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Criticality Safety Of Project W-151, 241-AZ-101 Retrieval System Process Test

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U.S. Department of Energy Contract DE-AC06-87RL10930

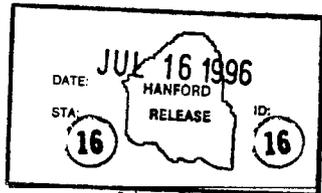
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Abstract: This Criticality Safety Evaluation Report (CSER) documents a review of the criticality safety implications of a process test to be performed in tank 241-AZ-101 (101-AZ). The process test will determine the effectiveness of the retrieval system for mobilization of solids and the practicality of the system for future use in the underground storage tanks at Hanford. The scope of the CSER extends only to the testing and operation of the mixer pumps and does not include the transfer of waste from the tank. Justification is provided that a nuclear criticality is extremely unlikely, if not impossible, in this tank.

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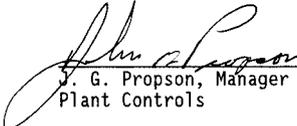
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CSER 96-014

Title: Criticality Safety Of Project W-151
 241-AZ-101 Retrieval System Process Test

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LIST OF TERMS

ALC	air lift circulators
AWF	Aging Waste Facility
CPS	Criticality Prevention Specification
CSER	Criticality Safety Evaluation Report
DST	double-shell tank
ECR	effective cleaning radius
NCAW	neutralized current acid waste
PUREX	Plutonium Uranium Extraction
SST	single-shell tank

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1.0 PURPOSE

This Criticality Safety Evaluation Report (CSER) documents a review of the criticality safety implications of a process test to be performed in tank 241-AZ-101 (101-AZ). The process test will determine the effectiveness of the retrieval system for mobilization of solids and the practicality of the system for future use in the underground storage tanks at the Hanford Site. The scope of the CSER extends only to the testing and operation of the mixer pumps and does not include the transfer of waste from the tank. Justification is provided that a nuclear criticality is extremely unlikely, if not impossible, in this tank.

This CSER is necessary because of the potential that mixing, suspension, and settling of fissile material bearing solids may result in a localized configuration that is a criticality safety concern. A primary objective of the process test for the two mixer pumps installed in tank 101-AZ is the suspension, mixing, and settling of plutonium bearing solids currently being stored in the tank.

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2.0 SUMMARY AND CONCLUSIONS

"CSER 94-004: Criticality Safety of Double-Shell Tanks, WHC-SD-SQA-CSA-20368," (Rogers 1994) spells out criteria against which waste can be evaluated to ensure an adequate margin of subcriticality. It provides the technical basis for limits and controls to be used in Criticality Prevention Specifications (CPS) (Vail 1995) to ensure that the waste remains in a highly subcritical state.

Unless the plutonium concentration in tank 101-AZ waste is increased by a large factor, criticality is not possible. Mixing within the waste tends to disperse the plutonium, and none of the mechanisms capable of increasing plutonium concentration appear capable of overcoming the dispersal and blending mechanisms. No identified scenario associated with the mixing test could credibly lead to criticality. It is concluded that the margin of safety is sufficient to permit testing of the mixer pumps. Also, the plutonium was not washed out of the solid phase by the water as evidenced by the low plutonium values of the water-washed supernate fraction of the samples. The rigorous laboratory procedure that centrifuged and tumbled the sample for several hours failed to dislodge the plutonium from the solid phase. The centrifuge and tumbling of the sludge is considered similar to the mixing action of the mixer pump.

The analysis of waste characterization samples taken in FY 1989 of the waste in tank 101-AZ indicates that the tank contains approximately 23,203 g of plutonium (63 g in the supernate and 23,140 g in the sludge layer). The majority of the waste is neutralized current acid waste (NCAW) which is the result of denitrating high-level waste with sugar, then neutralizing with sodium hydroxide. The tank pH is around 13.8. Because plutonium is a precipitate in alkaline salt solutions, it primarily resides in the solids layer of the waste tanks. The concentration of plutonium in all waste transfers is low; therefore, the sludge in tank 101-AZ contains a low concentration of plutonium at 0.175 g Pu/L (Gray et al 1993) and the supernate contains plutonium at a concentration of 0.000019 g Pu/L (Gray et al 1993). Because the plutonium concentration in the sludge is several orders of magnitude greater than the concentration in the supernate, even though there is 26 times more supernate, the data indicating that the sludge layer contains almost all the plutonium in the tank is reasonable. The highest concentration of plutonium in the supernate and sludge for the two core samples is used in this CSER, to provide some conservatism in the conclusions. The double-shell tank (DST) Fissile Material Tracking System currently estimates 19,249 g of plutonium in tank 101-AZ.

The upper limit on plutonium solubility in alkaline salt solutions is reported as 0.0017 g Pu/L (Hobbs et al. 1993). The concentration of plutonium in the supernate and interstitial liquids in tank 101-AZ, reported from analyzed samples, is less than the upper limit on solubility, as expected. The plutonium inventory and distribution as determined from the analysis of the samples is considered reasonable and representative of the tank waste. The plutonium concentration in the supernate is more than 378,000 times less than the minimum critical plutonium concentration in water of 7.2 g Pu/L (Rogers 1994).

Waste tank criticality safety is primarily focused on the plutonium in the solids phase because the plutonium concentration is higher in the solids than in the supernate (0.175 g Pu/L versus 0.000019 g Pu/L). The potential for an increase in the plutonium concentration in tank 101-AZ sludge up to the minimum critical concentration of an infinite system of waste tank solids under optimum conditions of 2.6 g Pu/L (Rogers 1993) of waste solids is extremely remote. An increase of plutonium concentration in the solid phase can be accomplished only by removing either the absorbers leaving the plutonium behind or precipitating additional plutonium without absorbers. The analytical data and laboratory procedures indicate that subjecting the sludge to many hours of centrifuging, water wash, and tumbling will not by itself separate the plutonium from the solid phase. Also, the rigorous laboratory procedure did not successfully remove neutron absorbers from the solid phase. One fraction of the solid phase of the samples was analyzed after the extreme chemical treatment of fusion with potassium hydroxide and another fraction was treated by sodium hydroxide. It can be concluded that the mechanical mixing of the solid material will not provide the dramatic chemical change required to separate the plutonium from the solid matrix.

The minimum critical areal density in tank waste is $2,582 \text{ g Pu/m}^2$ (240 g Pu/ft^2) (Carter et al. 1969). The settling of all the plutonium would need to occur within an area of 8.4 m^2 (90.6 ft^2) to achieve an areal density of $2,582 \text{ g Pu/m}^2$ (240 g Pu/ft^2). This assumes that all the plutonium in the supernate also settles out into the solids layer. The tank floor has an area of 409 m^2 ($4,400 \text{ ft}^2$) and there is no mechanisms available that would force the solids to settle within an area covering only 2.06% of the total floor area.

The macroscopic absorption cross section of the waste in tank 101-AZ compared to the macroscopic absorption cross section of the model (Rogers 1993). The comparison provides some knowledge of the margin of safety of the tank waste versus the model which was used to establish the minimum critical plutonium concentration of 2.6 g Pu/L. When the absorption cross section is calculated for one gram of waste material, it is found to be $0.01516 \text{ cm}^{-1}/\text{g}$ for the model composition. This can then be compared to $0.0334 \text{ cm}^{-1}/\text{g}$ for core 1 and to $0.0344 \text{ cm}^{-1}/\text{g}$ for core 2. The absorption cross section for the waste in tank 101-AZ is more than double the cross section of the model, when they are compared on the basis of the same mass per liter. Because the analyzed components of the waste samples comprise only about one-third of the total material in the waste, the total neutron absorption per liter of waste is expected to be more than twice that obtained for the analyzed components. The neutron absorbing qualities of the actual waste is therefore found to be greater than that of the waste composition used to calculate the minimum critical parameters.

It is reasonable to expect that before mixing, some radial and vertical heterogeneity with respect to the concentration of plutonium exists. The two 300 hp mixing pumps will sufficiently suspend and mix the majority of solids, providing a dispersing mechanism for the plutonium in the tank. The suspended solids will settle out of the supernate into a flat slab with a potential for the plutonium solids to form a thin slab at the bottom of the solids layer. If the plutonium is concentrated in a layer of waste at the bottom of the tank to 8 g Pu/L, the waste would be subcritical for waste thicknesses up to 38 cm

(15 in.) (Braun et al. 1994). The suspension and dispersing action of the pump is expected to preclude the settling of the plutonium solids over an area small enough to achieve the minimum critical areal density or create an increase in the plutonium concentration.

A postulated scenario considered in this CSER is the increase of plutonium concentration as a result of the plutonium solids settling at a faster rate than other solid material. Initially, the rigorous laboratory procedure of centrifuging, agitation, water washes, fusion with potassium hydroxide and acid dissolution supports the assertion that the plutonium and other solid-phase material will not separate. The thin slab of plutonium bearing solids will also include the other solid-phase material at the mass ratios calculated in Section 5.1.2, which is highly subcritical. Secondly, if all the plutonium in the tank settles out in a thin layer at the bottom of the tank the areal density will be 56.8 g Pu/m^2 (5.3 g Pu/ft^2), which is still highly subcritical and will not increase with additional mixing. Thirdly, if the plutonium solids settle into a thin slab at the bottom of the tank, the average concentration will depend on the thickness of the slab and the area over which the slab is distributed. Unless some mechanism for restricting the surface area over which the solids can settle is installed, the plutonium concentration will unlikely increase above the average. For waste thicknesses up to 38.1 cm (15 in.) the slab is subcritical for plutonium concentrations up to 8 g Pu/L, which requires an increase in the plutonium concentration of 46 times. Also, 38.1 cm (15 in.) of waste at 8 g Pu/L over the entire area of the tank requires over 1,000 kgs of plutonium, which far exceeds the quantity in the tank.

The estimated effective cleaning radius (ECR) of the pumps is 9.8 m (32 ft). The pumps are not in the center of the tank, so at least two areas of unsuspended solids called "dead zones" may exist; one on the east side of the tank and one on the west side. These areas are estimated to be 13.9 m^2 (147 ft^2) each, which is a little larger than 6.6% of the floor area. These "dead zones" are of little concern because the plutonium concentration in the undisturbed solids cannot change. Also, any plutonium rich material that may settle on top of these solids, after the pumps are turned off, will form a thin slab similar to the slab on the bottom of the tank and commingle with the unsuspended solid material. The discussion which supposes that all the plutonium in the tank separates and settles is conservative because the plutonium contained in the "dead zones" will not be available for concentrating in other areas of the tank.

Additional mixing and settling of all the plutonium in the tank cannot continually increase the concentration of plutonium above the average concentration allowed by the total mass of plutonium in the tank. An increase in plutonium concentration caused by separation of plutonium from the other solid-phase material in the waste would require an extremely efficient separation process to even begin to approach the concentration at which criticality is possible. If the plutonium inventory in tank 101-AZ did separate and concentrate to 8 g Pu/L at the bottom of the tank, the slab would only be 0.7 cm (0.26 in.) thick, which is highly subcritical.

The solubility of plutonium in alkaline salt solutions is sufficiently low so that tank 101-AZ supernate solution cannot hold enough dissolved plutonium to achieve a criticality. The solubility, concentration and distribution of plutonium in the supernate and solids are affected by many different elements and compounds (e.g., organic complexing agents, hydroxide, carbonate and metal oxides). This CSER considers the effect of these materials, only insofar as they impact criticality safety. Variations in the distribution of plutonium between the solids and the supernate will not impact critical safety, because all the plutonium could be either in the solids or supernate and the tank will remain subcritical.

The conservative plutonium concentration of the solids material as determined from core sample 2 (0.175 g Pu/L), is at least 14.9 times less than the minimum critical concentration in waste solids of 2.6 g Pu/L (Rogers 1993). The plutonium concentration in the supernate, as determined from core sample 2 (0.000019 g Pu/L), is at least 382,978 times less than the minimum critical concentration in water of 7.2 g Pu/L.

3.0 INTRODUCTION

High-level radioactive waste from nuclear fuels processing is stored in the underground double-shell storage tank 241-AZ-101 located in the 241-AZ Aging Waste Facility (AWF) tank farm on the Hanford Site. This newer DST is an active tank and may be used to receive waste.

Waste in tank 101-AZ storage contains low concentrations of fissile isotopes, primarily ^{235}U and ^{239}Pu . An important safety concern is the preclusion of a self-sustaining neutron chain reaction, also known as a nuclear criticality. This CSER reviews the process test (Symons 1996) and the first phase sludge mobilization test of the tank 101-AZ submersible mixer pumps and provides justification that a nuclear criticality cannot occur. This evaluation does not extend to the actual transfer of solids from the tank or sludge washing.

The initial activity in the disposal of Hanford Defense Waste is retrieving liquid and sludge from DSTs and converting the waste to solid forms. Project W-151 has been assigned the task to develop and demonstrate a method of retrieving the waste. Tank 241-AZ-101 has been selected as the first location for testing the retrieval system. The information and experience gained during the process test is expected to confirm the mobilization characteristics of the waste sludge, provide the bases to optimize the number, location, and the time cycles of the mixer pumps, and establish the effects of the mixer pump operation on the tank and other operating parameters.

Tank 101-AZ currently has 22 air lift circulators (ALCs) which have been used to mix the waste and suspend the solids. Because of the mixing action of the ALCs, the plutonium is expected to be relatively dispersed in the solids layer at the beginning of the process test. During the mixer pump tests, the ALCs will be turned off to allow for accurate evaluation of the effectiveness of the mixer pumps. Structural analysis was completed which showed the ALCs will withstand the mixer pump jet forces during the tests.

One 300 HP mixer pump is installed in each of the 01A and 01C risers. Each pump will take in fluid from the tank bottom and discharge the fluid horizontally through two opposing nozzles located 38 to 46 cm (12 to 18 in.) above the tank bottom. The nozzle assembly will rotate (180 degrees) for 360 degree mixing at 0.05 to 0.2 rpm to sweep the entire projected area of the tank bottom. The mixer pump is designed to operate within the temperature range of 10 to 130 °C and are capable of operation in 30 ft deep liquid waste at temperatures of 130 °C. The mixer pump nozzles are 15 cm (6 in.) in diameter with a designed flow rate of 19,680 L/min (5,200 gal/min). Based on the sludge shear strength of 10,000 dyn/cm² the expected ECR will be approximately 9.8 m (32 ft).

The composition and the distribution of waste components inside tank 101-AZ waste is uncertain because of the complexity of discharged waste and the mixing with previously stored tank waste. Because of this uncertainty, criticality safety depends on demonstrating inherent characteristics of waste that ensure subcriticality. Primary among waste characteristics that support criticality safety are the large proportion of waste solids to fissile

material and the relative uniform mixing of components within each waste layer. The continued dilution of fissile material in the solids during the mixing operations is key to the safety of the tank 101-AZ process test.

For criticality safety purposes, the Tank Farm Facility is classified as a limited control facility. The facility's status as a limited control facility requires a documented criticality safety evaluation which demonstrates that a criticality is prevented by the form or distribution of fissionable material, after allowing for credible accidents. The criticality safety evaluation for DSTs is provided in CSER 94-004 (Rogers 1994).

Critical parameters for tank waste are based on a hypothetical waste composition referred to as the conservative waste model. This waste composition is defined by Rogers (1993) and is based on 28 waste compositions analyzed for 16 single-shell tanks (SSTs). Although only samples from SSTs were used to derive the conservative waste model, critical parameters derived from the model may be applied to all tank waste because: the physics upon which the analyses are based is identical; DST waste is similar to SST waste; and considerable conservatism is included in the waste model. The conservative waste model defines a waste composition that has a smaller absorption cross section than any actual waste.

Additional information on the criticality safety of tank waste can be found in *High-Level Waste Subcriticality Safety Assessment* (Braun et al. 1994), which describes process history, waste streams, waste sample data, and waste tank chemistry. The basis for criticality safety is also discussed.

4.0 DESCRIPTION

Tank 101-AZ is a double-shell underground storage tank with components suspended into the tank and supported from the tank dome. The tank went into service in 1976 as one of four double-shell tanks designated to receive aging waste. It is 22.9 m (75 ft) in diameter and is designed to nominally store 3,785 kiloliter (kL) (1,000 kgal). The primary tank maximum waste level safety limit in tank 101-AZ is 3,849 kL (1,017 kgal) or 9.39 m (370 in.).

The tank presently contains approximately 3,497 kL (924 kgal) of waste in the form of supernate and solids. The total waste is the combined supernate and solids, it contains 3,365 kL (889 kgal) of supernate and 132 kL (35 kgal) of sludge (Hanlon, February 1996). The maximum temperature for the tank ranged from 74.4 to 84.4 °C (166 to 184 °F) for December 1993 through December 1994 (Hodgson and Tran 1995). The heat generation from radioactivity is estimated at 241,600 BTU/hr (70,700 watts) (Hodgson and Tran 1995).

Tank 101-AZ is an active receiver of waste so the waste volume is expected to change. Waste transfers since 1986 are mainly from a series of small waste additions from 241-AZ-102 and 241-AZ-102 and transfers of dilute noncomplexed waste. Waste volume fluctuations are mainly from evaporation and dilute solutions added to makeup losses. These small waste volume changes include only small quantities of solids and will not change the conclusions of this evaluation.

4.1 WASTE DESCRIPTION

The majority of waste in tank 101-AZ is aging waste or NCAW which is high-level first cycle solvent extraction waste from the Plutonium and Uranium Extraction (PUREX) plant. Between 1976 and the third quarter 1983, tank 101-AZ received and transferred out a mixture of evaporator feed, double-shell slurry feed, complexed, noncomplexed, and dilute noncomplexed waste. During the third quarter 1983, the tank was emptied in preparation for receiving aging waste exclusively from the PUREX plant. In March 1986, the tank reached its maximum aging waste fill. The NCAW waste is the result of denitrating high-level waste with sugar, then neutralizing with sodium hydroxide.

The sludge heel was initially measured in 1980 (Brevick et al. 1995). The latest solids volume update of September 30, 1990, indicate a sludge volume of 130 kL (35 kgal). The volume values of supernate and sludge used for this evaluation are 3,365 kL (889 kgal) of supernate and 132 kL (35 kgal) of sludge (Hanlon, February 1996).

4.2 WASTE CHARACTERIZATION

Since 1983, when tank 101-AZ was designated as a receiver for NCAW, approximately 20 samples have been taken. For this evaluation, only the most recent sludge and supernate analysis will be used. In March 1995, supernate samples were retrieved from tank 101-AZ using the bottle-on-a-string. The

sample analysis for these samples documented by internal memo, 75970-95-037, dated September 11, 1995, from Michelle D. Rollison to J. M. Jones, reports three ^{239/240}Pu values which are all "less than" values. Because the "less than" values are considered inaccurate they were not used in this evaluation. Eight solid sample analysis are reported in WHC-SD-WM-ER-400, *Tank Waste Source Term Inventory Validation* (Brevick et al. 1995) for tank 101-AZ. The laboratory analysis from core 2 has the highest plutonium concentration of the eight reported samples.

In FY 1989 WHC successfully obtained three core samples from tank 101-AZ. Two cores consisted of two segments each and the third core sample consisted of only one segment. The analysis of the third core is not used in this evaluation because the only planned analysis for the segment was the Miller number measurement. The first core sample obtained from riser #15F consisted of two 19-inch long segments of waste. Problems encountered during the sampling activity prevented the lower segment from maintaining the stratification of waste. The stratification of waste sample is not important to this evaluation because the intent of the process test is to mix at least 90% of the solid waste.

The first segment of the first core contained 280 g of only supernate. The second segment consisted of 200 g of dark brown solids and 118 g drainable liquid. The solids were soft, creamy, and sticky and did not maintain the cylindrical shape of the sampler. The supernate and solids had densities of 1.2 and 1.7 g/ml, respectively. The supernate had a pH of 13.7 and contained 26.9% dissolved solids (Peterson et al. 1989). Both segments were combined to form a composite core for which several physical properties were measured. The centrifuged solids and supernate from the composite core were analyzed for chemical and radiochemical properties (Peterson et al. 1989). Table 4-1 lists the supernate analysis and Table 4-2 lists the solids analysis.

The first segment of the second core contained 305 g of only solids with no drainable liquid. The second segment consisted of 208 g of dark brown solids and 109 g drainable liquid. The density and pH of the drainable liquid drained from the second segment were 1.22 g/L and 13.8, respectively (Gray et al. 1993). The solids from both segments were combined and homogenized and were titled "composite solids" (Gray et al. 1993). Table 4-1 lists the supernate analysis and Table 4-3 lists the solids analysis.

The estimated quantity of plutonium in the supernate, currently stored in tank 101-AZ is determined by multiplying the plutonium concentration by the quantity of supernate. The tank contains 3,364,865 L (889,000 gal) of supernate and the conservative approach is to use the highest concentration of plutonium found in the two supernate samples (core 2).

$$3,364,865 \text{ L} \times 9.55\text{E-}4 \frac{\mu\text{Ci}}{\text{g}} \times 1220 \frac{\text{g}}{\text{L}} \times \frac{\text{Ci}}{1\text{E}+6 \mu\text{Ci}} \times \frac{\text{g}}{0.062 \text{ Ci}} = 63.2 \text{ g Pu.}$$

Table 4-1. Selected Analyte Analysis of Centrifuged Supernate.
(all values in mmol/g supernate, except as noted)

Analysis	Core 1 ¹	Core 2 ²
pH	13.7	13.8
Al	0.332	0.0816
Ni	<0.0002	0.000043
Fe	0.0002	0.000351
Cr	0.013	0.00829
K	0.088	0.0521
Mn	0.00002	0.000008
Na	3.76	2.02
Density g/mL	1.2	1.22
^{239/240} Pu, uCi/g	0.00043	0.000955

Notes:

- ¹Peterson et al. (1989)
- ²Gray et al. (1993)

Table 4-2. Selected Analyte Analysis of Core 1 Sludge.
Results reported by Peterson et al. (1991)
(all values in mmol/g, except as noted).

Analysis	C-Solids ¹	Water-Wash Composite ²	Washed Solids ³
Na	3.42	1.53	0.769
Al	1.46	0.0739	0.277
Fe	1.5	4.98E-6	0.365
Cr	0.055	5.53E-3	0.00803
Mn	0.086	<2.E-6	0.0166
Ni	0.06	<2.E-5	<0.002
Density g/L	1800	1080	1400
^{239/240} Pu, mCi/g	0.0044	6.4E-8	0.00079

Notes:

- ¹Centrifuged solids from the core composite
- ²30 vol% supernate + 35 vol% wash 1 + 35 vol% wash 2
- ³Water-washed solids

Table 4-3. Selected Analyte Analysis of Core 2 Sludge.
 Results reported by Gray et al. (1993)
 (all values in mmol/g, except as noted).

Analysis	C-Solids ¹	Water-Wash Composite ²	Washed Solids ³
Na	3.89	0.769	0.299
Al	0.733	0.0344	0.312
Fe	2.500	0.000004	1.010
Cr	0.0163	0.00277	0.00354
Mn	0.0375	0.000001	0.0155
Ni	0.112	<0.000002	0.0688
Density g/L	1730	1220 ⁴	1140
^{239/240} Pu, mCi/g	0.00626	3.03E-7	0.00239

- Notes:
- 1 Centrifuged solids from the core composite
 - 2 Combined supernate from washed solids
 - 3 Water-washed solids
 - 4 Density of the water wash was not reported, the density of the supernate will be used.

The column headings in Tables 4-2 and 4-3 are explained as follows:

- C-Solids--Solids portion of the composite core after centrifuged supernate was decanted.
- Water-Wash Composite--deionized water was added to the centrifuged solids. Then agitated, allowed to settle and the supernate was decanted. This procedure was completed twice and the supernate from both washes was combined to form the composite.
- Washed Solids--the solid material remaining after the water washes is labeled washed solids.

The estimated quantity of plutonium in the sludge, currently stored in tank 101-AZ is determined by multiplying the plutonium concentration by the quantity of sludge. The tank contains 132,475 L (35,000 gal) of sludge and the conservative approach is to use the highest concentration of plutonium found in the two sludge samples (core 2).

$$132,475 \text{ L} \times 0.00626 \frac{\text{mCi}}{\text{g}} \times 1730 \frac{\text{g}}{\text{L}} \times \frac{\text{Ci}}{1000 \text{ mCi}} \times \frac{\text{g}}{0.062 \text{ Ci}} = 23,140 \text{ g Pu.}$$

The total quantity of plutonium in tank 101-AZ is the addition of the quantity of plutonium in the sludge and the supernate. The plutonium inventory is then estimated to be about 23,203 g.

The calculations indicate that almost all of the plutonium resides in the solid phase of the waste in the tank. If all of the plutonium is assumed to reside entirely in the sludge layer the concentration would be:

$$23,203 \text{ g Pu} \times \frac{1}{132,475 \text{ L}} = 0.175 \frac{\text{g Pu}}{\text{L}}$$

The composition of waste (sludge and supernate) in tank 101-AZ is expected to be represented by the analysis of the core samples taken in 1989. The minor fluctuations in waste volume is not significant because it is due mostly to evaporation and makeup additions. The DST Fissile Material Tracking System currently estimates 19,249 g of plutonium in tank 101-AZ. The plutonium inventory as determined from the core samples and the inventory tracking system are in good agreement; however, a quantified accuracy was not determined. The highest plutonium concentration of the eight laboratory analysis of solid samples from tank 101-AZ documented by Brevick (1995) is from core 2. Because the other seven samples are all lower in plutonium concentration than core 2, it can be concluded that an upper bounds of plutonium inventory was used in this evaluation.

4.3 COMPARISON BETWEEN THE TANK SUPERNATE AND SLUDGE

The total amount of actual solid-phase material in the sludge samples was reviewed. The two sample segments from each core were combined to form a core composite from which the volume percent (vol%) of settled solids and centrifuged solids were measured. Settled solids for the composite of core 1 measured 48 vol% and the centrifuged solids measured 16 vol%. The vol% settled solids for the composite of core 2 measured at 100 vol%, while the centrifuged solids measured 71 vol%. The difference between the amount of settled solids in the two core samples is the amount of drainable liquid obtained in the sample.

A comparison of the quantity of solid-phase material in terms of weight percent (wt%) solids in each sample is more relevant. The samples were allowed to air dry overnight, then transferred to a drying oven or furnace at $105 \pm 5^\circ\text{C}$. The wt% total solids in the two samples were in good agreement with core 1 at 58.9 wt% and core 2 at 57 wt%. The reported values for tank 101-AZ are considerably higher than typical Hanford waste which is about 8 wt% (Herting 1994).

The significance of the amount of solids lies with the determination of which analytes are actually solid-phase material and which are dissolved in the liquid portion of the solids. Therefore, every 100 g of sludge contains approximately 40 g of liquid phase material with a composition of the supernate.

The sample analysis of sludge material actually contains 40% liquid phase so any analyte that exists only in the liquid phase will have a concentration in the sludge of about 40% as high as in the supernate. Conversely, any analyte that is significantly higher in the sludge samples than in the supernate

samples can be presumed to be present in the solid phase. For the solids phase this is true for Fe, Mn, ^{239/240}Pu and to a lesser extent Al. This data supports the assertion that the plutonium resides primarily in the solids phase of the tank waste, along with the metal constituents necessary to ensure significant neutron absorption.

4.4 THE SLUDGE

The sludge volume in tank 101-AZ is approximately 132,475 L (35,000 gal). The distribution of plutonium and absorbers between the centrifuged solid material, the supernate and the washed solids are shown in Tables 4-1, 4-2, and 4-3. The various sample analysis strongly supports the conclusion that almost all the plutonium is in the solid-phase material. The solid phase of each sample was centrifuged, followed by a water wash to remove residual interstitial liquor. To measure the elements and nonvolatile radioisotopes in the solid samples, part of the solids were fused with 1) sodium hydroxide in a nickel crucible and 2) potassium hydroxide in a zirconium crucible. The fused material was dissolved in either nitric acid or hydrochloric acid, depending upon the analytical method used.

The relative distribution of plutonium between the solid phase and the liquid phase in the sludge layer was determined and is outlined below:

Core 1

Centrifuged solids of the composite sample	4.40E-3 mCi Pu/g	
Pu in the water-wash faction	6.40E-8 mCi Pu/g	(0.008%)
Pu in the water-wash solids	7.79E-4 mCi Pu/g	(99.992%)

Core 2

Centrifuged solids of the composite sample	6.26E-3 mCi Pu/g	
Pu in the water-wash faction	3.03E-7 mCi Pu/g	(0.013%)
Pu in the water-wash solids	2.39E-3 mCi Pu/g	(99.987%)

The relative distribution of plutonium in the sludge layer was calculated to provide an understanding of the distribution of plutonium between the different phases in the sludge. The calculations using values of the centrifuged solids provides supporting evidence that virtually all of the plutonium in the centrifuged portion of the sample is in the solid phase. Also, the plutonium was not washed out of the solid phase by the water as evidenced by the low plutonium values of the water-washed supernate fraction of the samples. The rigorous laboratory procedure that centrifuged and tumbled the sample for several hours failed to dislodge the plutonium from the solid phase. The centrifuge and tumbling of the sludge is considered similar to the mixing action of the mixer pump.

Note that subcriticality is assured when the plutonium concentration is less than 2.6 g Pu/L in dry waste solids (sludge). This is the minimum plutonium concentration that can be made critical in tank solid waste. Tank 101-AZ contains a plutonium concentration significantly less than the minimum critical concentration.

5.0 DISCUSSION

Waste contained in the Hanford Site underground storage tanks is a complex mixture of fission products and chemicals left over from plutonium separation processes. Some knowledge of the form and distribution of fissionable material and absorbers has been obtained from operations documents and waste characterization activities, but quantified accuracies of waste compositions are largely unknown. The demonstration of criticality safety depends on knowing the minimum critical parameters for the waste material combined with a qualitative discussion of the likelihood the parameters will be satisfied given the mixer pump operations. Section 6.0 contains more information which supports the context and conclusions in Section 5.0.

5.1 PRIMARY CRITICALITY SAFETY PARAMETERS

An important parameter for criticality safety is the solubility of plutonium. The dilution of plutonium with specific absorber elements depends on the physical state of the plutonium species under consideration. Plutonium which is dissolved or suspended in the supernate is more homogeneously distributed than plutonium in the solid-phase material. The variation in plutonium concentration in supernate is considered a minor concern because the upper boundary on solubility of plutonium in alkaline salt solutions is about 4,200 times lower than the minimum critical concentration in an optimized plutonium water system.

The parameter of primary importance in this evaluation is the plutonium concentration in the solid phase. The sludge samples clearly indicate the highest plutonium concentration is in the solid phase. In the waste solids, the plutonium is diluted with neutron absorbing materials, and the average dilution will remain unchanged when the waste is mixed. Mixing will tend to lower the plutonium concentrations where it is high and to increase the concentration where it is lower. This will reduce the probability of there being a region with high plutonium concentration.

5.1.1 MACROSCOPIC ABSORPTION CROSS SECTION

A good parameter to use for the measure of plutonium dilution is the mass ratio of waste solids to plutonium. When the typical waste solids to plutonium mass ratio exceeds 476, criticality is not possible in homogeneous waste (Rogers 1994). The presence of solids ensures that settling of suspended material and evaporation of liquid do not allow the plutonium concentration to increase to an unsafe level.

When the composition of the solids is known, then the subcritical mass ratios of specific elements, such as iron, aluminum or manganese, can be used to demonstrate a margin of subcriticality. If the plutonium in a solids matrix is diluted with a specific component such that the subcritical mass ratio is satisfied, the matrix will be subcritical regardless of the other components in the solid provided the specific component is homogeneously mixed in the

waste. However, a comparison of the solids to plutonium mass ratio is not complete without a comparison of the total absorption of the solids in tank 101-AZ with the total absorption of the waste model (Rogers 1993). This comparison is given in Tables 5-1 and 5.2.

Table 5-1. Total Absorption of the Solids in Core 1.

Element (g/L)	Atomic weight	Concentration (mmol/g)	Molarity (mol/L)	Quantity (g/L)	Absorption cross section	
					Microscopic (b/atom)	Molar x microscopic (mol-b/at-L)
Sodium (Na)	22.99	3.42	6.156	141.53	0.5300	3.263
Aluminum (Al)	26.982	1.46	2.628	70.91	0.2350	0.618
Iron (Fe)	55.847	1.5	2.700	150.79	2.2350	6.035
Chromium (Cr)	51.996	0.055	0.099	5.15	3.1000	0.307
Nickel (Ni)	58.71	0.06	0.108	6.34	4.8000	0.518
Manganese (Mn)	54.938	0.086	0.155	8.504	13.2000	2.046
Total Grams = 383.22			Total Absorption (TA) =		12.784	
			Macroscopic Cross Section =		0.0077 cm ⁻¹	

Table 5-2. Total Absorption Of The Solids In Core 2.

Element	Atomic weight	Concentration (mmol/g)	Molarity (mol/L)	Quantity (g/L)	Absorption cross section	
					Macroscopic (b/atom)	Molar x microscopic (mol-b/at-L)
Sodium (Na)	22.99	3.89	6.730	154.723	0.5300	3.567
Aluminum (Al)	26.982	0.733	1.268	34.213	0.2350	0.298
Iron (Fe)	55.847	2.500	4.325	241.538	2.2350	9.666
Chromium (Cr)	51.996	0.0163	0.028	1.456	3.1000	0.087
Nickel (Ni)	58.71	0.112	0.194	11.390	4.8000	0.931
Manganese (Mn)	54.938	0.0375	0.065	3.571	13.2000	0.858
Total Grams = 446.89			Total Absorption (TA) =		15.407	
			Macroscopic Cross Section =		0.00928 cm ⁻¹	

The macroscopic absorption cross section for the selected analytes in core sample 1 calculates to 0.0077 cm^{-1} and the cross section for core sample 2 calculates to 0.00928 cm^{-1} . The total macroscopic absorption cross section (XS) must exceed 0.01096 cm^{-1} for the absorption of the waste to be bounded by the calculations used in the model.

The macroscopic absorption cross section of the waste appears to be less than the cross section of the composition of waste used in the conservative waste model, but the opposite is true. The problem lies with the gross quantity of analytes, on a liter basis, used for the comparison. The quantity of solid material used for core 1 is 383 grams and for core 2 the selected analytes totaled 447 grams. The amount of solid material per liter used in the conservative waste model is 1,200 grams. So, if the absorption cross section is calculated on a gram basis, then the model has a cross section of $0.01516 \text{ cm}^{-1}/\text{g}$, while core 1 has $0.0334 \text{ cm}^{-1}/\text{g}$ and core 2 has $0.0344 \text{ cm}^{-1}/\text{g}$. The calculations indicate the absorption cross section for the waste in tank 101-AZ is more than double the cross section of the model per unit mass.

The difficulty in comparing real waste to a model lies in converting the real waste analysis to the same conditions used in the model. The model used a solids composition based on dry solids with a density of 1,200 g solids/L; however, the centrifuged solids in tank 101-AZ includes about 40% liquids with a combined density of 1,800 g/L for core 1 and 1,730 g/L in core 2. With 40% liquids, the samples only contained a little over 1,000 g of solids and only a portion of those solids were used to calculate the macroscopic cross section. In fact, less than half of the solids in the samples are included among the analyzed components (analytes). Therefore, the actual macroscopic absorption cross section would be expected to be at least twice that found above.

Because the comparison is based on a theoretical dry solids matrix used in the model, the sample must be converted to the same dry solid bases. A comparison of absorption cross sections can be done using the assumption that the water content of each sample is removed and replaced with solid material of the same composition as the sample. The solids would fill the void space left by removing the water. The result would be dry solids densities of about 2,500 g/L for the samples. In reality, the compaction of the solids would probably not be as great as the volume of the water removed. Nevertheless, the density of dry solids would be expected to be greater than the density in the original wet sample, and it would have a very high probability of exceeding 1,200 g/L. In any case, the higher neutron absorption per unit mass would ensure a greater macroscopic cross section than that assumed in the conservative waste model.

An equitable comparison of absorption cross sections could have been done with the assumption that the water content of each sample is removed and replaced with solid material of the same composition as the sample. The result would be sample densities of about 2,500 g/L and the molarity of each analyte would increase about 40%. The follow on assumption is that the solids would fill the void space left by removing the water. But, because the comparison is based on a theoretical dry solids matrix used in the model, the sample must be converted to the same theoretical dry solid bases. Converting the macroscopic absorption cross section to a per gram basis satisfies the requirement to compare the sample and model on the same basis.

5.1.2 SUBCRITICAL MASS RATIOS

An important characteristic of using mass ratios to show subcriticality is that conclusions remain valid for all densities of solids. It does not matter if the solids are suspended in water, are compacted in a centrifuge or calculated on a dry basis. Subcriticality is assured when the limiting subcritical mass ratios are exceeded throughout the waste. The subcritical mass ratio limit for selected components are listed in Table 5-3 (Rogers 1994).

Table 5-3. Mass Ratio Subcritical Limit.

Component	Absorber/Fissile Mass Ratio Limit
Aluminum (Al)	910
Chromium (Cr)	135
Nickel (Ni)	105
Nitrate (NO ₃)	270
Sodium (Na)	360
Iron (Fe)	160
Manganese (Mn)	32
Gross solids	476

Based on the sludge composition in tank 101-AZ obtained from sample analysis, a comparison of the mass ratio of gross solids to plutonium and mass ratios of specific elements to plutonium can be used to draw conclusions about the margin of subcriticality. The mass ratios of specified absorbers in the solid-phase and water-washed solids sludge are given in Table 5-4. The plutonium concentration for the mass ratio calculations in the water-washed solids and the sludge is taken from Tables 4-2 and 4-3.

Table 5-4. Mass Ratios of Absorber-to-Plutonium.

Absorber (Subcritical Ratio)	CORE SAMPLE 1		CORE SAMPLE 2	
	Composite Solids	Water Wash Solids	Composite Solids	Water Wash Solids
Aluminum (910)	555	587	196	218
Chromium (135)	40	33	8	5
Nickel (105)	50	<9	65	105
Sodium (360)	1,108	1,387	886	178
Iron (160)	1,180	1,600	1,383	1,463
Manganese (32)	67	72	20	22
Gross Solids (476)	14,091	78,481	9,904	25,941

A review of the mass ratios in Table 5-4 indicate the ratios of the analytes to plutonium are about the same for the composite and the water-wash solids. The reason these ratios are in good agreement is because these analytes are in the solid phase. As a result, the quantity of each analyte did not change with the water wash, centrifuge, and tumbling so the mass ratios of plutonium did not change significantly.

There is a significant difference in the mass ratio of gross solids to plutonium between the composite and the water-wash solids. One possible explanation for this difference is that the soluble salts were washed from the composite and replaced with lighter water so the density was decreased from 1,800 g/L to 1,400 g/L (about 20%) for core 1 and 1,730 g/L to 1,140 g/L (about 30%) for core 2. The quantity of plutonium per liter of water-washed solids was decreased by 86% for core 1 and 62% for core 2 as a result of diluting the composite solids portion of the sample with water. The laboratory analysis does not provide an explanation for the decrease in concentration of plutonium or the other insoluble analytes in the water-wash solids. Because the mass ratios of the insoluble analytes to plutonium remained fairly constant, the reason for the decrease is considered the same for all the specified analytes.

5.2 CHEMICAL CONSIDERATIONS

A discussion of the potential for mechanical mixing of the waste to separate the plutonium from the absorbers is not complete without reviewing the chemical aspects. Although all the plutonium could reside in either the solids or liquids and the waste would be highly subcritical. The solids sample preparation in the laboratory supports the contention that the plutonium is primarily a precipitate in the caustic environment of the waste. The transition of plutonium from the solid phase to the liquid phase would require increasing the plutonium solubility of the supernate. Significant changes in plutonium solubility can only be achieved with extreme changes in the chemical makeup of the waste. This would require adding significant quantities of organic or inorganic plutonium complexants, a change in the redox potential of the solution by adding oxidants or reductants, or acidifying the solution. None of these waste changes are planned nor are they part of the scope of the mixer pump operations.

The other half of the chemical consideration scenario is the subsequent precipitation of plutonium after the transition from solid phase to liquid phase. The operations planned under the scope of the mixer pump operations do not include the chemistry changes necessary to facilitate the transition of plutonium between phases and is not considered credible, so further discussion is not necessary. Suffice to conclude that after the waste is thoroughly mixed and the solids suspended, any precipitated plutonium would not be confined to settle out in an area small enough to achieve the minimum critical areal density, even if all the plutonium settled out in the sludge layer.

5.3 PUMP TEST AND SOLIDS DISTRIBUTION

The operational goal of the functional test of the mixer pumps is to achieve 90% mobilization of solids which have settled to the tank bottom and to demonstrate that a slurry suitable for transfer to the treatment facility can be maintained within the tank. Previous mixer pump tests and studies have shown that more than one mixer pump is required to achieve mobilization of a large fraction of the solids. The two 300 hp pumps will be orientated on the north and south of the tank centerline. The estimated ECR for each pump is 9.8 m (32 ft).

The minimum critical areal density in tank waste is $2,582 \text{ g/m}^2$ (240 g/ft^2) (Carter 1969). For plutonium spread evenly over the entire area of the tank, this correlates to a mass of slightly greater than 1,000 kgs of plutonium. The minimum critical mass at 4.0 g Pu/L of waste solids is 215 kg of plutonium and the minimum critical mass at 10.0 g Pu/L of waste solids requires 3.0 kg of plutonium (Rogers 1994). In a plutonium-pure water system the minimum critical plutonium concentration is 7.2 g Pu/L (Rogers 1994). The presence of neutron absorbers in the waste supernate ensures that the reactivity of the plutonium in the supernate is less than it is in pure water.

At 23,203 g of plutonium, the areal density, assuming the plutonium is dispersed homogeneously around the tank, calculates to 56.8 g/m^2 (5.3 g Pu/ft^2), which is extremely subcritical. Concern arises from the possibility of a localized area with a high concentration of plutonium. The concentration of plutonium in the solids in core 1 was 0.128 g Pu/L and in core 2 was 0.175 g Pu/L , both of which are highly subcritical. To approach the minimum critical concentration in waste solids of 2.6 g Pu/L the concentration in the core samples 1 and 2 would need to be increased by a factor of 20 and 15, respectively.

The rigorous laboratory procedure for analyzing plutonium strongly supports the conclusion that the plutonium remains in the solid phase after the water wash, agitation, and centrifuging, and most likely will continue to be a solid-phase material after mixing in the tank with the mixer pumps. Also, the solid phase will contain sufficient quantities of iron, manganese and other solid neutron absorbing material to ensure the mixture is highly subcritical. Any geometry, pile or configuration of solid material with the composition of the core samples will be highly subcritical regardless of the total quantity of plutonium. Consequently, discussions of possible concentrating mechanisms must include the assumption that the plutonium is separated from other absorbers as a result of the hydraulic dynamics of mixing.

The reasonable postulated scenario considers the suspension of 90% of the solids, which settle on top of the 10% unsuspended solids. Assume the unsuspended solids are in a flat slab on the bottom of the tank. The areal density and plutonium concentration will be exactly the same as indicated in the core samples. If the 10% solids, which are not suspended, are in one area of the tank, then the area would cover a minimum of 10% of the tank floor. Of course, this means that all the plutonium in the tank is settled into an area equivalent to 10% of the floor area. The resulting areal density would be 567.6 g Pu/m^2 (52.7 g Pu/ft^2). A value which is highly subcritical. For all the plutonium to settle in an area of the tank which exceeds the minimum

critical areal density the area would need to be no larger than 9.0 m^2 (96.7 ft^2) which is about 2% of the floor area. No mechanism which promotes the settling of solids into localized areas has been identified.

If the action of the mixer pumps actually separate the plutonium from the other solid-phase material, then a pile of plutonium in any desired geometry at any concentration can be contemplated. For this to happen, the mechanical forces of the pump must exceed the bonding forces which maintain the plutonium and the solid absorber material together in the solid phase. Without extensive research into the bonding forces of the coprecipitated solid material the discussion must suppose the separation takes place. The accumulation of 23 kgs of pure plutonium in a small area of the tank will certainly have the potential to go critical. Therefore, the discussion must investigate the possibility that the small area can be achieved.

The pumps are installed in risers 01A and 01C which are located about half way between the tank center and the tank wall north and south of the tank centerline. If the ECR of the pumps is 9.8 m (32 ft) then "dead zones" of unsuspended solids will exist at the east and west sides of the tank. The unsuspended material will be the same composition as the core samples because the solids are undisturbed. Any separated plutonium which settles on top of the undisturbed solids will settle in a flat slab the same as if it settled on the tank floor with some minor commingling with the undisturbed solids. The size of each "dead zone" will be about 13.9 m^2 (147 ft^2) which is about 6.6% of the floor area. This volume of undistributed solids would be expected to contain 766 g of plutonium in each "dead zone". If all other plutonium is suspended, the quantity of suspended plutonium will be 21,672 g. If all the suspended plutonium settles in one "dead zone" the areal density will be $1,643 \text{ g/m}^2$ (153 g/ft^2) which is still subcritical. If all the suspended plutonium settles on top of one "dead zone" at a concentration of 8 g Pu/L , the height of plutonium rich material will be 20.5 cm (8.1 in.). The waste is subcritical for waste thicknesses up to 38 cm (15 in.) at a plutonium concentration of 8 g Pu/L .

Consider the case where all the solids are suspended, the plutonium particulate separates from the absorbers and has a faster settling velocity than the absorber material. The plutonium would settle in a flat slab over the floor of the tank after the pumps are turned off. The areal density for this case is equivalent to the core samples, 56.8 g/m^2 (5.3 g Pu/ft^2). If the plutonium is concentrated in a layer of waste at the bottom of the tank to 8 g Pu/L , the waste would be subcritical for waste thicknesses up to 38 cm (15 in.) (Braun et al. 1994). If the plutonium inventory in tank 101-AZ did separate and concentrate to 8 g Pu/L at the bottom of the tank, the slab would only be 0.7 cm (0.28 in.) thick, which is highly subcritical.

Without extensive computer modeling, an increase in plutonium concentration can only be speculated. The first requirement includes the separation of plutonium from the other solid materials. If the plutonium settles in a flat slab at the bottom of the tank and additional mixing takes place, the plutonium could be moved along the tank floor instead of being suspended. This action could create a pile of plutonium rich material at the tank wall on the east and west side of the tank. With half of the plutonium inventory, 11,602 g Pu, in each pile and the objective of the test is met, i.e. 90% of

the solids are suspended, then each pile will have 5% the of the unsuspended solid material. The plutonium may be pushed and mixed with these solids resulting in a plutonium concentration as high as 1.8 g Pu/L (11,602 g in 5% of the solids or 6,624 L). This concentration of plutonium is about 10 fold higher than the core samples. However, the system would remain subcritical for any geometry of solids, because the minimum critical concentration is 2.6 g Pu/L.

All the plutonium in the tank must settle in no more than 8,924 L (2,358 gal) of waste solids to achieve a plutonium concentration of 2.6 g Pu/L of solids. This is only 6.7% of the solid material in tank 101-AZ. The design of this scenario requires the plutonium to separate from the other solid-phase material. As the plutonium concentration increases, the mass ratio of any absorber to plutonium decreases. The enriched plutonium solids would need to settle in a localized area of the tank at a concentration greater than 2.6 g Pu/L, while the plutonium depleted solids settle in another area of the tank. The plutonium also must not settle in a flat slab, but accumulate in a spherical geometry.

A 300-L sphere has a diameter of about 83 cm (32.7 in.). A sphere of this size requires a plutonium concentration of at least 10 g Pu/L or 3,000 g. To achieve a plutonium concentration of 10 g Pu/L and a plutonium mass of 3,000 g before criticality is possible. To achieve, a plutonium concentration of 10 g Pu/L, the plutonium content in core sample 2 would need to increase over 57 times. Also, because the solids volume in the tank calculates to an average height of 32.3 cm (12.7 in.) its unlikely the suspended solids will settle into a pile in a localized area of the tank to a height greater than the average. If the agitation of the tank supernate created an area of fluid flow conducive to the settling of plutonium particulate while the pumps are operating, the area would most likely be at the "dead zones". The undisturbed solids layer is 32.2 cm (12.7 in.) high and the settled plutonium-rich material would create a mound on top of these solids. If the mound is equivalent to the 300 L sphere it would increase the height of the undisturbed solids by 83 cm (32.7 in.) which would be about three times higher than the original solids layer. If the "dead zones" accumulate a slab of solids with the 300 L sphere contained inside, the volume of solids would be 31,495 L (8,321 gal), which is 24% of all the solids in the tank.

The above scenarios include some assumptions that are considered extremely unlikely if not impossible. The plutonium concentration of the solids material as determined from sample analysis (0.175 g Pu/L) is at least 57 times less than the concentration of 10 g Pu/L required to make 3,000 g of plutonium critical under optimum conditions. The plutonium concentration in the supernate as determined from sample analysis (0.000019 g Pu/L) is at least 378,947 times less than the minimum critical concentration in water of 7.2 g Pu/L.

6.0 BASIC PARAMETERS

The following discussion provides supporting evidence for the conclusions contained in this CSER.

6.1 SOLUBILITY OF PLUTONIUM IN WASTE

This discussion is provided verbatim (with the permission of the author) from WHC-SD-SQA-CSA-20368, *CSER 94-004: Criticality Safety Of Double-Shell Tank Waste Storage Tanks*, (Rogers 1994). The reader is encouraged to review the Rogers (1994) for a more extensive discussion.

An important parameter for criticality safety is the solubility of plutonium in high-level waste. The higher the solubility the more difficult it is to control the distribution of the plutonium. If the plutonium can be dissolved, for example, separation of the plutonium from other components might be possible by preferentially dissolving the plutonium. When plutonium is in solution, there are mechanisms, such as evaporation of liquid, settling, and precipitation, that are capable of increasing the concentration.

Perhaps the main problem associated with having a large fraction of the plutonium in solution would be the difficulty in estimating how much plutonium is in each tank. When plutonium is dissolved, the quantity transferred when waste is pumped between tanks is increased, and it becomes more difficult to estimate the distribution of the plutonium. It is therefore desirable to ensure a low solubility for plutonium to keep it combined with solids and to make it less mobile. Because plutonium is less soluble in an alkaline solution, the pH of the waste is controlled to ensure alkalinity.

Concentration of Dissolved Plutonium

Four documents were examined that discuss the solubility of plutonium under the conditions present in high-level waste. C. H. Delegard is the primary author for two of these studies, and D. T. Hobbs is the primary author of the other two.

Hobbs investigated the influence of hydroxide, nitrate, nitrite, aluminate, sulfate, carbonate, and temperature on the solubility of plutonium and uranium in alkaline salt solutions and reached the following conclusion:

For salt solutions within the range considered by this study, upper 95% tolerance limits for Pu and U solubilities, estimated from analytically measured specie concentrations, are 1.68 mg/L (6.36 mg/gal) and 17.1 mg/L (64.7 mg/gal), respectively. The alkaline salt solutions considered in this study should bound those that will be treated in the in-tank precipitation process (Hobbs et al. 1993).

Hobbs also concluded that:

"Conditions which increase the plutonium solubility do not necessarily increase the uranium solubility. Maximum plutonium solubility is predicted at high nitrate, high hydroxide, high carbonate, and high sulfate concentrations. Maximum uranium solubility is predicted at high hydroxide, high aluminate and high sulfate concentrations and low nitrate, low nitrite, and low carbonate concentrations (Hobbs et al. 1993)."

Effects of Waste Components on Solubility

Hobbs makes the following observation concerning the effect of other waste components on solubility:

- The solubilities reported in this document may be higher than those which will be observed in actual waste caused by the coprecipitation of the plutonium and the uranium with iron, manganese, and aluminum during neutralization of fresh waste. In a single experiment in which the plutonium and uranium were coprecipitated with iron, the solubility of plutonium was decreased by a factor of about five, and that of uranium increased by about a factor of two (Hobbs et al. 1993).
- Although the common understanding is that plutonium precipitates in alkaline solution, this simple understanding does not fully describe the complex nature of the chemistry involved in waste. Delegard shows that the solubility of plutonium increases for increasing NaOH.
- The solubility of Pu(IV) hydrous oxide, $\text{PuO}_2 \cdot x\text{H}_2\text{O}$, in air-equilibrated, synthetic, Hanford Site high-level waste (HLW) solutions was determined as a function of NaOH, $\text{NaAl}(\text{OH})_4$, NaNO_3 , NaNO_2 , and Na_2CO_3 concentrations. The solubility was found to increase with the square of the NaOH chemical activity. The components NaNO_3 and NaNO_2 increased $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ solubility by increasing NaOH activity (Delegard 1985).

Although the plutonium solubility is found to increase with addition of NaOH, the solubility nevertheless remains low. Delegard (1985) studied the solubility of plutonium in NaOH solutions over the range of NaOH concentration between 1 and 15 molar.

For typical waste, Delegard (1985) states that the NaOH concentration is 4 molar. At this concentration the maximum plutonium concentration is found to be about 0.0005 g/L (0.0019 g/gal or 2×10^{-6} molar). When allowed to set for a long time, the plutonium concentration in solution decreases to a value about 8 times smaller. When the NaOH is increased from 4 molar to 7 molar, the concentration of dissolved plutonium increases by about 10 times, and at 11 molar it is about 100 times greater than at 4 molar. At the high NaOH concentration of 11 molar, the plutonium concentration in solution should not exceed 0.05 g/L (0.19 g/gal) (Delegard 1985).

6.2 DENSITY OF SOLIDS

The following discussion provides supporting evidence for the conclusions about the density of solids and liquid content the contained in this CSER. This discussion is provided verbatim from Rogers (1994).

Importance of Solids

The presence of solids greatly increases the difficulty of achieving a critical configuration. Solids not only increase the neutron absorption, but also limit the ability of the plutonium to become more concentrated. After all liquids have been drained from the waste, the remaining solids ensure that the average plutonium concentration remains low.

The total mass of solids in all waste tanks is known to greatly exceed what is required to maintain subcriticality for the total quantity of plutonium available. However, the components of tank waste are not uniformly distributed among the various tanks, and the possibility must be considered that a localized region of high plutonium concentration and relatively low solids concentration might exist.

The conservative waste model defines a waste for which the neutron absorption is less than for any actual waste. Any homogenized real waste cannot be made critical when the mass ratio of waste solids to plutonium exceeds 476. This is the same as stating that the plutonium must be less than 2.1 g/kg of solids.

Many waste components are good absorbers of neutrons. For each of these components there is a corresponding absorber/plutonium mass ratio above which criticality is impossible. When the ratio of one particular absorber is decreased, it is likely that there will be other absorbers in the waste capable of ensuring subcriticality.

Total Quantity of Settled Plutonium

Settling of solids and evaporation of liquid can result in a layer of waste in which the plutonium concentration has increased. However, criticality is not possible unless the plutonium areal density exceeds 240 g/ft^2 ($2,582 \text{ g/m}^2$). This areal density over the area of a storage tank would require more than 1,000 kg of plutonium. There is a low probability that the inventory of any tank exceeds 10% of this quantity. Therefore, criticality would not be possible within a layer of settled waste, regardless of the solids content.

Density of Solids

Waste solids provide an effective way of controlling the plutonium concentration. When the plutonium is mixed with a high proportion of solids, it is difficult, if not impossible, to separate the plutonium from the solids by mechanical means. Stirring, mixing, pumping, or any other operation performed on the waste tends to more completely mix the plutonium with the solids.

When waste contains a large fraction of liquid, it is possible for solids to be suspended in the liquid. Removal of liquid may cause the density of the solids to increase. The highest density for the solids is obtained by removing all of the liquid to obtain dry solids. The volume of dry solids provides a lower limit on the volume of waste. When all plutonium is assumed confined to the dry solids, an upper limit is obtained on the plutonium concentration. Because the maximum possible plutonium concentration is determined by the minimum density of solids, the dry solids density is an important parameter for criticality safety.

Liquid Content

The high water content of the waste ensures that fissile material is highly overmoderated. However, there are operations designed to remove water from waste, such as saltwell pumping and passing waste through an evaporator. Although the degree of overmoderation decreases as liquid is removed, the low plutonium concentration ensures that the waste will remain overmoderated after completion of evaporation or pumping. If all water were to be removed, the scattering properties of the large fraction of material in the waste that is not fissile would provide appreciable moderation and absorption.

This evaluation assumes that optimal moderation of waste is possible. Therefore, the actual volume of liquid in the waste tank does not affect conclusions reached. No restrictions need be placed on the water content of tank waste, either as to how little or how much is allowed to be present.

6.3 PLUTONIUM CRITICAL PARAMETERS

The following discussion provides support for the critical parameters in different mediums that is cited in this CSER. This discussion is provided verbatim from Rogers (1994).

Plutonium in Water

Criticality is not possible for plutonium in a plutonium-water mixture unless the plutonium concentration exceeds 7.2 g/L.

When certain materials are present whose neutron absorption cross sections are small, in addition to water, criticality becomes possible at lower concentrations. For tank waste, criticality is possible at a lower plutonium concentration when the total macroscopic absorption cross section per plutonium atom is less than for water.

Plutonium in Waste

For criticality to be possible in tank waste, it is necessary for the plutonium concentration to be at least 2.6 g/L (9.84 g/gal) over a large volume. This value is based on the conservative waste model and occurs at an hydrogen/plutonium (H/Pu) atom ratio of about 100. Alternately, criticality is possible with a higher plutonium concentration over a smaller volume.

To achieve criticality with waste having a plutonium concentration of 4.0 g/L requires a 4.7-m (15.4-ft) diameter, 53,750-L (14,200-gal) sphere containing 215 kg of plutonium. Optimal moderation occurs for an hydrogen/plutonium atom ratio of 500.

The minimum critical areal density of plutonium in water is conservative when applied to waste. 2,582 g Pu/m² (240 g Pu/ft²) is the lowest areal density that can be made critical (Carter et al. 1969). The areal density includes all plutonium above a unit area of floor, including plutonium located all the way to the top surface.

6.4 MIXING MECHANISMS

The following discussion provides support for the conclusions about the dispersing of plutonium due to mixing waste. Rogers (1994) states the following about the dispersing tendency of mixing waste.

The only operation performed for many waste storage tanks is the pumping of new waste into the tank. The incoming solids from each batch of waste settle into a layer and the liquid portion mixes with the already present supernatant liquid. In these tanks the configuration of the waste should remain relatively unchanged over long periods of time.

Mixing tends to disperse a region of higher plutonium concentration. The concentration of each component in waste types that have been mixed together tends to become closer to an average value. Regions containing both higher and lower concentrations tend to become smaller. The overall waste mixture becomes increasingly uniform in composition as the mixing continues. Although the waste is initially well subcritical, mixing is expected to increase the margin of safety even farther by dispersing the plutonium and reducing the regions of higher plutonium concentration.

Although scenarios have been postulated in which mixing might lead to an increase in plutonium concentration, the conditions of waste in tank 101-AZ are such as to make it unlikely to occur. The extremely low plutonium concentration would require a highly efficient process of separating plutonium from other waste in order to even begin to approach the concentration at which criticality is possible. No such process can be postulated.

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APPENDIX A

ORIGINAL DATA AND CALCULATIONS

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A.1 APPENDIX DESCRIPTION

Tables in the appendix correlate with tables in the text of the document. The appendix tables will be identified with an "A" designator (i.e., Table A-4-1) contains original data for Table 4-1 and is in the appendix. There is no relevant need to include Table 5-3 in the appendix.

A.2 ORIGINAL DATA AND UNIT CONVERSION FOR SUPERNATE ANALYSIS

The units for values in Table 4-1 for core 1 are the same as the units reported in Peterson et al. (1989), except $^{239/240}\text{Pu}$ which is reported as mCi/g. The units for values in Table 4-1 for core 2 are mmol/g and are reported in Gray et al. (1993) Table 9, as $\mu\text{mol/g}$, except for $^{239/240}\text{Pu}$ which is reported in Gray et al. (1993) as $\mu\text{g/g}$ in Table 11. The original data as reported in the two documents are in Table A-4-1. The unit conversions are detailed below the table.

Table A-4-1. Selected Analyte Analysis of Centrifuged Supernate.

Analysis	Core 1 (mmol/g) ¹	Core 2 ($\mu\text{mol/g}$) ²
pH	13.7	13.5
Al	0.332	81.6
Ni	<0.0002	0.043
Fe	0.0002	0.351
Cr	0.013	8.29
K	0.088	52.1
Mn	0.00002	0.008
Na	3.76	2,020
Density g/mL	1.2	1.22
$^{239/240}\text{Pu}$	4.3E-7 mCi/g	0.0154 $\mu\text{g/g}$

Notes: ¹Peterson et al. (1989)
²Gray et al. (1993)

The conversion of core 2 data from $\mu\text{mol/g}$ to mmol/g of supernate is as follows:

$$\text{Conc.} \left(\frac{\mu\text{mol}}{\text{g}} \right) \times \left(\frac{\text{mol}}{1000 \mu\text{mol}} \right) = \text{Conc.} \left(\frac{\text{mmol}}{\text{g}} \right)$$

The conversion $^{239/240}\text{Pu}$ in core 1 from mCi/g to uCi/g is as follows:

$$\text{Pu Conc.} \left(\frac{\text{mCi}}{\text{g}} \right) \times \left(\frac{1000 \text{ uCi}}{\text{mCi}} \right) = \text{Pu Conc.} \left(\frac{\text{uCi}}{\text{g}} \right)$$

The conversion $^{239/240}\text{Pu}$ in core 2 from ug/g to uCi/g is as follows:

$$\text{Pu Conc.} \left(\frac{\text{ug}}{\text{g}} \right) \times \left(\frac{\text{g}}{1\text{E}+6 \text{ ug}} \right) \times \left(\frac{0.062 \text{ Ci}}{\text{g}} \right) \times \left(\frac{1\text{E}+6 \text{ uCi}}{\text{Ci}} \right) = \text{Pu Conc.} \left(\frac{\text{uCi}}{\text{g}} \right)$$

A.3 ORIGINAL DATA AND UNIT CONVERSION FOR SLUDGE ANALYSIS

The units for the values in Table A-2 are mmol/g of sludge. The original data documented in Peterson et al. (1991), Table 2, is also in units of mmol/g sludge, except the density, which is g/mL and $^{239/240}\text{Pu}$ which is reported as units of mCi/g in Table 7. The Table A-4-2 below contains the original data as found in Peterson et al. (1991). No unit conversions are necessary, the Table A-4-2 is included for completeness.

Table A-4-2. Selected Analyte Analysis of Core 1 Sludge.
Results reported by Peterson et al. (1991)
(all values in mmol/g, except as noted).

Analysis	C-Solids ¹	Water-Wash Composite ²	Washed Solids ³
Na	3.42	1.53	0.769
Al	1.46	0.0739	0.277
Fe	1.5	4.98E-6	0.365
Cr	0.055	0.00553	0.00803
Mn	0.086	<2.E-6	0.0166
Ni	0.06	<2.E-5	<0.002
Density g/mL	1.8	1.08	1.04
$^{239/240}\text{Pu}$, mCi/g	0.0044	6.4E-8	0.00079

Notes:

- ¹Centrifuged solids from the core composite
- ²30 vol% supernate + 35 vol% wash 1 + 35 vol% wash 2
- ³Water-washed solids

The units for the values in Table 4-3 are mmol/g of sludge. The original data documented in Gray et al. (1993), Table 9, is in units of umol/g sludge, except the density, which is g/mL (Table 8) and ^{239/240}Pu which is reported in units of ug/g in Table 11. The Table A-4-3 below contains the original data as found in Peterson et al. (1991). The only required unit conversion is for plutonium and is below the table.

Table A-4-3. Selected Analyte Analysis of Core 2 Sludge.
Results reported by Gray et al. (1993)
(all values in umol/g, except as noted).

Analysis	C-Solids ¹	Water-Wash Composite ²	Washed Solids ³
Na	3,890	769	299
Al	733	34.4	312
Fe	2,500	0.004	1,010
Cr	16.3	2.77	3.54
Mn	37.5	0.001	15.5
Ni	112	<0.002	68.8
Density g/mL	1.73	1.22 ⁴	1.14
^{239/240} Pu, ug/g	101	0.00488	38.6

Notes:

- ¹Centrifuged solids from the core composite
- ²Combined supernate from washed solids
- ³Water-washed solids
- ⁴Density of the water wash was not reported, the density of the supernate will be used.

For plutonium, the unit conversion from ug Pu/g of sludge to mCi Pu/g of sludge is as follows.

$$\text{Pu Conc.} \left(\frac{\text{ug}}{\text{g}} \right) \times \left(\frac{\text{g}}{1\text{E}+6 \text{ ug}} \right) \times \left(\frac{0.062 \text{ Ci}}{\text{g}} \right) \times \left(\frac{1000 \text{ mCi}}{\text{Ci}} \right) = \text{Pu Conc.} \left(\frac{\text{mCi}}{\text{g}} \right)$$

A.4 CALCULATIONS FOR ABSORPTION CROSS SECTION

The unit conversions and calculations for the absorption cross sections are below Table A-5-2. The original concentration data for each analyte is from Tables 4-2 and 4-3.

Table A-5-1. Total Absorption Of The Solids In Core 1.

Element	Atomic weight	Concentration (mmol/g)	Molarity (mol/L)	Quantity (g/L)	Absorption cross section	
					Microscopic (b/atom)	Molar x microscopic (mol-b/at-L)
Sodium (Na)	22.99	3.42	6.156	141.53	0.5300	3.263
Aluminum (Al)	26.982	1.46	2.628	70.91	0.2350	0.618
Iron (Fe)	55.847	1.5	2.700	150.79	2.2350	6.035
Chromium (Cr)	51.996	0.055	0.099	5.15	3.1000	0.307
Nickel (Ni)	58.71	0.06	0.108	6.34	4.8000	0.518
Manganese (Mn)	54.938	0.086	0.155	8.504	13.2000	2.046
Total Grams = 383.22			Total Absorption (IA)		=	12.784
			Macroscopic Cross Section		=	0.0077 cm ⁻¹

Table A-5-2. Total Absorption Of The Solids In Core 2.

Element	Atomic weight	Concentration (mmol/g)	Molarity (mol/L)	Quantity (g/L)	Absorption cross section	
					Microscopic (b/atom)	Molar x microscopic (mol-b/at-L)
Sodium (Na)	22.99	3.89	6.730	154.723	0.5300	3.567
Aluminum (Al)	26.982	0.733	1.268	34.213	0.2350	0.298
Iron (Fe)	55.847	2.500	4.325	241.538	2.2350	9.666
Chromium (Cr)	51.996	0.0163	0.028	1.456	3.1000	0.087
Nickel (Ni)	58.71	0.112	0.194	11.390	4.8000	0.931
Manganese (Mn)	54.938	0.0375	0.065	3.571	13.2000	0.858
Total Grams = 446.89			Total Absorption (IA)		=	15.407
			Macroscopic Cross Section		=	0.00928 cm ⁻¹

The unit conversion for each analyte from mmol/g to molarity is as follows.

$$\text{Conc.} \left(\frac{\text{mmol}}{\text{g}} \right) \times \left(\frac{\text{mol}}{1000 \text{ mmol}} \right) \times \text{density} \left(\frac{\text{g}}{\text{L}} \right) = \text{Conc.} \left(\frac{\text{mol}}{\text{L}} \right)$$

The unit conversion for each analyte from mmol/g to g/L is as follows.

$$\text{Conc.} \left(\frac{\text{mmol}}{\text{g}} \right) \times \left(\frac{\text{mol}}{1000 \text{ mmol}} \right) \times \text{density} \times \left(\frac{\text{g}}{\text{L}} \right) \times \text{atomic wt} \left(\frac{\text{g}}{\text{mol}} \right) = \text{Conc.} \left(\frac{\text{g}}{\text{L}} \right)$$

The TOTAL ABSORPTION (TA) for the sample is calculated by multiplying each analyte in units of molarity by the microscopic cross section for each analyte and adding all the microscopic cross sections.

The sample macroscopic absorption cross section (XS) is calculated as follows:

$$\begin{aligned} \text{XS} &= \text{total absorption (TA)} \times \text{Avogadro's Number} \\ &= \text{TA (mole-b/atom-L)} \times (6.023 \text{ E}23 \text{ atom/mole}) \times 1\text{E-}27 \text{ L/b-cm} \\ &= 6.023\text{E-}04 \times \text{TA cm}^{-1} \end{aligned}$$

The macroscopic absorption cross section for core 1 calculates to 0.0077 cm⁻¹ and core 2 calculates to 0.00928 cm⁻¹. The calculation of absorption per gram of sample is determined by dividing the macroscopic cross section by the grams of analytes used to calculate the total absorption.

For core 1 the absorption per gram is:

$$\frac{\text{TA } 12.784 \text{ cm}^{-1}}{383.22 \text{ g}} = 0.0334 \frac{\text{cm}^{-1}}{\text{g}}$$

For core 2 the absorption per gram is:

$$\frac{\text{TA } 15.407 \text{ cm}^{-1}}{446.89 \text{ g}} = 0.0344 \frac{\text{cm}^{-1}}{\text{g}}$$

For the conservative waste model (Rogers 1993) the absorption per gram is:

$$\frac{\text{TA } 18.197 \text{ cm}^{-1}}{1200 \text{ g}} = 0.01516 \frac{\text{cm}^{-1}}{\text{g}}$$

A.5 UNIT CONVERSION CALCULATION MASS RATIOS

The values in Table 5-4 are unitless ratios of the mass of plutonium to the specified analytes. Therefore, the units of the original data for each analyte must be consistent with the units of plutonium. The original data documented in Peterson et al. (1991) and Gray et al. (1993), for each phase of the sludge is given in Tables A-4-2 and A-4-3. The method of calculating mass ratios is to convert the analytes and plutonium concentration into g/L. The unit conversions are given below.

For core 1 the units are in mmol/g, so the conversion to g/L is:

$$\text{Conc.} \left(\frac{\text{mmol}}{\text{g}} \right) \times \left(\frac{\text{mol}}{1000 \text{ mmol}} \right) \times \text{atomic wt} \left(\frac{\text{g}}{\text{L}} \right) \times \text{density} \left(\frac{\text{g}}{\text{L}} \right) = \text{Conc.}$$

The conversion of plutonium from mCi/g to g Pu/L is:

$$^{239/240}\text{Pu Conc.} \left(\frac{\text{mCi}}{\text{g}} \right) \times \left(\frac{\text{Ci}}{1000 \text{ mCi}} \right) \times \left(\frac{\text{g}}{0.062 \text{ Ci}} \right) \times \text{density} \left(\frac{\text{g}}{\text{L}} \right) = ^{239/240}\text{Pu Conc.} \left(\frac{\text{g}}{\text{L}} \right)$$

For core 2 the units are in umol/g, so the conversion to g/L is:

$$\text{Conc.} \left(\frac{\text{umol}}{\text{g}} \right) \times \left(\frac{\text{mol}}{1\text{E}6 \text{ umol}} \right) \times \text{atomic wt} \left(\frac{\text{g}}{\text{Mol}} \right) \times \text{density} \left(\frac{\text{g}}{\text{L}} \right) = \text{Conc.} \left(\frac{\text{g}}{\text{L}} \right)$$

The conversion of plutonium from ug/g to g Pu/L is:

$$^{239/240}\text{Pu Conc.} \left(\frac{\text{ug}}{\text{g}} \right) \times \left(\frac{\text{g}}{1\text{E}6 \text{ ug}} \right) \times \text{density} \left(\frac{\text{g}}{\text{L}} \right) = ^{239/240}\text{Pu Conc.} \left(\frac{\text{g}}{\text{L}} \right)$$

APPENDIX B

REVIEWER'S COMMENTS

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B.1 APPENDIX DESCRIPTION

The following comments were received by the individuals indicated. All comments were appropriately resolved and incorporated into the document.

B.2 INDEPENDENT REVIEW

An independent review was completed by C. A. Rogers. Editorial comments were provided on a marked up copy of the evaluation.

Only a limited amount of analytical data is available on the composition of waste in tank 101-AZ. This data indicates a high degree of subcriticality. All available information on tank waste indicates that separation of the plutonium from the waste matrix is extremely unlikely. The nature of mixing itself has a strong tendency towards dispersal of waste components, rather than concentration. This report provides good justification that operation of the two mixer pumps would be very unlikely to produce any localized pockets in which the plutonium concentration would be much increased. A concentrating mechanism of very high efficiency would be required to bring together most of the available plutonium into a volume of less than 6% of the waste volume. Convincing arguments are provided that no such mechanism exists.

The following from page 4-7 provides important information showing criticality safety.

Also, the plutonium was not washed out of the solid phase by the water as evidenced by the low plutonium values of the water-washed supernate fraction of the samples. The rigorous laboratory procedure that centrifuged and tumbled the sample for several hours failed to dislodge the plutonium from the solid phase. The centrifuge and tumbling of the sludge is considered similar to the mixing action of the mixer pump.

This evaluation should discuss the accuracy of the two core samples and whether the associated uncertainty influences the conclusions of this report.

Some of the equations which show how to convert from one set of units to another do not balance. The formatting of some equations is not correct. These discrepancies are pointed out on a copy of the report.

The following specific comments are made.

1. (Page 2-2, Paragraph 3, Sentence 3) Suggest following rewrite of the discussion of calculating the absorption cross section per gram of waste.

When the absorption cross section is calculated for one gram of waste material, it is found to be $0.01516 \text{ cm}^2/\text{g}$ for the model composition. This can then be compared to $0.0334 \text{ cm}^2/\text{g}$ for core 1 and to $0.0345 \text{ cm}^2/\text{g}$ for core 2. The absorption cross section for the waste in 101-AZ is therefore found to be more than double the cross section of the model, when they are compared on the basis of the same mass per liter. Since the analyzed components of the waste samples comprise only about one-third of the total material in the waste, the total neutron absorption per liter of waste is expected to be more than twice that obtained for

the analyzed components. The neutron absorbing qualities of the actual waste is therefore found to be greater than that of the waste composition used to calculate the minimum critical parameters.

2. (Page 4-2, Paragraph 4, Line 6) The sentence beginning with "The Tank solids contained 74 vol%" is not clearly written.
3. (Page 5-1, Section 5.1, Paragraph 1) 42,000 in the next paragraph appears to be wrong. Is 4,200 the correct number?
4. Page 5-3, Bottom Paragraph) Suggest deleting last sentence in first paragraph and adding:

In fact, less than half of the solids in the samples are included among the analyzed components (analytes). Therefore, the actual macroscopic absorption cross section would be expected to be at least twice that found above.

(Page 5-4, top paragraph) Suggest replacing paragraph with something like:

Since the comparison is based on a theoretical dry solids matrix used in the model, the sample must be converted to the same dry solid bases. A comparison of absorption cross sections can be done using the assumption that the water content of each sample is removed and replaced with solid material of the same composition as the sample. The solids would fill the void space left by removing the water. The result would be dry solids densities of about 2500 g/L for the samples. In reality, the compaction of the solids would probably not be as great as the volume of the water removed. Nevertheless, the density of dry solids would be expected to be greater than the density in the original wet sample, and it would have a very high probability of exceeding 1,200 g/L. In any case, the higher neutron absorption per unit mass would ensure a greater macroscopic cross section than that assumed in the conservative waste model.

5. (Page 5-4, bottom paragraph) The reference to Table 4-7 is incorrect. Probably Table 5-4 is intended.
6. (Page 5-5) First paragraph is not clear. Suggest deleting it.
7. (Page 5-5) Bottom paragraph is not clear. A lower solids density in water-washed solids implies to me that the soluble solids are heavier than the insoluble.

B.3 AUTHOR OF THE CRITICALITY SAFETY ACCIDENT ANALYSIS FOR THE FSAR.

Mr. Robert M. Marusich provided the following comments.

1. I have a concern of using 478 as the solids to Pu subcriticality ratio without explicitly showing that the solids used have more absorption than Chuck's (Rogers 1993).

I also have a "sales" concern in that all reviewers have their own pet solids group. Use of this begs them to ask questions concerning low absorption solids, etc. It seems easier to me not to use the solids ratio.

2. Page 4-11,12 - While it is nice to speak in generalities, I think you need to get the dual mixer pump data from Greg Whyatt or Jeff Serne, determine the size of the dead zone, put the Pu in that zone(s) (plural as due to symmetry there may always be two zones or 4 zones) and show that the volume is subcritical. This is needed based on the topical's assertion that dual mixer pumps pose a criticality problem because of the dead zones.

The same comment applies to page 5-5 - paragraph 3 and the last paragraph. The dead zone is the mechanism to increase concentration. You cannot get off the hook by saying that it does not look like the Pu can concentrate that much.

3. page 5-2, If the tank has carbonate in it, even down to 0.001M, the solubility is much greater per the Topical. I did not see CO₃ in the listing, but the list was anions not cations.

B.4 CRITICALITY AND SHIELDING

Mr. Ed M. Miller provided the following verbal comments.

1. The SUMMARY AND CONCLUSIONS section should include a much more detailed discussion of the evaluation of the "dead zones" created by the two mixer pumps. The conclusions about the plutonium concentration in those dead zones should be clearly discussed in the summary sections.
2. The discussion about the rigorous laboratory procedure which prepared the solid sample for analysis should be expanded to explain the difference between the mechanical and chemical treatment of the sample. Not everyone understands what "fusion" is or how it relates to the conclusions.
3. The highest plutonium concentration of the two core samples was used to calculate the plutonium inventory and draw conclusions about that inventory. Using the highest plutonium concentration should be emphasized so that it is very clear to the reader that this evaluation is conservative.

Also, some attempt should be made to quantify the conservativeness or accuracy of the plutonium inventory in tank 101-AZ. There should be other samples, tanks, inventory or transfer sheets which could be used to quantify or at least provide a qualitative assessment of the accuracy of the plutonium inventory.

4. Page 4-9, primary criticality parameters, the discussion about why the mass ratio of water-washed solids to plutonium is significantly higher than the mass ratio for the composite is not clear. The value of the discussion is apparent, so the text should not be deleted only reworded to clarify the evaluation.

B.5 PROJECT W-151

The following comments were received from Mr. Edward M. Nordquist the Project Manager for Project W-151, representing DST Retrieval Projects.

1. Page 1-1, the last sentence, the objective is to resuspend the solids not mix and settle as that is a by-product of the resuspension.
2. Page 2-1, 3rd paragraph, suggest adding reference for statement in last sentence (i.e., for the Fissile Material Tracking System).
3. Page 2-2, first paragraph on page (carryover from previous page), the last sentence talks to dramatic chemical change but there's no mention of the heat input or material shearing. Would either of these mechanisms account for plutonium separation?
4. Page 2-3, 2nd paragraph last sentence, "... will not impact criticality safety, ..."
5. Page 3-1, is the third paragraph really needed? I'm not sure it adds any value to your analysis. If it stays, the first sentence needs to refer to construction, not Phase I activities.
6. Page 3-2, fifth paragraph need to delete fifth sentence. Also, the pumps are installed in riser 01A and 01C (don't add 241-AZ).
7. Page 4-1, first paragraph suggest you be consistent with kgal, not Mgal. Also, last paragraph suggest measured in 1980 (drop "about").
8. Page 4-5, first equation looks like a tab is missing for the denominators.
9. Page 4-7, first sentence change to "was" and "is". Similar comment page 4-8, first full sentence.
10. Page 4-10, first sentence in Section 4.7, shouldn't we convert the 135 kgal to xx" of sludge?
11. Page 4-11, last paragraph refer to the risers without the AZ on them, that is 01A and 01C.
12. Page 5-1, you only referenced one of each of the authors quoted in the Concentration section. Should you add the other references in Section 6.0?

13. Page 5-3, second paragraph you mention that the possibility of a localized region of high plutonium concentration and relatively low solids concentration must be considered. Do the following paragraphs discuss and refute the possibility?
14. Page 5-4, second paragraph under Plutonium in water you mention that criticality is possible for tank waste when the total macroscopic absorption cross-section per plutonium atom is less than for water. Is this asked and answered? It seems you leave the reader hanging.

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