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CRITICALITY SAFETY ASSESSMENT OF TANK 241-C-106 REMEDIATION

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Abstract: A criticality safety assessment was performed in support of Project 320 for the retrieval of waste from tank 241-C-106 to tank 241-AY-102. The assessment was performed by a multi-disciplined team consisting of expertise covering the range of nuclear engineering, plutonium and nuclear waste chemistry, and physical mixing hydraulics. Technical analysis was performed to evaluate the physical and chemical behavior of fissile material in neutralized Hanford waste as well as modeling of the fluid dynamics for the retrieval activity. The team has not found evidence of any credible mechanism to attain neutronic criticality in either tank and has concluded that a criticality accident is incredible.

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CRITICALITY SAFETY ASSESSMENT OF TANK 241-C-106 REMEDIATION

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EXECUTIVE SUMMARY

A multi-disciplined team consisting of members with expertise covering the range of nuclear engineering, plutonium and nuclear waste chemistry, and physical mixing hydraulics was assembled to assess the criticality aspects of the proposed tank 241-C-106 retrieval operations. Given this diverse range of backgrounds, the team considered an exhaustive set of possible scenarios and considered a set of bounding conditions to ascertain whether there was any reasonable probability of attaining criticality during the proposed operations. Figure ES-1 provides a summary of the mechanistic factors that must be achieved prior to a concern for a criticality event.

First, the donor and receiver waste tanks contain prodigious amounts of neutron absorbers. Over 6 times as much iron is present than is needed to prevent criticality in either donor tank 241-C-106 or receiver tank 241-AY-102, and over 4 times the required amount of manganese is present to independently prevent criticality. Numerous other neutron absorbers add to the degree of subcriticality. However, such absorbers are of little value if they could be completely separated from the plutonium. Consequently, the team devoted substantial effort to ascertain the form of the plutonium in the waste material to determine whether such separation was possible.

There is evidence that the plutonium in the waste tanks will be chemically bonded (sorbed) onto the surfaces of the metal oxyhydroxides of strong neutron absorbers such as iron, aluminum and manganese (all of which are in large abundance in both tanks). There is also evidence that such bonding will remain during the waste aging process. If sorption is the dominate precipitation mechanism in these strongly alkaline waste forms, there is absolutely no possibility of criticality--since any postulated fissile concentration mechanism would concentrate the neutron poisons in the same ratio.

On the other hand, it is difficult to prove that chemical sorption is the only precipitation mechanism. It is possible that plutonium oxide crystals could form as a separate phase in the sludge waste. Even though such a possibility would not give rise to criticality concerns for stable waste tank conditions (since massive amounts of neutron absorbers would always be in close proximity to the fissile material), it is conceivable that hydraulic forces associated with the proposed retrieval process could concentrate the plutonium oxide. This possibility leads to the second diamond of Figure ES-1, "Can an adequate plutonium concentration factor be achieved?"

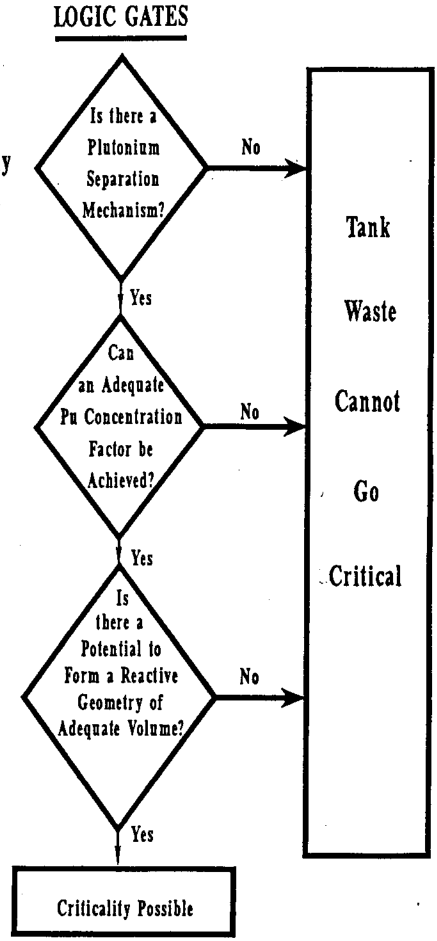
The team notes that in order for a neutronic criticality to be possible, the plutonium concentration in an infinite volume of waste must exceed 2.6 g Pu/L. Numerous layers of conservatism are built into this minimum fissile concentration, including optimal neutron moderation (i.e., optimal water moisture content), a waste medium containing a small fraction of the neutron absorbers actually present, and an infinite geometry. Since the maximum concentration of plutonium measured in either donor tank 241-C-106 or receiver tank 241-AY-102 was 0.13 g Pu/L, a plutonium concentration increase of at least 20 would be necessary to achieve criticality under the most ideal conditions.

Figure ES-1. Principal Conditions Necessary For Criticality in Tanks 241-C-106 or 241-AY-102.

- Massive neutron absorbers present
- Sorption of Pu onto metal oxyhydroxides likely
- PuO$_2$ crystals could form

- $\geq$ 2.6 g Pu/L
- Concentration increase > 20 required
- Maximum credible concentration from hydraulics < 10

- 108 Kg* at 4 g Pu/L requires 12 foot diameter sphere for criticality



* Total plutonium inventory available from tanks C-106 and AY-102.

Extensive hydraulic particle separation investigations were carried out to determine whether sufficient separation of plutonium from neutron adsorbers was possible. Computational modeling was conducted to test a wide range of possible settling patterns. Although it is possible to calculate concentration factors exceeding 20 (the margin between the maximum measured Pu concentration in the sludge and the minimum plutonium concentration required under idealized conditions to attain criticality), the parameters necessary to do so would require a unique combination of low probability events. Given our best estimate for physical parameters, the maximum concentration factors achievable are less than 10.

The final diamond of Figure ES-1, "Is there a potential to form a reactive geometry of adequate volume," is included to recognize the difficulty of achieving a critical geometry, even if the plutonium is concentrated in a form absent from the abundant neutron absorbers in the tanks. For instance, if all of the plutonium contained in tanks 241-C-106 and 241-AY-102 (108 kg, using the maximum estimates) were concentrated into a spherical ball to a concentration of 4 g Pu/L (twice the minimum concentration necessary for an infinite medium), the ball would be about 12 ft in diameter. The physical possibility of achieving such a scenario is highly unlikely. More realistic geometries would be considerably less reactive.

The important message is that all of the "gates" illustrated in Figure ES- 1 must be penetrated before there is even the remote possibility of a criticality. Any one of these "gates" provides a high degree of assurance that criticality is not possible. Taken in series, the potential for criticality is considered extremely unlikely.

As a consequence, the team has not found any evidence that would lead us to believe there is a credible mechanism to attain neutronic criticality in the tank 241-C-106 retrieval operations. Consequently, the team sees no technical basis to prevent proceeding with the proposed operations from the standpoint of criticality.

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ALARA	as low as reasonably achievable
CRW	cladding removal waste
DF	decontamination factor
DST	double-shell tank
EDTA	ethylenediaminetetraacetate
FSAR	Final Safety Analysis Report
HEDTA	N-2-hydroxyethylethylenediaminetriacetate
PCB	polychlorinated biphenyl
PFP	Plutonium Finishing Plant
PUREX	plutonium-uranium extraction
REDOX	reduction and oxidation
SST	single-shell tank
TOC	total organic concentration
TRU	transuranic
DOE	U.S. Department of Energy
WRSS	waste retrieval sluicing system

CRITICALITY SAFETY ASSESSMENT OF TANK 241-C-106 REMEDIATION

1.0 INTRODUCTION

A key part of the Hanford Tank Waste Remediation Program is to minimize any safety concerns associated with the tanks. In particular, tank 241-C-106 (subsequently referred to as tank 241-C-106), a 2 million L (0.53 million gal) single-shell tank (SST) built in the late 1940's, contains the highest heat load in the SST farm complex due to high levels of ^{90}Sr. As a consequence of this inventory, sufficient heat is generated by radioactive decay that the contents would boil if not cooled by routine additions of water to facilitate evaporative cooling.

Whereas the practice of controlling the temperature of this tank by regular additions of water is satisfactory, there is general agreement that the safety of tank 241-C-106 could be better assured if no regular, active intervention were necessary. The safety philosophy generally employed with the Hanford SSTs is to stabilize the waste content by removing as much moisture as possible. Such an approach minimizes the potential consequences of tank leakage (an ongoing concern with aging SSTs).

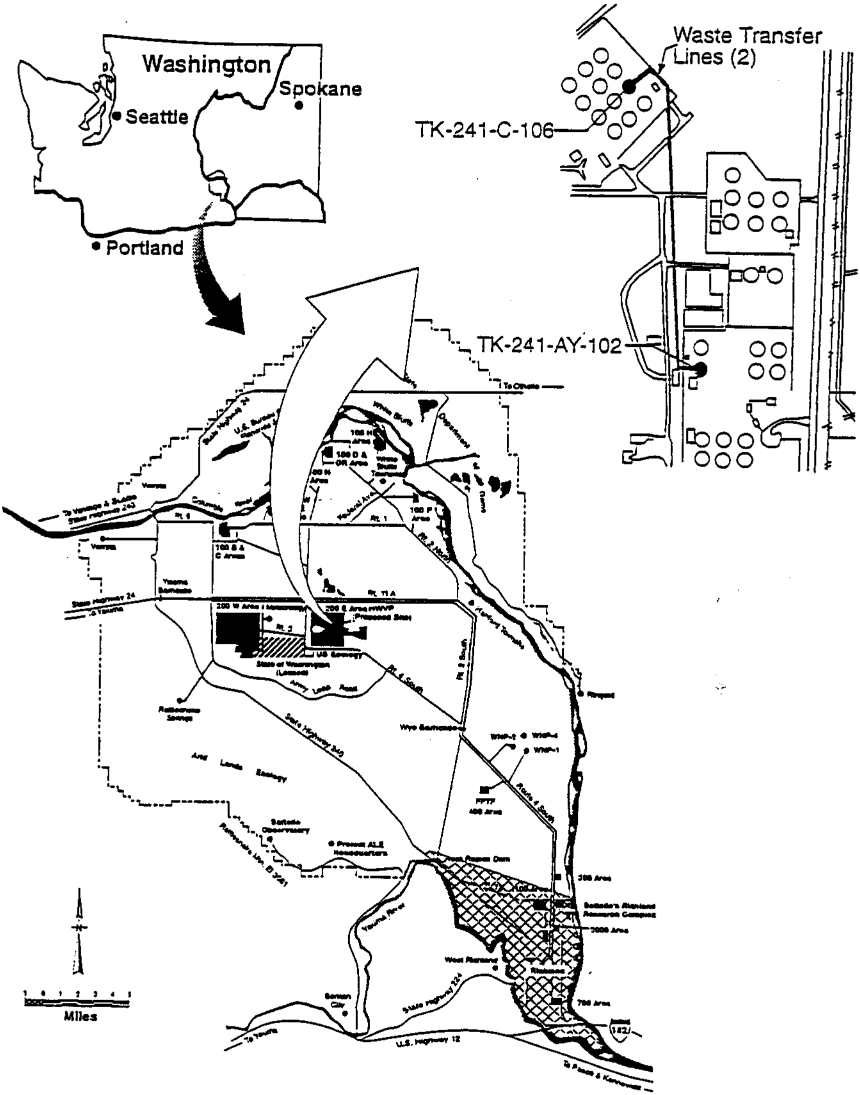
Consequently, the U.S. Department of Energy (DOE) has proposed transferring a major portion of the high-heat generating radioactive sludge from tank 241-C-106 to tank 241-AY-102, a larger double-shell tank (DST), which has a capacity of 4.4 million L (1.16 million gal). The double walled features of tank 241-AY-102, combined with its current waste inventory, provide the accommodation desired for dealing with the heat load from tank 241-C-106 waste.

Figure 1-1 illustrates the location of the Hanford 200-East area where the two tanks are located. The heavy line in the enlargement indicates the location of the slurry and sluice lines installed to effect the waste transfer.

The tank waste retrieval action envisioned is attracting particular attention because it is the first large waste transfer of slurries at Hanford in recent years, although the technology of the proposed sluicing/retrieval process has been employed on numerous past occasions at the Hanford Site. Another reason for the high visibility of this operation is because tank 241-C-106 is believed to contain the largest amount of plutonium in any Hanford waste tank; just under 100 kg by the most conservative estimates. The current inventory of tank 241-AY-102 is about 8 Kg plutonium; thus the maximum inventory possible in tank 241-AY-102 is approximately 108 Kg.

The purpose of the present report is to provide an assessment on the criticality implications of this waste transfer remediation project. In particular, the concern is whether there are any aspects of the proposed project that could concentrate the plutonium in the tanks to pose a serious criticality problem.

Figure 1-1. Location of Tanks 241-C-106 and 241-AY-102.



The present assessment is based on an expansion of the studies performed by the present authors in support of the Final Safety Analysis Report (FSAR) for the Hanford waste tanks. This expansion was necessary because the tank farm FSAR study was limited in scope to "safe storage" and did not explicitly include retrieval operations. Furthermore, the FSAR work was, by definition, tank farm generic. The present study is specific to the tanks 241-C-106 and 241-AY-102 retrieval program.

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2.0 TANK 241-C-106 REMEDIATION PROGRAM

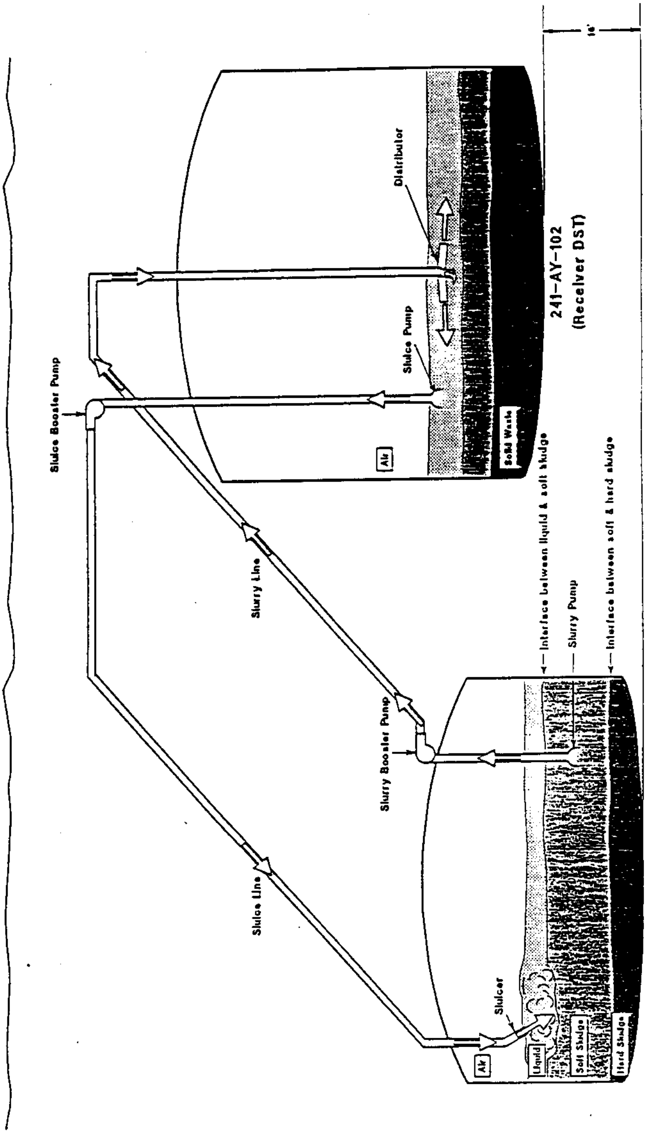
The DOE is taking action to eliminate safety concerns with regard to storage of high-heat waste in tank 241-C-106 and to demonstrate a tank waste retrieval technology. The proposed action is to move high-heat solid waste from tank 241-C-106 (a SST built in the mid 1940's) to DST, i.e., tank 241-AY-102. Past-practice sluicing technology, a mode of waste retrieval used extensively in the past at the Hanford Site, will be used to transfer high-heat waste from tank 241-C-106 to tank 241-AY-102, a process identified as the tank 241-C-106 waste retrieval sluicing system (WRSS), Project W-320, (Bailey 1995).

Tank 241-C-106 has been used for radioactive waste storage since 1947. Between mid-1963 and mid-1969, tank 241-C-106 received about 500,000 L (132,000 gal) of high-heat waste, including neutralized plutonium-uranium extraction (PUREX) high-level waste and strontium bearing solids from the strontium and cesium recovery program. The high temperatures in tank 241-C-106, relative to the other tanks at Hanford, are due principally to the high concentration of strontium and cesium. Temperatures in excess of 99 °C (210 °F) were measured in tank 241-C-106 in 1971. Tank 241-C-106 and adjoining tank 241-C-105 were placed in an "active exhauster" status and have water periodically added to facilitate heat removal. About 23,000 L (6,000 gal) of water are added to tank 241-C-106 each month to remove heat by evaporative cooling. A water cover is maintained over the solids, facilitating evaporative cooling to prevent the sludge from drying out and the tank from overheating. During the last 10 years, about 3,000,000 L (800,000 gal) of water have been added to tank 241-C-106 for cooling purposes. Water additions would need to continue until about the year 2045 to prevent overheating, a direct function of the approximately 30-year half-life of ^{90}Sr. A significant safety issue has been generated by concerns of eventual tank leakage (the tank will be 100 years old by the year 2045) and the requirement for continued water additions to prevent sludge dry-out, temperature excursions, and potential tank failure.

The radiogenic heat rate in tank 241-C-106 is presently calculated to be 116 MJ/h (110,000 Btu/h) +/- 21MJ/h (20,000 Btu/h) based on the current waste content of 746,000 L (197,000 gal) of sludge, (Bander 1993). Of this total, 655,000 L (173,000 gal) is soft sludge and 91,000 L (24,000 gal) is hardpan sludge material. The tank also contains 182,000 L (48,000 gal) of liquid. It is proposed to remove the softer, sluicable radioactive sludge from tank 241-C-106 and transfer that material to DST 241-AY-102. The transfer would eliminate the need for the addition of cooling water to tank 241-C-106. It would also stabilize the tank and resolve the existing safety issues.

Figure 2-1 contains a simplified illustration of the proposed retrieval sluicing system process. A variable speed, submersible sluice pump will be installed in tank 241-AY-102 to initially pump a high-volume, high-velocity stream of fluid from 241-AY-102 into tank 241-C-106 (through a remotely operated sluicer that will be installed in tank 241-C-106). The stream of AY-102 supernate will mobilize the waste sludge in tank 241-C-106, creating a slurry that can be removed by a submersible 75-hp slurry pump, in series with a variable speed 110-hp input booster pump, at about the same rate that

Figure 2-1. Schematic of the Sluicing/Retrieval Operation.



the sluicing fluid is introduced into tank 241-C-106. The sluice booster pump is rated at 1,300 L/min (350 gpm), operating at a temperature of 40 °C (120 °F).

The waste will be transferred to tank 241-AY-102 through a double encased, primary slurry transfer pipe (4 in. inner diameter, approximately 1,700 ft in length). The height of the submersible sluice and submersible slurry pumps may be individually adjusted via winches to compensate for liquid level changes.

The waste slurry from tank 241-C-106 will be directed into tank 241-AY-102 through a submerged distributor that spreads the slurry as evenly as possible over a large area by spraying it from four nozzles equidistant from each other to optimize the radial distribution of the discharged slurry while canceling out the bending moments on the distributor. The heavier particulate material will settle to the bottom of the tank, leaving a clarified supernatant for use as the sluicing agent. Unsettled solids in tank 241-AY-102 will be recycled to tank 241-C-106 for further sluicing.

Both slurry and supernatant transfer pipelines will be buried and bermed to provide freeze protection and shielding to maintain personnel radiation exposure as low as reasonably achievable (ALARA). Leakage from the primary transfer pipe (inner pipe) will be contained and detected by the secondary confinement system (encasement or outer pipe). The secondary confinement system has been designed to drain any fluid released from the primary piping to a common point for collection, detection, and removal.

A new ventilation system for tank 241-C-106 will be installed as part of the project. The ventilation system has been designed to maintain a negative tank pressure, remove heat from the tank and dehumidify the tank vapor space by recirculating a portion of the flow back to the tank through a condenser and heater, remove aerosols from ventilation emissions, and monitor the exhaust ventilation stream through the exhaust stack to the atmosphere. In addition, the design allows for the use of the existing ventilation system as a passive breather system for the tank during interruptions of sluicing operations or as a backup (higher capacity) ventilation system during periods of extended maintenance.

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3.0 CHEMICAL CONSIDERATIONS - PLUTONIUM CONTAINING SOLIDS

3.1 INTRODUCTION

This section examines chemical mechanisms that have been postulated to occur in the sludge. Our attention has been focused on the sludge, rather than the supernatant liquid, because it is only in the sludge that plutonium concentrations of potential concern could arise. The low solubility of plutonium in the liquid prevents a criticality concern in that medium.

There are three potential chemical mechanisms that need to be considered in determining the manner in which plutonium enters the sludge: 1) sorption onto precipitated metal oxide sludge particles, 2) precipitation as pure $PuO_2 \cdot xH_2O$ amorphous solids, and 3) solid-solid solution with metal oxyhydroxides. Once precipitated with the inorganic waste solids, the plutonium is believed to undergo an aging process that results in a slightly crystalline product. This results from a collapse of metal hydroxide bridges in favor of metal oxide bridges as water is eliminated. Figure 3-1 illustrates these three possibilities and how the mechanisms influence criticality considerations.

PFP waste was normally routed from 244-TX to tank 241-SY-102 where solids are allowed to settle. Supernate, which might contain a very small amount of plutonium as particulate crystalline PuO_2, was transferred to tank 241-AY-102. Estimates of waste content in tank 241-AY-102 show that PFP waste constitutes a negligible (<1%) of the total waste inventory of this tank (Agnew 1996).

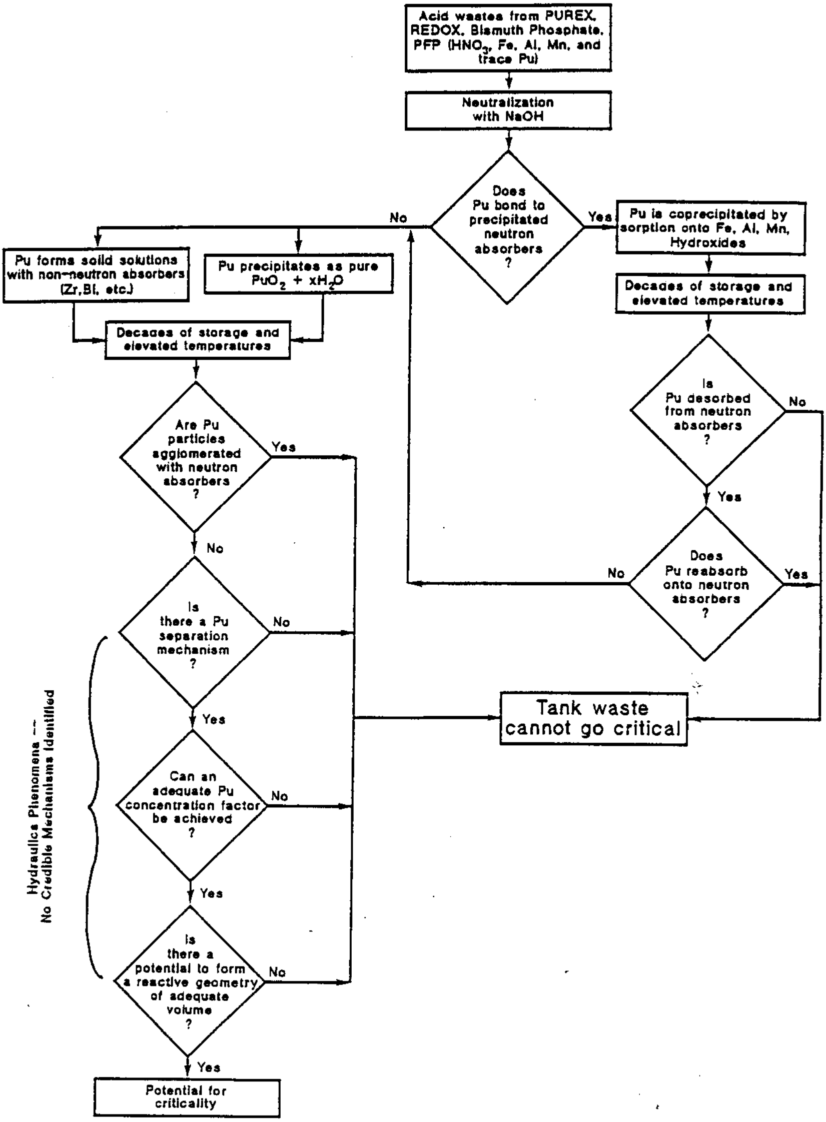
If sorption is the dominant mechanism, the direct bonding of plutonium to strong neutron-absorbing metals such as iron, aluminum, or manganese provides direct assurance that tank criticality cannot take place.

If pure hydrous plutonium oxide ($PuO_2 \cdot xH_2O$) forms a precipitate, such particles would agglomerate or mix with neutron absorbers. In such a case, criticality could not take place, unless hydraulic forces during retrieval would separate the absorber and fissile materials. The creation of neutron poison-free plutonium particles sufficiently large (e.g., tens of microns in size) to be significantly concentrated by retrieval hydraulics is not plausible, based on all the literature and calculations available to date. A thorough discussion of hydraulic separation mechanisms is provided in Section 4.0. The team agrees that whichever product of initial precipitation dominates, neither poses a serious risk from a criticality standpoint in tanks 241-C-106 and 241-AY-102.

The third potential fate for plutonium in the sludge is solid solution formation with large cation oxides. However, the absence of the necessary large cation metal oxides (zirconium and bismuth) in tanks 241-C-106 and 241-AY-102 effectively eliminates further concern for this mechanism.

Therefore, despite the uncertainties associated with the governing chemistry, there does not appear to be any technical basis for concluding that there are any forces associated with the proposed retrieval process that could cause sufficient separation/enrichment of the plutonium from neutron absorbers to cause a criticality concern.

Figure 3-1. Chemical Considerations Related to Tank Criticality in Tanks 241-C-106 and 241-AY-102.



The final subsection includes some discussion on how aging affects the three mechanisms identified above.

3.2 ADSORPTION

Dissolved plutonium has been shown to adsorb onto a wide variety of metal oxide and hydroxide surfaces, including surfaces of oxides that are known to exist in tank 241-C-106 and tank 241-AY-102 sludges. This section discusses the available evidence that adsorption may be an important mechanism for bonding plutonium in the sludge to neutron absorbers such as iron, aluminum and manganese hydroxides. If this mechanism prevails in the waste, concentration of plutonium during retrieval is not possible.

3.2.1 Formation Mechanisms

Most of the high-level radioactive waste solutions generated from chemical operations at Hanford were acidic solutions containing metals dissolved in nitric acid. Small concentrations of dissolved plutonium (typically $< 10^{-5}$ $\underline{M}$ Pu, [Braun et al. 1994]) that were not recovered in processing were also present in these waste solutions. Before sending the waste to underground tanks, the acid was neutralized with excess sodium hydroxide to prevent corrosion of the carbon steel tanks. Metals that were insoluble in basic solutions (including plutonium) were precipitated as oxyhydroxides during neutralization. These oxyhydroxides are the major components of sludge in the tanks.

Concentrations of plutonium were very small compared to the other metals dissolved in the waste solutions from the various processing operations (Braun et al. 1994). For example, typical mole ratios of iron/plutonium and aluminum/plutonium in the Hanford waste tanks were 12,000 and 28,000, respectively for bismuth phosphate waste; 1,400 and 132,000, respectively for reduction and oxidation (REDOX) waste; 63,000 and 1,400,000, respectively for PUREX aluminum clad wastes; 3,300 and 13,000, respectively for PUREX Zirflex waste; and 100 and 7,400 respectively for plutonium finishing wastes (this does not include iron added to the waste as a criticality control). In addition to iron and aluminum, other dissolved metals such as uranium, zirconium, manganese, bismuth, chromium, nickel, and tin were present in the acid waste and were precipitated as oxyhydroxides.

The waste composition in tank 241-C-106 (Sederburg 1994) consists mainly of sludge solids (746,000 L) and liquid supernate solution (182,000 L). The tank received tributyl phosphate waste from the uranium recovery process from 1954 to 1963, neutralized PUREX acid waste from 1958 to 1963, aluminum cladding waste from 1958 to 1963, PUREX organic wash waste from 1969 to 1974, and B-Plant complexed waste from 1974 to 1978. This resulted in a sludge with high concentrations of iron, aluminum, silicon and phosphate. The iron/plutonium and aluminum/plutonium mole ratios are about 4,500 and 5,800 in the sludge. The supernate solution has high concentrations of sodium (4.0 $\underline{M}$), nitrate (1.1 $\underline{M}$) and carbonate (0.75 $\underline{M}$). The plutonium concentration in the supernate is 0.0035 g/L (1.5×10^{-5} $\underline{M}$).

In a nitric acid solution containing Pu(IV) as the only dissolved hydrolyzable metal ion, neutralization with sodium hydroxide, as required for waste solutions sent to the tanks, would produce plutonium polymer along with plutonium hydroxide. However, because of the low solubility of iron and aluminum hydroxides and their much higher initial concentrations in the waste solution, these compounds will precipitate first as the waste is neutralized and plutonium will be coprecipitated with them. A comparison of the solubilities of amorphous $PuO_2 \cdot xH_2O$ (Rai et al. 1980), amorphous $Fe(OH)_3$ (Lindsay 1979), and crystalline $Al(OH)_3$ (gibbsite) (Lindsay 1979) are given for a range of pH values in Table 3-1. Assuming no significant kinetic differences, these data show that iron will precipitate before any plutonium can precipitate as plutonium oxyhydroxide during the waste neutralization process.

Amorphous iron is much less soluble than amorphous plutonium hydroxide. Since the wastes contain thousands of times more iron and aluminum than plutonium, a pure plutonium phase (plutonium hydroxide or polymer) may not form. Rather, the plutonium is expected to be coprecipitated by sorption on the iron and aluminum hydroxides that precipitate first in much larger quantities.

The rate of iron hydroxide precipitation during waste neutralization is rapid compared to the rate of plutonium hydroxide precipitation (or plutonium hydroxide polymer formation). As long as the initial molar ratio of $[OH^-]/[Fe^{3+}]$ is greater than 3, amorphous $Fe(OH_3)$ will precipitate immediately (Yariv 1979). During neutralization of the acidic wastes, this ratio greatly exceeded 3. Toth et al. (1981) have shown that the rate of plutonium hydroxide polymer formation is slow at the plutonium concentrations known to exist in the acidic wastes. The rate of polymer formation decreases with decreasing plutonium concentration. For example, only about 30% of the plutonium in a 0.05 M plutonium solution was polymerized after one hour at an acid concentration of 0.092 M. Because the plutonium concentration in the waste is about 10,000 times less than 0.05 M, polymer formation would be expected to be much slower.

Table 3-1. Comparison of Plutonium, Iron, and Aluminum Hydroxide Solubilities.

	Log of Solubilities (M)		
pH	$PuO_2 \cdot xH_2O$, Amorphous	$Fe(OH)_3$, Amorphous	$Al(OH)_3$, Crystalline
3	-3.6	-5.5	-1
4	-4.4	-7.1	-3
5	-5.3	-8.0	-6
6	-6.0	-9.2	-7
7	-6.8	-10.0	-7
8	-7.6	-10.3	-7
9	-8.4	-10.0	-6

Typical concentrations of plutonium in the acid wastes range from 10^{-5} to 10^{-6} M. At these low plutonium concentrations, incipient polymerization of plutonium hydroxide requires a relatively high pH. Also, polymerization is not instantaneous, but requires an induction period before it is formed (Toth et al. 1981). Although polymer formation is unlikely, any polymer that is formed has a strong affinity to adhere to other particles suspended in solution or on nearby surfaces (Dran et al. 1994).

There are several likely coprecipitation mechanisms that are important. First, sorption of plutonium hydroxide on the large surface areas of the solid metal oxyhydroxides is the most important mechanism. The oxyhydroxides of iron and aluminum, in particular, develop large, amorphous surfaces as they are formed that attract heavy metal ions and by inference lanthanide/actinide cations (Laitinen 1960).

The sorption capacity (in terms of available sorption sites) for iron oxyhydroxide gel has been estimated to be about 500 μmoles/millimole Fe (Kinniburgh and Jackson 1981). This capacity greatly exceeds the molar ratios of Pu/Fe in the waste tank sludges, which range from about 0.016 to 10 μmole Pu/millimole Fe. For tank 241-C-106, the ratio is 0.23 μmole Pu/millimole Fe.

The hydrolysis of metal ions has been studied extensively (Baes and Mesmer 1976). It has been shown that as these hydrolysis reactions occur, there is a tendency for the ions to aggregate through hydroxyl bridging, forming dimers, trimers, or extensive polymeric networks that can reach colloid dimensions. These polymers can then condense with the loss of water to form oxygen-bridged polymeric species (Thiyagarajan et al. 1990). The polymers can contain more than one metal hydroxide (hydroxides of other metal ions present in the initial solution mixtures) bonded to the polymer. For example, if uranium is present during plutonium or thorium hydroxide polymerization, the uranium is bonded through hydroxyl bridges to the polymer (Toth et al. 1981; and Toth et al. 1984). Hydroxyl bridge bonding is similar to that proposed for surface complexation models of sorption of hydrolyzable metal ions on oxide surfaces (Schindler 1981; and Davis et al. 1978). Surface complexation models have been successfully used to predict sorption of uranyl ions onto amorphous iron oxyhydroxide, goethite, and hematite solids (Hsi and Langmuir 1985). Structures of uranyl complexes at the surface of clay minerals have been identified by Chisholm-Brause et al. (1994). These studies suggest that the trace levels of plutonium hydroxide formed during neutralization of acidic wastes will be bonded to other oxyhydroxides that are present in much greater abundance in the sludge waste. Formation of individual crystals of $PuO_2 \cdot xH_2O$ was unlikely during neutralization because plutonium concentrations were thousands of times lower than the coprecipitated metal ions.

The above observations provide considerable evidence to support sorption as the primary plutonium precipitation mechanism for the subject waste forms. However, based on the fact that none of the experimental observations were conducted under the precise conditions existing in tank 241-C-106 or 241-AY-102, some extrapolation is necessarily required in arriving at this assessment that adsorption is the dominant mechanisms.

3.2.2 Composition of Solids and Sluicing Solutions

The composition of solids and liquids involved in the retrieval operation will affect the behavior of plutonium in the sludges. Both plutonium solubility and plutonium sorption/desorption on the sludge particles are affected by solid and liquid composition. The major components of the sludge and liquid phases in tank 241-C-106 are given in Table 3-2 (Sederburg 1994). The average concentration of plutonium in the sludge is 0.076 g/L, which is a factor of 34 lower than the minimum critical concentration of 2.6 g/L (see Section 5). The mass ratios for Fe/Pu, Al/Pu, and Mn/Pu are 1070, 653, and 147, respectively. The Fe/Pu and Mn/Pu mass ratios are much greater than the minimum critical mass ratios for these neutron absorbers (160 and 32, respectively from Braun et al. 1994). To reach these minimum criticality limits, the average sludge material must undergo a chemical alteration that concentrates the plutonium 34 times and that separates plutonium from iron and manganese by factors of 6.7 and 4.6, respectively.

The numbers in Table 3-2 correspond to the average values obtained, based on several samples. The highest value obtained for the concentration of plutonium in the sludge layer was 0.13 g Pu/L. Hence, even for this highest sample, the minimum concentration factor necessary to approach criticality concerns is 20.

Table 3-2. Major Components of Sludge and Liquid in Tank 241-C-106 (Sederburg 1994).

Component	Concentration in sludge, g/L	Concentration in liquid, g/L
Na	107	91.1
Fe	81.3	--
Al	49.6	0.27
Si	64.1	1.1
Ca	16.7	--
Mn	11.2	--
Ba	6.8	--
NO3	1.6	67.2
NO2	--	9.8
Cl	--	0.55
F	--	0.16
OH	--	0.00018
CO3	--	44.9
PO4	131	--
TOC	6.5	11.3
Pu	0.076	0.0035

The major components of the sludge and liquid phases in tank 241-AY-102 are given in Table 3-3. The concentration of plutonium in the sludge is 0.075 g/L, which is a factor of 35 lower than the minimum critical concentration (2.6 g/L). As noted above for Table 3-2, the values quoted in Table 3-3 are average values taken from several samples. If we use the highest plutonium concentrate recorded in tank 241-AY-102 sludge, namely 0.12 g Pu/L, the degree of concentration necessary to approach criticality concern is 22.

The mass ratios for Fe/Pu, Al/Pu, and Mn/Pu are 1560, 705, and 164, respectively. The Fe/Pu and Mn/Pu mass ratios are much greater than the minimum critical mass ratios for these neutron absorbers (160 and 32, respectively from Braun et al. 1994). To reach these minimum criticality limits, the sludge must undergo a chemical alteration that on average concentrates the plutonium 35 times and that separates plutonium from iron and manganese by factors of 9.8 and 5.1, respectively.

In addition to these waste compositions, the composition of the sluicing solution added to the tanks will affect the chemistry of retrieval operation. This solution will become a part of the supernates in the tanks. Sodium hydroxide was recently added to tank 241-AY-102 as part of the DST corrosion protection program to raise the free hydroxide concentration to 0.04 M.

Table 3-3. Major Components of Sludge and Liquid in Tank 241-AY-102. (Sederburg 1994)

Component	Concentration in sludge, g/L	Concentration in liquid, g/L
Na	58.0	2.2
Fe	117	--
Al	52.9	0.07
Si	16.9	--
Ca	19.6	--
Mn	12.3	--
Ba	2.9	--
NO3	1.0	11.7
NO2	4.1	1.0
Cl	11.7	0.36
F	3.7	0.17
OH	--	5.0
CO3	--	3.7
PO4	2.4	0.16
TOC	0.08	1.5
Pu	0.075	0.0000038

3.2.3 Important Chemical Parameters

Chemical parameters that are significant to criticality during retrieval operations are those that could affect plutonium concentration or separation of plutonium from solid neutron absorbers in the sludges. This would require either 1) dissolution or desorption of the plutonium from the sludge particles, 2) preferential dissolution of the metal oxyhydroxides that are the major components of the sludge particles, or 3) predominance of individual particles of plutonium oxide within the existing sludge.

Chemical factors that could significantly affect dissolution/desorption of plutonium from the sludge solids are hydroxide concentration, carbonate concentration, and organic complexant concentrations in the supernate solutions. Hydroxide concentration is the most important factor. If hydroxide concentrations are maintained at a high enough level, carbonate and organic complexants will not significantly affect plutonium solubility or desorption because soluble complexes (other than hydroxide complexes) of plutonium, iron, or manganese will not be formed to any appreciable extent. The solubilities of plutonium, iron, and manganese will be very low at this hydroxide concentration.

The carbonate concentration in tank 241-C-106 supernate is unusually high (about 0.75 $\underline{M}$) and the hydroxide concentration is low (1.0×10^{-5} $\underline{M}$). These conditions are optimal for dissolution of plutonium by forming a soluble Pu-hydroxyl carbonate complex (Yamaguchi et al. 1994 and Tait et al. 1983). This explains the relatively high plutonium concentration (0.0035 g/L) measured in that supernate. The 182,000 L of supernate in tank 241-C-106 contains about 637 g of plutonium, most of which will be precipitated or sorbed onto sludge particles when the tank 241-AY-102 supernate is mixed with the tank 241-C-106 waste. Mixing these supernates will lower the carbonate concentration and increase the hydroxide concentration in the supernate, resulting in a lower plutonium solubility.

The total organic concentration (TOC) in tank 241-C-106 supernate solution (11.3 g/L) is higher than for most tanks. Recent (April 1996) grab samples from tank 241-C-106 indicated that the TOC in the supernate is 2.27 g/L. The TOC is due to the presence of organic complexing agents, such as ethylenediaminetetraacetate (EDTA) and N-2-hydroxyethylethylenediaminetriacetate (HEDTA) sodium citrate or their degradation products. A small amount of the plutonium in solution will be complexed with the organic, but the extent of complex formation will be small at the high pH of the supernate. This is a result of complex formation constants being higher for hydroxide and carbonate complexes than for organic complexants. Thus, the organic ligand cannot compete with hydroxide as a ligand. For example, the formation constants for $Pu(OH)^0_4$, PuOHEDTA, and $Pu(OH)_4(CO_3)_2^{4-}$ are $10^{46.4}$ (Clark et al. 1995), $10^{17.7}$ (Weigel et al. 1986), and $10^{51.8}$ (Moriyama et al. 1994).

3.2.4 Plutonium/Absorber Ratios

Most plutonium in the high-level waste tanks exists as a solid phase mixture with other precipitated oxyhydroxides in sludge layers. The plutonium is either a discrete Pu oxyhydroxide phase, strongly sorbed onto the surfaces of these oxyhydroxides, or forms a solid solution with other precipitated oxyhydroxides. Sorption has been shown to be an important mechanism in the removal and fixation of plutonium from aqueous solution by a wide variety of metal oxyhydroxides, including those that are present in tank sludges. These oxyhydroxides include both pure phases and minerals that contain a mixture of phases. Plutonium sorption on goethite and hematite from basic solutions containing high dissolved salt was very strong (distribution coefficients, Kds, ranging from 170 to 1,400 mL/g) according to work reported by Ticknor (1993). Sorption/precipitation of Pu(IV) from solutions containing high concentrations of carbonate onto alumina, silica gel, and hydrous titanium oxide was also very strong (Pius et al. 1995). Carbonate lowered the sorption distribution coefficient for these adsorbents, but even at 0.5 M carbonate the coefficients were 60 mL/g, 1,300 mL/g, and 15,000 mL/g, respectively for alumina, silica gel, and hydrous titanium oxide. In bicarbonate solutions, the distribution coefficient for Pu(IV) sorption on alumina was lowered to about 30 mL/g at 0.5 M bicarbonate (Charyulu et al. 1991). This is likely due to a lower pH in bicarbonate solutions which, favors a carbonate complex over a hydroxide complex. Sanchez et al. (1985) measured sorption of Pu(IV) and Pu(V) on goethite over a range of pH values and carbonate concentrations. They found that Pu(V) was reduced to Pu(IV) and that the Pu(IV) was strongly sorbed above a pH of about 6. High carbonate concentrations decreased sorption at a pH of 8.6. At 1 M $NaHCO_3$, Pu sorption was inhibited completely.

Barney et al. (1992a) measured adsorption of plutonium from wastewater solutions onto commercial alumina adsorbents over a pH range of 5.5 to 9.0. Plutonium adsorption Kd values increased from about 10 mL/g at a pH of 5.5 to about 50,000 mL/g at a pH of 9.0. The slopes of Kd versus pH curves were close to one, which indicated that one hydrogen ion is released to the solution for each plutonium ion that is adsorbed on the alumina surface. This behavior is typical of adsorption reactions of multivalent hydrolyzable metal ions with oxide surfaces. Plutonium precipitation was not significant in these tests since changing the initial concentration of plutonium from about 10^{-9} to 10^{-10} M did not affect the Kd values. Also, the initial plutonium concentrations were below the measured solubility limits of plutonium hydroxide. Both of these effects should increase plutonium sorption on the sludge solids and prevent separation of plutonium from the neutron absorbers.

Delegard et al. (1984) performed screening tests to identify tank waste components that could significantly affect sorption of plutonium on three shallow sediments typical of the Hanford site. They found that sorption was decreased by the chelating agents, 0.05 M EDTA and 0.1 M HEDTA, but not by carbonate at 0.05 M. Sorption of Pu(IV) on a Hanford shallow sediment from a synthetic groundwater containing 0.003 M carbonate ranged from about 5,000 mL/g to 30,000 mL/g (Barney 1992).

Any chemical mechanism for concentrating the plutonium in a waste tank would require transport of plutonium from the solid phase to the aqueous liquid phase and then to a small volume solid phase. Hence, for the first step, sorbed plutonium must be desorbed into the aqueous phase of the waste mixture. Plutonium sorption on oxyhydroxides is known to be mostly irreversible (DOE 1988; and Alberts and Orlandini 1981) unless the solution composition in contact with the plutonium is dramatically altered. This would require (1) the addition of organic or inorganic plutonium complexants,

(2) a change in the REDOX potential of the solution by adding oxidants, or (3) acidification of the solution.

The supernate solutions have high concentrations of dissolved nitrite in them that act as a mild reducing agent, keeping the dissolved plutonium mainly as Pu(IV) (Yamaguchi et al. 1994; Charyulu et al. 1991). Since Pu(IV) is sorbed more strongly than Pu(V) or Pu(VI), the nitrite helps fix the plutonium on oxyhydroxide surfaces. To change the REDOX potential of the supernate solutions would require the addition of huge quantities of oxidizing or reducing agents to the tanks (enough to destroy the nitrite). Since all additions to the tanks are controlled, this is not a reasonable possibility.

Acidification of wastes in the tanks would cause partial dissolution of the oxyhydroxides on which the plutonium is sorbed and dissolution of some of the plutonium. Of greater consequence would be the large volumes of gases generated by acid reactions with nitrite to produce NO_x gases, with carbonate to produce CO_2, and potentially with the carbon steel tanks to produce hydrogen gas. Acidification would eventually cause failure of the carbon steel liner, allowing the liquid waste to leak. Because of these disastrous consequences, accidental acidification of the wastes seems highly unlikely. It would certainly be readily detected. As a matter of perspective, available inventories of acids on site are insufficient to acidify a waste tank.

The measured value of plutonium concentration in tank 241-C-106 supernate is 0.0035 g Pu/L, suggesting that sorption is probably the mechanism controlling plutonium concentration in this tank. This is illustrated in Figure 3-2, which shows the relationships between sorption, desorption, and solubility of plutonium in the tanks. Figure 3-2 is based on sorption and desorption isotherms for the sorption of neptunium, uranium, radium, and technetium on geologic materials (DOE 1988); sorption of zinc by soils (Elrashidi and O'Connor 1982); boron sorption on soils (Elrashidi and O'Connor 1982b); and polychlorinated biphenyl (PCB) adsorption on sediments (Di Toro and Horzempa 1982). The heavy line is the sorption isotherm that shows that as more plutonium is sorbed on the solid phase, plutonium concentrations in solution increase until the solubility limit for $PuO_2 \cdot xH_2O$ is reached. The desorption isotherms are nearly flat because of the irreversibility of the sorption reaction. The position of the desorption isotherm depends on the concentration of plutonium in the solid.

There is some disagreement among the chemists on the review team regarding whether sorbed plutonium on iron and aluminum hydrous oxides will dominate when the acidic waste stream is neutralized, and how that material will behave upon aging.

Almost all of the measured plutonium concentrations in tank supernate solutions are below the expected solubility limit for freshly precipitated $PuO_2 \cdot xH_2O$. Figure 3-3 shows the experimentally measured solubility limits for plutonium in carbonate solutions with pH = 10 and pH>12 (Yamaguchi et al. 1994) compared with measured supernate concentrations of plutonium in double-shell tanks. These data seem to indicate that sorption/desorption is lowering the plutonium concentrations in the supernate, although an alternate interpretation of this data is given in Section 3.3.

Figure 3-2. Model Sorption and Desorption Isotherms for Plutonium Sorption on Metal Oxyhyroxides.

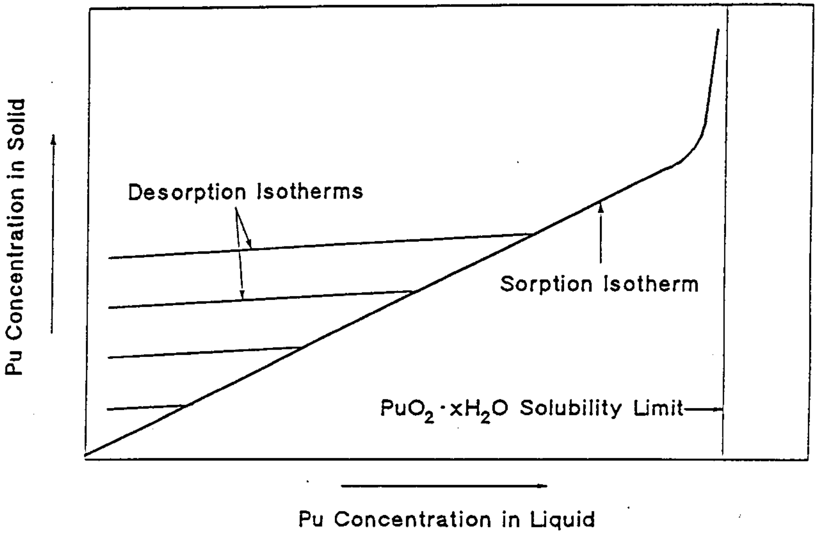
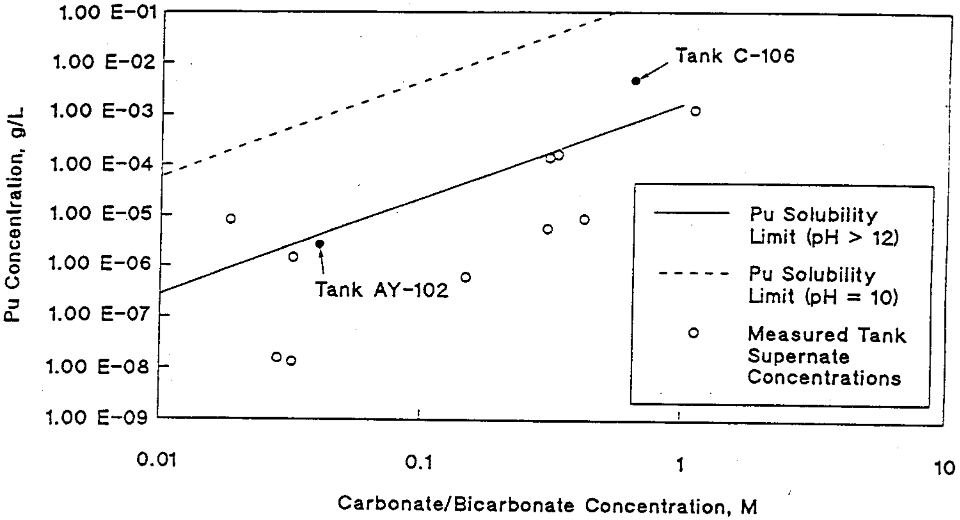


Figure 3-3. Plutonium Oxyhydroxide Solubilities Compared with Measured Plutonium Concentrations in Double-Shell Supernate Solutions for Various Carbonate Concentrations.



Tank supernate solutions cannot hold enough dissolved plutonium in them to reach criticality as long as the solutions remain basic. Extremely low concentrations (10^{-5} to 10^{-12} M) organic complexing agents present in the tanks will not affect the plutonium concentrations in supernate solutions since they cannot compete with hydroxide and carbonate as ligands for plutonium complexation in these solutions. Large carbonate concentrations will increase the plutonium concentration in solution, but by only a small amount. Measured hydroxide and carbonate concentration ranges in tank supernates are from about 4 $\underline{M}$ to 0.00001 $\underline{M}$ and 1.1 $\underline{M}$ to 0.005 $\underline{M}$, respectively. The highest concentrations of plutonium from experimental solubility measurements with hydroxide and carbonate concentrations in this range were about 0.2 g/L Pu at 1.1 $\underline{M}$ carbonate and 0.00001 $\underline{M}$ hydroxide. This concentration is well below the 2.6 g/L criticality limit and is far higher than any actual measured plutonium concentration in tank supernate solution. These arguments demonstrate the general nature of the phenomena beyond the tank 241-C-106 and tank 241-AY-102 retrieval.

3.3 SOLUBILITY

The concept of solubility/precipitation is well established from first principles and is often used in bounding fate and transport analyses to get an estimate of the distribution of actinides between the solution phase and solid phase. See the following articles for discussions and examples of why and how solubility is a valuable construct for addressing fate of Pu and other radionuclides: Nitsche (1991), Pennders et al. (1985), Pryke (1985), Pryke and Rees (1986), Rai and Ryan (1984), and Rees (1985). Solubility constructs for pure or solid solution phases give an upper bound on the concentrations that one would expect to be in a solution phase in equilibrium with solids.

When applied directly to Pu in the Hanford tanks, this would allow the assessment of the chemical impacts of Pu in supernatant liquids on criticality. As mentioned this has been assessed and the impact of the supernatant liquid has been dismissed as being a likely phase that could go critical (Serne et al. 1996). However, solubility can also impact criticality assessments if the Pu is present as a pure phase solid in the tank sludge because it could be redistributed/segregated in the sluiced tank 241-C-106 or the receiver tank 241-SY-102 in the mechanical disturbances in the proposed waste transfer remediation operation.

In its most simple form, solubility calculations require the identification of the "solubility-controlling" solid and the predominant (or if several aqueous species are present and contribute significantly to the overall solution concentration identification of the form and stability of each) aqueous species that forms upon dissolution of the controlling solid. Then use of the thermodynamic solubility product or constant, K_{sp}, and the stability constant(s), K_i is possible, that describes the formation of the predominant aqueous species to calculate the total solution concentration that should be present in the system of interest. In this example, assessment of the concentrations and solubilities is needed, relative to tanks 241-C-106 or 241-SY-102.

Waste stream data from Hanford (Agnew 1995) indicate that the acidic wastes were probably oversaturated with respect to $PuO_2 \cdot xH_2O$ after neutralization with caustic occurred. It is also known that hydrous Pu oxide [$PuO_2 \cdot xH_2O$] forms very rapidly under the conditions present during such neutralization as reported by Delegard (1987), Rai et al. (1980), Rai and Ryan (1982), Kim and Kanellakopulos (1989), Yamaguchi et al. (1994) Hobbs and Edwards (1993), and Hobbs (1995). There is some disagreement among the chemists on the review team as to whether pure Pu hydrous oxide will form when the acidic waste stream is neutralized. Since the waste stream contains copious amounts of other metal hydrous oxides, they could act as adsorption substrates that adsorb the Pu atoms out of solution before they can form discrete Pu solids. Perhaps the most germane experiments were conducted by Hobbs and his coworkers (referred to above). These experiments contained Pu, U, Al and Fe and, in some instances, other transition metals at mass levels much higher than the Pu. Plutonium and U were found to be "coprecipitating" with Al and Fe. Hobbs (personal communication) believes that such phenomena are probably coagulation of $PuO_2 \cdot xH_2O$ colloids by Al and Fe-hydroxides rather than the formation of true solid solution phases (Section 3.4). It is important to bear in mind that coagulation is a proven chemical process that is used in water treatment plants to remove colloidal suspended impurities (Clark 1990). In the case of physically-coagulated solid mass, the solubility of ions is controlled by each distinct relatively pure solid phase. Hobbs' observed solution Pu data will be discussed further along with actual Hanford tank supernatant solution data to see if they can be explained by solubility principles. In a recent undocumented study involving simulated tank waste supernatant typical of Savannah River wastes and similar to some of Hanford's, Hobbs and Karraker (personal communication) identified $PuO_2 \cdot xH_2O$ in the precipitated phase. Even if doubt of the existence of pure phase hydrous Pu oxides in the Hanford tanks is preferred, for completeness, the mechanism of pure Pu hydrous oxide phase formation is being studied to evaluate the possibility of nuclear criticality occurring during or after the tank 241-C-106 tank retrieval (see Figure 3-1).

The identification of the predominant aqueous solution species expected in Hanford tank chemical environments is less certain but we have concluded, mainly based on work by Yamaguchi et al. (1994), Tait et al. (1995), and Delegard (1995), that likely candidates are $Pu(OH)_2(CO_3)_2^{2-}$ when the free hydroxide content is low (<0.01 M, pH≤10 and total carbonate is ≥0.1 M), which are consistant with the measured conditions in tank 241-C-106 (see Table 3-2). At the higher pH values of 12 to 13, expected in most Hanford tanks, including tank 241-AY-102 (see Table 3-3), where carbonate is the predominant inorganic carbon species, the proposed soluble complex is $Pu(OH)_4(CO_3)_2^{4-}$ (see Serne et al. 1996 for more details).

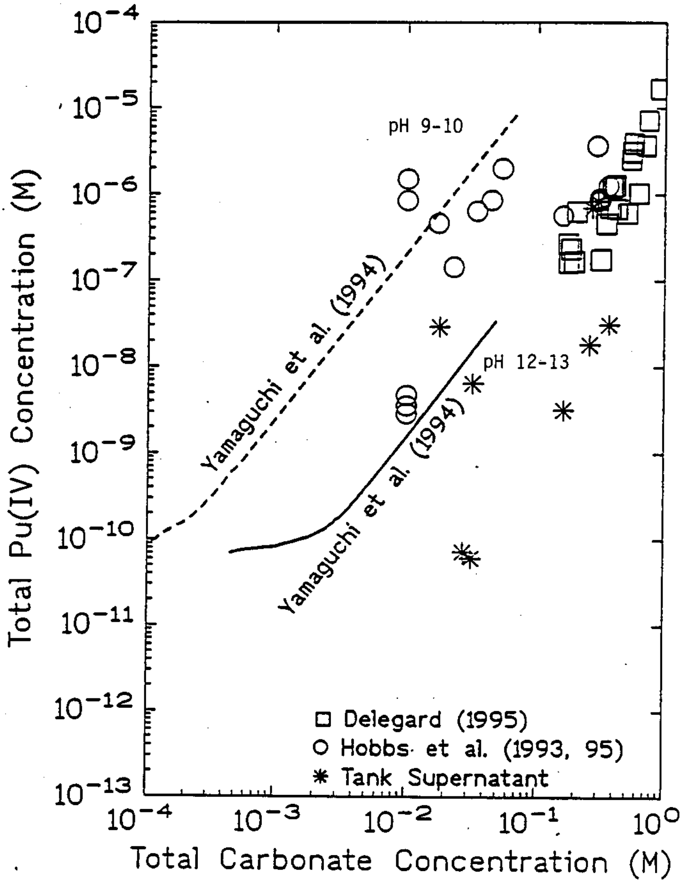
We do acknowledge that there are numerous articles in the literature for less alkaline, lower pH and lower salinity waters common in lakes, rivers, and oceans that suggest the predominant aqueous species should be Pu(V) species, but these reports may not be directly relevant given the highly sensitive nature of speciation to key variables such as pH, eH (e.g., presence of $NaNO_2$ in waste) and dissolved ligands concentrations such as carbonate.

Given the choice of fresh $PuO_2 \cdot xH_2O$ as the "solubility-controlling" solid and either $Pu(OH)_2(CO_3)_2^{2-}$ or $Pu(OH)_4(CO_3)_2^{4-}$ as the dominant aqueous species, dependent upon pH and in the presence of at least 0.1 M total carbonate, we can now predict the total Pu solution concentration in Hanford tanks. Expected Pu solution concentrations for high pH tanks should be $\approx 10^{-7}$ M

(0.025 ppm) at carbonate concentrations of ≥ 0.1 M as long as pH>12; $\approx 10^{-5}$ M (2.5 ppm) at carbonate concentrations of ≥ 1.0 M as long as pH >12. However, if pH is 10 or less, these values would increase by ≈300 for tanks with high carbonate but little free hydroxide. A plot of some of the Hobbs experimental data for relatively short term experiments (≤ 6 months) and Delegard data for $NaOH\text{-}Na_2CO_3$ solutions for time periods of (≈6 months), along with actual Hanford tank supernatant Pu concentrations as measured, are shown in Figure 3-4. The two lines shown and designated as Yamaguchi et al. are calculated lines based on Yamaguchi's chosen values for the K_{sp} for freshly precipitated hydrous Pu(IV) oxide and the stability constants for the two proposed mixed $Pu(IV)\text{-}OH\text{-}CO_3$ aqueous complexes. The lines are not extended to the far right hand edge of the figure because the ionic strength of the system at the right hand edge of the figure is higher than values where the assumption that Yamaguchi's thermodynamic activity corrections for ionic strength would hold. But for lack of more detailed high ionic strength calculation capabilities at the moment, one can project the lines to the right as a first approximation. The upper line would be used for low pH supernate solutions (pH ≤ 10) and the lower line would be applicable for high pH solutions (pH ≥ 12). Although Hobbs' data were for mixed electrolyte solutions at high pH (and thus they should plot near the lower line), many points fall considerably above the line. Note though, that none of the data plot below the line and about half the points are almost coincident with the lower calculated line. These results suggest that the solution concentrations in these experiments, some of which were co-precipitation tests where acid solutions containing Al, Fe, other transition metals and U, and Pu were neutralized with sodium hydroxide, could be controlled by the precipitation of pure phase, "freshly precipitated" hydrous Pu(IV) oxide. The data from Delegard should also plot on the lower line, and they do quite nicely. This corroborates that, in simple systems (Na-carbonate-hydroxide), the Yamaguchi results can be repeated by independent scientists. Five of the actual Hanford tank supernatant Pu solution concentration results fall below the appropriate solubility line for freshly precipitated hydrous Pu(IV) oxide at high pH.

Hydrous Pu(IV) oxide is only slightly soluble in all tank environments except at low pH and high carbonate systems as shown in Figure 3-4. Several references also note that the solubility of the freshly precipitated Pu compound drops as time progresses, as evidenced by continual slow losses of Pu left in the solutions in contact with the solids (see Delegard 1987, Rai and Ryan 1982 and Kim and Kanellakopulos 1989). Rai et al. (1980), Rai and Ryan (1982), and Delegard (1987) characterized the solids in their tests at very early times and after periods of time up to three years or longer. At first the solid is X-ray amorphous, which can mean that the solid lacks enough ordering in the structure to generate distinct X-ray patterns or that the size of discrete crystallites are too small to allow the X-ray analysis techniques to see the crystal ordering. But at longer times the hydrous Pu solid exhibits some of the characteristic X-ray patterns of high temperature formed crystalline PuO_2. In fact, Rai and Ryan (1982) and Kim and Kanellakopulos (1989) performed solubility tests where they monitored both the solution concentrations above freshly precipitated hydrous Pu oxide and crystalline Pu oxide and found that the final Pu solution concentrations between the two types of solids started to converge to values that were similar as time progressed over a period of several years. Rai and Ryan (1982) also showed, through X-ray diffraction, that the fresh precipitate went from being

Figure 3-4. Experimental and Calculated Data for Solubility of Freshly Precipitated $PuO_2 \cdot xH_2O$ as a Function of pH and Total Carbonate Concentration.



amorphous to somewhat crystalline and the crystalline material became less crystalline with time. We could conclude that in an aqueous solution, the fresh precipitate and the high temperature crystalline solid will both transform to the somewhat crystalline material that we will call "aged" hydrous Pu(IV) oxide. This would suggest that it is this "aged" hydrous Pu(IV) oxide that could be controlling the fate of Pu in the Hanford tanks, noting that the tanks have had about 40 years and elevated temperature conditions (≈25 - 90 °C) to promote the aging.

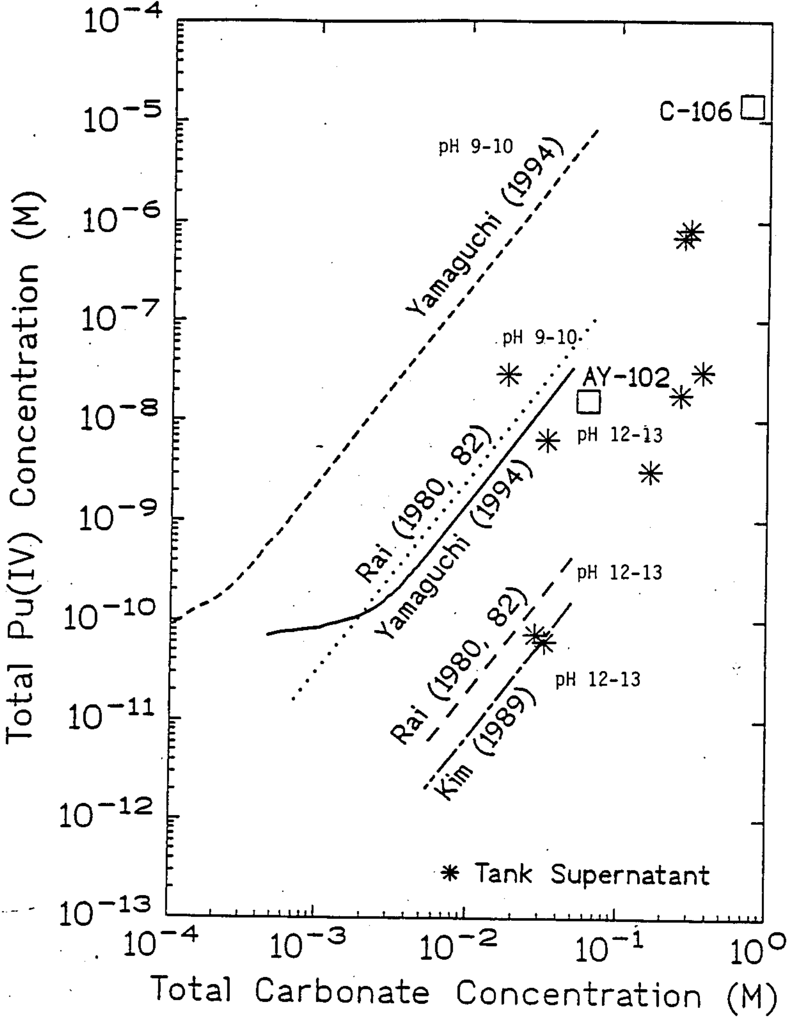
Using the K_{sp} for the "aged" hydrous Pu(IV) oxide as calculated by Rai or Kim, the lines on Figure 3-4 can be recalculated to get a new figure (Figure 3-5) that provides the solubility limit of the "aged" precipitate. There is some difference in Rai's and Kim's experiments, which leads to two lines being shown for the high pH solution condition. The Kim line was left out for low pH just for clarity because few tanks are expected to have low pH. Data from Tables 3-2 and 3-3 are also shown for the two specific tanks in question. Essentially, the aging process lowers the lines from Figure 3-4 down about 2 orders of magnitude for the Rai data and 2.4 orders of magnitude for the Kim data. Tank 241-C-106 is one of the few tanks known to have a relatively low pH and a very high carbonate content and, thus, should plot on the upper Rai or upper Kim line (not shown in the figure but just below the Rai line). The plotted point is very close to the extension of the Rai upper line. The tank 241-AY-102 supernatant solution should plot on the lower Rai and Kim lines but is significantly above the line and curiously near the line expected for freshly formed hydrous Pu(IV) oxide. Figure 3-5 shows that all the available Hanford supernatant solution Pu values fall near or above the appropriate predicted line for aged solid. Tank 241-AY-102 Pu solution data and perhaps some other tanks data fall near the freshly precipitated solubility line. We suggest that the available data do not allow a definitive statement to be made as to whether the observed Pu solution concentrations in tank supernatant liquors are controlled by solubility or adsorption.

However, observed and calculated Pu solution concentrations in the two tanks of interest are in the range of 0.003 to 0.35 ppm and are at least 8 times lower than values needed to allow nuclear criticality to occur in solution. Therefore, a key conclusion of this report is that criticality is implausible in tank supernate solutions from these two tanks and that criticality will require the concentration of Pu solids and separation of Pu-bearing or pure Pu solids from the large excess of neutron absorber solids found in the tank sludge.

3.4 SOLID-SOLID SOLUTION

Another coprecipitation mechanism is solid solution formation, in which a plutonium ion can replace an ion of another metal present at higher concentrations in a crystalline lattice. Because the ionic radius of Pu(IV) differs so much from those of Fe(III) and Al(III), such solid solution formation may be discounted for those metals. However, the ionic radii of Pu(IV), Zr(IV), La(III) and Bi(III) are quite similar. Thus, it is possible that some solid solution formation occurred in neutralized zircaloy cladding wastes, bismuth phosphate wastes, and perhaps other wastes. Though statistically possible, this formation mechanism is very unlikely for the

Figure 3-5. Experimental and Calculated Data for Solubility of Aged $PuO_2 \cdot xH_2O$ as a Function of pH and Total Carbonate Concentration.



waste in either tank 241-C-106 or 241-AY-102, since the amount of zirconium and bismuth in either of these tanks is very low. Zirconium and bismuth are the only two low neutron absorbers that have ionic radii compatible with a plutonium solid-solid formation mechanism. Lanthanum is a good neutron absorber. However, the absence of these elements in either tank leads to the conclusion that this mechanism is not applicable to these tanks.

Solid solution formation is a subset of coprecipitation phenomena in which two or more ions form a single solid phase. The solubility of a solid solution phase regulates the solution concentrations of each constituent ion at levels that may be significantly different from the solution concentrations of pure solid phases of each of the ions (Walton 1967). Typically, one of the conditions for solid solution formation is that the ionic radii of constituent ions should not differ significantly from each other (within 15% to 20%, Walton 1967). Based on ionic radii data (Shannon 1976) the ionic radii of Pu(IV) was compared with other ions in the Hanford waste stream to determine which may accommodate Pu(IV) and potentially form solid solution phases. The data show (Table 3-4) that only Bi, La, and Zr are likely to form true solid solutions with Pu(IV), whereas the Pu(IV) ion is too large to form solid solutions with either Al or Fe in six-fold coordination. Therefore, the observed removal of Pu(IV) from suspended colloidal form by Al and Fe(III) hydroxide gels is more than likely a coagulation or surface adsorption phenomena rather than the formation of thermodynamically definable solid solution phases that involves removal of Pu(IV) from dissolved aqueous phase and substitution into structural sites in gel phases.

Table 3-4. Differences (%) in Ionic Radii Between Pu(IV) and Potential Solid Solution Forming Ions in Hanford Waste Streams.

Ions	Coordination number*	
	VI	VIII
Bi(III)	-17	-18
La(III)	-17	-17
Zr(IV)	+19	+14
Al(III)	+61	--
Fe(III)	+33	--

*Ionic radii data from Shannon (1976).

Some experimental data exist to confirm the potential formation of Pu(IV) solid solutions in certain Hanford waste streams. For instance, bench-scale tests on cladding removal wastes (CRWs) by Hodgson et al. (1985) showed that Pu(IV) can coprecipitate with La as a solid solution. Their data showed that the decontamination factor (DF) (the ratio of initial Pu concentration in solution to the Pu solution concentration in equilibrium with the solid solution phase) ranged from 3 to 61 and was a function of La concentration. The DF of Pu showed an exponential relationship with La concentration represented by

$$DF = 47.4e^{(219.0\ X)} - 46.6e^{(98.9X)} + 4108.6X$$

where X represents molar concentration of La. These data showed that the mole fraction of Pu in La solid phase ranged from 2.9×10^{-3} to 3.18×10^{-2}, depending on the amount of La added to induce the precipitation of solid solution phase. Calculations indicate that within the range of La concentrations used in these experiments, the resulting solid solutions would contain La/Pu mole ratios of from 30 to 349. Hodgson et al. (1985) also indicated that when CRW was neutralized with sodium hydroxide, soluble transuranic (TRU) elements were found to be precipitating with zirconium hydroxide. The DFs for Pu(IV) coprecipitating as solid solution with zirconium hydroxide were estimated (John L. Swanson, personal communication) to range from 10 to 100. These data suggest that some of the Hanford waste streams containing constituents such as La, Zr and Bi upon neutralization may precipitate solid solution phases with Pu(IV). Since neither of the tanks of interest contain measurable amounts of the three possible metals that could form true solid-solid solutions, this mechanism is not applicable to these tanks.

3.5 EFFECTS OF AGING

3.5.1 Adsorption

Crystallization of the fresh, amorphous iron and aluminum oxyhydroxide precipitates no doubt occurs as these precipitates age in the tanks. This has been shown recently by Hobbs (1995) who precipitated insoluble metal oxyhydroxides from synthetic acidic Purex waste solutions containing plutonium by adding a sodium hydroxide solution. After standing for two months, the precipitated solids (mainly iron, aluminum, uranium, and nickel oxyhydroxides) were analyzed by X-ray diffraction. Most of the solids were amorphous, but crystalline goethite (α-FeOOH), gibbsite ($Al_2O_3 \cdot 3H_2O$), bayerite ($Al_2O_3 \cdot 3H_2O$), and sodium diuranite ($Na_2U_2O_7$) were also found. However, this crystallization did not affect the concentration of plutonium dissolved in the supernate over a 59-day period. The plutonium concentrations were more than 100 times lower than the solubility of freshly-precipitated $PuO_2 \bullet xH_2O$ when iron or uranium were present in the original solutions, strongly suggesting that plutonium was effectively coprecipitated with iron and aluminum oxyhydroxides.

The effects of iron oxyhydroxide crystallinity on sorption of metal ions was studied by Tochiyama et al. 1994. They measured Np(V) sorption on α-FeOOH that was prepared by adding a $Fe(NO_3)_3$ solution to 1 M NaOH. The crystallinity was increased by heating the α-FeOOH to 130 °C and 300 °C. At 300 °C, the diffraction pattern was similar to hematite (α-Fe_2O_3). Sorption distribution coefficients were lowered from about 10^4 cm^3/g Fe to $10^3 cm^3$/g Fe at a pH of 7 by the 300 °C heat treatment and were essentially unchanged by the 130 °C treatment. The lower Np sorption may also be due to a lower surface area after heating, but this was not measured. The sorption capacity of the oxyhydroxides for plutonium sorption probably decreases somewhat with aging, but the initial capacity is so large that the effect of crystallization is likely to be small.

Plutonium that was sorbed onto the surfaces of hydrated metal oxide sludge particles initially has undergone changes in chemical bonding over the aging period that the wastes have experienced. It is possible that the plutonium was incorporated into the evolving oxide structure (not necessarily in the crystalline structure) of the solids. This would increase the bonding strength between plutonium and the major oxyhydroxides present in the sludge. Metal ion sorption has been shown to retard the crystallization of hydrous oxide gels because of this type of bonding (Kinniburgh and Jackson 1981). Incorporation of calcium, strontium, barium, nickel, copper, zinc, and cadmium into the hydrated alumina gel structure has been reported (Kinniburgh et al. 1976). This was confirmed by isotopic exchange studies, where the percent of zinc adsorbed on aluminum gel that was exchangeable steadily decreased with time. After 400 hours of aging, only 10% of the sorbed zinc was isotopically exchangeable. Thus the zinc was steadily incorporated into the bulk structure of the aging gel. This type of bond formation between aluminum or iron oxyhydroxide with adsorbed plutonium would assure high concentrations of neutron absorbers in intimate contact with plutonium in the sludge. It is unlikely that solid solution formation could account for these observations since the metal ions studied have different oxidation states and larger ionic radii than aluminum. For example, the ionic radii of Ba(II), Sr(II), and Zn(II) are 160%, 120%, and 45% larger than aluminum, respectively.

3.5.2 Solubility

The effects of aging on the solubility of discrete Pu hydrous oxides have been aptly discussed in Section 3.3. We feel that the solubility of the discrete hydrous Pu(IV) oxide will decrease from the values found in the laboratory for freshly precipitated material by about 2 to 2.4 orders of magnitude.

If discrete Pu oxide particles are present in the sludge, it will be important to evaluate the particle segregation potential of various sludge components during the hydrodynamic sluicing operation. It could be possible to partially segregate the Pu-rich particles from the other sludge components (i.e., enrich the concentration of Pu-bearing particles or conversely deplete the neutron absorbers concentrations in some portion of the tanks). Knowledge of the particle size and density of the Pu-rich particles) would be required to quantitatively evaluate this potential. There are no data available of the particle size Pu or particle size neutron absorber relationships in the tank sludges. Therefore, at this time only expert opinions can be offered.

It is possible to estimate the upper size limit that crystalline particles may have and still remain X-ray diffraction amorphous to analysis using standard mineralogy techniques. That is, even crystalline particles will appear to be amorphous (showing no consistent lattice structure) if the average size of the particles is extremely small. Based on discussions in Klug and Alexander (1974), Bish and Post (1989) and Amonette and Zelazny (1994), it is estimated that the minimum size that crystallites must reach to be measured by traditional powder X-ray diffractiions studied havad peak is 0.003 to 0.004 μm. According to Bartram (1967), crystallites smaller than 0.003 μm do not scatter the primary X-ray beam coherently but contribute only to the background. Therefore, crystallites smaller than 0.003 μm have only short-range structural ordering and are thus X-ray amorphous. Peaks are still broad when the crystal size is up to nearly 0.1 μm (Hsu 1977, p 108). Hence, care must be taken when reviewing literature to discern whether the author is calling a mineral completely amorphous (based on absolutely no diffraction patterns above a background noise such as particles below 0.003 to 0.004 μm would give) or whether the author is calling very broad peaks amorphous. An author with this perspective might call such very broad spectra of particles that are as large as 0.1 μm as amorphous. A quantitative equation to estimate the crystallite size is known as the Scherrer equation and is defined as follows (Smith 1989):

$$D = (K \bullet \lambda)/[b \bullet \cos(\theta)]$$

where

D = Crystallite size in (Å)
K = A shape constant (usually ≈0.9)
λ = The wavelength of the incident X-ray in (Å)
b = The half-width of the diffraction profile due to the sample (measured breadth minus instrumental blank breadth at wavelength)
θ = Diffraction angle
Å = Angstroms (10^{-4} μm).

This equation cannot be used to estimate the size of a crystal when the sample gives no peak distinguishable from the instrument background (where b becomes zero) but experts on X-ray diffraction have used the value quoted above, 0.003 to 0.004 μm, as an estimate.

Thus, if the initial precipitates formed by the fast neutralization of the Hanford acidic waste streams with sodium hydroxide are actually forming very small Pu oxide and/or neutron absorbers crystalline particles with a size less than 0.003 to 0.004 μm, they would appear amorphous to the traditional instrumentation (powder X-ray diffraction) used to identify solids.

As described in various articles (e.g., Schwertmann and Cornell 1991, Stumm and Morgan 1981, Hsu 1977, and Cornell and Schwertmann 1979) many common oxides (such as Al, Fe, Cu and Zn) appear to form very small crystallites that have been interpreted as being amorphous at first but that grow in size and become "crystalline" with time. Schwertmann and Hsu prefer to conclude that the crystallites were essentially crystalline from the start but the individual particles were just too small to yield X-ray diffraction patterns that could be measured. Because small particles exhibit very large surface energy (Stumm and Morgan 1981), they are thermodynamically less stable than larger particles of the same mineral. Thus, there is a driving force for the small particles to agglomerate into more stable larger particles. Once the particles reach a size above ≈0.003 μm, they start looking "crystalline" to X-ray diffraction analyzers. In nature and in the laboratory, crystalline ferric oxides and aluminum oxides often are found as discrete particles with 0.1 to 10 μm sizes.

Schwertmann and Cornell (1991) show that pure ferric oxides follow the stated trends and transform into several larger-sized crystalline forms in a matter of days to a few weeks, depending on chemical and thermal conditions.

Cornell and Schwertmann (1979) and Hsu (1977) as well as others do concede that this recrystallization to form larger particles can be retarded/inhibited by other dissolved species in the system. Some of the most efficient inhibitors of this recrystallization process are simple organic acids such as citrate, and (to a much lesser extent) oxalate and fulvic acids from the decay of plant matter. Interestingly, these simple acids become much less effective at pH values of 11 or higher, which happens to be the range most common in Hanford tanks. The impact of these other ligands (anions) in the tank solutions is not easily quantified but there are some indications that the high pH, elevated temperatures and long time periods (≈30 to 50 years) available to react, all may favor the eventual recrystallization of crystalline and partly crystalline products.

There is evidence in the Hanford, Savannah River, and Russian literature germane to defense tanks that crystalline Al and Fe hydroxide, oxide, and oxyhydroxide compounds are present (Hobbs 1995, and Zakharova et al. 1995). There are no literature studies that have been identified that discuss the particle size or nature of Pu solids within Hanford or other nuclear defense sludges. However, it is logical to expect that Pu would act in a similar fashion to other metals such as Fe and Al, for which some literature has been assimilated (as discussed above).

Another interesting phenomena related to particle size is the variability of the solubility of a compound as a function of particle size. Stumm and Morgan (1981) describe and explain this phenomenon quite succinctly. Finely divided (small crystallites) exhibit enhanced (higher) solubility than large crystals. As a consequence, small crystals are thermodynamically less stable and should recrystallize into large ones. For particles smaller than about 1 μm or with a specific surface area greater than a few m^2/g (the proposed freshly precipitated Pu hydrous oxide appear to meet these two criteria), surface energy is sufficiently large to influence surface properties and the free energy of the solid. Experimenters such as Schindler (1967) and Schindler et al. (1965) have investigated the effect of particle size (and surface area of the particle) on the solubilities of ZnO, $Cu(OH)_2$, and CuO. Stumm and Morgan (1981) show that the solubility of the various compounds changes as a function of surface area by a theoretical ratio that relates the change in free energy of the particles to surface tension at the solid-solution interface.

For ZnO the solution concentration of Zn decreases by almost 30 times as the particle size of the ZnO increases from 0.0046 to 0.0560 μm. These particle sizes are generally smaller than those usually measured for the Al and Fe oxides discussed above, but the Pu solubility data discussed in Section 3.5.2 shows a similar drop in solubility. Perhaps this is because the Pu hydrous oxide crystallites are very small upon formation. Further, the particle size plays a role in the transformation of one polymorph to another, such as $Cu(OH)_2$ to CuO or Zn hydroxide to Zn oxide.

As discussed in Stumm and Morgan (1981), Schindler et al. describe how copper oxide that is ten times more stable than copper hydroxide becomes less and less stable as the particle size decreases, until at a size of 0.004 μm the oxide is less stable than the copper hydroxide. This results because the oxide exhibits a higher surface tension (interfacial energy) than the hydroxide; thus, there is a cross-over in overall Gibbs free energy (thermodynamic stability) as both compound's particle size decreases. The authors and cited experimental investigators suggest that this is why copper hydroxide forms first during the neutralization of acid solutions of copper ion. This phenomenon may be another mechanism that explains why scientists find or claim that hydroxides form first during the rapid neutralization of acidic solutions, but with time, crystalline oxides are found. The tank literature cited above suggests that this aging process may be occurring for Fe, Al, and Pu and, by inference, other components in the sludge.

Using available literature data, we are in a position to derive first approximation estimates of particle size distribution of freshly precipitated and aged $PuO_2 \cdot xH_2O$. Because freshly precipitated $PuO_2 \cdot xH_2O$ is X-ray amorphous, we can conclude that the bulk of this material may consist of particles smaller than 0.004μm. Studies conducted by Andelman and Rozzell (1970) showed that the bulk of freshly precipitated $PuO_2 \cdot xH_2O$ exists as colloids that are not settled thorough centrifuging. Studies of long-term aging of $PuO_2 \cdot xH_2O$ by Rai et al. (1980) and Delegard (1987) showed decreases in solubility, which indicates that there was particle growth with concomitant increase in crystallinity long-range structural ordering. Further, X-ray diffraction data obtained on aged (over 3 years) $PuO_2 \cdot xH_2O$ precipitates showed that the precipitate had crystallized, resulting in particle growth and decreased solubility (see Section 3.2).

If we assume that the solubility and particle size relationship for zinc hydroxide precipitates observed by Schindler (1967) are applicable to $PuO_2 \cdot xH_2O$ precipitates, we can calculate the diameter of the aged hydrous Pu(IV) oxide particle that we suggest in Section 3.2 may be controlling the tank supernatant solution concentrations. The relationship derived from this assumption was:

$$d\ (\text{Angstroms}) = 27.4 \exp\ (3 \times \Delta \log K_{sp}) + 35$$

where

d = Particle diameter in angstroms
$\Delta \log K_{sp}$ = The difference in equilibrium solubility between the crystalline phase and a phase with lower crystallinity.

The solubility data obtained by Rai et al. (1980), Rai and Ryan (1982) and Kim and Kanellakopulos (1989) indicated that the solubilities between freshly precipitated and aged $PuO_2 \cdot xH_2O$ differed by about two to two and half orders of magnitude. Using this assumption, it is calculated that the finest particles in aged $PuO_2 \cdot xH_2O$ material have average diameters of about 0.7 μm. This calculation provides the lower bound on particle size that controls the solubility. The upper bound for particle size can be estimated based on the particle-size distribution data obtained by Andelman and Rozell (1970), which showed that the upper bound is approximately an order of magnitude higher than the smallest particle size in the Pu-hydroxide colloidal mass. From these datacopper hydroxided that aged Pu(IV) oxyhydroxide has about 60% of the particles by mass less than 2 μm in size. About 40% of the mass of aged particles may range from about 2 to 8 μm in size. As shown by Andelman and

Rozell (1970), it is important to bear in mind that ionic strength, presence of ligands, and other particulates will affect the particle size distribution of $PuO_2 \cdot xH_2O$.

The crystal growth process discussed above has been recognized for at least a century and, in early literature, is referred to as "Ostwald Ripening." A succinct definition of this scientific term, Ostwald Ripening, is the process wherein small crystals, more soluble than large ones, dissolve and reprecipitate onto larger particles.

In summary, it can be inferred that the particle sizes of precipitates in the Hanford tank sludge should be the same as assessed from literature data. Some of the review team chemists believe that all the metals present in the acid waste stream that form insoluble hydroxide-like phases, and most likely those that form insoluble phosphate, sulfate, or carbonate compounds, all follow a similar history. At first, very small particles with a size range of less than one nanometer (<0.001 μm) to 0.004 μm form but, with fixed chemical structures. As time evolves, these crystallites grow larger, driven by the thermodynamic need to shed excess surface energy and reach a threshold size that is identified as "crystalline," using traditional techniques such as powder X-ray diffraction. Their size at this point is larger than 0.003 μm, depending on the author's criteria for calling the X-ray diffraction peaks as sharp enough to qualify as crystalline. Crystalline compounds of these metal oxides/hydroxides formed in the laboratory or isolated from natural soils/sediments are often in the 0.1 to 10 μm size range, although the details of particle size measurements or considerations of particles aggregation have not been explored in detail.

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4.0 PHYSICAL CONSIDERATIONS - SLUICING INDUCED SEPARATIONS

If the fissile content of the sludge cannot be shown to be intimately associated with neutron absorbers, it becomes necessary to demonstrate that the fluid dynamic forces to which the solids will be exposed will not result in segregation and redeposition of the plutonium in sufficient concentration and geometry to achieve criticality. The potential for fluid dynamic segregation is being addressed using several approaches. First, simple one-dimensional settling cases were calculated using assumed particle densities and sizes within a measured particle size distribution. Second, two-dimensional analytical models were used to examine situations that cannot be addressed in a one-dimensional model. Third, three-dimensional fluid dynamic simulations were performed to address specific processes within the tank 241-C-106 to tank 241-AY-102 retrieval project.

4.1 ONE-DIMENSIONAL SIMPLIFIED SETTLING SIMULATIONS

This section provides results based on a simplified one-dimensional analytical model. The results presented are based on 241-C-106 sludge uniformly suspended in a DST and settling under quiescent conditions.

That this particular scenario could result in a criticality is not a concern because the scenario results in a uniform distribution across the floor of the tank. No single tank has sufficient fissile content to exceed an areal concentration of 240 g/ft^2 Pu-239, which is the minimum areal concentration required to achieve criticality (Rogers et al. 1996). Formation of a uniform plutonium layer within a 75-ft diameter DST would require at least 1060 kg of Pu to attain a critical configuration, while the maximum combined plutonium inventory available in tanks 241-C-106 and 241-AY-102 is only 108 kg (WHC 1995).

However, the results of this scenario provide insight into the extent of segregation that might occur under differential settling (segregation) conditions. For example, while the larger or denser particles settle faster and would be expected to be more concentrated near the bottom of a settled layer, each deposited layer has a distribution of particles with a variety of sizes and densities. This distribution of particles will tend to limit the degree to which fissile material may concentrate.

4.1.1 Simplified Sedimentation Model

The conceptual model is based on a DST that initially contains a uniformly mixed slurry of tank 241-C-106 solids and is then allowed to settle under stagnant conditions. It is assumed, as a starting point, that the fissile material exists as discrete particles rather than existing within particles of mixed composition. If the fissile material can be shown to exist within discrete particles of mixed composition, fluid dynamic segregation calculations may be unnecessary.

The particles settle at their terminal settling velocity as calculated based on Stokes Law. In cases where the particle Reynolds number exceeds 2, an intermediate expression is applied for the friction factor. However, this adjustment is only required for calculation of the settling velocities of the PuO_2 particles larger than about 60 μm. Thus, the calculated results are not sensitive to the selection of viscosity because within the Stokes Law region, the velocity of all particles is inversely proportional to the viscosity.

The individual particles settle until they reach the floor and are allowed to pass through the floor. The particles passing through the floor over a given time increment is determined and the composition of the material is taken to represent the composition of a settled layer of sediment. The maximum fissile content of any layer of deposited sediment (expressed as mass fraction of solids) is divided by the initial fissile content of the uniform slurry (also expressed as mass fraction of solids) to determine a factor increase in fissile concentration. Thus, only the composition of the settled sludge solids is considered, not the degree of consolidation of the settled sludge layer.

The model does not include the effects of hindered settling. However, calculations were performed to determine that inclusion of hindered settling did not significantly affect the results. For completeness, calculations including hindered settling effects, are included at the end of this section. Particle agglomeration is not explicitly considered in the model although the agglomeration behavior is important for interpreting the results.

The uniform slurry is assigned a particle size distribution based on measured tank 241-C-106 particle size distributions. Data was obtained in 1977 as reported by Castaing (1994) and a second measurement was obtained by Weiss on a 1986 core (Weiss 1993). The 1986 core was a composite sample of the entire core. The specifics of the measurement technique and sample preparation are unclear. It is unknown whether larger particles in the distribution may actually be agglomerates of smaller particles. Also, no information is provided on sub-micron particulate. However, the size distributions were used for the current calculations. The particle size distributions used for the modeling are provided in Table 4-1

In all cases the fluid density was set to 1.0 g/cm^3 and the fluid viscosity to 1.0 cP. Iron was assumed to exist as hematite with a density of 5.26 g/cm^3, while aluminum was assumed to exist as gibbsite with a density of 2.4 g/cm^3. The am.68
sludge was based on waste characterization data (Castaing 1994). All other sludge components were arbitrarily assigned a density of 2.0 g/cm^3, which is believed to be conservatively on the low side. The PuO_2 was assigned a density of either 11.4 or 6.0 g/cm^3. The density of 11.4 g/cm^3 corresponds to crystalline PuO_2. In an aqueous environment, the density of PuO_2 may be lower than 11.4 g/cm^3 due to waters of hydration. Although definitive data is not available, it is the opinion of several people who have worked with precipitated PuO_2 that the particle density is less than 6 g/cm^3. The amount of plutonium assumed for tank 241-C-106 sludge simulations was set at 0.132 g/l, corresponding to a conservative 100 kg inventory. This initial PuO_2 concentration has little effect on the calculation of the degree of segregation but does influence the interpretation of a given degree of segregation.

Table 4-1. Particle Size Volume Distributions Used in Modeling.

Tank 241-C-106 (Castaing)		Tank 241-C-106 (Weiss 1993)	
Size, μm	Volume %	Size, μm	Volume %
52.5	6.1	90	0.49
47.5	7.4	80	0.68
42.5	10.8	67	0.49
37.5	8	58	0.00
32.5	0.8	49	0.49
27.5	4	41	0.98
22.5	12	35	1.96
17.5	5	29	4.01
12.5	11	26	5.87
7.5	36	21	8.31
		18	11.24
		15	13.49
		13	18.87
		11	14.37
		9	10.26
		7.8	3.42
		6.5	2.54
		5.5	2.54

The particle volume within the distributions in Table 4-1 were assigned identities based on the sludge composition. No data on variations of sludge composition with particle size is available. Therefore, except where noted, the iron, aluminum, and other components were assumed to exist uniformly throughout the entire size distribution. The plutonium was distributed uniformly across the size distribution for some cases and given a monodisperse size in other cases. Iron, aluminum, and PuO_2 were explicitly tracked with their own densities within the problem with all other sludge components being grouped into the category "other." Thus, using the Weiss particle size distribution, the problem becomes one of tracking (18 sizes)x(4 densities) = 72 different particles, each with its own concentration determined from characterization data, as they settle to the floor of the tank.

4.1.2 Simulation Results

The results of the simulations are summarized in Table 4-2. The factor increase represents the maximum increase in mass fraction PuO_2 (based on solids only) for any sediment layer within the sludge solids for the conditions shown. Calculations are provided for a uniform distribution of PuO_2 as well as for monodisperse PuO_2 at sizes greater than and less than 10 µm, which is estimated to be the approximate upper bound of PuO_2 size. A value of "2" in Table 4-2 indicates the mass fraction of PuO_2 has doubled compared to the initially uniform slurry. Interpretation of the results is provided in Section 4.1.2.3.

Table 4-2. Maximum Factor Increases in PuO_2 Mass Fraction in Sediment Layer.

	Maximum increase in sediment PuO_2 mass fraction	
Plutonium distribution	PuO_2 density = 11.4 g/cm^3	PuO_2 density = 6.0 g/cm^3
Tank 241-C-106 (particle size distribution from Castaing, 1994)		
Uniform over all sizes	5.7	2.7
Monodisperse, 17.5 µm	4.1	6.6
Monodisperse, 7.5 µm	6.5	5.3
Tank 241-C-106 (particle size distribution by Weiss 1993)		
Uniform over all sizes	5.5	2.7
Monodisperse, 21.5 µm	9.3	5.5
Monodisperse, 5.5 µm	3.4	8.0

4.1.2.1 Bounding Sensitivity Analysis. Additional bounding cases were calculated in which the PuO_2 is assigned the largest particle size within the distribution. This provides the greatest potential for segregation to the bottom of the sediment layer. These cases are not considered to be realistic cases in that plutonium oxide particulate would be expected to be small with an upper bounding size of approximately 10 µm (see Section 3.5.2). These cases are provided to indicate the sensitivity of the results to the establishment of the upper bound size of the plutonium particulate. Table 4-3 presents the results for each of the two particle size distributions. Interpretation of the results is provided in Section 4.1.2.3.

Table 4-3. Bounding Sensitivity Cases for Maximum PuO_2 Particle Size

Plutonium distribution	Maximum increase in sediment PuO_2 mass fraction	
	PuO_2 density = 11.4 g/cm^3	PuO_2 density = 6.0 g/cm^3
Tank 241-C-106 (52.5 µm PuO_2, particle size distribution from Castaing, 1994)		
Monodisperse, 52.5 µm	19.8	9.6
Tank 241-C-106 (90.0 µm PuO_2, particle size distribution by Weiss 1993)		
Monodisperse, 90.0 µm	93.9	55.3

4.1.2.2 Hindered Settling Effect. In the modeling described to this point, the settling velocity of particles is not dependent on the local concentration of suspended solids. However, at high solids concentrations the settling velocity of particles is slowed. Calculations were performed to determine if this could have a significant effect on the degree of segregation. The results indicate that a hindered settling model has very little impact on the degree of segregation predicted. Additional details of the hindered settling model are provided by Serne et al. (1996).

4.1.2.3 Interpretation of Results from One-Dimensional Settling Calculations. The conservative waste model developed by Rogers (1993) describes a sludge that is at least as neutronically reactive as any known tank sludge composition. A safe concentration has been established for the conservative waste model sludge at 2.6 g Pu/l for a sludge of infinite extent and optimal water moderation. Thus, for tank 241-C-106, the initial concentration of 0.132 g Pu/l must be concentrated by a factor of 20 to reach 2.6 g/l Pu content. For any factor less than 20, the plutonium-concentrated sludge could not be made critical even if collected from throughout the tank and placed into a favorable geometry. In all of the cases evaluated, no sediment layer exceeded a factor of 10 increase concentration. This leaves a 2x safety factor between the maximum sludge composition and the 2.6 g Pu/l concentration limit for infinite geometry. As discussed in Section 5.1, arranging 80 kg into a sphere 10 ft in diameter would require a concentration of 5 g/l to reach criticality. Thus, comparison to the 2.6 g/l level contains considerable conservatism.

The bounding case results were shown in Table 4-3. For the Castaing particle size distribution, the values indicate that even under bounding assumptions the concentration just reaches the conservative waste model limit of 2.6 g Pu/l. In the case of the Weiss particle size distribution though, the factor of 93.9 indicates a concentration of 12.4 g/l. This concentration would be cause for concern if it were actually to occur. Although it is not considered likely that PuO_2 would reach 90 µm, let alone be exclusively 90 µm, the case points out the importance of establishing that PuO_2 exists primarily at smaller sizes (see Section 3.5.2).

The particle size distribution data utilized did not include sub-micron particulates, presumably due to the limitations of the measurement technique. Therefore, simulations do not address the concentration of sub-micron particulate. The current model would predict that these very fine particulates could concentrate substantially in the upper levels of the sludge. However, particle flocculation is expected to interfere with segregation due to settling. If PuO_2 particles flocculate, then the fluid dynamic properton. Thus, for t will not be significantly different than other flocculants around them and the settling will not favor any particular material. Calculations have indicated that 10 μm particles should be agglomerated at the conditions expected within tank 241-AY-102, and sludge observations in hot-cell sludge settling tests indicate that no particles settle at sub-micron velocities indicating that flocculation is occurring among sub-micron particles. This is discussed in additional detail by Serne et al. (1996). Thus, for particles of 10 μm or less, flocculation is expected. It is also expected that the maximum plutonium particle size is on the order of 10 μm (see Section 3.5.2). Thus, the PuO_2 particulate would be expected to be agglomerated under quiescebly gaseous reacns. Additional work is needed to expand this conclusion to include the kinetics of flocculant destruction and reformation due to fluid shear.

The results of the one-dimensional models indicate that if the upper bound for plutonium particle size is approximately 10 μm, then it is extremely unlikely that segregation sufficient to achieve criticality will occur. However, this one-dimensional model is not sufficient by itself because it cannot address three-dimensional concerns that material might be selectively deposited in a localized area by fluid movements within the tank. This selective deposition issue is addressed by TEMPEST modeling in Section 4.3. Also, the one-dimensional and TEMPEST modeling cannot address processes such as film concentration, differential acceleration, Bagnold forces, flotation, and interstitial trickling. A review of these mechanisms, which are exploited in the mineral processing industry to achieve separations, has concluded that these mechanisms are unlikely to achieve the required segregation (Serne et al. 1996).

4.2 TWO-DIMENSIONAL ANALYTICAL MODELS

Two-dimensional analyses are still in progress. However, the outcome of the analysis is not expected to affect the safety basis or conclusions of this report. The two-dimensional analyses will be completed only to corroborate one-dimensional calculation results as additional conservatism.

4.3 THREE-DIMENSIONAL TEMPEST MODELING

TEMPEST is a time-dependent, three-dimensional model to simulate physical movements and chemical reactions by explicitly accounting for the interactions of aqueous chemical reactions, dissolution/precipitation, adsorption/desorption, possibly gaseous reactions, and associated rheology changes to simulate convective motion of physical and chemical species, solid settling/resuspension, and gas retention in the tank (Trent and Eyler 1994, and Onishi et al. 1995). To predict the physical movements, TEMPEST uses integral forms of the fundamental conservation laws (e.g., casted in the forms of Navier-Stokes equations for momentum, and advection-diffusion equations for mass and energy conservation) applied in the finite volume formulation to simulate flow, turbulence, heat transfer and mass transport of solids, liquid and gaseous constituents. It incorporates various physical properties and rheology correlations for non-Newtonian flows needed for the simulation of Hanford tank wastes (Mahoney and Trent 1995). The TEMPEST model being applied for these simulations accounts for a non-Newtonian flow properties and hindered solid setting.

Two TEMPEST simulations are being performed to evaluate what are believed to be the most likely locations for solids to segregate and accumulate. The first case simulates the removal of the solids from tank 241-C-106 while the second simulates settling of retrieved solids into tank 241-AY-102. Based on data in Castaing (1994), the sludge particle density was assumed to be 2.4 g/cm^3 with the particle size distribution as shown in Table 4-4 and the supernate assigned the density of 1.03 g/cm^3.

Table 4-4. Particle Size Distributions of Tank 241-C-106 Sludge

Size fractions	Particle sizes, μm	Percent weight
1	5 - 10	35
2	10 - 15	11
3	15 - 20	5
4	20 - 25	12
5	25 - 30	4
5	30 - 35	0.8
6	35 - 40	8
7	40 - 45	10.8
8	45 - 50	7.4
9	50 - 55	6
	Total	100

4.3.1 Tank 241-C-106 Pump Out Simulation

This simulation focuses on the point at which the slurried sludge is pumped out of tank 241-C-106. The current plan is to use the sluice jet to dig a 0.91 m deep, 1.52 m diameter hole (a well point) in the sludge from which the retrieval pump will withdraw the sluiced solids. The retrieval pump will withdraw the slurry generated by the sluicing operation at the approximate rate of 300 gpm.

The TEMPEST code was applied to this case as a full three-dimentional representation with approximately 2-ms time steps without simulating chemical reactions. The inlet slurry stream was assumed to contain 30 wt% solids, which is the maximum capacity of the pump. The solids were divided into nine size fractions by combing 25-30 micron and 30-35 micron as one of nine size fractions (see Table 4-2). The slurry enters the cylindrical hole through a

3.94 in. wide by 2 in. deep channel at the top edge. The slurry is withdrawn from the top at the center of the cylinder through a 10.2 m diameter pipe simulating the retrieval pump suction. With a retrieval rate of 300 gpm, the mean residence time in the cylindrical hole is about 1.5 min.

Early simulation results (up to 20 simulation minutes) show that concentrations of each of the nine solids is relatively uniformly distributed within the entire hole with Solid 1 (finest solids with 5-10 micron diameter, see Table 4-2) being the most uniformly distributed and Solid 9 (the coarsest solids with 50-55 micron diameter) least uniform. Figure 4-1 shows predicted distributions of flow (m/s) and Solid 9 (kg/m^3) in a vertical plane covering from the top to the bottom of the hole and the slurry inlet channel to the center of the hole at 20 simulation minutes. Figure 4-2 shows horizontal distributions at the bottom of the hole. As indicated in these figures, predicted concentrations of the Solid 9 (the largest solids) after 20 minutes vary from 22.1 kg/m^3 near the surface to 62.5 kg/m^3 near the bottom, revealing particle setting effects. The selected method of expressing the degree of segregation is the increase in mass fraction of solids for a particular size range particle. The largest size particles (50-55 micron) increase in mass fraction by a factor of 1.9 with smaller particles concentrating to a lesser degree. For sizes less than 30 micron the settled solids contain less than the mass fraction in the initial uniform solids.

The distribution of Solid 1 (the finest solids) are very uniform within the hole, ranging from 130 kg/m^3 near the top to 133 kg/m^3 near the bottom. Although, the highest Solid 1 concentrations are found near the bottom, based on a mass fraction of solids basis, the solids near the bottom contain 30% less of the finest fraction than at the inlet. This is an effect of the larger sizes concentrating in the lower layers.

4.3.2 Tank 241-AY-102

After transfer from tank 241-C-106, the retrieval stream containing 300 gpm of the slurry with 30 wt% solids will be introduced into tank 241-AY-102. It was assumed that the solid in the slurry has the size distribution of the tank 241-C-106 sludge (see Table 4-2). Tank 241-AY-102 initially contains .46 m of sludge and 4.6 m of supernate above the sludge layer. The sludge has the density of 1.4 g/cm^3 (Castaing 1994), and is assumed to have the same particle size distribution as that of tank 241-C-106.

Tank 241-AY-102 has a distributor consisting of four 2.54 m. diameter nozzles, oriented at right angles to each other to form a cross in the horizontal plane. The distributor is located 1.83 m off the tank center and 3.96 m above the tank bottom. A 10.2 m suction pipe opening to recirculate the tank 241-AY-102 supernate back to tank 241-C-106 is located at 6.7 m from the center (or 8.53 m from the distributor) at the surface of the supernate (5.03 m ft above the tank bottom). The suction pipe was located at 45 in. between the two of the injection nozzles. The outlet volumetric flow rate was set to 300 gpm to match the incoming slurry discharge. To simplify the simulation and still to maintain the conservativeness of the potential solid setting in the tank, the slurry distributor was located to the center of the tank, and the tank diameter was increased from the actual 22.9 m to 24.7 m.

Figure 4-1. Predicted Vertical Distribution of Solid 9 (with 50-55 μm Diameter) Concentration in kg/m^3 in the Retrieval Pump Well Point Within Tank 241-C-106 after 20 Minutes.

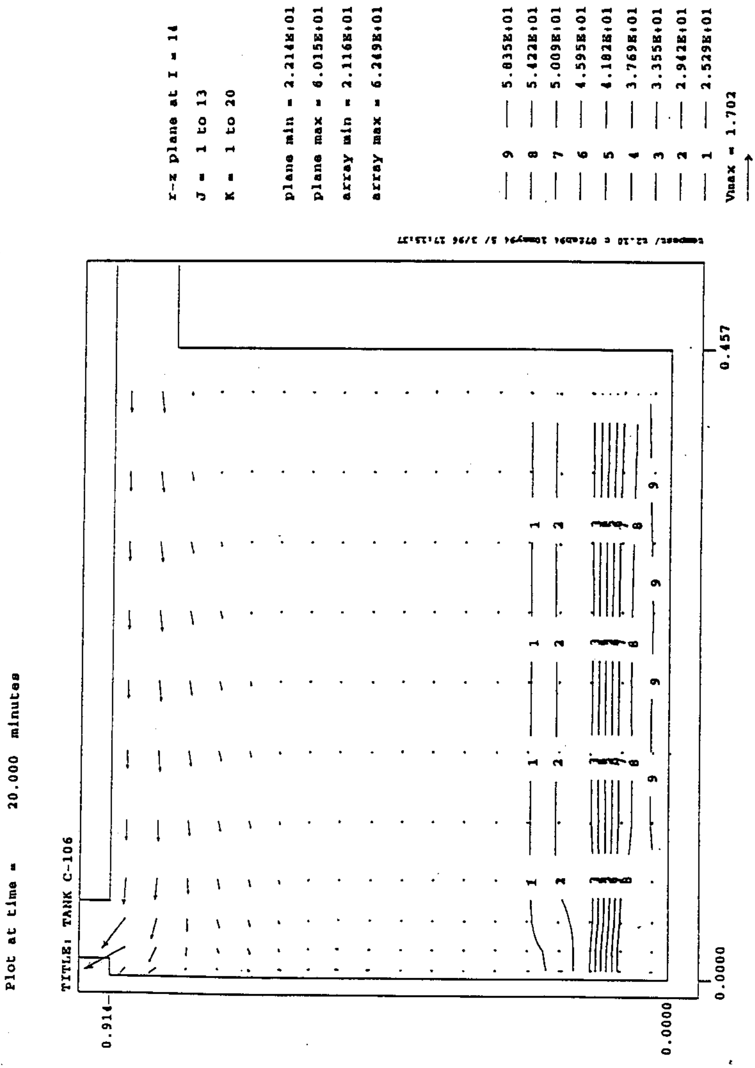
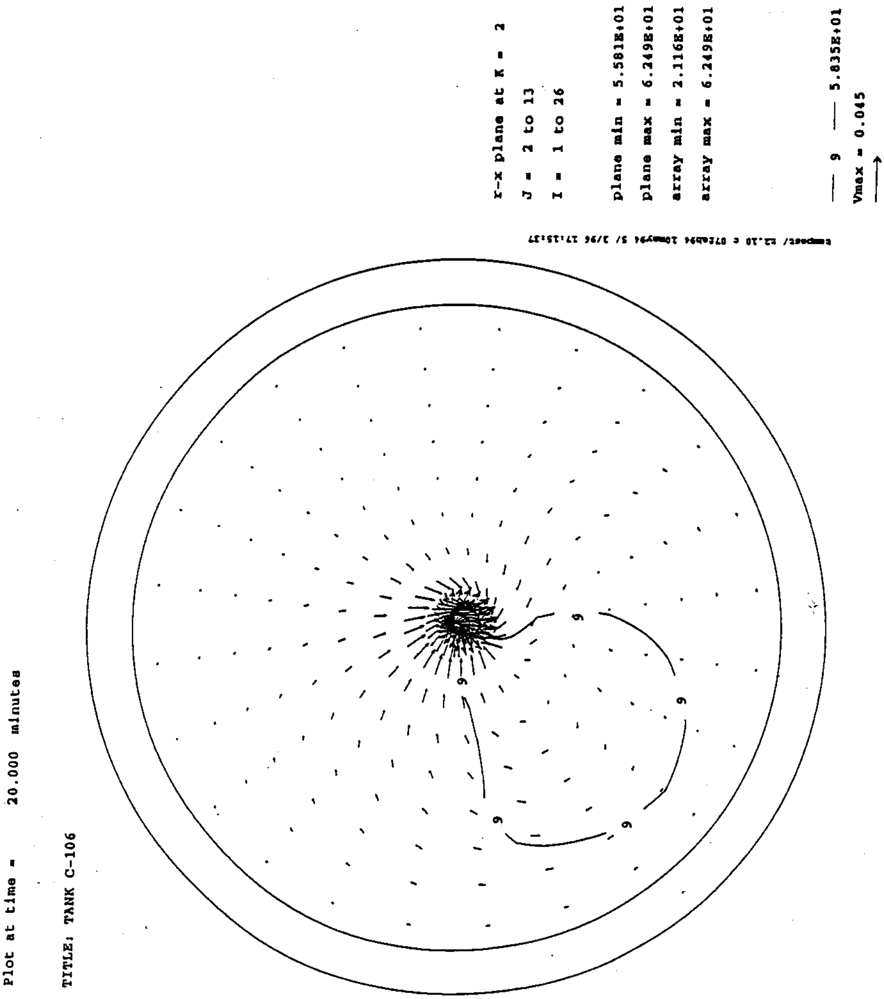


Figure 4-2. Predicted Horizontal Distribution of Solid 9 (with 50-55 μm Diameter) Concentration in kg/m^3 on the Bottom of the Retrieval Pump Well Point Within Tank 241-C-106 after 20 Minutes.



The TEMPEST code was applied to this tank as a full three-dimentional simulation case (without simulating chemical reactions) with approximately 3-ms time steps. Figure 4-3 shows the predicted vertical distribution of Solid 9 concentrations after six simulation minutes, depicting the slurry plume descending from one of the four nozzles toward the tank bottom and the density current spreading over the original 0.46 m tank 241-AY-102 sludge layer with a little mixing with the original tank sludge. Near the surface of the tank supernate, there is very little Solid 9 (the largest solids) present. Figure 4-4 shows the predicted Solid 9 concentrations on the horizontal plane above the original tank 241-AY-102 sludge layer after a 10 minute simulation, reflecting the density current movement. This figure shows that the Solid 9 accumulated more along the tank peripheral. Variations of Solid 9 concentrations within this horizontal plane vary over approximately factor of four (from 2.1 to 7.7 kg/m^3 at this time). The Solid 9 concentrations in this layer are expected to increase over time. Finer solids show similar patterns to that of Solid 9 with somewhat more uniform distribution patterns. These early simulation results indicate that most of the slurry introduced to the tank 241-AY-102 will be accumulated over the original tank 241-AY-102 sludge layer and the variations of Solid 9 accumulated there will vary over a factor of four, based on the conditions imposed on the modeling.

4.4 OTHER EFFECTS

In addition to the fluid dynamic investigations described above there are several miscellaneous investigations that are currently being pursued but for which results are currently not available.

Bubble attachment is a conceivable mechanism for removing fissile material from the bulk sludge, or conversely, for removing neutron absorbers from the sludge, leaving behind a sludge concentrated in fissile material. Bubbles may be formed by the sluice jet impacting on liquid surfaces or by air sucked into the retrieval pump if the level in the well point is not sufficiently maintained. Bubbles can also form from radiolysis of waste solutions. For the specific case of tank 241-C-106 retrieval, it is difficult to envision scenarios that might generate concern. Bubbles in tank 241-C-106 would eventually break and release the segregated component. Prior to bursting, any significant accumulation of foam would form a fairly uniform layer, which by its geometry would be unable to achieve criticality. Any deposition in a particular area from the bursting bubbles would be disturbed again as the sludge in the tank is sluiced from the tank. After reaching tank 241-AY-102, the extent of bubbles and foam would be expected to be fairly small due to the submerged pump suction. Any bubbles pulling neutron absorbers or Pu to the top of the tank would be in a safe geometry (thin layer) and after bursting, the solids would settle into the tank along with other solids over a large area. The possibility of there being sufficient bubbling to remove most of the neutron absorbers is considered very remote. However, additional investigation is being undertaken to look at the mechanisms of floatation separations and to determine what the potential for this type of segregation is for the sludge particles.

Figure 4-3. Predicted Vertical Distribution of Solid 9 (with 50-55 μm Diameter) Concentration in kg/m^3 in Tank 241-AY-102 after Six Minutes.

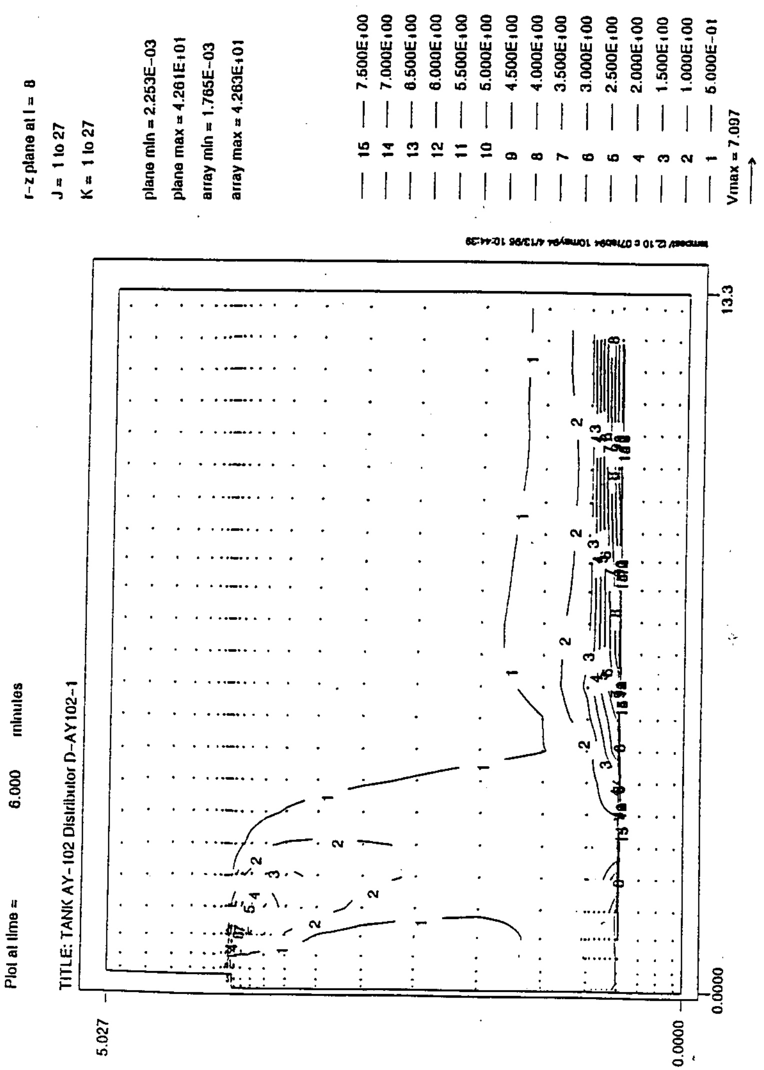
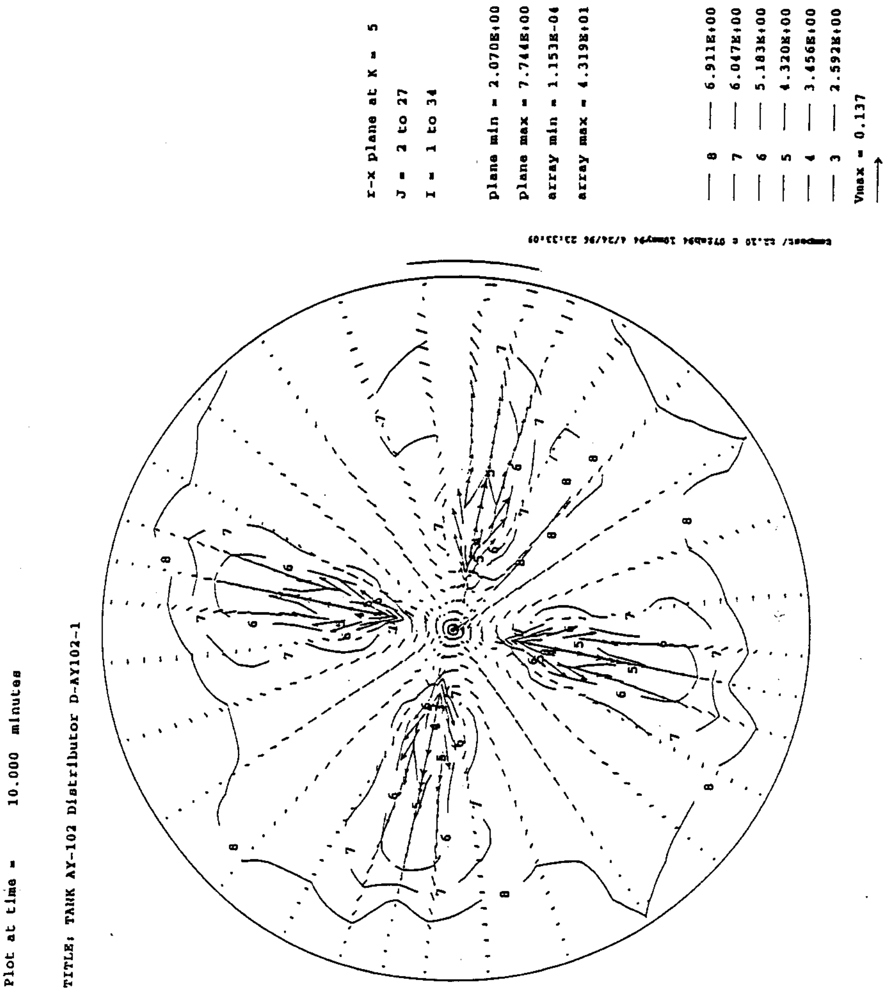


Figure 4-4. Predicted Horizontal Distribution of Solid 9 (with 50-55 μm Diameter) Concentration in kg/m^3 just above the Original Tank 241-AY-102 Sludge in Tank 241-AY-102 after 10 Minutes.



In addition, there are mechanisms that may act to segregate particles that are not simulated by the TEMPEST code. Many of these mechanisms are important to segregation in mining applications such as separation of placer gold from ore in sluice boxes, jigs, or other equipment. In TEMPEST (a passive-scaler code) the particles follow the flow streamlines with the addition of a settling velocity. Thus, the particles do not behave as if they have mass or momentum. These additional mechanisms will be investigated to determine if there is a potential effect on the degree of segregation observed.

4.5 CONCLUSIONS FROM FLUID DYNAMIC MODELING

Currently, there is no indication of a potential for criticality occurring during sluicing retrieval of tank 241-C-106. Only under very conservative (extreme) bounding assumptions can a one-dimensional case be formulated to exceed the minimum critically safe concentration of 2.6 g/l Pu for the conservative waste model. However, this case would still result in subcritical conditions because the scenario results in a uniform distribution across the floor of the tank (i.e., an inherently subcritical geometry). Using more realistic bounding assumptions (which we believe can be documented and defended) the degree of settling segregation will leave at least a factor of 2 difference between the maximum sludge composition and the minimum safe concentration of 2.6 g/l. Geometric arguments substantially widen this safety factor. In addition, TEMPEST modeling to date has indicated segregation of less than a factor of 2 increase in concentration, which would leave the maximum settled Pu content roughly a factor of 10 below the minimum before accounting for geometric considerations. Although additional investigation is required, there is no known credible scenario for criticality to be achieved due to fluid dynamic segregation of fissile material during sluicing retrieval of tank 241-C-106.

5.0 CRITICALITY CONSIDERATIONS FOR SLUICING

Waste tank criticality is a function of four factors:

- Fissile material concentration
- Neutron moderation
- Geometry
- Neutron absorbers

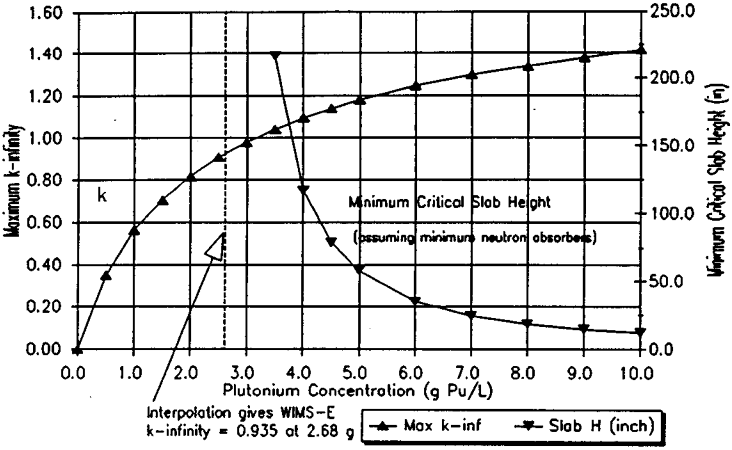
Fissile material consists of the odd numbered isotopes of uranium and plutonium (i.e., U^{233}, U^{235}, Pu^{239} and Pu^{241}). Any U^{235} in the tanks is generally present with sufficient U^{238} (an absorber) to render it infinitely subcritical; however, it adds to the reactivity of plutonium. Consequently, the critical concentrations derived in this report for Pu include the fissile and nonfissile Pu isotopes and the fissile U in order to be conservative.

The following discussion of parameters that effect the reactivity of stored waste assumes two things in all calculations and discussion: (1) all calculations are at optimum moderation (this means that the hydrogen [water] content for all systems has been assumed to be at a level that results in the lowest possible critical mass for the system being discussed), and (2) the nonfissile waste materials have a neutron absorption capacity equal to that of the Rogers Waste Model, a conservative model of the waste absorption properties of the waste (Rogers 1993 and 1996).

5.1 FISSILE MATERIAL CONCENTRATION

For Hanford waste, the plutonium concentration must be at least 2.6 g Pu/L before criticality becomes possible, even in an unlimited volume of waste. This value is based upon a uniform mixture of plutonium and other materials. The waste solids are conservatively assumed to be that of the Rogers Waste Model (Rogers 1993 and 1996) which defines a minimum neutron absorber composition, assumes a solids density of 1.2 g/cc, and assumes the water content is optimized. This subcritical limit is set for k_∞ not exceeding 0.95 at a 95% confidence level. After taking into account the uncertainty in the calculations, the 95% confidence level is satisfied when the calculated k_∞ is 0.935. Figure 5-1 shows that the critical slab height approaches infinity below a plutonium concentration of 3 g Pu/L.

Figure 5-1. Minimum Critical Slab Height.



Plutonium concentration has historically been used as the primary control on waste stream discharged to the storage tanks (Serne et al. 1996). Documents and procedures from the mid-1960's indicate control of discharge levels at 0.013 g Pu/L (0.05 g Pu/gal) in a waste mixture being routed to a waste tank and 1 g Pu/L in waste tank solids (Braun 1994). Reviews of flowsheets and transfer documents prior to 1960 indicate that the same level of control has always existed. A statistical analysis of the extensive number of waste tank characterization samples to date (>500) confirms the effectiveness of the concentration controls (Serne et al. 1996).

In addition to presenting the discussion of the minimum critical concentration, it is important to have an understanding of the concentration factor that would be required to increase the present concentration of Pu in waste to a level at which subcriticality could no longer be assured.

If the solids portions of both tanks 241-C-106 and 241-AY-102 were combined, the total mass would be about 108 Kg plutonium at a concentration of about 0.12 g/L. Based on the information in Figures 5-2 and 5-3 (Rogers and Schwinkendorf 1996), a subcritical sphere (K_{eff} = 0.935) with a mass of 108 Kg would require a plutonium concentration of at least 4 g/L. This would require a mechanism capable of producing a concentration factor of more than 33 for

Figure 5-2. Sphere Minimum Critical Diameter vs Plutonium Concentration (K_{eff} = 0.935).

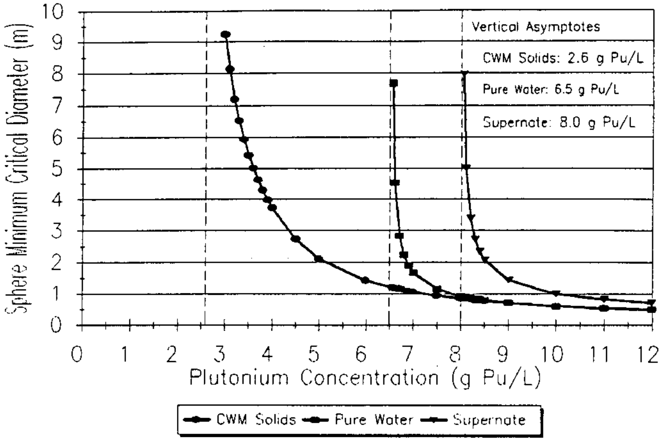
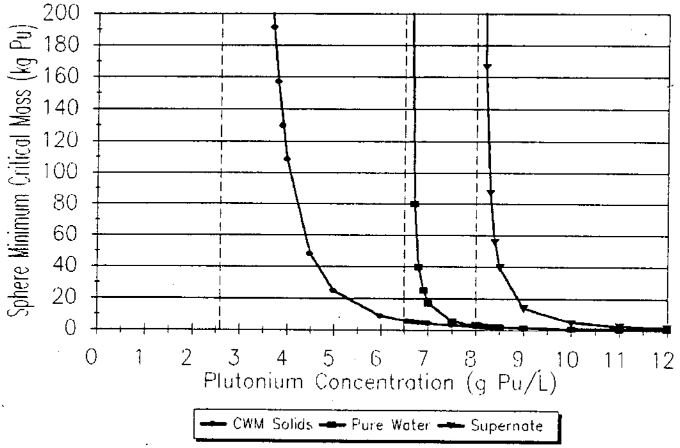


Figure 5-3. Sphere Minimum Critical Mass vs Plutonium Concentration (K_{eff} = 0.935).



all the plutonium in the combined tank and assemblage of a spherical geometry of about 3.5 m (12 ft) in diameter. A concentration factor closer to 40 would be required for criticality ($K_{eff} = 1.0$).

This perspective indicates that even under the most conservative conditions, a concentration factor in excess of 33:1 would be required for the tank average plutonium density to approach a critical system in tank 241-C-106. The resulting critical sphere would need to be as large as or larger than the thickness of the solids layer. It should be noted that spheres are calculated in this case for conservatism; more realistic slab-like layers would require considerably higher Pu concentrations before the subcritical nature of the waste could no longer be assured. A slab across the diameter of the entire tank would require on the order of 1000 Kg plutonium for criticality; this is more than the 108 Kg available in the system being reviewed.

5.2 DEFENSE IN DEPTH

The technical analysis provided in this report provides a bounding case to assure the tanks in question remain subcritical, based on insufficient concentration of the fissile material. The criticality analysis discussed in this report includes considerable conservatism to bound representative conditions. There are many additional factors that add to the margin of criticality safety for stored wastes. The following assessment provides additional defense in depth and conservatism to ensure the waste remains subcritical.

5.2.1 Neutron Moderation

Minimum critical mass is achieved by optimum moderation and infinite reflection. Any material, including water, coexisting with fissile atoms provides some parasitic absorption of neutrons. However, there is a certain amount of water that achieves optimal moderation, i.e., the neutron energy is reduced such that the ratio of absorption-to-fission cross section is minimized. Over moderation means that the additional water does little to further thermalize the neutron spectrum, but introduces additional neutron absorption, thereby also reducing the reactivity of the system. Since the waste tanks are nominally aqueous, water is the principal moderator. Generally, the waste form is over moderated, leading to higher minimum critical plutonium concentrations than those identified in Section 5.1. Sludge and liquid are both grossly over-moderated, and salt cake may be near optimal moderation. Water concentration in most tank layers ranges as follows:

- Liquid ≈65 - 95% water
- Sludge ≈20 - 70% water (may in some cases be as low as 5%)
- Salt Cake ≈5 - 65% water.

Salt cake and liquid are low in plutonium content. Over-moderation in sludge results in enhanced absorber effect (i.e., absorption cross sections are higher at the low neutron energy that results from an abundance of water moderation).

5.2.2 Areal Concentration Limit - ≈240 g Pu/ft^2 (2600 g Pu/m^2)

Carter et al. (1970) calculates the minimum critical areal density for plutonium in pure water as 240 g/ft^2. This means that criticality is not possible when the mass of plutonium in any vertical, full height column (square or circular) of waste 1 ft in cross sectional area does not exceed 240 g. In this case, the actual distribution of plutonium in the waste does not matter. As long as this areal density is not exceeded above any square foot of floor area, the waste will be subcritical, independent of the actual distribution and moderator content. This remains true even if the plutonium concentration exceeds the minimum critical volumetric concentration limits in localized regions and the water content is optimized. The areal concentration limit is of particular interest regarding tanks with an observable and measurable sludge layer.

Actual tank waste contains neutron absorbers that result in a higher minimum critical plutonium areal density, as illustrated in Figure 5-4. If an upper limit is assumed on the plutonium concentration in the waste, the minimum critical areal density increases even more. As the limiting plutonium concentration drops below 7 g Pu/L, the minimum critical areal density increases rapidly. Below 2.6 g Pu/L, the minimum critical areal density becomes infinite. Figure 5-4 shows the minimum criticality areal densities.

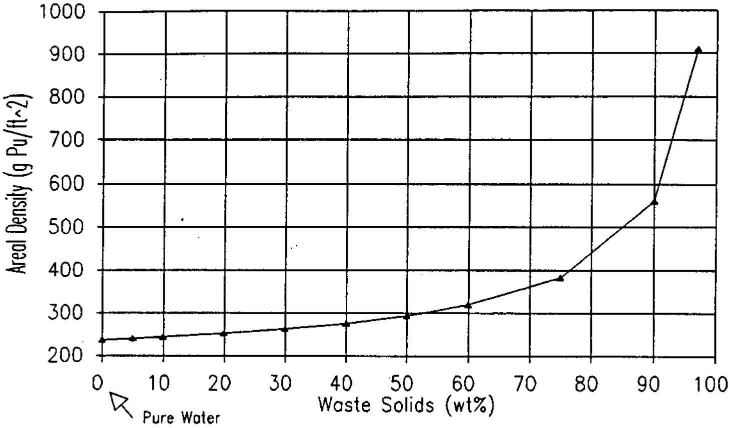
The data of Figure 5-4 was computed with WIMS-E (Gubbins et al. 1982) and GOLF (Schwinkendorf 1994) using the Rogers Waste Model (Rogers 1993) that contains the following materials at a density of 1200 g/L:

	Wt%
Oxygen	40.7
Phosphorous	6.9
Silicon	3.8
Sodium	21.5
Aluminum	7.2
Iron	19.9

This waste composition model was developed to conservatively represent the neutron absorption existing in any of the waste tanks. It is the percentage of this nuclide waste distribution that is plotted as the abscissa in Figure 5-4.

This calculation indicates a minimum areal density of 237 g Pu/ft^2. The plutonium concentration at this point is 17 g Pu/L, with an associated slab thickness of 15 m. The ARH-600 Criticality Handbook (Carter et al. 1970) contains a minimum published areal density of 242 g Pu/ft^2, at 15 g Pu/L, with a slab height of 17.8 m. These minimum values agree very well, considering that the optimum concentration limits are fairly broad. Note from Figure 5-4 that when solids are taken into account, the minimum critical areal density increases appreciably.

Figure 5-4. Minimum Critical Areal Density.



5.2.3 Neutron Absorbers

In the following discussion of the effects of neutron absorbers, two of the most effective absorber materials (boron and cadmium) have been excluded. Boron and cadmium are known to be present in Hanford waste tanks, sometimes in substantial quantities in waste solids. Their absorption properties would dominate the other absorbers such that they have been purposely excluded in order to better defend the conservatism of the waste model. Their exclusion adds considerable conservatism to the following discussion.

Neutron absorbers reduce the reactivity of any fissile assembly. There is a unique minimum absorber to plutonium ratio (X/Pu) for all absorbers, above which the system will remain subcritical, independent of any other influences. This mass ratio is calculated for a homogenous mixture of plutonium, absorber, and water and is applicable when the waste is homogeneous. Since waste is sent to tank farms as a more or less homogenized mixture, the absorber-to-plutonium ratio is a good indicator of subcriticality. This minimum has been calculated for the various elements in the sludge. The results are reported in Tables 5-1 and 5-2.

Table 5-1. Insoluble Absorber-to-Plutonium Minimum Subcritical Ratios (Sludge).

Element	Minimum subcritical ratio (X/Pu mass ratio)
Uranium (natural)	770
Iron	160
Manganese	32
Chromium	135
Nickel	105

Table 5-2. Soluble Absorber-to-Plutonium Minimum Subcritical Ratios (Salt Cake or Liquid).

Aluminum	910
Sodium	360
Nitrate	270

The relative importance of a component that ensures subcriticality can be found by dividing its actual mass ratio by the corresponding subcritical mass ratio. This ratio of mass is referred to as the absorber fraction. An absorber fraction greater than 1.0 means that a uniform mixture will be subcritical. Waste is composed of many different components, each with its own minimum absorber-to-plutonium subcritical ratio. The combined effect of these absorbers can be estimated using the sum of the individual absorber fractions. This is sometimes called the sum of the actual-to-minimum subcritical ratios. A formula for this sum is written as follows.

$$\text{If } \sum_{j=1}^{N} \frac{\left(\frac{X_j}{Pu}\right)_{\text{actual}}}{\left(\frac{X_j}{Pu}\right)_{\text{subcritical}}} \geq 1,$$

$$\text{then } k_\infty \leq 1$$

If we consider the neutron absorption effect of only two elements in abundance in the tanks, iron and manganese, we readily note that there is far more than enough neutron poison to render the tanks subcritical — assuming that the absorbers stay with the plutonium. Table 5-3 was prepared by taking the relevant concentrations from Tables 3-2 and 3-3 and comparing the ratios of absorber/plutonium with the ratios of Table 5-1 that define the minimum ratios needed to assure subcriticality. We note that the minimum safety factor or concentration factor, (determined by dividing the actual absorber/plutonium ratio by the minimum value for criticality) is about 5.

Table 5-3. Subcriticality Achieved in Tank 241-C-106 and Tank 241-AY-102 By Selected Neutron Absorbers.

	Tank 241-C-106	Tank 241-AY-102	Criticality limit	Minimum safety factors
Fe/Pu	1070	1560	160	6.7
Mn/Pu	147	164	32	4.6

5.2.4 Geometry

Geometry can play a strong role in determining critical conditions because of the neutron leakage effect. However, because of the immense size of the Hanford tanks, the geometry can normally be considered essentially infinite, at least in the lateral direction (slab geometry). If the tanks, can be shown to be subcritical for infinite conditions, any finite size will be even less reactive neutronically.

Plutonium in concentrations higher than the limits discussed in Section 4.1 can be tolerated in smaller volumes. For example, at 15 g Pu/L in pure water, the critical spherical radius is 9 in., per ARH-600 (Carter et al. 1970). For nominal waste compositions this critical sphere size is much larger. As noted earlier, the critical sphere size in pure water becomes infinite at 7.8 g Pu/L. This corresponds to the infinite subcritical concentration limit for Pu in pure water (Paxton and Pruvost 1986).

5.3 PERSPECTIVE ON PLUTONIUM CONCENTRATION WITHIN TANKS 241-C-106 AND 241-AY-102

Given the areal and volumetric concentration limits, some perspective can be gained on the safe plutonium concentration in various regions of the subject tanks. For the liquid (supernatant) regions, the concentration of plutonium is intrinsically low; 0.0035 g Pu/L in tank 241-C-106 and even lower in tank 241-AY-102. This highest concentration is about a factor of 740 below the concentration for criticality under ideal conditions.

The bulk of the plutonium resides in the sludge. Consequently, criticality concerns need to be addressed only in the sludge layer. As noted above, a significant concentration of plutonium would be required even in the sludge before any criticality potential would exist. If the nominal measured value of sludge plutonium concentration (i.e., 0.075 g Pu/L) is used, the concentration factor required to reach 2.6 g Pu/L would be 35. If the highest measured concentration (i.e., 0.13 g Pu/L) is used, the sludge would have to be concentrated by a factor of 20.

6.0 CONCLUSIONS

After assessing the underlying chemical and associated hydraulic forces operable in the tank 241-C-106 to tank 241-AY-102 retrieval program, it is concluded that there is no credible mechanism for plutonium to concentrate in sufficient quantities to constitute a nuclear criticality concern.

Although the total quantity of plutonium in tank 241-C-106 is believed to be among the highest of all Hanford SSTs, it has an insufficient concentration from a criticality perspective. During the waste neutralization process prior to sending the waste to the tanks, most of the plutonium precipitated out of solution. It is likely that the bulk of the plutonium coprecipitated with or adsorbed on the massive amounts of metallic oxyhydroxides (e.g., iron, manganese, aluminum). If adsorption is the principal precipitation mechanism, the processes expected during waste aging should not cause significant amounts of plutonium to dissolve and recrystallize. This would prevent separation of plutonium from the ubiquitous neutron absorbers (so long as the medium remains alkaline and is maintained at relatively low carbonate levels). Consequently, even if a plutonium concentrating mechanism could be identified, such concentration would not occur without the simultaneous concentration of neutron absorbers.

Even if sorption is not the dominant mechanism, and plutonium precipitates as small plutonium oxide crystals or as a solid-solid matrix with non-neutron absorbing elements, the degree of plutonium concentration necessary for any criticality problem to arise is larger than any identified concentration mechanism could produce.

In order for the sluicing and pumping operations in the proposed retrieval program to cause conditions approaching neutronic criticality, all of the following conditions would have to occur:

1) Plutonium would need to separate from iron and manganese by factors of 6.7 and 4.7, respectively;

2) Plutonium would need to concentrate by more than a factor of 20;

3) The geometry necessary to accommodate the plutonium concentration of concern would necessarily defy any realistic configuration.

It is recognized that the tank characterization data utilized for the numeric relationships identified in points 1 and 2 above may not be totally representative of all adverse conditions. Nevertheless, the margins are so large it is the judgment of the review team that attaining the combination of such factors is not credible. Consequently, the team sees no technical basis to prevent proceeding with the proposed operations from the standpoint of criticality.

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