Tank C6A Solids

by

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Recovery**INTER-OFFICE MEMORANDUM**

SAVANNAH RIVER PLANT

DPSPU-88-272-24

March 9, 1988

ACC# 244000

TO: J. L. ADAMS, 221-F B-LINE

FROM: H. P. HOLCOMB, 772-F

HPT

INFORMATION ONLYTANK C6A SOLIDSINTRODUCTION AND SUMMARY

The Separations Technology Laboratory was requested to characterize solids, removed as a slurry, from cleanout of Tank C6A last month. For some time, solids had been appearing in samples taken from this tank.

The sample was a rather viscous, tan-colored semiliquid. It consisted of two solid fractions: 1) large, easily centrifuged particles (16 mL total) and 2) fine particles that were difficult to centrifuge into a solid mass (23 mL solids plus interstitial liquid). The fractions were kept separate during all testing. Both were dried to a temperature of 300°C, in increasing steps, in order to remove water. The solids were finally collected in separate wide-mouthed plastic bottles and reduced in size and homogenized by vigorously shaking the capped containers.

The large fraction on drying yielded 13.840 g; the small, 3.714 g. Analysis by the F B-Line gamma pulse height analysis (PHA) waste monitor indicated a Pu²³⁹ content of 4.92 g (36.6 wt%) in the former and 1.73 g (55.5 wt%) in the latter after sampling had reduced the solids' weight by 0.4-0.6 g. The other primary constituent of the larger particles was aluminum. For the fines, aluminum and calcium were major cation contributors, other than plutonium. Isotopic analysis by gamma PHA indicated both materials to be 12% Pu²⁴⁰.

Particle size analysis of the smallest fines showed a distribution between 1 and 32 µm with the mean being 6.55 µm and the median, 6.18 µm. Some 22% of the particles were 2 µm or less.

95% of the plutonium, theoretically present in a sample of the large, dried particles, was recovered in solution by heating the solids in 8M HNO₃ at 90-95°C for 1.5 hours with efficient mixing.

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For the smaller particles, 96% of the theoretical Pu present was recovered under the same conditions. Small quantities (<0.1 mL) of residues persisted in both.

Small samples of each of the dried solids were equilibrated with hot, deionized water. Plutonium solubility of the larger particles was 0.6 wt%, sample weight basis; for the smaller particles, 0.3 wt%. Anion analysis by ion chromatography of a dilution of the larger particles' supernate showed F^- , NO_3^- , and SO_4^{2-} in a 2:1:3 molar ratio. Nitrate molarity (0.018 mmols NO_3^- /5 mL) was 2.6 times greater than the soluble plutonium. A repetitive experiment for the smaller particles yielded a similar molar ratio for F^- , NO_3^- , and SO_4^{2-} . Phosphate, at a molar level 10 times less than nitrate (0.007 mmols NO_3^- /5 mL), was also detected. Soluble nitrate molarity was 2.3 times that of soluble plutonium. Sulfate's origin in Tank C6A is unknown. I would suspect it to be an impurity in the 60% aluminum nitrate process solution.

The analytical evidence from this study shows the solids, although principally plutonium and aluminum, to be a complex mixture, stoichiometrically. The solids have likely been forming over the past few years due to conditions leading to insolubility, primarily of aluminum nitrate, in Tank C6A. This mode of formation is probably responsible for the larger particles. Since aluminum nitrate crystals can be highly hydrated, small quantities of plutonium could have been carried along from the 150-200 g Pu/L mother liquor. The smaller particles could have formed in the same manner, but since they contain more plutonium than the larger ones, they could have originated in upstream processing from C6A and have been fine enough to either bypass filtration or be passed along during line breaks to change filters or for other maintenance.

Routinely scheduled inspection and/or cleanout is recommended to prevent further buildup of solids in such process vessels.

EXPERIMENTAL AND DISCUSSION

Sample Furnished and Pretreatment

The sample sent to the Sep Tech Lab and placed in our glove box was contained in a wide-mouth plastic bottle. The sample was a thick, viscous slurry, tan in color. This color was similar to that of solids seen in previous C6A samples.

Using water, the slurry was divided between two Kimax® 30-mL centrifuge cones. First, the fines were transferred to one tube since they were easier to suspend. Finally, the remainder of

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the solids were transferred to another, similar tube. Since the water used to transfer the solids comprised the majority of the liquid, it was considered a wash and discarded.

Initial centrifugation produced 16 mL of larger particulates with a clear, almost colorless supernate, which was carefully decanted. These particles ranged from a few millimeters down to approximately one millimeter in rough diameter. Their color was primarily from dark shades of gray to off-white, although some tannish material was present.

Initial centrifugation of the finer material gave 23 mL of combined fines plus interstitial liquid with a supernate that contained the difficult-to-centrifuge particles. This supernate, containing the finest solids, was reserved for particle size analysis. The solids were a uniform tan color and appeared homogeneous throughout.

Drying of Solids

Each batch of solids was transferred to its individual porcelain crucible using a minimum quantity of water so that the crucible was filled to no more than one-third of its capacity.

The crucibles and their contents were placed in the muffle furnace in the glove box. The furnace was initially turned on at its lowest setting and took approximately one hour to reach 125°C, indicated. After another hour, the temperature had reached 150°C. At this point the furnace was turned off and left overnight to cool to ambient temperature. The next day, the furnace was slowly heated, in steps, over an eight-hour period to a final temperature of 300°C, at which it remained for approximately one hour. Again, the furnace was turned off and allowed to cool to ambient conditions overnight. There was no indication of splattering or of sample loss due to the heating process.

Both solid fractions were easily removed from their respective crucibles. They were placed in individual, tared wide-mouth plastic bottles, similar to the original sample container. Each was weighed on the balance in the glove box. The quantity of solids from the larger particles weighed 13.840 g; the smaller, 3.714 g.

Sampling for Emission Spectrographic Analysis

Each container was capped and then vigorously shaken to reduce the particle sizes to a powder-like material in each bottle. Also, by doing this, a more representative sample of each could be taken for emission spectrographic analysis. Following that sampling, the sample of larger particles weighed 13.444 g; the smaller, 3.117 g.

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NDA Determination of Pu in Solids

Each capped sample bottle with its solids was packaged in a $\frac{1}{2}$ -gal. ice cream carton. F B-Line operations arranged for pickup and transport of the solids to the gamma PHA waste monitor. By its analysis, there was 4.92 g Pu²³⁹ in the bottle of "large" particles and 1.73 g Pu²³⁹ in the "smaller" particles' fraction. Therefore, based on the weight of the solids following emission spec sampling, the larger particles were 36.6 wt% Pu²³⁹ and the smaller were 55.5 wt% Pu²³⁹.

Isotopic Composition of Solids

While B-Line had the samples, I requested that Laboratories Department determine the Pu isotopic distribution in each via their gamma PHA instrumentation. The following table gives their results.

TABLE 1ISOTOPIC COMPOSITION OF SOLIDS

Isotope	Weight Percent	
	"Large" Particles	"Small" Particles
238	0.09689	0.10235
239	86.04032	85.87396
240	12.15400	12.28329
241	1.45242	1.46929
242	0.25638	0.27110
Am-241 ($\mu\text{g/g Pu}$)	2827	3391

Therefore, both particle fractions consist of 12% Pu²⁴⁰ material, as would be expected.

Emission Spectrographic Analysis of Solids

The following table gives the major and minor constituents of the samples, other than plutonium, that were determined by emission spec:

TABLE 2COMPOSITION OF SOLIDS

	<u>"Larger" Particles</u>	<u>"Smaller" Particles</u>
Major	Al	Al, Ca
Minor	Ca, Cr, Cu, Fe, Mg, Ni, Pb, Si, Sn	Cr, Cu, Fe, Mg, Ni, Pb, Si, Sn.

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As a remark to this analysis, it was reported: "#1 (the 'larger' particles) was higher in everything with the exception of Ca, Ni, and Pb". Since #1 had less wt% plutonium as measured by NDA, this information that it had more contaminants supports the lower wt% Pu found in it and the higher wt% Pu found in #2 (the "smaller" particles).

Particle Size Analysis

The original sample of the fines slurry was given to Laboratories Department for particle size determination using their Coulter Counter®, Model TA-II. Table 3 on the following page is a copy of the actual printout from that analysis.

The "size" column lists the particle sizes in μm . The third column is the vol% of the total solids that particular particle size occupies. Of interest here is that the mean particle size of the fines was 6.55 μm ; the median, 6.18 μm . Also note that 21.7 vol% of the particles were 2 μm or less. Therefore, unless a filter were totally efficient for removing 1 μm particles, then some of these C6A solids could pass through a 1 μm -rated filter.

Dissolution of C6A Solids

In order to test dissolution characteristics of the dried C6A solids, an initial test, using 0.440 g of the "larger" particles and 0.446 g of the "smaller", was attempted in separate 10 mL portions of 0.5M (3%) HNO_3 since I was told by B-Line personnel that initial attempts at dissolution were being made with 2% (0.32M) HNO_3 . Since there was very little color throw to the acid upon vigorous mixing at ambient temperature, dissolution was essentially nil in the weak acid.

To the same weighed sample in each tube with the weak acid was added 10 mL of 15.7M HNO_3 . Therefore, the resulting acidity was 8M. Even in the cold upon mixing, there was a slight greenish color throw to the liquid. To speed up dissolution, the tubes were placed in a boiling water bath for 1.5 hours with vigorous mixing by hand of each tube and its contents every 5 minutes. At the end of this period, the liquid in each tube had a deep green color like that of the $\text{Pu}(\text{NO}_3)_6^{-2}$ complex. The samples were allowed to stand overnight to cool.

The following morning, the samples had the following parameters:

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TABLE 3PARTICLE SIZE ANALYSIS OF FINES

SAMPLE: H22222

ID: H2222251

VOLUME % STATISTICS

MEAN: 6.55 UM
MEDIAN: 6.18 UM
MODE 5.44 UM
STANDARD DEVIATION: 2.68 UM
COEF. VAR.: 40.96 %
SKEWNESS: 1.1 POSITIVE
KURTOSIS: 5.89 LEPTOKURTIC

DATE: 2/29/88

SAMPLE: H22222

ELECTROLYTE: 1

DISPERSANT: 1

EQUIPMENT: 1

APERTURES: 1

OPERATOR: GFP

COMMENTS: 1

CH.#	SIZE	DIFF VOL %	CUM VOL %
1	1	.55	100
2	1.26	7.31	99.45
3	1.59	6.53	92.14
4	2	7.31	85.61
5	2.52	6.56	78.3
6	3.17	6.96	71.75
7	4	7.61	64.79
8	5.04	8.15	57.18
9	6.35	7.06	49.03
10	8	6.51	41.97
11	10.08	6.16	35.46
12	12.7	6.01	29.3
13	16	5.74	23.29
14	20.16	5.21	17.56
15	25.4	6.93	12.34
16	32	5.41	5.41

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	<u>"Larger" Particles</u>	<u>"Smaller" Particles</u>
Total vol, mL	20.0	20.0
Vol. solids, mL	0.45	0.1
Total liquid volume, mL	19.5	19.9

Material Balance and Accountability - Quantity of Pu Recovered
On Dissolution

The contents of each of the centrifuge cones from the 8M HNO₃ dissolution were well mixed, then thoroughly centrifuged before taking the foregoing readings. Following these measurements, a 3-4 mL aliquot of each solution was submitted to Laboratories Department shift personnel for determination of its total plutonium content by the Pu⁺³ method using diode array spectrometry.

Their results showed the "Large" particle solution to be 9.12 g total Pu/L and the "Small" to be 13.99 g total Pu/L.

These data can be used to obtain a percent Pu recovery when combined with the data from the initial Pu value of each particle fraction and the isotopic analysis. The stepwise analytical progression follows:

	<u>"Larger" Particles</u>	<u>"Smaller" Particles</u>
(1) g dried solids taken for dissolution	0.440	0.446
(2) total g Pu/L in diss. solution by diode array	9.12	13.99
(3) g Pu/19.5 mL of diss. sol.	0.178	0.278
(4) g Pu/g sample, %, (3)(X100)/(1)	40.4	62.3

(5) original g solids counted on gamma waste monitor	13.444	3.117
(6) g Pu ²³⁹ in sample by WM	4.92	1.73
(7) wt% Pu ²³⁹ , (6)(X100)/(5)	36.6	55.5
(8) isotopic wt% Pu ²³⁹	86.04	85.87
(9) total wt% Pu in solids, (7)/(8)(X100)	42.5	64.6
(10) % Pu recovery by hot 8M HNO ₃ leach, (4)(X100)/(9)	95.0	96.4

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Therefore, the heated, 8M nitric acid leaching of the solids, even though dried to 300°C, recovered at least 95% of the total theoretical plutonium present as determined via gamma PHA. Efficient mixing was critical to effect such a high recovery.

Solubility of Solids in Water - Anion Analysis of Supernate

In an experiment to obtain information about the anionic content of the solids, approximately 0.2 g of each was equilibrated with separate 5-mL portions of deionized water in a boiling water bath for one hour. Vigorous hand shaking was employed every 5 minutes for thorough mixing. At the conclusion of the equilibration period, the samples were thoroughly centrifuged. Water was used as the solvent to prevent interference in ion chromatography analysis by a large quantity of anion that would be found in an acid dissolvent (e. g., nitrate from nitric acid).

An aliquot of the supernate was removed for alpha analysis and for ion chromatography (IC). Due to the alpha content of the contact water, a dilution of the supernate in deionized water had to be made in order to sufficiently reduce alpha activity levels to acceptable limits for IC.

The following table gives the results of the alpha and IC analyses.

TABLE 4

HOT WATER EQUILIBRATION OF SOLIDS - SUPERNATE CONTENTS

	<u>Larger Solids</u>	<u>Smaller Solids</u>
g sample in 5 mL DI H ₂ O	0.290	0.220
mmols dissolved/5 mL:		
Pu (wt% of sample)	0.007 (0.6%)	0.003 (0.3%)
F ⁻	0.036	0.012
NO ₃ ⁻	0.018	0.007
SO ₄ ⁻²	0.045	0.023
PO ₄ ⁻³	Not Detected	0.0007

Molar ratio: Pu:F ⁻ :NO ₃ ⁻ :SO ₄ ⁻²	1:5:3:6	1:4:2:7

To be noted from these data are the following:

- 1) The molar ratio of plutonium to the other ions in both samples is quite similar; i. e., plutonium:fluoride:nitrate:sulfate

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= approximately 1:5:2:7. This indicates that the water soluble species from each are similar in composition. Also, since the Pu/F ratio is close to 1/4, might not the insoluble Pu species be PuF_4 ? PuF_4 can precipitate from fairly acidic solutions, especially if there is minimal concentration of fluoride complexant (Al^{+3} , BO_3^{-3} , etc.) present.¹

- 2) Although the larger particles are about 40 wt% Pu and the smaller, about 60 wt%, about one-half as much plutonium dissolved in the water from the smaller as did from the larger particles. However, since less than 1 wt% of the plutonium from each particle sample was soluble in water, then the bulk of the plutonium in each is rather insoluble in hot water, but >95% soluble in hot 8M HNO_3 .
- 3) The question, "Where did the sulfate come from?", has to be asked. For both particulate samples, sulfate ion had the highest molarity in solution. Is it a reagent or feed impurity? Was sulfate (or something that gives rise to sulfate such as sulfamic acid or ferrous sulfamate) somehow improperly added to the process sometime previously? Or has sulfate solids gradually built up from the sulfate impurity in the 60% ANN process solution? At 25°C, in 6M HNO_3 , at 176 g Pu/L, limiting sulfate concentration is 0.103M in order to prevent precipitation of $\text{Pu}(\text{SO}_4)_2$. With increasing acidity, limiting sulfate concentration decreases.² So, under the proper conditions, sulfate could precipitate Pu^{+4} .

DCAP Analysis of Water Supernate For Cations

Aliquots taken from a nitric acid dilution of the water supernate, made for alpha analysis, were submitted to Laboratories for DCAP analysis of the following ions: Al, Ca, Fe, and Si. The following table gives the results of that analysis.

TABLE 5

DCAP ANALYSIS OF WATER SUPERNATE

	<u>Larger Particles</u>		<u>Smaller Particles</u>	
	<u>µg/5 mL</u>	<u>mmol/5 mL</u>	<u>µg/5 mL</u>	<u>mmol/5 mL</u>
Al	1190	0.044	1495	0.055
Ca	375	0.009	625	0.016
Fe	2625	0.047	4150	0.074
Si	5000	0.178	6100	0.218

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These molar compositions, except for silicon, are very similar in quantity to those found for the anions in the same solution. However, all of the experiments were conducted in glass vessels, and the DCAP samples were stored in glass vials, all a source of silicon. However, silicon is a component of each batch of solids as determined by emission spec, so not all of the soluble silicon is impurity from the glass vials. Emission spectrographic analysis found the major constituents, other than plutonium, of the "larger" particles to be aluminum; for the "smaller", they were aluminum and calcium. The emission spec findings are substantiated by the above data. These data also show that one of the minor constituents, iron, was a relatively large contributor to the soluble cationic components of the hot water leach.

Combining these data with those from the anionic analyses, it is apparent that the composition of each solid sample was complex and not readily stoichiometrically assignable to the elements found present.

Examination of Dried Solids by SEM/XRF

Portions of each dried solid sample were forwarded to D. F. Steedly of ADD, SRL, for examination by Scanning Electron Microscopy/X-Ray Fluorescence (SEM/XRF) to gather further information about their composition. ADD does not yet have a contained X-Ray Diffractometer, so a powder pattern of the solids, and possible identification of the crystal structure, is not possible onsite.

Initially, the solids showed the presence of plutonium and aluminum in one sample. However, immediately following this cursory examination, the SEM/XRF unit went down for maintenance and upgrading. Following this, problems have occurred with their instrument that will necessitate a visit by the factory representative next week. In order to facilitate issue of this report, a separate followup involving just the SEM/XRF findings will be published later.

CONCLUSIONS AND RECOMMENDATIONS

- 1) The solids have probably been slowly building up in Tank C6A over the past few years. They are there as the result of three factors, one being the insolubility of aluminum nitrate and other compounds under certain conditions in Tank C6A, another is that they formed or were present upstream of C6A and were transported and deposited there, and the final factor involves solid formers or solids themselves in cold feed solutions. The solids do not appear to be undissolved oxides since greater than 95% of the plutonium in them was soluble in hot 8M HNO₃.

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- 2) The solids contain a substantial quantity of plutonium as noted from the analyses. This could result from sorption or from occlusion of the 150-200 g Pu/L mother liquor during crystallization of the solids, or from coprecipitation of the plutonium itself with the solids.
- 3) The solids contain sulfate from an unknown source. Essential Materials Specifications (EMS) for process 60% aluminum nitrate (ANN) call for sulfate, as SO_4 , to be no more than 0.05 wt%, or 660 mg SO_4^{2-} per liter of 60% ANN. According to 772-F personnel, this analysis is still being conducted on vendor's samples. Another source of sulfate is from the hydrolysis of sulfamate ion, which is present in sulfamic acid or in ferrous sulfamate. Could either of these have been introduced into the process at some earlier time? I suspect the ANN impurity theory is much more plausible than the sulfamate one.
- 4) EMS for ANN solution also calls for "water insolubles" to be no greater than 0.01 wt%, or 132 mg/L 60% ANN. This is not part of the acceptance criteria, although it is a specification. There are no analyses for "water insolubles". Could these "water insolubles" be contributing to the solids buildup in C6A? It would be interesting to calculate how much aluminum nitrate goes through the system during a given time period, and then calculate, based on 0.01 wt% "water insolubles" in that aluminum nitrate, how much solids from this source would be available for formation of such residues.
- 5) Perhaps the best preventive measure for reducing solids buildup in such process tanks is regularly scheduled inspections and/or effective flushing operations for these vessels. For comparison, what does NSR plan to do with regard to such measures to prevent buildup of solids in their process tankage?

ACKNOWLEDGMENTS

Several other groups contributed to the gathering of data that are included in this report. They should be recognized for their cooperative efforts. They include my own technical analyst, N. W. McGahee, for the quality manner in which he routinely conducts the many various laboratory operations, G. M. Blessing of Laboratories for getting the isotopic data from gamma PHA, B-Line personnel for obtaining the Pu content of the solids via the gamma PHA Waste Monitor, P. B. Berry of Labs for conducting the particle size analysis, J. T. Coleman of Labs for the emission spec and DCAP analyses, W. R. Frazier of Labs for the IC analyses, and the Laboratories' shift personnel for their usual fine job in doing the diode array analyses for Pu on the 8M HNO_3 dissolvents.

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HPH/h