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Effects Influencing Plutonium-Absorber Interactions and Distributions in Routine and Upset Waste Treatment Plant Operations

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May 2015

U.S. DEPARTMENT OF
ENERGY

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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:

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

_____5/7/15_____
Date

Executive Summary

This report is the third in a series of analyses written in support of a plan to revise the Hanford Waste Treatment and Immobilization Plant (WTP) Preliminary Criticality Safety Evaluation Report (CSER) that is being implemented at the request of the U.S. Department of Energy (DOE) Criticality Safety Group. A report on the chemical disposition of plutonium in Hanford tank wastes was prepared as Phase 1 of this plan (Delegard and Jones 2015). Phase 2 is the provision of a chemistry report to describe the potential impacts on criticality safety of waste processing operations within the WTP (Freer 2014). In accordance with the request from the Environmental and Nuclear Safety Department of the WTP (Miles and Losey 2012), the Phase 2 report assessed the potential for WTP process conditions within and outside the range of normal control parameters to change the ratio of fissile material to neutron-absorbing material in the waste as it is processed with an eye towards potential implications for criticality safety. The Phase 2 study also considered the implications should WTP processes take place within the credible range of chemistry upset conditions. The study did not evaluate accidents or physical aspects of waste processing, such as re-suspension of solids, transfers, or mixing as a means of waste mobilization.

The Phase 2 study considered that the most likely means by which the fissile material-to-absorber ratio might change is by chemical processing. The Phase 2 study identified 28 phenomena by which chemical or physical changes of either fissile material or absorbers might occur and grouped those phenomena through changes in pH, through reduction/oxidation (redox) processes, and through other processes such as use of surfactants and anti-foam agents, leaks, and volatilization.

In the present Phase 3 analysis, the 28 phenomena described in the Phase 2 report were considered with respect to the disposition of plutonium and various absorber elements. Because the fissile ^{235}U and ^{233}U isotopes are diluted by the abundant and chemically identical ^{238}U also present in the waste, no consideration of the disposition of uranium itself as an element with fissile isotopes was considered except tangentially with respect to uranium's interaction as an absorber for plutonium.

In considering plutonium disposition in the WTP operations with respect to criticality safety, it is useful to know the limits that instigate criticality safety concern. The Criticality Safety Limit, structured to maintain a safety margin sufficient to allow the increase of criticality safety parameters for both normal and upset WTP operations, is 0.013 grams of plutonium per liter (Section 4 of Miles (2009)). The Criticality Safety Limit is based on the Safe Subcritical Limit of 6.3 g Pu/liter (Section 4 of Miles 2009 Miles (2009)) which is derived from criticality computations.

As a first step in the present Phase 3 analysis, the 28 Phase 2 phenomena were grouped into 10 categories based on the similarities of their chemical (or physical) effects:

- nitric acid effects, including nitric acid use in cesium ion exchange elution and in cleaning operations as well as inadvertent transfers or losses
- nitric acid/oxalic acid effects in cleaning of the ultrafilters
- sodium hydroxide effects in caustic leaching, pretreatment additions, oxidative leaching with permanganate, and inadvertent operations
- carbonate effects including its influence on plutonium solids dissolution and unwanted introduction from reserves used in glass-making

- permanganate effects from oxidative leaching of chromium solid phases and from use in organic complexant oxidation
- cerium/peroxide effects from the decontamination of the high-level waste (HLW) glass canisters using Ce(IV) and from the misrouting of hydrogen peroxide (H_2O_2)
- organic effects, encompassing high levels of organics present in the tank waste, use of anti-foam agents, and oxidative decomposition of organics
- temperature effects as they impact the solubilities of plutonium and the absorbers
- melter redox effects and the likelihood that iron or plutonium metal form in the melters and whether plutonium can be transported disproportionately from the melter
- physical sedimentation effects to determine whether physical processes such as mixing and sedimentation can alter the distribution of plutonium coprecipitated with absorbers

Each effect category then was addressed individually to ascertain its potential to alter the relative distributions of plutonium and the associated neutron absorbers.

Of the various phenomena and chemical effects considered, the issue of greatest potential criticality concern is treatment of PuO_2-bearing sludge with HNO_3 due to the likely existence of refractory PuO_2 in tank waste and its known and demonstrated resistance to dissolution in HNO_3 while absorber element compounds dissolve and segregate. Segregation of ~0.1-kg quantities of plutonium onto the cesium ion exchange (CsIX) columns, either with or without acidification, might occur based on lab test results, high nominal feed solution concentrations, and plausible process flow rates and durations. Limited testing shows the plutonium from the CsIX columns is accompanied by more-than-sufficient absorber. On the strongly alkaline side, the separation of the absorber element aluminum from intrinsic plutonium solids such as PuO_2 with increasing NaOH concentration is also of concern. Dissolution tests of twelve different actual sludges using NaOH solution show, however, that no significant plutonium dissolution occurs, implying that other (non-aluminum) sludge materials such as iron (hydr)oxides retain the plutonium in the solid phase even under conditions in which aluminum sludge solids dissolved. The solubility-limited plutonium potentially available to be carried from solution by dawsonite precipitation, ~0.002 M (~0.5 g Pu/L), may be of criticality concern in low-hydroxide and high-bicarbonate conditions engendered by organic oxidation reactions under inordinately long waste storage times. However, the actual amounts of plutonium available for dissolution from sludge are likely much lower than the plutonium solubility limits in high-bicarbonate solution. Likewise, inadvertent additions of high concentrations of carbonate, permanganate, cerium(IV), or peroxide are judged not to be problems because of the limited amounts of plutonium available to dissolve. Temperature changes, melter chemistry, and separation of plutonium from coprecipitated absorbers by physical sedimentation following vigorous agitation also are expected to have no deleterious effects on the relative distributions of plutonium and absorbers.

The specific findings for each of the ten effects are briefly summarized in the following paragraphs.

Nitric Acid Effects – Based on studies of actual tank waste radiochemical analyses, lab process testing, and plant process experience, most plutonium is known to be present in an intimate mixture with absorber materials through coprecipitation. Therefore, proportionate dissolution of the plutonium and the absorber should occur following treatment with HNO_3. Subsequent treatment of the resulting HNO_3 solution with NaOH solution, as would occur in WTP processing (e.g., during cesium recovery and neutralization), would cause the dissolved plutonium and absorber to re-precipitate and thus not alter their

relative distributions, even at intermediate pH given the parallel pH dependence of solubility on pH for plutonium and many absorbers (e.g., aluminum, chromium, iron, and uranium). Instances of disproportionate dissolution of absorber element materials away from the plutonium-bearing solids also are observed, perhaps because of refractory low-solubility PuO_2 being present. Plutonium accumulation at ~0.1-kg quantities also may occur onto the CsIX column, either with or without acidification, based on lab test findings, high nominal feed solution concentrations, and plausible process flow rates and durations. However, limited testing also shows the CsIX eluate includes absorber elements including chromium, iron, manganese, nickel, and sodium that are individually more-than-sufficient to maintain criticality safety for plutonium.

Nitric Acid/Oxalic Acid Effects – For most sludge, proportionate dissolution of plutonium and absorber are observed in the action of HNO_3, as noted in Nitric Acid Effects. The actions of oxalic acid, $H_2C_2O_4$, to alter the distribution of plutonium and absorber elements, including iron, are similar to those of HNO_3, but the degree of segregation from plutonium in the case of excess dissolution of absorbers is diminished by the potential formation of the solid absorber-element compounds Mn(II) oxalate and U(VI) oxalate, arising by the $H_2C_2O_4$ treatment, that would stay with the plutonium-enriched solids.

Sodium Hydroxide Effects – The propensity for plutonium to separate from most absorber elements by differential dissolution or precipitation of their compounds based on sodium hydroxide, NaOH, concentration changes is low. Only salts of the absorber elements aluminum, boron, and chromium as Cr(VI) have significant (molar) solubilities under alkaline conditions, while the solubility of plutonium as $PuO_2 \cdot xH_2O$ remains low. Oxidative leaching will convert many Cr(III) compounds to soluble Cr(VI) salts and may simultaneously dissolve any plutonium coprecipitated with the Cr(III). Plutonium coprecipitation with the prominent aluminum solid phase, gibbsite, is negligible and plutonium forms a solid phase separate from the aluminum solid phase. Therefore, complete dissolution of gibbsite can occur with high NaOH concentration to leave most plutonium in the solid phase. Thus, separation of the absorber element aluminum from plutonium might occur. However, dissolution tests of actual sludges from twelve different waste tanks using NaOH solution show no significant plutonium dissolution, implying that other materials in the sludge (e.g., iron (hydr)oxides) successfully retain the plutonium in the solid phase.

Carbonate Effects – Laboratory and waste analysis studies show that plutonium compound solubility is strongly enhanced by the presence of carbonate at pH ~12 and higher, and even more strongly enhanced by bicarbonate at pH 9 to 10. The extent of plutonium leaching depends on the susceptibility of the host solids that contain the plutonium to dissolution in carbonate or bicarbonate. Laboratory testing shows that iron-bearing precipitates are not susceptible to dissolution in (bi)carbonate and thus resist leaching of their contained plutonium, while uranium-bearing solids dissolve in (bi)carbonate solution and release their contained plutonium. It is expected that compounds of other absorbers that are known to be effective coprecipitating agents for plutonium (e.g., chromium(III), cobalt, lanthanum, manganese, and zirconium) will resist leaching of their contained plutonium by (bi)carbonate. Compounds of the absorber elements aluminum and nickel do not coprecipitate plutonium, such that plutonium forms a solid phase separate from the aluminum or nickel compound, and plutonium leaching from aluminum solids by (bi)carbonate has been demonstrated. Therefore, leaching of the discrete plutonium solids from the associated, but not coprecipitated, nickel solids by (bi)carbonate is also likely. Intrinsic plutonium solids present in the waste, such as PuO_2 discharged to the waste in that form or formed by plutonium compound hydrolysis, are expected to be susceptible to dissolution by (bi)carbonate, although at rates that may be low—especially for high-fired PuO_2.

Permanganate Effects – The solubilities of (hydr)oxide compounds of aluminum, cadmium, chromium, iron, and uranium (but not manganese and nickel), and of plutonium itself, increase with alkaline concentration and thus help preserve the plutonium/absorber ratio in solution. However, the ratio may be altered in permanganate oxidative dissolution of discrete plutonium phases such as PuO_2,$PuO_2 \cdot xH_2O$, or other low-solubility tetravalent plutonium because of oxidation to more soluble pentavalent or hexavalent plutonium. The ratio also may be altered because of oxidative leaching of Cr(III) phases while compounds of other absorber elements (e.g., aluminum, iron, nickel) are largely redox-indifferent. Plutonium dissolution from genuine washed sludge with permanganate is significantly enhanced by an increase in NaOH concentration, increasing by an average factor of 70 when permanganate oxidative leaching is undertaken at 3 M NaOH as compared with 0.1 or 0.25 M NaOH. The increase is likely due to plutonium being more readily oxidized to the more soluble hexavalent state. Dissolved plutonium species in alkaline solution, irrespective of oxidation state, are anionic so they are not expected to sorb onto the cation-sorbing resin used for ^{137}Cs removal. Indeed, such sorption is observed to be negligible. Excess permanganate does not appear to have an appreciable effect on the distribution of plutonium to solution based on oxidative leaching of REDOX Process sludge simulants and genuine Cr(III)-bearing Hanford tank sludges. In lab testing, intentional over-dosage of permanganate did not lead to enhanced plutonium leaching at lower alkalinity (0.09 to 0.25 M NaOH), while at higher alkalinity (3 M NaOH), the plutonium concentration increase to ~0.00036 g Pu/L was relatively low and could be mitigated by adding Cr(III) nitrate to the permanganate/manganate-bearing slurry to eliminate excess oxidant, form MnO_2, and remove ~95% of the solubilized plutonium by coprecipitation. Separate testing showed that plutonium dissolution in the presence of excess permanganate at 2 to 4 M NaOH also can be mitigated by addition of hydrogen peroxide, removing ~75% of the solubilized plutonium. In treatment with Sr/Mn(VII) for ^{90}Sr and transuranic element removal from Envelope C supernates, both coprecipitated plutonium that remains undissolved and the residual soluble plutonium, should be protected with 100 to 1000 times higher neutron absorber concentrations based on AN-102 supernate studies. Although experimental data on [239]Pu decontamination from AN-107 supernates are lacking, it is likely that plutonium decontamination by Sr/Mn(VII) treatment was similar to that of AN-102 supernates based on solution composition and total alpha analyses. Decontamination of tank SY-101 from dissolved plutonium by permanganate treatment also is found. Overall, treatment of Envelope C wastes by Sr/Mn(VII) should improve criticality safety by carrying plutonium into the solid phase in the presence of co-precipitated iron and especially manganese.

Cerium and Peroxide Effects – Phenomena involving the uses of the chemical redox agents Ce(IV) and H_2O_2 in the surface decontamination of stainless steel glass canister vessels were identified. The situation of greatest concern regarding the use of acidic Ce(IV) nitrate solution is its inadvertent introduction to alkaline tank waste under continued acidic conditions to cause the oxidative dissolution, in acid, of the waste sludges and their contained plutonium to form dissolved Pu(VI). While the dissolution itself would have no criticality safety consequence because of the accompanying dissolved absorbers, subsequent adjustment to alkaline conditions would precipitate most absorbers and leave the Pu(VI) in solution. However, the Pu(VI) would be accompanied by abundant sodium from the added NaOH and, potentially, chromium as soluble chromate to provide neutron absorption. The actual concentration of Pu(VI) would likely be small because of the relatively low concentration of plutonium in waste sludge. The inadvertent introduction of H_2O_2 to tank waste also could occur, oxidatively dissolving some of the less refractory Cr(III) solids and their contained plutonium or intrinsic plutonium solids, such as any less-refractory $PuO_2 \cdot xH_2O$, to form soluble Cr(VI), Pu(V), and perhaps Pu(V) peroxide complexes. Again, however, the amount of plutonium dissolved by this action would be low and would be

accompanied by chromium and the ubiquitous sodium ion as absorbers. With time and radiolysis, the peroxide would decompose and most of the plutonium would eventually be chemically reduced to precipitate onto the sludge while the chromate would remain in solution.

Organic Effects – Organic effects on the relative distributions of plutonium and absorber compounds to solid and solution phases are manifested by their actions to dissolve the plutonium or absorber elements and by their influence, in oxidative degradation, on the solubility of aluminum phases. Hanford process organic complexants and extractants such as EDTA and TBP, respectively, are expected to have little chemical interaction with plutonium or with iron, the principal absorber element, in alkaline waste media. These source organic compounds also are known to degrade by hydrolysis and radiolysis to simpler and less interactive organic species. Although partition of plutonium to separate aqueous-immiscible organic phases present in tank wastes has been observed, the partitioning appears to be physical and not plutonium-specific, as other low-solubility solid materials also partition at about equal fraction to the organic. Therefore, the presence of tank waste organics in the WTP is unlikely to dissolve and concentrate fissile material or otherwise separate fissile material from credited absorbers. Anti-foam agents also are being considered for use in the WTP operations. Although polyol chemical agents with compositions similar to that of the anti-foam agent constituent polyether polyol are known to enhance plutonium solubility in pH-12 systems, tests of plutonium dissolution from simulant sludge in the presence and absence of the anti-foam agent showed no preferential plutonium dissolution even with 85° C leaching using 3 M NaOH or 0.25 M NaOH with permanganate. Organic oxidative degradation reactions are unlikely to occur to a significant extent unless extended (months-long) storage in plant occurs. Organic degradation would decrease hydroxide concentration and form carbonate, leading to decreased aluminum solubility to form gibbsite and dawsonite, respectively. Gibbsite precipitated by making acidic aluminum-bearing solution alkaline does not carry plutonium and does not enhance iron precipitation. The carrying of plutonium by gibbsite precipitated by lowering the pH of alkaline solution, or by forming dawsonite by further pH lowering and the addition of carbonate, has not been studied. Precipitation of aluminum phases by waste blending to lower pH or add carbonate or silicate could lead to gibbsite, dawsonite, and sodium aluminosilicate precipitation, respectively. The plutonium available for carrying by gibbsite under carbonate conditions is likely to be small enough ($\sim 10^{-7}$ M) to be inconsequential, while solubility-limited plutonium potentially available to be carried from solution by dawsonite precipitation under bicarbonate conditions, should dawsonite carry plutonium, is ~0.002 M (~0.5 g Pu/L) and may be of criticality concern. Incorporation of plutonium into aluminosilicate matrices is unlikely. However, the actual amounts of plutonium available for dissolution from sludge are likely much lower than the solubility limits.

Temperature Effects – The influence of temperature change in alkaline waste slurries on the relative distributions of plutonium and absorber elements to the solid and solution phases is small except in the case of aluminum. For aluminum (hydr)oxides, the concentration in NaOH solution changes markedly with temperature change, such that if a waste slurry contains only $Al(OH)_3$ and $PuO_2 \cdot xH_2O$ in the solid phase and the $Al(OH)_3$ is leached by digestion in strong heated NaOH, separation of the absorber aluminum from the plutonium will occur and may impact the criticality safety. The reverse situation—removal of aluminum from solution by precipitation occasioned by dilution, cooling, or crystal seeding for supersaturated alkaline solutions—is not of criticality concern because of plutonium's low solubility.

Melter Effects – Criticality concerns have been raised about the possible formation of plutonium metal in the melter by introduction of excess sugar as a reductant, by the potential for iron metal to be

formed by chemical reduction and thus separate from the plutonium, and by volatilization of the plutonium. Criticality concerns related to separation of plutonium and absorbers in the melter by formation of plutonium metal are effectively excluded for several reasons. First, reduction of PuO_2 to metal by carbon requires temperatures of ~2300° C to be thermodynamically feasible, thus foreclosing the possibility of plutonium metal formation in the nominal 1150° C melter. In addition, for plutonium metal to be formed, a vast amount of SiO_2, other metal oxides, and sulfate first must be reduced. Finally, the low plutonium concentrations in the waste and plutonium dissolution into molten iron metal oppose any plutonium metal coalescence even if plutonium metal should form. Reduction of iron oxides to metal by massive sugar overdose is credible but unlikely. However, as already noted, plutonium oxide reduction to metal is not credible. Any plutonium metal initially present in the waste is of small inventory and would certainly be oxidized during heating by the strongly oxidizing conditions in the melter cold cap from nitrate decomposition. The disposition of plutonium thus would be in the oxide melt phase that might contain lower iron concentrations should iron metal be formed. In this case, the sodium, and particularly boron absorbers in the sodium borosilicate melt, will be sufficient to offset any iron lost to a separate dense-metal phase. Volatilization of plutonium in the melters is expected to be low. Although conditions to generate volatile oxidized plutonium species such as $PuO_2(OH)_2$ by the action of hot, humid oxygen gas (as would be present in the melter) are known in laboratory tests, the volatilization extent is low. Furthermore, the volatile plutonium species readily and quantitatively absorbs onto silica at temperatures below about 850° C. Therefore, any of the trace plutonium that might volatilize in the melt would readily be recaptured in the cold cap and be delivered to the melt. Finally, any volatilized plutonium escaping the cold cap would be overwhelmed by the absorbers carried into the melter plenum as aerosols, which are generally representative of the melt composition itself, and vapors which include boron absorber compounds.

Physical Sedimentation Effects – Mechanical segregation of dense plutonium-bearing solids from other solids is the subject of separate devoted studies. However, segregation of coprecipitated fissile material and absorbers by vigorous mixing according to the conditions provided by pulse jet mixing and spargers is not plausible. At most, de-agglomeration of the coprecipitates could occur, but the plutonium and absorber ratios in the comminuted solids would be preserved.

S.1 Objective

The objective of the Phase 1 report was to summarize and evaluate the large body of experimental work, theoretical understanding, and technical literature relating to the disposition of plutonium in tank waste and in its interactions with compounds of the neutron-absorbing elements aluminum, cadmium, chromium, iron, manganese, nickel, sodium, and uranium. Phenomena in routine and plausible process upset conditions within the WTP were identified in the Phase 2 report as having potential to affect the dispositions of plutonium and absorbers. In the present Phase 3 report, the phenomena identified in the Phase 2 report are evaluated in light of the Phase 1 report and other resources to determine the impacts these phenomena might have to alter the plutonium/absorber dispositions and ratios. The outcomes of the Phase 3 evaluations then can be used to inform subsequent engineering decisions and provide reasonable paths forward to mitigate or overcome real or potential criticality concern in plant operations. Table S-1summarizes the objectives that apply to this task.

Table S–1. Summary of Work Objectives and Results

Work Objective	Objective Met?	Discussion
Address the concerns raised by the Phase 2 report regarding potential means by which plutonium and absorbers might be separated under routine and upset process conditions.	Yes	This report addresses the concerns raised by the Phase 2 report regarding potential means by which plutonium and absorbers might be separated under routine and upset process conditions. The 28 phenomena under three types of process conditions (pH, redox, and other) identified by the Phase 2 report were addressed individually according to 10 groupings based on detailed review of the technical literature.

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 Task to Address Concerns Raised by the Phase 2 Report on Conditions That May Alter Relative Plutonium and Absorber Ratios in WTP Processing

Success Criterion	How Work Did or Did Not Meet the Success Criterion
Address concerns raised by the Phase 2 report regarding the potential means by which plutonium and neutron absorber elements might become separated under routine and upset WTP process conditions.	This success criterion was met. The present report incorporates findings from the Phase 1 report on the chemical disposition of plutonium in Hanford tank wastes and summarizes findings from additional technical publications found in journals, on Hanford, PNNL, and other US-DOE Sites, and in 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 to address the concerns raised in the Phase 2 report.

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 applied 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.

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

This report summarizes historical literature and government-sponsored reports that describe the chemistry of Hanford Site tank waste and plutonium and neutron absorber elements. Accordingly, no simulants were used in this literature review.

S.7 Discrepancies and Follow-on Work

No discrepancies were found, but subsequent laboratory work may be deemed prudent.

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

Acknowledgments

Acronyms and Abbreviations

BNI	Bechtel National, Incorporated
CITROX	Mixed citric/oxalic acids
CNP	Cesium nitric acid recovery process system
CSER	Criticality Safety Evaluation Report
CSL	Criticality Safety Limit
CsIX	Cesium ion exchange column
CXP	Cesium ion exchange and spent resin collection process system
DBP	Dibutyl phosphate
DF	Decontamination factor
DOE	U.S. Department of Energy
EDTA	Ethylenediaminetetraacetate
FEP	Waste feed evaporation process
HDH	HLW canister decontamination handling system
HEDTA	N-2-hydroxyethylethylenediaminetriacetate
HFP	HLW melter feed process system
HLP	HLW lag storage and feed blending process system
HLW	High level waste
HMP	HLW melter process system
HOP	HLW melter offgas treatment process
IDA	Iminodiacetate
LAW	Low activity waste
MBP	Monobutyl phosphate
NCRW	Neutralized cladding removal wastes
NITROX	Mixed nitric / oxalic acids
NPH	Normal paraffin hydrocarbon
PFP	Plutonium Finishing Plant
PJM	Pulse jet mixer
PNNL	Pacific Northwest National Laboratory
QA	Quality assurance
PUREX	Plutonium Uranium Extraction
R&T	Research and technology
REDOX/redox	Reduction oxidation (n.b.: the REDOX Process used at Hanford is distinguished from redox chemistry by case, as demonstrated here)
RF	Resorcinol-formaldehyde
SRS	Savannah River Site
SSL	Safe Subcritical Limit
TBP	Tributyl phosphate

TLP	Treated LAW evaporation process system
TRU	Transuranic
TWINS	Tank Waste Information Network System
UFP	Ultrafiltration process system
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WTPSP	Waste Treatment Plant Support Project
WVDP	West Valley Demonstration Project

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1.0   Introduction

A thorough understanding of the form, size, and density of plutonium that exists in the waste located at the Hanford Tank Farms, in light of their interactions with credited or potentially credited absorbers, is needed to ensure that the Hanford Waste Treatment and Immobilization Plant (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" (Losey 2010) identified by the U.S. Department of Energy (DOE) Criticality Safety Group.

In considering the disposition of plutonium throughout the WTP operations with respect to criticality safety, it is useful to know the limits that present criticality safety concern. The Criticality Safety Limit (CSL) for plutonium concentration is 0.013 grams of plutonium per liter (Section 4 of Miles (2009)) and is set to provide conservative margin to ensure the criticality safety of the WTP operations. The CSL is, in turn, based on the Safe Subcritical Limit (SSL) for plutonium concentration (6.3 g Pu/liter; Section 4 of Miles (2009)) which is derived from criticality computations. The SSL provides the plutonium concentration threshold below which subcriticality is safely maintained. As noted by Miles (2009), the CSL is structured to provide a safety margin below the SSL sufficient to allow the increase of criticality safety parameters for both expected changes during normal WTP operations and unexpected changes during upset or contingent conditions. Ratios of plutonium to candidate credited neutron absorbers also factor into criticality safety (Table 4-2 of Miles (2009)). Plutonium concentrations within matrices containing such absorbers must exceed certain values (e.g., 5.18 grams of plutonium per kilogram of iron) for criticality safety to be threatened.

This report is the third in a series of analyses written in support of a plan to revise the WTP Preliminary Criticality Safety Evaluation Report (CSER) that is being implemented at the request of the DOE Criticality Safety Group. A report on the chemical disposition of plutonium in Hanford tank wastes was prepared as Phase 1 of this plan (Delegard and Jones 2015). The objective of Phase 2 of the plan is to provide information to the preliminary CSER a chemistry report to describe the potential impacts on criticality safety of waste processing operations within the WTP (Freer 2014). In accordance with the request from WTP's Environmental and Nuclear Safety Department (Miles and Losey 2012), the Phase 2 report assessed the potential for WTP process conditions within and outside the range of normal control parameters to change the ratio of fissile material to neutron-absorbing material in the waste as it is processed with an eye towards potential implications for criticality safety. The Phase 2 study also considered the implications should WTP processes take place within the credible range of chemistry upset conditions such as misrouted or incorrect reagent concentrations. The study did not evaluate accidents or physical aspects of waste processing, such as re-suspension of solids, transfers, or mixing as a means of waste mobilization.

The Phase 2 study considered that the most likely means by which the fissile material-to-absorber ratio might change in the solution, especially in the solid phase, is by chemical processing. Based on the findings presented in the Phase 1 report, most plutonium in the Hanford tank waste is likely to have been simultaneously precipitated or co-precipitated with hydrated iron, nickel, and other low-solubility metal hydroxides or oxides in the highly alkaline waste. Extensive tank waste characterization shows that little of the plutonium is in solution. The two most likely ways for changes in the disposition of either fissile

material or absorbers to occur are through changes in pH, changes in carbonate complexation, and through reduction/oxidation (redox) processes. It has been found that pure hydrated tetravalent plutonium (Pu(IV)) oxide solubility (i.e., in the absence of other salts or metal compounds) is minimized at pH ~13 but increases steeply at higher pHs and in more acidic solutions. Higher carbonate concentrations, especially when coupled with lower pH, favor plutonium dissolution. Oxidizing conditions also favor plutonium solid-phase dissolution by formation of pentavalent and hexavalent plutonium (Pu(V) and Pu(VI)) compounds, which are significantly more soluble than those of Pu(IV) (Delegard and Jones 2015). Changes in pH and carbonate concentration also may affect the solubilities of absorber compounds, while redox changes can affect the solubilities of compounds of certain redox-sensitive absorber elements (e.g., chromium). The WTP processes considered in the Phase 2 report thus were divided into three categories: pH effects, redox chemistry, and other processes. The evaluation results summarized in Section 3 of the Phase 2 report (Freer 2014) are presented in Table 1-1, Table 1-2, and Table 1-3, respectively, for pH effects, redox chemistry effects, and other process effects.

The present report and its underlying analyses constitute Phase 3 of the plan to revise the WTP Preliminary CSER. The objective of Phase 3 is to evaluate and project the outcomes of the phenomena described in the Phase 2 analysis specifically as shown in Table 1-1, Table 1-2, and Table 1-3.

Table 1-1. pH Effects

Number	Process	WTP System(s)
Acid		
PE1	Transfer of nitric acid elution from Ion Exchange system to HLW lag storage system	CXP, HLP
PE2	Nitric acid used to unplug a WTP line or pump	WTP-wide
PE3	Nitric acid used to clean WTP vessel	WTP-wide
PE4	Nitric acid used to clean Evaporator scale	Pretreatment Evaporators (FEP, CNP, TLP)
PE5	Nitric acid elution of ion exchange columns	CXP
PE6	Inadvertent nitric acid addition prior to ultrafiltration	UFP
PE7	Nitric acid additions	WTP-wide
PE8	Nitric and/or oxalic acid used to clean the ultrafilters	UFP
Alkali		
PE9	Caustic leaching	UFP
PE10	Sodium hydroxide additions	Pretreatment
Other		
PE11	Water additions	WTP-wide

CNP – Cesium nitric acid recovery process system	**HLW – High level waste**
CXP - Cesium ion exchange process system	**PWD – Plant wash and disposal system**
FEP – Waste feed evaporation process	TLP - Treated LAW evaporation process system
HLP – HLW lag storage and feed blending process system	UFP – Ultrafiltration process system

Table 1-2. Redox Effects

Number	Process	WTP System(s)
RE1	Plutonium metal formation in HLW melter	HMP
RE2	Oxidative leaching	UFP
RE3	Excess permanganate added during oxidative leach	UFP
RE4	Reduction of iron due to excess sugar addition	HMP
RE5	Ceric nitrate solution added to plutonium-containing vessel heel	HDH
RE6	Hydrogen Peroxide added to plutonium-containing vessel heel	HDH
HDH – HLW canister decontamination handling system **HMP – HLW melter process system**		

Table 1-3. Other Process Effects

Number	Process	WTP System(s)
OP1	Carbonate formation results in plutonium dissolution	**WTP-wide** PJM-mixed vessels
OP2	WTP feed holds unexpected organic complexant	HLP, UFP
OP3	Waste over-concentration or dry out in evaporator	**Pretreatment Evaporators** (FEP, CNP, TLP)
OP4	Impact of Strontium/TRU precipitation	UFP
OP5	Pipe or jumper leak	WTP-wide
OP6	Temperature changes	WTP-wide
OP7	Aluminum precipitation carries down dissolved plutonium	UFP
OP8	Sodium carbonate addition	HFP
OP9	Plutonium transported into ventilation system	HOP
OP10	PJM impact on co-precipitated solids	**Pretreatment** PJM-mixed vessels
OP11	Anti-foam agents addition	WTP-wide
HFP – HLW melter feed process system **HOP – HLW melter offgas treatment process**		

As a first step in the Phase 3 analysis, the 28 phenomena described in the Phase 2 report and in Tables 1-1, 1-2, and 1-3 have been grouped into 10 categories based on the similarities of their chemical (or physical) effects. These ten groupings are shown in Table 1-4. Because of their potential impacts to relative distributions of plutonium and the absorber materials, both nitric acid (HNO_3) and sodium hydroxide (NaOH) effects are widespread and are manifest in 12 and 7, respectively, of the 28 phenomena. The combined effects of HNO_3 and oxalic acid ($H_2C_2O_4$) additions are addressed in a separate category. Effects of the other chemical reagents, carbonate (CO_3^{2-}), permanganate (MnO_4^-), organics, and cerium/peroxide (Ce, H_2O_2) are found in 2 to 4 of the 28 phenomena, while temperature and physical effects are found in separate single identified phenomena. The category that collectively addresses melter redox effects encompasses three of the 28 phenomena. The final category is physical sedimentation, which addresses this single identified phenomenon.

Table 1-4. Categorization of Effects

Category of Effect	Process Phenomena Numbers
Nitric acid effects	PE1, PE2, PE3, PE4, PE5, PE6, PE7, PE11, RE2, OP3, OP5, OP7
Nitric acid / oxalic acid effects	PE8
Sodium hydroxide effects	PE9, PE10, PE11, RE2, OP3, OP5, OP7
Carbonate effects	OP1, OP7, OP8
Permanganate effects	RE2, RE3, OP4
Cerium / peroxide effects	RE5, RE6
Organic effects	OP2, OP7, OP11
Temperature effects	OP6, OP7
Melter redox effects	RE1, RE4, OP9
Physical sedimentation effects	OP10

Some process phenomena appear in multiple effect categories. Thus, aluminum precipitation, addressed in phenomenon OP7, is subject to influence by pH changes incurred by HNO_3, NaOH, and carbonate concentration effects (as well as the influence of carbonate to form other aluminum solid phases), by pH and carbonate concentration changes arising from organic oxidation, and by temperature. Therefore, OP7 appears in five of the effect categories (nitric acid, sodium hydroxide, carbonate, organic, and temperature). Similarly, phenomenon RE2 on oxidative leaching appears in three effects categories because it depends on permanganate and sodium hydroxide concentrations (and, by extension, nitric acid). The phenomena OP3 and OP5 are both concerned with solution dry-out and thus influence effects of nitric acid and sodium hydroxide concentrations.

The effect categories are addressed individually in the following sections of this report to ascertain their potential impacts to alter the relative distributions of plutonium with the associated neutron absorbers.

2.0 Influence of Chemical and Physical Effects

The influences of the individual chemical and physical effects enumerated in Table 1-4 are described individually in the following sections in light of their impacts on plutonium and absorber element distributions, and subsequently the likelihood of their altering the plutonium and absorber element ratios.

2.1 Nitric Acid Effects

Potential issues surrounding the disposition and relative distributions of plutonium and absorber materials in the waste feed solution and solids arise from the use of nitric acid, HNO_3, at various places within the WTP. The issues were raised based on phenomena PE1, PE2, PE3, PE4, PE5, PE6, PE7, PE11, RE2, OP3, OP5, and OP7 as described in Tables 1-1, 1-2, and 1-3 and in Table 2-1.

Table 2-1. Chemical Phenomena Associated with Nitric Acid Chemistry Effects

Number	Process	WTP System(s)
PE1	Transfer of nitric acid elution from Ion Exchange system to HLW lag storage system	CXP, HLP
PE2	Nitric acid used to unplug a WTP line or pump	WTP-wide
PE3	Nitric acid used to clean WTP vessel	WTP-wide
PE4	Nitric acid used to clean Evaporator scale	Pretreatment Evaporators (FEP, CNP, TLP)
PE5	Nitric acid elution of ion exchange columns	CXP
PE6	Inadvertent nitric acid addition prior to ultrafiltration	UFP
PE7	Nitric acid additions	WTP-wide
PE11	Water additions	WTP-wide
RE2	Oxidative leaching	UFP
OP3	Waste over-concentration or dry out in evaporator	**Pretreatment Evaporators** (FEP, CNP, TLP)
OP5	Pipe or jumper leak	WTP-wide
OP7	Aluminum precipitation carries down dissolved plutonium	UFP

The impact of hydroxide concentration change (which can occur by HNO_3 solution misrouting) on phenomenon RE2 is addressed in the Permanganate Effects section. The influence of hydroxide concentration change (which also can occur by HNO_3 solution misrouting) is examined for phenomenon OP7 as part of various chemical processes that can affect aluminum and associated plutonium precipitation and dissolution in the Organic Effects section (2.7). Therefore, phenomena RE2 and OP7 will not be considered further in the present section.

Phenomena PE1, PE2, PE3, PE4, and PE5 are concerned with the potential for differential behaviors of plutonium and absorber materials by their interactions with HNO_3 under intended process operations. Phenomenon PE1 is concerned with the impact of HNO_3 encountering alkaline waste. Phenomena PE2, PE3, and PE4 are concerned with the reactions of HNO_3 with scales and other solid deposits on the plant process equipment. Phenomenon PE5 is concerned with the possible differential behavior of plutonium and absorbers in the cesium ion exchange columns. Intended (PE11) and unintended (PE6, PE7, OP3, and OP5) processes can influence HNO_3 concentration and alter the process chemistry of plutonium and the absorber elements. Phenomenon PE11 is concerned with the influence of water added during normal processing but which can dilute HNO_3 and thus alter its intended applications in various parts of the plant. Unintended addition of HNO_3 to the alkaline solution feed to the ion exchange column is of concern in phenomenon PE6. Phenomena OP3 and OP5 are concerned with unintended process solution evaporation with both phenomena having the effect of increasing the HNO_3 concentration.

2.1.1   PE1 – Transfer of Nitric Acid Elution from Ion Exchange System to HLW Lag Storage System

Acidic ion exchange eluate laden with ^{137}Cs will be concentrated by evaporation and then discharged into alkaline waste. In phenomenon PE1, concern is expressed that differential distribution of plutonium and compounds of the absorber elements could occur because of the ensuing acidification and neutralization processes. An enquiry into the effects of the addition of HNO_3 to alkaline tank waste within the WTP process vessels was prepared in 2001 based on reviews of laboratory studies with actual tank wastes, sludge characterization analyses published in the Tank Waste Information Network System (TWINS), tank sludge characterization results *not* available in TWINS, and examination of experience from acidifying Plutonium Uranium Extraction (PUREX) Plant tank waste sludge in fission product recovery operations (Batdorf and Larson 2001). In general, it was found that the fraction of plutonium dissolved approximately corresponded to the fractions of the compounds comprised of the bulk sludge elements. This was also true, in a very general fashion, for the acid processing of PUREX sludge. In this processing, the plutonium concentrations in the feed sludge and in the HNO_3-leached heel were approximately equal and thus would not alter the existing criticality safety. In some instances, the fraction of plutonium that dissolved was greater than that of some bulk sludge elements. In general, this also is of little criticality consequence because the quantity of plutonium available for leaching, no more than ~10^{-4} M in sludge (Figure 5-1 of Delegard and Jones (2015)),would lead to inconsequential plutonium concentrations in solution.

Results from additional examination of lab leaching tests to examine HNO_3 addition to actual tank waste solids and results from sludge characterization analyses were examined for the present report. The findings are presented as the percentages of plutonium and bulk element dissolved under various experimental leaching conditions as described in the "Sludge and Process Condition" column of Table 2-2. In some cases, preliminary washing of salts from the sludge was performed. If the solids contained fluoride salts, as is the case for neutralized cladding removal wastes (NCRW) tests (Swanson 1991a, b), acid leaching would create hydrofluoric acid, HF, and potentially help solubilize both $PuO_2 \cdot xH_2O$ and the zirconium solids also present in these sludges. The final acid concentration also is a factor in the amounts of plutonium and other elements dissolved. Water-soluble salts will be present for the received Hanford tank wastes but will be in much lower concentration for water-washed or NaOH-leached sludges. Therefore, the presence of salts and the final acid concentration are factors that come

into play when HNO_3 is discharged to HLP vessels. Overall, we note that published data are scant and, in many instances, the test conditions do not reflect the proposed PE-1 scenarios.

Table 2-2. Dissolution of Plutonium and Various Elements by Treatment of Hanford Tank Sludge with HNO_3

Report ID	Report Location	Sludge and Process Condition [a]	Waste Type [b]	Al	B	Bi	Ca	Cd	Cr	Fe	La	Mg	Mn	Na	Ni	P	Si	Th	U	Pu
Swanson (1991a)	p A.19, Table 7, assumes 5 mL 5 M HNO₃ dissolves all sludge	AW-105 ×leach unwashed with 1 M HNO₃; fluoride in matrix may have helped with dissolution; 3% of Zr dissolved	NCRW (neutralized cladding removal waste); CWZr× (TWINS)	12	NR	NR	45	NR	24	10	7	NR	84	73	NR	NR	NR	NR	72	4.8
		AW-105 leach unwashed with 3.5 M HNO₃; fluoride in matrix may have helped with dissolution; 84% of Zr dissolved		80	NR	NR	71	NR	77	83	84	NR	84	84	NR	NR	NR	NR	86	83.1
	pp B.17 & B.24, Tables 5 & 12	AW-105 expt. 15 App. B: Two water washes, then 0.2 M HNO₃ leach, end pH=3.1, 1-day RT contact; 3% of Zr dissolved		12	NR	NR	NR	NR	42	45	NR	NR	NR	6	NR	NR	NR	NR	90	15
		AW-105 expt. 15 App. B: Two water washes, 0.2 M HNO₃ leach, then 0.4 M HNO₃ leach; 3 days' RT contact with a 2-h 100°C digest; end pH=0.9; 5% of Zr dissolved		4	NR	NR	NR	NR	7	16	NR	NR	NR	1	NR	NR	NR	NR	10	40
	p C.12, Table 1	AW-103 acid strike with ~1.5 M HNO₃, RT; 96% of Zr dissolved		72	NR	NR	NR	NR	71	85	NR	NR	NR	100	NR	NR	NR	NR	NR	82
		AW-103 acid strike with ~2.5 M HNO₃, RT; 93% of Zr dissolved		76	NR	NR	NR	NR	92	93	NR	NR	NR	100	NR	NR	NR	NR	NR	95
		AW-103 acid strike with ~2.5 M HNO₃, 100°C; 55% of Zr dissd.		100	NR	NR	NR	NR	98	93	NR	NR	NR	99	NR	NR	NR	NR	NR	92
		AW-105 acid strike with ~1.7 M HNO₃, RT; 98% of Zr dissolved		72	NR	NR	NR	NR	96	95	NR	NR	NR	100	NR	NR	NR	NR	NR	96
Swanson (1991b)	pp 4.4-4.5, Tables 4.1 & 4.2	AW-103 contacted with ~2.6 M HNO₃ 2 h at RT. The UDS was further dissolved with 3 M HNO₃ + 0.2 M H₂C₂O₄, heated to 100°C for 2 h	CWZr2 (TWINS)	75	NR	NR	97.8	96.4	95.9	94.8	NR	NR	NR	99.97	95.5	57	98.4	NR	NR	98.7 tot-α
Lumetta and Swanson (1993)	pp 3.5 & 3.8, Tables 3.2 & 3.3	SY-102; solids previously treated with H₂O₂ were contacted with 2.1 M HNO₃	PFP or Z sludge; NA and Z (TWINS)	18.7	NR	NR	98.8	NR	59.6	94.7	NR	NR	95.1	NR	NR	60.3	NR	100	100	97.4
Lumetta et al. (1994)	pp 3.4 - 3.12; Table 3.2, Figure 3.4	C-109 washed with 0.1 M NaOH, then 0.7 M HNO₃ for 1 h at 100°C; large sludge fraction dissolved	TBP U extraction; 1C (TWINS)	17	NR	70 ±41	91	NR	22	48	49 ±42	29 ±22	45	13	NR	64	8	NR	≥54	82
		C-109 from previous test then contacted with 2 M HNO₃ for 1 h at 100°C	TBP U extraction; 1C (TWINS)	7	NR	30 ±17	2	NR	3	13	51 ±43	<4	11	0	NR	5	0	NR	<4	14
	pp 6.1 - 6.3, Tables 6.1 & 6.2	AN-102 leached with pH 1.08 HNO₃ heated to 100°C for 1 h; large fraction of sludge dissolved	TRUEX and SREX process; A2-SltSlr (TWINS)	92	NR	NR	95	NR	72	98	NR	NR	97	100	NR	≥64	73	NR	59	88
		AN-102 from above leached with 2 M HNO₃ at 100°C for 1 h	TRUEX and SREX process; A2-SltSlr (TWINS)	1	NR	NR	3	NR	13	1	NR	NR	2	0	NR	≤21	8	NR	18	10
Lumetta and Rapko (1994)	pp 3.1-3.9, Tables 3.1 & 3.3	U-110 core 14 washed and hydroxide and carbonate leached then leached twice with 2 M HNO₃ at 100°C for 2 h	3rd cycle; B1 (TWINS)	8	5	61	79	NR	27	50	NR	100	96	NR	100	1	4	NR	100	97

Report ID	Report Location	Sludge and Process Condition [a]	Waste Type [b]	Analyte Dissolved by HNO$_3$ Contact, % [c]																
				Al	B	Bi	Ca	Cd	Cr	Fe	La	Mg	Mn	Na	Ni	P	Si	Th	U	Pu
Krupka et al. (2004)	Table 3-10	AY-102 compared KOH/KNO$_3$ fusion in Ni crucible with HNO$_3$-H$_2$O$_2$ acid digestion per EPA SW-846 Method 3050B (EPA 2000); divided acid digest by fusion digest results. Acid digest method: contact sample with 8 M HNO$_3$ and heat at 95°C for 10 to 15 min, cool add 5 mL concentrated HNO$_3$ heat 30 min; repeat until no brown fumes form; cool then add 3 mL 30% H$_2$O$_2$, heat and warm, repeat H$_2$O$_2$ addition/heat until no further reaction; reduce volume to 5 mL. Parentheses results mean high variability.	NA and BL (TWINS); report does not define	106	(43)	19	(103)	(104)	116	90	NR	(102)	111	(119)	NA	151	3.3	NR	133	131
(Disselkamp 2009a)	p 169	AZ-101 Core 266 TWINS (acid, likely HCl, digestion)/(fusion)	P3AZ1 (TWINS)	149	6	<	85	116	102	135	125	<	73	NR	NA	36	17	<	<	92
	p 175	AZ-101 Core 269 TWINS (acid, likely HCl, digestion)/(fusion)		103	45	<	98	110	108	118	111	75	110	122	NA	<	37	<	138	85
	p 181	AZ-101 Core 283 TWINS (acid, likely HCl, digestion)/(fusion)		105	<	NA	103	107	131	108	96	83	100	98	NA	516	29	<	97	60
	p 186	AZ-101 core comp TWINS (acid, likely HCl, digestion)/(fusion)		115	24	<	92	110	104	124	112	<	93	112	NA	25	27	<	<	88
(Disselkamp 2009b)	p 96	C-204 solid 2007 Post-retrieval Finger Trap Sample TWINS (acid, likely HCl, digestion)/(fusion)	HS (TWINS)	42	<	<	<	<	86	79	<	<	74	95	NA	101	NR	82	102	82

Values highlighted in grey indicate that plutonium dissolution is <0.5× that of the noted element; values highlighted in yellow indicate plutonium dissolution is >2× that of the noted element.

(a) RT – room temperature; UDS – undissolved solids; EPA – Environmental Protection Agency; TWINS – Tank Waste Information Network System. Fusion digests assumed to provide complete sample dissolution for analysis.

(b) TRUEX – transuranic extraction; SREX – strontium extraction. For waste types such as 1C, B1, and A2-SltSlr, see Section 4.0 of Delegard and Jones (2015)

(c) NR – not reported; NA – not analyzed; < – "less than" reportable value result. Values >100% reflect the analytical uncertainty, sample heterogeneity, measurement uncertainty, and processing bias.

The laboratory leach testing (Lumetta and Swanson 1993; Swanson 1991a, b; Lumetta et al. 1994; Lumetta and Rapko 1994) and analytical acid digestion (Krupka et al. 2004; Disselkamp 2009a, b) findings show, in general, that plutonium leaches to approximately the same extent as other elements, particularly when sufficiently high acid concentrations and amounts are used.

For some conditions, particularly at low acid quantities, plutonium dissolution lags that of other elements, including elements that might be credited as neutron absorbers (aluminum, chromium, iron, manganese, and uranium – see Swanson (1991b) in Table 2-2). The results indicating lagging plutonium dissolution, identified in Table 2-2 by gray highlighting, are found mostly in cases of low added acid for NCRW sludge.

In other instances, plutonium dissolves to a greater extent than found for some elements (indicated by yellow highlighting in Table 2-2. Many of these elements having low extents of dissolution in acid (i.e., sodium, aluminum, and silicon and calcium/magnesium, phosphorus) are constituents in sodium aluminosilicate and calcium/magnesium phosphate phases that resist acid dissolution.

Of particular concern in criticality safety is the differential dissolution of absorber compounds away from refractory plutonium oxide particles, as might be found in wastes received from the Plutonium Finishing Plant (PFP). Tanks SY-102 and TX-118 received PFP wastes.[1] The digestion of waste from tank SY-102 in 2.1 M HNO_3 was examined and found to show relatively complete dissolution of plutonium with the absorber elements iron, manganese, and uranium (Lumetta and Swanson 1993). Aluminum and chromium leaching were less complete and the residue from leaching was aluminum-rich. By contrast, the ~2.6% of plutonium residue left in the heel was accompanied by 5.3% of the iron, 4.9% of the manganese, ~40% of the chromium, and ~81% of the aluminum, although virtually none of the uranium remained. These particular findings show that, aside from aluminum, significant plutonium segregation from its absorbers did not occur in these leach tests. Elutriation and sedimentation techniques have been used to characterize dense particles separated from sludges from tanks SY-102 and TX-118 and the results summarized in Section 5.3.3 of Delegard and Jones (2015) and in references cited therein. It was found that the fraction of the total plutonium that is present in such plutonium-rich particles is very small.

The findings summarized in Table 2-2 for tank waste process testing and characterization indicate that contact of the alkaline waste with HNO_3 can alter distributions of plutonium with absorber element materials. Although in many cases the relative fractions of plutonium and absorber element(s) that dissolve (or remain in the solids) are similar, situations arise wherein greater or lesser relative plutonium dissolution occurs. The re-neutralization of the resulting acidic waste (i.e., treatment with NaOH or added alkaline tank waste to make the mixture alkaline) will cause the dissolved plutonium to re-precipitate with the low-solubility compounds formed from many of the dissolved absorber elements (primarily, for example, iron, manganese, uranium, and any Cr(III)). Therefore, if the acidified HLW remains in the vessel and the contents are then made alkaline, no appreciable change in the relative plutonium:absorber distribution will occur in either the solids or solution. Some concern still would

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[1] Radiolytic spallation processes (metamictization) should diminish the crystallinity of PuO_2 with time (see, for example, Figure 5 of C. H. Delegard, *Effects of Aging on $PuO_2 \cdot xH_2O$ Particle Size in Alkaline Solution*, Radiochimica Acta 101.5 (2013).) and thus make this material easier to dissolve but the relative magnitude of this effect with respect to absorber compounds is not known.

remain regarding this pH adjustment if the transition from acid to alkaline paused at an intermediate point that favored the precipitation of either the plutonium or its absorbers, leaving plutonium without sufficient absorber in either the solid or solution. For most of the absorber elements (i.e., aluminum, cadmium, chromium, iron, and uranium), the solubilities of the corresponding (hydr)oxides decrease in parallel fashion with the solubility of plutonium as pH is raised. Therefore, the simultaneous precipitation, if not coprecipitation, of plutonium with absorber should occur. The solubilities of plutonium and the absorber elements are shown in Figure 6-3 of Delegard and Jones (2014). For nickel and manganese(IV), the solubility decrease with pH increase in the acid to neutral range does not track with plutonium's although both have low solubilities at neutral to high pH where plutonium solubilities are lowest meaning they are available to act as absorbers in the solid phase at these greater pH values. Sodium and boron solubilities remain high over the entire pH range and thus do not track with plutonium's solubility.

However, if the acidified waste, from acidic cesium ion exchange eluate or whatever source, is moved from the HLP vessel(s) and that solution is plutonium-enriched, or, alternatively, plutonium-enriched solids remain in the heel, the relative plutonium concentration in the respective solution or heel stream has increased. Because the plutonium concentration in Hanford tank wastes is generally low (maximum of ~10^{-4} M or ~0.02 g Pu/L in solution and sludge from 27 and 19 different tanks, respectively; Figure 5-1, Delegard and Barney (1983)), the opportunity for the solution to exceed a level of criticality concern is likewise low, but not negligible (the CSL is 0.013 g Pu/liter). It is of greater concern that methods (here undefined) be instituted in the WTP processes to address the potential impacts of plutonium concentration increases in the solid residues remaining after acidification of tank wastes. The likely existence of refractory PuO_2 in tank waste and its known resistance to dissolution in HNO_3 (Sections 5.3.2 and 5.3.3, respectively, of Delegard and Jones (2015))—proven by the fact that much of the PuO_2 present in the tank waste originated from dissolver heels from the PFP—makes this an issue of particular criticality concern in WTP operations.

2.1.2 PE2 – Nitric Acid Used to Unplug a WTP Line or Pump, PE3 – Nitric Acid Used to Clean WTP Vessel, and PE4 – Nitric Acid Used to Clean Evaporator Scale

As noted in Table 2-1, phenomena PE2, PE3, and PE4 are concerned with the reactions of HNO_3 with blockages, deposits, and evaporator scales, respectively, to remove these solids from plant process equipment in planned operations. These various solids mostly arise from the tank waste itself but also can include the underlying corrosion products from the 304L stainless steel, which constitutes most of the wetted material of construction in the plant. Deposits also include sodium aluminosilicates (e.g., cancrinite; see Section 6.1 of Delegard and Barney (1983)) from tank waste reactions with silica added as a glass-former. For these reasons, the solids themselves have the plutonium:absorber ratios of the starting waste abetted by added absorber from the stainless steel corrosion product. It is likely, and desirable from a plant-longevity perspective, that the contribution of 304L corrosion products to the solids is minimal. Therefore, the question to be considered is whether preferential dissolution of either the plutonium or the absorber materials from the sludge might occur upon addition of acid.

The dissolution of waste blockages by HNO_3 under phenomenon PE2, to a first approximation, should be similar to the dissolution of sludge as considered in phenomenon PE1. To a lesser extent, dissolution of solids deposits on process vessels and piping by use of HNO_3 under phenomenon PE3 also should be analogous to PE1. Therefore, differential dissolution of plutonium leads to greater

plutonium:absorber ratios in the solids or in the solution. As shown in Table 2-2, differential dissolution of plutonium and various absorber element solids arising from tank wastes is credible. The situation in the case of higher plutonium:absorber ratio in the residual solids may be ameliorated by the close proximity of the stainless steel plant process equipment and the intrinsic neutron absorption properties of the constituent iron, chromium, and nickel, upon which the solids rest (note that the impact of process vessel wall absorbers on criticality safety is beyond the scope of the present assessment). Plutonium-enriched solution then becomes a concern. However, as noted in consideration of phenomenon PE1, above, where no more than ~10^{-4} M plutonium is present in sludge, it is unlikely that total plutonium concentrations in the acidic solution can rise to levels high enough to be of concern.

Phenomenon PE4 is associated with the removal of evaporator scales. The scales that form are likely to consist of solids that, by dehydration reactions, are more refractory than the starting compounds. For example, the formation of boehmite, $AlOOH$, from gibbsite, $Al(OH)_3$, and hematite, Fe_2O_3, from goethite, $FeOOH$, and ferric hydroxide, $Fe(OH)_3$, by way of thermal dehydration processes is well known. Significantly for the WTP, evaporator scales consisting of the sodium aluminosilicate mineral cancrinite have been observed at the Savannah River Site occurring just after commencement of operation of the Defense Waste Processing Facility, a waste vitrification plant (Section 6.1 of Delegard and Jones (2015) and references therein). Information on plutonium incorporation into aluminosilicates was not found in the technical literature but is unlikely given the much smaller size of the anions (e.g., nitrate, chloride, and carbonate) enclathrated in cancrinite and other aluminosilicates compared with the size of the alkaline plutonium anions. However, precipitated plutonium silicate deposits might occur (Section 5.3.1 and 6.2 of Delegard and Jones (2015)). Increased dehydration also occurs for $PuO_2 \cdot xH_2O$ as hydrothermal aging temperature increases at least over the range of 10 to 200° C (Krot et al. 1998c; Yusov et al. 2000a). The differential dissolution of plutonium and solids of the absorber elements from such thermally aged materials is not known, however, except to the extent that tank wastes also have been thermally aged by decades-long storage at temperatures that sometimes have exceeded boiling. Indeed, the presence of boehmite in some tank wastes is *prima facie* evidence that elevated waste temperatures have been attained. Thus, leaching or dissolution of tank waste with nitric acid for chemical analysis (see Table 2-2) already is known to some extent. In the end, the considerations that must be given to the differential dissolution occasioned by treating boiler scales with HNO_3 under phenomenon PE4 do not differ materially from the considerations that apply to phenomenon PE1.

2.1.3   PE5 – Nitric Acid Elution of Ion Exchange Columns

Phenomenon PE5 is concerned with the potential for differential behaviors of plutonium and absorbers in the cesium ion exchange (CsIX) columns. Of particular concern would be the absorption or interaction of plutonium with the ion exchange medium itself and unintended collection of plutonium on that solid. The feed for the CsIX is filtered alkaline solution from the Hanford tank wastes. Plutonium concentrations in such feeds are thus limited by solubility and carbonate complexation conditions as shown in Figures 5-5 and 5-6 of Delegard and Jones (2015). Practically, however, the highest plutonium concentrations found in tank waste solution are on the order of 10^{-4} M, about 0.02 g Pu/liter (see Figure 5-1 of Delegard and Jones (2015)). Furthermore, the dissolved plutonium species found in alkaline tank waste are anionic (negatively charged) and highly unlikely to be attracted to the CsIX media, which are designed to attract the positively charged cesium ion, Cs^+.

Tests have been conducted to determine the behavior of plutonium from a blend of genuine tank waste solution when processed using the resorcinol-formaldehyde (RF) CsIX media (Fiskum et al. 2009). In these extended tests, it was found that only about 0.2% of the plutonium present in the actual waste was fed, as filtered solution, to the CsIX column (i.e., 99.8% remained in solids), that only 4.5% of the 0.2% that was fed to the column (i.e., 0.009% of the initial plutonium in the waste) was retained on the CsIX resin, and that only 0.2% of the 4.5% of the 0.2% (i.e., 1.8×10^{-5}% of the initial plutonium) still remained on the CsIX resin after elution with 15 bed volumes of HNO_3. Nevertheless, if the feed solution contains 10^{-4} M plutonium (~0.02 g Pu/L; i.e., already above the 0.013 g Pu/L CSL), about the maximum observed in Hanford tank waste solutions (Figure 5-1 of (Delegard and Jones 2015)), and the resin bed loading occurs at 120 liters/minute for 20 hours (a nominal but hypothetical process flow rate), about 130 g of plutonium would accumulate on the resin bed before elution. Associated tests with simulated tank waste solutions showed that about 15% of the dissolved plutonium was retained on the resin (Duignan and Nash 2009) as compared with 4.5% observed with genuine waste (Fiskum et al. 2009). In this case, about 400 g of plutonium might accumulate and concentrations in the eluate would be multiplied well above the CSL.

The criticality potential in the eluate likely is mitigated by the co-elution of cationic absorbers from tank feed, primarily sodium (Fiskum et al. 2009). At one significant figure, the Pu:absorber mass ratios in the eluate, in grams of plutonium per kilogram of absorber, were: Cr – 0.7 (6.28), Fe – 0.5 (5.18), Mn – 2 (25.5), Ni – 0.8 (9.68), and Na – 0.0003 (2.47) (based on Tables 5.10 and 5.11 of Fiskum et al. (2009)). Uranium and particularly boron are also present in the eluate. The numbers in parentheses indicate the upper threshold values for plutonium:absorber mass ratios, based on Table 4-2 of Miles (2009), and show that all of the listed absorbers provide safety factors of about ten and, for sodium, almost a factor of 10,000. The simultaneous precipitation or coprecipitation of plutonium with these absorbers upon making the CsIX eluate alkaline should be expected for at least chromium and iron, as indicated in Figure 6-3 of Delegard and Jones (2015).

Based on these findings, and depending on the plutonium concentration in the waste solutions, some risk to criticality safety is posed by even the minimal interactions of plutonium with the CsIX, the elution by HNO_3 of plutonium from the CsIX, and the evaporative concentration of the eluate, but absorbers also present in the eluate would strongly mitigate the risk.

2.1.4   PE6 – Inadvertent Nitric Acid Addition Prior to Ultrafiltration and PE7 – Nitric Acid Additions

Under phenomenon PE6 we consider the impacts of inadvertent (but otherwise undefined) nitric acid addition to the alkaline waste solution feed prior to ultrafiltration and subsequent introduction of the acidified waste to the CsIX. If the amount of nitric acid added were insufficient to make the waste feed itself acidic, no change in the expected behavior of the CsIX process is anticipated aside from precipitation of metal ions having greater solubility in stronger NaOH concentrations (e.g., iron, chromium, plutonium, and particularly aluminum; see Figure 6-3 of Delegard and Jones (2015)). These precipitated solids would be removed by filtration. However, one might also postulate an increased plutonium solubility if carbonate were present in the initial alkaline waste and the waste solution pH were lowered to ~10. In this case, an enhanced plutonium concentration might be attained through carbonate complexation with solubility up to ~0.5 g Pu/liter in 1 M carbonate attainable (see Figure 5-6 of Delegard and Jones (2015)), depending on the availability of plutonium in the solution. However, the maximum

plutonium concentration observed in actual waste solution is about 0.02 g Pu/liter (Figure 5-1 of Delegard and Jones (2015)). Because the dissolved plutonium carbonate species is anionic, it should pass through the cation-absorbing resin but the dissolved plutonium would be separated from other metal ions including aluminum, chromium, iron, nickel, and manganese though not from uranium, which also forms anionic carbonate complexes, nor from sodium.

If sufficient acid were added to make the feed solution acidic, the plutonium and ions of the absorber elements could distribute themselves differentially onto the CsIX. Aluminum also would precipitate as $Al(OH)_3$; this solid may be difficult to redissolve in acid without vigorous mixing, heating, and generally aggressive treatment. It is noted that the CsIX RF resin is designed to sorb cationic (positively charged) species, such as the radioactive $^{137}Cs^+$ desired to be removed from solution, and H^+, the agent used to displace the Cs^+ during elution. If the feed were made acidic, it would include typical sludge and salt-cake waste constituents such as sodium, iron, chromium(III), aluminum, nickel, manganese, and uranium, all of which are cationic in acid, and the dissolved plutonium, which in <6 M HNO_3 is also cationic. In this case, these cationic materials would sorb onto the RF resin and the resin's capacity would be quickly exceeded, particularly given the preference of the RF resin for the H^+ present, and no effective separation would occur.

At higher HNO_3 concentrations (e.g., >6 M HNO_3), however, the plutonium would be present as an anionic species and not sorb on the resin. At the higher H^+ concentration, the cationic metal ions also would be readily displaced to join the plutonium. Therefore, limited, but little, segregation of plutonium from the cationic absorber ions (e.g., Al^{3+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Na^+, and UO_2^{2+}) would occur as they all would exit the CsIX column. We also note that the RF resin is highly susceptible to degradation in strong HNO_3 (King et al. 2006). The plutonium concentration available in solution again would be limited to ~0.02 g/L.

Inadvertent addition of HNO_3, at concentrations up to 8 M, could occur at many points in the WTP process. Should this happen, it could cause preferential precipitation or dissolution of absorbers or fissile material, or preferential precipitation once the acidified waste is neutralized. The range of impacts such inadvertent addition might incur are considered within the other phenomena discussed in this section of the report.

2.1.5   PE11 – Water Additions, OP3 – Waste Over-Concentration or Dry Out in Evaporator, and OP5 – Pipe or Jumper Leak

Phenomenon PE11 involves the influence of water addition through normal processing. With respect to the influence of HNO_3, this action would only have the effect of diluting HNO_3, and thus only altering its intended utility in plant application. Phenomena OP3 and OP5 are concerned with unintended process solution evaporation; both phenomena have the effect of increasing the HNO_3 concentration for HNO_3 solutions. Thus, because the influences of these phenomena are solely to change HNO_3 concentration, their impacts are not any different than those already considered for phenomena PE1 through PE6.

Conclusions to Section 2.1 – The potential of HNO_3 to alter the distribution of plutonium and absorber elements in WTP processes have been considered. The greatest effect HNO_3 might have on criticality safety seems to be the disproportionate dissolution of absorber element materials away from the plutonium solids as considered under phenomena PE1, PE2, PE3, and PE4. In the cases of PE2, PE3, and PE4, the expected

impact of leaving plutonium-rich solids behind after HNO₃ treatment would be tempered by the close attachment such solids (blockages, coatings, scales) would have with the underlying stainless steel and its complement of iron, nickel, and chromium absorber. The likely existence of refractory plutonium oxide, PuO₂, in tank waste and its known resistance to dissolution in HNO₃ (evident in that much of the PuO₂ present in the tank waste originated from dissolver heels from the PFP) makes this issue of particular criticality concern even though radiolytic spallation (metamictization) should diminish the crystallinity of PuO₂ with time. In general, however, based on studies of actual tank waste radiochemical analyses, lab process testing, and plant process experience, most plutonium is present in an intimate mixture with absorber materials through coprecipitation. Therefore, proportionate dissolution of the plutonium and the absorber should occur following treatment with HNO₃. Subsequent treatment of the resulting HNO₃ solution with NaOH solution, as would occur in WTP processing, would cause the dissolved plutonium and absorber to re-precipitate and thus not alter their relative distributions even at intermediate pH given the parallel precipitation dependence of pH of plutonium and the absorbers aluminum, chromium, iron, and uranium in the acid to neutral range and the low solubilities of manganese(IV) and nickel at neutral pH. Potential accumulation of ~0.1-kg quantities of plutonium on the ion exchange column might occur based on lab test results, nominally high plutonium feed solution concentrations, and plausible process flow rates and durations. However, in limited testing, the plutonium in the eluate is accompanied by absorber elements including chromium, iron, nickel, manganese, and sodium.

2.2 Nitric Acid / Oxalic Acid Effects

Potential issues regarding the disposition and relative distributions of plutonium and absorber materials in the waste feed solution and solids arise from the use of HNO₃, and/or oxalic acid, H₂C₂O₄, to clean the cross-flow ultrafilters in the WTP. These issues were raised based on phenomenon PE8 as described in Table 1-1 and in Table 2-3.

Table 2-3. Chemical Phenomena Associated with
Nitric Acid / Oxalic Acid Chemistry Effects

Number	Process	WTP System(s)
PE8	Nitric and/or oxalic acid used to clean the ultrafilters	UFP

Cross-flow ultrafilters are used to clarify the alkaline feed to the CsIX modules which contain the RF ion exchange media. Solids entering the CsIX have the potential to block solution flow through the RF granules and necessitate costly replacement of the media. This ultrafiltration occurs through 0.1-μm sintered metal pipe filter in which the upstream slurry flows tangentially across the filter surface along the inside of the pipe, driving the solution outward through the pores (as permeate), while the tangential flow prevents accumulation of a deep filter cake that would obstruct solution flow through the filter (Section 2.3.5.2 of Jenkins et al. (2013)). With continued operation, a solid film nevertheless forms, decreasing the permeate flow. To overcome this slowing of flow, the ultrafilters will be cleared of occluding solids by pressurized backpulsing to force the occluding solids back into the flowing slurry (2.3.5.3 of Jenkins et al. (2013)). Periodically, however, chemical cleaning of the filters using 2 M HNO₃

is envisioned, followed by a treatment with 2 M NaOH (Section 2.3.4.4 of Jenkins et al. (2013)). Laboratory testing indicates that supplemental treatment with $H_2C_2O_4$ solution may be effective in dissolving iron-bearing solids (Section 2.3.5.4 of Jenkins et al. (2013)).

Chemical agents were investigated for their efficacies in dissolving $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, MnO_2, and $Na_2U_2O_7$, solids known to be present in Hanford tank waste sludges (Sinkov 2003). Scoping tests investigated 22 individual agents, all aqueous solutions, including organic acids and their salts; hydroxycarboxylic acids; organic alcohols; aminocarboxylic acids and their salts; and two mineral acids, HNO_3 and hydrofluoric acid, HF. Testing of mixed citric/oxalic acids (CITROX) and mixed $HNO_3/H_2C_2O_4$ acids (NITROX) in various ratios also was performed (note that both citrate and oxalate may be present in tank waste solution such that acidification could produce a weak CITROX-like reagent). Overall, $H_2C_2O_4$ was the most effective single reagent, dissolving all of the solid phases to some extent. However, re-precipitation soon followed dissolution for MnO_2 and $Na_2U_2O_7$. The MnO_2 also oxidized $H_2C_2O_4$ and citric acid as shown by bubbling when these components were combined. The mixed CITROX and NITROX reagents showed no beneficial synergistic sludge dissolution effects. Based on this testing, a sequential addition of individual pure reagents such as initial treatment with citric acid to dissolve MnO_2 and $Na_2U_2O_7$ followed by $H_2C_2O_4$ to dissolve the $Fe(OH)_3$, $Cr(OH)_3$, and $Al(OH)_3$, may be more effective than individual or blended reagents in dissolving Hanford tank waste sludges.

2.2.1   PE8 – Nitric and/or Oxalic Acid Used to Clean the Ultrafilters

In phenomenon PE8, concern is expressed that HNO_3 and $H_2C_2O_4$ solutions, individually (or perhaps combined as NITROX) may differentially dissolve plutonium and/or absorber material caught in the ultrafilters. This material could then precipitate in the plant wash and disposal system when the acidic dissolver solution is treated with NaOH.

The potential differential dissolution of plutonium and sludge components by use of HNO_3 is considered in the "Nitric Acid Effects" (Section 2.1 of the present document), specifically in consideration of phenomenon PE1. The differential dissolution of plutonium and sludge components by use of $H_2C_2O_4$ is examined in the present section.

The action of $H_2C_2O_4$ to dissolve $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, MnO_2, and $Na_2U_2O_7$ bulk tank waste sludge components show this reagent to be effective for $Fe(OH)_3$, $Cr(OH)_3$, and $Al(OH)_3$. It also will attack MnO_2 and $Na_2U_2O_7$ but the manganese and uranium re-precipitate as $MnC_2O_4 \cdot 2H_2O$ and $UO_2C_2O_4 \cdot 2H_2O$, respectively (Sinkov 2003). Of the 22 reagents tested to dissolve $Fe(OH)_3$, $H_2C_2O_4$ was found to be the most effective. The transition metal ions, such as Fe^{3+}, Mn^{2+}, and Cr^{3+}, form complexes with oxalate and thus can buffer the free oxalate concentration to limit the efficacy of $H_2C_2O_4$.

The plutonium contained as coprecipitate within bulk sludge components dissolved by $H_2C_2O_4$ is also expected to dissolve. Small discrete $PuO_2 \cdot xH_2O$ particles that had been formed by hydrolysis of plutonium nitrate, oxalate, fluoride, and organic "crud" compounds in alkaline solution are likely to exist in Hanford tank waste sludges (see Sections 5.3.1 and 5.3.2 of Delegard and Jones (2015)). Because of their small (nanometer-scale) size, these particles are expected to dissolve by the action of $H_2C_2O_4$ as a complexant under acidic conditions, but experimental evidence of such action was not found in the technical literature. If such dissolution were to occur, the plutonium would join the plutonium released by dissolution of the host iron and other bulk sludge coprecipitate. In contrast, dissolution of plutonium

present in the sludge as particles from PuO_2 scrap recovery is unlikely owing to the large (tens-of-microns-scale) size of the particles and correspondingly low specific surface areas, as well as the refractory nature of PuO_2, which is notoriously difficult to dissolve even in much more aggressive process conditions.

Once in solution, the potential exists that plutonium, if sufficiently concentrated, might precipitate with oxalate to form $Pu(C_2O_4)_2 \cdot 6H_2O$. This precipitation chemistry is exploited in plutonium processing as the means to purify plutonium by separating it from other metals present as contaminants (e.g., aluminum, chromium, iron, nickel, and uranium; Facer Jr and Harmon (1954)), and as a pathway to form plutonium dioxide, PuO_2, by subsequent calcination of the Pu(IV) oxalate precipitate. As shown in Figure 2-1, however, Pu(IV) oxalate is relatively soluble (e.g., ~0.03 to 0.3 g Pu/L in 0.05 to 0.2 M $H_2C_2O_4$ in 0.1 M HNO_3) as compared with its concentration in sludge (maximum ~0.02 g Pu/kg dry sludge; see Figure 5-1 of Delegard and Jones (2015)). Furthermore, much of the oxalic acid would be complexed with iron, thus lowering its effective concentration (e.g., Section 3.3 of Nash (2012)). Therefore, because of low concentration and competition from iron and other metals, it is very unlikely that the Pu(IV) oxalate will precipitate as a discrete phase by treating plutonium-bearing sludge with $H_2C_2O_4$.
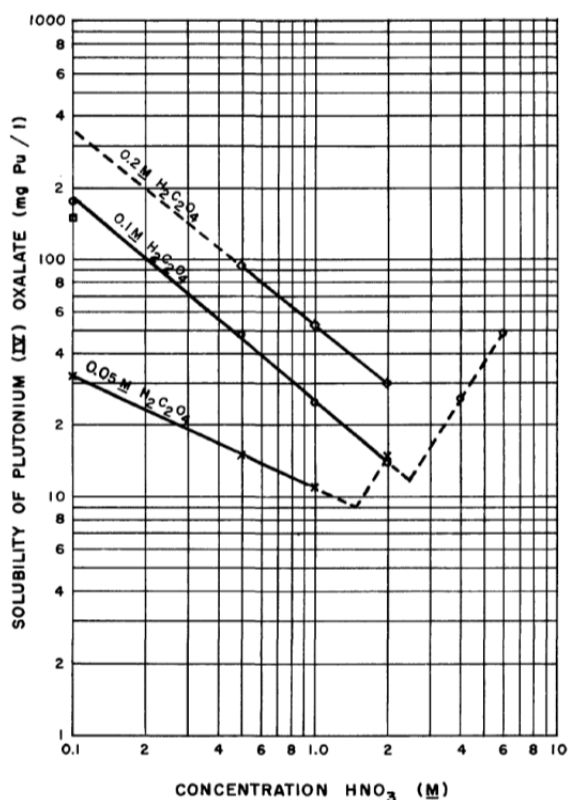
Figure 2-1. Pu(IV) Oxalate Solubility in HNO_3-$H_2C_2O_4$ Solutions (Facer Jr and Harmon 1954)

However, coprecipitation of Pu(IV) oxalate with $MnC_2O_4 \cdot 2H_2O$ or $UO_2C_2O_4 \cdot 2H_2O$, should they form by treatment of sludge solids with $H_2C_2O_4$, cannot be excluded. The coprecipitation of Pu(IV) within $MnC_2O_4 \cdot 2H_2O$ or $UO_2C_2O_4 \cdot 2H_2O$ (Mn(II) and U(VI) oxalate, respectively) has not been demonstrated. However, Pu(IV) (and Pu(III)) are known to coprecipitate with Th(IV), U(IV), Bi(III), and La(III)

oxalates (Table IV-14 of Coleman (1965)) and with Ca(II) and Pb(II) oxalates (Jarvinen 2009). Therefore, the carrier precipitation of plutonium with Mn(II) or U(VI) oxalate is plausible.

The solution arising from treatment of sludge solids collected on ultrafilters using $H_2C_2O_4$ is therefore expected to contain dissolved aluminum, iron, chromium, and, likely, nickel oxalate complexes. The solution will also include oxalate complexes of any plutonium coprecipitated with the sludge solids that had been dissolved and oxalate complexes of plutonium dissolved from the nanometer-scale $PuO_2 \cdot xH_2O$ crystallites formed in waste disposal operations from alkaline hydrolysis of plutonium nitrate, oxalate, fluoride, and organic "cruds." Solids present after treatment of sludge with $H_2C_2O_4$ would include materials not susceptible to attack by $H_2C_2O_4$ such as silica (SiO_2), refractory PuO_2, and the solids formed by metathesis and ensuing precipitation processes such as $MnC_2O_4 \cdot 2H_2O$ and $UO_2C_2O_4 \cdot 2H_2O$. As noted, the solid Mn(II) and U(VI) oxalates may incorporate dissolved plutonium by carrier precipitation processes that are analogous to the Pu(III) and Pu(IV) carrier precipitation processes observed with other metal oxalates.

The solution and solids mixture arising from the $H_2C_2O_4$ treatment would, upon being made alkaline with NaOH, largely revert to their original state, with the hydroxide displacing the oxalate from the metal ion to form the corresponding hydroxide or, in the case of U(VI), the sodium diuranate salt $Na_2U_2O_7 \cdot xH_2O$. The Mn(II) oxalate, formed by MnO_2 reduction and then Mn(II) precipitation by $H_2C_2O_4$ during the sludge dissolution step, is readily hydrolyzed and the Mn(II) oxidized by dissolved atmospheric oxygen to restore MnO_2.

However, if solid/solution separation occurred after the sludge dissolution step by use of $H_2C_2O_4$, the solids would contain undissolved particulate PuO_2 that could have lower relative amounts of absorber than the starting sludge. Therefore, according to conditions accessible under phenomenon PE8, segregation of plutonium from absorber elements potentially can occur in $H_2C_2O_4$ treatment of sludge solids collected onto ultrafilter surfaces. This segregation is similar to the segregation that might occur by treatment of sludge with excess HNO_3, as considered in phenomenon PE1, but the severity of the segregation under phenomenon PE8 is tempered by the potential distribution of the absorber element compounds Mn(II) oxalate and U(VI) oxalate to the solid phase containing the undissolved PuO_2.

> *Conclusions to Section 2.22.2 – The influence of HNO_3 and $H_2C_2O_4$ to alter the distribution of plutonium and absorber elements in Hanford tank wastes within WTP processes are considered in phenomenon PE8. The actions of HNO_3 by itself are considered under phenomenon PE1, which indicates the potential for refractory particles of PuO_2 to segregate from any of the absorber elements whose compounds can dissolve in HNO_3. The actions of $H_2C_2O_4$ to alter the distribution of plutonium and absorber elements are similar to those of HNO_3 but the severity of the segregation is tempered by the probable, but untested, distribution of the solid absorber element compounds Mn(II) oxalate and U(VI) oxalate to remain with the undissolved PuO_2.*

2.3 Sodium Hydroxide Effects

There are widespread potential issues surrounding the disposition and relative distributions of plutonium and absorber materials in the waste feed solution and solids as a result of the influence of hydroxide concentration. These issues were raised in phenomena PE9, PE10, PE11, RE2, OP3, OP5, and OP7 as shown in Tables 1-1, 1-2, and 1-3 and in Table 2-4.

Table 2-4. Chemical Phenomena Associated with Hydroxide Chemistry Effects

| Number	Process	WTP System(s)
PE9	Caustic leaching	CXP, HLP
PE10	Sodium hydroxide additions	Pretreatment
PE11	Water additions	WTP-wide
RE2	Oxidative leaching	UFP
OP3	Waste over-concentration or dry-out in evaporator	Pretreatment Evaporators (FEP, CNP, TLP)
OP5	Pipe or jumper leak	WTP-wide
OP7	Aluminum precipitation carries down dissolved plutonium	UFP

Two of these phenomena, RE2 and OP7, pertain to specific processing steps and absorber materials, respectively. In RE2, the influence of improperly controlled hydroxide concentration on oxidative leaching by permanganate is considered. In OP7, the influence of changes in hydroxide concentration is considered as part of various chemical processes that can affect aluminum precipitation and dissolution in association with plutonium. The impacts of hydroxide concentration changes on phenomenon RE2 are addressed in Permanganate Effects, Section 2.5 below. Many of the impacts of hydroxide concentration on phenomenon OP7 are found in Section 2.7, Organic Effects. Further, while phenomenon OP1 (related to absorption of atmospheric carbon dioxide into alkaline process solution) decreases hydroxide concentration, its outcomes are addressed in Carbonate Effects, Section 2.4.

Phenomena PE9, PE10, PE11, OP3, and OP5 are concerned with the outcomes of alterations or incorrect levels in hydroxide concentration occasioned by sodium hydroxide (NaOH) overdose (PE9 and PE10), sodium hydroxide underdose (PE9), process solution evaporation (OP3 and OP5), and process solution dilution (PE11). These phenomena and their influences on the relative distributions of plutonium and absorber compounds will be considered together as they are functionally equivalent.

2.3.1 PE9 – Caustic Leaching, PE10 – Sodium Hydroxide Additions, PE11 – Water Additions, OP3 – Waste Over-Concentration or Dry-Out in Evaporator, and OP5 – Pipe or Jumper Leak

The concerns arising from phenomena PE9, PE10, PE11, OP3, and OP5 relate to relative differences in the dissolution or precipitation of plutonium and absorber compounds incurred by increases or decreases in hydroxide concentration. The solubilities of hydrated Pu(IV) oxide and of various (hydr)oxide compounds of absorber elements as functions of hydroxide concentration are compared in Figure 2-2 (taken from Figure 6-1 of Delegard and Jones (2015)). It is noted that up to 19 M NaOH solution is available in the WTP but that solubility data at NaOH concentrations higher than indicated in Figure 2-2 were not found in the technical literature. Absorber element compounds include those of cadmium, chromium (as Cr(III)), iron, manganese(II), manganese(IV), nickel, and uranium. The absorber element aluminum has relatively high but complicated solubility behavior in molar NaOH solution (see Figure 6-2 of Delegard and Jones (2015)). Much of the behavior of aluminum is considered in the Organic Effects section, but the effect of hydroxide concentration on the solubility of the more common

aluminum compound gibbsite (Al(OH)₃) is considered in the present section. Sodium salts of the absorber elements boron and hexavalent chromium (Cr(VI)) and sodium itself have molar solubilities in NaOH solution and thus effectively partition to the solution phase. These soluble salts are present interstitially within the solids in amounts proportional to the solids' interstitial volume fraction and the salt solution concentrations. It is also noted that solubilities can be influenced by the presence of dissolved salts, which, in general, can increase the chemical activity of NaOH in solution. Temperature also can impact solubility. The effects of temperature increase on the solubilities of aluminum and iron phases in NaOH solution are described in Sections 2.8.1 and 2.8.2, respectively. Though the impact of temperature increase on solubility is appreciable, it is only about a factor of 2-3 over a normal solution process range of ~20 to 70° C, while NaOH concentration increase over normal process ranges (e.g., 0.5 to 5 M NaOH) can effect order-of-magnitude solubility changes for some metals, as seen in Figure 2-2.
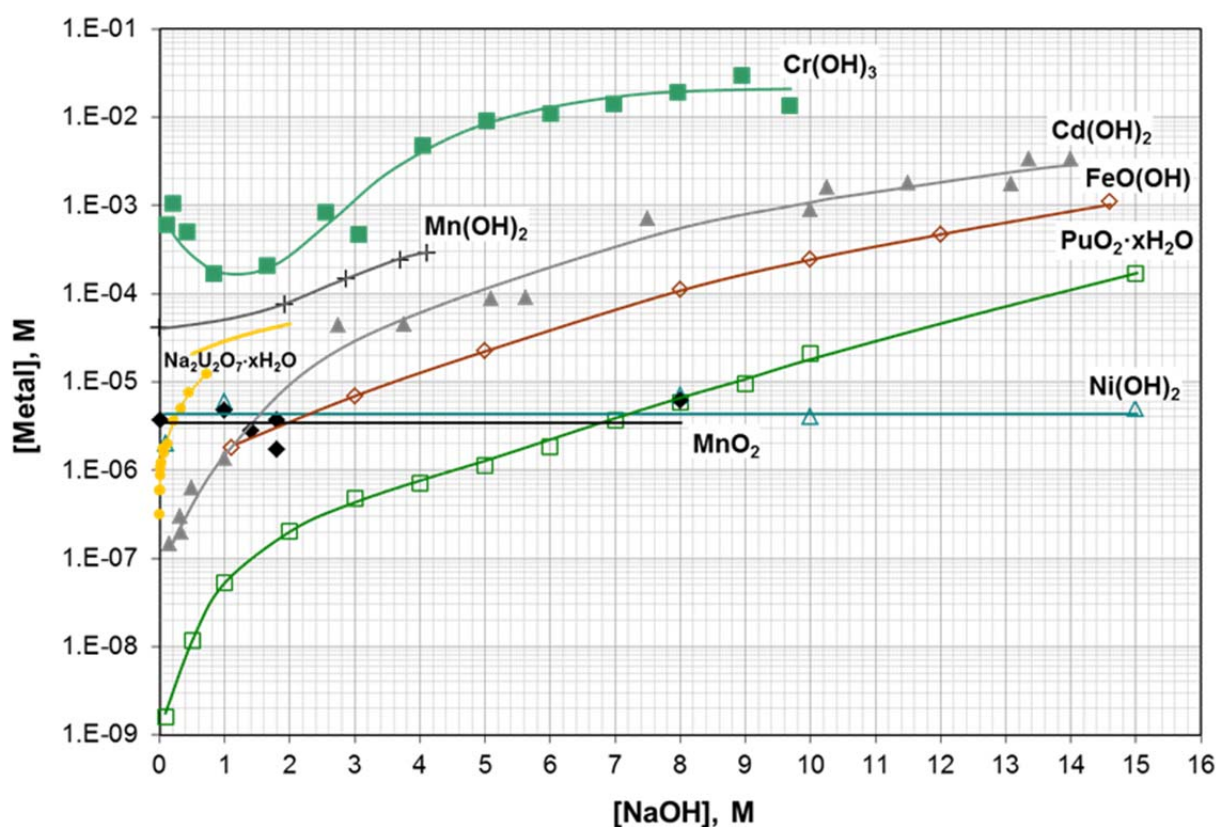
Figure 2-2. Solubilities of PuO₂·xH₂O and Various (Hydr)Oxides of Absorber Elements as Functions of Sodium Hydroxide Concentration

As shown by the following arguments, NaOH concentrations varying from 1 M to multi-molar values are not expected to significantly alter the relative distributions between the solids and the solution phases of plutonium and the solid phase absorber compounds identified in Figure 2-2.

From Figure 2-2, it is seen that the solubility behaviors of the (hydr)oxide compounds can be grouped into two types. For nickel as $Ni(OH)_2$ and manganese as MnO_2, no discernable change of solubility occurs as the NaOH concentration varies, whereas for $PuO_2 \cdot xH_2O$ and the absorber element compounds $Cd(OH)_2$, $Cr(OH)_3$, $FeOOH$[1], $Mn(OH)_2$, and $Na_2U_2O_7 \cdot xH_2O$, the solubilities increase in parallel with increasing hydroxide concentration.

For $Ni(OH)_2$ and MnO_2, the solubilities, at $\sim 4 \times 10^{-6}$ M, are relatively small, as is the solubility of $PuO_2 \cdot xH_2O$—2×10^{-5} M or less (i.e., ≤ 0.005 g Pu/L) below 10 M NaOH. Therefore, the propensity for manganese as MnO_2 or nickel absorbers to separate from plutonium by selective dissolution is small as NaOH concentration changes. This small differential between $PuO_2 \cdot xH_2O$ and $Ni(OH)_2$ or MnO_2 dissolution still occurs even though plutonium coprecipitates well with MnO_2 but does not coprecipitate with $Ni(OH)_2$ (see Sections 6.1.6 and 6.1.5, respectively, of Delegard and Jones (2015)).

For $PuO_2 \cdot xH_2O$ and the $Cd(OH)_2$, $Cr(OH)_3$, $FeOOH$, $Mn(OH)_2$, and $Na_2U_2O_7 \cdot xH_2O$ absorber compounds, the solubilities change in a parallel manner with NaOH concentration changes. In the case of iron, the most important absorber, the molar solubility of FeOOH, goethite, is ~ 200-times higher than that of $PuO_2 \cdot xH_2O$ (Figure 2-2), while the iron itself is present at ~ 3000-times higher molar concentration than is plutonium in the tank waste inventory (data from Delegard and Jones (2015)). This means that even for the small amount of plutonium that dissolves, a similar relative fraction of iron will dissolve and that the plutonium dissolved upon increased NaOH concentration will remain accompanied, in 200-fold molar excess, by its most prevalent neutron absorber. The responses of the cadmium, Cr(III), Mn(II), and uranium absorber compounds are similar to that of iron.

Overall, despite the increasing solubility of the plutonium and absorber compounds with NaOH concentration, their concentrations remain relatively low so that the driving force for their dissolution and thus their separation is small even if NaOH concentrations are raised inordinately. At low, but still alkaline, hydroxide concentrations, the solubilities of plutonium and the absorber (hydr)oxide compounds are even smaller and thus offer even less opportunity for segregation by selective dissolution.

The potential sorption of dissolved plutonium onto sludge solids also should be considered. As discussed in Section 6.2 of Delegard and Jones (2015), however, evidence for plutonium sorption onto iron (hydr)oxide solid phases must be examined carefully as some tests showing extremely high sorption were conducted under conditions exceeding plutonium's solubility. In the most careful and relevant tests, uptake onto tank waste sludge solids, including iron (hydr)oxide phases, decreased plutonium concentrations about a factor of two to three. Sorption of Pu(V) species from alkaline solution onto hydrated thorium oxide, lanthanum hydroxide, and silicate minerals as well as plutonium sorption onto engineered sodium titanate absorbents also is observed (Delegard and Jones (2015) and references therein and Hobbs and Pulmano (1999), respectively).

Of the absorber elements, only aluminum, boron, and Cr(VI) salts have significant solubilities under alkaline conditions. The Cr(VI) salts are present in alkaline waste solution but are also formed by permanganate-mediated oxidative dissolution of low-solubility Cr(III) compounds such as $Cr(OH)_3$.

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[1] [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 $\sim 100°$ C (Fedoseev et al. 1998). Goethite and other FeOOH phases have been identified in Hanford tank sludges (Delegard and Jones (2014) and references therein).

Because the $Cr(OH)_3$ can contain coprecipitated plutonium and oxidative leaching will convert the $Cr(OH)_3$ and related compounds to soluble $Cr(VI)$ salts, plutonium dissolution (and oxidation) may also occur. Chemical phenomena related to oxidative leaching of $Cr(III)$ are addressed in Section 2.5, Permanganate Effects. Boron is soluble as its sodium salts and is not likely to be present to a significant extent in the solid phase. Boron concentrations in Hanford tank waste solutions are low but concentrations in WTP solutions may become appreciable because of the boric acid introduced in borosilicate glass production.

Coprecipitation of plutonium with the $Al(III)$ hydroxide compound gibbsite, $Al(OH)_3$, is known to be negligible and the solubility of gibbsite increases with increased NaOH concentration (Delegard and Jones (2015) and references therein). Therefore, the separation of the absorber element aluminum from plutonium with increasing NaOH concentration is likely because the aluminum will dissolve under strongly alkaline conditions while most of the plutonium will remain in the solid phase.

The fraction of plutonium dissolved from actual sludge by treatment with strong NaOH solution is small. The propensity of plutonium to be leached from sludge by NaOH solution has been investigated as part of testing of aluminum-bearing solid dissolution by NaOH solutions (Rapko et al. 2004). Results of prior leach testing, including leaching by NaOH solution in the absence of oxidants (e.g., permanganate, MnO_4^-, or ozone, O_3) aside from air or oxygen (O_2) for sludges from twelve different waste tanks are provided in Tables 1.3 and 1.4 of Rapko and colleagues' 2004 report. Leaching tests were run for 24 to 203 hours at 30° C to 100° C using 0.1 to 4.8 M NaOH. For most tests, less than 1% of the plutonium dissolved. The amounts exceeded 1% only for tests at higher (≥3 M) NaOH concentrations, but did not exceed 3% for any test. Therefore, even for dissolution of aluminum-bearing phases in strong and heated NaOH solution, little plutonium dissolution occurred. Based on plutonium-bearing tests in which various combinations of aluminum, iron, and uranium solid phases were present (Fedoseev et al. 1998; Krot et al. 1998b), it is likely that it was the iron in the actual waste sludge solids reported by Rapko and colleagues (2004), Table 4-1) that contributed to the low plutonium leaching.

> *Conclusions to Section 2.3 – The propensity for plutonium to separate from absorber elements cadmium, trivalent chromium, iron, manganese, nickel, or uranium by differential dissolution or precipitation of their compounds based on changes in NaOH concentration is low. Of the absorber elements, only aluminum, boron, and Cr(VI) salts have molar solubilities under alkaline conditions, such that most of the absorber element is dissolved, while the solubility of plutonium as $PuO_2 \cdot xH_2O$ remains low. Because the $Cr(OH)_3$ can contain coprecipitated plutonium and oxidative leaching will convert the $Cr(OH)_3$ and related compounds to soluble Cr(VI) salts, plutonium dissolution also has potential to occur under oxidative dissolution conditions. Coprecipitation of plutonium with gibbsite is negligible, but gibbsite can dissolve while appreciable $PuO_2 \cdot xH_2O$ remains by treatment with high concentration NaOH solution. This means that separation of the absorber element aluminum from plutonium with increasing NaOH concentration is likely. However, in caustic dissolution tests with actual sludges from twelve different waste tanks, no significant plutonium dissolution was observed implying that other materials present in the sludge (e.g., iron (hydr)oxides) successfully retained the plutonium in the solid phase even under conditions in which aluminum (hydr)oxide phases dissolved.*

2.4 Carbonate Effects

Potential issues on the disposition and relative distributions of plutonium and absorber materials in the waste feed solution and solids as a result of the influence of carbonate were raised in phenomena OP1, OP7, and OP8 as shown in Table 1-3 and in Table 2-5.

Table 2-5. Chemical Phenomena Associated with Carbonate Chemistry Effects

Number	Process	WTP System(s)
OP1	**Carbonate formation results in plutonium dissolution**	WTP-wide PJM-mixed vessels
OP7	Aluminum precipitation carries down dissolved plutonium	UFP
OP8	Sodium carbonate addition	HFP

The chemical phenomena associated with carbonate in the waste are of two types. Phenomena OP1 and OP8 can potentially alter the plutonium:absorber ratio in the solid and solution phases by selectively dissolving the plutonium by carbonate complexation. Dissolution of absorber element compounds by carbonate is expected to be low except in the case of uranium. The OP1 and OP8 phenomena differ only in the source of the carbonate, with OP1 arising from scrubbing of carbon dioxide from air by capture in alkaline solution, and OP8 occurring by addition of sodium carbonate, Na_2CO_3, by misrouting (Na_2CO_3 is a component used in glass-making).

In contrast, the carbonate of concern in phenomenon OP7 arises from the oxidative decomposition of organics present in the alkaline waste. Organic oxidation reactions also decrease hydroxide concentration. These carbonate and hydroxide concentration changes would only occur to a significant extent if the waste were stored an inordinate length of time (months or more) and then would act to decrease aluminum solubility by lowering the pH to favor precipitation of gibbsite from solutions that contain aluminum dissolved as aluminate, $Al(OH)_4^-$. At even lower pH, the increasing carbonate concentration in the waste also can precipitate dawsonite, $NaAlCO_3(OH)_2$. Precipitations of these aluminum phases can potentially affect plutonium:aluminum distributions. Mention of the OP7 phenomenon is provided here for completeness, but full discussion is found in Section 2.7, Organic Effects, and therefore will not be addressed further in the present section.

Holmesmith (2014) examines in detail the roles of absorption of atmospheric carbon dioxide and the decomposition of organic compounds by chemical or radiolytic effects to increase carbonate concentrations in Hanford tank wastes. Holmesmith (2014) also adapted an empirical model of carbon dioxide absorption by alkaline radioactive tank wastes at the Savannah River Site (Hobbs 1987) to Hanford tanks.

2.4.1 OP1 – Carbonate Formation Results in Plutonium Dissolution and OP8 – Sodium Carbonate Addition

Carbonate addition to plutonium-bearing waste solid slurries can occur by air infusion via the pulse jet mixers (PJMs) and spargers, phenomenon OP1, and by inadvertent addition of sodium carbonate,

Na_2CO_3, a glass frit component, to the wastes, phenomenon OP8. In air infusion, atmospheric carbon dioxide, CO_2, reacts with the NaOH in the alkaline waste slurry to form sodium carbonate, Na_2CO_3. Further CO_2 addition would form sodium bicarbonate, $NaHCO_3$, from the Na_2CO_3:

$$2\ NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2\ NaHCO_3.$$
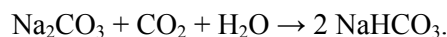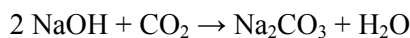
Because NaOH is consumed by the reaction to form Na_2CO_3, the solution pH necessarily decreases. For example, equimolar $NaHCO_3$-Na_2CO_3, with pH ~10, is created by treating NaOH with CO_2 at a 3:2 NaOH:CO_2 mole ratio.

It is known that plutonium solid-phase solubility in sodium carbonate and bicarbonate solution is markedly higher than the solubilities observed in carbonate-free solution and that the plutonium solubility increases with the square of sodium carbonate and bicarbonate concentration (Figure 5-6 of Delegard and Jones (2015)). Thus, in highly alkaline (i.e., pH ≥12) solution containing 1 M Na_2CO_3, plutonium concentrations are 10^{-6} to 10^{-5} M 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 (see, respectively, Figures 5-6, 5-5, and 6-3 of Delegard and Jones (2015) and Figure 13 of Delegard (1985)). It is noted that while the impact of carbonate on plutonium solubility decreases as the alkalinity increases to molar hydroxide concentration, up to ten-fold increase in plutonium concentration can be attained even in 3 to 5 M NaOH in the presence of 1 M carbonate. It is significant to note that observations of high plutonium solubility made in genuine Hanford tank waste solutions are consistent with the concentrations found in lab testing with simpler idealized systems (Figure 5-6 of Delegard and Jones (2015)). Plutonium concentrations in less-alkaline but bicarbonate-bearing pH 9 to 10 solution are ~200-times greater than for a pH ≥12 solution having equivalent carbonate concentration. Plutonium concentrations found in bicarbonate-free pH 9 to 10 solution are about 10^{-10} M to 5×10^{-9} M (Figures 5-6 and 6-3, respectively, of Delegard and Jones (2015)). However, if such solutions are made 1 M in bicarbonate, the contained plutonium solubility becomes ~2×10^{-3} M, an increase in solubility by a factor of ~10^6.

At issue is whether the carbonate or bicarbonate in solution is sufficient to leach plutonium from plutonium-bearing precipitates containing absorber elements and whether compounds of the absorber elements themselves are susceptible to dissolution by carbonate or bicarbonate. Limited tests of plutonium leachability were conducted for alkaline precipitates prepared from nitric acid solutions containing varying initial concentrations of uranium(VI) (0-0.16 M), iron(III) (0-0.60 M), and aluminum(III) (0-1.1 M) in 1 M HNO_3 containing 0.001 M Na_2SiO_3 (Krot et al. 1998b). Each solution contained 1.9×10^{-4} M Pu(IV) (and americium) and each solution was precipitated by addition of 16 M NaOH titrated to reach 0.01 M excess NaOH (i.e., pH ~12) at 40° C. The plutonium concentrations in the mother solutions derived from the precipitation tests were all on the order of 10^{-8} M and apparently were independent of precipitate composition.

The separated product solids then were contacted with a 5 M sodium nitrate ($NaNO_3$) / 1 M Na_2CO_3 solution to determine the leachability of plutonium. If the bulk precipitate contained only uranium or uranium plus aluminum, the degree of plutonium leaching by the carbonate solution was similar to that of the uranium itself. 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. It is likely that because uranium is very susceptible to carbonate dissolution and carbonate leaching is

used, in fact, to dissolve uranium from ores in the ground or in ore heaps, carbonate leaching of the uranium solids succeeded in dissolving not only uranium solids but also the accompanying plutonium. However, the degree of plutonium leaching into the carbonate solution in these tests decreased markedly in proportion to 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 carbonate-resistant Fe(III) hydroxide precipitate.

The iron solid phase generally was found to be amorphous, i.e., showed no crystal pattern by x-ray diffractometry; but x-ray evidence of goethite, FeOOH, was found in some tests. In tests of simulant sludges for which uranium was present and iron was present in Fe:Pu mole ratios ranging from 360:1 to 3200:1 (mass ratios from 84:1 to 750:1), the quantity of plutonium dissolved by leaching in 1 M Na_2CO_3 ranged from about 7% to 27% while uranium dissolution ranged from about 27% to 89% (Krot et al. 1998b). Based on these findings, it is likely that much of the leached plutonium arose from dissolution of the uranium with which it was associated.

In further testing, mixed uranium, iron, and aluminum precipitates containing minor concentrations of added plutonium were prepared by precipitation of their 1 M HNO_3 solutions with excess NaOH solution (Fedoseev et al. 1998). These conditions are similar to those occurring in treatment of acidic Hanford process wastes in anticipation of disposal into the mild steel underground waste tanks. The simulated sludge solids were water-washed and the washed solids leached using 0.25 and 0.5 M $NaHCO_3$. The sludge solids' compositions and leach test outcomes are shown in Table 2-6 (Fedoseev et al. 1998).

Table 2-6. Composition of Samples and Plutonium Quantities Leached by Bicarbonate

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	

Tests 1 and 2 (Table 2-6), prepared without iron, dissolved completely in the bicarbonate, while the iron-bearing solids in Tests 3 and 4 had undissolved residue after bicarbonate leaching. The amounts of plutonium dissolved by $NaHCO_3$ solution leaching were highly dependent on whether or not iron was present. With iron present (at a Fe:Pu mass ratio of ~100), plutonium dissolution decreased from about 95% to about 6%. Unlike iron, the presence of aluminum did not affect the resistance of the solid phase to plutonium leaching by bicarbonate.

The findings from these two studies show that carbonate and bicarbonate act as effective dissolving agents or leachants for plutonium from absorber materials that contain aluminum or uranium, but that the effectiveness drops significantly for plutonium associated with iron. Results of supplemental tests by Fedoseev and colleagues (1998) indicate that plutonium chemical association with the iron and uranium solid phases formed in alkaline solution by coprecipitation is strong but that plutonium does not coprecipitate with aluminum.

The results of these two studies (Krot et al. 1998b; Fedoseev et al. 1998) and the known chemistry of the aluminum, iron, and uranium absorbers in these alkaline and alkaline/carbonate solutions indicate that plutonium interactions with iron (hydr)oxides and sodium diuranate by way of coprecipitation are strong. However, because sodium diuranate and hydrated plutonium oxide dissolve in (bi)carbonate solution, any plutonium associated with the sodium diuranate is susceptible to leaching. In contrast, because plutonium associates strongly with iron (hydr)oxides under alkaline coprecipitation conditions, and because iron (hydr)oxide resists dissolution by (bi)carbonate, plutonium remains with the iron solid phase in (bi)carbonate leaching. The association of plutonium with aluminum is poor, with the result that plutonium leaching from sludge solids containing only aluminum solid phase (gibbsite, in this case) should be complete.

The following inferences might be made based on these findings and on the expected responses of other absorber compounds to carbonate leaching. The selectivity of carbonate as a uranium lixiviant for *in-situ* and heap leaching means that oxides of most other metals are not susceptible to solubilization by such treatment (Edwards and Oliver 2000). Therefore, oxides of metals other than uranium known to be effective in coprecipitating plutonium (e.g., iron, chromium, cobalt, lanthanum, manganese, and zirconium; see Section 6.1 of Delegard and Jones (2015)) should resist carbonate/bicarbonate dissolution and, in chemical analogy with iron, retain any contained coprecipitated plutonium.

Oxides or hydroxides of nickel and aluminum, which do not incorporate plutonium by coprecipitation (Fedoseev et al. 1998), would be ineffective in shielding plutonium from leaching by (bi)carbonate. In addition, plutonium that had not been discharged into the tank waste under coprecipitation mechanisms but instead is present in the waste as solids (e.g., process losses as PuO_2 particles and hydrolysis products of plutonium compounds such as plutonium nitrate, oxalate, various fluorides, and plutonium-bearing solvent extraction crud; Section 5.3 of Delegard and Jones (2015)) likewise should be susceptible to leaching and dissolution by (bi)carbonate. Freshly formed hydrated plutonium oxide, called plutonium hydroxide, dissolves readily in carbonate solution (Cunningham 1954) but the rates of dissolution by (bi)carbonate of other hydrolyzed and aged hydrolysis products are unknown and the rates are likely to be low for refractory materials such as high-fired PuO_2.

Finally, the potential sorption of dissolved plutonium onto sludge solids should be considered. However, evidence for sorption onto iron (hydr)oxide solid phases must be examined with care. Some tests that show extremely high sorption were conducted under conditions exceeding plutonium's solubility. In the most careful and relevant tests, uptake onto tank waste sludge solids, including iron (hydr)oxide phases, decreased plutonium concentrations about a factor of two to three (Section 6.2 of Delegard and Jones (2015)) and it would seem that carbonate complexation of the plutonium would diminish any tendencies to sorption. And while sorption of Pu(V) species from alkaline solution onto hydrated thorium oxide, lanthanum hydroxide, silicate minerals, and non-speciated plutonium onto engineered sodium titanate absorbents is observed (Section 6.2 of Delegard and Jones (2015) and references therein), again, carbonate complexation of the dissolved plutonium would be expected to diminish sorption on these solids as well.

> *Conclusions to Section 2.4 – Plutonium compound solubility is strongly enhanced by the presence of carbonate at pH ~12 and higher, and even more strongly enhanced by bicarbonate, at pH 9 to 10. The plutonium concentrations in both cases increase with the square of the (bi)carbonate concentration. The extent of leaching of plutonium from solids that contain coprecipitated plutonium depends on the susceptibility of the host*

solids that contain the plutonium to dissolution in (bi)carbonate. Laboratory testing shows that iron-bearing precipitates are not susceptible to dissolution in (bi)carbonate and thus resist leaching of their contained plutonium, while uranium-bearing solids dissolve in (bi)carbonate solution and thus release their contained coprecipitated plutonium. It is expected that compounds of other absorbers that are known to be effective coprecipitating agents for plutonium (e.g., chromium, cobalt, lanthanum, manganese, and zirconium) and which have themselves low susceptibility to (bi-)carbonate leaching, will resist leaching of their contained plutonium by (bi)carbonate. Compounds of the absorber elements aluminum and nickel do not coprecipitate plutonium, and plutonium leaching from aluminum solids by (bi)carbonate has been demonstrated. Therefore, leaching of plutonium from nickel solids by (bi)carbonate is also highly likely. Intrinsic plutonium solids present in the waste, such as PuO_2 discharged to the waste in that form or formed by plutonium compound hydrolysis, are expected to be susceptible to dissolution by (bi)carbonate, although at rates that may be low—especially for high-fired PuO_2.
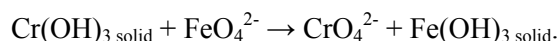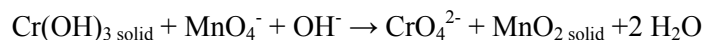
2.5   Permanganate Effects

Phenomena RE2, RE3, and OP4 raise potential issues surrounding the disposition and relative distributions of plutonium and absorber materials in the waste feed that could result from the influence of permanganate (see Tables 1-2 and 1-3 and Table 2-7).

Table 2-7. Chemical Phenomena Associated with Permanganate Chemistry Effects

Number	Process	WTP System(s)
RE2	Oxidative leaching	UFP
RE3	Excess permanganate added during oxidative leach	UFP
OP4	Impact of strontium/TRU precipitation	UFP

Sodium permanganate, $NaMnO_4$, and other oxidants including persulfate, $S_2O_8^{2-}$, ferrate, FeO_4^{2-}, and peroxynitrite, $ONOO^-$, were extensively tested for their efficacies in the oxidative dissolution of trivalent chromium, Cr(III), solid phases from both sludge simulants and actual Hanford tank waste sludges (Rapko et al. 2002; Rapko and Vienna 2002; Rapko et al. 2004). Permanganate and ferrate proved to be the most efficient reagents for oxidative dissolution of the Cr(III) solid sludge component to form soluble chromate, CrO_4^{2-}, from the Cr(III) solid. Low solubility manganese dioxide, MnO_2, and ferric hydroxide, $Fe(OH)_3$, are the respective products from these oxidants. The permanganate and ferrate oxidative dissolution processes for $Cr(OH)_3$, a representative Cr(III) sludge solid, are described by the following reactions:

$$Cr(OH)_{3\ solid} + MnO_4^- + OH^- \rightarrow CrO_4^{2-} + MnO_{2\ solid} + 2\ H_2O$$

$$Cr(OH)_{3\ solid} + FeO_4^{2-} \rightarrow CrO_4^{2-} + Fe(OH)_{3\ solid}.$$

As indicated, dissolution of one mole of Cr(III) hydroxide by permanganate consumes one molar equivalent of hydroxide while the oxidation by ferrate has no hydroxide ion dependence. Therefore, to ensure complete dissolution using permanganate, the initial hydroxide concentration should be maintained at a sufficient level to avoid hydroxide depletion and termination of the desired oxidative dissolution

reaction. Although both permanganate and ferrate efficiently dissolve the Cr(III) solids, ferrate was not considered for further testing or WTP implementation because of its much lower thermal stability with respect to oxidizing water itself, thus requiring refrigerated storage of this aqueous reagent (Rapko et al. 2004).

We note that oxidative leaching at high alkalinity also may produce other chemical effects including partial dissolution of certain sludge components. Greater dissolution of chromium, iron, uranium, and cadmium and aluminum solid phases can occur solely by increase in the alkalinity (Figures 6-1 and 6-2, respectively, of Delegard and Jones (2015)). Significantly, the solubility of plutonium as its tetravalent hydrated dioxide ($PuO_2 \cdot xH_2O$) also increases as alkalinity increases by the formation of negatively charged Pu(IV) hydroxide complexes. However, the oxidative action of permanganate in alkaline solution has a stronger effect by converting Pu(IV) to the much more soluble Pu(VI) (Figures 5-4 and 5-5 of Delegard and Jones (2015)). For example, the solubility-limited concentrations for Pu(VI) as shown in Figure 5-5 of Delegard and Jones (2015) are ~0.0001 M (~0.02 g/L) and 0.01 M (~2 g/L) at 0.25 and 3 M NaOH, respectively, assuming excess permanganate and access by the permanganate to the plutonium solid phase. The solubility of Pu(IV) solids in the absence of oxidation is lower at the same NaOH concentrations by about a factor of 10^4. The enhanced plutonium solubility afforded by permanganate oxidation thus can impact the distribution of plutonium and absorber element compounds in the sludge.

The interaction of permanganate with redox-sensitive constituents of Hanford tank sludges in alkaline media can be better understood by comparison of the electrochemical potential-versus-pH equilibrium diagrams of the subject elements (Pourbaix 1974). Thus, we note that Fe(III) potentially can be oxidized to its highest known oxidation state of +6 (ferrate) in a strongly alkaline medium by permanganate. This behavior, among others, is considered in the following discussion.

2.5.1   RE2 – Oxidative Leaching

In phenomenon RE2, concern is expressed that inadvertent use of excessive NaOH concentrations can dissolve plutonium by oxidative leaching. This can occur directly by reagent addition, as well as by failing to drain and rinse the original waste solution from the feed sludge. While it is known that the solubilities of key non-radioactive absorber components (aluminum, cadmium, chromium(III), and iron) as well as uranium and plutonium increase with increased NaOH concentration in the absence of oxidizers (Figures 6-1 and 6-2 of Delegard and Jones (2015)), permanganate in alkaline solution can further enhance plutonium solubility by converting Pu(IV) to Pu(VI) (Figures 5-4 and 5-5 of Delegard and Jones (2015)).

A series of studies conducted with genuine sludge washed of contained soluble salts using permanganate in low (0.1 M) and high (3 M) NaOH were performed by Rapko and colleagues (1997; 1998; 2002; 2002); these findings are conveniently summarized in Table 1.3 of Rapko et al. (2004)). The leaching generally was done at 80° C but tests at 30° C also were reported. In these tests, conducted with sludge from eight different tanks, plutonium dissolution was invariably enhanced by increasing the NaOH concentration to 3 M. From 0.01 to 1.5% of the plutonium dissolved (depending on the starting sludge) at 0.1 M NaOH while at 3 M NaOH, under otherwise similar conditions, from 2% to 69% of the plutonium dissolved. Overall, an average 70-fold enhancement in the amount of plutonium dissolution occurred by leaching at 3 M NaOH compared with leaching at 0.1 M NaOH.

Subsequent studies with genuine sludges from tanks 241-SY-102 and 241-SX-101 show that permanganate addition to the standard 3 M NaOH leach solution produces the greatest plutonium dissolution enhancement of all the leach strategies tested (Rapko et al. 2004). However, Rapko and colleagues (2004) noted that further increasing the initial NaOH concentration from 3 M to 5 M in the presence of a greater permanganate excess lowers plutonium dissolution. They also found that a standard 3 M NaOH leach that takes place after permanganate addition with 0.25 M NaOH dissolves more plutonium than reversing the order (i.e., performing the standard 3 M NaOH caustic leach followed by the permanganate leach in 0.25 M NaOH). This delayed plutonium dissolution is believed to occur due to kinetic effects in the following manner. First, the plutonium actually dissolved during the initial oxidative leach step. However, the plutonium re-precipitated during cooling and washing in the low-alkalinity solution. This freshly precipitated plutonium then was available to rapidly re-dissolve during the subsequent relatively short 8-hr standard 3 M NaOH caustic leach. Rapko and colleagues (2004) also showed that a small enhancement in plutonium dissolution occurs by conducting oxidative leaching at 85° C rather than at 25° C.

We also note that a change in the reduction pathway of permanganate is likely at higher hydroxide concentrations. At lower hydroxide concentrations, permanganate, Mn(VII), reduces to MnO_2, Mn(IV), a three-electron process. However, at higher (3 M) hydroxide concentrations, permanganate may reduce only to manganate, Mn(VI), a one-electron process, because of the increased stability of manganate with respect to disproportionation. Manganate was observed during simulant sludge dissolution testing at 3 M NaOH (Sinkov 2007). If permanganate reduces to manganate only, as favored by higher alkalinity, then Cr(III) phase dissolution may be incomplete. Although this would limit the desired Cr(III) oxidative dissolution with ensuing impacts to vitrification, this situation would benefit criticality safety by leaving the plutonium incorporated with the undissolved Cr(III) solids and other insoluble sludge components having good neutron absorption properties.

Based on the laboratory testing and knowledge of the potential-pH (Pourbaix) diagrams, Fe(III) hydroxide is redox-inert to the oxidative action of permanganate in mildly alkaline solution. Most of the oxidative leach testing on sludge simulants and genuine tank sludges was performed at mild 0.1 M to 3 M NaOH. Consideration of phenomenon RE2 makes it important to examine the possibility that much higher alkalinity might induce partial or complete dissolution of the Fe(III) phase from the sludge by permanganate oxidation of Fe(III) (hydr)oxides to soluble Fe(VI) species (i.e., ferrate, FeO_4^{2-}) as shown by the relevant electrode potentials. Although Fe(VI) is a strong oxidant, it is stabilized in concentrated hydroxide solutions. According to data on standard electrode potentials (Bratsch 1989), the Fe(VI)/Fe(III) couple potential at pH 14 (1 M NaOH) is +0.71 V to +0.81 V, depending on the crystallinity of the Fe(III) phase, while for the soluble Fe(III) species, $Fe(OH)_4^-$, the potential is +0.62 V. The Fe(VI)/Fe(III) couple potential also is highly dependent upon the hydroxide concentration:

$$FeO_4^{2-} + 4\ H_2O + 3\ e^- \rightleftharpoons Fe(OH)_3 + 5\ OH^-,$$
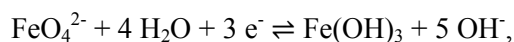
meaning that the reduction potential decreases by $0.0591 \times 5/3 \cong 0.10$ V for each log unit of hydroxide chemical activity increase. Assuming that a ten-fold increase in NaOH concentration yields a ten-fold increase in chemical activity of hydroxide, the above-listed Fe(VI)/Fe(III) potentials would decrease by at least ~0.10 V. Because the actual increase in hydroxide activity with NaOH concentration increases at a greater rate than this, the change in potential is even greater than 0.10 V.

Although the Fe(VI)/Fe(III) potential decreases markedly with increasing NaOH concentration, the Mn(VII)/Mn(VI) couple potential, +0.56 V (Bratsch 1989), is independent of NaOH concentration (Delaude and Laszlo 1996):

$$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}.$$
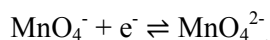
This means that at ~10 M NaOH, the Fe(VI)/Fe(III) and Mn(VII)/Mn(VI) potentials become comparable such that oxidative dissolution of amorphous Fe(III) hydroxide by permanganate at very high alkalinity cannot be excluded. Practically, however, accumulation of soluble ferrate will be limited by the initial moderate permanganate dosage and by the ready permanganate consumption by Cr(III) conversion to chromate. In addition, any soluble ferrate formed under these conditions is expected to oxidize water to oxygen with the reduction of Fe(VI) back to the much less soluble Fe(III) species.

Both Pu(IV) and Pu(VI) form anionic species in alkaline solution such as $Pu(OH)_5^-$ for Pu(IV) and $PuO_2(OH)_3^-$ for Pu(VI) (Section 5.2 of Delegard and Jones (2015)). Increased NaOH concentration increases the number of hydroxide ions entering the primary coordination sphere of these species, which may cause these initial anionic forms to acquire additional negative charge such as $Pu(OH)_6^{2-}$ for Pu(IV) as noted by Delegard and Jones (2015) and references therein. This negative charge is expected to prevent any uptake of plutonium complexes by cation-exchange RF resin columns to be used for the removal of cesium and other unhydrolyzable metal cations. However, the chemical reduction of the more soluble Pu(VI) hydroxide complex to the less soluble $Pu(OH)_5^-$ or $Pu(OH)_6^{2-}$ complex is plausible and could lead to deposit of finely divided $PuO_2 \cdot xH_2O$ solids within the RF resin bed especially as the RF resin could be a chemical reductant.

> *Conclusions to Section 2.5.1– Significant enhancement of plutonium dissolution from genuine washed sludge occurs when oxidative leaching using permanganate occurs with 3 M NaOH as compared with 0.1 or 0.25 M NaOH. The greater plutonium leaching at higher NaOH concentration may require supplemental NaOH concentration process controls. The enhanced leaching, by an average factor of ~70, is likely due to plutonium being oxidized to the more soluble hexavalent state. Dissolved plutonium species in alkaline solution are anionic and their sorption on cation-sorbing RF resin should not occur to a great extent, although limited sorption is observed (Section 2.1.3). While the solubilities of (hydr)oxide compounds of aluminum, cadmium, iron, and uranium (but not manganese and nickel) increase with leach solution alkalinity, helping preserve the plutonium/absorber ratio in solution, the plutonium/absorber ratio may be altered in oxidative dissolution of discrete plutonium phases such as PuO_2 or $PuO_2 \cdot xH_2O$. In this case, some separation of plutonium from absorbers could occur. Deposition of $PuO_2 \cdot xH_2O$ solids within the RF resin bed also is plausible by chemical reduction of dissolved Pu(VI) hydroxide complexes.*

2.5.2   RE3 – Excess Permanganate Added during Oxidative Leach

The concern expressed in phenomenon RE3 is that excessive permanganate addition during the oxidative leach could preferentially oxidize and dissolve the plutonium or absorbers to alter their ratios in the solution or residual solids. The process intent in oxidative leaching is that solid Cr(III)-bearing phases present in Hanford tank sludge be converted to soluble Cr(VI) species. Tests with actual waste sludges indicate that in most cases, better than 85% dissolution can be achieved with stoichiometric addition of permanganate with respect to molar equivalents of Cr(III) in the sludge (Rapko et al. 2004; Rapko and

Vienna 2002; Rapko et al. 2002). These studies also show that slightly super-stoichiometric addition of permanganate at up to 15% excess increases Cr(III) dissolution efficiency to ~95% and higher. The chemical reduction product of permanganate in the Cr(III) oxidation process is mostly insoluble MnO_2. However, when excess permanganate is present and the Cr(III) is dissolved, the remaining permanganate slowly oxidizes water to form manganate. Manganate itself has limited stability in weakly alkaline (i.e., <1 M NaOH) media and can either disproportionate to MnO_2 and permanganate or simply oxidize water itself to form MnO_2. In either event, the ultimate reduction product is MnO_2.

In a recent study, the WTP pretreatment flowsheet steps were applied to Group 5 (i.e., REDOX Process) waste combined with Group 6 (i.e., S-Saltcake) waste on a laboratory scale basis (Fiskum et al. 2009). Parametric testing was conducted to determine the oxidant dosage required to dissolve chromium solid phases as well as characterize concomitant plutonium dissolution. Additionally, the fates of boron and cadmium, two potent neutron absorbers, were evaluated through all flowsheet processing steps. Among other things, it was found that a small fraction of plutonium dissolved during the oxidative leaching of the Cr(III) phases. As the NaOH concentration increased from 0.25 M to 1.4 M, the plutonium concentration increased ~7-fold (from 0.017 μM to 0.12 μM). These plutonium concentrations, as a function of the free hydroxide concentration, were consistent with the hydroxide dependence of Pu(IV) solubility exhibited in previously reported data ((Delegard 2006); see also Figure 5-5 of Delegard and Jones (2015)). Thus, no enhancement of solubility caused by oxidation to Pu(VI) was evident given that Pu(VI) is about four orders of magnitude more soluble than Pu(IV) at these NaOH concentrations. It was also found that there was no effect of Mn(VII)/Cr(III) ratio in the range from 0.95:1 to 1.7:1 on the extent of plutonium dissolution in the range of 0.09 M to 1.1 M NaOH.

During the demonstration test of the cross-flow ultrafilter for feed slurries conducted at a 1.7:1 Mn:Cr molar ratio and at 0.09 M NaOH (Fiskum et al. 2009), it was established that

- greater than 90% of the Cr but only 0.04% of the [239,240]Pu had leached from the solids

- the observed plutonium solubility from parametric testing at low alkalinity agreed with previously published data on plutonium solubility presented in a variety of studies

- the plutonium in the ion exchange feed largely partitioned to the effluent with ~4.2% found in the subsequent eluate and 0.18% found on the ion exchanger bed after elution was complete

- although the extent of boron partitioning during oxidative leaching was not determined, the final slurry contained less than 18% of the initial boron; 57% and 25% of the boron was removed from the sludge at the caustic leach and wash steps, respectively (i.e., the boron largely partitioned to solution)

- cadmium partitioning during oxidative leaching was less than 0.003% with about 90% of the cadmium present in the final slurry (i.e., the cadmium remained in the sludge solids).

Note that the tests done by Fiskum and colleagues (2009), though illustrative, may not represent worst-case conditions.

In other tests, a number of interesting observations was made on dissolution of solid $Pu(OH)_4$ (nominally $PuO_2 \cdot xH_2O$) in 0.25 M NaOH permanganate and manganate solutions in the absence of other solid phases (Sinkov 2007). The observations can be summarized as follows:

- significant $Pu(OH)_4$ dissolution by alkaline (0.25 M NaOH) permanganate solution occurred with up to 53% dissolved at a 3.4:1 Mn(VII):Pu(IV) molar ratio

- manganate is a much less efficient $Pu(OH)_4$ dissolving agent than is permanganate, dissolving only 6% to 15% under conditions otherwise similar to those in which permanganate dissolved 53%

- permanganate consumption in experiments with aged $Pu(OH)_4$ exceeded the expected 2:1 stoichiometry for even the least efficient reaction, $Pu(IV) + 2 Mn(VII) \rightarrow Pu(VI) + 2 Mn(VI)$. This gives evidence that catalytic reduction of Mn(VII) by water occurred in the presence of undissolved $Pu(OH)_4$.

- a 3:1 molar oxidation reduction stoichiometry was found with *in situ*-formed $Pu(OH)_4$ in an alkaline solution of Mn(VII), based on plutonium dissolution.

In the same report, preparation of a simplified REDOX Process sludge simulant was described. The simulant was based on NaOH solution treatment of an initially homogeneous acidic solution containing $Fe(NO_3)_3$, $Cr(NO_3)_3$, and $Pu(NO_3)_4$. The Fe:Cr:Pu molar ratios in the sludge simulant were 28500:21400:1. Oxidative leaching of this Fe:Cr:Pu coprecipitate with permanganate was performed at two NaOH concentrations.

At the lower 0.25 M NaOH concentration

- quantitative dissolution of the Cr(III) fraction by $NaMnO_4$ occurred, with stirring, in the first three minutes after Mn(VII) addition using a stoichiometric 1:1 Mn(VII)/Cr(III) mole ratio

- no radiometrically detectable plutonium was found in the leachate at 0.25 M NaOH regardless of contact time (up to 3 days) and a Mn(VII) molar excess of 1.12:1 with respect to Cr(III). The dissolved plutonium fraction was less than 1.8% and the estimated soluble plutonium was less than 10^{-7} M. The excess oxidant remained in the leachate solution as permanganate.

At the higher 3.0 M NaOH concentration

- dissolution of Cr(III) from the sludge simulant was very fast and quantitative if a sufficient amount of permanganate was added

- the leachate contained 32% of the plutonium (at 1.5×10^{-6} M) within the first three minutes after oxidant addition at a 1.15:1 Mn(VII)/Cr(III) mole ratio, but increasing to 1.45:1 Mn(VII)/Cr(III) mole ratio led to no further increase in the amount of plutonium dissolved

- the excess oxidant in the leachate was present as manganate although the amounts of manganate decreased with leach time

- the dissolved plutonium fraction left in contact with the metathesized sludge simulant decreased with time in the order 32% (3 min) $\rightarrow$ 21% (1 hour) $\rightarrow$ 18% (4.5 hours) $\rightarrow$ 13% (3 days) $\rightarrow$ 12% (6 days)

- no detectable plutonium was present in the leachate at substoichiometric Mn(VII)/Cr(III) mole ratios

- excess oxidant could be quenched by Cr(III) nitrate addition according to the following reaction:

$$3 \, MnO_4^{2-} + 2 \, Cr^{3+} + 4 \, OH^- \rightarrow 3 \, MnO_2 + 2 \, CrO_4^{2-} + 2 \, H_2O,$$
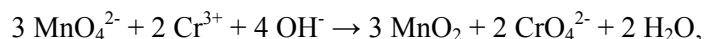
resulting in an additional 95% removal of plutonium from the leachate. As result of this treatment, the dissolved plutonium concentration decreased from 0.67 µM to 0.032 µM. Separate tests in which plutonium-bearing NaOH solution containing permanganate was treated with H_2O_2 corroborate these results and show 75% removal of plutonium from 2 and 4 M NaOH solution and >98% removal from 1 M

NaOH (Krot et al. 1998a). In the experiments by Krot and colleagues (1998a), the test solutions contained 0.02 M permanganate and 10^{-4} M Pu(VI) in 2 to 4 M NaOH, sufficient H_2O_2 was added to make the final concentration 0.05 M, and the tests were conducted at 50° C with separation after 3 hours.

> *Conclusions to Section 2.5.2 – With mitigation (i.e., removal), excess permanganate does not appear to have any supplemental effect on the distribution of plutonium to solution based on oxidative leaching of REDOX Process sludge simulants and genuine Cr(III)-bearing Hanford tank sludges. Accidental over-dosage of permanganate should not lead to enhanced plutonium leaching at lower alkalinity (0.09 to 0.25 M NaOH) while at higher alkalinity (3 M NaOH) the plutonium concentration increase to ~1.5 µM (only ~0.00036 g Pu/L) can be mitigated by addition of Cr(III) nitrate to the permanganate/manganate-containing slurry to eliminate excess oxidant and remove ~95% of the solubilized plutonium from solution via coprecipitation with and sorption onto freshly formed MnO_2. Plutonium dissolution by permanganate over-dosage at 2 to 4 M NaOH also may be mitigated by H_2O_2 addition, removing ~75% of the solubilized plutonium by coprecipitation with MnO_2. The behavior of plutonium in permanganate leaching is likely a combination of the lower stability of its more soluble Pu(V) and Pu(VI) forms at lower NaOH concentration, sorption onto undissolved sludge heel and MnO_2 solids, and coprecipitation with MnO_2.*

2.5.3   OP4 – Impact of Strontium/TRU Precipitation

According to Section 2.3.2.2 of Jenkins et al. (2013),

> Envelope C waste contains organic complexing agents that have complexed with some radioactive metals, resulting in the metals being dissolved in the liquid phase rather than remaining in the solid phase. The Envelope C treatment processing involves steps to break up the complexing agents precipitating TRU species. In addition, the remaining soluble radioactive strontium isotopes are diluted by the addition of nonradioactive strontium nitrate ($Sr[NO_3]_2$) diluting the radioactive species (p. 2, 3-2).

Removal of ^{90}Sr and TRU elements from Envelope C solutions may be done by treatment with non-radioactive strontium nitrate to carry ^{90}Sr and addition of sodium permanganate and sodium hydroxide to oxidize the organic complexing agents that solubilize the TRU. The TRU activity is provided primarily by americium and curium with some plutonium. Extensive work to study the removal of ^{90}Sr and TRU elements from the supernatant fraction in Envelope C wastes has been performed by Hallen and colleagues (2003; 2005; 2000). This team also developed a pretreatment process initially proposed by Orth et al. (1995) to remove not only ^{90}Sr and TRU elements but also ^{137}Cs and the entrained solids. The ^{90}Sr removal process consists of isotopic dilution by nonradioactive $Sr(NO_3)_2$ addition and precipitation of $SrCO_3$. The TRU removal process involves permanganate addition, organic complexant oxidation by way of stepwise manganese reduction (Mn(VII) → Mn(VI) → Mn(IV)), precipitation of Mn(IV) as MnO_2, and concomitant TRU coprecipitation. Characterization of plutonium, neptunium, and strontium on manganese solids, based on tests with waste simulants and using chemical and structural analysis, was performed by a team of Westinghouse Savannah River Company researchers (Duff et al. 2002). These studies showed the manganese-bearing solids to be sodium birnessite ($Na_4Mn_{14}O_{27}\cdot 9H_2O$) and the plutonium to be incorporated by coprecipitation. The entrained solids and Sr/TRU precipitate would be removed by crossflow filtration while the ^{137}Cs would be removed by ion exchange. One study was devoted to assessing Sr/TRU removal mechanisms using

241-AN-102 and 241-AN-107 tank waste samples (Hallen et al. 2003). This study aimed to apply earlier experiments on reaction mechanisms of TRU removal from simulants to actual waste samples from Envelope C tanks by added nonradioactive strontium and permanganate. The effectiveness of the various treatment conditions for TRU removal, measured as total alpha emitters, from AN-102 and AN-107 tank wastes is shown in Table 2-8.

Table 2-8. Comparison of TRU (sum of alpha) Decontamination Factors for AN-102 and AN-107 Waste Samples (24 hrs of exposure to precipitating and/or oxidizing agents)

Treatment agent	Decontamination factors (% removed) for TRU as (total alpha)	
	AN-102	AN-107
Sr/permanganate	**4.1 (76)**	6.8 (85)
Sr/permanganate duplicate	4.0 (75)	7.3 (86)
Permanganate	4.1 (76)	No data
Sr/manganate	No data	7.6 (87)
Sr/permanganate/hydroxide	3.1 (68)	No data
Sr/permanganate/no mixing	5.7 (82)	5.2 (81)
Sr/manganese dioxide solid	1.9 (47)	No data
Sr/manganese(II) salt	2.7 (63)	7.2 (86)

We note that about 90% of total alpha activity in the Envelope C wastes is represented by americium and curium isotopes which are of much less importance for criticality safety than plutonium as ^{239}Pu. However, the specific activity of ^{241}Am is about 55-times higher than that of ^{239}Pu. Therefore, neglecting the contribution of curium, the molar concentration of plutonium is about five-times greater than that of americium. However, decontamination factors for the combined ^{239,240}Pu were measured only for tests with AN-102 liquid waste and not AN-107 (Table 2-9).

Table 2-9. Comparison of Pu239, 240 Decontamination Factors for AN-102 Waste Samples (24 hrs exposure to action of precipitating and/or oxidizing agents)

Treatment agent	Decontamination factors (% removed) for ^{239,240}Pu
Sr/permanganate	**3.0 (67)**
Sr/permanganate duplicate	3.0 (67)
Permanganate	3.1 (68)
Sr/permanganate/hydroxide	2.1 (52)
Sr/permanganate/no mixing	2.9 (66)
Sr/manganese dioxide solid	1.2 (17)
Sr/manganese(II) salt	1.4 (29)

The molar concentration of ^{239,240}Pu in AN-102 supernatant is ~0.4 µM (Barney and Delegard 1999; Urie et al. 2002) while the concentrations of major neutron absorbers and their removed fractions are shown in Table 2-10.

Table 2-10. Concentrations of Major Neutron Absorbers in AN-102 Supernatant and Their Fraction Removed after Introduction of Precipitating and/or Oxidizing Agents (all data are for 24 hours of treatment)

Element	Initial conc., M	Amount removed, %, based on the treatment agents						
		Sr/Mn(VII)	Sr/Mn(VII) dup	Mn(VII)	Sr/Mn(VII) /OH	Sr/Mn(VII) no mixing	Sr/MnO$_2$	Sr/Mn(II)
Al	**0.22**	4	-3	8	6	5	-2	-5
Cd	0.00029	3	-2	7	5	6	-1	-3
Cr	0.0019	22	23	27	18	39	24	39
Fe	0.00017	73	74	74	72	83	49	61
Mn	0.000044	>39	37	2	>35	-126	-23	-233
Ni	0.0037	2	1	5	3	4	2	-1
Na	5.2	4	-6	8	0	3	-4	-5

A comparison of the two lowest transition metal concentrations (manganese and iron) with that of [239,240]Pu shows that the manganese- and iron-to-fissile-plutonium molar ratios are 110:1 and 425:1, respectively. The concentrations of three other transition metals (cadmium, chromium, and nickel) are several times higher than those of manganese and iron, but of those three, only chromium is removed from solution in appreciable quantities (18% to 39%). The most important aspect of all these transition metals' behaviors is that the percentage of iron removed (72 to 74%) is very close to that of plutonium (decontamination factor (DF) of 2.8 to 3.1, corresponding to 64% to 68% plutonium removed from solution). This means that both soluble and co-precipitated fractions of plutonium will be accompanied by a ~400-fold molar excess of iron, one the most efficient neutron absorbers. The precipitated fraction of plutonium will be additionally loaded with a very high excess of manganese in the form of freshly formed hydrated manganese dioxide, further reducing criticality concerns for this plutonium. More than 95% of the cadmium will remain in solution, allaying any potential criticality concerns for the soluble fraction of plutonium, which should contain no more than 0.13 µM plutonium (~0.00003 g Pu/L) after the Sr/Mn(VII) treatment.

Unfortunately, no DFs for [239,240]Pu were determined during the Sr/TRU removal from AN-107 supernatant. For this reason, neutron absorber-to-plutonium ratios cannot be calculated for any of the same seven treatment options as described above for the AN-102 liquid waste. Hallen and co-workers (2005) commented that

> … treatment of AN-107 waste under similar conditions gave much different results than AN-102. TRU removal (as sum of alpha) was significantly higher for most treatment schemes compared with correspondingly treated AN-102 sample. The results for Mn(II), IO$_4^-$, and Zr(IV) show that oxidation is not as important for TRU decontamination in AN-107 waste. This was somewhat surprising because AN-107 is initially higher in total organic carbon (TOC) and concentrations of soluble Fe and Mn. Co-precipitation, sorption, and ligand exchange result in high TRU removal from AN-107 waste. AN-102 waste may have higher concentrations of active complexants that require oxidation for effective TRU removal (p. 181).

The [239]Pu concentration in AN-107 supernate is 4.2 µM (Urie et al. 1999), about 10 times higher than that in AN-102 waste. Soluble iron and manganese concentrations are 30 and 26 times higher than the respective values for AN-102. Efficiencies of removal of these transition metals using the Sr/Mn(VII)

treatment are 97% (iron) and 94 ± 3% (manganese). The DF for TRU (total alpha) for these conditions is 7.1 ± 0.2. This corresponds to 86% of TRU removed from solution. However, no data are available on the percentage of ^{239}Pu that may contribute to the total alpha activity complement in AN-107 waste.

Assuming that all TRU activity is represented by ^{239}Pu, it can be deduced that the co-precipitated fraction of plutonium will be slightly enriched with co-precipitated iron and manganese compared with their concentration ratios in the initial solution. These precipitates also will be highly loaded with the manganese dioxide generated by permanganate reduction. If, on the other hand, we were to assume the opposite situation, i.e., that the DF for the TRU fraction results exclusively from ^{241}Am and that all of the plutonium remains in solution, then the TRU would be accompanied by soluble cadmium at a 450:1 Cd:Pu mole ratio (~210:1 mass ratio). No measureable cadmium is removed from solution by the Sr/Mn(VII) treatment. Therefore, all initially soluble cadmium will remain in solution to serve as a highly efficient neutron absorber for the soluble plutonium. Because the ^{239}Pu concentration is ~10-times greater in the AN-107 supernate than in the AN-102 supernate and the iron and manganese concentrations also are greater, it is most likely that plutonium decontamination using the Sr/Mn(VII) treatment of AN-107 is comparable to that of AN-102.

> *Conclusions to Section 2.5.32.5.3 – Comparison of decontamination factors for ^{239}Pu with those of major neutron absorbers for the AN-102 supernate suggests that after treatment with Sr/Mn(VII), both the co-precipitated plutonium and the residual soluble plutonium should be protected with 2 to 3 orders-of-magnitude higher molar concentrations of neutron absorbers. Despite lack of experimental data on ^{239}Pu DFs in tank AN-107 supernate, it is likely that Sr/Mn(VII) treatment was effective in removing plutonium. Evidence of decontamination of tank SY-101 from dissolved plutonium also is found through experimental studies. Overall, treatment of Envelope C wastes by Sr/Mn(VII) should improve criticality safety by carrying plutonium into the solid phase in the presence of co-precipitated iron and especially manganese.*

2.6 Cerium and Peroxide Effects

Phenomena RE5 and RE6 raise potential issues on the disposition and relative distributions of plutonium and absorber materials in the waste feed solution and solids from the application of tetravalent cerium and hydrogen peroxide within the HLW glass canister decontamination steps. These phenomena are also described in Table 1-2 and in Table 2-11.

Table 2-11. Chemical Phenomena Associated with Cerium Peroxide Chemistry Effects

Number	Process	WTP System(s)
RE5	Ceric nitrate solution added to plutonium-containing vessel heels	HDH
RE6	Hydrogen peroxide added to plutonium-containing vessel heel	HDH

The cerium (RE5) and peroxide (RE6) chemistry effects involve separate reactions but occur in sequential processes, as described in Table 2-11, and thus are addressed together in the present section. In phenomenon RE5, ceric nitrate, $Ce(NO_3)_4$, in nitric acid, HNO_3, is used to decontaminate the stainless steel HLW canisters by chemical milling; i.e., oxidative dissolution of the outer layer of the stainless steel canister. If the $Ce(NO_3)_4/HNO_3$ solution is misrouted, it may encounter plutonium or absorber material and cause differential dissolution and subsequent precipitation.

Phenomenon RE6 considers the effects of using hydrogen peroxide, H_2O_2, to chemically reduce any residual strongly oxidizing $Ce(NO_3)_4$ reagent remaining from the HLW canister decontamination step to relatively benign cerous nitrate, $Ce(NO_3)_3$. This concern arises from the potential differential distribution of plutonium and absorber materials occasioned by inadvertent overdose, excess addition, or misrouting to the process of H_2O_2.

Under flowsheet conditions, the acidic decontamination solution and associated acidic and water rinses are treated with H_2O_2 and then made alkaline with NaOH for subsequent processing with other wastes.

Ceric nitrate in nitric acid is used for HLW canister decontamination. It functions by oxidatively dissolving the outer layer of stainless steel from the canister to undercut any surface contamination deposits (Section 4.6.3.2.3 of Jenkins et al. (2013)). The reagent for this process is 0.047 M Ce(IV) in ~0.91 M HNO_3 (calculated from information in Section 4.6.3.2.2 of Jenkins et al. (2013)) and the processing occurs by immersion of the HLW canister in a bath of Ce(IV)/HNO_3 at 65° C. Under phenomenon RE5, it is postulated that this reagent also may differentially dissolve plutonium and/or absorber solids through similar oxidative processes. Hydrogen peroxide is used to treat the solution and rinses arising from the HLW canister decontamination process. Issues of potential separation of plutonium and absorbers related to the use of H_2O_2 are raised under phenomenon RE6.

The general outlines and quantities involved in these chemical processes are considered in the following paragraphs. The potential influences of tetravalent cerium, Ce(IV), in HNO_3, and H_2O_2 on plutonium chemistry also are described. Consideration of the outcomes under the designed process and process upset conditions are then examined.

The technical literature shows that PuO_2 dissolves at increased rates in HNO_3 solution that contains more than about 0.005 M Ce(IV) compared with Ce(IV)-free acid. For example, it has been found that the PuO_2 dissolution rate in 4 M HNO_3 containing 0.005 to 0.1 M Ce(IV) is approximately proportional to the solution's Ce(IV) concentration (Uriarte and Rainey 1965; Horner et al. 1977 for 0.01 to 0.1 M Ce(IV)). The PuO_2 dissolution rate observed in boiling 4 M HNO_3 containing 0.05 M Ce(IV) corresponds to a particle corrosion penetration rate of ~0.22 µm/hour—about a factor of 10 higher than the plateau rate prevailing in much lower Ce(IV) concentrations. At the 0.22-µm/h rate, a nominal 10-µm

diameter PuO_2 particle that is typical from oxalate processing (Section A.2 of Delegard and Jones (2015)) would require about one day to dissolve. The rate interpolated at 0.91 M HNO_3 containing 0.047 M Ce(IV) (i.e., the concentration to be used for HLW decontamination) is about half of that observed in 4 M HNO_3 (Harmon 1975), meaning that a nominal 10-µm diameter PuO_2 particle would require about two days to dissolve in boiling 0.047 M Ce(IV) / 0.91 M HNO_3.

The PuO_2 dissolution rate in Ce(IV)/HNO_3 solution also has an Arrhenius temperature dependence with activation energy of 14.5 kcal/mole or 61 kJ/mole (Horner et al. 1977). Therefore, the rate at the 65° C decontamination process temperature would be ~0.38 times the rate at boiling (~104° C), meaning that the nominal 10-µm diameter PuO_2 particle would require about five days to dissolve in 65°-C, 0.91 M HNO_3 containing 0.047 M Ce(IV) assuming no Ce(IV) concentration depletion.

Cerium(IV), Ce^{4+}, reacts with PuO_2 according to the following stoichiometry (Horner et al. 1977):

$$2\ Ce^{4+} + PuO_{2\ solid} \rightarrow 2\ Ce^{3+} + PuO_2^{2+}$$
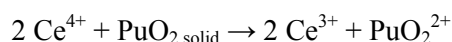
However, the reaction rate falls steeply once the Ce^{4+} concentration equals the product Ce^{3+} concentration (see Figure 6 of Horner et al. (1977)). Therefore, only about half of the Ce(IV) remains effective in oxidatively dissolving Pu(IV) oxide solids. Horner et al. (1977) posit that this effect is due to drop in the Ce(IV) oxidation potential as Ce(IV) concentration decreases and Ce(III) concentration builds.

The outer 304L stainless steel surfaces of each HLW canister will be cleaned in the WTP by use of ~810 liters of 65°-C, 0.047-M $Ce(NO_3)_4$ in 0.91 M HNO_3 (Section 4.6.3.2.2 of Jenkins et al. (2013)). The 304L is nominally 70 wt% iron, 19 wt% chromium, and 10 wt% nickel—other constituents ignored and being about 1 wt%—to give a mole ratio of about 0.70 Fe:0.20 Cr:0.10 Ni. Ceric nitrate acts by oxidative dissolution of the outermost layers of stainless steel according the following balanced chemical reaction:

$$3.5\ Ce^{4+} + \text{stainless steel (0.70 Fe, 0.20 Cr, 0.10 Ni)} + 0.7\ H_2O \rightarrow$$

$$3.5\ Ce^{3+} + 0.70\ Fe^{3+} + 0.10\ Cr_2O_7^{2-} + 0.10\ Ni^{2+} + 1.4\ H^+$$

According to the envisioned decontamination process, about 10 µm of thickness will be chemically milled from each 2-ft diameter, 14.75-ft tall, 304L stainless steel HLW canister during treatment (Sections 4.6.2 and 4.6.1 of Jenkins et al. (2013)). These dimensions correspond to a ~99 ft^2, or ~9.2×10^4 cm^2, canister surface area. Therefore, chemical milling to a 10-µm depth would remove about 92 cm^3 of stainless steel. At an 8.03-g/cm^3 density and Fe:Cr:Ni weight ratio of 70:19:10, the 92 cm^3 (~740 grams) of 304L stainless steel corresponds to ~517 g (9.3 moles) of iron, 140 g (2.7 moles) of chromium, and 74 grams (1.3 moles) of nickel. This corresponds to 46.5 chemical equivalents of metal oxidized to Fe(III), Cr(VI), and Ni(II) by the Ce(IV). The amount of Ce(IV) stock solution used to prepare the decontamination bath, 20 gallons of 0.5 M Ce(IV), only corresponds to 37.9 moles or chemical equivalents (based on Section 4.6.3.2.2 of Jenkins et al. (2013)). This apparent discrepancy between the amount of 304L stainless steel dissolved and the amount of Ce(IV) available to achieve this dissolution, given that all metal oxidation occurs by way of Ce(IV) reduction to Ce(III) (Section 4.6.3.2.3 of Jenkins et al. (2013)) may be due to unattributed metal oxidation dissolution reactions by the hydrogen ion, H^+. In any event, the spent solution produced in normal decontamination operations, even before subsequent treatment with H_2O_2, should be incapable of dissolving any PuO_2 it might encounter. Assuming negligible dilution, this ~810 liters of spent solution should contain about 0.047 M (6.6 g Ce/L)

Ce^{3+}, 0.011 M (0.64 g Fe/L) Fe^{3+}, 0.0016 M (0.17 g Cr/L) $Cr_2O_7^{2-}$, and 0.0016 M (0.09 g Ni/L) Ni^{2+}, based on the stated chemically unbalanced cerium versus 304L values (Jenkins et al. 2013).

Trace amounts of plutonium dissolved from the surface of the HLW canister would be hexavalent, present as PuO_2^{2+}, and be accompanied by the iron, chromium, and nickel credited neutron absorbers dissolved from the 304L present as Fe^{3+}, $Cr_2O_7^{2-}$, and Ni^{2+}. The nominal Ce^{3+} concentration in the spent cleaning solution would be 0.047 M meaning that, according to the above balanced chemical reaction, the corresponding respective iron, <u>total</u> chromium, and nickel concentrations from oxidative dissolution of the stainless steel would be 0.0094, 0.0027, and 0.00134 M and the HNO_3 concentration would be 0.93 M (0.91 M from the initial solution and 0.019 M from the acid produced by the reaction).

The decontamination solution is drained and the HLW canister rinsed with 200 gallons of 1 M HNO_3 spray followed by 200 gallons of water spray. The two rinses are combined with the 214 gallons of decontamination solution (Section 4.6.3.2.2 of Jenkins et al. (2013)). The resulting acidic solution is composed of 0.65 M HNO_3, 0.0164 M Ce^{3+}, 0.00328 M Fe^{3+}, 0.000468 M $Cr_2O_7^{2-}$, and 0.000468 M Ni^{2+}, assuming additive volumes (i.e., 614 gallons or 2324 liters) and proceeding from the nominal 10-µm depth of the chemical milling. This solution then is treated with 0.5 gallons of 30 wt% (9.77 M) H_2O_2 to chemically reduce any Ce(IV) that might still be present so that inadvertent corrosion of stainless steel apparatus downstream does not occur. Finally, the solutions collected from two HLW canister decontaminations are neutralized (made alkaline) by treatment with 5 M NaOH (Section 4.6 of Jenkins et al. (2013)).

The reaction of H_2O_2 with Ce^{4+} occurs by the following stoichiometry:

$$H_2O_2 + 2\ Ce^{4+} \rightarrow 2\ Ce^{3+} + O_2 + 2\ H^+$$
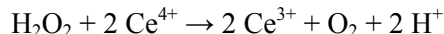
It is also known that H_2O_2 reacts with $Cr_2O_7^{2-}$ in acid solution to produce Cr^{3+}, although this reaction is not considered in the most germane process documents (Jenkins et al. 2013; Barton 2011). The dichromate reduction reaction occurs according to the following stoichiometry:

$$8\ H^+ + 3\ H_2O_2 + Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 3\ O_2 + 7\ H_2O$$
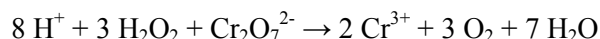
In acid solution, PuO_2^{2+} can be reduced by H_2O_2 to form Pu^{4+}. This reaction proceeds through Pu^{3+} but nitrate in the acid solution readily oxidizes Pu^{3+} to Pu^{4+} (Marsh and Gallegos 1987). The potentials for the PuO_2^{2+}/Pu^{4+} and PuO_2^{2+}/Pu^{3+} redox couples are nearly identical in 1 M acid, 1.0 V, and oxygen gas is formed from the H_2O_2. The potential of the $Cr_2O_7^{2-}/Cr^{3+}$ couple is 1.36 V and that of the Ce^{4+}/Ce^{3+} couple is 1.72 V, while the potential of H_2O_2 oxidation to oxygen gas (i.e., the H_2O_2/O_2 couple) is -0.695 V—all in unit H^+ activity (Bratsch 1989) while the HNO_3 concentration in the decontamination and rinse solution is 0.65 M HNO_3. Based on these electrochemical potentials, H_2O_2 is thermodynamically capable of reducing Pu(VI) to Pu(IV), Pu(VI) to Pu(III), Cr(VI) to Cr(III), as well as Ce(IV) to Ce(III) in acid.

Because the amount of H_2O_2 added is about 17.5 moles—much more than the amount of dichromate (1.09 moles) present after the chemical milling by the redox potentials and the quantities involved—there is more than sufficient H_2O_2 to convert all of the dichromate to Cr^{3+} and any trace PuO_2^{2+} to Pu^{4+}. Any excess H_2O_2, especially that catalyzed by the Fe^{3+} present, is rapidly lost through disproportionation to form water and oxygen gas:

$$2 \, H_2O_2 \rightarrow 2 \, H_2O + O_2.$$
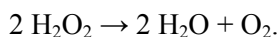
Because of this rapid gas-evolving reaction, H_2O_2 addition must be conducted in a measured manner to limit excessive disproportionation and foaming.

Based on full completion of the metal ion reduction reactions, the acid decontamination and rinse solution composition after treatment with 0.5 gallons of 30 wt% H_2O_2 would be 0.65 M HNO_3, 0.0164 M Ce^{3+}, 0.00328 M Fe^{3+}, 0.000936 M Cr^{3+}, and 0.000468 M Ni^{2+}, assuming additive volumes (i.e., 614 gallons or 2326 liters). Because the H_2O_2 disproportionation leaves no condensable residue aside from water, negligible dilution of all components and small chemical decrease in HNO_3 would occur, with the major change being the chemical reduction of dichromate and any Pu(VI).

It is important to note that if the Ce(IV) did not first spend itself on decontaminating the HLW canister by chemical milling of the 304L, the ~17.5 moles of H_2O_2 provided by the 0.5 gallons of 30 wt% solution would be slightly insufficient to reduce all of the Ce^{4+} (~38 moles based on 20 gallons of 0.5 M Ce^{4+}) to Ce^{3+} according to the 2:1 $Ce:H_2O_2$ molar reaction stoichiometry.

The final step in the HLW canister decontamination process is treatment of the solution with 5 M NaOH to neutralize the acid (Section 4.6.3.3.4 of Jenkins et al. (2013)). The amount of excess NaOH is not stated but by making the solution alkaline, the Ce^{3+}, Fe^{3+}, Cr^{3+}, Ni^{2+} and any trace Pu^{4+} would precipitate to form their respective (hydr)oxides, such as $Ce(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$, and $Ni(OH)_2$, with the plutonium coprecipitated and captured intimately within the $Fe(OH)_3$ and $Cr(OH)_3$ solids as demonstrated by Fedoseev et al. (1998). The $Ce(OH)_3$ likewise would capture plutonium based on chemical analogy with $La(OH)_3$, which is known to coprecipitate plutonium intimately (Fedoseev et al. 1998). The $Ce(OH)_3$ is readily oxidized by dissolved atmospheric oxygen to form $CeO_2 \cdot xH_2O$ in alkaline solution (Hayes et al. 2002), while peroxide under alkaline conditions is even more effective at accomplishing this oxidation (Yu et al. 2006). It is likely that the precipitating $CeO_2 \cdot xH_2O$ would readily coprecipitate any of the trace plutonium dissolved in the alkaline solution within its crystalline matrix based on the marked structural similarities of $CeO_2 \cdot xH_2O$ and hydrated Pu(IV) oxide, $PuO_2 \cdot xH_2O$. Interactions of plutonium with $Ni(OH)_2$ are not chemically intimate (Fedoseev et al. 1998), but this is not necessary given the higher concentrations of the other bulk metal hydroxides.

2.6.1 RE5 – Ceric Nitrate Solution Added to Plutonium-Containing Vessel Heels

Several outcomes arise in consideration of the dispositioning of the combined decontamination and rinse solutions under phenomenon RE5. For example, if the H_2O_2 were not added, even if the Ce(IV) were spent and only Ce(III) present, the chromium would be present as dichromate and the trace plutonium present as Pu(VI). The acid solution, when made alkaline by treatment with 5 M NaOH, would produce the hydroxide precipitates of Fe(III), Ni(II), and Ce(III) and the soluble $Cr_2O_7^{2-}$ convert to soluble chromate (CrO_4^{2-}). The plutonium dislodged from the HLW canister surface is relatively soluble Pu(VI) in alkaline solution (see Figure 5-5 of Delegard and Jones (2015)); however, Pu(VI) does not coprecipitate with Fe(III) or Al(III) when the acidic solution is made alkaline with excess NaOH. Pu(VI) does eventually precipitate in the presence of Cr(III), presumably by oxidizing some of the Cr(III) solids and forming much less soluble Pu(IV) (Fedoseev et al. 1998). Pu(VI) also can be carried by Pu(IV) solids (Budantseva et al. 1998). Therefore, the Pu(VI) formed from the HLW canister decontamination initially would remain in solution with the chromate. The chromium is almost certainly present in sufficiently high concentration to maintain a satisfactory plutonium:absorber ratio in solution. With time,

radiolysis ultimately will chemically reduce the Pu(VI) to the less soluble Pu(IV) and this plutonium would precipitate (Section 5.2 of Delegard and Jones (2015)) to join the Fe(OH)$_3$ and other sludge solids rich in neutron absorbing properties even though it would not be intermingled by coprecipitation.

However, the spent decontamination solution with rinse also could remain acidic overall if the quantity of NaOH added was insufficient or even zero. In this case, the acidic decontamination solution could dissolve solids, including plutonium, when added to alkaline sludge. In this case, the dissolved plutonium would be present with its original dissolved absorber compounds and would also have the iron, nickel, cerium, and chromium complement from the stainless steel dissolution. The plutonium:absorber ratio in the resulting acid solution would be much lower than the original ratio in the alkaline solids. If or when the solution would be made alkaline, the iron, chromium, nickel, and cerium from the decontamination solution would precipitate with the dissolved absorbers from the initial sludge and carry the plutonium, providing a lower plutonium:absorber ratio in the solids than was present in the starting solution.

Another possible upset is the direct misrouting of the 0.047 M Ce(NO$_3$)$_4$ in 0.91 M HNO$_3$ stainless steel HLW canister decontamination solution, or even the 0.5 M Ce(IV) used to prepare the decontamination solution, to encounter plutonium-bearing alkaline waste. For this scenario to be of greater risk than that of the contained acid alone, the active dissolving agent in the decontamination solution, Ce(IV), first must survive its own demonstrated reaction with the stainless steel piping and vessels it would encounter on the way to the alkaline waste. At the nominal 65°-C process temperature, the stainless steel corrosion penetration rate of the 0.047 M Ce(IV) decontamination solution is about (10 μm/6 h =) 1.7 μm/h. To a first approximation, the corrosion rate is proportional to Ce(IV) concentration at 2 M HNO$_3$ (Lerch 1968) and in 0.5 M HNO$_3$ (Bray et al. 1992). Therefore, the corrosion rate of stainless steel exposed to the 0.5 M Ce(IV) stock solution should be about 10 times that afforded by 0.047 M Ce(IV) at a given temperature. Should any Ce(IV) survive the stainless steel pipe and vessel passage, two different outcomes might occur when the Ce(IV)-bearing solution encounters the alkaline waste, depending on whether the resulting mixture is alkaline or acidic.

In the first case, the acidic decontamination solution and alkaline waste mixture might, together, be alkaline because of the excess alkaline capacity of the waste. Under alkaline conditions, the Ce(IV) would precipitate to form CeO$_2$ (Anis-ur-Rehman and Abdullah 2011). The oxidizing potential of CeO$_2$ in alkaline solution, -0.5 V (Bratsch 1989), is insufficient to cause oxidative dissolution of any solid phase Pu(IV) to more soluble Pu(V) or Pu(VI) oxidation states. This potential is also too low to oxidize any Cr(OH)$_3$ to soluble chromate. While it is likely that the precipitating CeO$_2$ would coprecipitate any trace Pu(IV) dissolved in the alkaline solution within its crystalline matrix because of the marked similarities of CeO$_2$ and hydrated Pu(IV) oxide, PuO$_2$·xH$_2$O structures, it is unlikely that Ce(IV) would carry down any Pu(V) and Pu(VI) dissolved from the original HLW canister decontamination processing or produced by Ce(IV) when it encountered the sludge but before the mixture became alkaline. The fully reacted alkaline product would have lower NaOH concentration than the starting alkaline waste, and thus would decrease further the already low plutonium and absorber metal solubilities (see Figure 6-1 of Delegard and Jones (2015)) and retain most of the plutonium in a solid phase that is even richer in absorber materials, thus improving criticality safety. However, the Pu(V) and Pu(VI) created by the acidic Ce(IV) would remain in the alkaline solution with any dissolved sodium salts and chromate to act as absorbers. It is unlikely that the Pu(V) and Pu(VI) concentrations would be sufficient to be of criticality concern, especially given the accompanying sodium and chromate.

In the second case, the Ce(IV) and alkaline waste mixture might remain acidic. The acid would dissolve to some extent the plutonium-bearing absorber solids such as $Fe(OH)_3$, and the Ce(IV) would oxidize the plutonium dissolved from the alkaline solids to Pu(VI), Pu(V) not being stable in acid solution, and oxidize any $Cr(OH)_3$ or related Cr(III) compound present to soluble dichromate. The Ce(IV) also would attack the stainless steel vessel holding the alkaline waste according to the reactions outlined for HLW canister decontamination until the Ce(IV) was spent and fully converted to Ce(III). The acidic solution thus would contain Pu(VI) dissolved from the sludge, the associated sludge neutron absorbers dissolved by the acid, and the additional iron, chromium, and nickel plus spent Ce(III) produced by stainless steel oxidative dissolution. The absorber:plutonium ratio in the acid solution would necessarily be greater than the ratio found for the original alkaline solids.

However, once the acid solution was made alkaline, the degree of coprecipitation of Pu(VI) with the bulk Fe(III), Ni(II), and Ce(III) precipitating solid phases must be considered and likely would be lower than the high coprecipitation of Pu(IV) observed with iron, lanthanum, and other elements observed in alkaline solution. As noted previously, Pu(VI) does not coprecipitate with Fe(III) or Al(III) when the acidic solution is made alkaline with excess NaOH, but does eventually precipitate in the presence of Cr(III)—presumably by oxidizing some of the Cr(III) solids and forming much less soluble Pu(IV) (Fedoseev et al. 1998). In a related study, little association of neptunium(V) or neptunium(VI) [Np(V) and Np(VI)] during alkaline coprecipitation with Fe(III) from acid solution was found, based on Mössbauer spectroscopy techniques, while the expected strong association of Pu(IV) with Fe(III) was found (Grigor'ev et al. 2001). Based on Np(VI) and Pu(VI)'s close chemical similarities and based on the findings of Grigor'ev and colleagues (2001), little association of Pu(VI) with Fe(III) by coprecipitation is expected.

In the end, the amount of soluble chromium, as chromate in alkaline solution from sludge dissolution and stainless steel attack by Ce(IV), might not be adequate to guarantee criticality safety in solution if the quantities of dissolved plutonium, present as Pu(VI), are sufficiently high. However, the sodium present in solution from the NaOH used to achieve alkaline conditions would be present, making it highly unlikely that a condition of criticality concern could be attained. Furthermore, it is also unlikely that plutonium concentrations sufficient to be of criticality concern, i.e., 0.013 grams plutonium per liter, $\sim5.4\times10^{-5}$ M, for the criticality safety limit based on the WTP contract limit, and 6.3 g plutonium per liter, for the safe subcritical limit (Section 4 of Miles (2009)), could be reached in the acid solution derived by dissolving alkaline tank waste sludge.

2.6.2   RE6 – Hydrogen Peroxide Added to Plutonium-Containing Vessel Heel

The impacts of inadvertent loss or misrouting of the 30 wt% (9.77 M) H_2O_2 to alkaline waste solutions and sludges must be considered as outlined in phenomenon RE6.

Early studies show that a red Pu(V) peroxide complex exists in 1 M NaOH, but is only stable in cold solution (Musikas 1971). In later work, freshly precipitated $Pu(OH)_4$ solids in NaOH solutions of various concentrations were contacted with H_2O_2 (functionally, the peroxide species in alkaline solution is HO_2^-) and the solution concentrations and spectra monitored (Shilov et al. 1996). It was found that the peroxide oxidized the $Pu(OH)_4$ (i.e., hydrated Pu(IV) oxide or $PuO_2 \cdot xH_2O$) to form soluble Pu(V); brown Pu(V) peroxide complexes were found at 12 M NaOH. At NaOH concentrations below about 6 M, where Pu(V) is unstable to disproportionation to form low-solubility Pu(IV) and dissolved Pu(VI) (see Figure 5-4 of

Delegard and Jones (2015)), the addition of peroxide was postulated to increase plutonium concentration in solution by stabilizing the more soluble Pu(V) at rates that exceeded the Pu(V) disproportionation rate. Subsequent studies in the same laboratory showed that HO_2^- chemically reduces Pu(VI) to Pu(V) in alkaline solution (Shilov and Budantseva 1998). If the HO_2^- was used in stoichiometric excess (i.e., the peroxide:Pu(VI) mole ratio was greater than two), a highly colored and relatively soluble Pu(V) peroxide complex was observed.

The only absorber having compounds potentially susceptible to dissolution in alkaline media using H_2O_2 is chromium. Studies of the effects of H_2O_2 on the oxidative leaching of Cr(III) solids from simulated and actual Hanford tank waste sludges have been conducted (results surveyed by Rapko et al. (2004); see also Delegard (1995) and Rapko et al. (1997)). Greater efficacy of H_2O_2 treatment has been experienced in tests with simulated sludge materials than with actual sludge. The rate of Cr(III) oxidation for various *dissolved* Cr(III) hydroxide species by hydrogen peroxide under alkaline conditions showed that the oxidation rate of Cr(III) to Cr(VI) was first-order in Cr(III) and hydrogen peroxide concentrations and inverse first-order in hydroxide concentration (Rao et al. 2002). The dissolved Cr(III) species' oxidation rates also decrease with increasing Cr(III) species polymerization with the monomer oxidation being the most rapid.

The interaction of H_2O_2 with Cr(III) hydroxides and mixed Cr(III)-Ni(II) and Cr(III)-Fe(III) hydroxides has been studied in 0.2 to 2 M NaOH solution (Fedoseev et al. 2002). These studies followed related studies by researchers from the same laboratory (Krot et al. 1999). In both studies, oxidative dissolution to form soluble chromate was observed for "pure" Cr(III) (hydr)oxides. The dissolution increased with increasing digestion temperature and for $Cr_2O_3 \cdot xH_2O$ solids hydrothermally aged to lower temperatures and which, not coincidentally, contained higher amounts of water ("x" in the formula). Dissolutions were performed using 1 M H_2O_2 that was added in a stepwise manner to minimize H_2O_2 disproportionation. The dissolution rate increased with peroxide concentration and temperature, but decreased with NaOH concentration. In the presence of Fe(III) and other transition-metal hydroxides (e.g., nickel, copper, cobalt), catalytic loss of peroxide occurred during attempted Cr(III) (hydr)oxide dissolution by H_2O_2. Substantial catalytic loss of H_2O_2 also was observed for dissolution tests of $NiCr_2O_4 \cdot xH_2O$ and mixed Fe(III)-Cr(III) hydroxides. This loss of peroxide, of course, severely diminished the desired oxidative dissolution of contained chromium. In summary, the various tests of the effects of H_2O_2 on oxidative dissolution of Cr(III) solids for genuine Hanford tank waste sludge indicate that little net chromium solid dissolution by peroxide could be expected because of the refractory nature of the sludge solids and the marked catalytic loss of peroxide to disproportionation.

Based on these findings, the inadvertent addition of H_2O_2 to the sludge by way of misrouting will cause minimal oxidative dissolution of Cr(III) solids. For any Cr(III) solids that might dissolve and the accompanying plutonium or plutonium solids that are present in an uncombined form (e.g., as $PuO_2 \cdot xH_2O$), oxidative dissolution also would occur and chromate, soluble Pu(V), and perhaps even the corresponding Pu(V) peroxide complexes, would form. The plutonium solution concentrations achieved by such limited dissolution would be low and would be accompanied by much greater quantities of the chromium absorber and the ubiquitous sodium salts. With time and radiolytic processes, most of the Pu(V) and Pu(V) peroxide complexes would chemically reduce to Pu(IV) and revert to the solid phase with its abundant absorbers. The dissolved chromium, present as chromate, likely would remain in solution given the relative stability of chromate as demonstrated by its presence in tank waste solutions.

Conclusions to Section 2.62.6 – The phenomena RE5 and RE6 involve, respectively, the uses of the chemical redox agents Ce(IV) and hydrogen peroxide and their potential effects to alter the relative plutonium and absorber element distributions by dissolution or precipitation reactions under process or upset conditions. Consideration of phenomenon RE5 indicates that the situation of most concern is the inadvertent introduction of acidic Ce(IV) to alkaline tank waste and the continuation of acidic conditions to occasion the oxidative dissolution, in acid, of the waste sludges and their contained plutonium to form Pu(VI). While the dissolution itself would have no criticality safety consequence because of the accompanying dissolved absorbers (including iron), subsequent adjustment to alkaline conditions would precipitate most absorbers and leave the Pu(VI) in solution. In this case, however, abundant sodium from the added NaOH and potentially dissolved chromium as chromate also would be present to provide neutron absorption. It is noted, however, that testing to substantiate this proposed reaction sequence has not been performed. Consideration of phenomenon RE6 shows that inadvertent introduction of H_2O_2 to tank waste could only affect freshly precipitated Cr(III) solids and the contained associated plutonium or non-aged intrinsic plutonium solids such as $PuO_2 \cdot xH_2O$ by oxidative dissolution to form soluble Cr(VI), Pu(V), and perhaps Pu(V) peroxide complexes. The amount of plutonium dissolved by this action would be low and would be accompanied by chromium absorbers and the ubiquitous sodium ion. With time and radiolysis, most of the plutonium would eventually be chemically reduced and precipitate into the sludge, while the chromate would remain in solution.

2.7 Organic Effects

Potential issues on the disposition and relative distributions of plutonium and absorber materials in the waste feed as a result of the influence of organic constituents were raised in phenomena OP2, OP7, and OP10 as shown in Table 1-3 and in Table 2-12.

Table 2-12. Chemical Phenomena Associated with Waste Organic Chemistry Effects

Number	Process	WTP System(s)
OP2	WTP feed holds unexpected organic complexant	HLP, UFP
OP7	Aluminum precipitation carries down dissolved plutonium	UFP
OP11	Anti-foam agents addition	WTP-wide

The chemical phenomena associated with organic chemicals in the waste are of two types. Phenomena OP2 and OP11 may alter plutonium and absorber distribution and ratios in the solid and solution phases by selectively dissolving either the plutonium or the credited absorber. Phenomenon OP7 arises from the chemical impact of organic oxidative decomposition in the alkaline waste to produce carbonate and to decrease hydroxide concentration. These changes then can decrease aluminum solubility by lowering the pH, which favors precipitation of gibbsite, $Al(OH)_3$, and by increasing the carbonate concentration in the waste to favor the precipitation of dawsonite, $NaAlCO_3(OH)_2$, with potential associated impacts on plutonium and absorber distributions.

2.7.1   OP2 – WTP Feed Holds Unexpected Organic Complexant

Early studies of plutonium chemistry in alkaline media simulating Hanford tank waste and containing organic complexing agents and other waste components within 1 to 4 M NaOH containing sodium salts of nitrate, nitrite, carbonate, and others show that EDTA (ethylenediaminetetraacetate), citrate ($^-O_2CCH_2C(OH)(CO_2^-)CH_2CO_2^-$), glycolate ($HOCH_2CO_2^-$), and HEDTA (N-2-hydroxyethylethylenediaminetriacetate) have little effect on plutonium solubility (Delegard and Gallagher 1983). These four organic complexing agents had been used in high concentrations in Hanford tank waste processing, with their primary application being dissolution of iron-bearing sludge phases in acid (Buckingham 1967). These starting components plus formate (HCO_2^-), oxalate ($^-O_2CCO_2^-$), acetate ($H_3CCO_2^-$), iminodiacetate ($HN(CH_2CO_2^-)_2$), and others that largely are degradation products of EDTA, HEDTA, glycolate, and citrate starting materials also are present in tank waste (Section 1.3.1.2 and Table 1.3-4 of Jenkins et al. (2013)).

Because the precipitation of the stable $PuO_2 \cdot xH_2O$ in alkaline solution is not affected by the presence of oxalate, glycolate, citrate, EDTA, or HEDTA (Krot et al. 1998b; Yusov et al. 2000b), the influence of organic complexing agents on the dissolution of plutonium in alkaline tank waste is expected to be low.

More recent studies confirm that EDTA is not effective in complexing plutonium at high hydroxide concentrations (Rai et al. 2008). This research showed that Pu(IV) experiences strong competition for EDTA with ions of other metals, including Fe^{3+} and calcium, Ca^{2+} (Rai et al. 2008), and it is known that EDTA and HEDTA strongly affect the solubilities of strontium, cobalt, and americium ions (Sr^{2+}, Co^{2+}, and Am^{3+}, respectively) in alkaline solution (Delegard and Gallagher 1983). Rai et al. (2008) conclude that in environmental systems where iron and calcium minerals are ubiquitous, EDTA would be primarily complexed with the iron and calcium and thus be unavailable to complex plutonium. They also note that surface complexation of the EDTA onto mineral solids occurs, although more so at lower pH, effectively removing EDTA (and, presumably, other complexing agents) from solution. Finally, Rai et al. (2008) note that EDTA is subject to chemical degradation in the environment.

The ameliorating influences noted by Rai et al. (2008) also pertain to the tank waste situation in which high concentrations of competing metal ions exist, large quantities of solid phases are present, and in which degradation reactions to simpler organic components occur. It is also noted, however, that the organic complexing agents can diminish plutonium uptake onto sludge solids (Section 6.2 of Delegard and Jones (2015) and references therein).

The separation of plutonium from iron-bearing solids (amorphous ferric hydroxide and goethite, FeOOH) by leaching with alkaline EDTA solutions was studied by Krot et al. (1998c). They examined the physical characteristics of the bulk precipitates and the susceptibilities of the precipitated products to leaching by use of 0.1 M EDTA in 1 M NaOH containing 5 M $NaNO_3$. The investigations showed that plutonium interactions with iron were strong because very little plutonium leaching from the iron solids occurred. Therefore, little separation of plutonium from iron solids occurred because of EDTA complexation.

Some TBP has been observed in a recent waste sample taken from tank 241-AN-106, leading to the speculation that dibutyl phosphate (DBP) also might have been present, although analyses to establish this were not performed (Dodd et al. 2014). The TBP was associated with an organic liquid analyzed as "diesel #2," but which was likely normal paraffin hydrocarbon (NPH), a special kerosene cut used as

diluent in solvent extraction processing at the PUREX Plant. The continuing existence of TBP in Hanford tank waste had been considered unlikely because of acid hydrolysis in plant operations and alkaline and radiolytic decomposition to DBP and butanol, $H_3CCH_2CH_2CH_2OH$; further hydrolysis to monobutyl phosphate (MBP) proceeds at a much lower rate and was deemed unlikely. Although ~100-fold higher plutonium concentrations were found in the organic liquid than were found in the associated aqueous phase, uranium concentrations in the organic liquid were about 300-times higher than in the aqueous phase. Because uranium concentration in the aqueous sample exceeded the solubility of sodium diuranate, it is likely that the higher uranium and plutonium concentrations in the organic phase were because of incorporation of solids and not by solvent extraction. Gerber et al. (1992) remark that inorganic solids can accumulate organic phases onto their surfaces:

> Adsorption of organics onto the surfaces of the solids.*[sic]* Many of the organics in the tank are polar compounds and thus capable of adsorbing onto the solids surfaces of the sludge and salt cake. Among these compounds are surfactants that were used during plant decontamination operations and (C_8 or more) carboxylic acids that are products of solvent degradation and are known to have surfactant behavior. Under optimum conditions these compounds can concentrate as high as $7.5(10)^{-2}$ mol/m^2 of surface. This in turn can produce carbon concentrations on the solids as high as several percent if the solids have high surface areas. However, several parameters (pH, ionic strength of solution, organic compounds adsorbing, and organic compound inventory) affect the adsorption mechanism and can result in much lower concentrations at nonoptimum conditions (p. iv).

The interactions of TBP and even its primary organic degradation product, DBP, with plutonium and with iron or other absorbers, when observed, are therefore likely to result in a coagulated water-insoluble scum by physical interactions akin to the interaction of soap with soil solids rather than by chemical complexation. Thus, TBP, its decomposition products, and the NPH diluent interact indiscriminately with plutonium and other solids and absorb sludge solids by physical processes. Specific organic hydraulic fluids potentially leaked into the tank wastes from waste sample retrieval equipment have been shown to have no chemical affinity for plutonium (Dodd et al. 2014).

> *Conclusions to Section 2.7.12.7.1 – Hanford-origin organic complexants and compounds such as EDTA and TBP have little chemical interaction with plutonium and iron, the principal absorber element, in alkaline waste media. Furthermore, these organic compounds degrade by hydrolysis and radiolysis to simpler and less interactive compounds. Some partition of plutonium to separate organic phases present in tank wastes has been observed but the partitioning appears to be physical and non-specific in that other low-solubility solid materials also partition at about equal fraction to the organic. Overall, introduction of such organics into the WTP is unlikely to dissolve and concentrate fissile material or otherwise separate fissile material from credited absorbers as speculated under phenomenon OP2.*

2.7.2   OP11 – Anti-Foam Agents Addition

Anti-foam agents are to be added to improve processing in WTP evaporators. Under phenomenon OP11, such materials might pose a criticality concern if they were to alter the plutonium-to-absorber ratios during these and follow-on processes. The anti-foam agents to be added are 40 to 70 wt% polypropylene glycol, 40 to 70 wt% polydimethylsiloxane, 3 to 7 wt% octylphenoxy polyethoxy ethanol,

3 to 7 wt% proprietary treated silica, and 3 to 7 wt% polyether polyol (Section 2.2.3.5 of Jenkins et al. (2013)). Heating and irradiation reportedly decomposes about 20 wt% of the first two ingredients every 24 hours (Section 2.2.3.5 of Jenkins et al. (2013)), but no information on the stability of the remaining organic constituent, polyether polyol, is provided. Polyols are organic compounds having multiple alcoholic (-OH) functional groups arrayed along the carbon chain.

Organic complexing agents known to be effective in increasing plutonium solubility in alkaline (pH 12) media include gluconate, $CH_2OH(CHOH)_4CO_2^-$, arabinoate, $CH_2OH(CHOH)_3CO_2^-$, and isosaccharinate, $CH_2OHCHOHCH_2COH(CH_2OH)CO_2^-$ (Moreton 1993). Significantly, all three of these agents are polyols, like the polyether polyol present in the anti-foam agent; however, each has a terminal organic acid function, unlike the polyether polyol. The gluconate, arabinoate, and isosaccharinate increased plutonium concentrations by a factor of about 3000 when ligand concentration increased from 10^{-6} M to 10^{-2} M. Thus, at 10^{-6} M ligand, the plutonium concentration was 3×10^{-9} M plutonium, while at 10^{-2} M ligand, the plutonium concentration ranged from 10^{-5} to 5×10^{-4} M. Further testing showed that the deprotonated hydroxyl ligands likely were responsible for the enhanced complexation of plutonium, based on observations of similar solubility enhancements in tests using pure alcohol ligands in which hydroxy groups replaced the carboxylate groups of the gluconate, arabinoate, and isosaccharinate. Similar stability constants were calculated for the respective alcohol-acid and latter purely alcohol complexes, which are akin to the structure of the polyether polyol used in the anti-foam agent. Similarly, polysulfonic acid and polycarboxylic acid cement additives at ~1 g/L concentrations enhanced plutonium compound solubility about 300-fold in pH 12 cement waters (Greenfield et al. 1998). The effectiveness of these polyol agents in enhancing plutonium compound solubility in more alkaline solution such as the tank wastes is not known.

However, in more directly pertinent tests with a plutonium-spiked simulated sludge containing the anti-foam agent, plutonium dissolution by preparation of the sludge in 3 M NaOH was 0.087% (Rapko et al. 2010). The plutonium(IV) was coprecipitated with iron(III), both as nitrates in acid, using NaOH solution. Under otherwise similar conditions but without the anti-foam agent, 0.076% plutonium leaching was observed, a difference that is not statistically significant based on the stated measurement errors. Only 0.005% to 0.014% of the plutonium leached from the simulant sludge over a wide range of anti-foam agent concentrations using eight hours of 3 M NaOH treatment at 85° C. Under oxidative leaching conditions using 0.25 M NaOH and permanganate as the oxidant in quantities equimolar to the chromium contained in the sludge, plutonium leaching was 0.15% or lower and completely independent of the anti-foam concentration. Thus, negligible plutonium is dissolved under varied alkaline conditions by the addition of anti-foam agent.

> *Conclusions to Section 2.7.2 – Although polyol chemical agents, with compositions similar to that of the anti-foam agent constituent polyether polyol, are known to enhance plutonium solubility in pH-12 systems, tests of plutonium dissolution from simulant sludge in the presence and absence of the anti-foam agent showed no preferential plutonium dissolution. Additional tests at 85° C using 3 M NaOH and with 0.25 M NaOH containing permanganate likewise showed negligible plutonium leaching. Overall, anti-foam agents are highly unlikely to dissolve plutonium away from absorbers present in Hanford tank sludge. Therefore, the impact to criticality safety of the use of anti-foam agents under phenomenon OP11 is expected to be negligible. However, confirmation testing with genuine wastes or simulant wastes after thermal and radiolytic aging should be performed.*

2.7.3   OP7 – Aluminum Precipitation Carries Down Dissolved Plutonium

Organic compound decomposition by oxidation in the alkaline waste produces carbonate and decreases hydroxide concentration. Although such reactions would only occur to a significant extent if the waste were stored an inordinate length of time (months or more), they would impact aluminum solubility. Absorption of atmospheric carbon dioxide into the waste solution can have the same effect. The following reaction of acetate with nitrate is illustrative and by no means exceptional, in that hydroxide is consumed by organic oxidation reactions irrespective of the starting organic compound:

$$H_3CCO_2^- + NO_3^- + 2\ OH^- \rightarrow 2\ CO_3^{2-} + NH_3 + H_2O.$$
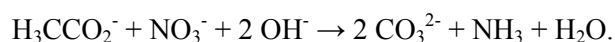
Thus, the decomposition of organics present in the waste can decrease aluminum solubility as aluminate, $Al(OH)_4^-$, by lowering the pH. As shown in Figure 6-2 of Delegard and Jones (2015), this leads to $Al(OH)_3$ (e.g., gibbsite) precipitation:

$$Al(OH)_4^- \rightleftharpoons Al(OH)_{3\ (solid)} + OH^-.$$
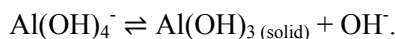
Furthermore, by increasing the carbonate concentration in the waste and decreasing hydroxide concentration, conditions are created favoring precipitation of the sodium aluminum carbonate hydroxide salt dawsonite, $NaAlCO_3(OH)_2$ (Reynolds et al. 2012). Finally, blending of wastes can precipitate aluminum as gibbsite, dawsonite, or sodium aluminosilicates such as cancrinite (see Section 2.1.2).

As noted in Section 6.1.1 of Delegard and Jones (2015), the association of Pu(IV) with $Al(OH)_3$ precipitates, prepared by neutralization of acidic solutions with NaOH, is poor (Fedoseev et al. 1998; Krot et al. 1998b; Hobbs 1999). Tests from the opposite direction, i.e., to determine whether plutonium is carried from solution by $Al(OH)_3$ precipitation incurred by treatment of aluminate solutions with acid, have not been conducted. However, unless highly oxidizing conditions prevail, the solubility of plutonium in, for example, 1 M NaOH, is relatively low ($\sim 10^{-7}$ M or ~ 0.000024 g Pu/L), and is about only 10^{-5} M in 1 M NaOH containing 1 M carbonate (Figures 5-5 and 5-6 of Delegard and Jones (2015)). This means that the amounts of plutonium that are available to be carried by gibbsite precipitation are very small and may not be of criticality consequence.

It is noted that compounds of aluminum with chromium, iron, uranium, bismuth or mixtures of their compounds have been reported in tank waste characterization (Table 4-8 of Delegard and Jones (2015)). Regarding iron, the tests by Krot and colleagues (1998b) indicate that joint aluminum/iron precipitation must be low because discrete $Al(OH)_3$ and FeOOH (goethite) phases are observed by x-ray diffractometry and mixed aluminum-iron phases are not. Thus, even though both aluminum and iron have steeply lower solubilities at intermediate pH than in strongly alkaline solution (Figure 6-3 of Delegard and Jones (2015)), aluminum precipitation as $Al(OH)_3$ is not responsible for removing the iron absorber from solution. Formation of aluminum-chromium mixed hydroxides is more likely, as evidenced by the presence of Al-Cr solid phases in the tank wastes (Table 4-8 of Delegard and Jones (2015)).

The association of plutonium with dawsonite is not known. The high-carbonate and low-hydroxide concentrations needed to precipitate dawsonite, however, favor high plutonium compound solubility. For example, plutonium compound solubility in conditions that cause dawsonite precipitation, 1 M bicarbonate, HCO_3^-, at pH 9 to 10, is ~ 0.002 M, or nearly 0.5 g Pu/L (Figure 5-6 in Delegard and Jones (2015)). This concentration is about 200,000 times higher than it would be ($\sim 10^{-8}$ M; Figure 6-3 of

Delegard and Jones (2015)) at pH 9 to 10 in the absence of bicarbonate. Dissolved plutonium concentrations reaching 0.002 M concentrations in solution, however, is unlikely unless the sludge solid phase itself has a sufficiently high plutonium concentration to provide the plutonium to solution and unless the bicarbonate can successfully dissolve the plutonium from the solid phase. At most, $\sim 10^{-4}$ moles plutonium per kilogram of dry sludge was found in a limited survey of sludge compositions (Barney and Delegard 1999). This concentration, perhaps 20 times lower than the solubility-limited ~ 0.002 M plutonium concentration in 1 M bicarbonate solution, may indicate that removal of plutonium from solution by dawsonite precipitation engendered by organic decomposition and the associated increase in carbonate concentration and decrease in hydroxide concentration does not impact criticality safety.

Plutonium incorporation into sodium aluminosilicates such as cancrinite has not been studied but is unlikely because anions typically enclathrated in cancrinite and other aluminosilicates (e.g., nitrate, chloride, and carbonate) are much smaller than alkaline plutonium anions (e.g., $PuO_2(OH)_4^{3-}$).

Conclusions to Section 2.7.3 – Post-leaching, low-rate precipitation of aluminum is possible. Aluminum also can precipitate as gibbsite or as dawsonite by the consequences of oxidative decomposition of organic compounds (if extended, months-long, waste storage occurs) to produce carbonate and consume hydroxide, and by the absorption of atmospheric carbon dioxide into the waste solution. Aluminum precipitates also may arise as a consequence of waste blending operations. Tests show that gibbsite precipitated by making acid solution alkaline does not carry plutonium and does not enhance iron precipitation, although aluminum-chromium compounds are likely form from neutralization from acid solution. The carrying of plutonium by gibbsite precipitated by lowering the pH of alkaline solution or by forming dawsonite by further pH lowering and the addition of carbonate has not been studied. In the case of gibbsite, the plutonium concentration available for carrying may be small enough ($\sim 10^{-7}$M) to be inconsequential. The solubility-limited plutonium potentially available to be carried from solution by dawsonite precipitation can be as high as 0.002 M (~0.5 g Pu/L) and may be of criticality concern. However, the risk of attaining such high concentrations may be limited by the amount of plutonium available to be leached from the sludge, and by the poor ability of bicarbonate to achieve the leaching, particularly for plutonium coprecipitated with elements besides uranium. Plutonium incorporation as an alkaline anion into aluminosilicates is unlikely.

2.8 Temperature Effects

Temperature changes can potentially alter the disposition and relative distributions of plutonium and absorber materials in the waste feed solution and solids in the WTP. This issue was raised directly under phenomenon OP6 and arises indirectly as part of phenomenon OP7 regarding aluminum precipitation as its hydroxide, $Al(OH)_3$. These phenomena are outlined in Tables 1-3 and in Table 2-13.
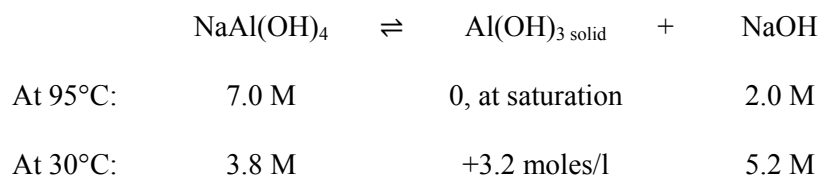
Table 2-13. Chemical Phenomena Associated with Temperature Effects

Number	Process	WTP System(s)
OP6	**Temperature changes**	**WTP-wide**
OP7	Aluminum precipitation carries down dissolved plutonium	UFP

In phenomenon OP6, the impact of heating or cooling to change the relative distribution of plutonium and absorber materials by precipitation or dissolution reactions is considered. Phenomenon OP7 considers the potential for precipitation of aluminum phases such as gibbsite, $Al(OH)_3$, to carry down plutonium or other absorbers after alkaline (NaOH) leaching. The case of aluminum under phenomenon OP7 is illustrative and will be addressed first.

2.8.1   OP7 – Aluminum Precipitation Carries Down Dissolved Plutonium

A marked manifestation of the effect of temperature on solubility is seen for aluminum (hydr)oxide solid phase dissolution in sodium hydroxide, NaOH, solution as shown in Figure 6-2 of Delegard and Jones (2015). At 95° C, a 2 M NaOH solution that is at saturation in $Al(OH)_3$ solid phase contains 7 M $NaAl(OH)_4$. By cooling this clear solution to 30° C, 3.2 moles (~250 grams) of $Al(OH)_3$ precipitates per liter of solution, the $NaAl(OH)_4$ concentration drops to ~3.8 M, and the NaOH concentration increases to about 5.2 M, assuming constant solution volume. These changes are tabulated according to the following equilibrium:

$$NaAl(OH)_4 \quad \rightleftharpoons \quad Al(OH)_{3\ solid} \quad + \quad NaOH$$

At 95°C:	7.0 M	0, at saturation	2.0 M
At 30°C:	3.8 M	+3.2 moles/l	5.2 M

The substantial changes in aluminum solubility with temperature are exploited in the Bayer process to produce refined gibbsite, $Al(OH)_3$, from bauxite ore (impure $Al(OH)_3$) for aluminum metal production (Wiberg 2001, pp. 1000-1001; Hudson et al. 2002). In the WTP, the Bayer process chemistry also is exploited, but in the opposite direction, to effect $Al(OH)_3$ dissolution from Hanford tank waste sludges that are poor in other components (e.g., REDOX sludge) using heated NaOH solution (Sections 1.3.4.2 and 2.3.5.5 of Jenkins et al. (2013)). However, the sodium salts that are abundant in most tank waste can markedly alter the dissolution or solubility behavior of $Al(OH)_3$, practically eliminating the effect of temperature in the range 20 to 80° C (also in Figure 6-2 of Delegard and Jones (2015)).

In the Bayer process, $Al(OH)_3$ is precipitated from the pregnant bauxite dissolution liquors by cooling and dilution. The precipitation rate is accelerated by addition of gibbsite seed crystals. In phenomenon OP7, concern is expressed that $Al(OH)_3$ solids may precipitate inadvertently but by similar actions (e.g., cooling, dilution, seeding) such that absorbers or plutonium are removed from solution to adversely alter the ratio of plutonium to absorber in the solution or solid phase.

The potential for this to occur is small, however. Figure 6-3 of Delegard and Jones (2015) demonstrates that the solubilities of the various (hydr)oxide absorber compounds in 1 M NaOH solution

are 10^{-4} M or lower, while the solubility of plutonium as $PuO_2 \cdot xH_2O$ is $\sim 5 \times 10^{-8}$ M. It is noted that the metal (hydr)oxide compound solubilities may be increased by the presence of dissolved salts, which can, in general, increase dissolved NaOH chemical activity. Nevertheless, little absorber material (aside from chromate, CrO_4^{2-}, and the sodium salts) is available to be captured by the precipitating $Al(OH)_3$. Although the capture of dissolved plutonium from the alkaline side has not been tested, the plutonium available in solution for coprecipitation is miniscule. Plutonium capture into the $Al(OH)_3$ matrix would seem to be unlikely as it does not occur when acidic mixed aluminum-plutonium nitrate solutions are treated with NaOH solution to cause the separate precipitation of $Al(OH)_3$ and $PuO_2 \cdot xH_2O$ (Fedoseev et al. 1998).

The Bayer process is used to refine aluminum for metal production because it achieves decontamination from most other elements present in the bauxite ore. In particular, the decontamination from iron is good (Wiberg 2001, p. 1000; Hudson et al. 2002) such that nearly all of this impurity element appears in the bauxite residue. The properties of the bauxite residue are described below:

> *[The bauxite residue]* is primarily composed of the insoluble fraction of the bauxite ore that remains after extraction of the aluminum-containing components. Iron oxides (10-30%), titanium dioxide (2-15%), silicon oxide (5-20%) and undissolved alumina (0-20%) make up the residue, together with a wide range of other oxides which will vary according to the initial bauxite source. The high concentration of iron compounds in the bauxite gives the by-product its characteristic red colour, and hence its common name "Red Mud".

> Initially, the residue is washed, to extract as much valuable caustic soda and dissolved alumina as possible. The caustic soda is recycled back into the digestion process, reducing production costs and in turn lowering the alkalinity of the residue. The pH level of the residue is generally up to 13 or higher in some cases, due to the presence of alkaline sodium compounds, such as sodium carbonate and sodium hydroxide.

> Like most ores and soils, bauxite can contain trace quantities of metals such as arsenic, beryllium, cadmium, chromium, lead, manganese, mercury, nickel and naturally-occurring radioactive materials, such as thorium and uranium. Most of these trace elements remain with the residue after extraction of the alumina (The International Aluminium Institute 2012).

Thus, the absorbers iron, cadmium, most of the chromium, manganese, nickel, and uranium remain in the bauxite residue. Dissolved gallium, vanadium, and chromate remain in the liquor, increase in concentration with recycle, and therefore must be removed.

Finally, iron(hydr)oxides, like gibbsite itself, can act as crystallization seed for gibbsite (Webster et al. 2011). However, because the actual quantity of iron (hydr)oxide available in the clarified aluminate solution is small and the quantity of iron present in the seed is likewise small compared with the precipitating $Al(OH)_3$, the impact on $Al(OH)_3$ purity is relatively low.

2.8.2   OP6 – Temperature Changes

As is the case for $Al(OH)_3$, heating the alkaline sludge may increase solubilities of absorber compounds. For example, as shown in Figure 2-3, the solubility of hematite, Fe_2O_3, in ~ 2 to 10 M NaOH

solution increases by a factor of two to three as the temperature is raised from 30° C to 76° C (Ishikawa et al. (1997); data as a function of temperature at higher NaOH concentrations were not found in the technical literature). Although the Fe_2O_3 solubility increase by heating occurs by approximately the same multiplicative factor as the solubility of $Al(OH)_3$, the solubility of Fe_2O_3 is only 10^{-4} to 10^{-3} M over the ~2 to 10 M NaOH and 30° C to 76° C range, much lower than the molar solubility of $Al(OH)_3$. Therefore, on an absolute basis, little iron will report to solution by raising the temperature of the alkaline solution.
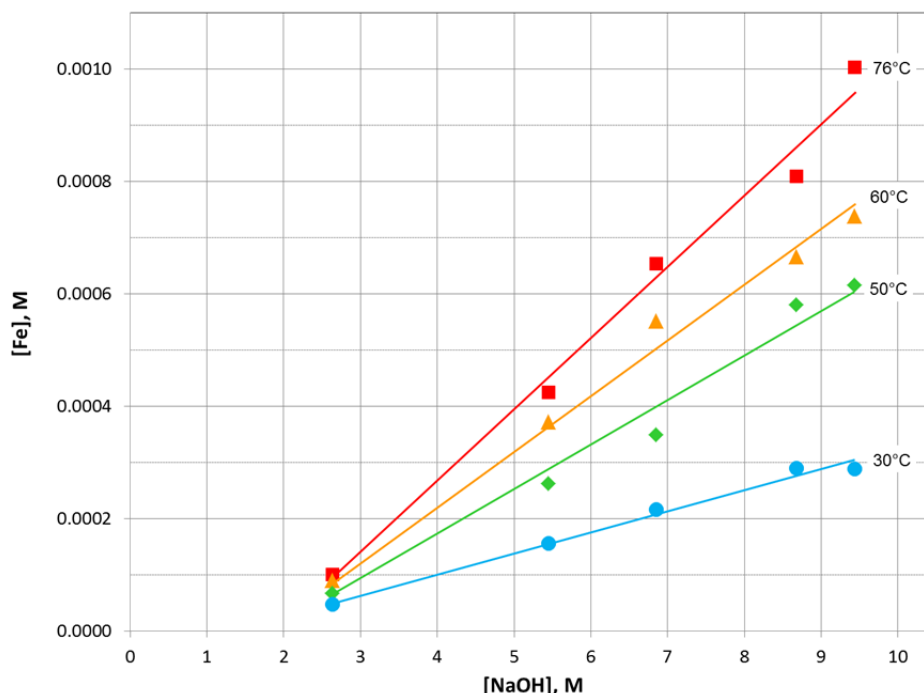
Figure 2-3. Solubility of Hematite as Functions of NaOH Concentration and Temperature (Ishikawa et al. 1997)

The effects of temperature on the solubilities of sludge solids were examined for actual wastes from Hanford tanks 241-AW-101 (Lumetta and Lettau 1999), AN-102 (Burgeson et al. 2003), C-104 (Lumetta et al. 2000b), and C-106 (Lumetta et al. 2000a) and found, in general, to be much smaller than the effects shown for Fe_2O_3 in pure NaOH solution (Figure 2-3). In the AW-101 study, the aluminum, chromium, and uranium concentrations increased modestly (as much as ~13%) by increasing the temperature to 50° C compared with the concentrations found at 30° C while iron and nickel concentrations decreased as much as 23% (Lumetta and Lettau 1999). The hydroxide concentration was not measured, but the total sodium concentration was about 6.4 M. No plutonium analyses were performed. For the AN-102 sludge, aluminum, chromium, iron, manganese, nickel, and uranium metal concentrations all increased, but by no more than ~8%, at 50° C compared with the concentrations measured at 30° C (Lumetta et al. 1999). Again, however, hydroxide and plutonium concentrations were not measured, while sodium was about 6.0 M. In the tests with C-106 sludge, the sodium concentration was only ~0.63 M because of dilution using 0.1 M NaOH; the hydroxide and plutonium concentrations were not measured (Lumetta et al. 2000a). Under these dilute conditions, chromium and nickel concentrations approximately tripled (but were so low at $<5\times10^{-5}$ M as to be of no practical consequence) in raising the temperature from 30° C to 50° C and uranium concentration increased about 25%. The results for aluminum and iron were too scattered to discern a trend and manganese was below detection (<2 µM). For sludge from tank C-104,

the sodium concentration was about 1.4 M, hydroxide and plutonium were not measured, and the aluminum concentration decreased by a factor of ~2 by raising the solution temperature from 30° C to 50° C (Lumetta et al. 2000b). The findings for chromium, iron, manganese, nickel, and uranium were too low or too scattered to reveal a trend. For a later AN-102 study, about 0.25 M hydroxide and ~8.5 M sodium were present in solubility tests run at 15° C and 50° C (Burgeson et al. 2003). Of the absorber elements, only manganese showed a significant concentration change, decreasing 26% from an initial concentration of about 0.00024 M, when the temperature was raised. The plutonium concentration at 15° C was about 0.08 g/liter ($\sim3.3\times10^{-7}$ M), and remained virtually unchanged with heating to 50° C. Overall, these tests with actual wastes, albeit at unknown but likely relatively dilute hydroxide concentrations, showed that temperature change had a small and scattered effect on absorber element concentrations in solution.

In a set of statistically-designed tests, the effect of temperature change in the range 25° C to 60° C was found to have no effect on the solubility of plutonium in 0.5 to 2.0 M NaOH solutions. These test solutions also contained a variety of other sodium salts including nitrate, nitrite, aluminate, and carbonate, and were meant to broadly emulate the compositions of tank waste at the Savannah River Site (Hobbs and Karraker 1996).

Examination of Figure 6-3 of Delegard and Jones (2015) shows that, like Fe_2O_3, the solubilities of ferrihydrite ($Fe_5O_7OH\cdot4H_2O$), $FeOOH$, $Cr(OH)_3$, MnO_2, $Ni(OH)_2$, $Cd(OH)_2$, and $Na_2U_2O_7\cdot xH_2O$ also are much lower than that of $Al(OH)_3$ in 1 M NaOH. For all of these compounds, the solubilities are less than 10^{-4} M and most are less than 10^{-5} M. Therefore, even ten-fold enhancement in the solubilities of these compounds would dissolve only trivial concentrations of the respective absorber elements. More importantly, the solubility of $PuO_2\cdot xH_2O$ in 1 M NaOH, about 5×10^{-8} M, is even lower than that of any of the named absorber element compounds. Therefore, the potential for appreciable quantities of any solid phase absorber of plutonium to dissolve into the alkaline mother solution by temperature increase is low. By the same arguments, the quantities of absorber elements and plutonium available for precipitation, should the waste temperature decrease, are also low, would have negligible impact on the ratios of plutonium and absorber elements in the solid phase, and could not alter the criticality safety of the solution phase because of its already-low plutonium concentration.

Of the absorber element compounds present in solid phase, and thus in physical and intimate chemical association with plutonium, only $Al(OH)_3$, by reaction with NaOH, and $Cr(OH)_3$, by oxidation, are subject to dissolution at molar concentrations in alkaline solution. Of the plausible absorber element compounds, only $Al(OH)_3$ and the related compound $AlOOH$ are subject to substantially increased solubility by increase in temperature and thus of concern under phenomenon OP6.

> *Conclusions to Section 2.8 – The influence of temperature change in the alkaline waste slurries on the relative distributions of plutonium and absorber elements to the solid and solution phases is small, due to their low solubilities; aluminum is the exception. For Al(OH)$_3$ and the related compound AlOOH, the aluminum solution concentration can increase markedly in strong NaOH solution with temperature increase for relatively "pure" REDOX sludge containing low concentrations of other salts. Thus, if a waste slurry contains only Al(OH)$_3$ and plutonium in the solid phase, and the Al(OH)$_3$ is leached by digestion in strong heated NaOH, an opportunity exists to separate the relevant absorber, aluminum, from the plutonium and impact the criticality safety. However, the reverse situation, removal of aluminum from solution by precipitation occasioned by dilution, cooling, or even crystal seeding for supersaturated solutions, is*

not cause for criticality concern because of plutonium's low solubility in alkaline solution.

2.9 Melter Redox Effects

Potential issues regarding the disposition and relative distributions of plutonium and absorber materials in the WTP HLW and low-activity waste (LAW) melters as a result of redox chemistry were raised in phenomena RE1, RE4, and OP9 as shown in Table 1-2, Table 1-3, and Table 2-14.

Table 2-14. Chemical Phenomena Associated with Melter Redox Chemistry Effects

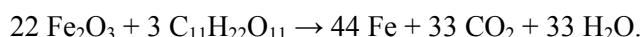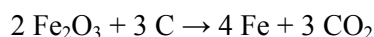| Number	Process	WTP System(s)
RE1	Plutonium metal formation in HLW melter	HMP
RE4	Reduction of iron due to excess sugar addition	HMP
OP9	Plutonium transported into ventilation system	HOP

The outcomes of these three phenomena hinge on the redox behavior of plutonium and absorber elements, primarily iron, in the LAW and HLW melters and the behavior of excess sugar during its decomposition in the cold cap. Note that it is not certain that sugar will be used in the HLW melter (Section 4.1.3.4.8 of Jenkins et al. (2013)), where the majority of the plutonium- and iron-bearing Hanford tank waste sludge would be expected, although sugar addition can decrease foaming (Section 4.1.3.4.10 of Jenkins et al. (2013)).

To understand chemical behaviors in the melter(s), the chemical composition of the waste, the glass formers, and the redox additives, such as sugar (sucrose, $C_{11}H_{22}O_{11}$) must be considered. Sugar is added to the LAW and potentially HLW melter feed to react with sodium nitrate and nitrite ($NaNO_3$ and $NaNO_2$, respectively), nominally forming nitrogen gas (N_2), limited amounts of ammonia (NH_3), and a complicated plethora of other minor volatile organic compounds such as acetonitrile (H_3CCN). The sugar addition also decreases the foaming of the melt that would otherwise occur by reducing multivalent oxides before they are incorporated into a high-viscosity melt and by supplying reaction heat to the cold cap / melt surface to decrease the glass' viscosity (Sections 3.1.3.5.1, 3.1.3.5.5, and 3.2.3.4.3 of Jenkins et al. (2013); Peeler et al. (2001); Ryan (1995); Hrma et al. (2010); Smith et al. (1995)).

The nominal concentration of sugar added to both LAW and HLW (0.75 moles of TOC per mole of NO_x) will result in an iron redox ratio of less than 6% Fe(II), divalent iron, to total Fe. Studies show that increased sugar dosage to the LAW melter feed linearly increases the redox ratio (Fe(II)/total Fe) in the product glass (Section 3.1.3.5.6 of Jenkins et al. (2013); see also Darab et al. (2001)and Goles et al. (2001)). Although the dependence of the extent of Fe(III) reduction on sugar dosage seems less distinct in HLW glass (Section 4.1.3.4.9 of Jenkins et al. (2013)), this is not generally true. Other studies with defense glasses for Hanford, the Savannah River Site (SRS), and the West Valley Demonstration Project, WVDP, have shown clear trends on the effect of reductant concentration on glass redox (for Hanford, Goldman et al. (1986) and Russell et al. (2001); for SRS, Bickford and Choi (1991) and Ramsey et al. (1991); for WVDP, Jain (1993); for the Idaho National Engineering and Environmental Laboratory, Darab et al. (2001)). Conversion of Fe(III) to Fe(II) in the LAW glass under flowsheet conditions is ≤6%

(Table 3.1-11 of Jenkins et al. (2013)) and much of the iron oxidation state decrease is countered by bubbling air into the melt (Section 3.1.3.5.6 of Jenkins et al. (2013)). Over-batching of sugar by a factor of 2.5 results in a Fe(II)/total Fe value of 0.6.

It is argued, as postulated in phenomenon RE4, that sugar available in gross overdose under process upset conditions could potentially chemically reduce the Fe(III) oxides present in the melt past Fe(II) and all the way to iron metal. If sulfate were present, reduction to metal sulfides could also occur (Section 3.1.3.5.5 of Jenkins et al. (2013)). To a first approximation, the reaction of iron oxides with sugar to form metal is credible because the oxidation state of carbon in sucrose is zero, making it equivalent to the elemental carbon present in coke (see page 2.26 of Ryan (1995)), the agent used to chemically reduce iron oxides in the blast furnace process to produce iron metal (Wiberg 2001, page 1435). The following two reactions, which compare the production of iron metal from Fe_2O_3 using carbon and using sugar, respectively, as reductant, show that they differ only in the production of water in the latter reaction:

$$2 \ Fe_2O_3 + 3 \ C \rightarrow 4 \ Fe + 3 \ CO_2$$

$$22 \ Fe_2O_3 + 3 \ C_{11}H_{22}O_{11} \rightarrow 44 \ Fe + 33 \ CO_2 + 33 \ H_2O.$$

While the heat needed to drive the blast furnace process is provided by the burning of coke as well as the iron oxide reduction reaction itself, the heat in the vitrification process is provided externally and thus can guarantee completion of the Fe(III) oxide-sucrose reaction. Because the iron blast furnace reaction operates at ~900° C, carbon monoxide (CO), which forms above about 600° C from the reaction of elemental carbon with any CO_2, is the functional reductant (Wiberg 2001; Miller and Reimann 1993). The same would be true for the WTP melters, which operate at 1150° C glass pool temperatures (3.2.1.2 and 4.2.3.6 of Jenkins et al. (2013) for the LAW and HLW melters, respectively). Therefore, the actual reductant in blast furnaces and in vitrification of organic-bearing wastes is CO (Wiberg 2001; Miller and Reimann 1993).

It is noted that iron-phosphorus metal inclusions were formed by graphite electrodes within early versions of the in-container vitrification process with simulated Hanford LAW (Kim et al. 2003) and that metal sulfides were formed in a test with simulated waste valley sludge purposefully over-reduced (Perez et al. 1984).

2.9.1   RE1 – Plutonium Metal Formation in HLW Melter

Consideration of the thermodynamic feasibility of chemically reducing iron and plutonium oxides to their metals (phenomena RE4 and RE1, respectively) can be conveniently assessed by use of Ellingham diagrams. In an Ellingham diagram, the Gibbs free energies of formation per mole of oxygen, O_2, of, in these cases, the oxides from the pertinent elements or compounds (i.e., CO_2-C, CO-C, Fe_2O_3-Fe, and PuO_2-Pu) are plotted as functions of temperature. Although Ellingham diagrams generally include reactions of the elements, it is useful for the present work to consider the reaction of magnetite, Fe_3O_4, with oxygen to form hematite, Fe_2O_3. It is notable that the free energy of formation of PuO_2, the most likely form of plutonium in the tank waste (Delegard and Jones 2015), from plutonium metal is very similar to that of uranium dioxide, UO_2, from uranium metal, U (Kleykamp 1985). From the Ellingham diagram presented in Figure 2-4 (based on Darken and Gurry (1953, p. 349) and Kleykamp (1985)), we see that temperatures well above 2000° C (~2300° C, according to the Ellingham diagram, Figure 8, of

Miller and Reimann (1993)), and thus well above the nominal 1150°-C glass pool temperature, would be necessary for the negative Gibbs free energy of formation of CO_2 from CO to exceed that of PuO_2 (near that of UO_2); i.e., for the following reaction to have a negative Gibbs free energy and thus be thermodynamically feasible:

$$2\ CO + PuO_2 \rightarrow 2\ CO_2 + Pu.$$
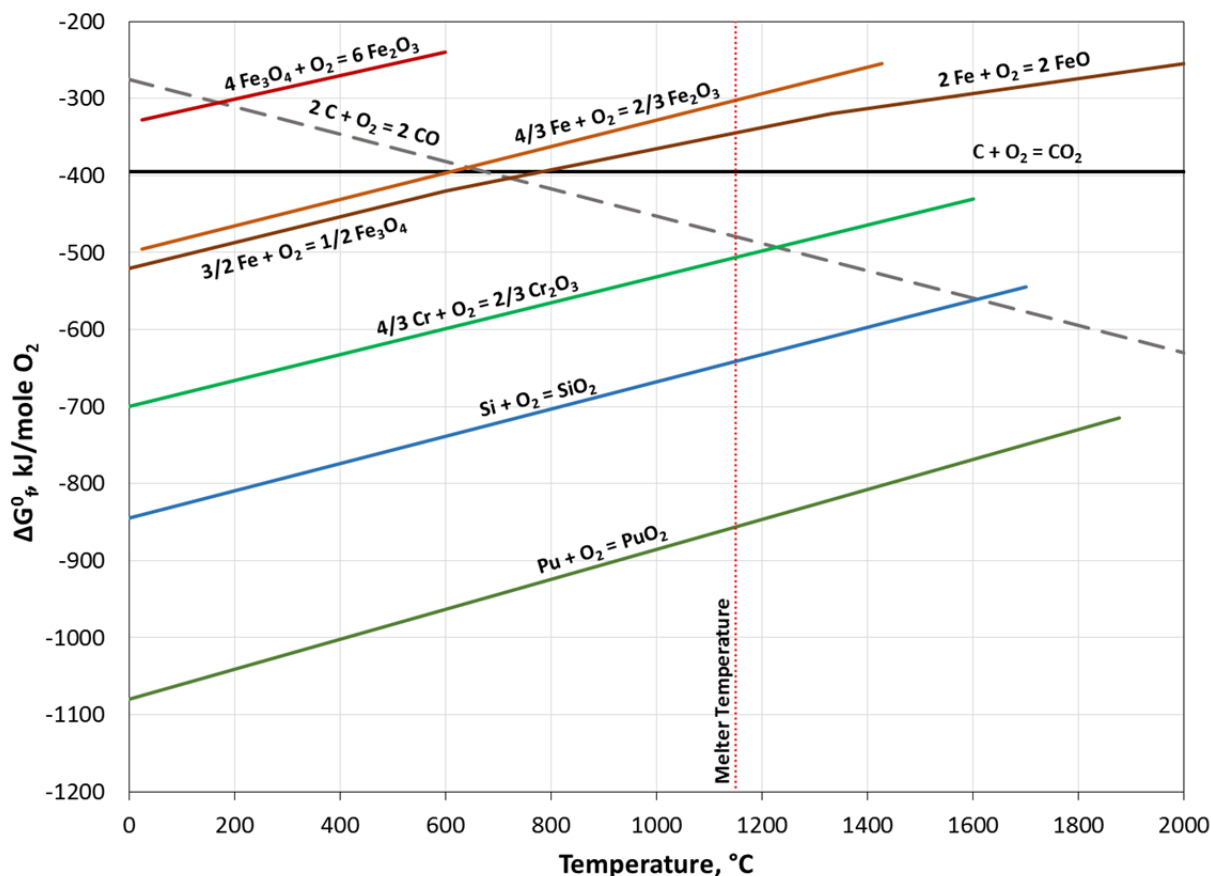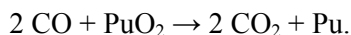
Figure 2-4. Ellingham Diagram for Carbon, Iron, Chromium, Silicon, and Plutonium and Their Oxides (Darken and Gurry 1953; Kleykamp 1985)

The Ellingham diagram (Figure 2-4) also shows that conditions sufficiently reducing to take PuO_2 to plutonium metal would be more than enough to reduce silica, SiO_2, a major glass-forming component, to elemental silicon, Si. Therefore, PuO_2 reduction to plutonium metal is shielded or buffered by the huge surfeit of SiO_2, which would first have to be reduced before any PuO_2 could be reduced. Other metal oxides present in the waste glass melt, including those of iron, chromium, nickel, and manganese, and of sulfate are similarly positioned in the Ellingham diagram by having to be reduced before PuO_2 could be reduced. Because plutonium quantities are very small, even if plutonium were reduced to metal, coalescence of the metal would be precluded. In fact, the plutonium metal is highly unlikely to survive as metal under melter conditions and even if it should, would be dissolved in metallic iron, as will be shown in the following paragraphs.

In practice, the iron oxides present in the glass provide a buffer more-than-sufficient to prevent iron metal formation in the event of inadvertent sugar over-dosage. As noted in Section 2.9, over-batching of sugar by a factor of 2.5 compared with the nominal flowsheet condition results in a Fe(II)/total Fe value of 0.6, meaning that the iron complement still is 40% Fe(III). The Fe(II) that did form still would require massive additional reductant (sugar) to proceed to iron metal. Thus, as seen in Figure 2-4, the oxidation conditions in the glass still lie well above those required to form iron metal.

> *Conclusions to Section 2.9.1 – Criticality concerns related to the occurrence of phenomenon RE1 are effectively excluded because: 1) reduction of PuO_2 to metal by carbon requires ~2300° C to be thermodynamically feasible, 2) the PuO_2 reduction to metal is shielded by a vast amount of SiO_2 (and other metal oxides) that must first be reduced, and (3) the low concentrations of plutonium in the waste and dissolution of plutonium into molten iron metal oppose any plutonium metal coalescence even if plutonium metal should form.*

2.9.2   RE4 – Reduction of Iron Due to Excess Sugar Addition

However, phenomenon RE4, the reduction of iron oxides in the glass to iron metal by sugar, is thermodynamically credible, meaning that the separation of iron, the primary credited neutron absorber, as metal from the plutonium present in the glass melt can occur. To address this concern in other (*in-situ* and *ex-situ*) vitrification processes, the dispositions of iron, other metals, including uranium and plutonium, and their oxides have been determined (Miller and Reimann (1993) and references therein). In particular, the behaviors of plutonium and uranium oxides in the presence of mild and stainless steel melts have been examined in work conducted at the Argonne and Oak Ridge National Laboratories and these findings have been examined and reviewed by Miller and Reimann (1993). The laboratory findings, which are in line with the thermodynamic analyses made by use of Ellingham diagrams, allowed Miller and Reimann (1993) to conclude that "experimental evidence substantiates the idea that uranium and plutonium oxides will preferentially remain in the slag or glass phase rather than be reduced to the metallic state and be dissolved into the molten iron" (p. 16).

Small amounts of plutonium metal postulated to have survived from plutonium metal recovery process losses from the Plutonium Finishing Plant may still be present in the tank waste feed (Delegard and Jones 2015). It is extremely unlikely that any such plutonium metal could resist the extremely oxidizing conditions incurred during the thermal decomposition of nitrate and nitrite salts during heat-up of the tank waste charge in the WTP melters. Instead, the plutonium metal would convert to PuO_2 or an oxidized plutonium salt and thus report to the glass phase. The distribution of up to 11.4 wt% plutonium oxide to glass has been demonstrated for lanthanum borosilicate glasses specially formulated to accommodate high plutonium concentrations (Vienna et al. 1996). A PuO_2 solubility of ~1% to 7% is more typical for defense HLW glass melted at 1150° C (e.g., Marra et al. (2010) and Muller et al. (2002)). The molten plutonium metal also would be unlikely to survive exposure to molten silica as the Ellingham diagram shows plutonium metal capable of reducing SiO_2 and many other metal oxides, including Fe_2O_3, to their elemental forms. However, if plutonium metal did somehow survive and if iron metal were present, the trace plutonium metal would dissolve in the much more abundant iron metal. The solubility of plutonium metal in iron at the nominal 1150°C melter temperature is about 5 wt% (Figure 13 of Miller and Reimann (1993)). With slow freezing of the melt below 912° C, the necessarily miniscule amounts of α-Fe_2Pu could crystallize within α-Fe (Fe-Pu metal phase diagram, Figure 13 of Miller and Reimann

(1993)). Based on this interpretation of the Fe-Pu phase diagram, Miller and Reimann (1993) state the following for melting of ferrous materials containing plutonium and other actinides:

> It is conceivable that the higher specific gravity intermetallic compounds could settle to form regions of high fissile material concentration. Because it is thermodynamically favorable for large crystals to grow from smaller crystals, it might be possible for locally high concentrations of the intermetallic phases to form without significant settling in the molten mass. (p. 16).

The settling mentioned above by Miller and Reimann (1993) is credible given that the α-Fe_2Pu density at ambient temperature is 12.72 g/cm^3 (Table 7.17 of Clark et al. (2006)), well above that of α-Fe ($\sim$7 g/cm^3). The intermetallic compound α-Fe_2Pu is not intrinsically safe with respect to criticality by the Pu-Fe mass ratio. However, the maximum plutonium concentration within the metallic iron and plutonium metal system still would be very small, meaning that the ability of trace amounts of α-Fe_2Pu to "find" other such material in the pool of cooling iron metal would be severely constrained. Thus, the likely outcome in the thermodynamically impossible event that sufficient plutonium metal could be present in this system to form any α-Fe_2Pu would be that only microscopic islands of the intermetallic phase would exist immersed in a sea of α-Fe and the plutonium would remain critically safe.

Again, reduction of PuO_2 to metal is thermodynamically impossible and the survival of any plutonium metal in the oxidizing decomposition of nitrate/nitrite salts and in the presence of silica, SiO_2, is practically foreclosed.

Therefore, the plutonium will partition to the more buoyant oxide/glass phase of the melt rather than to the denser molten iron in the impossible event plutonium metal should form or still be present from the waste feed. This behavior is also stated elsewhere for plutonium disposition in molten steel environments, which indicates only 0% to 1% of the plutonium partitions to steel, $\sim$95% to 100% to slag, and 0% to 5% to dust (Table 6.2 of NCRP (2002)).

Another issue arising from phenomenon RE4 is the criticality safety of plutonium within an iron-free glass. However, in this case, the silicon and particularly the sodium and boron in the sodium borosilicate glass should be more than sufficient to assure criticality safety. For example, a HLW glass produced by vitrification of pretreated (leached) actual waste from tank 241-AZ-101 contained 44.69 wt% SiO_2, 11.87 wt% Na_2O, 10.63 wt% B_2O_3, and 11.16 wt% Fe_2O_3 ((Hrma et al. 2004). The boron concentration in this glass was 3.30 wt%. Because comparable levels of boron are to be used for nominal LAW and HLW vitrification products, the boron alone will provide more than adequate margin for criticality safety to compensate for any loss of iron from the glass melt should overdose of sugar occur given that boron is 1450-times more effective for neutron absorption than is iron (Table 4-2 of (Miles 2009)).

> *Conclusions to Section 2.9.2 – Reduction of iron oxides to metal by massive sugar overdose is credible. However, plutonium oxide reduction to metal is not credible, as shown by consideration of phenomenon RE1. Any plutonium metal initially present in the waste is of small inventory and will certainly be oxidized. Therefore, the disposition of plutonium in the oxide/glass phase bereft of iron is of more concern in phenomenon RE4. However, it is seen that the levels of sodium, and particularly boron in the sodium borosilicate vitrification glass, is more than adequate to compensate for any iron lost to a separate dense metal phase in a waste/glass melt that has been overdosed in sugar.*

Overall, no deleterious impact to criticality safety is expected based on the phenomenon RE4, "Reduction of iron due to excess sugar addition."

2.9.3   OP9 – Plutonium Transported into Ventilation System

In phenomenon OP9, it is postulated that volatile plutonium phases might be generated in the melters because of the high melter temperatures and chemical effects. If volatile plutonium compounds form, they could be transported away from the melters to the offgas system, where they might concentrate, perhaps by condensation or dust collection.

The only known volatile plutonium phases that might arise in the melter systems are plutonium hexafluoride, PuF_6; plutonium oxyhalides such as PuO_2Cl_2; and plutonium trioxide, PuO_3, hydroxide-oxide, $PuO_2(OH)_2$, and plutonium tetroxide, PuO_4. All of these compounds require strongly oxidizing conditions to form; strongly oxidizing conditions are available in the vitrification melter.

Plutonium hexafluoride, however, cannot form under any credible conditions in the LAW or HLW melters because it requires fluorine gas or other powerful fluorinating agents to form. Such agents are not available in any WTP system. Furthermore, PuF_6 is extremely unstable and readily decomposes to form non-volatile plutonium tetrafluoride, PuF_4, and fluorine gas, F_2, and would be readily hydrolyzed in the moist melter cold cap even if it were formed. The halide (e.g., fluoride, F^-, and chloride, Cl^-) concentrations in the waste are inadequate to produce plutonium oxyhalides such as PuO_2Cl_2 and, like PuF_6, would be readily hydrolyzed in the cold cap.

The existences of volatile PuO_3, $PuO_2(OH)_2$, and PuO_4 have been proposed to explain the observation of volatile plutonium arising from exposure of PuO_2 to oxygen gas at high temperatures (page 1036 of Clark et al. (2006) and references therein; Hübener et al. (2008)). Apparent volatilization of plutonium from PuO_2 has been observed under heated and oxidizing conditions using helium/oxygen (He/O_2) mixtures (Ronchi et al. 2000; Domanov et al. 2002; Domanov and Lobanov 2009; Hübener et al. 2008). The latest investigations by Hübener et al. (2008) cast some doubt on the claims of PuO_4 formation made by Domanov and colleagues (2002; 2009) and also on their observations on the volatility of the plutonium gaseous species, while agreeing more closely with the findings of Ronchi and colleagues (2000).

The careful tests by Hübener and colleagues (2008) were conducted under conditions near those of the melters using oxygen and humid oxygen as oxidants and silica-based apparatus to study plutonium volatilization from a PuO_2 starting material. They found that PuO_2 began to volatilize above ~1000° C in the presence of humid oxygen gas, but that no volatilization occurred with oxygen gas alone. They found that not more than 0.6% of the total plutonium (the total being about 10^{16} atoms or ~0.01 micromole) could be volatilized from a silica crucible and that if quartz (i.e., silica) wool were used as the substrate, only about 0.1% of the plutonium could be volatilized. The experiments, which are described as thermochromatography, followed the deposition of the plutonium onto silica glass tubes as the volatile plutonium species migrated down the flow (and temperature) gradient of the silica glass tubes. The volatilized plutonium deposited downstream onto the tube, with deposition amounts greatest at the ~1000°-C zone and deposition complete by ~850° C. Even stronger plutonium deposition than for silica was observed when alumina, Al_2O_3, or zirconia, ZrO_2, apparatus was used (Hübener et al. 2008).

Based on these findings, negligible plutonium loss from the melters through volatilization is expected. The melters, indeed, provide conditions for PuO_2 oxidation and volatilization by the action of

oxygen gas and water vapor streams produced, respectively, by thermal decomposition of nitrate and nitrite salts and solution evaporation. However, based on the tests by Hübener et al. (2008), any of the trivial amount of plutonium that would be volatilized under these hot, moist, and oxidizing conditions would soon be captured onto silica surfaces within the cold cap (whose temperature ranges between the ~1150° C of the melt to the nominally 400° C of the plenum) and returned to the melt.

We also note that significant carry-over of entrained aerosols into the melter plenum occurs and that the entrained aerosol compositions are broadly representative of the melt compositions while the concentrations of vaporized but then plenum-condensed elements are slightly greater than the melt. Thus, the concentrations of semi-volatile elements such as boron, cesium, and chromium collected in the offgas plenum are modestly enriched over the nominal feed composition concentrations while the non-fuming components such as calcium, lanthanum, manganese, and zinc (and iron, which is considered to be non-volatile) are present at much lower to nominally equivalent feed melt concentrations (Section 7.3 of Goles et al. (2004)). In tests with a "Research-Scale Melter" of ~4.5-liter volume, about 0.6% to 2.5% of the non-volatile charge mass partitioned to the off-gas system (Goles et al. 2004). The loss of melter feed to the off-gas as particulate with more prototypical melters has been modeled and shown to be ~0.17% (Nelson 2013). Therefore, any plutonium entering the plenum will be accompanied by appreciable quantities of absorbers, including the semi-volatile neutron absorber, boron.

> *Conclusions to Section 2.9.3 – In phenomenon OP9, it is proposed that plutonium might volatilize in the melters and that the volatile plutonium could thus separate from the absorbers present in the glass, impacting criticality safety. Although conditions are available to generate volatile oxidized plutonium species such as $PuO_2(OH)_2$ by the action of hot, humid oxygen gas, laboratory tests show that the extent of plutonium volatilization is low and that the volatilized species readily and quantitatively absorb onto silica at temperatures below about 850° C. Therefore, any of the trace plutonium that might volatilize in the melt would be readily recaptured in the cold cap and be delivered to the melt. Overall, no deleterious impact to criticality safety from phenomenon OP9, "Plutonium transported into ventilation system," is expected.*

2.10 Physical Sedimentation Effects

Physical sedimentation of particles in the waste feed solution and solids in the WTP could alter the disposition and relative distributions of plutonium and absorber materials. The other phenomena considered in this document are related to the alteration of plutonium and absorbers through chemical effects. However, physical sedimentation relies on the disparate hydrodynamic behaviors of discrete plutonium-bearing particles and absorber-bearing particles. In phenomenon OP10, it is postulated that the vigorous mixing actions of the PJMs or spargers could cause the coprecipitated absorber and plutonium solids to separate. This phenomenon is outlined in Table 1-3 and repeated in Table 2-15.

Table 2-15. Phenomena Associated with Physical Sedimentation Effects

Number	Process	WTP System(s)
OP10	PJM impact on co-precipitated solids	Pretreatment PJM-mixed vessels

The meaning of the term coprecipitation and related terms will be considered in light of phenomenon OP10 to ascertain the specific risk to criticality safety that might be posed by vigorous mixing.

2.10.1   OP10 – PJM Impact on Co-Precipitated Solids

It is pertinent to know the disposition of plutonium within various solid phases in consideration of phenomenon OP10, the physical separation of plutonium solids from absorber solids by vigorous mixing. Solids containing plutonium arise in tank waste by several mechanisms. Probably the greatest amount of plutonium added to the Hanford tank waste is present by treatment of HNO_3 solutions containing plutonium nitrate, as $Pu(NO_3)_4$ and $PuO_2(NO_3)_2$, other metal ions such as Fe(III), Ni(II) and/or other anions (e.g., sulfate, phosphate) with NaOH solution. These mechanisms were examined in Sections 6.1 and 5.3.1, respectively, of the Phase 1 report (Delegard and Jones 2015). Plutonium also was discharged to the tank farms in the form of various intrinsic plutonium solid materials. Plutonium sent to the tank farms as intrinsic solids include plutonium fluoride salts, plutonium oxalate, plutonium in organic "cruds," plutonium dioxide, and plutonium metal. The formation and disposition of these solids were considered in Section 5.3.2 of the Phase 1 report. Finally, plutonium can be present in solid phase by being adsorbed from solution onto other solid phases, as was discussed in Section 6.2 of the Phase 1 report. The expected and observed plutonium dispositions in tank wastes arising by these various mechanisms are summarized in Table 2-16.

Table 2-16. Plutonium Disposition in Alkaline Tank Wastes

Starting Plutonium Disposition	Other Agent	Plutonium Disposition in Waste after NaOH Treatment
With Anions – (Section 5.3.1 of Delegard and Jones (2015))		
$Pu(NO_3)_{4\ solution}$	HNO_3 only	**$PuO_2 \cdot xH_2O$;** crystallites 0.002 to 0.005 µm
$PuO_2(NO_3)_{2\ solution}$	HNO_3 only	**Eventually $PuO_2 \cdot xH_2O$;** crystallites ~0.01 µm
$Pu(NO_3)_{4\ solution}$	Nitrate plus: nitrite, carbonate, sulfate, chromate, ferrocyanide, oxalate, glycolate, citrate, EDTA, or HEDTA	**$PuO_2 \cdot xH_2O$;** crystallites 0.002 to 0.005 µm
	Nitrate plus phosphate	**"$Pu(PO_4)O$"** **where P:Pu≤0.15;** unknown but small particle size
	Nitrate plus silicate	**"$Pu(SiO_4)O$"** **where Si:Pu = 0.3-1.8;** unknown but small particle size
With Metal Ions – (Section 6.1 of Delegard and Jones (2015))		
$Pu(NO_3)_{4\ solution}$	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 $PuO_2 \cdot xH_2O$ in

Starting Plutonium Disposition	Other Agent	Plutonium Disposition in Waste after NaOH Treatment
		nanometer-scale crystallites
	Dissolved Mn	**Coprecipitation likely**
	Dissolved nitrate salt of Cd(II)	Unknown
$PuO_2(NO_3)_2$ 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 of Delegard and Jones (2015))		
PuF_4 solid and fluoride double salt solids	None	**$PuO_2 \cdot xH_2O$;** likely micron-scale agglomerates of nanometer-scale small crystallites
$Pu(C_2O_4)_2 \cdot 6H_2O$ solid	None	
Pu in organic "cruds"	None	
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 of Delegard and Jones (2015))		
Dissolved plutonium	Various solids	Surface adsorption

The opportunity for plutonium in these solids to become separated from the associated absorbers is foreclosed for coprecipitation and for surface adsorption. In these two instances, the plutonium is chemically bound, generally as a trace constituent, either within the crystalline or even the amorphous phase absorber solid matrix (in coprecipitation), or onto the surface of the absorber solid matrix (in surface adsorption). Mechanical agitation cannot break the plutonium-absorber bonds in a significantly selective manner. If anything, mechanical agitation only will serve to break agglomerates apart while not altering the plutonium:absorber ratio in the subdivided particles.

Mechanical partitioning of intrinsic plutonium solids from discretely different absorber element solids particles is conceivable. However, for this to occur, the PuO_2 particle size must be sufficiently large for hydrodynamic force separation from the absorber constituent solids to take place (Serne et al. 1996). Plutonium particles arising from precipitation of "pure" plutonium nitrate solutions are nanometer-scale crystallites, largely of $PuO_2 \cdot xH_2O$, with dimensions similar to those of the absorber solids $Fe(OH)_3$ and $Na_2U_2O_7 \cdot xH_2O$ precipitated in the same manner (Section 5.3.1 of Delegard and Jones (2015)). The particles arising from precipitation with phosphate or silicate are also likely nanometer scale owing to their favored formation over the nanometer-scale $PuO_2 \cdot xH_2O$.

Intrinsic plutonium particles having dimensions of 10 to 30 μm and largely PuO_2 arising from scrap recovery or fuels reprocessing operations are found in waste and PuO_2 particles of 100-μm dimension or greater have been measured for products from plutonium metal burning (Section 5.3.3 and Appendix C, respectively, of Delegard and Jones (2015)) although transport of particles larger than 100 μm from the PFP to tank farms is highly unlikely. Images of angular plutonium-rich solids having the appearance of splintered wood have been collected from tank SY-102 and TX-118 waste and from Z-9 crib soils. These particles have dimensions in the tens-of-microns range (Figure 5-7 of Delegard and Jones (2015)). These

tanks and the Z-9 crib received waste from the Plutonium Finishing Plant. The same samples also have round plutonium-only particles and anomalous plutonium-bearing particles also containing bismuth and bismuth with phosphorus whose process origin is as yet unknown. Unburnt plutonium metal also may exist in the tank wastes and, in fact, may be the materials with the splintered wood appearance (Section 5.3.3 of Delegard and Jones (2015)).

Mechanical segregation of dense plutonium-bearing solids is the subject of separate, devoted studies. However, segregation of "coprecipitated fissile material and absorbers" by vigorous mixing according to the concerns expressed under phenomenon OP11 is not plausible.

> *Conclusions to Section 2.10 – The segregation of "coprecipitated fissile material and absorbers" by vigorous mixing according to the concerns expressed under phenomenon OP11 is not plausible.*

3.0   Conclusion

In the Phase 2 report, *"Process Engineering Chemistry Study to Support WTP Criticality Safety - WTP Process Analysis"* (Freer 2014), 28 phenomena arising from pH change processes, redox processes, and others were identified as having the potential within normal and upset WTP process conditions to alter the ratio of fissile material to neutron-absorbing material in the waste. In the present Phase 3 analysis, these 28 phenomena were grouped into 10 categories based on the similarities of their chemical or physical effects. These ten groupings are nitric acid effects, nitric acid / oxalic acid effects, sodium hydroxide effects, carbonate effects, permanganate effects, cerium / peroxide effects, organic effects, temperature effects, melter redox effects, and physical sedimentation effects. Each effect category then was addressed individually to ascertain its potential to alter the relative distributions of plutonium and the associated neutron absorbers. The overall conclusions reached for each category are summarized in the following paragraphs. We note that because the fissile ^{235}U and ^{233}U isotopes are diluted by the abundant and chemically identical ^{238}U also present in the waste, no consideration of the disposition of uranium itself as an element with fissile isotopes was made except tangentially with respect to uranium's interaction as an absorber for plutonium.

Nitric Acid Effects – Based largely on published studies of actual tank waste radiochemical analyses, lab process testing, and plant process experience, the presence of most plutonium as an intimate mixture with absorber materials through coprecipitation means that treatment with HNO_3 causes the proportionate dissolution of the plutonium and the absorber. Subsequent treatment of the resulting HNO_3 solution with NaOH solution, as would occur in WTP processing, would cause the dissolved plutonium and absorber to re-precipitate and thus not alter their relative distributions even at intermediate pH, given the parallel precipitation dependence of pH of plutonium and the absorbers aluminum, chromium, iron, and uranium in the acid to neutral range. However, in some instances, disproportionately greater dissolution of absorber element materials away from the plutonium solids is observed by HNO_3 treatment. The likely existence of refractory plutonium oxide, PuO_2, in tank waste and its known resistance to dissolution in HNO_3—made even more evident in that much of the PuO_2 present in the tank waste originated from dissolver heels from the PFP—makes this an issue of potential criticality concern even though metamictization should diminish PuO_2 crystallinity with time. Potential accumulation of ~0.1-kg quantities of plutonium on the ion exchange column may occur based on lab test results, high nominal feed solution plutonium concentrations, and plausible process flow rates and durations. However, the limited testing also shows that the plutonium in the eluate is accompanied by more-than-sufficient quantities of absorber elements including chromium, iron, manganese, nickel, and sodium.

Nitric Acid / Oxalic Acid Effects – As noted, the actions of HNO_3 by itself indicate that for most sludge, proportionate dissolution of plutonium and absorber are observed. However, the potential exists for refractory particles of PuO_2 to segregate from any of the absorber elements whose compounds can dissolve in HNO_3. The actions of $H_2C_2O_4$ to alter the distribution of plutonium and absorber elements are similar to those of HNO_3 but the degree of segregation in the case where plutonium-bearing residue exists is tempered by the potential formation of the solid absorber element compounds Mn(II) oxalate and U(VI) oxalate by the $H_2C_2O_4$ treatment. These solids would remain with the undissolved PuO_2 and thus provide neutron absorption should manganese or uranium be present.

Sodium Hydroxide Effects – The propensity for plutonium to separate from absorber elements cadmium, chromium as Cr(III), iron, manganese, nickel, or uranium by differential dissolution or

precipitation of their compounds based on changes in NaOH concentration is low. Only salts of the absorber elements aluminum, boron, and Cr(VI) have significant solubilities under alkaline conditions, while the solubility of plutonium as $PuO_2 \cdot xH_2O$ remains low from a criticality perspective. Because Cr(III) compounds can contain coprecipitated plutonium and alkaline oxidative leaching will convert many Cr(III) compounds to soluble Cr(VI) salts, plutonium dissolution also may occur under oxidative dissolution. Plutonium coprecipitation with gibbsite is negligible and complete dissolution of gibbsite can occur with high NaOH concentration, potentially leaving most plutonium in the solid phase. This means that separation of the absorber element aluminum from plutonium with increasing NaOH concentration is likely. However, dissolution tests of actual sludges from twelve different waste tanks using NaOH solution show that no significant plutonium dissolution occurred, implying that other materials present in the sludge (e.g., iron (hydr)oxides) successfully retained the plutonium in the solid phase even under conditions in which aluminum (hydr)oxide phases dissolved.

Carbonate Effects – Laboratory and waste analysis studies show that plutonium compound solubility is strongly enhanced by the presence of carbonate at pH $\gtrsim 12$, and even more strongly enhanced by bicarbonate at pH 9 to 10. The extent of plutonium leaching from solids that contain coprecipitated plutonium depends on the susceptibility of the host solids that contain the plutonium to dissolution in carbonate or bicarbonate. Laboratory testing shows that iron-bearing precipitates are not susceptible to dissolution in (bi)carbonate and thus resist leaching of their contained plutonium, while uranium-bearing solids dissolve in (bi)carbonate solution to release their contained plutonium. It is expected that compounds of other absorbers that are known to be effective coprecipitating agents for plutonium but have low solubility in (bi)carbonate (e.g., chromium(III), cobalt, lanthanum, manganese, and zirconium) will resist leaching of their contained plutonium. Compounds of the absorber elements aluminum and nickel do not coprecipitate plutonium, and plutonium leaching from aluminum solids by (bi)carbonate has been demonstrated. Therefore, leaching of plutonium from nickel solids by (bi)carbonate is also likely. Intrinsic plutonium solids present in the waste, such as PuO_2 discharged to the waste in that form or formed by plutonium compound hydrolysis, are expected to be susceptible to dissolution by (bi)carbonate, although at rates that may be low—especially for high-fired PuO_2.

Permanganate Effects – The solubilities of (hydr)oxide compounds of aluminum, cadmium, iron, and uranium (but not manganese(IV) and nickel) increase with alkaline leaching and thus help preserve the plutonium/absorber ratio in solution. However, the ratio may potentially be altered in permanganate oxidative dissolution of discrete plutonium phases such as PuO_2 or $PuO_2 \cdot xH_2O$ as a result of oxidation to the more soluble pentavalent or hexavalent oxidation states. Plutonium dissolution with permanganate is significantly enhanced with any increase in NaOH concentration, as demonstrated in tests of ten different genuine washed sludges. The amount of dissolved plutonium increased an average factor of 70 when leaching was performed using 3 M NaOH as compared with 0.1 or 0.25 M NaOH. The enhanced leaching likely was due to plutonium being oxidized to the more soluble hexavalent state. We note that dissolved plutonium species in alkaline solution, irrespective of oxidation state, are anionic so that their sorption on the cation-sorbing resin used for ^{137}Cs removal is not expected to occur. Based on oxidative leaching of REDOX Process sludge simulants and genuine Cr(III)-bearing Hanford tank sludges, however, excess permanganate does not appear to have any supplemental effect on the distribution of plutonium to solution. Accidental over-dosage of permanganate should not lead to enhanced plutonium leaching at lower alkalinity (0.09 to 0.25 M NaOH) while at higher alkalinity (3 M NaOH), the plutonium concentration increase to ~0.00036 g Pu/L can be mitigated by addition of Cr(III) nitrate to the permanganate/manganate-bearing slurry to eliminate excess oxidant, form MnO_2, and remove ~95% of

the solubilized plutonium by coprecipitation; permanganate elimination by H_2O_2 with concomitant removal of plutonium from solution also has been demonstrated. In treatment of Envelope C supernates with strontium nitrate and permanganate for ^{90}Sr and TRU removal, both coprecipitated plutonium and the residual soluble plutonium should be protected with 100- to 1000-fold higher neutron absorber concentrations based on AN-102 supernate studies. Although explicit experimental data on ^{239}Pu decontamination from AN-107 supernates are lacking, plutonium decontamination by Sr/Mn(VII) treatment similar to that of AN-102 should occur based on solution composition and total alpha analyses. Decontamination from dissolved plutonium of tank SY-101 solution also is found. Overall, Envelope C waste treatment by Sr/Mn(VII) should improve criticality safety by carrying plutonium into the solid phase in the presence of co-precipitated iron and supplemental manganese.

 Cerium and Peroxide Effects – Phenomena involving the uses of the chemical redox agents Ce(IV) and H_2O_2 in the surface decontamination of stainless steel glass canister vessels were identified. The situation of greatest concern in the use of acidic Ce(IV) nitrate solution is its inadvertent introduction to alkaline tank waste under continued acidic conditions, causing the oxidative dissolution of the waste sludges and their contained plutonium to form Pu(VI). While the dissolution itself would have no criticality safety consequence because of the accompanying dissolved absorbers, subsequent adjustment to alkaline conditions would precipitate most absorbers and leave the Pu(VI) in solution. However, the Pu(VI) would be accompanied by abundant sodium from the added NaOH and, potentially, chromium as soluble chromate to provide neutron absorption. The actual concentration of Pu(VI) likely would be small because of the relatively low concentration of plutonium in waste sludge. The inadvertent introduction of H_2O_2 to tank waste also could occur to oxidatively dissolve Cr(III) solids and their contained plutonium or intrinsic plutonium solids such as $PuO_2 \cdot xH_2O$ to form soluble Cr(VI), Pu(V), and perhaps Pu(V) peroxide complexes. Again, however, the amount of plutonium dissolved by this action would be small and would be accompanied by chromium and the ubiquitous sodium ion as absorbers. With time and radiolysis, most of the plutonium would eventually be chemically reduced to precipitate onto the absorber solids in the sludge while the chromate would remain in solution.

 Organic Effects – The effects of organic compounds on the relative distributions of plutonium and absorber compounds to solid and solution phases are manifest by their potential actions to dissolve the plutonium or absorber elements, and by their influence in oxidative degradation, on the solubility of aluminum phases. Hanford process organic complexants and extractants such as EDTA and TBP, respectively, are expected to have little chemical interaction with plutonium and iron, the principal absorber element, in alkaline waste media. These source organic compounds also are known to degrade by hydrolysis and radiolysis to simpler and less interactive compounds. Although partition of plutonium to separate aqueous-immiscible organic phases present in tank wastes has been observed, the partitioning appears to be physical and not plutonium-specific because other low-solubility solid materials also partition at about equal fraction to the organic. Therefore, the presence of tank waste organics in the WTP is unlikely to dissolve and concentrate fissile material or otherwise separate fissile material from credited absorbers. Anti-foam agents also are being considered for use in the WTP operations. Although polyol chemical agents with compositions similar to that of the anti-foam agent constituent polyether polyol are known to enhance plutonium solubility in pH-12 systems, tests of plutonium dissolution from simulant sludge in the presence and absence of the anti-foam agent showed no preferential plutonium dissolution even with 85° C leaching using 3 M NaOH or 0.25 M NaOH with permanganate. Organic oxidative degradation reactions are unlikely to cause significant composition changes during timely plant processing but may occur under extended storage. The organic reactions would decrease hydroxide

concentration and form carbonate, leading to decreased aluminum solubility to form gibbsite and dawsonite, respectively. Waste blending also can precipitate aluminum as gibbsite or dawsonite by pH and carbonate concentration changes or sodium aluminosilicates such as cancrinite by addition of silicates to aluminum-rich solutions. Gibbsite precipitated by making acidic aluminum-bearing solution alkaline does not carry plutonium and does not enhance iron precipitation, but the carrying of plutonium by gibbsite precipitated by lowering the pH of alkaline solution or by forming dawsonite by further pH lowering and the addition of carbonate has not been investigated. Plutonium incorporation into aluminosilicates is unlikely. The plutonium available for carrying by gibbsite is likely to be small enough ($\sim10^{-7}$ M) to be inconsequential, while solubility-limited plutonium potentially available to be carried from solution by dawsonite precipitation, ~0.002 M (~0.5 g Pu/L) may be of criticality concern. However, the actual amounts of plutonium available for dissolution from sludge likely are much lower than the solubility limits.

Temperature Effects – The influence of temperature change in alkaline waste slurries on the relative distributions of plutonium and absorber elements to the solid and solution phases is small except in the case of aluminum. For aluminum (hydr)oxides, the aluminum concentration in NaOH solution changes markedly with temperature change such that if a waste slurry contains only $Al(OH)_3$ and $PuO_2 \cdot xH_2O$ in the solid phase, and the $Al(OH)_3$ is leached by digestion in strong heated NaOH, separation of the absorber aluminum from the plutonium will occur and potentially impact the criticality safety. The reverse situation, removal of aluminum from solution by precipitation occasioned by dilution, cooling, or crystal seeding for supersaturated alkaline solutions, is not of criticality concern because of plutonium's low solubility.

Melter Effects – Criticality concerns arise in the possible formation of plutonium metal in the melter by introduction of excess sugar as reductant, by the potential for iron metal or metal sulfides to be formed by chemical reduction and thus separate from the plutonium, and by volatilization of the plutonium. Criticality concerns related to the separation of plutonium and absorbers in the melter by plutonium metal formation are effectively excluded for several reasons. First, reduction of PuO_2 to metal by carbon requires $\sim2300°$ C to be thermodynamically feasible, thus foreclosing the possibility of plutonium metal formation in the nominal $1150°$ C melter. In addition, for plutonium metal to be formed, a vast amount of SiO_2, other metal oxides, and sulfate first must be reduced, effectively shielding the plutonium from reduction to metal by the surfeit of silica and other oxides that are more easily reduced. Finally, the low plutonium concentrations in the waste and plutonium dissolution into molten iron metal oppose any plutonium metal coalescence even if plutonium metal should form. Reduction of iron oxides to metal and to its sulfide by massive sugar overdose is credible. However, as already noted, plutonium oxide reduction to metal is not credible. Any plutonium metal initially present in the waste is of small inventory and certainly would be oxidized during heating by the strongly oxidizing initial conditions in the melter during thermal decomposition of nitrate and nitrite. The disposition of plutonium thus would be in the oxide melt phase that might contain lower iron concentrations should iron metal be formed. In this case, the sodium and particularly boron in the sodium borosilicate melt (and glass) should be sufficient as a neutron absorber to offset any iron lost to a separate dense-metal phase. Volatilization of plutonium in the melters is expected to be low. Although conditions to generate volatile oxidized plutonium species such as $PuO_2(OH)_2$ by the action of hot, humid oxygen gas (as would be present in the melter) are known in laboratory tests, the volatilization extent is low. Furthermore, the volatile plutonium species readily and quantitatively absorbs onto silica at temperatures below about $850°$ C. Therefore, any of the trace plutonium that might volatilize in the melt would be readily recaptured in the cold cap and be delivered to

the melt. Finally, any volatilized plutonium would be overwhelmed by the absorbers carried into the melter plenum as aerosols, which are generally representative of the melt composition itself, and the boron-rich compound vapor condensates.

Physical Sedimentation Effects – Mechanical segregation of dense plutonium-bearing solids is the subject of separate, devoted studies. However, segregation of coprecipitated fissile material and absorbers by vigorous agitation according to the conditions provided by pulse jet mixing and spargers is not plausible. At most, de-agglomeration of the coprecipitates could occur, but the plutonium and absorber ratios in the smaller solids would be preserved.

Summary – Of the various phenomena and chemical effects considered, the likely existence of refractory PuO_2 in tank waste and its known and demonstrated resistance to dissolution in HNO_3 while absorber element compounds dissolve and thus segregate, make treatment of PuO_2-bearing sludge with HNO_3 an issue of potential criticality concern. Segregation of ~0.1-kg quantities of plutonium onto the CsIX columns, either with or without acidification, might occur based on lab test results, high nominal feed solution concentrations, and plausible process flow rates and durations. On the strongly alkaline side, the separation of the absorber element aluminum from intrinsic plutonium solids such as PuO_2 with increasing NaOH concentration also is of concern. Dissolution tests of twelve different actual sludges using NaOH solution show, however, that no significant plutonium dissolution occurs implying that other (non-aluminum) sludge materials such as iron (hydr)oxides retain the plutonium in the solid phase even under conditions in which aluminum sludge solids dissolved. The solubility-limited plutonium potentially available to be carried from solution by dawsonite precipitation, ~0.002 M (~0.5 g Pu/L), may be of criticality concern in low hydroxide and high bicarbonate conditions engendered by organic oxidation reactions under inordinately long waste storage times. However, the actual amounts of plutonium available for dissolution from sludge are likely much lower than the plutonium solubility limits in high bicarbonate solution. Likewise, inadvertent additions of high concentrations of carbonate, permanganate, cerium(IV), or peroxide are judged not to be problems because of the limited amounts of plutonium available to dissolve. Temperature changes, melter chemistry, and separation of plutonium from coprecipitated absorbers by physical sedimentation following vigorous agitation also are expected to have no deleterious effects on the relative distributions of plutonium and absorbers.

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