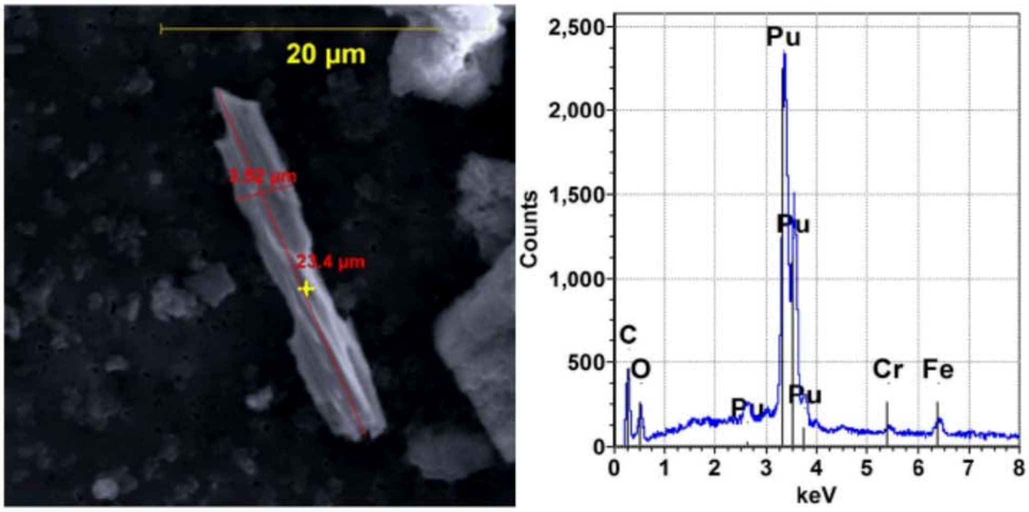

Figure 82. Sample S1R000475C Tank 241-TX118 >45 Micron.

BEI image to left, EDS spectrum to right from area marked with +

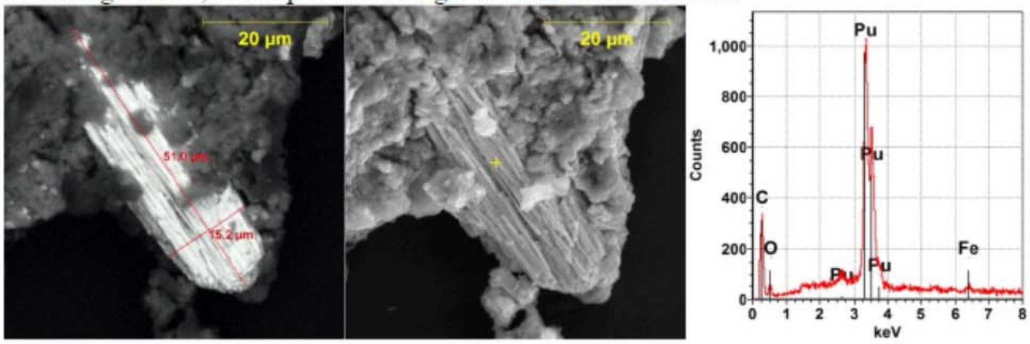

Figure 159. 216-Z-9 Sample 5A, >40-Micron Fraction.

BEI to Left, SEI in Middle, EDS Spectrum to Right.

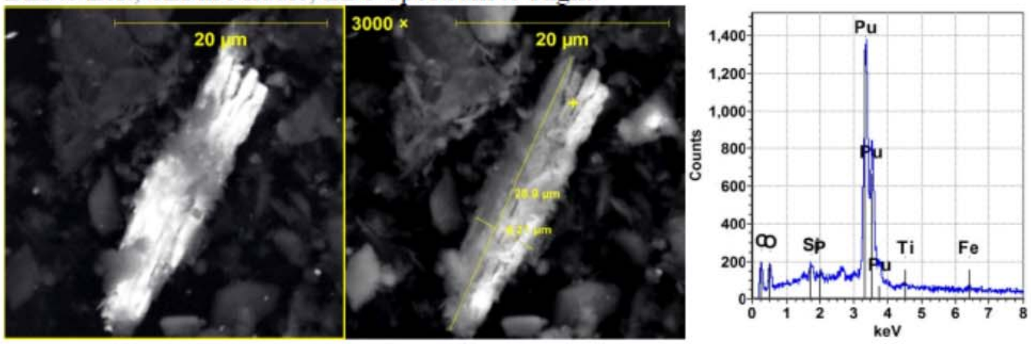

Figure 5-7. Plutonium-rich Particles from Tank SY-102 (top), Tank TX-118 (middle), and the Z-9 Crib (bottom) (taken from McCoskey and Cooke (2013))

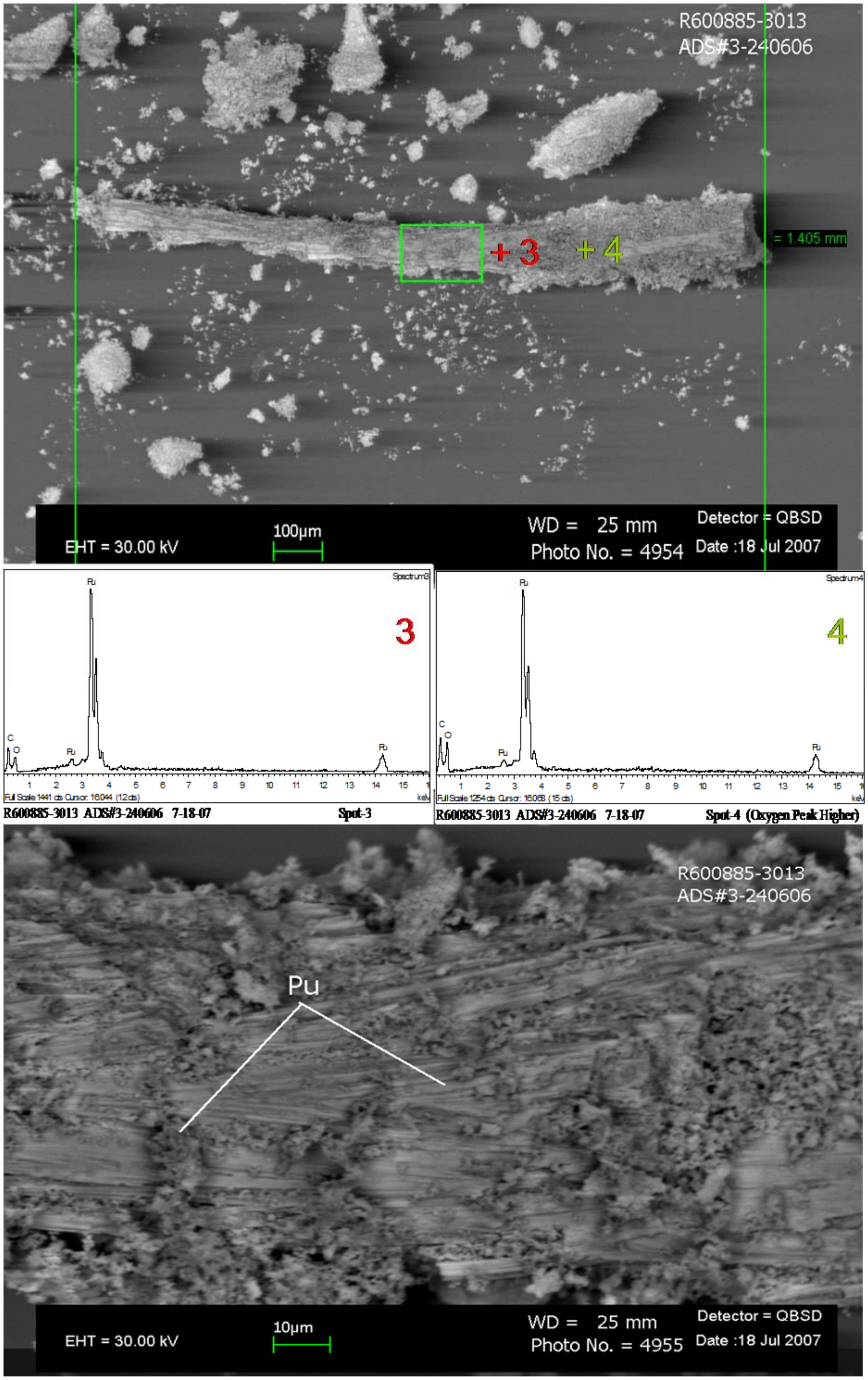

Figure 5-8. Particle from Burnt Plutonium Metal from Rocky Flats 3013 Item R600885 EDS Spectra at Spot-3 (red +) and Spot-4 (green +); lower image area from green box in upper image

Particles with the wood splinter appearance also have been observed in product from plutonium direct metal oxidation, DMO (Wayne 2014); see Figure 5-9. The oxidation is performed using metered introduction of 75% O_2/25% He, maintaining temperature between 475° C and 575° C and below the 640° C melting point of plutonium metal (Bluhm et al. 2008). Particles with similar wood splinter textures were found in furnace-stabilized plutonium metal electrorefining Rocky Flats residues (Narlesky et al. 2012, Figures 22 and 23). Based on process origin, these particles also were PuO_2 from plutonium metal burnt in air.

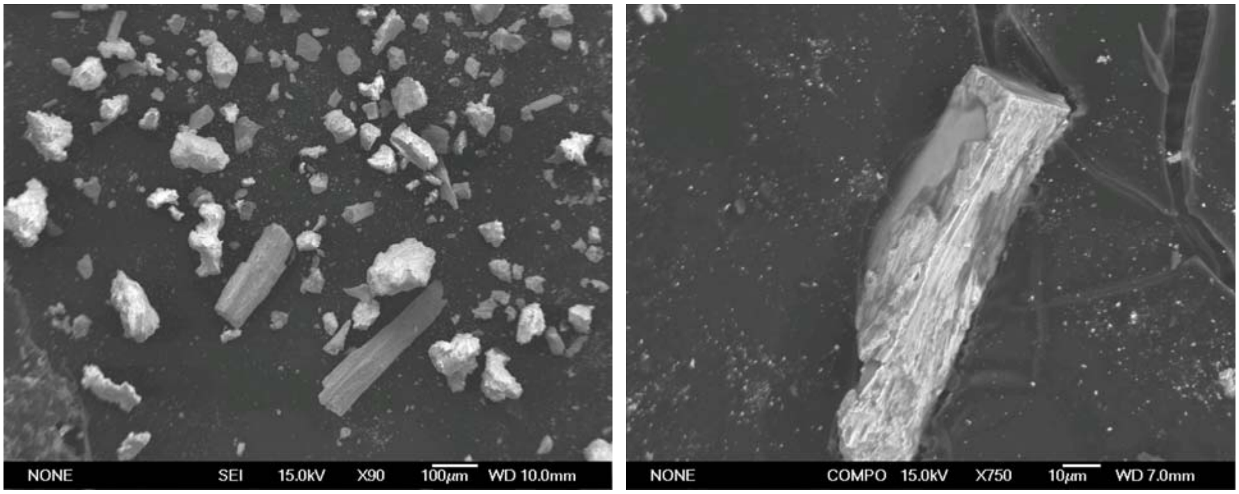

Figure 5-9. Particles from DMO of Plutonium Metal at LANL (courtesy David Wayne, LANL)

Although the SY-102, TX-118, and Z-9 particles are 0.02 to 0.05 mm long (Figure 5.7) and the acicular plutonium particle is 1.4 mm long (Figure 5.8), the microscopic grains and wood-like textures are of similar scale and also are similar to the DMO product (Figure 5.9). The EDS spectra for the SY-102, TX-118, Z-9, and R600885 particles show peaks for plutonium and oxygen. Because of the high chemical activity of plutonium metal, oxygen would be observed even on a fresh plutonium metal surface once it has been exposed to air (Haschke et al. 2000). Direct comparison of the relative EDS spectra plutonium and oxygen peak intensities for the three Hanford samples with those of R600885-3013 to assess their similarities cannot be done with confidence because of matrix effects, including the very limited depth of interrogation into the highly shielding plutonium matrix, the weakness of the oxygen x-rays, and detector sensitivity differences. The EDS spectra for the two different locations on the Rocky Flats particle can be compared with greater confidence and show that the area with the splintered wood-like texture at Spot 3 in Figure 5-8 has a lower oxygen-to-plutonium signal ratio than the granule-coated area at Spot 4. This might suggest that the wood-textured region is unburnt plutonium metal with density 19.86 g/cm^3 and the granule-coated area is PuO_2 with density of 11.46 g/cm^3. However, the higher O:Pu ratios for the granules also might reflect their relatively greater surface area and thus greater water vapor adsorption compared with the wood-textured region. In that case, both types of particles might be PuO_2.

Particle size distribution data from three different studies of bulk plutonium metal oxidation in air at ≥500° C have been spliced into a single size distribution (Haschke (1992); see also Appendix C). The resulting mass-based spliced size distribution is bimodal with maxima centered at ~30 μm and 600 μm. The SY-102, TX-118, and Z-9 sample particle sizes are in line with the smaller mode and the R600885-3013 needle with the larger. It is likely that only the smaller particles could have arrived at the waste tanks and crib because of the size-classification engendered by the lengthy pipeline transits and the high particle densities.

> *Conclusions – Discrete plutonium-bearing solids have been found in the TX-118 and SY-102 waste tanks and in the Z-9 crib, all receivers of wastes from the PFP while no discrete plutonium-bearing solids were found from tank AZ-101 which contained abundant plutonium but not from PFP. The plutonium-bearing solids were plutonium only (with oxygen), plutonium-bismuth, or plutonium-bismuth-phosphorus and all likely from PFP sources. Some plutonium-oxygen particles have splintered wood-like texture strikingly similar to those found in oxides from burnt plutonium metal and likely is* PuO_2*, although plutonium metal, for the time being, cannot be excluded for some materials based on the present evidence.*

6.0 Plutonium Interactions with Absorber Compounds

The intimate and robust interaction of plutonium with compounds of the seven absorber elements is a key factor in criticality safety considerations for WTP operations. The seven absorber elements are aluminum, cadmium, chromium, iron, manganese, nickel, and uranium. Sodium also is considered an absorber due to its ubiquity in the tank wastes. The interactions can take place by coprecipitation of plutonium with compounds of the neutron absorber elements, by sorption or adsorption of plutonium onto neutron absorber particle surfaces, and by proximity as in the presence of dissolved sodium salts by themselves and within tank waste solids.

Bismuth is a poor neutron absorber as it is used as a coolant constituent in liquid metal cooled reactors (e.g., naval reactors). However, it is relatively abundant in the tank wastes, present at levels about a factor of three lower (on a mole basis) than manganese, nickel, and chromium, and its compounds are demonstrated to be good coprecipitation agents for plutonium. Therefore, limited discussion of the chemistry of bismuth in alkaline tank waste solution is provided for completeness.

6.1 Coprecipitation

Three studies conducted by the IPC/IPCE for the Hanford Site under U.S. DOE support (Fedoseev et al. 1998; Krot et al. 1998c; Krot et al. 1998b) and the subsequent journal articles based on these studies provide key foundational information on coprecipitation. The IPC/IPCE examined the interactions of Pu(IV) with the metal ions Al(III), Co(II), Cr(III), Fe(III), La(III), Ni(II), U(VI), and Zr(IV) and Pu(VI) with the Al(III), Cr(III), and Fe(III) metal ions under alkaline coprecipitation conditions, akin to those practiced in Hanford Site processing plants (Fedoseev et al. 1998). To aid in understanding the Pu-metal ion solid phase interactions (e.g., so that XRD and spectroscopic methods could be used and the plutonium species identified), the tests were performed using widely varying Pu:metal mole ratios. That same year, many of the same scientists conducted additional investigations of the interactions of Pu(IV) and Am(III) with Al(III), Fe(III), and U(VI) at various mole ratios under alkaline coprecipitation conditions. This work was done for potential application to disposal of Hanford Site K Basin sludges to the Hanford tank farms after their acid-treatment to dissolve their contained uranium metal and subsequent adjustment with NaOH (Krot et al. 1998b). They examined the physical characteristics of the resulting Al(III), Fe(III), and U(VI) bulk precipitates and the susceptibilities of the precipitated products to leaching by alkaline carbonate and EDTA solutions. In the third IPC/IPCE study, experiments to determine the interactions of Pu(IV) with numerous sodium salts under alkaline coprecipitation conditions were performed (Krot et al. 1998c).

In the first set of tests, dissolutions in hydrochloric acid were performed of the solids formed by alkaline coprecipitation of macro amounts of Pu(IV) with separate aliquots of Al(III), Co(III), Cr(III), Fe(III), La(III), Ni(II), U(VI), and Zr(IV). The rates of dissolution showed whether the plutonium combined intimately with the metal ion, as indicated by dissolving at the same rate, or if the plutonium did not combine intimately, in which case the separate generally more recalcitrant $PuO_2 \cdot xH_2O$ phase dissolved more slowly than the complementary metal ion compound. The tests and spectroscopic measurements showed that the coprecipitates of Pu(IV) with Fe(III), Co(III), Cr(III), La(III), Zr(IV), and U(VI) were intimately mixed; the structures of the resulting metal oxide/hydroxide solids were also altered from those of the individual pure phases (Fedoseev et al. 1998). For the coprecipitation tests of Pu(IV) with Ni(II) and Al(III), however, no such atomic-scale intimate mixture was evident. Instead,

$PuO_2 \cdot xH_2O$ was found to precipitate by itself. Because only small amounts of aluminum precipitated, the $PuO_2 \cdot xH_2O$ solids themselves were examined and found to contain little trace of aluminum, even in relatively dilute NaOH solutions where aluminum solubility is low, confirming the lack of interaction. The dissolution rate tests of the mixed Pu(IV)-Ni(II) precipitate showed that the Pu(IV) dissolved at the same rate as $PuO_2 \cdot xH_2O$ by itself.

The additional investigations of the interactions of Pu(IV) with Al(III), Fe(III), and U(VI) at various mole ratios under alkaline coprecipitation conditions confirmed the initial findings and showed that Pu(IV)-Fe(III) interactions are strong (Krot et al. 1998b). The Pu(IV)-U(VI) interactions also are strong, but lower than Pu(IV)-Fe(III). Little to no Pu(IV)-Al(III) interaction was found.

As discussed in the previous section, Pu(IV) does not precipitate with the anions of most sodium salts to form anion-specific compounds. The precipitated phase was $PuO_2 \cdot xH_2O$, the same as observed for precipitation using NaOH alone (Krot et al. 1998c) and no incorporation of sodium within the $PuO_2 \cdot xH_2O$ precipitate was seen (Yusov et al. 2000c). Likewise, no aluminum-bearing plutonium compound is formed in the presence of aluminate (Fedoseev et al. 1998). However, interactions of plutonium with phosphate and silicate to form plutonium phosphate and silicate compounds from alkaline solution were identified.

Thus, these three studies (Fedoseev et al. 1998; Krot et al. 1998b; Yusov et al. 2000c) encompass the interactions of Pu(IV) with five of the seven absorber elements of interest, as will be described. The absorbers not examined by the IPC/IPCE scientists were cadmium and manganese. However, in earlier studies, many of the same IPC/IPCE investigators examined the interactions of the alkali-soluble manganese species Mn(II) and permanganate, MnO_4^-, as vehicles to carry, by coprecipitation, dissolved actinide ions under alkaline conditions.

For perspective, the solubilities of hydroxides, oxides, or oxyhydroxides of six of the seven absorber elements (cadmium, chromium, iron, manganese, and nickel and sodium salts of uranium) in strong NaOH solution are compared, in Figure 6-1, with that of freshly precipitated Pu(IV). Because of its high solubility in strongly alkaline solution, the behavior of the absorber aluminum is not presented in Figure 6-1. The crystallinities of the non-plutonium solid phases shown in Figure 6-1 are not defined, in general, but preference was given to using data for less aged precipitates (e.g., FeO(OH) rather than Fe_2O_3; $Cr(OH)_3$ rather than Cr_2O_3) which would have higher relative solubilities. The solubilities of two manganese phases, $Mn(OH)_2$ and MnO_2, are plotted. At the 0.017-V electrode potential established by the NO_3^-/NO_2^- couple at pH 14, effectively 1 M NaOH (Bratsch 1989), Mn_2O_3 should be the stable manganese oxide phase (Pourbaix 1966). However, no solubility data in highly alkaline solution were found in the technical literature for either the Mn_2O_3 or the Mn_3O_4, which is predicted by Pourbaix (1966) under slightly more reduced conditions. It is also noted that at the potential established by the nitrate/nitrite couple, chromium should exist as chromate, CrO_4^{2-} [i.e., hexavalent chromium, Cr(VI); Pourbaix (1966)]. In fact, both dissolved chromate and precipitated $Cr(OH)_3$ and other Cr(III) solid phases (Table 4-8) are observed in tank waste. The potential for the electrochemical couple of CrO_4^{2-} versus freshly precipitated $Cr(OH)_3$ at pH 14 is -0.12 V (Bratsch 1989). The nitrate/nitrite and $CrO_4^{2-}/Cr(OH)_3$ couples (Figure 5.4) may bracket the plausible range of tank waste redox potentials in the absence of any supplemental redox agents.

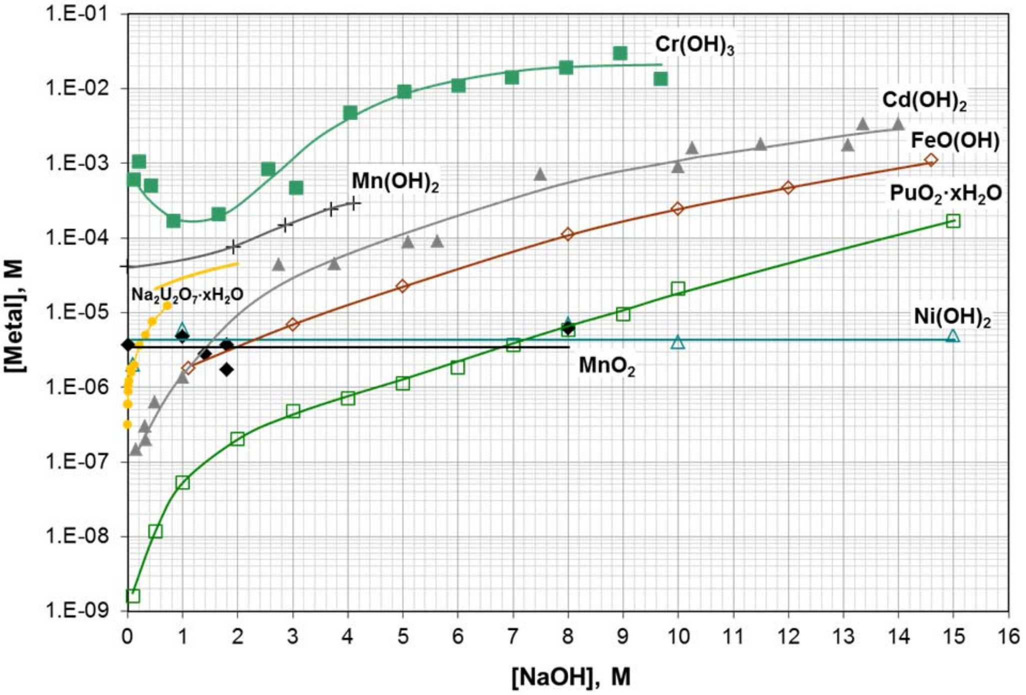

Figure 6-1. Solubility of Metal (Hydr)Oxides. $Cd(OH)_2$ (Rai et al. 1991b; Solov'eva et al. 1973b; Solov'eva et al. 1973a); $Cr(OH)_3$ (Rai et al. 2002); FeO(OH) (Kamnev et al. 1986); MnO_2 (Pokrovskii et al. 1997); $Mn(OH)_2$ (Fox et al. 1941); $Ni(OH)_2$ (Gayer and Garrett 1949); $Na_2U_2O_7 \cdot xH_2O$ (Yamamura et al. 1998; Hobbs and Karraker 1996); and ~2-day-old $PuO_2 \cdot xH_2O$ precipitate (Delegard 1985b) in NaOH solution. *(The plutonium data for the two points below 1 M NaOH are from as-yet unpublished findings of Delegard.)*

Figure 6-1 shows that $Cd(OH)_2$, $Cr(OH)_3$, FeO(OH), $Mn(OH)_2$, $Na_2U_2O_7 \cdot (0\text{-}5H_2O)$, and $PuO_2 \cdot xH_2O$ generally increase in solubility with increase in NaOH concentration while $Ni(OH)_2$ and MnO_2 solubilities show no apparent dependence on NaOH concentration. The solubility of $Na_2U_2O_7$ may decrease with further increase in NaOH concentration (Hobbs and Karraker 1996) because precipitation of the sodium salt caused by the increased sodium ion concentration may be more influential than increase in hydroxide ion concentration to stabilize the anionic complex. Other sodium salts are not included in Figure 6-1 because of their relatively high solubilities; the solubilities of double anionic sodium salts are described elsewhere (Felmy and MacLean 2001). Data for $Al(OH)_3$ are not plotted in Figure 6-1 because of the relatively high $Al(OH)_3$ solubility that occurs with increasing NaOH concentration.

The solubility of the aluminum phases $Al(OH)_3$ and $NaAl(OH)_4$ in simulated Hanford tank waste solution containing NaOH and saturated in $NaNO_3$, $NaNO_2$, $Al(OH)_3$/ $NaAl(OH)_4$, Na_2SO_4, and Na_2CO_3 media has been determined (Barney 1976b). Note that double salts such as $Na_3NO_3SO_4$ may have formed (Herting et al. 2002) but were not identified. As seen in Figure 6-2, the dissolved aluminum concentration increases steeply to ~4 M as NaOH concentration increases to ~1.6 M and then decreases with further increase in NaOH concentration, all in solutions saturated in $NaNO_3$, $NaNO_2$, $Al(OH)_3$/ $NaAl(OH)_4$, Na_2SO_4, and Na_2CO_3. For systems below ~1.6 M NaOH, the aluminum solid phase is $Al(OH)_3$; for systems above ~1.6 M NaOH, the aluminum solid phase is $NaAl(OH)_4$, described as $NaAlO_2$ by Barney (1976b). The solubilities of $Al(OH)_3$ and $NaAl(OH)_4$ in the dissolved

$NaOH$-$NaAl(OH)_4$ system as functions of temperature also are shown in Figure 6-2. The $NaOH$-$NaAl(OH)_4$ system represents conditions that might occur in caustic leaching of, for example, aluminum-rich REDOX sludge to dissolve its contained gibbsite [γ-$Al(OH)_3$] and boehmite (γ-$AlOOH$). Under these conditions, the concentrations of other tank waste salts (e.g., sodium nitrate, sodium carbonate) could be low. In practice, achieving the concentrations shown in Figure 6-2 could be challenged by slow aluminum phase dissolution rates.

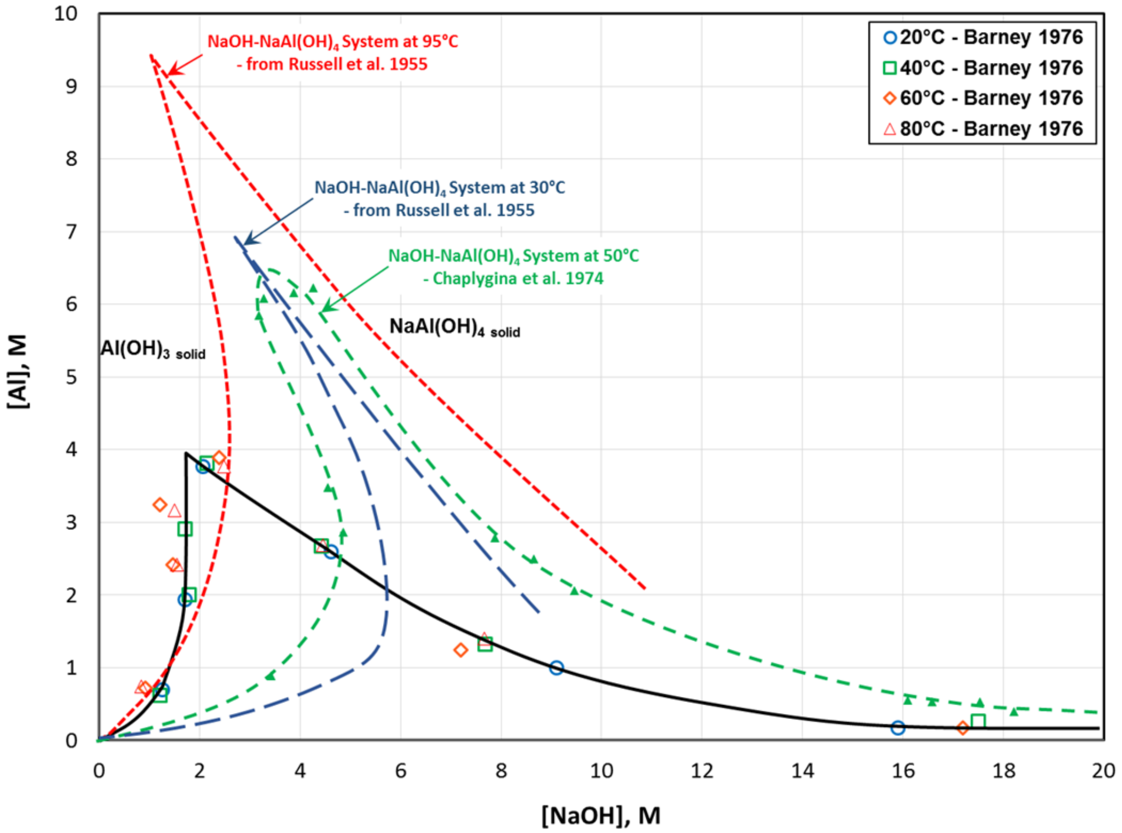

Figure 6-2. Solubility of Aluminum Phases in NaOH Solutions. Saturated in $NaNO_3$, $NaNO_2$, $Al(OH)_3$/ $NaAl(OH)_4$, Na_2SO_4, and Na_2CO_3 (Barney 1976a), and in pure NaOH solutions (Russell et al. 1955 and references therein; Chaplygina et al. 1974)

Finally, it is evident that aluminate and silicate readily react in 1:1 mole ratios to form aluminosilicate minerals in alkaline solution as shown by the frequent observation of cancrinite in Hanford tank waste (Table 4-8), the presence of cancrinite in Savannah River Site tank wastes brought on by discharge of high-silica wastes from the Defense Waste Processing Facility (vitrification plant) to their aluminate-bearing alkaline tank waste system (Wilmarth et al. 2000)[1], tests of reaction of simulated Hanford tank wastes with siliceous sediments (Mashal et al. 2004), and in investigations of waste forms

---

[1] This is based on the authors' assignment of an XRD scan of the deposit to powder diffraction file 38-0513, $Na_8[AlSiO_4]_6(NO_3)_2 \cdot 4H_2O$, cancrinite. Significantly for the WTP, the Savannah River Site observations were linked to the mixing of high-silicate wastes from their vitrification plant, beginning in 1997, with alkaline aluminum-rich streams for evaporation. Soon, low solubility sodium-aluminosilicate deposits began to form in the evaporator. The conditions leading to sodium aluminosilicate formation in the silicate-bearing Savannah River Site tank wastes has been studied both from thermodynamic and experimental perspectives. See CM Jantzen et al. 2002 and SV Mattigod et al. 2006.

for Hanford tank wastes in the "Aqueous Silicate Process" (Barney 1976a, chapter 8, pp 108-125). Given the ~10:1 Al:Si mole ratio in tank waste (Figure 3-1) and the results of lab studies (Mattigod et al. 2006), little silicon is expected to remain in alkaline tank waste solution in the presence of aluminum. Stated differently, to a first approximation, virtually all silicon and ~10% of the aluminum in alkaline Hanford tank waste may be present as solid sodium aluminosilicates.

Reviews of the studies of plutonium coprecipitation with aluminum, cadmium, chromium, iron, manganese, nickel, and uranium solids in NaOH solution are presented in the following subsections.

6.1.1 Aluminum

Over 97% of the aluminum present in Hanford tank waste came from chemical dissolution of the aluminum metal cladding from the uranium metal fuel used in the eight single-pass reactors (~45%; Section 3.1) and aluminum nitrate used as a salting agent in the REDOX Process (~52%; Section 3.3). Most of the remainder came from use of aluminum nitrate to mask the corrosive fluoride ion (i.e., bind it through chemical complexation) (Kupfer et al. 1999). Approximately 8700 metric tons, or 3.2×10^8 moles of aluminum are present in the waste (PNNL n.d.).

The association of Pu(IV) with aluminum precipitates made by neutralization of acidic solutions with NaOH is poor (Fedoseev et al. 1998; Krot et al. 1998b; Hobbs 1999) and becomes poorer with increasing pH into the alkaline regime because the aluminum is amphoteric, dissolving as the aluminate ion at high alkalinity (see Figure 6-2). The uptake of plutonium within cage-like aluminosilicate structures, formed by the presence of both dissolved aluminum and silicon in alkaline solution, is unknown but is not likely given the dimensions of plutonate anions (e.g., $PuO_2(OH)_4^{3-}$) compared with anions ordinarily found in the cancrinite or sodalite cages (e.g., chloride, carbonate, nitrate).

Thus, the aluminum hydroxide [$Al(OH)_3$] precipitate formed by treatment of an acidic Pu(IV)-Al(III) solution with NaOH will dissolve to form soluble $Al(OH)_4^-$ with further increase in pH as shown in the following reaction sequence:

$$Al^{3+} + 3\ NaOH \rightarrow Al(OH)_{3\ (solid)} + 3\ Na^+ \qquad \text{[precipitation complete between ~pH 4 and 12]}$$

$$Al(OH)_{3\ (solid)} + NaOH \rightarrow Al(OH)_4^- + Na^+ \qquad \text{[the } Al(OH)_3 \text{ solid begins dissolving above ~pH 12]}$$

Hanford tank waste contains both dissolved $Al(OH)_4^-$ (the aluminate anion), precipitated aluminum primarily as $Al(OH)_3$, i.e., gibbsite but also bayerite and nordstrandite, and the partially dehydrated form, AlOOH, boehmite, and, with increasing NaOH concentration or chemical activity, $NaAl(OH)_4$ solids. As seen in Table 4-8, other aluminum solid phases exist [e.g., aluminum phosphates or $NaAlCO_3(OH)_2$, known as dawsonite] but no Pu(IV) coprecipitation studies with Al(III) compounds other than $Al(OH)_3$ are known. Studies also show that Pu(VI) coprecipitation with Al(III) in alkaline media is poor (Fedoseev et al. 1998; Yusov et al. 2000a).

The propensity of plutonium to be leached from genuine Hanford tank waste sludge by NaOH solution has been investigated as part of testing of aluminum-bearing solid dissolution by NaOH solutions (Rapko et al. 2004). A review of results of prior leach testing, including leaching by NaOH solution alone in the absence of oxidants (e.g., permanganate, MnO_4^-, or ozone, O_3), is provided in Tables 1.3 and 1.4 of the cited report. Leach tests were run for 24 to 203 h at 30° C to 100° C with NaOH concentrations ranging from 0.01 to 4.8 M. For most tests, the amounts of plutonium dissolved were less than 1%. The amounts exceeded 1% only for tests at higher (≥3 M) NaOH concentrations but did not exceed 3% for any test. These data suggest that plutonium present in genuine sludge is not associated with the dissolving aluminum phases.

Because $Al(OH)_3$ is amphoteric, there is the possibility that the Pu(IV) or Pu(V) dissolved in alkaline solution might coprecipitate with $Al(OH)_3$ should dissolved $Al(OH)_4^-$ be present and the NaOH concentration decrease. The NaOH concentration decrease can occur by absorption of CO_2 from the air or by inadvertent or intentional addition of HNO_3 to the solution. As shown in Figure 5-5, decreasing NaOH concentration decreases plutonium solubility in any studied oxidation state. If the pH decrease is occasioned by CO_2 absorption, the carbonate quantities would increase and potentially increase the Pu(IV) solubility. However, many, if not most, of the tank waste solutions already are saturated in Na_2CO_3 such that additional carbonate could just precipitate more Na_2CO_3 or, with aluminum, precipitate dawsonite, $NaAlCO_3(OH)_2$. Therefore, Pu(IV) coprecipitation with $Al(OH)_3$ caused by NaOH concentration decrease occurring due to CO_2 absorption is unlikely; the interaction of plutonium with dawsonite is unknown.

No experimental evidence is known to predict whether Pu(IV) coprecipitation with $Al(OH)_3$ would occur if an alkaline $Al(OH)_4^-$ solution containing dissolved Pu(IV) were contacted with mineral acid (e.g., HNO_3). Therefore, the question of whether dissolved plutonium will coprecipitate with $Al(OH)_3$ precipitated from the alkaline side cannot be answered with certainty and must be investigated by laboratory testing.

> *Conclusions – Little association of plutonium with $Al(OH)_3$ under alkaline conditions is observed. Potential association of plutonium with other Al-bearing phases such as dawsonite is unknown.*

6.1.2 Cadmium

About 8 tons of cadmium are projected to be present in Hanford tank waste (PNNL n.d.; Kupfer et al. 1999), similar to the ~10-ton value shown in Figure 3-1. Inventory data for cadmium are not available in TWINS (PNNL n.d.). About two-thirds of this total is estimated to have been used as a soluble neutron absorber for secondary criticality control in dissolving PRTR fuel at the PUREX Plant in 1968 and in rework of the plutonium product because the head-end PUREX process vessels were not designed for plutonium-rich feed (Kupfer et al. 1999). Prior flowsheets for processing PRTR and Shippingport fuel at the REDOX Plant do not mention using cadmium. The cadmium was added as cadmium nitrate solution. The raffinates from processing the PRTR fuel in the PUREX Plant went to tanks AZ-101 and AZ-102 to be combined with the more typical PUREX wastes from Hanford production reactor fuel processing. The remaining ~⅓ of the cadmium expected in waste is projected to be distributed about equally to the single-shell and double-shell tanks (Kupfer et al. 1999).

No information was found in the technical literature on coprecipitation interactions of plutonium with cadmium. In alkaline solution, cadmium precipitates as its hydroxide, $Cd(OH)_2$, or oxide, CdO (Rai et al. 1991b). In the presence of carbonate, cadmium carbonate would precipitate, $CdCO_3$ (Rai et al. 1991a). As shown in Figure 6-1, $Cd(OH)_2$ is mildly amphoteric with a solubility that increases from about 10^{-7} M in 0.1 M NaOH to ~10^{-4} M in 10 M NaOH (Rai et al. 1991b; Solov'eva et al. 1973b; Solov'eva et al. 1973a).

Conclusions – Association of plutonium by coprecipitation with cadmium phases stable under alkaline conditions [e.g., low solubility $Cd(OH)_2$*] has not been studied. Most of the cadmium used at Hanford was disposed to only two tanks – AZ-101 and AZ-102.*

6.1.3 Chromium

Chromium in Hanford tank waste primarily came from dichromate used as an oxidant in both the Bismuth Phosphate and REDOX Processes, chromium(III) used to chemically reduce permanganate, chromium from corrosion of stainless steel process equipment, and chromic acid used as a decontamination agent (Kupfer et al. 1999). About 590 metric tons or 1.1×10^7 moles of chromium are estimated to be present in the tank waste (PNNL n.d.).

Fedoseev et al. (1998) has studied the association of Pu(IV) with Cr(III), and other metal ions, under coprecipitation conditions. Infrared (IR) spectroscopy, XRD, and the differential dissolution rates of the hydrated plutonium/metal (hydr)oxide precipitates in HCl solution showed strong interactions between Pu(IV) and Cr(III). The mixed Pu(IV)-Cr(III) systems' IR spectra differed greatly from those of the individual components and no $PuO_2\cdot xH_2O$ was found in the mixed compounds by XRD meaning that Pu(IV) preferred to interact with Cr(III) during precipitation rather than with itself. Because plutonium dissolution rates in HCl were more rapid for the mixed compounds than for similarly prepared pure $PuO_2\cdot xH_2O$, intimate interaction of the plutonium within the Cr(III) matrix was inferred. The $Cr(OH)_3$ solubility is relatively high compared with hydrated Pu(IV) oxide and the other polyvalent metals in strongly alkaline solution (Figure 6-1).

In other tests, trace amounts of plutonium were homogeneously coprecipitated with Fe(III) and Cr(III) nitrate mixtures in HNO_3 by addition of excess NaOH solution and the susceptibility of the prepared precipitates to oxidative leaching by permanganate in 0.25 M NaOD and 3 M NaOD was studied (Sinkov 2007). The iron:chromium:plutonium mole ratio used was 28000:21000:1. In 0.25 M NaOD, the oxidative dissolution of Cr(III) by permanganate, Mn(VII), was rapid and quantitative, showing 1:1 chromium-to-manganese stoichiometry indicating the reduction of permanganate to MnO_2 by Cr(III) oxidation to Cr(VI). At the same time, undetectable (<2.1%) amounts of the plutonium dissolved, even with excess permanganate addition and extended leaching times, in two separate sets of experiments. Similarly, no detectible (<1.8%) plutonium dissolved in the 3 M NaOD tests using substoichiometric amounts of permanganate and the solutions rapidly became bright yellow, indicating dissolved Cr(VI) and also indicating, by color, that no residual permanganate (purple) or manganate (green) remained. However, when 15 to 45% excess permanganate was used in 3 M NaOD, from 32 to 36% of the plutonium dissolved within three minutes. This percentage may reflect the 43 molar% of chromium in the precipitate; the presence of excess permanganate and manganate was indicated by the solution color. With extended time, however, the excess permanganate converted to manganate and then, over time, to solid MnO_2. By four hours, about 17% of the plutonium remained in solution and by three to six days, the amount of plutonium remaining in solution decreased to about 12%. Subsequent quenching of the excess oxidant with Cr(III) left only ~0.7% of the total plutonium in solution. These tests indicate that $Cr(OH)_3$ in the mixed $Fe(OH)_3/Cr(OH)_3$ precipitate is an excellent carrier of plutonium but that the plutonium naturally is susceptible to becoming soluble by oxidative dissolution of the host $Cr(OH)_3$. At the same time, the associated $Fe(OH)_3$ retains the plutonium in the solid phase roughly in proportion to its mole fraction. In the case of oxidative dissolution of $Cr(OH)_3$ by permanganate, it is seen that the MnO_2 reduction product can efficiently return the plutonium to the solid phase.

The chromium-bearing solids observed in tank waste (Table 4-8), besides the $Cr(OH)_3$ solids or related oxyhydroxides tested by Fedoseev et al. (1998), include $FeCr_2O_4$; oxides of chromium with iron and manganese; compounds of chromium combined with aluminum, calcium; $(Ca,Sr)_3(Cr,Al)_2(OH)_{12}$; and chromium phosphate. The $FeCr_2O_4$ is a spinel phase, and thus should have high plutonium affinity in analogy to that exhibited by magnetite. The oxides of chromium with iron and manganese likewise should have high plutonium affinity given their complements of iron and chromium (and manganese) and the demonstrated affinities of these individual metal hydroxides for plutonium. The affinity of plutonium for the $(Ca,Sr)_3(Cr,Al)_2(OH)_{12}$ phase is not known. The affinity for the chromium phosphate likely is high given the low solubility of Pu(IV) phosphate (Krot et al. 1998c). The hydroxide concentration likely is low for the solution surrounding solid chromium phosphate. Were the pH higher, the chromium phosphate would metathesize to form the corresponding hydroxide or oxyhydroxide solid, $Cr(OH)_3$ or CrOOH in analogy to what is observed for iron(III) phosphate (Lumetta et al. 2010).

The Cr(III) (hydr)oxides can be dissolved by strong oxidants to form soluble chromate (e.g., Rapko et al. 2004 and associated studies cited therein). Dissolution of Cr(III) solid phases by permanganate is part of planned waste pretreatment strategies. Under oxidizing conditions, the association of plutonium by coprecipitation with Cr(III) would be lost.

> *Conclusions – Association of plutonium by coprecipitation with Cr(III) hydroxide under alkaline conditions is strong. However, oxidative dissolution of chemically reduced chromium phases using permanganate is planned in waste pretreatment. Such treatment will eliminate any association of plutonium with chromium.*

6.1.4 Iron

The ~1270 metric tons (~2.3×10^7 moles) of iron present in the Hanford tank wastes (PNNL n.d.) arose from process chemical additions mostly as ferrous sulfamate reductant, ~76%, and stainless steel corrosion, ~24% (Kupfer et al. 1999).

Scavenger precipitation of dissolved plutonium with Fe(III) in alkaline solution has been practiced from the earliest laboratory work with plutonium and is a well-known laboratory and plant technology to decontaminate solutions and to recover plutonium (Christensen and Maraman 1969). Solution concentrations of $<4\times10^{-8}$ M plutonium can be reached routinely but the amorphous or poorly crystalline $Fe(OH)_3$ gels are flocculent and difficult to filter. To overcome the poor filterability, magnetite, Fe_3O_4, also has been tested to coprecipitate plutonium (Slater et al. 1997 and references therein). The effects of magnetite concentration, pH, Fe(II)/Fe(III) ratio, direct or reverse strike mixing, temperature, and cation, anion, and organic complexing agent interferences were investigated. Decontamination factors (DFs) of 1000 to more than 100,000 were achieved at ~15 g magnetite carrier per liter concentrations. Later experiments by many in the same group found DFs for in-situ formed magnetite of ~200 when tested with an iron loading of 2.2 mg per mL of a simulated Savannah River Site alkaline tank waste solution (Arafat et al. 2003). The magnetite was formed in-situ by addition of dissolved Fe(II) and Fe(III) to the alkaline solution.

The association of Pu(IV) with Fe(III) and other metal ions under alkaline coprecipitation from HNO_3 solutions has been studied (Fedoseev et al. 1998; Fedoseev et al. 2000; Grigor'ev et al. 2001). Infrared (IR) spectroscopy, XRD, and the differential dissolution rates of the plutonium/metal hydrous oxide precipitates in HCl solution showed strong interactions between Pu(IV) and Fe(III). The mixed

Pu(IV)-Fe(III) systems' IR spectra differed significantly from those of the individual components. No $PuO_2 \cdot xH_2O$ was found in the compound mixtures by XRD meaning that Pu(IV) preferred to interact with Fe(III) during precipitation rather than with itself. Interactions of Pu(IV) with Fe(III) also were studied by Mössbauer spectroscopy, a technique sensitive to iron phases. The presence of Pu(IV) was found to impact the Fe(III) solid phase structure significantly, causing it to differ from that of the pure goethite formed in the absence of Pu(IV). Because plutonium dissolution rates in HCl were more rapid for the mixed compounds than for similarly prepared pure $PuO_2 \cdot xH_2O$, intimate interaction of the plutonium within the Fe(III) matrix was inferred.

The relative affinities of plutonium with aluminum, iron, and uranium were studied in additional experiments by Fedoseev et al. (1998). In these tests, mixed uranium, iron, and aluminum precipitates containing added plutonium were prepared by precipitation of their 1 M HNO_3 solutions with excess NaOH solution and then water washing the solids. The test ratios are as shown in Table 6-1. The precipitates then were leached using 0.25 and 0.5 M sodium bicarbonate, $NaHCO_3$.

Table 6-1. Composition of Samples Prepared for Bicarbonate Dissolution

Test	Solids Content, mg				Pu Dissolved
	Pu(IV)	U(VI)	Fe(III)	Al(III)	
1	0.020	20	0	0	95%
2	0.020	20	0	0.9	
3	0.020	20	1.8	0	5-8%
4	0.020	20	1.8	0.9	

As shown in Table 6-1, the amounts of plutonium dissolved by $NaHCO_3$ solution leaching were highly dependent on whether or not iron was present. With iron present (at an iron-to-plutonium mass ratio of ~100), plutonium dissolution decreased from about 95% to about 6%. These results show the high preference of plutonium for iron, even in the presence of much greater uranium concentrations.

The solubilities of both iron oxyhydroxide [FeO(OH), goethite][1] and hydrated Pu(IV) oxide increase in a parallel manner with increasing NaOH concentration, as shown in Figure 6-1, with the goethite solubility being about a factor 200-times higher than that of hydrated Pu(IV) oxide. The higher solubility of goethite than $PuO_2 \cdot xH_2O$ and the approximate 300-times higher iron concentration in the Hanford tank waste sludge compared with plutonium suggest that even for the small amount of plutonium that dissolves, a similar relative fraction of iron will dissolve. Thus, the plutonium coprecipitated with iron will remain accompanied by its most prevalent neutron absorber when contacted with NaOH solution.

The crystallite size of the freshly precipitated Fe(III) hydroxide generated under Hanford tank waste conditions is ~2 to 3 nm (Krot et al. 1998b), similar to the ~2-nm crystallite size observed for $PuO_2 \cdot xH_2O$ generated under similar conditions (Delegard 2013 and references therein). The similarity of crystallite sizes suggests that hydrodynamic separation of mixtures of these two solids is unlikely should they exist in a non-coprecipitated form. However, the size of their respective agglomerates, not the crystallites, is of greater importance.

---

[1] Goethite (α-FeOOH) forms from ripening of ferrihydrite in NaOH solution at room temperature and is relatively stable but will convert to hematite (α-Fe_2O_3) with heating above ~100°C (Fedoseev et al. 1998). Goethite and unnamed FeOOH phases have been identified in Hanford tank sludges (Rapko and Lumetta 2000; see also Table 4-8 in the present report).

Solutions with plutonium at trace concentrations in various simulated acidic PUREX waste solutions containing Al(III), Fe(III), Ni(II), and U(VI) were treated with 0.6 M NaOH to observe the coprecipitation behavior (Hobbs 1999). Partial crystallization of the bulk metal precipitates occurred with aging; after two months, the precipitated iron, aluminum, uranium, and nickel solids were analyzed by XRD. Although most of the solids were amorphous, crystalline goethite, gibbsite, bayerite, and sodium diuranate were identified. Aging did not affect the plutonium solution concentration. It was found that with iron or uranium present, plutonium concentrations were ~100-times lower than the concentrations found for $PuO_2 \cdot xH_2O$ prepared separately in side-by-side tests. However, little plutonium removal occurred from solutions containing aluminum with low iron or uranium concentrations. Thus, plutonium effectively coprecipitates with iron and uranium but not with the aluminum solid phases.

In contrast with the situation for Pu(IV), little association of Pu(VI) in alkaline solution with freshly precipitated Fe(III) and Cr(III) hydroxides was observed (Fedoseev et al. 1998; Fedoseev et al. 2000). In the same set of tests, little affinity of Pu(VI) for Al(III) hydroxide was observed (Fedoseev et al. 1998; Yusov et al. 2000a). In a related study, little association of neptunium(V) or neptunium(VI) during alkaline coprecipitation with iron(III) from acid solution was found, based on Mössbauer spectroscopy techniques, while the expected strong association of plutonium(IV) with iron(III) was found (Grigor'ev et al. 2001). Based on these findings, and because of the close chemical similarities of neptunium(VI) and plutonium(VI), little association by coprecipitation of Pu(VI) with Fe(III) is expected.

Tests also were performed to coprecipitate Pu(IV) with Ni(II) and Fe(III) at Pu(IV)-Ni(II)-Fe(III) component ratios of 1:1:1 and 2:1:1 (Fedoseev et al. 1998; Fedoseev et al. 2000). In these cases, no evidence of a separate plutonium phase, such as $PuO_2 \cdot xH_2O$, was found by IR spectroscopy. Because no test of the mixed solids dissolution rates was performed to determine if the plutonium dissolved at the same rate as the nickel or iron, this measure of the extent of interaction of the plutonium with the nickel and iron precipitate cannot be assessed. However, the lack of IR evidence for $PuO_2 \cdot xH_2O$ in the mixed Pu(IV)/Ni(II)/Fe(III) solid suggests that incorporation of Pu(IV) into the transition element matrix occurred.

Herting (1995) examined addition of ~0.3 M supplemental acidic Fe(III) to genuine alkaline tank waste, and Worl et al. (1995) examined addition of ~0.2 M Fe(II)/Fe(III) mixtures to simulated alkaline tank waste, to enhance plutonium removal from solution. Both tests met with some success with removals varying from 20-27% in the tests with actual waste (Herting 1995) to nearly quantitative in some tests with simulants (Worl et al. 1995).

Tests of oxidative dissolution of Cr(III) hydroxide from mixed $(Fe,Cr)(OH)_3$ by permanganate in 0.25 M and 3 M NaOD (Sinkov 2007) were described in the previous section on chromium. The fact that the quantity of trace plutonium initially dissolved mirrored that of the chromium mole fraction in the 3 M NaOD tests suggests that plutonium dissolution from the $Fe(OH)_3$ portion did not occur. No detectible plutonium dissolved by permanganate in the 0.25 M NaOD tests. Because the plutonium that did dissolve in the 3 M NaOD tests when stoichiometric permanganate excess was present could be virtually completely re-precipitated when the excess permanganate was quenched by added Cr(III) indicates that the permanganate reduction product, MnO_2, is also a good carrier of plutonium into the solid phase.

Iron-bearing solids other than goethite, hematite, and magnetite are observed in genuine Hanford tank waste (Table 4-8). These include $FeCr_2O_4$; Fe_2MnO_4; $BiFeO_3$; oxides of iron with chromium and manganese; compounds of iron combined with bismuth, lead , and chromium; iron phosphates; other Fe(III) hydroxides; iron oxalates; and lepidocrocite, another FeOOH phase. The dispositions of plutonium within these phases are not explicitly known. However, it is likely that Pu(IV) coprecipitates well with the spinel phases, $FeCr_2O_4$ and Fe_2MnO_4, owing to their similarity to ferrite, $FeFe_2O_4$ (i.e., Fe_3O_4). The poorly defined oxides and compounds of iron with chromium, manganese, bismuth, and lead and lepidocrocite likely are excellent carriers of plutonium, given the high affinity of plutonium for iron, which is present in all these compounds. The affinity of plutonium for iron oxalates is not known. However, Pu(IV) oxalate has low stability in alkaline solution and will decompose to form hydrated Pu(IV) oxide (Gel'man and Sokhina 1958) (see also discussions in Appendix A of this report). Similarly, the affinity of plutonium for iron phosphate is not known but likely is high in light of the low solubility of Pu(IV) phosphate (Krot et al. 1998c). The presence of iron phosphate indicates that hydroxide concentration is low for the solution surrounding this solid. If the pH were higher, the iron phosphate would metathesize to form $Fe(OH)_3$ or goethite (e.g., Lumetta et al. 2010).

> *Conclusions – Association of plutonium(IV) by coprecipitation with Fe(III) hydroxide under alkaline conditions is very strong but little association of Pu(VI) with Fe(III) hydroxide is observed. The Fe(III) matrix is stable to EDTA and carbonate leaching and is stable to oxidative leaching by permanganate.*

6.1.5 Manganese

Most of the manganese found in the Hanford tank wastes arose from use of permanganate as a process oxidant (~21% to oxidize plutonium in the Bismuth Phosphate Process, 58% to oxidize ruthenium to volatile RuO_4 in the REDOX Processes, and ~18% for solvent treatment in PUREX) with the balance, about 3%, introduced by fuel fabrication (Kupfer et al. 1999). The total manganese inventory is ~164 metric tons or $\sim3.0\times10^6$ moles (PNNL n.d.).

Manganese was not included in the survey of behaviors of Pu(IV) with transition metal ions and other metal ions performed by Fedoseev et al. (1998). However, experiments conducted by IPC/IPCE scientists on the behavior of plutonium in coprecipitation with manganese using permanganate, MnO_4^-, as an alkali-soluble precursor, were performed. Permanganate is a strong oxidizing agent and, if present in solution, can oxidize Pu(IV) to the more soluble pentavalent and especially hexavalent states (see Figure 5-4 and results of Sinkov (2007)). Permanganate also was used as a process reagent at the REDOX Plant and the PFP. Tests were conducted to determine plutonium coprecipitation with $Mn(OH)_2$ achieved by treating the alkaline Pu-bearing solutions containing permanganate with hydrazine and hydroxylamine (Krot et al. 1998a) and with MnO_2 and $Mn(OH)_2$ formed using sulfite and hydroxylamine, respectively (Bessonov et al. 1999). In the latter tests, the effects of other dissolved tank waste salts also were investigated. These findings arose from more general reports on decontamination of alkaline solutions from transuranium elements by a variety of alkali-soluble transition metal and uranium precursors (Krot et al. 1996; Bessonov et al. 1997).

With sufficiently high NaOH concentrations, DFs of 100 or more were achieved using ~0.004 to 0.03 M permanganate and reductant to precipitate $Mn(OH)_2$ carrier (Krot et al. 1996; Krot et al. 1998a). Decontamination factors for plutonium from alkaline solution in the tens to hundreds were found for permanganate reduction to $Mn(OH)_2$ and MnO_2 in the presence of complexing agents (Bessonov et al. 1997; Bessonov et al. 1999). Carrier precipitation of plutonium from alkaline solution with manganese using permanganate also was observed by Orth et al. (1995). Later, more detailed study of the carrying of plutonium from alkaline solution by permanganate established that the plutonium was removed from solution by coprecipitation and that the solid phase was sodium birnessite, ($Na_4Mn_{14}O_{27}\cdot 9H_2O$), a mixed Mn(III)/Mn(IV) phase (Duff et al. 2002). Tests of the oxidative destruction of organic complexants citrate, oxalate, gluconate, glycolate, and EDTA by permanganate in 3 M NaOH that contained trace dissolved ^{238}Pu were conducted (Nash et al. 2005). While permanganate did not oxidize citrate or oxalate, as determined by production of MnO_2 reduction product, it was effective in destroying gluconate, glycolate, and EDTA. The fraction of plutonium removed from solution was found to be proportional to the amount of MnO_2 produced.

Indirect evidence for the coprecipitation of plutonium with manganese solids was observed in the coincident dissolution of manganese and plutonium during exhaustive treatment of diluted genuine waste from tank SY-101 with bubbling ~10% ozone in oxygen gas (Delegard et al. 1993). Ozone, an extremely strong oxidant, was used in an effort to destroy organic complexing agents such as EDTA and HEDTA in the SY-101 waste solution. To achieve the organic destruction, the nitrite within the waste first had to be oxidized to nitrate which then was accompanied by the oxidative dissolution of Cr(III) to form soluble chromate, CrO_4^{2-}. By the end of ozonation, an organic residue of oxalate generated in the destruction of the larger organic species comprised about 10% of the original organic carbon inventory. Only when the oxalate reached its residual plateau concentration and the Cr(III) fully oxidized to chromate did the dissolution of the manganese solids occur, yielding a root beer-colored solution that, with the intense yellow caused by chromate, most likely indicated that permanganate was present. Accordingly, solution samples from the end of the ozonation treatment showed enhanced manganese and dissolved plutonium concentrations. The plutonium oxidation state was not determined, its concentration being too low to determine by spectrophotometry, but likely was Pu(VI) in the ~0.3 M NaOH solution present at the end of ozonation (Krot et al. 1977).

Further indirect evidence for plutonium incorporation into manganese solid phases also was seen in laboratory testing of calcination/dissolution of genuine tank waste (Delegard et al. 1994 and succeeding publications on this topic). In these tests, various types of Hanford tank waste underwent aqueous leach processing and parallel calcination/dissolution experiments in which the waste was first calcined by heating to ~800° C to form a strongly oxidizing melt, giving conditions akin to an alkaline fusion digestion as implemented in chemical assays of ores and minerals. The melt then was cooled and contacted with water. In most cases, both the manganese (if present) and plutonium dissolved. Then, when the strongly alkaline solutions containing manganese and plutonium were treated with chemical reductants, the plutonium precipitated from solution with the manganese.

As discussed in the prior sections dealing with chromium and iron, the recent tests by Sinkov (2007) of oxidative dissolution of Pu-bearing $(Fe,Cr)(OH)_3$ using permanganate show that MnO_2 arising from permanganate reduction is an effective carrier of plutonium dissolved by the oxidative dissolution of the host $Cr(OH)_3$. The quenching of the excess permanganate oxidant with Cr(III) confirmed this behavior and showed that the MnO_2 reduction product efficiently captures dissolved plutonium.

As Figure 6-1 shows, the solubility of manganese, as MnO_2, is relatively constant at about 4×10^{-6} M in NaOH solution. Although $Mn(OH)_2$ is predicted to be present by thermodynamics (Table 4-8), it is expected to be susceptible to oxidation by radiolytically-generated peroxide in alkaline solution to form MnO_2. Besides MnO_2, manganese is present as Mn_2CrO_4, $Mn_3Cr_3O_8$, Mn_2MnO_4, and other oxides and oxyhydroxides of manganese with iron in tank waste (Table 4-8). The spinel phases, Mn_2CrO_4 and Mn_2MnO_4, might have high affinity for plutonium based on the experience with the spinel ferrite for carrier precipitation (Slater et al. 1997). The undefined oxides and oxyhydroxides of manganese with iron likely have high plutonium affinity because of the iron complement in these solids.

Together, these finding suggest that manganese is an effective agent to coprecipitate plutonium and also forms strong interactions with the contained coprecipitated plutonium. Further experimentation would help confirm these speculations.

> *Conclusions – Association of plutonium by coprecipitation with Mn(IV) phases such as* MnO_2 *under alkaline conditions is very strong, as shown by carrier precipitation tests under alkaline conditions and in testing of genuine waste processing by ozone and calcination/dissolution. The stability of the manganese matrix towards EDTA and carbonate leaching is unknown but likely is high.*

6.1.6 Nickel

About 99 metric tons, or 1.7×10^6 moles, of nickel are present in the Hanford tank wastes (PNNL n.d.). Of this, about 34% is from stainless steel corrosion, 27% from cladding (mostly from aluminum single-pass reactor fuel), and 39% from nickel ferrocyanide scavenging operations (Kupfer et al. 1999).

The association of Pu(IV) with Ni(II), and other metal ions, under alkaline coprecipitation conditions has been studied (Fedoseev et al. 1998; Fedoseev et al. 2000). The Pu-metal ion solid phase interactions were determined using XRD and IR spectroscopic methods and widely varying Pu:metal mole ratios were used. The nickel(II) hydroxide, $Ni(OH)_2$, solubility in NaOH solution is low, $\sim4\times10^{-6}$ M, and invariant as NaOH concentration changes as seen in Figure 6-1 (Gayer and Garrett 1949).

In the tests by Fedoseev and colleagues (1998; 2000), the IR spectra in the Pu(IV)/Ni(II) system were found to be equivalent to the sum of the spectra of the individual components precipitated separately from alkaline solution. The separate precipitation of hydrated Pu(IV) oxide and $Ni(OH)_2$ upon adding NaOH solution to acidic solution containing both Pu(IV) and Ni(II) nitrate was confirmed by studying the dissolution rate of the resulting precipitates in 3 M HCl at 60° C. No difference in plutonium dissolution behavior was found between pure $PuO_2{\cdot}xH_2O$ and the products obtained by alkaline coprecipitation of 1:1 mole ratio Pu(IV):Ni(II) mixtures, aged for 1 hour at 60° C over a wide range of NaOH concentrations. Together, these studies show that Pu(IV) does not coprecipitate well with Ni(II) under alkaline conditions.

The tests to coprecipitate Pu(IV) with Ni(II) and Fe(III) at Pu(IV)-Ni(II)-Fe(III) component ratios of 1:1:1 and 2:1:1 (Fedoseev et al. 1998; Fedoseev et al. 2000) have been described in the earlier section addressing plutonium coprecipitation with iron. Again, no evidence of formation of a separate plutonium phase, such as $PuO_2{\cdot}xH_2O$, was found by IR spectroscopy. This suggests that Pu(IV) was incorporated into the transition element matrix.

> *Conclusions – Plutonium does not associate by coprecipitation with* $Ni(OH)_2$ *under alkaline conditions.*

6.1.7 Uranium

The estimated amount of uranium present in the Hanford tank waste is 645 metric tons or about 2.7×10^6 moles (PNNL n.d.). About 43% arose from process losses from the REDOX and PUREX Plant operations, ~44% from uranium not recovered from the Bismuth Phosphate Process metal wastes in the

Uranium Recovery Process, and ~13% from process losses from the Uranium Recovery Process (Kupfer et al. 1999).

The association of Pu(IV) with U(VI) and other metal ions under alkaline coprecipitation conditions was studied by Fedoseev et al. (1998). Although IR spectroscopy was used for other Pu(IV)-metal oxide/hydroxide interactions, no IR spectra were gathered for the Pu(IV)-U(VI) system. However, differential dissolution rates of the plutonium/uranium precipitates in HCl solution showed strong interactions. Because plutonium dissolution rates in HCl were more rapid for the mixed Pu(IV)-U(VI) solids than for pure $PuO_2 \cdot xH_2O$, intimate interaction of plutonium within the U(VI) matrix was inferred.

Limited tests of carbonate leaching were conducted for alkaline precipitates prepared from HNO_3 solutions containing varying initial concentrations of U(VI) at 0 to 0.096 M, Fe(III) at 0 to 0.246 M, Al(III) at 0 to 0.033 M, and 0.001 M Na_2SiO_3 in 1 M HNO_3 (Krot et al. 1998b). Each solution contained 1.9×10^{-4} M Pu(IV) and was precipitated by addition of 16 M NaOH to reach pH ~12 (i.e., 0.01 M excess NaOH), 0.1, and 1 M excess NaOH at 40° C. Plutonium concentrations in all of the precipitation test mother solutions were $\sim 3 \times 10^{-8}$ M and thus apparently were independent of precipitate composition. The $Na_2U_2O_7$ crystallites arising under these alkaline conditions were 3 to 5 nm in size (Krot et al. 1998b).

The separated product solids were contacted with a 5 M sodium nitrate ($NaNO_3$) solution containing 1 M Na_2CO_3 to determine the nature of the interaction of plutonium with the bulk precipitates. It was found that for the precipitates that contained only uranium or uranium plus aluminum, the degree of plutonium leaching by the carbonate solution was similar to that of the uranium leaching. From this it was inferred that the plutonium partitioned to the uranium solids (which proved to be sodium diuranate, $Na_2U_2O_7$) and not to the generally amorphous aluminum hydroxide phase. Because uranium is very susceptible to dissolution by carbonate and carbonate leaching is used, in fact, as a means to dissolve uranium from ores in the ground or in heaps, carbonate leaching of the uranium solids succeeded in dissolving the accompanying plutonium. However, the degree of plutonium leaching into the carbonate solution in these tests decreased markedly in proportion to the increase in the amount of iron in the solid phase. This finding confirmed that, when iron was present, the plutonium preferentially, though not exclusively, associated with the iron and reported to the Fe(III) hydroxide precipitate. The iron solid phase generally was found to be amorphous, showing no crystal pattern by XRD, but XRD evidence of goethite, FeOOH, was found in some tests. In leaching tests of solids with uranium present in every case but with iron present in Fe:Pu mole ratios ranging from 360 to 3200 (mass ratios from 84 to 750), the quantity of plutonium leached by 1 M carbonate ranged from about 7% to 27% while uranium dissolution ranged from about 27% to 89%. It is likely that much of the leached plutonium arose from dissolution of the uranium with which it was associated.

As noted, in other tests (Hobbs 1999) plutonium at tracer concentrations in various simulated acidic PUREX waste solutions containing Al(III), Fe(III), Ni(II), and U(VI) was treated with 0.6 M NaOH. Crystallization of the bulk metal precipitates occurred with aging; after 2 months, crystalline goethite, gibbsite, bayerite, and $Na_2U_2O_7$ were identified (Hobbs 1999). Plutonium effectively coprecipitated with iron and uranium but not with the aluminum solid phases.

The solubilities of sodium diuranate, $Na_2U_2O_7 \cdot (0\text{-}5)H_2O$, and $PuO_2 \cdot xH_2O$ as functions of NaOH concentration are compared in Figure 6-1. It is seen that the solubilities parallel each other but that the $Na_2U_2O_7 \cdot (3\text{-}5)H_2O$ is about 200-times more soluble than the $PuO_2 \cdot xH_2O$. Solubility information for sodium diuranate above 2 M NaOH was not found in the technical literature but likely trends downward based on limited data in the presence of other sodium salts (Hobbs and Karraker 1996). Uranium-bearing phases identified in genuine tank waste (Wells et al. 2011) include the $Na_2U_2O_7$ identified in the coprecipitation testing (Fedoseev et al. 1998; Krot et al. 1998b; Hobbs 1999) but also include UO_2, UO_3, U_2O_7, U_3O_8, $NaUO_2OOH$, uranium and uranium-aluminum phosphates, $Na_4UO_2(CO_3)_3$, $Ca(UO_2)_3CO_3OH{\cdot}3H_2O$, and CaU_2O_7. The affinities of plutonium for these phases are not known. However, it is likely that $PuO_2{\cdot}xH_2O$ is effectively scavenged by the isomorphic uraninite phase, UO_2, even though UO_2 is likely an analytical artifact and not actually present in tank waste. The abilities of UO_3, $NaUO_2OOH$, $Na_4UO_2(CO_3)_3$, $Ca(UO_2)_3CO_3OH{\cdot}3H_2O$, and CaU_2O_7 to incorporate $PuO_2{\cdot}xH_2O$ may be good based on the uranium phase structural similarities to $Na_2U_2O_7{\cdot}(3\text{-}5)H_2O$.

The findings from these various studies show that $Na_2U_2O_7$ is an effective scavenging agent for plutonium in NaOH solution. However, carbonate and bicarbonate are effective dissolving agents or leachants for plutonium associated with uranium. The effectiveness of (bi)carbonate drops significantly for plutonium that is associated with iron. Thus, plutonium associates well with uranium but shows preferential coprecipitation with iron.

> *Conclusions – Association of plutonium by coprecipitation with $Na_2U_2O_7$ under alkaline conditions is strong as shown by various carrier precipitation tests. However, the $Na_2U_2O_7$ is susceptible to dissolution in carbonate solution, freeing the plutonium.*

6.1.8 Bismuth

According to the BBI, the Hanford tank waste contains 561 metric tons of bismuth, or about $2.7{\times}10^6$ moles (PNNL n.d.), practically identical with the inventory of uranium in the waste tanks. Nearly all of the bismuth arose from wastes of the Bismuth Phosphate Process, either as precipitation agent introduced as $BiONO_3$, ~70%, or as oxidant introduced as $NaBiO_3$, ~30% (Kupfer et al. 1999). Very small amounts of $NaBiO_3$ were also used in the REDOX Process.

As noted in Section 3.1, the carrier precipitation of plutonium(IV) by bismuth phosphate, $BiPO_4$, and corresponding absence of plutonium(VI) carrying by bismuth phosphate in acid solution were key to the plutonium recovery from irradiated fuel in the Bismuth Phosphate Process. The re-dissolution of the plutonium-bearing $BiPO_4$ in nitric acid constituted necessary steps in this process. It was demonstrated in both laboratory (Perlman et al. 1947) and plant operations (page 610 of Hanford Works (1944)) that this re-dissolution could be accomplished more efficaciously if the $BiPO_4$ were first metathesized by potassium hydroxide, KOH, or other alkali solution (including NaOH) to produce bismuth hydroxide, $Bi(OH)_3$. Plutonium losses of only ~0.4% demonstrated that plutonium remained associated with the bismuth solid phases through the metathesis steps.

Based on these findings, it is expected that plutonium present in bismuth-bearing Bismuth Phosphate Process tank farm wastes can be present as a coprecipitate with $Bi(OH)_3$. While $Bi(OH)_3$ itself has not been identified in tank waste solids (based on Table 5-1 of Harrington (2011)), potentially because of low crystallinity, the corresponding dehydrated $Bi(OH)_3$ product, Bi_2O_3, has been identified. Bismuth phosphate is also found in tank waste solids, as are combinations of bismuth with iron, chromium, aluminum, and silicate (Table 5-1 of Harrington (2011); see also Section 2.5.4.2 of McCoskey and Cooke (2013)). An x-ray amorphous compound with hypothetical formula $FeBiO_3$ is postulated to exist in water-washed sludge, based on both electron microprobe and infrared analyses of actual tank waste from the Bismuth Phosphate Process and comparison with waste simulants prepared in manners similar to the plant process flowsheets (Lumetta et al. 2010). The actual water-washed waste sludge solids contained ~12 wt% Bi, 11 wt% Fe, ~13 wt% Na, ~10 wt% P, and 6 wt% Si with lesser quantities of Al and U. The sludge solids also contained about 10^{-5} g plutonium per gram of sludge. Based on laboratory and process experience, it is likely that plutonium has remained coprecipitated with $Bi(OH)_3/Bi_2O_3$, with $BiPO_4$, and with the more complex mixed bismuth/metal compounds, including compounds with iron, in the tank waste.

> *Conclusions – Plutonium association with bismuth as $Bi(OH)_3$, Bi_2O_3,, $BiPO_4$, and in mixed bismuth/metal compounds in alkaline tank wastes is likely.*

6.2 Sorption/Adsorption

The sorption of trace sub-micro-molar plutonium onto precipitating (hydr)oxides of iron or other metallic absorber elements present at many thousands-of-times higher concentrations during acid waste neutralization with sodium hydroxide solution is very likely the first step in coprecipitation. The plutonium ions are simply too disperse to form "pure" plutonium phases and instead, once sorbed onto the precipitating (hydr)oxides, soon become incorporated into the bulk solids through accretion. However, the possibility of plutonium sorption onto neutron absorber compounds within the alkaline solution also should be considered. For example, at least 99.9% sorption of plutonium from pH 10 to 12 Rocky Flats process waste solutions onto pre-formed crystalline magnetite (Fe_3O_4) was observed (Boyd et al. 1983). It has been noted that plutonium coprecipitation with magnetite was effective in decreasing plutonium concentrations (Slater et al. 1997). In a supplemental part of the same study, adsorption of plutonium onto preformed magnetite also was investigated. In the adsorption tests, 5.5×10^{-9} M plutonium was found at pH 12 and 1.6×10^{-8} M plutonium at pH 14, yielding DFs of 5000 to 15,000, respectively (Slater et al. 1997). However, we note that the plutonium concentration at pH 14 used in these tests is similar to that found in ultrafiltered solution without magnetite or other sorbents (Figure 5.5). Therefore, the magnetite may only have functioned as a filter aid and not as a sorbent. Later, many of the same researchers found Pu(IV) sorption DFs were <2 onto commercial magnetite at 2.2 mg iron per mL simulated Savannah River Site alkaline waste solution (Arafat et al. 2003). Plutonium sorption onto goethite was found to be low from simulated alkaline Hanford wastes containing high concentrations of the organic complexing agents EDTA, HEDTA, nitrilotriacetate, citrate, iminodiacetate, and gluconate whereas goethite sorbed about 39% of the plutonium from an actual Hanford waste containing high organic carbon concentrations (Worl et al. 1995). The mechanism of the organic effect, whether plutonium complexation or goethite surface alteration, is not known.

Tetravalent plutonium (Pu(IV)) distribution coefficients (K_ds) from 0.5 M carbonate solution (pH ~12) onto alumina, silica gel, and hydrous titanium oxide were 60, 1300, and 15,000 mL/g, respectively (Pius et al. 1995). In less alkaline 0.5 M bicarbonate (pH ~10), the Pu(IV) K_d decreased to about 30 mL/g (Charyulu et al. 1991). The lower distribution coefficient in bicarbonate likely reflects the increased stability of carbonate complexation at lower pH compared with hydroxide complexation in analogy with the increased Pu(IV) solubility found in pH ~10 bicarbonate solution versus pH ~12 carbonate solution (Yamaguchi et al. (1994); Figure 5-6). At near neutral pH, plutonium effectively competes for sorption onto goethite and hematite in high salt solutions showing K_ds ranging from 170 to 1400 mL/g (Ticknor 1993). Sanchez et al. (1985) measured sorption of Pu(IV) and Pu(V) on goethite over a range of pH values and carbonate concentrations. They found that Pu(V) was reduced to Pu(IV) and that the Pu(IV) was strongly sorbed above a pH of about 6. High carbonate concentrations decreased sorption at pH 8.6. At 1 M $NaHCO_3$, plutonium sorption was completely inhibited.

Distribution coefficients of 10^{-10} M plutonium in the presence of sodium dithionite, a strong reductant, onto bentonite altered to form the aluminosilicate mineral analcite from pH 12.2 solution containing ~0.003 M calcium hydroxide solution ranged from ~50,000 to 300,000 cm^3/g (Brownsward et al. 2000). Although the plutonium uptake was high, these solutions were relatively dilute in macro-components and of low pH compared with Hanford tank waste. The results, therefore, likely are not meaningful for tank waste considerations unless the waste pH is decreased significantly (e.g., sluicing of tank heel solids by water).

Sorption of dissolved plutonium from actual SRS tank waste solution onto actual SRS tank waste solids containing sodium aluminosilicate, hematite (Fe_2O_3), carbon black, and other solid phases has been demonstrated (Oji et al. 2010). The actual waste solution contained 6.81 M NaOH, 0.95 M $NaNO_3$, 0.68 M $NaNO_2$, 0.30 M aluminate, and 0.11 M carbonate plus other dissolved constituents at smaller concentrations. Uptake tests with a simulant waste solution containing 1.33 M NaOH, 2.60 M $NaNO_3$, and other salts also were conducted. The actual waste solution had been stripped of dissolved cesium as well as plutonium and other actinides, and plutonium spiked in at known concentration of $\sim 6.3\times10^{-7}$ M, somewhat below the plutonium solubility of $\sim 10^6$ M in the ~6.8 M NaOH present based on Figure 6-3. The simulant solution contained $\sim 8.4\times10^{-7}$ M plutonium, somewhat above the $\sim 10^{-7}$ M plutonium expected at ~1.3 M NaOH. For both solutions, however, plutonium uptake was registered onto both the tank waste solids and onto the hematite with greater mass-specific uptake onto the hematite in 24-hour contacts conducted at 26° C. About 60% of the plutonium was removed from the actual waste solution when contacted with actual tank waste solids at 3 mL/g solution/solid ratio; the amount decreased to ~20% when the ratio increased to 10 mL/g. Similar findings were obtained for contact of the simulant waste solution with the actual tank waste solids. The specific amounts of uptake approached limits as the solids were loaded. The maximum plutonium loading onto the mixed tank waste solids was ~2.0 µg/g while the hematite could be loaded to ~5.5 µg/g. Tests using granulated activated carbon showed intermediate terminal loading of ~3.4 µg/g (Oji et al. 2010).

Besides sorption of plutonium ions onto solid phases, sorption of hydrated plutonium oxide colloids onto solids may occur. This was shown in tests for which 2-5-nm colloids of $PuO_2{\cdot}xH_2O$ were prepared at pH ~8.5 by adding NaOH solution and buffer to an acidic Pu(IV) solution (Zavarin et al. 2012). The plutonium colloid particle size range is remarkably consistent with that observed in various other investigations, including $PuO_2{\cdot}xH_2O$ prepared in molar NaOH solution (Delegard (2013) and references therein). Uptake of the plutonium particles onto goethite, also synthesized hydrothermally, was observed at pH 8.5. In similar tests by the same group, uptake of plutonium colloids onto quartz and goethite at pH 7 was studied (Powell et al. 2011). Again, the intrinsic plutonium nano-colloids were 2-5 nm in diameter. Little interaction of the plutonium colloids with quartz or goethite was noted when the plutonium was introduced as a nano-colloid. However, epitaxial growth of plutonium onto the goethite was seen when the plutonium was added as a solution with the plutonium present as Pu_4O_7. In this work and the work of Zavarin and colleagues (2012), transmission electron microscopy and electron diffraction were used to characterize the solids. Although uptake of plutonium colloids onto Hanford tank waste sludge solids would be an attractive property for criticality safety, unfortunately, no studies determining the sorption behavior of plutonium colloids onto solids in strongly alkaline solution were found.

Sodium titanates have been found to be strong Pu(IV) sorbents from alkaline solution and have been tested with Hanford tank waste to yield final plutonium concentrations less than 6×10^{-11} M (Schulz 1979). Later studies with simulated and actual alkaline waste supernates from the PFP achieved $<(1\text{-}3)\times10^{-10}$ M plutonium, a DF of >1000, when the solutions were treated with sodium titanate powder (Schulz et al. 1980). The sodium titanate, $Na(Ti_2O_5H)$, was produced by alkaline hydrolysis of titanium isopropoxide. Another sodium titanate, $Na_2Ti_3O_7$, was found to decrease plutonium concentrations in pH 13.7 simulated West Valley alkaline waste solution containing 7 M total sodium by about a factor of 1000 by using 0.1 M of the solid and by 30 to 80 using 0.01 M (Bray et al. 1984).

Decontamination factors of about 10 to 30 were obtained for simulated alkaline Savannah River Site waste containing 2 M NaOH and 5 M of other sodium salts by use of 0.14 to 0.43 g of monosodium titanate (MST) per liter (Hobbs and Walker 1992). The MST was produced similarly to the sodium titanates used by Schulz et al. (1980). The DFs increased linearly with MST loading, but uranium competed with plutonium in adsorption. Complexing agents also decreased solution decontamination. Later testing examined the effects of waste dilution (ionic strength), MST concentration, temperature, mixing rate, the presence of PUREX sludge solids, and initial plutonium concentration on decontamination of simulated Savannah River Site alkaline waste (Hobbs et al. 1999). As might be expected, plutonium adsorption increased with higher waste dilution, higher MST concentration, and lower temperature and also increased slightly in the presence of the PUREX sludge solids and with better mixing. Final plutonium concentrations were about 4×10^{-10} to 2×10^{-8} M, corresponding to DFs of 1 for the $(2\text{-}40)\times10^{-8}$ M initial plutonium concentrations in 7.5 M sodium solutions to about 100 for 8×10^{-7} M initial plutonium in 4.5 M sodium. Kinetic studies showed that most plutonium uptake on MST occurred in the first 20 hours but seven days were required for equilibrium (Hobbs and Pulmano 1999a). Linear uptake again was observed with twice as much sorption occurring at 0.4 g MST/liter than at 0.2 g MST/L. Plutonium uptake on MST using actual Savannah River alkaline waste was similar to that found for simulated waste (Hobbs and Pulmano 1999b). The DFs were about 8 in diluted 4.5 M sodium waste (5×10^{-8} M plutonium initially) and about 2 in 7.5 M sodium solution (3×10^{-8} M Pu). However, apparent equilibrium was not reached after one week of contact. Implementation of MST technology at the Savannah River Site and the impacts of varying the MST loading and the contact time are described in a recent report (Hobbs 2012a).

Unlike the Hanford Site tank wastes, the Savannah River Site tank wastes do not contain the organic complexants that can decrease plutonium uptake onto sodium titanate. Thus, sodium titanate removal of plutonium from a simulated pH 13.7 to 13.9 Hanford waste containing complexing agents ranged from 16 to 30% for a 1:1 diluted (in 1 M NaOH) waste, 35 to 39% from a 3:1 diluted waste, and 26 to 66% from gamma-irradiated 1:1 diluted waste (Worl et al. 1995). In the same study, titanium-loaded zeolites sorbed 80 to 85% of the plutonium from actual complexant-bearing Hanford waste solutions.

Tests to identify Hanford tank waste components that affect plutonium sorption onto three typical shallow Hanford sediments were performed (Delegard and Barney 1983). The plutonium oxidation state was not controlled but likely was Pu(IV). To ensure that sorption and not solubility limitations were operating, the testing was performed using $\sim(2\text{-}3)\times10^{-9}$ M plutonium as ^{238}Pu in 1 to 4 M NaOH solution containing a statistically-designed range of sodium salt concentrations. The sediment minerals primarily were quartz, feldspar, montmorillonite, and vermiculite as determined by XRD and likely contained amorphous glassy basalt phases. The tests showed that the chelating agents, 0.05 M EDTA and 0.1 M HEDTA, decreased sorption while carbonate, at 0.05 M, had no effect, possibly because the sediments themselves contain carbonate. Higher hydroxide and aluminate concentrations decreased plutonium sorption. Over the range of simulated waste compositions, the K_ds ranged from about 1.4 to 40 mL/g but were >200 mL/g in 1 M NaOH in the absence of other waste components. Investigations of the reactions between the bulk minerals and the strongly alkaline aluminate-bearing simulated waste were not performed (Delegard and Barney 1983) but such reactions are certain. Feldspathoid minerals such as sodalite and cancrinite as well as silica gel have been observed in tests of the reactions between simulated Hanford tank waste solutions and Hanford sediments (Mashal et al. 2004). In light of the interaction noted between plutonium and silicate (Krot et al. 1998c) and the observation of silica gels by Mashal et al. (2004), the strong plutonium uptake observed in the 1 M NaOH system may be because a low-solubility plutonium silicate phase formed. The interactions of plutonium and americium, Am, with Hanford soils is the subject of a recent review (Cantrell and Felmy 2012).

Sorption of plutonium from highly alkaline simulant radioactive waste containing ~0.26 M NaOH, 0.52 M $NaNO_3$, and 0.02 M Na_2CO_3 onto quartz-clay soil ranged from K_d ~130 mL/g at 20°C after 100 hours to ~ 500-970 mL/g at 70°C after 100 hours and further increasing at 70°C to 1000-1300 after 500 hours (Rumynin 2011, pp. 681-711). However, the initial plutonium concentration was $\sim 2.4 \times 10^{-6}$ M, well about the $\sim 10^{-8}$ M solubility of plutonium at that NaOH concentration. In fact, the plutonium concentrations after contact with the soils became $\sim 10^{-8}$ M and thus indistinguishable from the expected solubility.

Hydrated Pu(IV) oxide itself can sorb Pu(V) from strongly alkaline solution while sorption of Pu(VI) is negligible (Budantseva et al. 1998b). Sorption of Pu(V) from NaOH solution onto hydrated thorium oxide, $ThO_2 \cdot xH_2O$, and lanthanum hydroxide, $La(OH)_3$, also was found in the same study.

Dissolution of plutonium and americium from samples of two genuine Hanford waste sludges was tested using pH 8 bicarbonate solution, bicarbonate solution combined with permanganate and ozone chemical oxidants, and mineral acid (Lumetta et al. 1993). Both sludges had been leached previously with NaOH solution and thus removed $Al(OH)_3$ phases. Bicarbonate leaching dissolved about 4 to 15% of the alpha (plutonium plus americium) activity from these sludges. Oxidant use improved dissolution to about 6 to 22%. However, only strong acid, which also dissolved the sludge matrix, completely dissolved the plutonium and americium. Thus, carbonate and oxidizing conditions favor limited Pu/Am dissolution by desorption, but much of the plutonium and americium evidently is entrapped or sorbed irreversibly onto sludge particles and is not readily removed by complexants, leachants, or even strong oxidants.

> *Conclusions – Studies of sorption of plutonium from alkaline solution onto solid substrates are limited. Information found in the technical literature on plutonium sorption onto iron phases such as magnetite and soil mineral can be ambiguous with uncertainty about whether plutonium concentration decrease was caused by sorption or solubility limits because the tests were conducted with plutonium spike concentrations that exceed solubility for the solution conditions. However, tests with actual and simulated SRS waste solutions and tank waste solids with the SRS wastes having compositions similar to Hanford wastes show that limited plutonium sorption occurs with only about half of the plutonium removed. The same testing also showed plutonium uptake onto hematite and granulated activated carbon from simulated and actual waste solution. Plutonium uptake onto iron phases also is diminished by organic complexants. Uptake of Pu(V) onto hydrated thorium oxide and lanthanum hydroxide and onto silicate minerals has been observed. Studies show that engineered sodium titanate absorbents are effective for plutonium sorption from alkaline solution.*

6.3 Sludge Solids Dissolution in Acid

The dissolution of sludge solids by treatment with nitric acid is planned to occur in routine WTP processing such as cleaning of plugged filters or removal of residual deposits on process equipment. Therefore, the response of sludge to nitric acid treatment, particularly the relative distributions of plutonium and the absorber elements to the solution and to the undissolved solid phase residues, is of interest. An initial appreciation of the potentials for differential dissolution of plutonium and absorber elements (aluminum, boron, cadmium, chromium, iron, manganese, nickel, and uranium) can be assessed by considering the solubilities of their hydrated oxides, hydroxides, oxides, and their sodium salts as functions of pH as shown in Figure 6-3. Note that, unlike the tank wastes, these systems are free of other salts whose effects on solubility may be significant. For example, increase in plutonium solubility at pH 9-10 caused by carbonate complexation can be many orders of magnitude (Section 5.2). Ionic strength changes caused by added salts also may change the solubility, but effects would likely be by factors of ten or less (e.g., see the aluminum concentration decrease by added sodium salts demonstrated in Figure 6-2 or the plutonium concentration increase by added $NaNO_3$ and $NaNO_2$ described in Section 5.2).

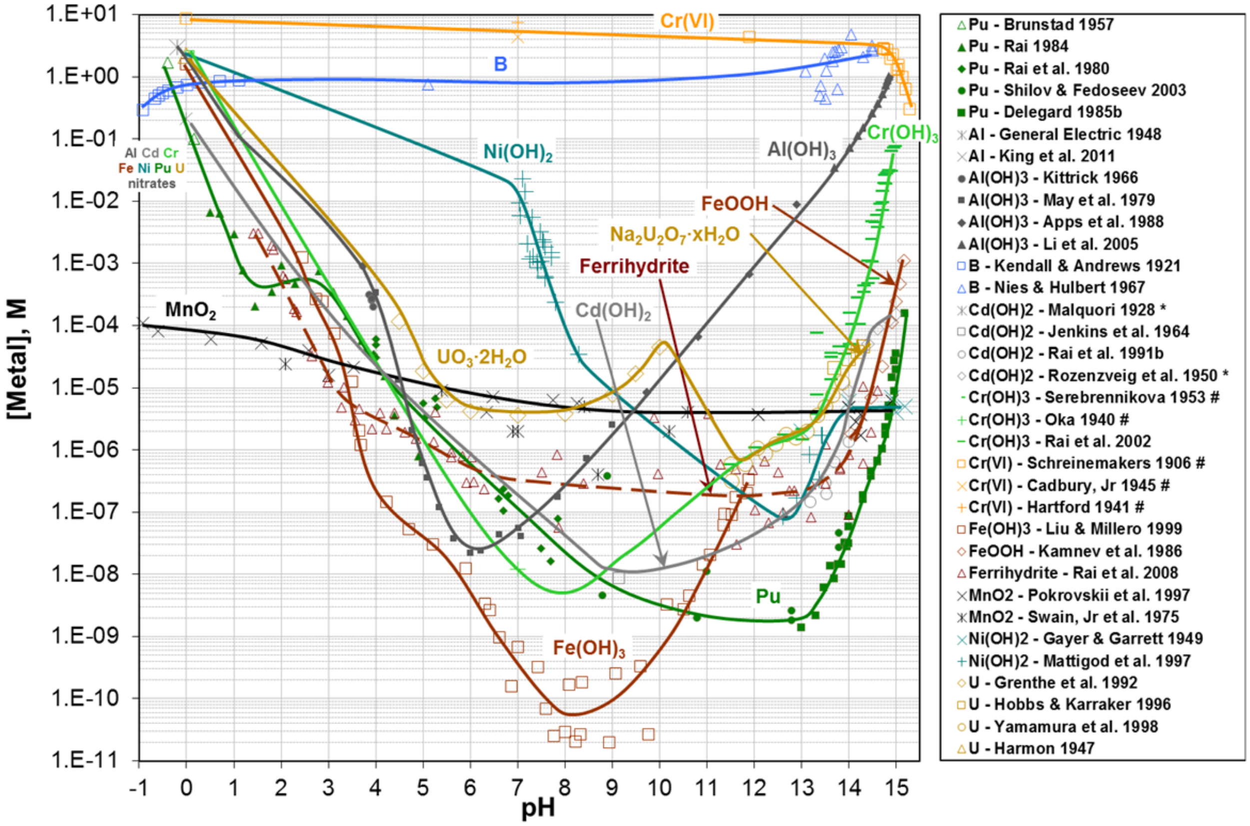

Figure 6-3. Solubility of Plutonium and Absorber Element Compounds as a Function of pH. (* denotes $Cd(OH)_2$ data taken from Dirkse (1986)). (# denotes $Cr(OH)_3$ and Cr(VI) data taken from Linke (1958))

Hexavalent chromium (Cr(VI)), as its sodium dichromate and chromate salts, and boron, as sodium borate salts, have relatively high solubilities across a wide pH range. The abundant sodium nitrate and nitrite salts, not shown in Figure 6-3 for simplicity, also have high (molar) solubilities across a wide pH range. Such salts require only water and would not require acid to dissolve. Note that sodium nitrite, $NaNO_2$, is unstable to disproportionation in strong acid to form NO gas and nitrate.

Many element compounds show amphoteric behavior in Figure 6-3 as demonstrated by their having higher solubilities at low (acidic) and high (alkaline) pH than at intermediate pH. Those element compounds showing amphoteric behavior are aluminum hydroxide, $Al(OH)_3$, cadmium hydroxide, $Cd(OH)_2$, chromium(III) hydroxide, $Cr(OH)_3$, iron (hydr)oxides including $Fe(OH)_3$, FeOOH, and ferrihydrite, $Fe_5O_7OH\cdot 4H_2O$, nickel hydroxide, $Ni(OH)_2$, and the U(VI) (hydr)oxide hydrate metaschoepite, $UO_3\cdot 2H_2O$, which converts to sodium diuranate, $Na_2U_2O_7\cdot xH_2O$, at pH ≅ 10-11 as well as plutonium. The rising solubilities as alkalinity increases demonstrates the formation of anionic and hydroxide-complexed dissolved species [e.g., $UO_2(OH)_4^{2-}$ for uranium(VI) but also $Al(OH)_4^-$ for aluminium, $Cr(OH)_4^-$ for chromium(III), and $Fe(OH)_4^-$ for iron]. At pH 14 (effectively 1 M NaOH), only $Al(OH)_3$ has appreciable solubility; the cadmium, chromium(III), iron, nickel, uranium, and plutonium compound solubilities are 10^{-4} M or lower. However, at pH 0 (effectively 1 M acid), the aluminium, chromium(III), iron, and uranium can dissolve to ≥1 M concentrations while cadmium and plutonium dissolve to ~0.1 M.

Manganese, as MnO_2, maintains low solubility over the entire pH range and increases in solubility only slightly, to ~10^{-4} M, in strong acid.

The solubility behaviours diagrammed in Figure 6-3 are provided for HNO_3 and NaOH solutions at low and high pH, respectively, and do not include the effects of complexation by, for example, carbonate or EDTA. As such, Figure 6-3 illustrates the treatment with HNO_3 or NaOH of water-washed or leached sludge containing these compounds. The solubility behaviours of other (hydr)oxide compounds such as the transition metal spinels (Fe_3O_4, $FeCr_2O_4$, Mn_3O_4, Fe_2MnO_4) and other mixed element compounds such as sodium aluminosilicates (e.g., cancrinite and sodalite) which also may be present in washed and leached sludge (see Table 4-8) are not captured in Figure 6-3.

The solubility of plutonium across the pH range reflects its existence as $PuO_2\cdot xH_2O$ in the solid phase and with the system in contact with air atmospheres. As discussed previously, the oxidation state for plutonium in strongly alkaline solution is expected to be as Pu(IV) and Pu(V) with radiolysis and greater hydroxide concentration stabilizing Pu(V). At intermediate pH, the dissolved plutonium is widely acknowledged to be present as Pu(V) (Rai 1984) while multiple oxidation states may be present in dilute nitric acid (Figure 6-4) owing to the proximities of the relevant redox potentials.

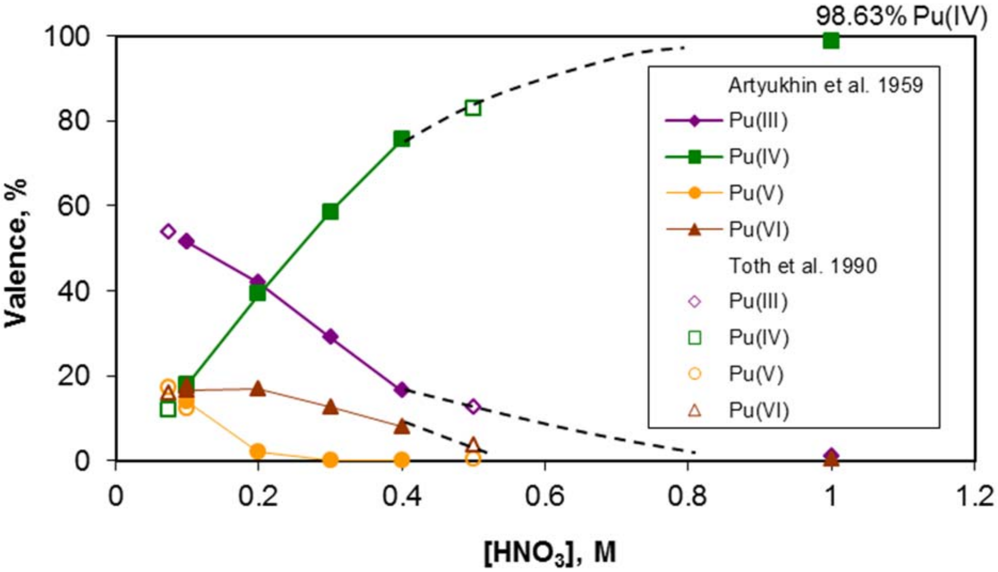

Figure 6-4. Plutonium Oxidation State Distribution in Dilute Nitric Acid in Air

The response of sludge to nitric acid treatment has been examined based on prior lab studies of tank waste processing, waste characterization by chemical and radiochemical analysis, and actual sludge processing for strontium-90 recovery. A brief survey of these findings in 2001 showed that differential dissolution in acid does occur and that it varies with waste type (Section 6 of Batdorf and Larson (2001) and references therein). Conclusions from these findings are summarized in the following three paragraphs.

Lab-scale nitric acid leaching studies with actual neutralized current acid waste (NCAW), Bismuth Phosphate Process waste, and PFP waste were considered in Section 6.1 of Batdorf and Larson (2001). The NCAW testing showed uneven results but seemed to indicate that plutonium could remain coprecipitated with zirconium, a poor neutron absorber, if the waste had been aged under hydrothermal conditions with NaOH. For water-leached Bismuth Phosphate Process tank 241-U-110 sludge, treatment with four strikes of 2 M HNO_3 dissolved 99% of its transuranic (americium and plutonium) complement but left much of the iron, silicon, and aluminum in the heel and hence showed separation of plutonium from iron, the potent neutron absorber. Leaching of PFP sludge from tank 241-SY-102 with nitric acid containing hydrogen peroxide dissolved 97.5% of the plutonium, 100% of the uranium, 92% of the chromium(III), and 95% of the iron and manganese. Thus, for this sludge, the extents of plutonium and absorber element dissolution by nitric acid treatment were comparable.

Examination of sludge analysis data from the Tank Waste Information Network System was described in Section 6.2 of Batdorf and Larson (2001). The survey found that analytical data from four tanks (241-AW-103, 241-AZ-101, 241-AZ-102, and 241-AX-103) had paired data showing plutonium disposition to both nitric acid and fusion digests – i.e., had data showing how well nitric acid dissolves particular analytes (e.g., plutonium, iron) compared with the complete digestion achieved by analytical fusion. The results for the four tanks for six selected absorber analytes (iron, manganese, lanthanum, chromium, aluminum, and phosphorus) and plutonium were compiled and averaged. Within analytical error, it was found that plutonium was completely dissolved by the acid digest for these four tank wastes.

However, for waste from tanks 241-AW-103 and 241-AX-103, the acid digest left much of the iron and manganese. For 241-AW-103, lanthanum also was left largely undissolved. Phosphorus was found to dissolve poorly and erratically for all of the four tank wastes. Thus, in two of the four sludge types tested, the plutonium dissolved preferentially away from iron and manganese neutron absorbers by nitric acid digestion. It should be pointed out that these results may not be typical for all tank wastes because of atypical phases being present.

The experience of processing PUREX acidified sludge for strontium-90 recovery in B Plant in the Waste Fractionization Process was examined in Section 6.4 of Batdorf and Larson (2001). It was found that the PUREX sludge, which was retrieved into the 244-AR Vault for processing by 12 M HNO_3, left 5 to 25% of the sludge undissolved in a plutonium-bearing residue despite repeated nitric acid contacts. The strontium recovery flowsheet indicates that the solid residues contained between 0.001 and 0.1 g plutonium per liter while the Best Basis PUREX HLW sludge contained between 0.04 and 0.2 g Pu/liter. Because the range in plutonium concentration for the 244-AR Vault residues overlapped the plutonium concentration in PUREX HLW sludge, it was judged that no significant change in the relative concentration of plutonium in the sludge solids occurred because of treatment with strong HNO_3. It was speculated that the solids residue remaining from 244-AR Vault was a ferro-strontium silicate mineral - such a material might be a host for entrapped plutonium. It was also speculated that aged iron (hydr)oxides such as hematite and goethite also arise by heating and that these phases resist HNO_3 leaching.

Conclusions – Plutonium hydrated oxide and the (hydr)oxide compounds of many of the candidate neutron absorber elements (aluminum, cadmium, trivalent chromium, iron, nickel, and uranium) show amphoteric behavior, meaning that they have much greater solubilities in acidic and strongly alkaline solution compared with intermediate pH. Survey of the dissolution behavior of actual Hanford tank waste sludges upon treatment with HNO_3 *based on lab testing, sludge characterization, and plant processing shows both equal and unequal response of plutonium and absorber element solids containing iron and manganese. Unexpectedly, the iron- and manganese-bearing sludge constituents are occasionally more difficult to dissolve in* HNO_3 *than the contained plutonium.*

7.0 Summary

The chemical disposition of plutonium in Hanford Site tank wastes by itself and in its observed and potential interactions with compounds of the neutron absorbers aluminum, cadmium, chromium, iron, manganese, nickel, and sodium are examined in this report. Consideration also is given to the interactions of plutonium with uranium.

A brief review of Hanford Site plutonium processes examined the various means used to recover plutonium from irradiated fuel and from scrap and also examined the intermediate processing of plutonium to prepare useful chemical forms. This review showed the origin of various Hanford tank defined waste types and their compositions and indicated the ratios of plutonium to absorber elements for some of these waste types based on Hanford tank waste inventory data derived from separate published expert assessments of tank disposal records, process flowsheets, and chemical/radiochemical analyses.

The distribution and expected speciation of plutonium in tank waste solution and solid phases were examined with respect to plutonium oxidation state redox potentials for dissolved Pu(VII), Pu(VI), Pu(V), and Pu(IV) and the freshly precipitated $PuO_2 \cdot xH_2O$ species. The solubilities of the various plutonium oxidation states were shown to increase with increasing NaOH concentration and with increasing carbonate concentration, particularly in instances of low NaOH concentration (e.g., pH 10). Based on these studies, it was shown that, with time, plutonium present in NaOH solution will precipitate to form $PuO_2 \cdot xH_2O$ solids and Pu(IV) dissolved species. Only with higher NaOH concentrations, higher ionic strength (or salt effects), and lower temperatures is dissolved Pu(V) favored to form in NaOH solution. The valuable and interesting findings of Callaway III and Cooke (2004) and McCoskey and Cooke (2013) regarding particulate plutonium found in tank wastes from SY-102 and TX-118 and solids from the Z-9 crib, all receptacles of alkaline wastes from the PFP, were examined and compared with the latter study's findings of the lack of plutonium-bearing particles in the AZ-101 tank waste. Plutonium, plutonium-bismuth, and plutonium-bismuth-phosphorus particles were found in the Z-9 sediments and in the tank SY-102 and TX-118 solids. The splinter-like appearances of the SEM/EDS-observable plutonium-only particles compare closely with plutonium-rich splinters in scrap that arose from plutonium metal burning and suggest that the tank waste and crib samples also may contain product from plutonium metal burning.

The interactions of plutonium with the seven absorber elements then were examined. These assessments of plutonium chemistry largely are based on analyses of idealized or simulated tank waste or strongly alkaline systems. Both coprecipitation and sorption/adsorption studies were examined. The very limited information on plutonium behavior, disposition, and speciation in genuine tank waste also was discussed.

The assessments show that plutonium coprecipitates strongly with chromium, iron, manganese, and uranium absorbers. Plutonium's chemical interactions with aluminum, nickel, and sodium are minimal to non-existent. No information on the potential interaction of plutonium with cadmium was found in the technical literature.

All absorber compounds except MnO_2 are susceptible to dissolution in strong acid. For those absorber element compounds with which plutonium strongly coprecipitates (chromium, iron, manganese, and uranium), the susceptibilities to plutonium separation by carbonate complexation, organic complexation, or oxidative dissolution were assessed. The uranium compound, $Na_2U_2O_7$ is susceptible to dissolution in carbonate solution while chromium, iron, and manganese (hydr)oxides are not. The iron and uranium compounds are resistant to dissolution by organic complexation under alkaline conditions and the chromium and manganese compounds are postulated to be resistant. Chromium(III) compounds are susceptible to oxidative dissolution to form chromate. Under extreme, and perhaps incredible, oxidation conditions, Mn(II) and Mn(IV) compounds also might be susceptible to oxidation to soluble permanganate. Oxidative dissolutions of Fe(III) and U(VI) compounds are not probable because these elements are already at their maximum plausible oxidation states. It is noted that oxidation of Fe(III) to soluble Fe(VI) requires at least 0.71 V at 1 M NaOH, well above the 0.56 V potential provided by permanganate; see Figure 5-4.

The inventories of the absorbers in the tank farm system and the mass ratios of plutonium to the individual absorber elements are shown in Table 7-1 with the coprecipitation and leaching summaries. It is seen that for aluminum, cadmium, chromium, iron, and manganese, the individual plutonium-to-absorber ratios are each about 5- to 10-fold beyond that needed to maintain criticality safety. For nickel, the margin is about a factor of 1.1, for uranium, the factor is about 3, and for sodium, the factor is 143. Iron is the most broadly effective absorber. It enjoyed wide use in Hanford processing, largely as a chemical reductant in the form of ferrous, Fe(II), salts, but also with 24% of the total iron in the waste arising from stainless steel corrosion product (Kupfer et al. 1999). It coprecipitates plutonium in $Fe(OH)_3$, goethite, hematite, and magnetite forms and has broad leaching and dissolution resistance. Manganese is the next most effective absorber with broad leach resistance; including in acid as MnO_2.

Table 7-1. Candidate Absorber Element Inventories, Compounds, and Plutonium Interactions

Absorber Element	Inventory, MT[a]	Pu/Abs Mass Ratio, g/kg[b]		Excess Absorber Factor[d]	Representative Solid Phases	Pu Coprecip-itation	Susceptibility to Pu Separation by Leaching		
		Target[c]	Tank Waste				Carbonate	Organic Complexant	Oxidation
Al	8690	0.638	0.0975	6.55	$Al(OH)_3$	No	NA	NA	NA
Cd	8.20	993	103	9.64	$Cd(OH)_2$	Unknown	Unknown	Unknown	Unknown
Cr	591	6.28	1.43	4.39	$Cr(OH)_3$	Yes	No	No	Yes
Fe	1270	5.18	0.667	7.76	FeOOH	Yes	No	No	No
Mn	164	25.5	5.16	4.94	$Mn(OH)_2$ MnO_2	Yes	No	No	Yes, if strong
Na	49000	2.47	0.0173	143	Many sodium salts	No	NA	NA	NA
Ni	98.8	9.68	8.57	1.13	$Ni(OH)_2$	No	NA	NA	NA
U	645	4.20	1.31	3.21	$Na_2U_2O_7$	Yes	Yes	No	No

a From PNNL (n.d.).
b Based on 847 kg plutonium inventory in tanks (PNNL n.d.).
c Calculated from Table 4-2 of Miles (2009).
d Excess Absorber Factor = Target (Pu/Abs)/Tank Waste (Pu/Abs)

Sorption or adsorption of plutonium onto various solid phases from alkaline media is less clear-cut, perhaps owing to fewer studies and uncertainty in the experimental findings because some tests were run under conditions exceeding the solubility of the plutonium. Most of the studies examined iron phases such as goethite and the artificial sodium titanate sorbents tested for Hanford, West Valley, and particularly Savannah River Site application. Limited plutonium sorption is observed onto tank waste solids and onto other solids (e.g., hematite, granulated activated carbon, hydrated thorium oxide, and lanthanum hydroxide). Plutonium sorbs more effectively onto the sodium titanate phases. It was found that carbonate and the organic complexants present in many Hanford tank waste solutions decrease plutonium uptake onto solids.

The chemical and physical dispositions of plutonium in the starting Hanford process materials, in solution by itself and with various anions and other metal ions, as solid compounds, in adsorption reactions, and after treatment with NaOH to be made alkaline for tank waste storage are summarized in Table 7-2.

Table 7-2. Plutonium Disposition in Alkaline Tank Wastes

Starting Plutonium Disposition	**Other Agent**	**Plutonium Disposition in Waste after NaOH Treatment**
With Anions – (Section 5.3.1)		
$\mathrm{Pu(NO_3)_{4\ solution}}$	$\mathrm{HNO_3}$ only	$\mathrm{PuO_2{\cdot}xH_2O}$; crystallites 0.002 to 0.005 µm
$\mathrm{PuO_2(NO_3)_{2\ solution}}$	$\mathrm{HNO_3}$ only	Eventually $\mathrm{PuO_2{\cdot}xH_2O}$; crystallites ~0.01 µm
$\mathrm{Pu(NO_3)_{4\ solution}}$	Nitrate plus: nitrite, carbonate, sulfate, chromate, ferrocyanide, oxalate, glycolate, citrate, EDTA, or HEDTA	$\mathrm{PuO_2{\cdot}xH_2O}$; crystallites 0.002 to 0.005 µm
	Nitrate plus phosphate	“$\mathrm{Pu(PO_4)O}$” where P:Pu≤0.15; unknown but small particle size
	Nitrate plus silicate	“$\mathrm{Pu(SiO_4)O}$” where Si:Pu = 0.3-1.8; unknown but small particle size
With Metal Ions – (Section 6.1)		
$\mathrm{Pu(NO_3)_{4\ solution}}$	Dissolved nitrate salts of Co(III), Cr(III), Fe(III), La(III), U(VI), Zr(IV)	Coprecipitation
	Dissolved nitrate salts of Al(III), Ni(II)	Simultaneous precipitation; Pu exists separately as $\mathrm{PuO_2{\cdot}xH_2O}$ in nanometer-scale crystallites
	Dissolved Mn	Coprecipitation likely
	Dissolved nitrate salt of Cd(II)	Unknown
$\mathrm{PuO_2(NO_3)_{2\ solution}}$	Dissolved nitrate salts of Al(III), Cr(III), Fe(III)	Separate precipitation; Pu likely exists as nanometer- to sub-micron-scale crystallites
Plutonium Solid Compounds – (Sections 5.3.2 and 5.3.3)		
$\mathrm{PuF_{4\ solid}}$ and fluoride double salt solids	None	$\mathrm{PuO_2{\cdot}xH_2O}$; likely micron-scale agglomerates of nanometer-scale small crystallites
$\mathrm{Pu(C_2O_4)_2{\cdot}6H_2O_{\ solid}}$	None	
Pu in organic “cruds”	None	

Starting Plutonium Disposition	**Other Agent**	**Plutonium Disposition in Waste after NaOH Treatment**
$PuO_{2\ solid}$ from scrap or fuels	None	PuO_2 with little alteration; ~10-20 µm from oxalate; ~30 µm from burnt metal
Plutonium metal	None	Unknown (may or may not corrode)
Unknown	Unknown	Pu-Bi, Pu-Bi-P phases
Plutonium adsorption – (Section 6.2)		
Dissolved plutonium	Various solids	Surface adsorption

8.0 References

Alenchikova IF, LL Zaitseva, LV Lipis, VV Fomin, and NT Chebotarev. 1958. *Preparation and Properties of Certain Double Fluorides of Tetrapositive Plutonium*. Presented at The Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. 28, Basic Chemistry in Nuclear Energy, Geneva, Switzerland, United Nations, New York, NY.

Altmaier M, V Neck, R Muller, and T Fanghänel. 2005. "Solubility of $ThO_2 \cdot xH_2O$(am) in Carbonate Solution and the Formation of Ternary Th(IV) Hydroxide-Carbonate Complexes." *Radiochimica Acta* 93:83-92.

Ames LL. 1974. *Characterization of Actinide Bearing Soils: Top Sixty Centimeters of 216-Z-9 Enclosed Trench*. Report No. BNWL-1812, Pacific Northwest National Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/4313915.

Apps JA, JM Neil, and C-H Jun. 1988. *Thermochemical Properties of Gibbsite, Bayerite, Boehmite, Diaspore, and the Aluminate Ion between 0° and 350° C.* Report No. LBL-21482, Lawrence Berkeley Laboratory, Berkeley, CA. http://www.osti.gov/scitech/biblio/6481805.

Arafat HA, SB Aase, AJ Bakel, DL Bowers, AV Gelis, MC Regalbuto, J Sedlet, and GF Vandegrift. 2003. *Parametric Studies on the Use of In-Situ Formed Magnetite for the Removal of Sr and Actinides from Tank Waste at the Savannah River Site*. Report No. ANL/CMT/MAGNETITE-2002/02, Argonne National Laboratory, Argonne, IL. www.ipd.anl.gov/anlpubs/2003/04/46360.pdf.

Artyukin PI, VI Medvedovskii, and AD Gel'man. 1959. "Disproportionation of Pu(IV) and Pu(V) in Nitric Acid Solutions." *Russian Journal of Inorganic Chemistry* 4(6):596-99.

Barney GS. 1976a. "Fixation of Radioactive Waste by Hydrothermal Reactions with Clays." In *High-Level Radioactive Waste Management, Advances in Chemistry*, ed. MH Campbell, Vol. 153. American Chemical Society, Washington, DC. (See also Report No. ARH-SA-174, Atlantic Richfield Hanford Company, Richland, WA. http://www.osti.gov/scitech/biblio/4242703.).

Barney GS. 1976b. *Vapor-Liquid-Solid Phase Equilibria of Radioactive Sodium Salt Wastes*. Report No. ARH-ST-133 , Rev. 0, Atlantic Richfield Hanford Company, Richland, WA. http://www.osti.gov/scitech/biblio/7355628.

Barney GS. 1988. "*Particle Size Analyses of Plutonium Fluoride Samples from the RMC Line in 234-5 Building.*" Internal Memo 12221-PSL88-005. Westinghouse Hanford Company, Richland, WA.

Barney GS, and CH Delegard. 1999. "Chemical Species of Plutonium in Hanford Site Radioactive Tank Waste." In *Actinide Speciation in High Ionic Strength Media,* eds. DT Reed, SB Clark and L Rao. Kluwer Academic / Plenum Publishers, New York, NY.

Barr MJ, MW Urie, JL Daniel, and SJ Mayhan. 1970. *Characterization of Some UO_2 and PuO_2 Powders*. Report No. BNWL-1441, Battelle Memorial Institute, Richland, WA. http://www.osti.gov/scitech//servlets/purl/4102315/.

Batdorf J, and S Larson. 2001. *Addition of Nitric Acid and Sodium Hydroxide to Hanford Tank Waste*. Report No. RPT-W375-TE00044, Rev 0, CH2M Hill Hanford Group, Incorporated, Richland, WA.

Bennett DA, D Hoffman, H Nitsche, and RJ Silva. 1987. *Preliminary Results on the Hydrolysis and Carbonate Complexation of Dioxoplutonium(V)*. Report No. LBL-24254, Lawrence Berkeley Laboratory, Berkeley, CA. http://www.osti.gov/scitech/biblio/60363.

Bessonov AA, NA Budantseva, AV Gelis, MV Nikonov, and VP Shilov. 1997. *Investigation on the Coprecipitation of Transuranium Elements from Alkaline Solutions by the Method of Appearing Reagents. Study of the Effects of Waste Components on Decontamination from Np(IV) and Pu(IV)*. Report No. PNNL-11625, Pacific Northwest National Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/554187.

Bessonov AA, AV Gelis, VP Shilov, and NN Krot. 1999. "Coprecipitation of Transuranium Elements from Alkaline Solutions by the Method of Appearing Reagents. IV. Coprecipitation of Pu(IV) with Manganese Dioxide and $Mn(OH)_2$." *Radiochemistry* 41(2):124-26.

Bluhm E, K Fisher, K Martinez, L Christensen, and M Keddy. 2008. "Direct Metal Oxidation: A Process-Oriented Approach." *Actinide Research Quarterly* 2008(1st/2nd Quarters). http://arq.lanl.gov/source/orgs/nmt/nmtdo/AQarchive/1st_2ndQuarter08/page4.shtml.

BNL. 2000. *National Nuclear Data Center Nuclear Wallet Cards*. 6th ed., Brookhaven National Laboratory, Upton, NY. http://www.nndc.bnl.gov/wallet/wallet-2000.pdf.

Bourges J. 1972. "Preparation Et Identification Du Plutonium a L'etat D'oxydation-V En Milieu Basique." *Radiochemical and Radioanalytical Letters* 12:111-15.

Bourges J. 1973. *Etude Electrochimique des Etats D'oxydation Du Plutonium En Milieu Hydroxyde De Sodium*. Report No. CEA-R-4406 (in French), Commissariat a I'Energie Atomique, Bâtiment Le Ponant, France. http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/05/093/5093628.pdf.

Boyd TE, RL Kochen, and JD Navratil. 1983. "Actinide Aqueous Waste Treatment Using Ferrites." *Radioactive Waste Management and the Nuclear Fuel Cycle* 4:195-209.

Bratsch SG. 1989. "Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K." *Journal of Physical and Chemical Reference Data* 18(1):1-21.

Bratzel DR. 1984. "*"Plutonium Finishing Plant Laboratory Study",* Internal Letter 65453-84-360 to DM Tulberg." In *Process Aids - A Compilation of Technical Letters - Evaporator Process & PFP & Misc Studies by Process Development Group*, Vol. 16, Book B, RHO-RE-SR-84-26-16. Rockwell Hanford Operations, Richland, WA.

Bratzel DR. 1985. "Characterization of Complexant Concentrate Supernatant." In *Process Aids - A Compilation of Technical Letters*. Report No. WHC-IP-0711, 17, Westinghouse Hanford Company, Richland, WA.

Bratzel DR, WW Schulz, R Vornehm, AE Waltar, H Babad, GS Barney, J Greenborg, LH Rodgers, RE Felt, DW Jeppson, CA Rogers, KW Schwinkendorf, TS Vail, RJ Serne, and GA Whyatt. 1996. *Tank Farm Criticality Review*. Report No. WHC-SD-WM-TI-725, Rev. 0, Westinghouse

Hanford Company, Richland, WA. http://rkc.pnl.gov/docs/files/webviewable-WHC-SD-WM-TI--725.pdf.

Bray LA, LK Holton, TR Myers, GM Richardson, and BM Wise. 1984. *Experimental Data Developed to Support the Selection of a Treatment Process for West Valley Alkaline Supernatant*. Report No. PNL-4969, Pacific Northwest Laboratory, Richland, WA. http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=E0015599.

Bruns LE. 1960. *Solvent Extraction Flowsheet for New Plutonium Reclamation Facility*. Report No. HW-64851, Hanford Atomic Products Operation, Richland, WA. https://192.107.175.222/opennet/detail.jsp?osti_id=16447031&query_id=0.

Brunstad A. 1957. *Polymerization and Precipitation of Plutonium(IV) in Nitric Acid*. Report No. HW-54203, Hanford Atomic Products Operation, Richland, WA. https://192.107.175.222/opennet/detail.jsp?osti_id=16442705&query_id=0. Also published in *Industrial and Engineering Chemistry* 51(1):38-40 (1959).

Buckingham JS. 1967. *Waste Management Technical Manual*. Report No. ISO-100, Isochem, Incorporated, Richland, WA.

Budantseva N, A Bessonov, I Tananaev, A Fedosseev, and CH Delegard. 1998a. "Behavior of Plutonium(V) in Alkaline Media." *Journal of Alloys and Compounds* 271-273:813-16.

Budantseva NA, IG Tananaev, AM Fedoseev, AA Bessonov, and CH Delegard. 1997. *Investigation of the Behavior of Plutonium(V) in Alkaline Media*. Report No. PNNL-11624, Pacific Northwest National Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/554209.

Budantseva NA, IG Tananaev, AM Fedoseev, and CH Delegard. 1998b. "Capture of Pu(V), Np(V) and Pu(VI) from Alkaline Solutions by Hydroxides of Pu(IV), Th(IV) and La(III)." *Journal of Alloys and Compounds* 271-273:231-35.

Burger LL. 1955. *The Chemistry of Tributyl Phosphate – A Review*. Report No. HW-40910, Hanford Atomic Products Operation, Richland, WA. http://www.osti.gov/scitech/biblio/4334996.

Burney GA, and FW Tober. 1965. "Precipitation of Plutonium Trifluoride." *I&EC Process Design and Development* 4(1):28-32.

Cadbury Jr WE. 1945. "The System Sodium Chromate—Sodium Molybdate—Water." *Journal of the American Chemical Society* 67(2):262-68. http://dx.doi.org/10.1021/ja01218a035. As presented in Linke 1958.

Callaway III WS, and GA Cooke. 2004. Letter report to KH Abel (Bechtel National Incorporated) from WS Callaway and GA Cooke (CH2M HILL Hanford Group, Inc.), "Distribution of Plutonium-Rich Particles in Tank 241-SY-102 Sludge, CH2M-0400872." July 3, Richland, WA.

Campbell MH, and JV Panesko. 1971. Internal letter to LM Knights (Manager) from MH Campbell and JV Panesko, Research Staff, "Tentative Indications from the Burning of a Portion of One Dow Button and Dissolution of Oxide." 13 October 1971, Richland, WA.

Cantrell KJ, and AR Felmy. 2012. *Plutonium and Americium Geochemistry at Hanford: A Site-Wide Review*. Report No. PNNL-21651, Pacific Northwest National Laboratory, Richland, WA. http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-21651.pdf.

Cash RJ, GT Dukelow, and JM Atwood. 1992. *Quarterly Report on Defense Nuclear Facilities Safety Board Recommendation 90-7 for the Period Ending December 31, 1991*. Report No. WHC-EP-0474-3, Westinghouse Hanford Company, Richland, WA. http://pdw.hanford.gov/arpir/pdf.cfm?accession=E0019224.

Castaing BA. 1993. *101-AY, 102-AY, & 106-C Data Compendium*. Report No. WHC-SD-WM-TI-578, Rev. 0, Westinghouse Hanford Company, Richland, WA.

Certa PJ, PA Empey, and MN Wells. 2011. *River Protection Project System Plan*. Report No. ORP-11242, Rev. 6, Office of River Protection, Richland, WA.

CH2M Hill Hanford. 2006. *Tank Farm Contractor Operation and Utilization Plan*. Report No. HNF-SD-WM-SP-012, Rev 6, CH2M HILL Hanford Group, Inc., Richland, WA.

Chaplygina NM, LS Itkina, and EV Petrova. 1974. "Solubility and Solid Phases of the $Al(OH)_3$-NaOH-H_2O and $Al(OH)_3$-KOH-H_2O Systems at 50° C." *Russian Journal of Inorganic Chemistry* 19(5):762-66.

Charyulu MM, IC Pius, A Kadam, M Ray, CK Sivaramakrishnan, and S Patil. 1991. "The Behaviour of Plutonium in Aqueous Basic Media." *Journal of Radioanalytical and Nuclear Chemistry* 152:479-86.

Christensen EL, and WJ Maraman. 1969. *Plutonium Processing at the Los Alamos Scientific Laboratory*. Report No. LA-3542, Los Alamos Scientific Laboratory, Los Alamos, NM. http://permalink.lanl.gov/object/tr?what=info:lanl-repo/lareport/LA-03542.

Clark DL. 2000. "The Chemical Complexities of Plutonium." *Los Alamos Science* 26:373. http://fas.org/sgp/othergov/doe/lanl/pubs/00818038.pdf.

Clark DL, SS Hecker, GD Jarvinen, and MP Neu. 2006. "Plutonium." In *The Chemistry of the Actinide and Transactinide Elements,* eds. LR Morss, et al. Springer, Dordrecht, The Netherlands.

Clark SB, and CH Delegard. 2002. "Plutonium in Concentrated Solutions." In *Advances in Plutonium Chemistry 1967-2000,* ed. DC Hoffmann. American Nuclear Society, La Grange Park, IL.

Cleveland JM. 1970. *The Chemistry of Plutonium*. Gordon and Breach Science Publishers, Inc., New York, NY.

Cunningham B. 1954. "Preparation and Properties of the Compounds of Plutonium." In *The Actinide Elements,* eds. GT Seaborg and JJ Katz, pp. 398-99. McGraw-Hill Book Company, New York, NY.

Dawson JK, RWM D'Eye, and AE Truswell. 1954a. "The Hydrated Tetrafluorides of Uranium and Plutonium." *Journal of the Chemical Society*:3922-29.

Dawson JK, RM Elliott, R Hurst, and AE Truswell. 1954b. "The Preparation and Some Properties of Plutonium Fluorides." *Journal of the Chemical Society*:558-64.

Deichman EN, and IG Tananaev. 1962. "Plutonium Fluorides." *Soviet Radiochemistry* 4(1):56-62.

Delegard CH. 1985a. Internal letter #65454-85-032 to E Abramowski (Manager) from CH Delegard, Scientist, "Chemical Analysis of Rocky Flats Oxide Sludge and Heel." 25 February 1985, Richland, WA.

Delegard CH. 1985b. *Solubility of $PuO_2 \cdot xH_2O$ in Alkaline Hanford High-Level Waste Solution*. Report No. RHO-RE-SA-75 P, Rockwell Hanford Operations, Richland, WA. http://www.osti.gov/scitech/biblio/5402793. (Also published in 1987 in *Radiochimica Acta* 41:11-21).

Delegard CH. 1987. *Solubility of $PuO_2 \cdot xH_2O$ in PUREX Plant Metathesis Solutions*. Report No. RHO-RE-ST-53P, Rockwell Hanford Operations, Richland, WA.

Delegard CH. 1997. *Liaison Activities with the Institute of Physical Chemistry, Russian Academy of Sciences: FY 1997*. Report No. PNNL-11682, Pacific Northwest National Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/552764.

Delegard CH. 2013. "Effects of Aging on $PuO_2 \cdot xH_2O$ Particle Size in Alkaline Solution." *Radiochimica Acta* 101(5):313-22.

Delegard CH, and GS Barney. 1983. *Effects of Hanford High-Level Waste Components on Sorption of Cobalt, Strontium, Neptunium, Plutonium and Americium on Hanford Sediments*. Report No. RHO-RE-ST-1 P, Rockwell Hanford Operations, Richland, WA. http://www.osti.gov/scitech/biblio/6180868.

Delegard CH, TD Elcan, and BE Hey. 1994. *Chemistry of Application of Calcination/Dissolution to the Hanford Tank Waste Inventory*. Report No. WHC-EP-0766, Westinghouse Hanford Company, Richland, WA. http://rkc.pnl.gov/docs/index.php/home/view/683.

Delegard CH, and SA Gallagher. 1983. *Effects of Hanford High-Level Waste Components on the Solubility of Cobalt, Strontium, Neptunium, Plutonium and Americium*. Report No. RHO-RE-ST-3 P, Rockwell Hanford Operations, Richland, WA. http://www.osti.gov/scitech/biblio/5335758.

Delegard CH, AM Stubbs, and SD Bolling. 1993. *Laboratory Testing of Ozone Oxidation of Hanford Site Waste from Tank 241-SY-101*. Report No. WHC-EP-0701, Westinghouse Hanford Company, Richland, WA. http://www.osti.gov/scitech/biblio/10117009.

Dirkse TP. 1986. "Cadmium Oxide and Hydroxide." In *Copper, Silver, Gold and Zinc, Cadmium, Mercury Oxides and Hydroxides*, Vol. 23 in Solubility Data Series, pp. 270-306. Pergamon Press, Oxford, U. K.

Duff MC, DB Hunter, DT Hobbs, AR Jurgensen, and SD Fink. 2002. *Characterization of Plutonium, Neptunium, Strontium on Manganese Solids from Permanganate Reduction*. Report No. WSRC-TR-2002-00366, Rev. 0, Westinghouse Savannah River Company, Savannah River Site, Aiken, SC. http://www.osti.gov/scitech/biblio/807670.

Duffield RB. 1960. "Metathesis of Plutonium Carrier Lanthanum Fluoride Precipitate with an Alkali." US Patent No. 2,931,702. http://www.google.com/patents/US2931702.

Eller PG, RW Szempruch, and JW McClard. 2004. *Summary of Plutonium and Oxide Storage Package Failures*. Report No. LA-UR-04-1453, Los Alamos National Laboratory, Los Alamos, NM. http://lib-www.lanl.gov/cgi-bin/getfile?01054987.pdf.

Engineers of Plutonium Process Engineering. 1968. *Z Plant Report Task I-II & Recovery Operations, January 1, 1968 through December 31, 1968.* Report No. ARH-294 RD (with deletions), Atlantic Richfield Hanford Company, Richland, WA.

Fedoseev AM, NA Budantseva, MV Nikonov, and MS Grigor'ev. 2000. "Interaction of Pu(IV) Hydroxide with Hydroxides of Some D and F Elements in Alkaline Solutions: I. Systems Pu(IV)-Fe(III) and Pu(IV)-Ni(II)." *Radiochemistry* 42(5):405-12.

Fedoseev AM, NN Krot, NA Budantseva, AA Bessonov, MV Nikonov, MS Grigor'ev, AY Garnov, VP Perminov, and LN Astafurova. 1998. *Interaction of Pu(IV,VI) Hydroxides/Oxides with Metal Hydroxides/Oxides in Alkaline Media*. Report No. PNNL-11900, Pacific Northwest National Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/665966.

Felmy AR, and GT MacLean. 2001. *Development of an Enhanced Thermodynamic Database for the Pitzer Model in ESP: The Fluoride and Phosphate Components, Rev. 0*. Report No. PNWD-3120, WTP-RPT-018, Pacific Northwest National Laboratory, Richland, WA. http://www.pnl.gov/rpp-wtp/documents/WTP-RPT-018.pdf.

Felt RE. 1967. *Burning and Extinguishing Characteristics of Plutonium Metal Fires*. Report No. ISO-756, Isochem, Incorporated, Richland, WA.

Fountain MS, RT Brigantic, and RA Peterson. 2013. *Statistical Methods and Tools for Hanford Staged Feed Tank Sampling, Rev. 0*. Report No. PNNL-22901, Pacific Northwest National Laboratory, Richland, WA. http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22901.pdf.

Fox RK, DF Swineheart, and AB Garrett. 1941. "The Equilibria of Manganese Hydroxide, $Mn(OH)_2$, in Solutions of Hydrochloric Acid and Sodium Hydroxide." *Journal of the American Chemical Society* 63(7):1779-82.

Gayer KH, and AB Garrett. 1949. "The Equilibria of Nickel Hydroxide, $Ni(OH)_2$, in Solutions of Hydrochloric Acid and Sodium Hydroxide at 25° C." *Journal of the American Chemical Society* 71(9):1973-2975.

Gel’man AD, AI Moskvin, LM Zaitsev, and MP Mefod'eva. 1962. *Complex Compounds of Transuranium Elements*. Consultants Bureau, New York, NY.

Gel’man AD, and LP Sokhina. 1958. "Oxalate Complex Compounds of Plutonium (IV)." *Journal of Inorganic Chemistry, USSR* 3(5):49-56.

General Electric. 1948. *REDOX Technical Data Handbook* Report No. HDC-826, General Electric Company, Richland, WA.

Gephart RE. 2003. *A Short History of Hanford Waste Generation, Storage, and Release, Rev. 4*. Report No. PNNL-13605, Pacific Northwest National Laboratory, Richland, WA. http://www.pnl.gov/main/publications/external/technical_reports/PNNL-13605rev4.pdf.

Gerber MS. 1993. *A Brief History of the PUREX and UO_3 Facilities*. Report No. WHC-MR-0437, Westinghouse Hanford Company, Richland, WA. http://www.osti.gov/scitech/biblio/10115226.

Gerber MS. 1996. *Plutonium Production Story at the Hanford Site: Processes and Facilities History*. Report No. WHC-MR-0521, Westinghouse Hanford Company, Richland, WA. http://www.osti.gov/scitech/biblio/664389.

Gerber MS. 1997. *History and Stabilization of the Plutonium Finishing Plant (PFP) Complex, Hanford Site*. Report No. HNF-EP-0924, Fluor Daniel Hanford, Inc., Richland, WA. http://www.osti.gov/scitech/biblio/325360.

Granquist DP. 1955. *Simplified Study Flowsheet No. 2 Modified Redox Process*. Report No. HW-40230, Hanford Atomic Products Operation, Richland, WA.

Grenthe I, J Fuger, RJM Konings, RJ Lemire, AB Muller, C Nguyen-Trung, and H Wanner. 1992. "Chemical Thermodynamics of Uranium, Figure V.5." In *Chemical Thermodynamics,* eds. H Wanner and I Forest, Vol. 1. North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands. https://www.oecd-nea.org/dbtdb/pubs/uranium.pdf.

Griffo JS, WB Brown, and FD Lonadier. 1964. *Solubility of Plutonium Compounds*. Report No. MLM 1191, Mound Laboratory, Miamisburg, OH. http://www.osti.gov/scitech/biblio/4659828.

Grigor'ev MS, AM Fedoseev, AV Gelis, NA Budantseva, VP Shilov, VP Perminov, MV Nikonov, and NN Krot. 2001. "Study of the Interaction of Pu(IV) and Np(IV,V, VI) with Fe Hydroxides to Predict the Behavior of Actinides in Environmental Media." *Radiochimica Acta* 89:95-100.

Guillaumont R, T Fanghänel, J Fuger, I Grenthe, DA Palmer, and MH Rand. 2003. *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*. Elsevier, Amsterdam, The Netherlands. https://www.oecd-nea.org/dbtdb/pubs/vol5-update-combo.pdf.

Haire RG, MH Lloyd, ML Beasley, and WO Milligan. 1971. "Aging of Hydrous Plutonium Dioxide." *Journal of Electron Microscopy* 20:8-16.

Hanford Works. 1944. *Hanford Engineer Works Technical Manual*. Report No. HW-10475 C-DEL, Hanford Atomic Products Operation, Richland, WA.

Harlow DG, and LJ Olguin. 1977. Internal letter to RB Gelman (Manager) from DG Harlow and LJ Olguin, ARHCO Researchers, "Current Status and Safety Hazards in Miscellaneous Treatment." 8 Mar 1977, Richland, WA.

Harmon KM, and WH Reas. 1957. *Conversion Chemistry of Plutonium Nitrate*. Report No. HW-49597 A, Hanford Atomic Products Operation, Richland, WA. http://www.osti.gov/scitech/biblio/4364697.

Harmon MK. 1947. *Freezing Point Data for UNH-H_2O-HNO_3 Systems*. Report No. HW-8309, General Electric Company, Richland, WA. http://www.osti.gov/scitech/biblio/4374237.

Harrington SJ. 2011. *Hanford Waste Mineralogy Reference Report*. Report No. RPP-RPT-46618, Rev. 2, Washington River Protection Solutions LLC, Richland, WA.

Hartford WH. 1941. "Note on the System Sodium Dichromate-Water." *Journal of the American Chemical Society* 63(5):1473-74. As presented in Linke 1958.

Haschke JM. 1992. *Evaluation of Source-Term Data for Plutonium Aerosolization*. Report No. LA-12315-MS, Los Alamos National Laboratory, Los Alamos, NM. http://lib-www.lanl.gov/cgi-bin/getfile?00193529.pdf.

Haschke JM. 1995. *Reactions of Plutonium and Uranium with Water: Kinetics and Potential Hazards*. Report No. LA-13069-MS, Los Alamos National Laboratory, Los Alamos, NM. http://lib-www.lanl.gov/cgi-bin/getfile?00285828.pdf.

Haschke JM, and TH Allen. 2002. "Equilibrium and Thermodynamic Properties of the PuO_{2+X} Solid Solution." *Journal of Alloys and Compounds* 336:124-31.

Haschke JM, TH Allen, and LA Morales. 2000. "Surface and Corrosion Chemistry of Plutonium." In *Los Alamos Science,* ed. NG Cooper, pp. 252-73. Los Alamos National Laboratory, Los Alamos, NM. http://library.lanl.gov/cgi-bin/getfile?26-30.pdf.

Haschke JM, TH Allen, and LA Morales. 2001. "Reactions of Plutonium Dioxide with Water and Hydrogen-Oxygen Mixtures: Mechanisms for Corrosion of Uranium and Plutonium." *Journal of Alloys and Compounds* 314:78-91.

Haschke JM, and JL Stakebake. 2006. "Handling, Storage, and Disposition of Plutonium and Uranium." In *The Chemistry of the Actinide and Transactinide Elements,* eds. LR Morss, et al. Springer, Dordrecht, The Netherlands.

Herting DL. 1994. "Characterization of Sludge Samples from Tank 241-AN-107." In *Process Aids-A Compilation of Technical Letters by Process Laboratories and Technology*. Report WHC-IP-0711-26. Westinghouse Hanford Company, Richland, WA.

Herting DL. 1995. *Report of Scouting Study on Precipitation of Strontium, Plutonium, and Americium from Hanford Complexant Concentrate Waste*. Report No. WHC-SD-WM-DTR-040, Westinghouse Hanford Company, Richland, WA. http://www.osti.gov/scitech/biblio/273259.

Higley BA, SL Lambert, DE Place, and MJ Kupfer. 2001. *Best-Basis Inventory Template Compositions of Common Tank Waste Layers*. Report No. RPP-8847, Rev. 0, CH2M Hill Hanford Group, Richland, WA. http://rkc.pnl.gov/docs/index.php/home/view/2466.

Higley BA, DE Place, RA Corbin, and BC Simpson. 2004. *Hanford Defined Waste Model*. Report No. RPP-19822, Rev. 5, CH2M Hill Hanford Group, Inc., Richland, WA.

Hobbs DT. 1999. "Precipitation of Uranium and Plutonium from Alkaline Salt Solutions." *Nuclear Technology* 128:103-12.

Hobbs DT. 2012a. *Decontamination Factors and Filtration Flux Impact to ARP at Reduced MST Concentration*. Report No. SRNL-STI-2012-00299, Westinghouse Savannah River Company, Aiken, SC. http://www.osti.gov/scitech/biblio/1044792.

Hobbs DT. 2012b. *Form and Aging of Plutonium in Savannah River Site Waste Tank 18*. Report No. SRNL-STI-2012-00106, Revision 0, Savannah River National Laboratory, Aiken, SC. http://sti.srs.gov/fulltext/SRNL-STI-2012-00106.pdf.

Hobbs DT, MG Bronikowski, TB Edwards, and RL Pulmano. 1999. *Final Report on Phase III Testing of Monosodium Titanate Adsorption Kinetics*. Report No. WSRC-TR-99-00134, Westinghouse Savannah River Company, Aiken, SC. http://www.osti.gov/scitech/servlets/purl/12507.

Hobbs DT, and TB Edwards. 1993. *Solubility of Plutonium in Alkaline Salt Solutions*. Report No. WSRC-TR-93-131, Westinghouse Savannah River Company, Aiken, SC. http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/24/075/24075626.pdf.

Hobbs DT, TB Edwards, and SD Fleischman. 1993. *Solubility of Plutonium and Uranium in Alkaline Salt Solutions*. Report No. WSRC-TR-93-00056, Westinghouse Savannah River Company, Aiken, SC. http://www.osti.gov/scitech/servlets/purl/10136590.

Hobbs DT, and DG Karraker. 1996. "Recent Results on the Solubility of Uranium and Plutonium in Savannah River Site Waste Supernate." *Nuclear Technology* 114:318-24.

Hobbs DT, and RL Pulmano. 1999a. *Phase IV Simulant Testing of Monosodium Titanate Adsorption Kinetics*. Report No. WSRC-TR-99-00219, Westinghouse Savannah River Company, Aiken, SC. http://www.osti.gov/scitech/biblio/963951.

Hobbs DT, and RL Pulmano. 1999b. *Phase IV Testing of Monosodium Titanate Adsorption with Radioactive Waste*. Report No. WSRC-TR-99-00286, Westinghouse Savannah River Company, Aiken, SC. http://www.osti.gov/bridge//product.biblio.jsp?query_id=0&page=0&osti_id=750092.

Hobbs DT, and DD Walker. 1992. *Plutonium and Uranium Adsorption on Monosodium Titanate*. Report No. WSRC-RP-92-093, Westinghouse Savannah River Company, Aiken, SC. http://www.osti.gov/scitech/biblio/10114343.

Hoekstra HR. 1945. *Some Phases of the Alkaline Chemistry of Plutonium – Memo Report*. Report No. SE-PC-#69, HW-3-2921, Hanford Atomic Products Operation, Richland, WA.

Jantzen CM, JE Laurinat, and KG Brown. 2002. *Thermodynamic Modeling of the SRS Evaporators: Part I. The 2H and 2F Systems*. Report No. WSRC-TR-2000-00293, Rev. 1, Westinghouse Savannah River Company, Aiken, SC. http://sti.srs.gov/fulltext/tr2000293r1/tr2000293r1.pdf.

Jenkins IL, FH Moore, and MJ Waterman. 1963. "X-Ray Powder Crystallographic Data on Plutonium Oxalates and Their Isomorphs." *Chemistry and Industry (London)* 1:35-36.

Jenkins IL, FH Moore, and MJ Waterman. 1965a. "X-Ray Powder Crystallographic Data on Plutonium and Other Oxalates—I: The Oxalates of Plutonium(III) and Plutonium(VI) and Their Isomorphs." *Journal of Inorganic and Nuclear Chemistry* 27(1):77-80. http://www.sciencedirect.com/science/article/pii/0022190265801932. http://dx.doi.org/10.1016/0022-1902(65)80193-2.

Jenkins IL, FH Moore, and MJ Waterman. 1965b. "X-Ray Powder Crystallographic Data on Plutonium and Other Oxalates – II: Plutonium(IV) Oxalate Dihydrate, Uranium(IV) Oxalate Hexahydrate, Uranium(IV) Oxalate Dihydrate and Thorium Oxalate Dihydrate." *Journal of Inorganic and Nuclear Chemistry* 27(1):81-87.

Jenkins SH, DG Keight, and RE Humphreys. 1964. "The Solubility of Heavy Metal Hydroxides in Water, Sewage and Sewage Sludge. I. The Solubility of Some Metal Hydroxides." *Air and Water Pollution* 8:537-56.

Kamnev AA, BB Ezhov, OG Malandin, and AV Vasev. 1986. "Investigation of the Solution Process of Goethite (α-FeOOH) in Alkaline Solutions." *Journal of Applied Chemistry, USSR* 59(8):1560-64.

Karraker DG. 1993. *Solubility of Plutonium in Waste Evaporation*. Report No. WSRC-TR-93-578, Westinghouse Savannah River Company, Aiken, SC. http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/25/064/25064588.pdf.

Katz JJ, and GT Seaborg. 1957. *The Chemistry of the Actinide Elements*. Methuen & Company, Limited, London, U. K.

Keller C. 1963. "Untersuchen Über Die Germanate Und Silikate des Typs ABO_4 Der Vierwertigen Elemente Thorium Bis Americium." *Nukleonik* 5:41-48.

Keller C, and M Salzer. 1967. "Ternäre Fluoride des Typs $Me^{II}Me^{IV}F_6$ mit LaF_3-Struktur." *Journal of Inorganic and Nuclear Chemistry* 29:2925-34.

Kendall J, and JC Andrews. 1921. "The Solubilities of Acid in Aqueous Solutions of Other Acids." *Journal of the American Chemical Society* 43:1545-60.

Kessinger GF, PM Almond, NJ Bridges, MG Bronikowski, ML Crowder, JM Duffey, DM Missimer, JH Scogin, ME Summer, RR Livingston, MM McElwee, and AR Jurgensen. 2010. "Material Properties of Plutonium-Bearing Oxides Stored in Stainless Steel Containers." *Journal of Nuclear Materials Management* XXXVIII(3):82-95. Also, as Report No. SRNL-STI-2010-00065, Savannah River National Laboratory, Aiken, SC. http://sti.srs.gov/fulltext/SRNL-STI-2010-65.pdf.

King WD, MS Hay, BJ Wiersma, and FM Pennebaker. 2011. *EM-31 Alternative and Enhanced Chemical Cleaning Program for Sludge Heel Removal*. Presented at Waste Management 2011, Phoenix, AZ. http://www.wmsym.org/archives/2011/papers/11220.pdf, Savannah River National Laboratory, Aiken, SC.

Kittrick JA. 1966. "The Free Energy of Formation of Gibbsite and $Al(OH)_4^-$ from Solubility Measurements." *Soil Science Society of America Journal* 30:595-98.

Klem MJ. 1972. "*Evaluation of Process Test PRF 67-5 Filtration of CA Column Interface Jettings*." Internal note, June 20, 1972. Atlantic Richfield Hanford Company, Richland, WA.

Knights LM. 1970. *Monthly Report – Plutonium Process Engineering Section*. Report No. ARH-423-RD-DEL, Atlantic Richfield Hanford Company, Richland, WA.

Kolman DG. 2002. *The Aqueous Corrosion Behavior of Plutonium Metal Exposed to Nitric Acid Solution*. Report No. LA-UR-02-5920, Los Alamos National Laboratory, Los Alamos, NM.

Kolman DG, and LP Colletti. 2008. "Aqueous Corrosion Behavior of Plutonium Metal and Plutonium–Gallium Alloys Exposed to Aqueous Nitrate and Chloride Solutions." *Journal of the Electrochemical Society* 155(12):C565-C70.

Krot NN, AA Bessonov, AV Gelis, and VP Shilov. 1998a. "Coprecipitation of Transuranium Elements from Alkaline Solutions by the Method of Appearing Reagents. II. Coprecipitation of Pu(VI,V) with $Mn(OH)_2$." *Radiochemistry* 40(6):578-81.

Krot NN, AD Gel'man, MP Mefod'eva, VP Shilov, VF Peretrukhin, and VI Spitsyn. 1977. "Семивалентное Состояние Нептуния, Плутония, Америция (Semivalentnoe Sostoyanie Neptuniya, Plutoniya, Ameritsiya)." *Nauka* (Available in English as *Heptavalent States of Neptunium, Plutonium, and Americium*, Report No. UCRL-trans-11798, from Lawrence Livermore National Laboratory, Livermore, CA.).

Krot NN, AD Gel'man, FA Zakharova, VF Peretrukhin, and AK Pikaev. 1972. "The Possibility of Production of Plutonium(VIII)." *Soviet Radiochemistry* 14(6):922-24.

Krot NN, VP Shilov, AA Bessonov, NA Budantseva, IA Charushnikova, VP Perminov, and LN Astafurova. 1996. *Investigation on the Coprecipitation of Transuranium Elements from Alkaline Solutions by the Method of Appearing Reagents*. Report No. WHC-EP-0898, Westinghouse Hanford Company, Richland, WA. http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/30/047/30047157.pdf.

Krot NN, VP Shilov, AM Fedoseev, AB Yusov, AA Bessonov, NA Budantseva, SI Nikitenko, GM Plavnik, TP Puraeva, MS Grigor'ev, AY Garnov, AV Gelis, VP Perminov, LN Astafurova, and CH Delegard. 1998b. *Alkali Treatment of Acidic Solution from Hanford K Basin Sludge Dissolution*. Report No. PNNL-11944, Pacific Northwest National Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/2507.

Krot NN, VP Shilov, AB Yusov, IG Tananaev, MS Grigor'ev, AY Garnov, VP Perminov, and LN Astafurova. 1998c. *Plutonium(IV) Precipitates Formed in Alkaline Media in the Presence of Various Anions*. Report No. PNNL-11901, Pacific Northwest National Laboratory, Richland, WA. http://www.osti.gov/bridge/purl.cover.jsp?purl=/665911-NwS0BW/webviewable/.

Kupfer MJ, AL Boldt, KM Hodgson, LW Shelton, BC Simpson, RA Watrous, MD LeClair, GL Borsheim, RT Winward, BA Higley, RM Orme, NG Colton, SL Lambert, and DE Place. 1999. *Standard Inventories of Chemicals and Radionuclides in Hanford Site Tank Wastes*. Report No. HNF-SD-WM-TI-740, Rev. 0C, Lockheed Martin Hanford Company, Richland, WA. http://www.hanford.gov/files.cfm/HNF-SD-WM-TI-740_Rev_0.pdf and http://www.hanford.gov/files.cfm/HNF-SD-WM-TI-740_Rev_0C.pdf.

Latimer WM. 1952. *Oxidation Potentials*. 2nd ed., Prentice Hall, Inc., New York, NY.

Li H, J Addai-Mensah, JC Thomas, and AR Gerson. 2005. "The Influence of Al(III) Supersaturation and NaOH Concentration on the Rate of Crystallization of $Al(OH)_3$ Precursor Particles from Sodium Aluminate Solutions." *Journal of Colloid and Interface Science* 286:511-19. http://ac.els-cdn.com/S0021979705000937/1-s2.0-S0021979705000937-main.pdf?_tid=18057852-dfd9-11e4-843b-00000aab0f6c&acdnat=1428708603_03e209026025c4a0c759abb938500fc8.

Linke WF. 1958. *Solubilities – Inorganic and Metal-Organic Compounds*. Fourth ed., American Chemical Society, Washington, D. C.

Liu X, and FJ Millero. 1999. "The Solubility of Iron Hydroxide in Sodium Chloride Solutions." *Geochimica et Cosmochimica Acta* 63:3487-97.

Lloyd MH, and RL Fellows. 1985. *Alpha Radiolysis and Other Factors Affecting Hydrolysis of Tributyl Phosphate*. Report No. ORNL/TM-9565, Oak Ridge National Laboratory, Oak Ridge, TN. http://web.ornl.gov/info/reports/1985/3445600515930.pdf.

Lloyd MH, and RG Haire. 1978. "The Chemistry of Plutonium in Sol-Gel Processes." *Radiochimica Acta* 25:139-48.

Lumetta GJ, JC Braley, MK Edwards, O Qafoku, AR Felmy, JC Carter, and PJ MacFarlan. 2010. *Removing Phosphate from Hanford High-Phosphate Tank Wastes: FY 2010 Results*. Report No. PNNL-19778, Pacific Northwest National Laboratory, Richland, WA. http://www.pnl.gov/main/publications/external/technical_reports/PNNL-19778.pdf

Lumetta GJ, MJ Wagner, NG Colton, and EO Jones. 1993. *Underground Storage Tank Integrated Demonstration, Evaluation of Pretreatment Options for Hanford Tank Wastes*. Report No. PNL-8537, Pacific Northwest Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/10167322.

MacCready WK. 1957. Letter to AT Gifford (Atomic Energy Commission) from WK MacCready, Hanford Operations Office, "Lay-Away of TBP Plant and Metal Removal Facilities." HAN-64642. 4 April 1957, Hanford Operations Office, Richland, WA.

Machuron-Mandard X, and C Madic. 1996. "Plutonium Dioxide Particle Properties as a Function of Calcination Temperature." *Journal of Alloys and Compounds* 235(2):216-24. http://dx.doi.org/10.1016/0925-8388(95)02122-1.

Malquori G. 1928. "Sugli Idrati Dei Nitrati Di Cadmio, Zinco E Magnesio (On the Hydrates of Nitrates of Cadmium, Zinc and Magnesium)." In *Gazzetta Chimica Italiana*, Vol. 58, pp. 209-16, As presented in Dirske 1986.

Mandleburg CJ, KE Francis, and RC Smith. 1961. "The Solubility of Plutonium Trifluoride, Plutonium Tetra-Fluoride, and Plutonium(IV) Oxalate in Nitric Acid Mixtures." *Journal of the Chemical Society*:2464-68.

Martell CJ. 1974. *The Effect of Particle Size on the Carrier-Distillation Analysis of PuO_2*. Report No. LA-UR-74-356, Los Alamos Scientific Laboratory, Los Alamos, NM. http://lib-www.lanl.gov/cgi-bin/getfile?00354254.pdf.

Martz JC, JM Haschke, and JL Stakebake. 1994. "A Mechanism for Plutonium Pyrophoricity." *Journal of Nuclear Materials* 210:130-42.

Mashal K, JB Harsh, M Flury, AR Felmy, and H Zhao. 2004. "Colloid Formation in Hanford Sediments Reacted with Simulated Tank Waste." *Environmental Science and Technology* 38:5750-56.

Mattigod SV, DT Hobbs, KE Parker, DE McCready, and L-Q Wang. 2006. "Effects of Sodium Hydroxide and Sodium Aluminate on the Precipitation of Aluminum Containing Species in Tank Wastes." In *Nuclear Waste Management – Accomplishments of the Environmental Management Science Program,* eds. PW Wang and T Zachry. American Chemical Soceity, Washington, DC. *See also* SV Mattigod, DT Hobbs, KE Parker, and DE McCready. 2002. "Precipitation of Aluminum Containing Species in Tank Wastes". Report No. PNNL-13881, Pacific Northwest National Laboratory, Richland, WA. http://www.pnl.gov/main/publications/external/technical_reports/PNNL-13881.pdf.

Mattigod SV, D Rai, AR Felmy, and L Rao. 1997. "Solubility and Solubility Product of Crystalline $Ni(OH)_2$." *Journal of Solution Chemistry* 26(4):391-403.

May HM, PA Helmke, and ML Jackson. 1979. "Gibbsite Solubility and Thermodynamic Properties of Hydroxy-Aluminum Ions in Aqueous Solution at 25° C." *Geochimica et Cosmochimica Acta* 43:861-68.

McCoskey JK, and GA Cooke. 2013. *Characterization of Plutonium-Bearing Waste in the High-Level Waste Storage Tanks 241-SY-102, 241-TX-118, and 241-AZ-101 and the Plutonium Finishing Plant Z-9 Crib, Rev. 1.* Report No. LAB-RPT-12-00006, Washington River Protection Solutions, LLC, Richland, WA.

Miles RE. 2009. *Preliminary Criticality Safety Evaluation Report for the WTP*. Report No. 24590-WTP-CSER-ENS-08-0001, Rev. 0b, Bechtel National Incorporated, Richland, WA.

Mishima J. 1966. *Plutonium Release Studies II. Release from Ignited Bulk Metallic Pieces*. Report No. BNWL-357, Battelle Northwest Division, Richland, WA. http://www.osti.gov/scitech/biblio/4453507.

Molen GF, and RD White. 1967. *Properties of Plutonium Oxide, Part II.* Report No. RFP-927, The Dow Chemical Company, Golden CO. http://www.osti.gov/scitech/biblio/4339665. *Note that Part I is the report by Moseley and Wing (1965).*

Moore JD, RL Walser, and JJ Fritch. 1980. *PUREX Technical Manual*. Report No. RHO-MA-116, Rockwell Hanford Operations, Richland, WA.

Moseley JD, and RO Wing. 1965. *Properties of Plutonium Dioxide*. Report No. RFP-503, The Dow Chemical Company, Golden, CO. http://www.osti.gov/scitech/biblio/4613823.

Myers MN. 1956. *Thermal Decomposition of Plutonium (IV) Oxalate and Hydrofluorination of Plutonium (IV) Oxalate and Oxide*. Report No. HW-45128, Hanford Atomic Products Operation, Richland, WA. http://www.osti.gov/scitech/biblio/4181389.

Narlesky JE, MA Stroud, PH Smith, DM Wayne, RE Mason, and LA Worl. 2012. *Characterization of Representative Materials in Support of Safe, Long Term Storage of Surplus Plutonium in DOE-STD-3013 Containers*. Report No. LA-UR-12-23790, Los Alamos National Laboratory, Los Alamos, NM. http://www.osti.gov/scitech/biblio/1048356.

Nash KL, M Borkowski, M Hancock, and I Laszak. 2005. "Oxidative Leaching of Plutonium from Simulated Hanford Tank-Waste Sludges." *Separation Science and Technology* 40:1497-512.

Nies NP, and RW Hulbert. 1967. "Solubility Isotherms in the System Sodium Oxide-Boric Oxide-Water. Revised Solubility-Temperature Curves of Boric Acid, Borax, Sodium Pentaborate, and Sodium Metaborate." *Journal of Chemical and Engineering Data* 12(3):303-13.

Nikonov MV, and BF Myasoedov. 2010. "Oxidation of Pu(VI) with Ozone and Stability of the Oxidation Products, Pu(VII) and Pu(VIII), in Concentrated Alkali Solutions." *Radiochemistry* 52(1):17-21.

Oji LN, WR Wilmarth, and DT Hobbs. 2010. "Loading Capacities for Uranium, Plutonium, and Neptunium in High Caustic Nuclear Waste Storage Tanks Containing Selected Sorbents." *Nuclear Technology* 169(2):143-49.

Oka Y. 1940. "The Fundamental Reactions in Analytical Chemistry. IX. Summary." *Nippon Kagaku Kaishi (Journal of the Chemical Society of Japan)* 61:311-20, as presented in Linke 1958.

Oma KH. 1977. *Plutonium Metal Electrolytic Dissolution Flowsheet for the Plutonium Reclamation Facility*. Report No. ARH-F-109, Atlantic Richfield Hanford Company, Richland, WA.

Orth RJ, AH Zacher, AJ Schmidt, MR Elmore, KR Elliott, GG Neuenschwander, and SR Gano. 1995. *Removal of Strontium and Transuranics from Hanford Tank Waste Via Addition of Metal Cations and Chemical Oxidant - FY 1995 Test Results*. Report No. PNL-10766, Pacific Northwest Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/109670.

Pallmer PG. 1956. *Crystallite Sizes of PuO_2 Powder*. Report No. HW-44585, Hanford Atomic Products Operation, Richland, WA. http://www.osti.gov/scitech/biblio/4162958.

Panesko JV. 1971a. Internal letter to AJ Low (ARHCO Manager) from JV Panesko, ARHCO Researcher, "CA Column Interface Crud Sampled on September 27, 1971." 1 Oct 1971, Richland, WA.

Panesko JV. 1971b. Internal letter to AJ Low (ARHCO Manager) from JV Panesko, ARHCO Researcher, "CAW Centrifuge Solids from Burnt Oxide Run." 26 Aug 1971, Richland, WA.

Panesko JV. 1972. *Hydrofluoric Acid Scrubber Systems*. Report No. ARH-2343, Atlantic Richfield Hanford Company, Richland, WA. http://www.osti.gov/bridge/servlets/purl/1016165-iGj45w/1016165.pdf.

Peretrukhin VF, and DP Alekseeva. 1974. "Polarographic Properties of Higher Oxidation States of Plutonium in Aqueous Alkali Solutions." *Soviet Radiochemistry* 16:823-26.

Peretrukhin VF, SV Kryutchkov, VI Silin, and IG Tananaev. 1996. *Determination of the Solubility of Np(IV)-(V), Pu(III)-(VI), Am(III)-(VI) and Tc(IV),(V) Hydroxo Compounds in 0.5 - 14 M NaOH Solutions*. Report No. WHC-EP-0897, Westinghouse Hanford Company, Richland, WA. http://www.osti.gov/bridge//product.biblio.jsp?query_id=0&page=0&osti_id=331672.

Peretrukhin VF, VP Shilov, and AK Pikaev. 1995. *Alkaline Chemistry of Transuranium Elements and Technetium and the Treatment of Alkaline Radioactive Wastes*. Report No. WHC-EP-0817, Westinghouse Hanford Company, Richland, WA. http://www.osti.gov/bridge//product.biblio.jsp?osti_id=92064.

Peretrukhin VF, and VI Spitsyn. 1982. "Electrochemical Determination of the Oxidation Potentials and the Thermodynamic Stability of the Valence States of the Transuranium Elements in Aqueous Alkaline Media." *Bulletin of the Academy of Sciences USSR, Division of Chemical Sciences* (4):826-31.

Perlman I, SG Thompson, and BB Cunningham. 1947. "Metathesis of Bismuth Phosphate Plutonium Carrier with an Alkali." United States. US Patent No. 2,990,245. US Patent Office, Washington, DC. http://pdfpiw.uspto.gov/.piw?Docid=2990245&idkey=NONE&homeurl=http%3A%252F%252Fpatft.uspto.gov%252Fnetahtml%252FPTO%252Fpatimg.htm

Pius IC, MM Charyulu, B Venkataramani, CK Sivaramakrishnan, and SK Patil. 1995. "Studies on Sorption of Plutonium on Inorganic Ion Exchangers from Sodium Carbonate Medium." *Journal of Radioanalytical and Nuclear Chemistry Letters* 199(1):1-7.

PNNL. n.d. *Tank Waste Information Network System*. Accessed on 14 September, 2014 at https://twins.labworks.org/twinsdata/Forms/About.aspx (last updated January 2014).

Pokrovskii OS, VS Savenko, and KN Timofeev. 1997. "Solubility of MnO_2 and Forms of Manganese Occurrence in Aqueous Solutions (English Translation)." *Doklady Akadamii Nauk SSSR* 354(4):591-94.

Pourbaix M. 1966. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. Pergamon Press, Oxford, UK.

Powell BA, Z Dai, M Zavarin, P Zhao, and AB Kersting. 2011. "Stabilization of Plutonium Nano-Colloids by Epitaxial Distortion on Mineral Surfaces." *Environmental Science and Technology* 45:2698-703.

Price SM, and LL Ames. 1975. *Characterization of Actinide-Bearing Sediments Underlying Liquid Waste Disposal Facilities at Hanford*. Report No. ARH-SA-232, Atlantic Richfield Hanford Company, Richland, WA. http://0-www.osti.gov.iii-server.ualr.edu/scitech/biblio/4155335.

Rai D. 1984. "Solubility Product of Pu(IV) Hydrous Oxide and Equilibrium Constants of Pu(IV)/Pu(V), Pu(IV)/Pu(VI), and Pu(V)/Pu(VI) Couples." *Radiochimica Acta* 35:97-106.

Rai D, AR Felmy, and DA Moore. 1991a. "Thermodynamic Model for Aqueous Cd^{2+}-CO_3^{2-} Ionic Interactions in High-Ionic-Strength Carbonate Solutions, and the Solubility Product of Crystalline $CdCO_3$." *Journal of Solution Chemistry* 20(12):1169-87.

Rai D, AR Felmy, and RW Szelmeczka. 1991b. "Hydrolysis Constants and Ion-Interaction Parameters for Cd(II) in Zero to High Concentrations of NaOH-KOH, and the Solubility Product of Crystalline $Cd(OH)_2$." *Journal of Solution Chemistry* 20(4):375-90.

Rai D, NJ Hess, L Rao, Z Zhang, AR Felmy, DA Moore, SB Clark, and GJ Lumetta. 2002. "Thermodynamic Model for the Solubility of $Cr(OH)_{3(am)}$ in Concentrated NaOH and NaOH–$NaNO_3$ Solutions." *Journal of Solution Chemistry* 31(5):343-67.

Rai D, DA Moore, KM Russo, AR Felmy, and H Bolton Jr. 2008. "Environmental Mobility of Pu(IV) in the Presence of Ethylenediaminetetraacetic Acid: Myth or Reality." *Journal of Solution Chemistry* 37(7):957-86. http://link.springer.com/article/10.1007%2Fs10953-008-9282-2#.

Rai D, and JL Ryan. 1982. "Crystallinity and Solubility of Pu(IV) Oxide and Hydrous Oxide in Aged Aqueous Suspensions." *Radiochimica Acta* 30:213-16.

Rai D, RJ Serne, and DA Moore. 1980. "Solubility of Plutonium Compounds and Their Behavior in Soils." *Soil Science Society of America Journal* 44:490-95.

Rapko BM. 1998. *Oxidative Dissolution of Chromium from Hanford Tank Sludges: Results of FY 98 Studies*. Report No. PNNL-11908, Pacific Northwest National Laboratory, Richland, WA. http://rkc.pnl.gov/docs/files/webviewable-PNNL--11908.pdf.

Rapko BM, CH Delegard, and MJ Wagner. 1997. *Oxidative Dissolution of Chromium from Hanford Tank Sludges under Alkaline Conditions*. Report No. PNNL-11571, Pacific Northwest National Laboratory, Richland, WA. http://rkc.pnl.gov/docs/index.php/home/view/2318.

Rapko BM, JGH Geeting, SI Sinkov, and JD Vienna. 2004. *Oxidative-Alkaline Leaching of Washed 241-SY-102 and 241-SY-101 Tank Sludges*. Report No. WTP-RPT-117, Rev. 0; PNWD-3512, Bechtel National, Inc., Richland, WA. www.pnl.gov/rpp-wtp/documents/wtp-rpt-117.pdf.

Rapko BM, GJ Lumetta, and MJ Wagner. 1996. *Oxidative Dissolution of Chromium from Hanford Tank Sludges under Alkaline Conditions*. Report No. PNNL-11233, Pacific Northwest National Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/266870.

Rapko BM, and JD Vienna. 2002. *Selective Leaching of Chromium from Hanford Tank Sludge 241-U-108*. Report No. PNNL-14019, Pacific Northwest National Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/860129.

Rapko BM, JD Vienna, SI Sinkov, J Kim, and AJ Cisar. 2002. *Alkaline Leaching of Key, Non-Radioactive Components from Simulants and Hanford Tank Sludge 241-S-110: Results of FY01 Studies*. Report No. PNNL-14018, Pacific Northwest National Laboratory, Richland, WA. http://www.osti.gov/scitech/biblio/860128.

Rasmussen JH. 2013. *Derivation of Best-Basis Inventory for Tank 241-AN-101 as of July 1, 2013.* Report No. RPP-RPT-44814, 2013, Rev. 12, Washington River Protection Solutions, LLC, Richland, WA.

Ray M, IC Pius, MM Charyulu, and CK Sivaramakrishnan. 1988. *Spectrophotometric Studies on the Behaviour of Plutonium in Basic Media*. Presented at Radiochemistry and Radiation Chemistry Symposium, Bombay, India, IAEA, Vienna, Austria.

Reynolds JG, GA Cooke, DL Herting, and RW Warrant. 2013. "Salt Mineralogy of Hanford High-Level Nuclear Waste Staged for Treatment." *Industrial and Engineering Chemistry Research* 52:9741−51.

Rodgers MJ. 2010. *Waste Tank Summary Report for Month Ending March 31, 2010*. Report No. HNF-EP-0182 , Rev. 264, Washington River Protection Solutions, Richland, WA. http://pdw.hanford.gov/arpir/index.cfm/docDetail?accession=1006100795.

Roetman VE, SP Roblyer, and H Toffer. 1994. *Estimation of Plutonium in Hanford Site Waste Tanks Based on Historical Records*. Report No. WHC-EP-0793, Westinghouse Hanford Company, Richland, WA. http://www.osti.gov/bridge/servlets/purl/10186404-mmajWH/webviewable/10186404.pdf.

Rozentzveig SA, BV Ershler, EL Shtrum, and MM Ostanina. 1950. "The Electrochemical Properties of Cadmium in Alkaline Solutions." *Trudy Soveshchaniya Elektrokhim. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1950:571-78. As presented in Dirkse 1986.

Rudisill TS. 2011. Email to CH Delegard (Scientist) from TS Rudisill, Scientist, "$PuF_4 \cdot 2.5H_2O$." 23 June 2011, Richland, WA.

Rudisill TS, DT Hobbs, and TB Edwards. 2010. "Plutonium Solubility in Simulated Savannah River Site Waste Solutions." *Separation Science and Technology* 45(12-13):1782-92.

Rudisill TS, and MC Thompson. 2011. *Enhanced Chemical Cleaning of SRS Waste Tanks to Improve Actinide Solubility*. Report No. SRNL-STI-2011-00521, Savannah River National Laboratory, Aiken, SC. http://www.sti.srs.gov/fulltext/SRNL-STI-2011-00521.pdf.

Rumynin VG. 2011. "Tomsk-7 and Krasnoyarsk-26 Sites for Deep-Well Injection Radioactive Waste Disposal, and Lake Karachai Site of Near-Surface Disposal of Radioactive Brine." In *Subsurface Solute Transport Models and Case Histories with Applications to Radionuclide Migration*, pp. 681-711. Springer, New York, NY.

Russell AS, JD Edwards, and CS Taylor. 1955. "Solubility and Density of Hydrated Aluminas in NaOH Solutions." *Journal of Metals* 7(10):1123-28.

Sams TL. 2012. *Executive Summary: Review of Plutonium Oxide Receipts into Hanford Tank Farms*. Report No. WRPS-51744, Rev. 0, Washington River Protection Solutions, Richland, WA.

Sanchez AL, JW Murray, and TH Sibley. 1985. "The Adsorption of Plutonium IV and V on Goethite." *Geochimica et Cosmochimica Acta* 49:2297-307.

Schneider KJ. 1951. *Flow Sheets and Flow Diagrams of Precipitation Separation Processes*. Report No. HW-23043, Hanford Atomic Products Operations, Richland, WA.

Schreinemakers FAH. 1906. "Alkali Chromates." *Zeitschrift fuer Physikalische Chemie, Stoechiometrie und Verwandtschaftslehre* 55:71-98 (in German), as presented in Linke 1958.

Schulz WW. 1979. "Removal of Plutonium and Americium from Alkaline Waste Solutions." US Patent No. 4,156,646. US Patent Application No. 05/916,179. https://docs.google.com/viewer?url=patentimages.storage.googleapis.com/pdfs/US4156646.pdf.

Schulz WW, RE Burns, and EM Duke. 1962. "Nitric Acid Dissolution of Uranium-Molybdenum Alloy Reactor Fuels." *Industrial & Engineering Chemistry, Process Design and Development* 1(2):156-60.

Schulz WW, JW Koenst, and DR Tallent. 1980. "Application of Inorganic Sorbents in Actinide Separations Processes." In *Actinide Separations,* eds. JD Navratil and WW Schulz, pp. 17-32. American Chemical Society, Washington, D. C.

Serebrennikova MT. 1953. "Solubility of Chromic Nitrate in Aqueous Solutions of Nitric Acid." *Zhurnal Prikladnoi Khimii (Russian Journal of Applied Chemistry)* 26:1011-15 (in Russian), as presented in Linke 958.

Shilov VP. 1997. "Disproportionation of Plutonium(VI) in Alkaline Media." *Radiochemistry* 39(4):328-31.

Shilov VP. 1998. "Probable Forms of Actinides in Alkali Solutions." *Radiochemistry* 40(1):12-17.

Shilov VP, and AM Fedoseev. 2003. "Solubility of Pu(IV) in Weakly Alkaline Solutions (pH 9-14) Containing Silicate Anions." *Radiochemistry* 45(5):491-94.

Shilov VP, NN Krot, NA Budantseva, AB Yusov, AY Garnov, VP Perminov, and LN Astafurova. 1996. *Investigation of Some Redox Reactions of Neptunium, Plutonium, Americium, and Technetium in Alkaline Media*. Report No. WHC-EP-0886, Westinghouse Hanford Company, Richland, WA.

Sinkov SI. 2007. *Plutonium Speciation in Support of Oxidative-Leaching Demonstration Test.* Report No. WTP-RPT-165, Rev. 0; also as PNNL-16844, Pacific Northwest National Laboratory, Richland, WA. http://www.pnl.gov/rpp-wtp/documents/WTP-RPT-165.pdf and http://www.pnl.gov/main/publications/external/technical_reports/PNNL-16844.pdf.

Slaathaug E. 2013. *ICD 19 - Interface Control Document for Waste Feed*. Report No. 24590-WTP-ICD-MD-1-019, Rev. 6, River Protection Project, Waste Treatment Plant, Bechtel National, Inc., Richland, WA.

Slater SA, DB Chamberlain, SA Aase, BD Babcock, C Conner, J Sedlet, and GF Vandegrift. 1997. "Optimization of Magnetite Carrier Precipitation Process for Plutonium Waste Reduction." *Separation Science and Technology* 32:127-47.

Solov'eva VD, VV Bobrova, LG Orlova, and EU Adeishvili. 1973a. "Solubility of Copper, Cadmium, and Indium Hydroxides in Sodium Hydroxide Solutions." *Trudy Instituta Metallurgii i Obogashcheniya, Akademiya Nauk Kazakhskoi SSR* 49:45-48. As reported in Dirkse 1986.

Solov'eva VD, EG Svirchevskaya, VV Bobrova, and NM El'tsov. 1973b. "Solubility of Copper, Cadmium, and Indium Oxides in Sodium Hydroxide Solutions." *Trudy Instituta Metallurgii i Obogashcheniya, Akademiya Nauk Kazakhskoi* 49:37-44. As reported in Dirkse 1986.

Stakebake JL. 1981. "Kinetics for the Reaction of Hydrogen with a Plutonium-1 Weight Percent Gallium Alloy Powder." *Journal of the Electrochemical Society* 128(11):2383-88.

Stakebake JL, and LM Steward. 1973. "Water Vapor Adsorption on Plutonium Dioxide." *Journal of Colloid and Interface Science* 42(2):328-33.

Stewart K. 1961. *Vixen-A Trials: Experiments to Study the Release of Particulate Materials During the Combustion of Plutonium, Uranium and Beryllium in a Petrol Fire*. Report No. AWRE T15/60, Atomic Weapons Research Establishment, Aldermaston, United Kingdom. As cited by Haschke 1992.

Swain Jr. HA, C Lee, and RB Rozelle. 1975. "Determination of the Solubility of Manganese Hydroxide and Manganese Dioxide at 25° C by Atomic Absorption Spectrometry." *Analytical Chemistry* 47(7):1135-37.

Tananaev IG. 1989. "Forms of Hexavalent Plutonium and Americium in Basic Aqueous Solutions." *Soviet Radiochemistry* 31:303-07.

Thompson MA. 1966. *The Oxidation and Ignition of Plutonium*. Report No. RFP-491, The Dow Chemical Company, Rocky Flats Division, Golden, CO. http://www.osti.gov/scitech/biblio/4558003.

Ticknor KV. 1993. "Actinide Sorption by Fracture-Filling Minerals." *Radiochimica Acta* 60:33-42.

Toth LM, JM Bell, and HA Friedman. 1990. "The Disproportionation of Pu^{4+} in Nitric Acid Solutions." *Radiochimica Acta* 49:193-99.

Waber JT, and ES Wright. 1961. "The Corrosion of Plutonium." In *The Metal Plutonium,* eds. AS Coffinberry and WN Miner. The University of Chicago Press, Chicago, IL.

Wagman DD, WH Evans, VB Parker, RH Schumm, I Halow, SM Bailey, KL Churney, and RL Nuttall. 1982. "The NBS Tables of Chemical Thermodynamic Properties – Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units." *Journal of Physical and Chemical Reference Data* 11(Supplement 2). http://www.nist.gov/data/PDFfiles/jpcrdS2Vol11.pdf.

Wayne DM. 2014. *Thermal and Physical Properties of Plutonium Dioxide Produced from the Oxidation of Metal: A Data Summary*. Report No. LA-UR-14-20201, Los Alamos National Laboratory, Los Alamos, NM. http://permalink.lanl.gov/object/tr?what=info:lanl-repo/lareport/LA-UR-14-20201.

Wells BE, MA Knight, EC Buck, RC Daniel, LA Mahoney, PA Meyer, AP Poloski, JM Tingey, WS Callaway III, GA Cooke, ME Johnson, MG Thien, DJ Washenfelder, JJ Davis, MN Hall, GL Smith, SL Thomson, and Y Onishi. 2007. *Estimate of Hanford Waste Insoluble Solid Particle Size and Density Distribution*. Report No. PNWD-3824 (WTP-RPT-153, Rev. 0), Battelle - Pacific Northwest Division, Richland, WA. www.pnl.gov/rpp-wtp/documents/wtp-rpt-153.pdf.

Wells BE, Y Onishi, CA Burns, RC Daniel, DE Kurath, JL Huckaby, EC Buck, KK Anderson, LA Mahoney, SK Cooley, and JM Tingey. 2011. *Hanford Waste Physical and Rheological Properties: Data and Gaps*. Report No. PNNL-20646, Pacific Northwest National Laboratory, Richland, WA. http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-20646.pdf.

Westrum Jr. EF. 1949. "The Preparation and Properties of Plutonium Oxides." In *The Transuranium Elements - Research Papers,* eds. GT Seaborg, JJ Katz and WM Manning, pp. 936-44 of paper 6.57. McGraw-Hill Book Company, Inc., New York, NY.

Wheelwright EJ. 1972. *Development of an Electrolytic Dissolver for Plutonium Metal*. Report No. BNWL-1642, Battelle Pacific Northwest Laboratories, Richland, WA.

Wilmarth WR, CJ Coleman, JC Hart, and WT Boyce. 2000. *Characterization of Samples from the 242-16H Evaporator Wall*. Report No. WSRC-TR-2000-00089, Westinghouse Savannah River Company, Aiken, SC. http://sti.srs.gov/fulltext/tr2000089/tr2000089.html.

Worl LA, SM Bowen, JM Berg, DD Padilla, and MR Cisneros. 1995. *Actinide Removal from Hanford Supernatant Tank Waste*. Report No. LA-UR-95-3743, Los Alamos National Laboratory, Los Alamos, NM. (See also “TRU Removal from Underground Storage Tank Waste.” In *Proceedings of the Embedded Topical Meeting, DOE Spent Nuclear Fuel & Fissile Material Management,* 1996, pp. 428-437. American Nuclear Society, LaGrange Park, IL).

Yamaguchi T, Y Sakamoto, and T Ohnuki. 1994. "Effect of the Complexation on Solubility of Pu(IV) in Aqueous Carbonate System." *Radiochimica Acta* 66/67:9-14.

Yamamura T, A Kitamura, A Fukui, S Nishikawa, T Yamamoto, and H Moriyama. 1998. "Solubility of U(VI) in Highly Basic Solutions." *Radiochimica Acta* 83:139-46.

Yusov AB, NA Budantseva, AV Anan'ev, and AM Fedoseev. 2000a. "Coprecipitation of Aluminum with Hydroxides of Tetra-, Penta-, and Hexavalent Actinides." *Radiochemistry* 42(5):413-16.

Yusov AB, AM Fedoseev, OV Isakova, and CH Delegard. 2005. "Complexation of Np(V) with Silicate Ions." *Radiochemistry* 47(1):39-44.

Yusov AB, AY Garnov, VP Shilov, IG Tananaev, MS Grigor'ev, and NN Krot. 2000b. "Plutonium(IV) Precipitation from Alkaline Solutions. I: Effect of Precipitation and Coagulation Conditions on Properties of Hydrated Plutonium Dioxide $PuO_2 \cdot xH_2O$." *Radiochemistry* 42(2):151-56.

Yusov AB, AY Garnov, VP Shilov, IG Tananaev, MS Grigor'ev, and NN Krot. 2000c. "Plutonium(IV) Precipitation from Alkaline Solutions: II. Effect of Anions on Composition and Properties of Hydrated Plutonium Dioxide $PuO_2 \cdot xH_2O$." *Radiochemistry* 42(2):157-60.

Zavarin M, P Zhao, Z Dai, SA Carroll, and AB Kersting. 2012. *Sorption Behavior and Morphology of Plutonium in the Presence of Goethite at 25 and 80°C.* Report No. LLNL-TR-561456, Lawrence Livermore National Laboratory, Livermore, CA. https://e-reports-ext.llnl.gov/pdf/622965.pdf.

Zimmer E, and J Borchardt. 1986. "Crud Formation in the PUREX and Thorex Processes." *Nuclear Technology* 75:332-37.

Appendix A

Metathesis of Pu(IV) Oxalate and Pu(III)/(IV) Fluorides in Alkaline Media to Form $PuO_2 \cdot xH_2O$

A.1 Introduction

Plutonium oxalate ($Pu(C_2O_4)_2 \cdot 6H_2O$) and plutonium tetrafluoride (PuF_4) were solid-phase chemical intermediates formed in the preparation of plutonium metal from plutonium nitrate solutions in the Plutonium Finishing Plant (PFP). Plutonium oxalate also was an intermediate in the preparation of plutonium dioxide, PuO_2, at both the PFP and at N Cell operations in PUREX. Hydrated plutonium tetrafluoride, $PuF_4 \cdot 2.5H_2O$, and the double salts $NaPuF_5$ and Na_2PuF_6, all solid phases with low aqueous solubility, were likely formed in fluoride-assisted dissolution of PuO_2 values in scrap processing and in other points in Hanford processes. The hydrate $PuF_4 \cdot 2.5H_2O$ also could form during the stripping of Pu(IV) from the organic phase in the Plutonium Recovery Facility (PRF) solvent extraction operations within the PFP, in which fluoride was added to enhance the stripping process while the trivalent fluoride salt $PuF_3 \cdot xH_2O$ could form in reductive stripping.

Inadvertent discharge of $Pu(C_2O_4)_2 \cdot 6H_2O$, $PuF_3 \cdot xH_2O$, PuF_4, $PuF_4 \cdot 2.5H_2O$, $NaPuF_5$, and Na_2PuF_6 solids to the Hanford waste tanks could have occurred due to process operation upsets and as trace material losses in scrubber solutions and process wastes from these facilities. The chemical behaviors of $Pu(C_2O_4)_2 \cdot 6H_2O$, $PuF_3 \cdot xH_2O$, PuF_4, $PuF_4 \cdot 2.5H_2O$, and $NaPuF_5$, and Na_2PuF_6 with aging and after contacting alkaline tank wastes are of interest in understanding their likely current disposition in the tank farms.

The technical chemical literature was examined to determine the outcomes of interactions of Pu(IV) oxalate, $Pu(C_2O_4)_2 \cdot 6H_2O$, Pu(III) fluoride, and Pu(IV) fluoride as PuF_4, $PuF_4 \cdot 2.5H_2O$, $NaPuF_5$, and Na_2PuF_6 with alkaline solution. The following analysis and discussion was prepared to determine whether these compounds are unstable with respect to the formation of PuO_2 or $PuO_2 \cdot xH_2O$, either by radiolysis or by alkaline hydrolysis. Information on the initial particle size of $Pu(C_2O_4)_2 \cdot 6H_2O$, $PuF_3 \cdot xH_2O$, PuF_4, $PuF_4 \cdot 2.5H_2O$, $NaPuF_5$, and Na_2PuF_6 and the expected particle sizes of their products after contact with alkaline solution also is discussed.

A.2 Plutonium Oxalate

Tetravalent plutonium (Pu(IV)) oxalate was prepared in PFP operations by co-addition of ~1 M oxalic acid solution and ~0.2 M Pu(IV) in ~1-3 M nitric acid (HNO_3) to a stirred and warmed precipitation vessel. The solution mixture was digested at ~60° C to encourage crystal growth and the slurry decanted for filtration in a continuous MSMPR crystallizer. The product $Pu(C_2O_4)_2 \cdot 6H_2O$ particle size was 5 to 7 µm as determined by x-ray analysis during development work (Myers 1956). Continuous processing by co-addition of the Pu(IV) and oxalic acid reagents in the PFP MSMPR produced ~5 to 20 µm plutonium oxalate particles (Barr et al. 1970). Processing in 2001-2002 to recover plutonium from stored nitrate solutions during the de-inventory of the PFP also used Pu(IV) oxalate precipitation. In this case, the precipitation occurred in an air-sparged batch reactor by adding solid oxalic acid crystals to the feed Pu(IV)-bearing solution in HNO_3. The precipitation occurred at plant temperature and digestion time was about 1 hour before filtration. However, under these conditions, solids formation attributed to Pu(IV) oxalate post-precipitation was observed in the process filtrates. The process filtrates, including precipitated solids, were discarded to waste and ultimately to tank farms. The particle size distribution of the Pu(IV) oxalate solids in this stream is not known.

No information on the particle density of Pu(IV) oxalate hexahydrate, or even of the Th(IV) or U(IV) chemical analogues, was found in the technical literature. The densities of Pu(IV) oxalate dihydrate and the thorium analogue are 3.085 and 3.391, respectively, while that of Pu(III) oxalate decahydrate is 3.115 g/cm^3 (Jenkins et al. 1965a, b). Based on these values, Pu(IV) oxalate hexahydrate density is estimated to be between 3 and 4 g/cm^3.

The stabilities of Pu(IV) oxalate hexahydrate to radiolysis and to alkaline hydrolysis are examined in this section.

Radiolysis

Radiolytic decomposition of $Pu(C_2O_4)_2 \cdot 6H_2O$ is observed with the ultimate formation of $PuOCO_3 \cdot 2H_2O$ (Gel'man et al. 1962; Gel'man and Sokhina 1958). The half-life of the material to decomposition by its own alpha radiation is 64 days (Jenkins et al. 1963 as described in Cleveland 1970, page 407). A similar rate was observed by Myers (1956). The intermediate presence of trivalent plutonium, as $Pu_2(C_2O_4)_3 \cdot nH_2O$, is observed during radiolytic decomposition (Gel'man and Sokhina 1958). Based on these observations, $Pu(C_2O_4)_2 \cdot 6H_2O$ particles are not stable to chemical decomposition with respect to autogenous alpha radiolysis.

Alkaline Hydrolysis

Tetravalent plutonium oxalate is known to hydrolyze in strong alkaline solution to form plutonium "hydroxide" (or plutonium hydrous oxide, $PuO_2 \cdot xH_2O$). The balanced chemical reaction is:

$$Pu(C_2O_4)_2 \cdot 6H_2O + 4\ OH^- \rightarrow PuO_2 \cdot xH_2O + 2\ C_2O_4^{2-} + (8-x)\ H_2O$$

The most direct account found in the technical literature of the reaction of Pu(IV) oxalate with hydroxide ion, OH^-, describes metathesizing $Pu(C_2O_4)_2 \cdot 6H_2O$ in 4 M KOH solution. This was done to release the oxalate ion, $C_2O_4^{2-}$, for analysis after first filtering out the precipitated plutonium hydroxide (Myers 1956).

Other laboratory tests show that $PuO_2 \cdot xH_2O$ forms exclusively when dissolved acidic Pu(IV) nitrate solution is added to 60° C alkaline solutions, at 0.2 and 1 M NaOH, containing 0.1 M oxalate (Yusov et al. 2000c). The precipitated $PuO_2 \cdot xH_2O$ contained no detectible oxalate (<5 mol% with respect to plutonium) and has the same hygroscopic (water absorption) properties as the $PuO_2 \cdot xH_2O$ prepared by precipitation in the absence of oxalate. Together, the experiments of Yusov et al. (2000c) and those of (Myers 1956) indicate that Pu(IV) oxalate is unstable with respect to the formation of $PuO_2 \cdot xH_2O$ in alkaline solutions, at least above 0.2 M NaOH.

The stability of Pu(IV) oxalate at lower alkalinity can be inferred by studying the behavior of sodium plutonium oxalate double salts (Gel'man and Sokhina 1958). In these tests, the double salt of formula $Na_4[Pu(C_2O_4)_4] \cdot 5H_2O$ was prepared by mixing $Pu(C_2O_4)_2 \cdot 6H_2O$ solids in water, adding sodium oxalate, $Na_2C_2O_4$, solids and heating at ~80° C until both solids dissolved by formation of higher Pu(IV) oxalate complexes. The sodium-plutonium oxalate double salt then was precipitated from the aqueous solution by adding ethyl alcohol. The $Na_4[Pu(C_2O_4)_4] \cdot 5H_2O$ precipitate, when dissolved in water, was found to produce a solution of pH 4.5 to 4.7. However, raising the pH to about 7.5 to 8 caused destruction of the double salt and precipitation of plutonium hydroxide. Therefore, even with a stoichiometric excess of oxalate compared to formation of $Pu(C_2O_4)_2 \cdot 6H_2O$, as would be the case for $Na_4[Pu(C_2O_4)_4] \cdot 5H_2O$ dissolution, $PuO_2 \cdot xH_2O$ forms preferentially under very mildly alkaline (pH ~8) conditions.

Analysis of the thermodynamic stability of Pu(IV) oxalate to form $PuO_2 \cdot xH_2O$ by hydrolysis in alkaline solution was not possible because the Gibbs free energy of formation (ΔG_f^0) values for $Pu(C_2O_4)_2 \cdot 6H_2O$ were not found in the technical literature. Despite this paucity of thermodynamic knowledge, abundant chemical observation shows that $Pu(C_2O_4)_2 \cdot 6H_2O$ is unstable, to even mildly alkaline hydrolysis conditions, to formation of $PuO_2 \cdot xH_2O$.

A.3 Plutonium(III) and Plutonium(IV) Fluoride Salts

The process sources and properties of $PuF_3 \cdot xH_2O$ and the Pu(IV) fluorides PuF_4, $PuF_4 \cdot 2.5H_2O$, $NaPuF_5$, and Na_2PuF_6 and their stabilities to alkaline hydrolysis are examined based on findings reported in the technical literature.

A.3.1 Plutonium(III) and (IV) Fluoride Sources and Properties

The process sources and properties of the Pu(IV) fluorides $PuF_3 \cdot xH_2O$, PuF_4, $PuF_4 \cdot 2.5H_2O$, $NaPuF_5$, and Na_2PuF_6 are examined below.

$PuF_3 \cdot xH_2O$

A report of the potential presence of PuF_3 (likely $PuF_3 \cdot xH_2O$ with x ~0.75 or 0.4; Clark et al. (2006)) was reported to be the cause of decreased "CAX" flow in May 1968 (Engineers of Plutonium Process Engineering 1968, pages 53-54). CAX was the extractant, 20% TBP in carbon tetrachloride, used in the process in the Plutonium Reclamation Facility (PRF). $PuF_3 \cdot xH_2O$ agglomerate, described as "golf ball size" and readily and completely soluble in warm aluminum nitrate solution, was collected downstream of the process feed tank filter. The particle size of $PuF_3 \cdot xH_2O$ that could have formed in the process is not known but, given the low solubility of PuF_3 (Griffo et al. 1964), the individual particles likely were small. Studies designed to optimize the precipitation of PuF_3 by mixing of Pu(III) in nitric acid with hydrofluoric acid solution showed that 10-15 µm agglomerates could be made with moderate agitation but that with greater agitation, the particle size was ~2-3 µm (Burney and Tober 1965). Subsequent lab tests at PFP under the same chemical process conditions that produced the golf ball size agglomerates also produced black solids at the filter.

The $PuF_3 \cdot xH_2O$ is blue-violet in color, and thus may have appeared black when observed in plant processing; the anhydrous PuF_3's particle density is 9.32 g/cm^3 (Clark et al. 2006).

PuF_4

The particle size of PuF_4 formed by hydrofluorination using hydrogen fluoride (HF) gas under conditions used at the PFP is 2 to 10 µm (Myers 1956). Measurement of PuF_4 particle size produced by the Remote Mechanical C (RMC) Line under routine 1980s operation in the PFP showed the weight-average particle size to be ~22 µm with about 87 wt% of the material being greater than 10 µm and about 0.5 wt% less than 2 µm (Barney 1988). The density of PuF_4 is 7.04 g/cm^3 (Clark et al. 2006). It is noted that the solid particulate PuF_4 (or starting PuO_2) was most likely to report to the downstream system used to scrub excess corrosive and toxic HF from the offgas would have been that lofted by flow of the impinging HF gas and therefore should be strongly skewed to the finer particles.

$PuF_4 \cdot 2.5\ H_2O$

Plutonium(IV) fluoride, in the form $PuF_4 \cdot 2.5\ H_2O$, arises by precipitation of Pu(IV) from acid solution containing fluoride (Dawson et al. 1954b). Conversion of PuF_4 to $PuF_4 \cdot 2.5\ H_2O$ is known to occur in HF solution (Dawson et al. 1954a) and it is likely that this conversion also transpires in water.

Precipitation of pink $PuF_4 \cdot 2.5\ H_2O$ was often observed in dissolution of scrap plutonium oxides because fluoride ion was added to HNO_3 to complex Pu^{4+} as dissolved PuF^{3+} to improve plutonium dissolution from the source PuO_2. At PFP, the fluoride often was added as hydrofluoric acid (dissolved HF). The fluoride ion concentration used in the dissolution processing generally ranged up to ~0.5 M, while the HNO_3 concentration ranged from about 6 to 12 M. During scrap dissolution, the fluoride was consumed by the PuF^{3+} complex and also by reaction with silica (SiO_2; to form SiF_4) and by complexation with aluminum ion (Al^{3+}) or other metal ions present as impurities in the scrap. Because of these reactions, additional fluoride would be required for the plutonium scrap dissolution to continue. However, if the fluoride concentration became too high, Pu(IV) fluoride precipitated as $PuF_4 \cdot 2.5\ H_2O$.

Precipitates of what was probably $PuF_4 \cdot 2.5\ H_2O$, but was reported as pink PuF_4, also have been observed in the organic wash column (i.e., the “CO” column) of the PRF (Knights 1970). The precipitation of the pink compound was found to be enhanced due to the presence of DBP, a hydrolytic and radiolytic decomposition product of the TBP extractant used at PFP. The solubility of $PuF_4 \cdot 2.5H_2O$ in the 2.5 M HNO_3 / 0.25 M HF process stream is reported to be in excess of 8 grams of plutonium per liter. However, the pink precipitate was observed even at concentrations less than 3 grams of plutonium per liter. According to the process report, the “pink PuF_4 precipitate coagulated and was heavy enough to exist with the organic effluent” (which contained carbon tetrachloride diluent and thus was the lower phase in the extraction process). Solids reported to contain PuF_4, but likely $PuF_4 \cdot 2.5\ H_2O$, and other miscellaneous solids, were noted to be plugging a filter between Tank 39 and the solvent clean-up (known as the “CX”) column in May 1968 (Engineers of Plutonium Process Engineering 1968, 50). The solids were attributed to prior process operations.

No information was found in the process or technical literature on $PuF_4 \cdot 2.5\ H_2O$ particle size. However, the conditions under which the $PuF_4 \cdot 2.5\ H_2O$ formed during scrap dissolution, such as extended times at high temperature followed by slow cooling and relatively high concentrations of fluoride and Pu(IV), would favor crystal growth while the low solubility would limit crystal size. The particle size is likely to be 1-10 μm based on related formation condition and properties of $PuF_3 \cdot xH_2O$ (Burney and Tober 1965). The density of $PuF_4 \cdot 2.5\ H_2O$ is 4.89 g/cm^3 (Clark et al. 2006).

$NaPuF_5$ and Na_2PuF_6

The precipitation of Pu(IV) fluoride in the form of $NaPuF_5$ or Na_2PuF_6 is likely if NaF were used as the fluoride source in dissolving plutonium-bearing scrap, as it often was at PFP. Sodium also was present in many plutonium-bearing scrap materials processed at PFP, most obviously in electroreduction (ER) scrap containing NaCl/KCl (eutectic sodium/potassium chloride salt) from the Rocky Flats Site.

Lab studies show that $NaPuF_5$ forms when $PuF_4 \cdot 2.5H_2O$ solids are mixed with NaF in water (Deichman and Tananaev 1962). With NaF concentrations above about 0.25 M, the salt Na_2PuF_6 is observed. The starting $PuF_4 \cdot 2.5H_2O$, which has solubility of ~0.00013 M in water, is described as large acicular (needle-shaped) crystals, but the particle size is not given. The product $NaPuF_5$ (solubility decreasing from ~0.00013 to ~0.000001 M as NaF concentration increased to 0.25 M) is described as fine gray-green needles. The density of $NaPuF_5$ is 6.03 g/cm^3 (Clark et al. 2006).

The Na_2PuF_6, with ~0.000001 M solubility in ~0.25 to 0.5 M NaF, is described as large brown needles, but no quantitative particle size information is provided (Deichman and Tananaev 1962); it has a density of 5.84 g/cm^3 (Clark et al. 2006).

It is reported separately that when an excess of NaF is added to a solution of Pu(IV) in nitric acid, $NaPuF_5$ is obtained as a dense green precipitate. On standing, the green solid becomes pink, converting to the Na_2PuF_6 salt (Alenchikova et al. 1958). Tenuous XRD evidence of a sodium-plutonium fluoride double salt in the heel of a Rocky Flats oxide laboratory dissolution test at the PFP also has been reported (Delegard 1985a).

Other Pu(IV) Fluoride Salts

Savannah River Site operations used potassium fluoride (KF) in their digestions of plutonium oxide values and have identified the analogous $KPuF_5$ salt as well as KPu_2F_9 by x-ray diffractometry (Rudisill 2011). However, the particle size of the potassium double salts was not measured. Based on these observations, potassium-Pu(IV) fluoride double salts also might have formed in PFP scrap recovery operations for scraps, such as ER salts, which contained potassium.

The precipitation of Pu(IV) fluoride in the form of $CaPuF_6$ or other calcium-Pu(IV) fluoride double salts also might be credible if calcium were present in the scrap. For example, calcium fluoride, CaF_2, is present in sand, slag, and crucible (SS&C) scrap. Calcium fluoride also was used as a source of fluoride in dissolution of plutonium values in scrap recovery operations at the PFP. The density of $CaPuF_6$ is 6.65 g/cm^3 (Keller and Salzer 1967). Plant-scale preparation of this compound is reported to have occurred by mixing approximately two volumes of ~50 g Pu(IV)/liter solution containing ~9 g Ca^{2+}/liter in 4.5 M HNO_3 with one volume of 5.6 M HF to make $CaPuF_6$ under a solution containing only 0.3 g Pu/liter (Harmon and Reas 1957). No information on the existence of the analogous $MgPuF_6$ compound was found in the technical literature, but its existence is likely. It could have formed in processing SS&C scrap, which contained magnesium oxide (MgO) sand and crucible materials.

A.3.2 Alkaline Hydrolysis of Plutonium(IV) Fluoride Compounds

Direct experimental and process plant observations of the interaction of plutonium tetrafluoride with alkaline solution have been recorded in the technical literature. These observations and supporting thermodynamic analyses indicate that Pu(IV) fluoride compounds are unstable to formation of $PuO_2 \cdot xH_2O$ in sodium-rich alkaline media.

The earliest information on the stability of PuF_4 in alkaline solution was developed during the Manhattan Project for plutonium separations from irradiated uranium fuel. In the “Concentration” step in the Bismuth Phosphate Process to recover plutonium, metathesis (double decomposition) of lanthanum fluoride (LaF_3) and coprecipitated trace PuF_4 was performed, in which the LaF_3/PuF_4 solids were converted to their respective hydroxides $La(OH)_3/PuO_2 \cdot xH_2O$ in hydroxide solution (Hanford Works 1944; Duffield 1960)

$$LaF_3/PuF_{4\,(s)} + 3\ KOH_{\,(aq)} \rightarrow La(OH)_3/PuO_2 \cdot xH_2O_{\,(s)} + 3\ KF_{\,(aq)}$$

It is likely that the neat plutonium(IV) fluoride would be $PuF_4 \cdot 2.5H_2O$ when precipitated under these conditions. The LaF_3-PuF_4 precipitate, produced by treating mixed La(III) and Pu(IV) nitrate solution with 0.2 M to 0.5 M HF by either direct or reverse strike, took place using 15% KOH (~4 M KOH). To assure completeness in this plutonium-rich stream, the KOH metathesis was run at 80° C for 90 minutes. It was found that at KOH concentrations lower than 15% or at temperatures lower than 75° C the metathesis conversion was less rapid.

The behavior of carrier-free plutonium and the performance in NaOH are similar to the behaviors observed with carrier and with KOH:

> "It is to be understood that the process may be carried out with equally good results with a plutonium fluoride uncontaminated by carrier when the plutonium is in sufficient concentration and it will form precipitates without a carrier. As to the reagents used in the metathesis steps of my process, the hydroxide or carbonate of sodium may be used in place of the potassium basic salts" (Duffield 1960).

The metathesized solids resemble the original LaF_3/PuF_4 mixture in appearance. The LaF_3 characteristics are described as follows:

> "Lanthanum fluoride as normally precipitated is a finely divided amorphous, hydrated, flocculent mass, which even under the electron microscope shows no definite crystalline structure, but rather a small ill-defined mass less than 0.01 micron in size" (page 706 of Hanford Works 1944).

These observations imply that the metathesized solids likewise should be very finely particulate.

Plutonium fluoride decomposition in KOH solution also occurred in the step immediately following the chemical removal of Zircaloy cladding from irradiated N Reactor uranium metal fuel in the Zirflex process at the PUREX plant at Hanford. The Pu(IV) fluoride was present with much greater quantities of U(IV) fluoride and undissolved irradiated uranium metal fuel in the cladding dissolver heels. Both compounds were likely present as the respective actinide fluoride hydrate salts of the form $AnF_4 \cdot 2.5H_2O$. The metathesis reaction in the KOH solution converts uranium and plutonium fluorides to uranium and plutonium oxides to permit dissolution in HNO_3 and solvent extraction recovery, and to limit corrosion of the dissolvers with the fluoride removed from the dissolvers in the spent metathesis solution as soluble potassium fluoride.

Laboratory testing undertaken to support the flowsheet modifications showed that solid plutonium trifluoride, $PuF_3 \cdot xH_2O$, oxidizes instantly to Pu(IV), as indicated by change from its original lavender color to form a green solid precipitate when added to solutions of 25 different compositions composed of mixed KOH (1 to 3 M) and KF (0 to 2 M). Plutonium(III) nitrate, initially blue in color, instantly precipitated to a lavender solid that, with shaking, turned green when added to the same KOH/KF solutions. These observations gave qualitative demonstration of the preferential formation of green $PuO_2 \cdot xH_2O$ over the pink PuF_4 or $PuF_4 \cdot 2.5H_2O$ during oxidation of the Pu(III) even though abundant fluoride was present in many of these experiments (Delegard 1987). Plutonium solution concentrations for these tests tended to the same concentrations observed for Pu(IV) addition to KOH solutions of the same chemical activity, further supporting the thesis that Pu(IV) hydrous oxide, $PuO_2 \cdot xH_2O$, is the solubility-controlling solid phase.

For most of the PFP history, the hydrofluorinator offgas scrubber used concentrated KOH solution. For other periods, the scrubber solution was monobasic aluminum nitrate [Monoban, $AlOH(NO_3)_2$] or aluminum nitrate [$Al(NO_3)_3$] (Panesko 1972).

Small PuF_4 particles were lofted from flowing HF gas and captured in KOH, $AlOH(NO_3)_2$, or $Al(NO_3)_3$ scrubber solutions in hydrofluorination operations in the PFP. The PuF_4 particles metathesize upon contact with KOH solution to form Pu(IV) hydrous oxide:

$$PuF_{4\,(s)} + 4\ KOH_{(aq.)} + (x\text{-}2)\ H_2O_{(aq.)} \rightarrow PuO_2 \cdot xH_2O_{(s)} + 4\ KF_{(aq.)}$$

Contact of the PuF_4 particles with the $AlOH(NO_3)_2$ or $Al(NO_3)_3$ solution decompose the PuF_4 compound by abstracting fluoride in a series of steps to culminate in the following net reaction to dissolve the plutonium as $Pu(NO_3)_4$ or as soluble plutonium-fluoride complexes in excess $Al(NO_3)_3$:

$$3\ PuF_{4\,(s)} + 4\ Al(NO_3)_{3\,(aq.)} \rightarrow 3\ Pu(NO_3)_{4\,(aq.)} + 4\ AlF_{3\,(s)}$$

During much of PFP operating history, these scrubber solutions were ultimately discharged to the underground waste storage tanks and thus entered NaOH solution where the $Pu(NO_3)_4$ or Pu(IV) fluoride complexes would have hydrolyzed.

As outlined in Table A - 1, thermodynamic analysis shows that the PuF_4 hydrolysis reaction,

$$PuF_{4\,(s)} + 4\ NaOH_{(aq.,\ 1\ m)} \rightarrow PuO_{2\,(s)} + 4\ NaF_{(aq.,\ 1\ m)} + 2\ H_2O_{(aq.)},$$

is favored (i.e., the free energy of the reaction, ΔG_{rxn}, is negative) in 1 molal (~1 M) sodium hydroxide, NaOH, solution to form PuO_2 solid and 1 molal (~1 M) sodium fluoride, NaF, solution.

Table A - 1. Free Energy of the PuF_4 Hydrolysis Reactions in 1 Molal NaOH and in Water

PuF_4 Hydrolysis Reaction in 1 m NaOH			
$PuF_{4\,(s)} + 4\ NaOH_{(aq.,\ 1\ m)} \rightarrow PuO_{2\,(s)}$ (or $PuO_2{\cdot}xH_2O_{(s)}$) $+ 4\ NaF_{(aq.,\ 1\ m)} + 2\ H_2O_{(aq.)}$			
PuF_4 Hydrolysis Reaction in Water			
$PuF_{4\,(s)} + 2\ H_2O_{(aq.)} \rightarrow PuO_{2\,(s)}$ (or $PuO_2{\cdot}xH_2O_{(s)}$) $+ 4\ HF_{(aq.,\ 1\ m)}$			
Reactants	**ΔG_f^0, kJ/mol**	**ΔG_f^0, kJ/mol, in**	
		1 m NaOH	**Water**
$PuF_{4\,(s)}$	-1756.741	1756.741	1756.741
$NaOH_{(aq,\ 1\ m)}$	-419.150	1676.600	N/A
$H_2O_{(aq.)}$	-237.129	N/A	474.258
Products	N/A	N/A	N/A
$PuO_{2\,(s)}$ or	-998.113	-998.113	-998.113
$PuO_2{\cdot}xH_2O_{(s)}$*	-965.520	-965.520	-965.520
$NaF_{(aq.,\ 1\ m)}$	-540.680	-2162.720	N/A
$HF_{(aq.\ 1\ m)}$	-296.820	N/A	-1187.280
$H_2O_{(aq.)}$	-237.129	-474.258	N/A
ΔG_{rxn}	**Product**	**ΔG_{rxn}, kJ/mol, in**	
		In 1 m NaOH	**In Water**
$\Delta G_{rxn} = \Delta G_f^0$ (products) - ΔG_f^0 (reactants) =	PuO_2	-201.750	45.606
	$PuO_2{\cdot}xH_2O$	-169.157	78.199

Thermodynamic data for PuF_4 and PuO_2 from (Guillaumont et al. 2003).
Thermodynamic data for non-Pu phases from (Wagman et al. 1982).
* The $\log_{10}K_{sp}$ for PuO_2 = -64.04 and the $\log_{10}K_{sp}$ for $PuO_2{\cdot}xH_2O$ = -58.33 where K_{sp} is the solubility product of the respective PuO_2 and $PuO_2{\cdot}xH_2O$ phases (Guillaumont et al. 2003).
$\Delta G_{rxn.}$ ($PuO_2 \rightarrow PuO_2{\cdot}xH_2O$) = -2.303 RT log K = -2.303 RT (-64.04+58.33) = 32.593 kJ/mol.
ΔG_f ($PuO_2{\cdot}xH_2O$) = ΔG_f (PuO_2) + 32.593 = -998.113 + 32.593 = -965.520 kJ/mol.

However, as also shown in Table A - 1, the reaction of PuF_4 in neutral water,

$$PuF_{4\,(s)} + 2\ H_2O_{(aq.)} \rightarrow PuO_{2\,(s)} + 4\ HF_{(aq.,\ 1\ m)},$$

to form PuO_2 solid and 1 molal hydrogen fluoride, HF, aqueous solution is <u>not</u> favored (i.e., ΔG_{rxn} is positive).

Thermodynamic data on the standard ΔG_f^0 of $PuF_4{\cdot}2.5H_2O$, $NaPuF_5$, and Na_2PuF_6 were not found. However, none of these compounds form even in the presence of excess fluoride and sodium in alkaline solution. Instead, $PuO_2{\cdot}xH_2O$ is found from metathesis of $PuF_4{\cdot}2.5H_2O$ in alkaline solution abundant in both sodium and fluoride.

The experimental observations, PUREX plant experience, and the thermodynamic analyses show that PuF_4 is unstable to hydrolysis to PuO_2 or $PuO_2{\cdot}xH_2O$ in alkaline solution. The compounds $PuF_4{\cdot}2.5H_2O$, $NaPuF_5$, and Na_2PuF_6 are demonstrably unstable to formation of $PuO_2{\cdot}xH_2O$ in alkaline solution. Thermodynamic and experimental information on PuF_4 stability in mildly alkaline solution (e.g., pH 8-10) was not found. Discussion of tests to measure the solubility of PuF_4 in water and in HNO_3 solution does not include information on the stability of PuF_4 in water but does indicate that PuF_4 has low water solubility (0.00025 M plutonium while the solubility of PuF_3, likely as $PuF_3{\cdot}xH_2O$, in excess fluoride and 0.05 M HNO_3 is ~0.0002 M plutonium; Mandleburg et al. (1961)). Anhydrous PuF_4 converts to $PuF_4{\cdot}2.5H_2O$ in aqueous HF solution. The solubility of $PuF_4{\cdot}2.5H_2O$ in water (0.00012 M plutonium; Deichman and Tananaev (1962)) is similar to that of PuF_4 suggesting both likely are controlled by the same $PuF_4 \cdot 2.5H_2O$ solid phase. The thermodynamic analysis also shows that PuF_4 is stable to hydrolysis by water alone. The thermodynamic analyses indicate that chemically sufficient hydroxide ion must be present to satisfy the reaction stoichiometry of one hydroxide per fluoride.

A.4 Particle Size Impacts

Whenever a very insoluble solid quickly forms due to reaction such as metathesis, the product's particle size tends to be very small. On this basis, the $PuO_2 \cdot xH_2O$ formed by Pu(IV) fluoride or Pu(IV) oxalate metathesis also should be small [noting that Pu(III) fluoride is rapidly oxidized to Pu(IV)]. If the tank waste system is relatively quiescent when the reaction takes place, the insoluble product could loosely adhere to the surface of the reactant particle and thus form an agglomerated $PuO_2 \cdot xH_2O$ product. In such a case, the surface "shell" formed by the precipitating $PuO_2 \cdot xH_2O$ product might seal the underlying particle undergoing metathesis and protect or at least impede the underlying material from further metathesis. However, given the decade or more time that the Pu(IV) fluoride and Pu(IV) oxalate particles have been present in the waste tanks, the survival of such "armored particles" is unlikely. Nevertheless, if left undisturbed, weak $PuO_2 \cdot xH_2O$ agglomerates of dimension similar to the original Pu(IV) fluoride and Pu(IV) oxalate particles may remain.

Given the anticipated small size of the $PuO_2 \cdot xH_2O$ formed by Pu(IV) fluoride compound or Pu(IV) oxalate metathesis and the expected weak inter-particle adherence of the product $PuO_2 \cdot xH_2O$, the agglomerated plutonium-bearing particles are unlikely to survive even minimal slurrying and pumping. Instead, the particles are likely to be significantly size-reduced and blended with the accompanying waste solids.

A.5 Conclusions

Process and laboratory chemical evidence shows that Pu(IV) oxalate, Pu(IV) fluoride, and sodium-plutonium fluoride double salts are unstable to decomposition by metathesis to $PuO_2 \cdot xH_2O$ in alkaline solution and that Pu(III) fluoride is rapidly oxidized to Pu(IV). Plutonium(IV) oxalate also is unstable to hydrolysis in neutral pH solution. Thermodynamic calculations show that PuF_4 is unstable to alkaline hydrolysis but stable to hydrolysis in neutral solution. Lack of ΔG_f^0 data on Pu(IV) oxalate, $PuF_4 \cdot 2.5H_2O$, and the sodium-plutonium fluoride double salts preclude calculation of the thermodynamic stabilities of these compounds to hydrolysis to form $PuO_2 \cdot xH_2O$ in neutral or alkaline solution.

The particle size of Pu(IV) oxalate prepared under routine PFP production conditions was ~5-7 μm. Later de-inventory processing produced limited quantities of post-precipitated Pu(IV) oxalate [i.e., Pu(IV) oxalate precipitating downstream of solid-liquid separation at pan filters] that ultimately was discharged to tank farms and had unknown particle size. The particle size of PuF_4 lost as aerosols to HF scrubbers in hydrofluorination processing of PuO_2 at the PFP also is unknown but, because the PuF_4 left as an aerosol, likely was micron to sub-micron scale. The particle sizes of $PuF_4 \cdot 2.5H_2O$ and the sodium-plutonium fluoride double salts arising from plutonium scrap dissolution operations and the $PuF_4 \cdot 2.5H_2O$ from organic solvent wash operations also are unknown but are expected to be ~1-10 μm. The particle densities of $Pu(C_2O_4)_2 \cdot 6H_2O$ (~3-4 g/cm^3), $PuF_3 \cdot xH_2O$ (9.32 g/cm^3), PuF_4 (7.04 g/cm^3), $PuF_4 \cdot 2.5H_2O$ (4.89 g/cm^3), $NaPuF_5$ (6.03 g/cm^3), and Na_2PuF_6 (5.84 g/cm^3) are lower than that of PuO_2 (11.46 g/cm^3; Clark et al. (2006)).

Overall, the constituent particle sizes of the $PuO_2 \cdot xH_2O$ hydrolysis products arising from the metathesis reactions of Pu(IV) oxalate and the Pu(III) and Pu(IV) fluoride compounds, and the mechanical resilience of agglomerates produced by these reactions in quiescent alkaline solutions, are unknown. However, the $PuO_2 \cdot xH_2O$ metathesis product has extremely low solubility with the outcome being that the particles from the oxalate and fluoride compound metatheses are likely to be small (sub-micron). In addition, the product $PuO_2 \cdot xH_2O$ agglomerates are likely to be weak and have minimal resistance to shear caused by slurrying and pumping. No such $PuO_2 \cdot xH_2O$ agglomerates have yet been observed in actual tank waste samples.

A.6 References

Alenchikova IF, LL Zaitseva, LV Lipis, VV Fomin, and NT Chebotarev. 1958. Preparation and Properties of Certain Double Fluorides of Tetrapositive Plutonium. Presented at The Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. 28, Basic Chemistry in Nuclear Energy, Geneva, Switzerland, United Nations, New York, NY.

Hanford Works. 1944. Hanford Engineer Works Technical Manual. Report No. HW-10475 C-DEL, Hanford Atomic Products Operation, Richland, WA.

Barney GS. 1988. "Particle Size Analyses of Plutonium Fluoride Samples from the RMC Line in 234-5 Building." Internal Memo 12221-PSL88-005. Westinghouse Hanford Company, Richland, WA.

Burney GA and FW Tober. 1965. "Precipitation of Plutonium Trifluoride." I&EC Process Design and Development 4(1):28-32.

Clark DL, SS Hecker, GD Jarvinen, and MP Neu. 2006. "Plutonium." In The Chemistry of the Actinide and Transactinide Elements, eds. LR Morss, et al. Springer, Dordrecht, The Netherlands.

Cleveland JM. 1970. The Chemistry of Plutonium. Gordon and Breach Science Publishers, Inc., New York, NY.

Dawson JK, RWM D'Eye, and AE Truswell. 1954. "The Hydrated Tetrafluorides of Uranium and Plutonium." Journal of the Chemical Society:3922-29.

Dawson JK, RM Elliott, R Hurst, and AE Truswell. 1954. "The Preparation and Some Properties of Plutonium Fluorides." Journal of the Chemical Society:558-64.

Deichman EN and IG Tananaev. 1962. "Plutonium Fluorides." Soviet Radiochemistry 4(1):56-62.

Delegard CH. 1985a. Internal letter #65454-85-032 to E Abramowski (Manager) from CH Delegard, Scientist, "Chemical Analysis of Rocky Flats Oxide Sludge and Heel." 25 February 1985, Richland, WA.

Delegard CH. 1987. Solubility of $PuO_2 \cdot xH_2O$ in PUREX Plant Metathesis Solutions. Report No. RHO-RE-ST-53P, Rockwell Hanford Operations, Richland, WA.

Duffield RB. 1960. "Metathesis of Plutonium Carrier Lanthanum Fluoride Precipitate with an Alkali." US Patent No. 2,931,702.

Engineers of Plutonium Process Engineering. 1968. Z Plant Report Task I-II & Recovery Operations, January 1, 1968 through December 31, 1968. Report No. ARH-294 RD (with deletions), Atlantic Richfield Hanford Company, Richland, WA.

Gel'man AD, AI Moskvin, LM Zaitsev, and MP Mefod'eva. 1962. Complex Compounds of Transuranium Elements. Consultants Bureau, New York, NY.

Gel'man AD and LP Sokhina. 1958. "Oxalate Complex Compounds of Plutonium (IV)." Journal of Inorganic Chemistry, USSR 3(5):49-56.

Griffo JS, WB Brown, and FD Lonadier. 1964. Solubility of Plutonium Compounds. Report No. MLM-1191, Mound Laboratory, Miamisburg, OH. http://www.osti.gov/scitech/biblio/4659828.

Guillaumont R, T Fanghänel, J Fuger, I Grenthe, DA Palmer, and MH Rand. 2003. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Elsevier, Amsterdam, The Netherlands.

Harmon MK. 1947. Freezing Point Data for UNH-H_2O-HNO_3 Systems. Report No. HW-8309, General Electric Company, Richland, WA. http://www.osti.gov/scitech/biblio/4374237.

Haschke JM, TH Allen, and LA Morales. 2001. "Reactions of Plutonium Dioxide with Water and Hydrogen-Oxygen Mixtures: Mechanisms for Corrosion of Uranium and Plutonium." Journal of Alloys and Compounds 314:78-91.

Jenkins IL, FH Moore, and MJ Waterman. 1963. "X-Ray Powder Crystallographic Data on Plutonium Oxalates and Their Isomorphs." Chemistry and Industry (London) 1:35-36.

Jenkins IL, FH Moore, and MJ Waterman. 1965. "X-Ray Powder Crystallographic Data on Plutonium and Other Oxalates – II: Plutonium(IV) Oxalate Dihydrate, Uranium(IV) Oxalate Hexahydrate, Uranium(IV) Oxalate Dihydrate and Thorium Oxalate Dihydrate." Journal of Inorganic and Nuclear Chemistry 27(1):81-87.

Jenkins SH, DG Keight, and RE Humphreys. 1964. "The Solubility of Heavy Metal Hydroxides in Water, Sewage and Sewage Sludge. I. The Solubility of Some Metal Hydroxides." Air and Water Pollution 8:537-56.

Keller C and M Salzer. 1967. "Ternäre Fluoride des Typs MeIIMeIVF_6 mit LaF_3-Struktur." Journal of Inorganic and Nuclear Chemistry 29:2925-34.

Knights LM. 1970. Monthly Report – Plutonium Process Engineering Section. For December 1970. Report No. ARH-423-RD-DEL, Atlantic Richfield Hanford Company, Richland, WA.

Mandleburg CJ, KE Francis, and RC Smith. 1961. "The Solubility of Plutonium Trifluoride, Plutonium Tetra-Fluoride, and Plutonium(IV) Oxalate in Nitric Acid Mixtures." Journal of the Chemical Society:2464-68.

Myers MN. 1956. Thermal Decomposition of Plutonium (IV) Oxalate and Hydrofluorination of Plutonium (IV) Oxalate and Oxide. Report No. HW-45128, Hanford Atomic Products Operation, Richland, WA. http://www.osti.gov/scitech/biblio/4181389.

Panesko JV. 1972. Hydrofluoric Acid Scrubber Systems. Report No. ARH-2343, Atlantic Richfield Hanford Company, Richland, WA. http://www.osti.gov/bridge/servlets/purl/1016165-iGj45w/1016165.pdf.

Rudisill TS. 2011. Email to CH Delegard (Scientist) from TS Rudisill, Scientist, "$PuF_4 \cdot 2.5H_2O$." 23 June 2011, Richland, WA.

Stakebake JL and LM Steward. 1973. "Water Vapor Adsorption on Plutonium Dioxide." Journal of Colloid and Interface Science 42(2):328-33.

Wagman DD, WH Evans, VB Parker, RH Schumm, I Halow, SM Bailey, KL Churney, and RL Nuttall. 1982. "The NBS Tables of Chemical Thermodynamic Properties – Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units." Journal of Physical and Chemical Reference Data 11(Supplement 2).

Yusov AB, AY Garnov, VP Shilov, IG Tananaev, MS Grigor'ev, and NN Krot. 2000. "Plutonium(IV) Precipitation from Alkaline Solutions: II. Effect of Anions on Composition and Properties of Hydrated Plutonium Dioxide PuO2·Xh2o." Radiochemistry 42(2):157-60.

Yusov AB, AY Garnov, VP Shilov, IG Tananaev, MS Grigor'ev, and NN Krot. 2000c. "Plutonium(IV) Precipitation from Alkaline Solutions: II. Effect of Anions on Composition and Properties of Hydrated Plutonium Dioxide $PuO_2 \cdot xH_2O$." Radiochemistry 42(2):157-60.

Appendix B

Interfacial Crud Disposition in Alkaline Tank Waste

B.1 Introduction

Interfacial crud was generated by the interaction of plutonium and other metal ions with solvent degradation products in the Plutonium Reclamation Facility of the Plutonium Finishing Plant, and in the third product purification cycle in the PUREX Plant, as well as by the presence of fine particulate solids that sought the organic-aqueous interface in solvent extraction processing. These crud materials, all of which could contain plutonium, acted as vectors for plutonium losses from the Plutonium Finishing Plant and PUREX.

Plutonium recovery occurred in the PFP Plutonium Reclamation Facility (PRF) by solvent extraction in 20% tributyl phosphate [TBP; $OP(O(CH_2)_3CH_3)_3$] dissolved in carbon tetrachloride (CCl_4) diluent or in normal paraffin hydrocarbon in the PUREX Plant. An early PRF flowsheet outlines the key features of this process (Bruns 1960) and will be used to illustrate the formation of crud.

The plutonium, originating from dissolved impure scrap and present in the tetravalent oxidation state, Pu(IV), was extracted from aqueous solution containing ~2.5 M nitric acid (HNO_3) and other dissolved metal nitrate salts (principally magnesium, calcium, iron, and aluminum, as well as trace ^{241}Am in-grown from radioactive decay of ^{241}Pu). The extraction by the TBP-CCl_4 organic solution, which is denser than the aqueous phase, occurred in a pulse column in the PRF glove box canyon. Scrub solution, nominally 1 M HNO_3, was used to remove impurities from the plutonium-loaded TBP by another pulse column operation. The purified plutonium then was stripped from the TBP-CCl_4 into the aqueous phase by contact in another pulse column with solution containing a chemical reductant, usually hydroxylamine, $HONH_2$. The hydroxylamine served to chemically reduce the Pu(IV) dissolved in the TBP-CCl_4 to trivalent plutonium, Pu(III), which is not extracted in TBP-CCl_4. The organic solution then was recycled to repeat the process while the plutonium aqueous solution was processed further to plutonium metal and oxide product forms.

Both chemical and radiolytic decomposition of TBP occur because of the respective effects of acid hydrolysis in HNO_3 (Burger 1955; Lloyd and Fellows 1985) and alpha radiation damage (Lloyd and Fellows 1985). The decompositions in both cases involve the stepwise loss of butoxy [$-O(CH_2)_3CH_3$] groups as butanol, $H_3C(CH_2)_2CH_2OH$, to make, in order, dibutyl phosphate [DBP; $^{-}O_2P(O(CH_2)_3CH_3)_2$], monobutyl phosphate [MBP; $^{2-}O_3P(O(CH_2)_3CH_3)$], and phosphate, PO_4^{3-}. When the solvent is properly maintained by alkaline clean-up steps in the solvent extraction process, decomposition beyond DBP normally has no opportunity to occur.

However, complexes form by the interaction of DBP with polyvalent metal ions, including Pu^{4+} and Pu^{3+}, and, in the PRF, the Pu(III,IV)-DBP complexes have high affinity for the TBP-CCl_4 phase that resists stripping. Precipitation of Th(IV), chemically analogous to Pu(IV), as the compound $Th(DBP)_4$ occurs and appears at the interface between the organic and aqueous phases. This has led to speculation that $Pu(DBP)_4$ also can precipitate (Zimmer and Borchardt 1986). Finely divided solids such as silica gels and clays present in solvent extraction systems also seek the organic-aqueous interface and can create and stabilize emulsions that impede and ultimately thwart the rapid organic-aqueous disengagement needed for successful solvent extraction operations. The solids appearing at the interface can also include undissolved solid plutonium dioxide, PuO_2. These solid materials and the less soluble metal-organic complexes appearing at the organic-aqueous interface are known collectively as “crud”.

In the PFP, dissolution of plutonium-bearing scrap almost invariably produced silica gels from the acid decomposition of tramp silicate minerals present in the scrap (e.g., ash, crucible impurities) or present in infiltrated dust particles. In practice, any time solution feeds with high solids loading were processed, problems with crud formation would arise. Therefore, crud was an early and continuing challenge in proper solvent extraction operations in the PRF.

To help address problems with crud accumulating randomly in the organic-aqueous mixtures, the PRF operation flowsheet called for addition of Mistron®, a magnesium talc mineral, to the solvent extraction system. The Mistron®, added at about 100 ppm to the feed solution (Bruns 1960), served to coagulate the crud materials at the interface and help in efficiently sweeping them from the interface by occasional decantation. As described by (Klem 1972),

> CA Column interface solids (crud) are a complex mixture formed by mistron ($MgSiO_3$) and other impurities in the feed or by combination of metallic impurities with solvent decomposition product to form insoluble compounds. The crud fills the column's glass disengaging section and must be removed to prevent it overflowing with the high-salt aqueous waste stream (CAW) to the Waste Treatment Facility. Crud removal is achieved by jetting the solids together with up to 10 liters of aqueous and organic to the Z-18 crib.

The crud would appear at the organic-aqueous interface or, occasionally, at the top of the aqueous layer in the column that provided the primary plutonium solvent extraction contact (i.e., the "CA" column). When the interface crud layer became too thick in the CA column (i.e., measured in feet, not inches), the crud was pushed to overflow to the CA column aqueous waste (called "CAW") centrifuge by raising the interface level. The supernatant solution from the centrifuge would be discharged to the CAW while the solids were collected for later processing (burning and leaching) or for crib Z-18 discharge (Klem 1972). However, overloading of the centrifuge would cause loss of crud with the supernatant solution for discharge with the CAW that, after 1973, ultimately would go to tank farms.

B.2 Plutonium Losses through Crud Discards

Crud solids would contain not only the silica gels and the Mistron® but also some undissolved plutonium, most likely as PuO_2, as well as plutonium contained in poorly soluble organic complexes such as DBP. The decanted crud was sometimes collected for burning and plutonium recovery, but in the 1970s, crud also was lost to the Z-18 crib with the CAW discharges and later, entrained with the CAW, inadvertently sent to direct discard in the tank farms. With decreasing drive to recover plutonium from relatively lean and hard-to-process scraps like crud, simple discard of collected crud by cementation occurred by the late 1980s, even as inadvertent loss to the tank farms by entrainment with the CAW continued.

The crud contained highly variable amounts of plutonium. In one account (Panesko 1971a), a 500-mL sample of crud was filtered, washed with CCl_4, and dried to produce 6.7 grams of fine, light, gray solids containing about 2.5 grams of plutonium (i.e., 37 wt% plutonium in the solids or 5 grams Pu/liter of initial wet crud). Other crud samples reported in the same letter contained solids that were 26 wt% and 0.8 wt% plutonium (the original crud volumes were not reported). In another account, 120 grams of dried centrifuged solids collected from the CAW of a "burnt oxide" run were described as "light, gray, homogeneous (flour-like) solids"(Panesko 1971b). The 120 g of dried solids arose from ~300 mL of settled crud sludge. The dried solids contained 13 to 16 wt% plutonium (i.e., ~60 grams of Pu/liter of initial wet crud), with the major other elements being silicon and phosphorus. As noted in the letter report, the presence of phosphorus suggested that an organic emulsion was the source of the centrifuged crud and the silicon suggested the presence of Mistron®.

Plutonium losses also occurred by its retention in Pu-DBP compounds that would partition to the crud or be removed from the organic phase by the organic clean-up performed with sodium carbonate, Na_2CO_3, solution. With the carbonate treatment, the Pu-DBP complex would be decomposed to form water-soluble sodium dibutyl phosphate, NaDBP, and either dissolved aqueous Pu(IV) carbonate complexes (if the carbonate concentration were sufficiently high) or precipitated Pu(IV) hydrous oxide, $PuO_2 \cdot xH_2O$, as an extremely finely divided solid (nanometer-scale) in the wash (if the carbonate concentration were depleted).

B.3 Fate of Plutonium-Crud in the Tank Waste

As described, plutonium in crud took two forms: as Pu(III)- or Pu(IV)-organic complexes, generally with DBP, and as undissolved scrap solids, primarily as PuO_2. These plutonium-bearing streams would have been discharged by entrainment in the CAW. Also present in the organic phase would be plutonium-DBP complexes that were scrubbed from the organic by carbonate wash in the solvent scrubbing (“CO”) column and sent to waste. Both CAW and CO column wastes would have been treated in waste tank D-5 in preparation for their discharge to tank farms, and so would have been blended with ferric nitrate as a neutron absorber in D-5 and with excess sodium hydroxide, either in D-5 or in waste-blending operations further downstream.

The Pu-DBP complexes, whether present in the crud or scrubbed from the organic, would hydrolyze and, in the case of Pu(III), oxidize in the highly alkaline tank waste to form finely divided $PuO_2 \cdot xH_2O$. Because ferric nitrate was also present, coprecipitation of the Pu(IV) with the ferric hydroxide, $Fe(OH)_3$, would occur when the stream was made alkaline.

However, any solid PuO_2 or other solid that had already resisted acid digestion at PFP prior to solvent extraction treatment in the PRF would remain in that form when discharged to tank farms; given the low solubility of PuO_2 in alkaline media, it would have remained unchanged.

B.4 References

Bruns LE. 1960. Solvent Extraction Flowsheet for New Plutonium Reclamation Facility. Report No. HW-64851, Hanford Atomic Products Operation, Richland, WA. https://192.107.175.222/opennet/detail.jsp?osti_id=16447031&query_id=0.

Burger LL. 1955. The Chemistry of Tributyl Phosphate – a Review. Report No. HW-40910, Hanford Atomic Products Operation, Richland, WA. http://www.osti.gov/scitech/biblio/4334996.

Klem MJ. 1972. "Evaluation of Process Test PRF 67-5 Filtration of CA Column Interface Jettings." Internal note, June 20, 1972. Atlantic Richfield Hanford Company, Richland, WA.

Lloyd MH and RL Fellows. 1985. Alpha Radiolysis and Other Factors Affecting Hydrolysis of Tributyl Phosphate. Report No. ORNL/TM-9565, Oak Ridge National Laboratory, Oak Ridge, TN.

Panesko JV. 1971a. Internal letter to AJ Low (ARHCO Manager) from JV Panesko, ARHCO Researcher, "CA Column Interface Crud Sampled on September 27, 1971." 1 Oct 1971, Richland, WA.

Panesko JV. 1971b. Internal letter to AJ Low (ARHCO Manager) from JV Panesko, ARHCO Researcher, "CAW Centrifuge Solids from Burnt Oxide Run." 26 Aug 1971, Richland, WA.

Zimmer E, and J Borchardt. 1986. "Crud Formation in the PUREX and THOREX Processes." Nuclear Technology 75:332-37.

Appendix C

Plutonium(IV) Oxide and Unburned Plutonium Metal from Operations to Burn Plutonium Metal

C.1 Introduction

Alpha-phase unalloyed plutonium metal was prepared at the Hanford Site PFP in a series of chemical process steps by conversion of Pu(IV) nitrate through Pu(IV) oxalate, Pu(IV) oxide, and Pu(IV) fluoride intermediates. The pure product alpha (α) phase plutonium metal, which was prepared by reduction using calcium metal as the reductant, took the physical form of a "button" with size and shape similar to that of a hockey puck. Plutonium metal was then assayed, and any material found not to meet product specifications for purity was recycled through PFP unit operations. Plutonium metal also was alloyed with gallium to stabilize the softer and more machinable delta (δ) phase for use in weapons. Fabrication of weapons parts at the PFP produced machining "swarf" (turnings and cuttings). This swarf also was recycled through PFP operations.

Over most of the PFP process history, the first step in the recycle of plutonium metal was burning the metal to form plutonium dioxide, PuO_2. Ignition of the plutonium metal was performed by either flame (gas torch) or by Calrod-type electrical resistance loops. Once ignited, the plutonium metal continued burning until complete or near-complete oxidation. The materials occasionally were stirred during burning to enhance air access to the metal and improve the completeness of the oxidation step.

Oxide from metal burning in Hood 1 of Miscellaneous Treatment (MT-1) would be screened and charged directly into the dissolver pots in MT-2A and MT-5. However, if the oxide was to be packaged for storage or shipment, it would generally be sieved and thoroughly oxidized by heating in a pot or muffle furnace. This secondary oxidation was required to ensure complete oxidization of the metal. Observations of "gains-on-ignition" (GOIs) often were made for oxide from metal burning when analyzed for moisture content by gravimetric loss-on-ignition. The weight gains were caused by oxidation of unburned or unreacted metal by atmospheric oxygen during heating and would offset or mask any actual moisture content. Incomplete oxidation of metal also was suspected in incidents where food pack containers holding burnt metal collapsed in storage from residual unburned metal consuming the packaging atmosphere and creating a vacuum sufficient to lead to can collapse (see, for example, cases PANEL-5 and PANEL-8 in Table 3 of Eller et al. (2004)).

Over the period 1973 to 1976, off-specification plutonium metal also was digested for subsequent processing by an electrolytic dissolver. The dissolution occurred in a strong HNO_3/HF acid medium that became depleted in nitrate by the accompanying reduction of nitrate to oxides of nitrogen, NO_x during electrolysis (Wheelwright 1972; Oma 1977; Harlow and Olguin 1977). In practice, however, metal dissolution in the electrolytic dissolver was incomplete with very fine and readily suspendible solids observed particularly if HNO_3/HF concentrations were not maintained above 10 M and 0.05 M, respectively. The two electrolytic plutonium metal dissolvers operated in MT-3.

Finally, non-coalesced plutonium metal also could be found in sand, slag, and crucible scrap from the calciothermic reduction step used to produce the plutonium metal buttons at PFP and from various pyrochemical processing scrap received from offsite sources. One such scrap was from electrorefinining conducted at Rocky Flats. The first step in processing these scraps for recovery of their contained plutonium values was dissolution in "B" acid, a mixture of ~6 to12 M HNO_3 containing ~0.5 M fluoride.

C.2 Characteristics of Burning Plutonium Metal in Air

Korinko (2009) recently prepared an overview of plutonium metal burning. As shown there and elsewhere, the product of burning plutonium metal in air is PuO_2. However, Pu_2O_3 is an intermediate that forms on the surface of the burning metal (Haschke et al. 2000). The ignition temperature, metal oxidation rate, and the PuO_2 particle size distribution from burning plutonium metal are strong functions of the atmosphere and the oxidation temperature (Haschke et al. 2000). In one set of tests conducted at Rocky Flats, plutonium metal (in the form of flat sheet 1.27×0.51×0.1 or 0.2 cm) ignited in air at 35% relative humidity between 310° C and 505° C and reached a maximum temperature of 780° C (Thompson 1966). The burning temperature thus exceeded the plutonium metal melting point of 640° C (Clark et al. 2006). The plutonium metal ignition temperature increases step-wise with increase in the size of the solid. For plutonium metal thickness less than about 0.2 mm, which includes powder and most machining chips, ignition in air occurs at ~150-200° C; at greater thicknesses, ignition occurs between ~450-520° C (Figure 29.6 of Haschke and Stakebake (2006)).

With massive plutonium metal pieces, such as buttons, the oxidation is self-heating (autothermic) and the reaction rate in air is about 0.14 g Pu cm^{-2} min^{-1}, irrespective of alloying, humidity, or temperature within the range of 500° C to ~1000° C. This corresponds to a linear penetration rate of about 5 mm plutonium metal thickness per hour (Haschke and Allen 2002). The invariance of the burning rate over this broad temperature span has been attributed to imposition of an oxygen gas-depleted zone around the burning metal with non-reactive nitrogen gas providing a diffusion impediment to inflowing atmospheric oxygen. Because of the combined opposing effects of high reaction exothermicity and oxygen gas diffusion limits, significant but steady reaction temperatures can be attained such that bulk burning plutonium metal often glows to a bright orange color (see, for example, Figure 3 of Haschke et al. (2000)) and are observed to be 930° C to 1000° C within bulk pieces ranging from 570 to 1770 grams (Mishima 1966). With smaller plutonium metal pieces, the reaction is not autothermic; external heat must be supplied to sustain burning. Thus, smaller pieces ignited by a flame may be extinguished if, for example, the piece is held in a forceps that conducts heat away.

Characteristics of burning plutonium metal; including the burning of 1- to 3-kg plutonium metal buttons and smaller 0.2- to 1-kg plutonium metal pieces (both α-phase), ~0.7-kg δ-phase metal pieces, casting skulls, and turnings; are described in detail by Felt (1967). The burning of plutonium metal buttons was described as follows:

> Metal ignition usually required 60 to 70 sec[onds] of torch contact to establish a satisfactory burn. Spread of the burn throughout the metal took 12 to 15 min[utes], and reached a peak temperature of about 825° C. Following the peak temperature, a decrease of 200° C occurred in the next 30 min[utes], leveling to 600° C; with a gradual decrease of 20° C per hour until completely oxidized. The burning metal was a bright cherry-red color with a gradually-increasing surface oxide coating. There was no flaming or flashing from the burning mass. After reaching the peak temperature, the metal was 150° C above its melting point. Containment and extinguishment became a problem of handling molten plutonium metal encased by an oxide-molten metal shell. Any disturbance of the shell would cause the metal to spew.

At later stages, autothermic conditions diminish and smothering by product PuO_2 and oxygen depletion or nitrogen blanketing increase. As a result, incomplete combustion is frequently observed in burning large metal pieces. Anecdotes from PFP experience tell of storage of oxide from burnt metal in food pack cans under air atmosphere resulting in inward collapse of the cans (see also Table 3 of Eller et al. (2004)). This inward collapse has been attributed to the presence of unburned metal that reacted with both oxygen to form PuO_2 and nitrogen to form plutonium nitride (PuN). Note that it is only by consumption of nitrogen that sufficient differential pressure; i.e., >0.2 atmospheres; is generated to collapse a food pack can. Therefore, complete oxidation of plutonium metal buttons often required supplemental furnace heating in air (to make so-called “twice-burned” plutonium oxide) for extended storage. By contrast, subsequent scrap recovery processing of burnt plutonium metal buttons that had not undergone supplemental furnace heating had to deal with variable but generally small amounts of unburned metal.

C.3 Plutonium Oxide Particle Size Found by Burning Plutonium Metal in Air

The high temperatures attained by burning large plutonium metal pieces, such as buttons, cause sintering of the product PuO_2 to occur and lead to increased PuO_2 particle agglomerate size compared with that from oxidation of plutonium metal in air at lower temperatures. Because of the high sintering temperature and the nature of the plutonium metal burning process, in which spallation of oxide layers from the massive metal occurs, the PuO_2 particle agglomerate size distribution tends to much greater size than observed for PuO_2 prepared from other starting materials. For example, at 300° to 620° C, calcination of 5-to 7-μm diameter Pu(IV) oxalate particles produces 2 to 5 μm PuO_2 particles (Myers 1956).

The PuO_2 particles prepared by calcining plutonium salts themselves are agglomerates of much smaller crystallites that become larger with increase in calcination temperature. Crystallite sizes as functions of source material and calcination temperature as determined by x-ray diffraction line broadening techniques (i.e., mean crystallite size by the Scherrer equation) are shown in Table C - 1 (Moseley and Wing 1965; Pallmer 1956). The Pu(IV) oxalate particles calcined at 300° to 620° C thus are agglomerates with diameters equivalent to about 800 to 1000 crystallite diameters. Later studies confirm that increasing Pu(IV) oxalate calcination temperature from 450° to 1050° C increases PuO_2 crystallite size and decreases the specific particle surface area (e.g., surface area per gram); however, the agglomerate particle size distribution remains relatively unchanged with increasing calcination temperature and is centered at about 5 μm (Machuron-Mandard and Madic 1996).

Table C - 1. PuO_2 Mean Crystallite Size as Functions of Plutonium Compound and Calcination Temperature

Calcination Temp., C	**Crystallite Size,[(a)] nm, for PuO_2 Prepared from**				**Calcination Temp., ° C**	**Size, nm**
	Nitrate	**Peroxide**	**Oxalate[(b)]**	**Hydroxide**		**Metal[(c)]**
240	11.5	3.8	4.1	5.6	100	105
400	13.0	5.2	5.7	6.1	300	122
600	11.8	27.7	13.7	10.0	500	167
800	100	48.0	27.5	29.1	700	269
1000	100	100	100	55.0	900	442

Calcination Temp., C	Crystallite Size,[(a)] nm, for PuO_2 Prepared from				Calcination Temp., ° C	Size, nm
	Nitrate	Peroxide	Oxalate[(b)]	Hydroxide		Metal[(c)]

(a) (Moseley and Wing 1965).

(b) Crystallite sizes for PuO_2 prepared by calcination of Pu(IV) oxalate at 270, 300, 480, 510, 550, and 600° C were 3, 11, 11, 17, 25, and 28 nm, respectively (Pallmer 1956).

(c) Metal air-oxidized at room temperature and then calcined at 100, 300, 500, 700, and 900° C (Molen and White 1967).

As shown in Table C - 1, PuO_2 crystallite sizes produced by room temperature air-oxidation of plutonium metal and then calcined at 100° to 900° C also increase with increasing calcination temperature (Molen and White 1967). However, the crystallites are much larger than the PuO_2 crystallites produced by calcination of the plutonium nitrate, peroxide, oxalate, and hydroxide compounds. Like the PuO_2 agglomerates produced by calcining the plutonium compounds, the particle size of the PuO_2 agglomerates produced by calcining PuO_2 obtained by room-temperature oxidation of metal did not change appreciably with subsequent increased calcination temperature. Over 90% of the size distribution was in the range of 1 to 5 µm, with the largest particles being about 16 to 45 µm. The larger sizes were observed at calcination temperatures of 700° and 900° C.

Particle size distribution data from three different studies of high-temperature bulk plutonium metal oxidation in air (Stewart 1961; Mishima 1966; Stakebake 1981) have been spliced into a single size distribution as shown in Table C - 2 and Figure C - 1 (Haschke 1992). The resulting mass-based spliced size distribution is seen to be bimodal with maxima centered at about 30 µm and 600 µm.

Table C - 2. Size Distribution for PuO_2 Prepared by Burning Plutonium Metal above 500° C

Size, µm	Mass Fraction	Cumulative Mass Fraction	Particle Fraction*	Cumulative Particle Fraction
0.25	3.80E-09	3.80E-09	1.24E-01	1.24E-01
0.35	9.10E-09	1.29E-08	1.10E-01	2.34E-01
0.5	6.70E-08	7.99E-08	6.90E-02	3.03E-01
1.5	4.20E-07	5.00E-07	1.10E-01	4.13E-01
3	4.50E-05	4.55E-05	2.04E-01	6.17E-01
5	6.40E-05	1.09E-04	6.30E-02	6.80E-01
8	4.20E-04	5.29E-04	1.02E-01	7.82E-01
15	1.90E-03	2.43E-03	1.24E-01	9.06E-01
30	1.70E-02	1.94E-02	8.00E-02	9.86E-01
52	8.40E-03	2.78E-02	7.30E-03	9.93E-01
77	1.10E-02	3.88E-02	3.80E-03	9.97E-01
150	9.20E-02	1.31E-01	3.20E-03	1.00E+00

Size, µm	Mass Fraction	Cumulative Mass Fraction	Particle Fraction*	Cumulative Particle Fraction
300	1.55E-01	2.86E-01	7.10E-04	1.00E+00
600	2.63E-01	5.49E-01	1.50E-04	1.00E+00
1000	2.23E-01	7.72E-01	2.80E-05	1.00E+00
1700	2.18E-01	9.90E-01	5.50E-06	1.00E+00
2500	4.90E-03	9.95E-01	3.80E-08	1.00E+00
3000	6.80E-03	1.00E+00	2.30E-08	1.00E+00
* Particle fractions calculated assuming spherical particle shape.				

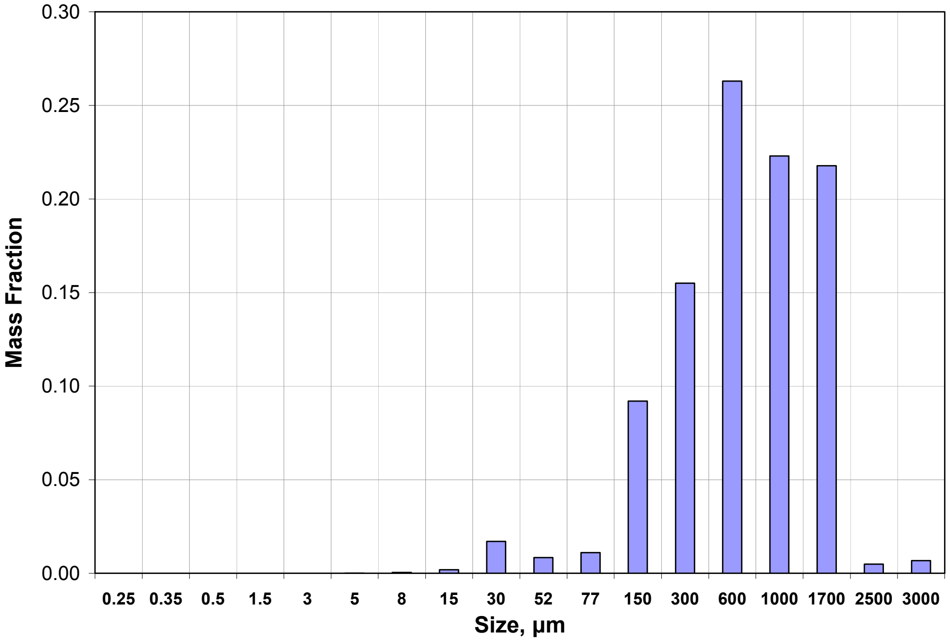

Figure C - 1. Plutonium Oxide Mass Size Distribution for Plutonium Metal Burned above 500° C

The PuO_2 particle size data presented in Table C - 2 is depicted in log (size) -normal (cumulative mass fraction) form is represented in Figure C - 2. The slope break into two segments demonstrates that the particle size distribution is bimodal. The particle size data provided in Figure C - 1 are supported by an Arrhenius correlation of the logarithm of plutonium oxide scale thickness as a function of inverse temperature based on observations of oxidation of plutonium metal in air at 90°, 257°, and 400° C (Martz et al. 1994). According to the Arrhenius correlation equation,(1) the plutonium oxide thickness should be about 120 µm at 500° C and 280 µm at 1000° C. These extrapolated scale thickness data are consistent with the particle sizes shown in Table C - 2 and Figure C - 1. The particle size distribution of PuO_2 derived by burning metal and then grinding it for an unspecified time in a mortar was 20 wt% between 75 and 150 µm, 46 wt% between 45 and 75 µm, and 34 wt% below 45 µm (Martell 1974). Further grinding was successful in decreasing all PuO_2 below 45 µm. In yet another study, the burning of a portion of a gallium-bearing “Dow metal” button (apparently from Rocky Flats) at 600° to 650° C produced such

---

(1) PuO_2 thickness, µm = 1043 $e^{(-1673/T)}$ where T is in K.

coarse oxide that 29 wt% did not pass a 600-µm screen (Campbell and Panesko 1971). According to this report, "Most of this coarse oxide consisted of small layers curled at the edges; with a few bigger, brittle layers which were retrievable with tweezers". These accounts thus confirm the coarseness of the PuO_2 produced by self-burnt metal.

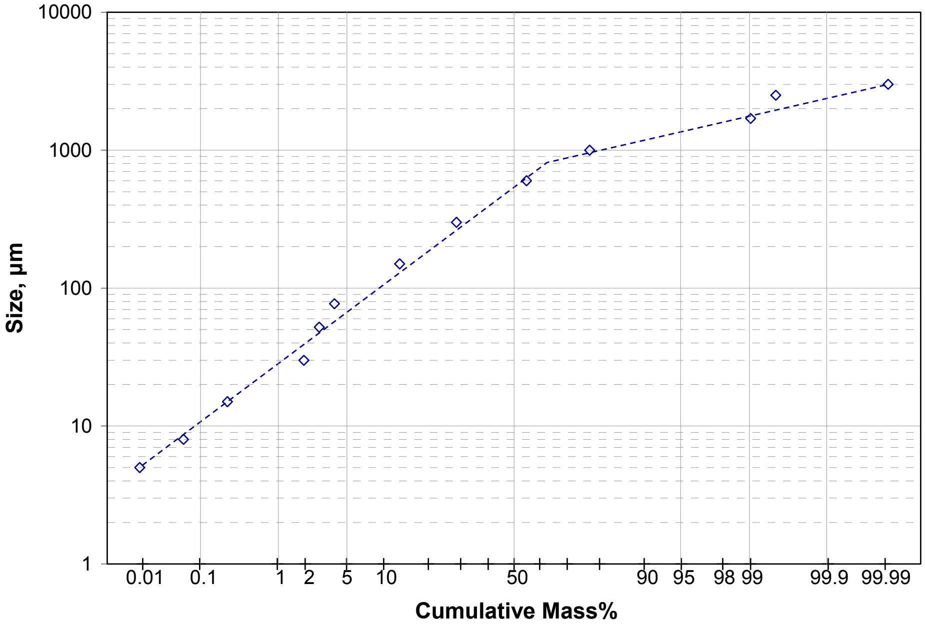

Figure C - 2 Cumulative Mass Size Distribution for Plutonium Oxide from Metal Burned above 500° C

Efforts to find information in the technical literature on the size of the constituent PuO_2 crystallites arising from high temperature burning of metal were not successful. However, if behavior is analogous with 900° to 1000° C calcination of other plutonium-bearing materials to form PuO_2, crystallite sizes about a factor of 10- to 50-times smaller than the agglomerated particles arising from burning plutonium metal in air would be expected.

The PuO_2 particles generated by burning bulk plutonium metal pieces in air are thus uncommonly large compared with the PuO_2 particles prepared by calcination of plutonium compounds or the PuO_2 found from room temperature air-oxidation of plutonium metal. According to Figure C - 2, 50 mass% of the PuO_2 particles produced by burning plutonium metal in air are greater than ~500 µm diameter and 99.9 mass% are greater than 10 µm diameter.

The size of the PuO_2 particles, arising from burning of bulk plutonium metal and which reached the tank farms, is expected to be limited to the lower end of the size distribution shown in Figure C - 2. Thus, the PuO_2 from metal burning that might be present in the waste tanks has a (maximum) particle size from 40 to 100 µm and a density of 8 to 11 g/cm^3 where 11 g/cm^3 is the nominal crystal density of PuO_2 (Sams 2012). The unburnt plutonium metal fines have the same (maximum) particle size of 40 to 100 µm (Sams 2012) and a density of about 19 g/cm^3, the nominal density of plutonium metal. It has been estimated that the PFP discarded to the tank farms as much as 2.5 kg of plutonium as fine metal particles (Sams 2014).

C.4 Corrosion of Plutonium Metal Residues from Burnt Plutonium Metal in Tank Waste Solution

Besides containing large agglomerates, the product from burning scrap plutonium metal in air at PFP, which was almost exclusively α-plutonium when PFP wastes were being sent to tank farms, likely also contained small amounts (as much as 2.5 kg; Sams 2012) of unburned plutonium metal because of the diminishing quantity of burning material and self-extinguishing by smothering.

The plutonium oxide and the associated unburned metal were processed for recovery at the PFP by dissolution in "B" acid. Both PuO_2 and the plutonium metal dissolve in this reagent, but dissolution rates for the large particle size and "high-fired" oxide (formed at temperatures around 800°-1000° C) present in burnt metal would be slow. Dissolution of plutonium metal coated in high-fired oxide in this reagent also would be slow. Furthermore, the metal likely would have relatively low surface area relative to its size (i.e., the metal particles would be millimeter- rather than µm-scale). The large particle size and high density of these plutonium-rich solids means they settle rapidly, making discharge from PFP to the tank farms difficult. However, these particles also represent the materials of most concern to criticality safety in tank farms.

The PuO_2 and plutonium metal discharged to Hanford tank farms are not expected to be altered by interaction with the alkaline tank farm waste solutions. As noted elsewhere, PuO_2 is thermodynamically stable in alkaline solution. Therefore, the large sintered PuO_2 particles formed by burning plutonium metal would remain as large PuO_2 particles in tank waste.

Studies of plutonium metal corrosion rate in aqueous solution are few but indicate unobservable rates in alkaline solution. An overview of plutonium metal corrosion rates in aqueous solution provided in Table C - 3 shows it to be stable in alkaline solution (Kolman (2002), as abstracted from prior studies including the statement, "The metal appears inert to alkaline solution" from Katz and Seaborg (1957). No attack of plutonium metal was observed in the presence of 2.5 M NaOH; the experimental conditions were not further elaborated (Table 1 of Waber and Wright (1961)).

Table C - 3. Summary of Aqueous Corrosion Rates for Plutonium Metal (Kolman 2002)

Rapid Attack	**Slow Attack**	**No Attack**
HNO_3/0.005 M HF	H_2O	HNO_3
HCl	HF	Conc. H_2SO_4
HBr	Dilute H_2SO_4	Alkaline solution
72% $HClO_4$	Dilute CH_3COOH	Glacial CH_3COOH
85% H_3PO_4	Conc. CF_3COOH	
Conc. CCl_3COOH	Dilute CCl_3COOH	
Artificial sea water	Tap water	

More recent studies and compilation of prior work shows that plutonium metal corrosion rates increase with increasing salt concentration (see Figure 1 of Haschke (1995)). Delta-phase plutonium-gallium alloy in saturated alkaline lithium hydroxide (~ 4.8 M LiOH; pH ~13.7) showed no measureable corrosion occurred as determined by weight change or hydrogen gas evolution and the metal itself appeared untarnished even after three weeks' exposure (Haschke 1995). The initial corrosion product observed in pH neutral room-temperature water was PuOH, an oxide-hydride, had 7-nm particle size, and, with time, proceeded through intermediate compounds to form PuO_2 (Haschke (1995) and references therein). The corrosion rate for gallium alloy δ-plutonium found in phosphate-buffered pH 7 solution at 49° C was 2×10^{-3} mg $Pu/cm^2\cdot day$ and was markedly lower, 7×10^{-7} mg $Pu/cm^2\cdot day$, in a pH 10 borate buffer under otherwise similar conditions. The latter value corresponds to a linear penetration rate of $\sim3\times10^{-3}$ μm/year. Although plutonium metal corrosion rates increase with increasing sodium chloride (NaCl) concentration and decreased pH, sodium nitrate ($NaNO_3$), the solute generally of highest concentration in Hanford tank waste, has much less impact (Kolman and Colletti 2008).

No studies of the corrosion of plutonium metal in simulant or genuine Hanford tank waste were found. Based on the published literature, which shows that plutonium metal is uncommonly stable to corrosion in alkaline solution and is only marginally affected by $NaNO_3$, it is likely that plutonium metal corrodes at very slow and perhaps unobservable rates in tank waste solution. However, Hanford tank waste is complex and contains many dissolved components. The impacts of redox-active materials present in the tank waste, such as nitrite, NO_2^-, or organics (e.g., glycolate, $HOCCO_2^-$), have not been examined and may be significant. Any plutonium metal that has corroded is certain to be $PuO_2\cdot xH_2O$ and would likely have characteristically small particle size owing to its extremely low solubility. Because no studies of plutonium metal corrosion in Hanford tank waste have been performed and other studies of plutonium metal corrosion in alkaline solution showed the metal to be stable, no plutonium metal corrosion product could have been made to be studied to determine the actual particle size.

C.5 Conclusions

The products of plutonium metal burning operations in the PFP, PuO_2 and unburned plutonium metal, are expected to be the largest and most dense plutonium-bearing materials potentially discharged to the Hanford tank waste system. Over 99 wt% of the plutonium oxide particles produced by burning scrap plutonium metal buttons (and possibly other metal forms such as turnings and skulls) are expected to be greater than 10 μm. Residues of unburned plutonium metal are predicted to be present in the products from plutonium metal button burning unless supplemental furnace oxidation had been used. The residual plutonium metal and the large and high-fired PuO_2 particles produced in burning plutonium metal scrap would be difficult to dissolve in PFP operations and, with difficulty (owing to their high sedimentation rates), could have been discharged to the Hanford waste tanks. Thus, the maximum particle sizes for plutonium metal and PuO_2 arriving in the Hanford waste tanks from plutonium metal scrap burning operations would be 40 to 100 μm (Sams 2012). Once there, little change in the chemical or physical form of the high-fired PuO_2 would be expected, as this material is stable in the extant alkaline solution conditions. Plutonium metal corrosion rates in simple alkaline solution are abysmally low. However, no meaningful measurement of the actual corrosion rate is known for α-plutonium metal in simulant or actual Hanford tank waste solution. Although it would seem that any plutonium metal discharged to the Hanford tank waste would have corroded in the ensuing ~20+ years, in the absence of experimental evidence aside from the uniform observations of "no attack" or "inert" in tests in alkaline solution, the survival of plutonium metal in tank waste must be assumed. If corrosion did occur, the product would be $PuO_2\cdot xH_2O$ having the extremely small particle size characteristic of this material when formed in aqueous solution.

C.6 References

Campbell MH and JV Panesko. 1971. Internal letter to LM Knights (Manager) from MH Campbell and JV Panesko, Research Staff, "Tentative Indications from the Burning of a Portion of One Dow Button and Dissolution of Oxide." 13 October 1971, Richland, WA.

Clark DL, SS Hecker, GD Jarvinen, and MP Neu. 2006. "Plutonium." In The Chemistry of the Actinide and Transactinide Elements, eds. LR Morss, et al. Springer, Dordrecht, The Netherlands.

Eller PG, RW Szempruch, and JW McClard. 2004. Summary of Plutonium and Oxide Storage Package Failures. Report No. LA-UR-04-1453, Los Alamos National Laboratory, Los Alamos, NM. http://lib-www.lanl.gov/cgi-bin/getfile?01054987.pdf.

Felt RE. 1967. Burning and Extinguishing Characteristics of Plutonium Metal Fires. Report No. ISO-756, Isochem, Incorporated, Richland, WA.

Harlow DG and LJ Olguin. 1977. Internal letter to RB Gelman (Manager) from DG Harlow and LJ Olguin, ARHCO Researchers, "Current Status and Safety Hazards in Miscellaneous Treatment." 8 Mar 1977, Richland, WA.

Haschke JM. 1992. Evaluation of Source-Term Data for Plutonium Aerosolization. Report No. LA-12315-MS, Los Alamos National Laboratory, Los Alamos, NM. http://lib-www.lanl.gov/cgi-bin/getfile?00193529.pdf.

Haschke JM. 1995. Reactions of Plutonium and Uranium with Water: Kinetics and Potential Hazards. Report No. LA-13069-MS, Los Alamos National Laboratory, Los Alamos, NM. http://lib-www.lanl.gov/cgi-bin/getfile?00285828.pdf.

Haschke JM, TH Allen, and LA Morales. 2000. "Surface and Corrosion Chemistry of Plutonium." In Los Alamos Science, ed. NG Cooper, pp. 252-73. Los Alamos National Laboratory, Los Alamos, NM.

Haschke JM and TH Allen. 2002. "Equilibrium and Thermodynamic Properties of the PuO2+x Solid Solution." Journal of Alloys and Compounds 336:124-31.

Haschke JM and JL Stakebake. 2006. "Handling, Storage, and Disposition of Plutonium and Uranium." In The Chemistry of the Actinide and Transactinide Elements, eds. LR Morss, et al. Springer, Dordrecht, The Netherlands.

Katz JJ and GT Seaborg. 1957. The Chemistry of the Actinide Elements, Methuen & Company, Limited, London, UK, page 271.

Kolman DG. 2002. The Aqueous Corrosion Behavior of Plutonium Metal Exposed to Nitric Acid Solution. Report No. LA-UR-02-5920, Los Alamos National Laboratory, Los Alamos, NM. See also Kolman, DG. 2003. “The Aqueous Corrosion Behavior of Plutonium Metal Exposed to Nitric Acid Solutions”, Electrochemical and Solid State Letters 6(2):B1-B3.

Kolman DG and LP Colletti. 2008. "Aqueous Corrosion Behavior of Plutonium Metal and Plutonium–Gallium Alloys Exposed to Aqueous Nitrate and Chloride Solutions." Journal of the Electrochemical Society 155(12):C565-C70.

Korinko P. 2009. Review of Plutonium Oxidation Literature. Report No. SRNL-L7100-2009-00046 Rev. 1, Savannah River National Laboratory, Aiken, SC. http://sti.srs.gov/fulltext/SRNL-L7100-2009-00046R1.pdf.

Machuron-Mandard X and C Madic. 1996. "Plutonium Dioxide Particle Properties as a Function of Calcination Temperature." Journal of Alloys and Compounds 235(2):216-24. http://dx.doi.org/10.1016/0925-8388(95)02122-1.

Martell CJ. 1974. The Effect of Particle Size on the Carrier-Distillation Analysis of PuO_2. Report No. LA-UR-74-356, Los Alamos Scientific Laboratory, Los Alamos, NM. http://lib-www.lanl.gov/cgi-bin/getfile?00354254.pdf.

Martz JC, JM Haschke, and JL Stakebake. 1994. "A Mechanism for Plutonium Pyrophoricity." Journal of Nuclear Materials 210:130-42.

Mishima J. 1966. Plutonium Release Studies II. Release from Ignited Bulk Metallic Pieces. Report No. BNWL-357, Battelle Northwest Division, Richland, WA. http://www.osti.gov/scitech/biblio/4453507.

Molen GF and RD White. 1967. Properties of Plutonium Oxide, Part II. Report No. RFP-927, The Dow Chemical Company, Golden CO. http://www.osti.gov/scitech/biblio/4339665. Note that Part I is the report by Moseley and Wing (1965).

Moseley JD and RO Wing. 1965. Properties of Plutonium Dioxide. Report No. RFP-503, The Dow Chemical Company, Golden, CO. http://www.osti.gov/scitech/biblio/4613823.

Myers MN. 1956. Thermal Decomposition of Plutonium (IV) Oxalate and Hydrofluorination of Plutonium (IV) Oxalate and Oxide. Report No. HW-45128, Hanford Atomic Products Operation, Richland, WA. http://www.osti.gov/scitech/biblio/4181389.

Oma KH. 1977. Plutonium Metal Electrolytic Dissolution Flowsheet for the Plutonium Reclamation Facility. Report No. ARH-F-109, Atlantic Richfield Hanford Company, Richland, WA.

Pallmer PG. 1956. Crystallite Sizes of PuO_2 Powder. Report No. HW-44585, Hanford Atomic Products Operation, Richland, WA. http://www.osti.gov/scitech/biblio/4162958.

Sams TL. 2012. Executive Summary: Review of Plutonium Oxide Receipts into Hanford Tank Farms. Report No. WRPS-51744, Rev. 0, Washington River Protection Solutions, Richland, WA.

Stakebake JL. 1981. "Kinetics for the Reaction of Hydrogen with a Plutonium-1 Weight Percent Gallium Alloy Powder." Journal of the Electrochemical Society 128(11):2383-88.

Stewart K. 1961. Vixen-A Trials: Experiments to Study the Release of Particulate Materials During the Combustion of Plutonium, Uranium and Beryllium in a Petrol Fire. Report No. AWRE T15/60, Atomic Weapons Research Establishment, Aldermaston, United Kingdom. As cited by Haschke 1992.

Thompson MA. 1966. The Oxidation and Ignition of Plutonium. Report No. RFP-491, The Dow Chemical Company, Rocky Flats Division, Golden, CO. http://www.osti.gov/scitech/biblio/4558003.

Waber, JT and ES Wright. 1961. "The Corrosion of Plutonium". Chapter XVIII of The Metal Plutonium. AS Coffinberry and WN Miner, editors, The University of Chicago Press, Chicago, IL.

Wheelwright EJ. 1972. Development of an Electrolytic Dissolver for Plutonium Metal. Report No. BNWL-1642, Battelle Pacific Northwest Laboratories, Richland, WA.

Distribution*

No. of
Copies

9 Pacific Northwest National Laboratory

M Brady Raap	K8-34
CH Delegard	P7-25
SK Fiskum	P7-25
SA Jones	P7-25
RA Peterson	P7-25
SI Sinkov	P7-25
LP Staudinger	(PDF)
Information Release	(PDF)
Project File	K3-52

6 Bechtel National, Inc.

TK Campbell	H4-02
DL Herting	H4-02
TG Lewis	H4-02
RE Miles	H4-02
AH Wells	H4-02
WTP R&T Docs	H4-02

*All distribution will be made electronically.

Pacific Northwest
NATIONAL LABORATORY

U.S. DEPARTMENT OF
ENERGY

Proudly Operated by **Battelle** *Since 1965*

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)

www.pnnl.gov