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Characterization of Sludge and Water Samples Obtained from the General's Tanks during April, 2010 Sampling, Rev.0

by

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II. Executive Summary

This report presents the results of radiological, physical, and chemical studies of material sampled from the Generals Tanks during the April, 2010 sampling campaign. The General's Tanks, located at Material Disposal Area (MDA) A, Technical Area (TA) 21consist of two, 50,000-gal. cylindrical steel storage tanks, designated the East (21-108) and West (21-107) Tanks, which were constructed in 1945 for underground storage of plutonium-bearing sludge from waste solutions. Water and sludge were sampled from the tanks during April 2010 by LANL Environmental Programs in order to better characterize these materials to evaluate a remediation strategy. Specifically this report focuses on:

1. The elemental composition of water and sludge from each tank
2. The concentration and isotopic composition of plutonium, and other radionuclides in sludge and water samples from each tank
3. Density and settled porosity of sludge from each tank; and,
4. Radionuclide inventory estimates for each tank

Elemental composition of water and sludge from each tank were performed by Inductively Couple Plasma (ICP) – Atomic Emission Spectroscopy (AES), and ICP-Mass Spectrometry (MS) and are presented. Concentrations of plutonium and other radionuclides were analyzed by a number of methods including ICP-MS, alpha and gamma spectroscopy, liquid scintillation counting, and Thermal Ionization Mass Spectrometry (TIMS). Total activity in each sample and sample heterogeneity were examined by total dissolution, Toxicity Characteristic Leaching, and acid leaching of a large number of sub-samples. The data show that the sludge samples are heterogeneous in plutonium concentration, but very consistent in plutonium isotopic composition. The plutonium concentration in the samples varied from no detectable activity to 410 ug/g. Plutonium concentrations also varied significantly within subsamples from the same sample. Isotopic characterization shows that most of the activity in the sludge and sediment samples is from Pu-239/Pu-240 with minimal contributions from Am-241, U-235 and Sr-90. The data show that the water contains low concentrations of radionuclides.

Calculations of plutonium inventory in the tanks are based on the measured volume of sludge in the tanks, the range of concentration of plutonium in the sludge, the sludge density, and the settled porosity. Measurements indicate that plutonium and other radionuclide inventory in the water is negligible to the total tank inventory. The plutonium inventory for the East tank varies from 0.78 kg for a high sludge-volume estimate and 0.4 kg for a low sludge-volume estimate. The inventory in the West tank is estimated at between 2.4 and 2.9 kg, values that correspond to

different plutonium concentration values. There are considerable uncertainties in these values. For the east tank the plutonium concentration, density and porosity measurements are reasonably consistent and the largest uncertainty is due to the uncertainty in sludge volume. The west tank is known to contain sediment from the surface that mixed with the sludge. The samples analyzed in this study contained variable amounts of this sediment resulting in a large spread of plutonium concentrations in subsamples. Uncertainty in the average plutonium concentration for the sludge in the west tank is the largest uncertainty in this inventory estimate. An additional uncertainty that applies to both tanks is the question of sample representativeness. The samples we obtained were limited to the area beneath the tank opening. Calculations of total inventory assume that these samples are representative of the entire tank.

III. Brief Background on Waste Disposal in the General's Tanks

The General's Tanks, known as the east and west tanks, are each 50,000 gallon steel tanks that were used for the storage of low level retrievable waste streams derived from plutonium reprocessing and recovery operation carried out at LANL from 1945 to 1947. The tanks received basic supernatant solutions from which no further plutonium recovery was practical, but which contained levels deemed too great to discard. These residual solutions were reported to contain approximately 1 mg/L (10^{-3} g/L) of plutonium (LASL 1947). The final recovery processes for the bulk (over 90%) of solutions were generated by one of 2 processes. The first process involved solutions that were treated with hydrogen peroxide and sodium hydroxide that resulted in solutions sent to the west tank that contained little or no calcium and magnesium. The second involved a final treatment with ammonium nitrate and ammonium hydroxide to precipitate aluminum hydroxide as a plutonium carrier and was sent to the east tank. The resulting supernatant solutions were high in calcium and magnesium.

As the availability of plutonium increased in the following years the recovery of plutonium from the General's Tanks was deemed uneconomical. The tanks were sealed and buried in place until 1974. In 1974, the tanks were partially excavated; the soil and concrete were removed from the top of the tanks and holes about 16-inch diameter were cut in the top of each tank. It was determined that an estimated 40,000 gallons of liquid and solid material was held in the west tank from the sodium hydroxide process and 9,000 gallons was in the east tank from the ammonium hydroxide process (Rogers, 1977). It was also recognized that the wastes in the tanks had separated and that solid sludge material had collected in the bottoms of the tanks. The sludge was overlain by a layer of supernatant water that comprised the bulk of the material in the tanks. The holes in the tanks remained open for 4 or 5 years, and the water in the west tank was pumped periodically as rainwater collected in the tank. The tanks were sealed and buried in 1985 to prevent further rainwater infiltration (Emelity, 1996).

IV. Sample Description

In 2010, the tanks were re-excavated and the holes in the concrete and tops of the tanks were re-opened for access to the tanks and wastes in the bottoms of the tanks. Aluminum shoring boxes with steel covers were installed to cover the openings when not in use. Precision measurements of the interior dimensions of the tanks, including levels of the liquid and sludge, were obtained with a laser device, and as-found drawings were compiled to document the results (LANL 2011). Estimates of solid and water volumes are given in Table 1.

Table 1. Volumes of sludge and water contained in the Generals Tanks.

	Total volume (gal)	**Sludge Volume (gal)**	**Water Volume (gal)**
east tank	2728	Min 327 Max 640	2401 2088
west tank	2729	1846	883

In April, 2010 several sludge and water samples and were obtained from both the east and west Generals Tanks. Samples were collected from the region directly below the openings in both tanks and by angling the sampling tool to the sides in order to test for sample heterogeneity. In this manner samples were obtained from approximately 3 to 4 feet along the long axis of the tanks from the point vertically below the opening. The samples received were heterogeneous, especially those from the west tank. The west tank samples contained varying amount of sediment that consists of fine to coarse grained soil components (quarts, feldspar, clay, plant debris), that apparently washed into the tanks while it was open in the 1970s. The east tank contained little such material.

Samples were placed in Teflon containers, assayed for radioactivity by gamma spectroscopy, and shipped to either TA48 or the CMRR. Water samples were collected via peristaltic pump and shipped to TA50 for chemical analysis. Table 2 gives the amount of samples received at TA48 and the CMR and a brief description. Table 3 presents pH measurements and activity of the supernatant in samples determined shortly after arrival at TA 48.

Table 2. Inventory of the samples received from TA-21

Sample ID	**Sample description**	**Sample activity measured at the site**	**Picture of the sample**
5317	About 5 g of dry tank scrapings	No measurable activity	

4943	100 g of single rock and rope that was used in the past to measure depth in the tank	Total activity from gamma measurements 4.51e-7 Ci from 241Am	
4952	916 g of wet sandy like sludge	Total activity from gamma measurements 4.41e-8 Ci from 241Am	
5319	About 10 g of tank scrapings	Total activity from gamma measurements 3.69e-8 Ci from 241Am	
4950	About 800 g of sludge	Total activity 1.49e-7 Ci of 241Am	
4946	About 2223 grams of wet sludge split into two plastic container	No measurable activity	
4944	About 893 g of tank water	No measurable activity	
4951	173 g of sandy sludge	Total activity 241Am 3.9e-7, 239Pu 3.85e-5 Ci, 240Pu 9.01e-6 Ci	
4935	About 887 grams of tank water	Total activity 239Pu 2.53e-5 Ci, 240Pu 5.92e-6 Ci 234U 6.75 e-8 Ci, U235 1.67e-9 Ci	ok
4937	2129 grams of tank water	Total activity 137Cs 2.77e-9 Ci, Sr90 2.77e-9 Ci, 234U 1.4e-7 Ci, U235 3.46e-9 Ci	
21GTW11-4948	Brown granular mud with a good deal of integrity. 46.87 g of the sample was transferred to	Total activity 0.000027 Ci/g from 98.4 wt% 239Pu and 1.6 % 240Pu with traces of 238Pu,	

	TA-48 (ARF)	241Am and 235U (analysis performed at the CMR by mass spectrometry)	
21GTE11-4942	Loose solids and also contained what looked like pieces of leaves or paint chips and sticks in it. 64.02 g was transferred to TA-48 (ARF)	0.000020 Ci/g from 98.4 wt% 239Pu and 1.6 % 240Pu with traces of 238Pu, 241Am and 235U (analysis performed at the CMR by mass spectrometry)	

Table 3. Results of pH and activity in the supernatant sampled from the generals tanks.

Sample ID	**pH**	**Activity in Ci**	**Storage location**
4937	6.317, 6.460, 6.460	No measurable activity in the supernatant	TA-48, RC-1, room 308
4946	8.713, 8.658, 8.665, 8.617	No measurable activity in the supernatant	TA-48, RC-1, room 308
4950	8.443, 8.445	No measurable activity in the supernatant	TA-48, RC-1, room 308
4951	7.988, 8.012, 8.057	No measurable activity in the supernatant	TA-48, RC-1, room 308
4952	8.470, 8.482, 8.476	No measurable activity in the supernatant	TA-48, RC-1, room 308
4941	6.966, 7.021, 7.002	No measurable activity in the supernatant	TA-48, RC-1, room 308
GTW			TA-48, RC-1, room ARF
GTE			TA-48, RC-1, room ARF

V. Sludge and Sediment Samples Characterization

Sludge samples from the east and west tanks were characterized using different techniques to determine chemical, physical and radiological characteristics. Experimental details and results are summarized below:

1. Density and porosity measurements

Density and porosity measurements were performed on sludge samples 21GTW11-4948 and 21GTE11-4942 (Table 4). Density measurements were made as follows. Sludge samples were fully dried and the mass determined. This material was placed in a tared gravimetric cylinder and a measured volume of deionized water was added to the cylinder. The volume and mass were determined. The volume occupied by the sludge sample is determined by the subtracting the volume of the water added from the measured volume of the sludge plus the water. The dry sludge density (ρ_{dry}) is the ratio of the mass of the air-dried sludge sample to the volume of the sample. Porosity is determined as follows. The fully-saturated sludge from the density measurements was allowed to settle in the graduated cylinder for 24 hours. The cylinder was then lightly tamped to further pack the sludge. Tamping the sample was thought to best approximate the porosity of the tank sludge, which has had decades to compact. The volume of the fully-saturated sludge was then determined in the gravimetric cylinder. Porosity values (n) were determined as the percentage of the volume occupied by water in the fully-saturated sludge over the total volume of the fully-saturated sludge. Analyses were replicated for five samples splits from the east tank and two from the west tank. Errors are given at one standard deviation and reflect experimental reproducibility.

Table 4. Density and porosity values for sludge samples from the General's Tanks

Sediment sample ID	Density (ρ_{dry})	Porosity in %
21GTE11-4942	1.84 ± 0.1	43 ± 2
21GTW11-4948	2.5 ± 0.1	59 ± 6

2. Characterization of the water chemistry

Characterization of the water chemistry in the east and West tanks were obtained from TA-50 radiological Liquid Waste facility. These were performed in accordance with their Waste Acceptance Criteria (P930-1) and are included herein for completeness. Abbreviations used in Tables 5 and 6 are given in Table 7.

Table 5. West General's Tank water analysis

Sample #	**Analytical Method**	**Analysis Name**	**Result**	**Report Units**	**Detection Limit**
11.76055	COLOR	COD	3300	mg/L	10
11.76055	ELEC	pH	8.5	pH	0.1
11.76055	ELEC	COND	64000	umho/cm	5
11.76055	GRAV	TDS	53100	mg/L	20
11.76055	GRAV	TSS	3640	mg/L	4
11.76055	GSPEC	Am-241	0	nCi/L	0.1
11.76055	IC	Cl	1340	mg/L	0.04
11.76055	IC	ClO4	1.1	mg/L	0.001
11.76055	IC	F	0	mg/L	0.01

11.76055	IC	NO3-N	6500	mg/L	0.01
11.76055	IC	SO4	1210	mg/L	0.03
11.76055	ICP-MS	Pu-238	9.3	nCi/L	1
11.76055	ICP-MS	Pu-239	13	nCi/L	1
11.76055	ICP-MS	Pu-240	1.3	nCi/L	1
11.76055	ICP-MS	Th-232	0.24	pCi/L	0.1
11.76055	ICP-MS	U-234	300	pCi/L	100
11.76055	ICP-MS	U-235	13	pCi/L	0.1
11.76055	ICP-MS	U-238	64	pCi/L	0.1
11.76055	ICP-MS	Ag	22	ug/L	3
11.76055	ICP-MS	As	0	ug/L	10
11.76055	ICP-MS	B	440	ug/L	30
11.76055	ICP-MS	Ba	61	ug/L	1
11.76055	ICP-MS	Be	0	ug/L	5
11.76055	ICP-MS	Ca	32000	ug/L	300
11.76055	ICP-MS	Cd	0	ug/L	1
11.76055	ICP-MS	Co	5.9	ug/L	0.5
11.76055	ICP-MS	Cr	78	ug/L	1
11.76055	ICP-MS	Cu	1400	ug/L	5
11.76055	ICP-MS	Fe	0	ug/L	100
11.76055	ICP-MS	Hg	30	ug/L	2
11.76055	ICP-MS	K	20000000	ug/L	1000
11.76055	ICP-MS	Mg	330000	ug/L	1
11.76055	ICP-MS	Na	2900000	ug/L	1000
11.76055	ICP-MS	Ni	34	ug/L	10
11.76055	ICP-MS	Pb	1.9	ug/L	1
11.76055	ICP-MS	Se	530	ug/L	20
11.76055	ICP-MS	Si	3100	ug/L	1000
11.76055	ICP-MS	V	0	ug/L	1
11.76055	ICP-MS	Zn	48	ug/L	30
11.76055	ICP-MS	Al	0	ug/L	40
11.76055	LSC	Alpha	24	nCi/L	1
11.76055	LSC	Beta	0	nCi/L	2
11.76055	LSC	H-3	0	nCi/L	2
11.76055	LSC	Sr-89	0	nCi/L	1
11.76055	LSC	Sr-90	0	nCi/L	2
11.76055	TITR	PALK	0	mg/L	5
11.76055	TITR	TALK	2400	mg/L	5

Table 6. East tank water analysis

Sample #	Analytical Method	Analysis Name	Result	Report Units	Detection Limit
11.76056	COLOR	COD	1180	mg/L	10
11.76056	ELEC	pH	6.3	pH	0.1
11.76056	ELEC	COND	43000	umho/cm	5
11.76056	GRAV	TDS	22500	mg/L	20
11.76056	GRAV	TSS	2090	mg/L	4
11.76056	GSPEC	Am-241	0	nCi/L	0.1
11.76056	IC	F	0	mg/L	0.01
11.76056	IC	NO3-N	5200	mg/L	0.01
11.76056	IC	SO4	236	mg/L	0.03
11.76056	IC	Cl	400	mg/L	0.04
11.76056	IC	ClO4	0.6	mg/L	0.001
11.76056	ICP-MS	Pu-238	1.7	nCi/L	1
11.76056	ICP-MS	Pu-239	5.3	nCi/L	1
11.76056	ICP-MS	Pu-240	1	nCi/L	1
11.76056	ICP-MS	Th-232	0	pCi/L	0.1
11.76056	ICP-MS	U-234	100	pCi/L	100
11.76056	ICP-MS	U-235	5.5	pCi/L	0.1
11.76056	ICP-MS	U-238	26	pCi/L	0.1
11.76056	ICP-MS	Cu	20	ug/L	5
11.76056	ICP-MS	Fe	5800	ug/L	100
11.76056	ICP-MS	Hg	7.7	ug/L	2
11.76056	ICP-MS	K	1600000	ug/L	100
11.76056	ICP-MS	Mg	500000	ug/L	1
11.76056	ICP-MS	Na	1700000	ug/L	1000
11.76056	ICP-MS	Ni	250	ug/L	10
11.76056	ICP-MS	Pb	1.1	ug/L	1
11.76056	ICP-MS	Se	360	ug/L	20
11.76056	ICP-MS	Si	1100	ug/L	1000
11.76056	ICP-MS	V	38	ug/L	1
11.76056	ICP-MS	Zn	0	ug/L	10
11.76056	ICP-MS	Ag	190	ug/L	3
11.76056	ICP-MS	Al	100	ug/L	40
11.76056	ICP-MS	As	15	ug/L	10
11.76056	ICP-MS	B	330	ug/L	30
11.76056	ICP-MS	Ba	660	ug/L	1
11.76056	ICP-MS	Be	0	ug/L	5
11.76056	ICP-MS	Ca	1400000	ug/L	300

11.76056	ICP-MS	Cd	1.1	ug/L	1
11.76056	ICP-MS	Co	7.9	ug/L	0.5
11.76056	ICP-MS	Cr	4.9	ug/L	1
11.76056	LSC	H-3	0	nCi/L	2
11.76056	LSC	Sr-89	0	nCi/L	1
11.76056	LSC	Sr-90	0	nCi/L	2
11.76056	LSC	Alpha	8	nCi/L	1
11.76056	LSC	Beta	0	nCi/L	2
11.76056	TITR	PALK	0	mg/L	5
11.76056	TITR	TALK	31	mg/L	5

Table 7. List of abbreviations used in the water analysis tables.

Analytical Method		**Analysis Name**	
COLOR	Colorimetric (HACH Kit)	COD	Chemical Oxygen Demand
ELEC	Electrode	COND	Conductivity
GRAV	Gravimetric	TDS	Total Dissolved Solids
GSPEC	Gamma Spectroscopy	TSS	Total Suspended Solids
IC	Ion Chromatography	Alpha	Gross Alpha
ICP-MS	Mass Spectrometry	Beta	Gross Beta
LSC	Liquid Scintillation Counting	H-3	Tritium
TITR	Titration	PALK	Phenophthalein Alkalinity
		TALK	Total Alkalinity
		NO3-N	Nitrate as Nitrogen

3. Characterization of the sludge samples radiological content

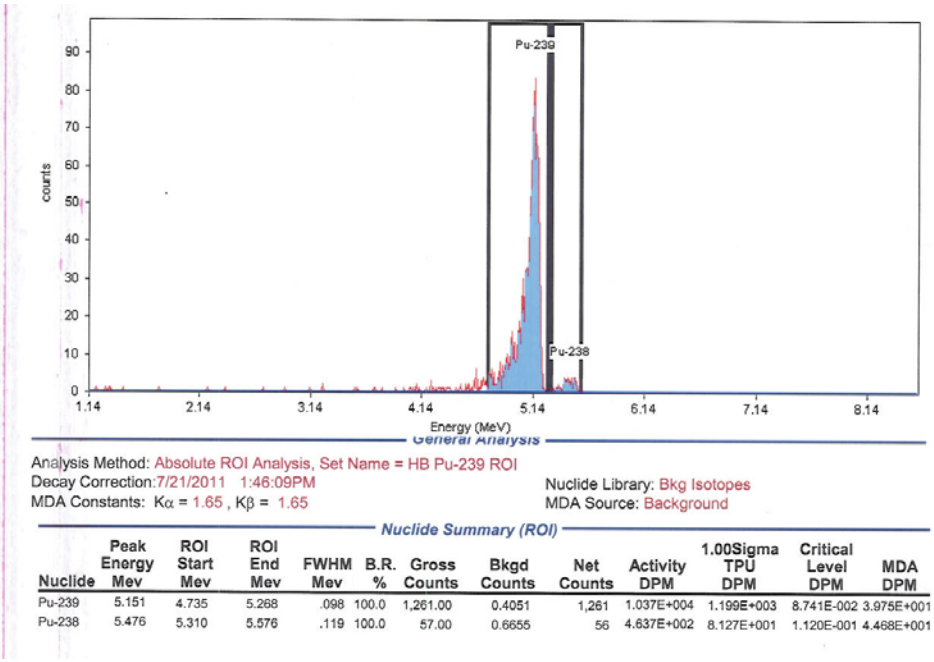
Alpha spectrometry

Sample Preparation

We prepared a dilute sludge suspension in 6.0 M HNO_3 using sludge sample 4951 by dispersing a weighed mass of moist sludge in 5.0 mL of acid. The solutions were left to equilibrate for 24 hours. After equilibration, the solutions were centrifuged to separate the supernatant from the remaining solids. Aliquots of the solutions were diluted 1:100 with 8 M HNO_3. One quarter of a

milliliter of this solution was directly stippled onto a 5/8's inch electro-deposition disk. The samples were counted for 24-50 hours using an alpha spectrometer fitted with 450 mm Passivated Implanted Planar Silicon (PIPS) detectors manufactured by Ortec Inc to determine total activity.

Results



Nuclide	Peak Energy Mev	ROI Start Mev	ROI End Mev	FWHM Mev	B.R. %	Gross Counts	Bkgd Counts	Net Counts	Activity DPM	1.00Sigma TPU DPM	Critical Level DPM	MDA DPM
Pu-239	5.151	4.735	5.268	.098	100.0	1,261.00	0.4051	1,261	1.037E+004	1.199E+003	8.741E-002	3.975E+001
Pu-238	5.476	5.310	5.576	.119	100.0	57.00	0.6655	56	4.637E+002	8.127E+001	1.120E-001	4.468E+001

Figure 1. Alpha spectrum of sample 4951

The data indicate (Figure 1) that the sample is mostly Pu-239 with very little activity in the Pu-238/Am-241 area. Alpha spectrometry cannot distinguish between 239Pu and 240Pu which show peaks at energy levels (Pu-239 at 5156.59 keV with 73.3% yield and Pu-240 at 5168.17 keV a with 72.8% yield) that cannot be separated by alpha spectrometry. The total activity from this sample was determined to be 1.41 x10^6 CPM/g of sludge.

Mass spectrometry

Two splits from sample 21GTW11-4948 (west tank) and two splits from sample 21GTE11-4942 (east tank) were selected from 1 liter sample containers by scooping using a long spoon. Importantly, the sludge in sample 21GTW11-4948 remained as a coherent mass after transport, which allowed subsampling from the top of the container as well as from farther down in the container. In contrast the sample from the east tank was loosely dispersed in the container, which did not allow for spatial subsampling. Samples were dissolved using a mixture of HNO_3 and HF acids heated to 140°C for up to three days in sealed Savillex pressure vessels. Splits

were made from the digested material for Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Thermal-ionization mass spectrometry (TIMS).

Splits from 21GTW11-4948 (west tank) and 21GTW11-4948 were also prepared according to the Toxicity Characteristic Leaching Procedure (TCLP, EPA Method 1311), a method designed to evaluate the mobility of inorganic analytes in multiphasic waste. The leachates generated were analyzed by ICP-AES and ICP-MS for the Resource Recovery and Conservation Act (RCRA) metals.

ICP-MS and AES Analysis (ANC 102, 211)

A serial dilution was performed prior to the analyses. Two techniques were used to obtain the trace elemental concentrations: the Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and the ICP-MS. For ICP-AES method, a peak search was performed to locate the emission lines position and an external standard calibration was used to calibrate the Horiba Jobin Yvon (JY-2) ICP-AES instrument on the day of the analysis. For the ICP-MS method, the VG Elemental PlasmaQuad S (PQS) ICP-MS (Thermo Fisher) was tuned for optimum ion counts at mass 114 for ^{114}Indium before calibrated externally. Internal standards, ^{45}Sc, ^{103}Rh, and ^{169}Tm, were added to standards and samples for drifting correction. The final concentrations for the internal standards are 100ng/mL. Results of totally digested material are given in Tables 8 and 9. Results for TCLP analyses are given in Table 10.

TIMS analysis

For TIMS analysis, the splits were spiked to determine elemental concentration by isotope dilution using a ^{244}Pu spike, and for U and Am analysis using a ^{233}U and ^{243}Am spike. Samples were mixed with spike, equilibrated, and dried in their respective spike vials. Two sequential column procedures were then used to separate the actinide elements from the sludge matrix and then separate the actinide elements (Pu, Am, U) from each other. All samples were then analyzed using Daly ion counting techniques on a Sector-54 mass spectrometer (for Pu, U and Am) and using an Isoprobe-T mass spectrometer equipped with an energy filter for trace Pu isotopes. Spikes have been previously calibrated against Pu and U standard reference materials. The Am spike was calibrated against an Am radioisotope standard and also against the Am ingrowth in Pu standards with known purification ages. Isotopic standards analyzed for QC purposes are CRM126a for Pu and IRM-199 for U. No isotopic standard exists for the Am analysis. Results are given in Tables 11 and 12.

Table 8. Elemental analysis of the sludge samples 21GTW (west tank) and 21GTE (east tank) by PQS-ICP-MS

Element	GT-BLK	21GTW-11-4948-(1)	21GTW-11-4948-(2)	21GTE-4942-(3)	21GTE-4942-(4)
	ppm	ppm	ppm	ppm	ppm
ANTIMONY	<.01	2.46	3.59	1.44	1.96
BARIUM	2.02	229.25	288.89	324.88	293.69
BISMUTH	1.74	9.04	16.24	9.67	8.18
CADMIUM	0.51	8.03	18.27	1.37	1.73
CERIUM	0.22	95.46	55.51	77.97	69.68
CESIUM	0.29	4.34	2.73	5.70	4.95
DYSPROSIUM	0.29	7.09	4.53	5.56	5.13
ERBIUM	0.22	3.62	2.50	3.10	2.71
EUROPIUM	0.29	1.52	0.55	0.79	0.86
GADOLINIUM	0.29	7.81	4.84	6.64	5.99
GALLIUM	0.43	22.20	21.78	20.86	17.74
GERMANIUM	0.43	16.85	11.79	23.82	26.89
HAFNIUM	3.11	3.18	2.97	3.54	2.94
HOLMIUM	0.29	1.88	0.94	1.23	1.15
INDIUM	0.22	1.01	0.47	0.36	0.23
IRIDIUM	8.53	1.01	1.33	0.43	0.17
LANTHANUM	0.22	61.25	42.55	95.30	87.53
LUTETIUM	0.22	1.30	0.39	0.51	0.40
MOLYBDENUM	0.65	9.47	6.09	8.95	12.90
NEODYMIUM	0.22	37.39	23.74	31.48	28.22
NEPTUNIUM	0.29	1.08	0.23	0.22	0.23
NIOBIUM	0.80	33.92	31.00	29.46	26.60
PALLADIUM	0.72	1.88	1.64	1.73	1.44
PLATINUM	<.28	2.89	4.14	1.37	1.32
PRAESEODYMIUM	0.22	11.35	7.50	10.40	8.98
RHENIUM	<.69	<.7	<.7	0.22	0.17
RUBIDIUM	<.48	98.35	28.58	102.52	85.23
RUTHENIUM	0.87	1.23	0.16	0.14	0.12
SAMARIUM	<.55	7.74	5.08	6.28	6.05
SILVER	<.21	1.16	1.25	0.72	0.46
STRONTIUM	0.22	75.93	83.54	83.75	74.29
TANTALUM	8.97	0.87	2.97	0.87	0.86
TERBIUM	0.14	1.95	0.94	1.23	0.98
THORIUM	0.94	14.25	4.29	26.78	23.44
TIN	0.43	31.89	53.02	13.64	16.01
TUNGSTEN	2.82	3.54	3.28	2.24	2.30
URANIUM	0.43	12.29	15.54	19.13	19.35
YTTERBIUM	<.35	3.54	2.11	2.67	2.42
YTTRIUM	0.22	28.71	16.79	24.62	22.23

Table 9. Elemental analysis of the sludge samples 21GTW (west tank) and 21GTE (east tank) by J-Y ICP-AES

Element	GT-BLK	21GTW-11-4948-(1)	21GTW-11-4948-(2)	21GTE-4942-(3)	21GTE-4942-(4)
	ppm	ppm	ppm	ppm	ppm
ALUMINUM	<1.8	47658.22	30216.33	49958.59	41576.72
ARSENIC	<5.8	23.29	16.32	27.00	27.58
BERYLLIUM	<0.06	1.59	1.64	2.67	2.36
BORON	<0.6	13.81	13.59	23.82	25.80
CALCIUM	<0.6	25962.52	35135.27	27433.91	41979.82
CHROMIUM	<1.2	107.03	252.97	301.77	290.23
COBALT	<1.8	7.59	8.43	12.20	13.76
COPPER	<1.8	562.64	999.40	168.94	232.07
IRON	<4.2	56987.37	40522.67	74360.33	90985.06
LEAD	<12	100.52	198.32	98.18	86.95
LITHIUM	<1.2	14.90	16.71	16.53	14.74
MAGNESIUM	<0..12	4295.75	3224.64	4281.13	4054.02
MANGANESE	<0.24	1070.32	1530.34	456.99	563.76
NICKEL	<0.24	263.24	423.18	308.27	308.08
PHOSPHOROUS	<0.42	292.89	417.72	408.62	386.97
POTASSIUM	<3	29506.15	32480.60	21874.93	18427.35
SELENIUM	<12	30.01	18.19	31.77	30.17
SILICON	8.1	18152.07	12726.77	14150.12	13014.32
SODIUM	<12	13234.38	12336.38	10179.42	8637.82
TITANIUM	<.6	652.32	1061.87	1169.55	904.09
VANADIUM	<1.2	16.20	24.91	31.26	28.04
ZINC	<2.4	1930.92	3833.65	420.89	450.89

Table 10. Results of TCLP analyses for RCRA metals from the Generals Tanks. All analytes are determined using ICP-AES except for mercury, which was determined using ICP-MS.

Element	RCRA Limit	21GTW-11-4948	21GTE-4942
	ppm	ppm	ppm
Silver	5	<0.02	<0.02
Arsenic	5	0.010	0.032
Barium	10	0.42	0.33
Cadmium	1	0.075	0.23
Chromium	5	<0.01	<0.01
Lead	5	<0.1	<0.1
Selenium	1	<0.1	<0.1
Mercury	0.2	<0.015	<0.015

Table 11. Isotopic composition of concentration of the sludge samples 21GTW (west tank)

subsample	Split 1	Split 2	
TOTAL Pu, ug/g,	156	410	
Isotopic composition	Atom%	Atom%	
238Pu	0.002	0.002	at detection limits
239Pu	98.40	98.41	
240Pu	1.60	1.59	
241Pu	0.002	0.003	at detection limits
242Pu	ND	ND	below detection limits
TOTAL U, ug/g	9.10	15.49	
isotopics	Atom %	Atom %	
234U	0.03%	0.03%	
235U	3.39%	4.02%	
236U	0.16%	0.20%	
238U	96.42%	95.74%	
241Am, ug/g	0.076	0.208	

Table 12. Isotopic composition of concentration of the sludge samples 21GTE (east tank)

Subsample	Split 1	Split 2	
TOTAL Pu, ug/g,	312	300	
Isotopic composition	Atom%	Atom%	
238Pu	0.002	0.003	at detection limits
239Pu	98.45	98.45	
240Pu	1.54	1.54	
241Pu	0.002	0.002	at detection limits
242Pu	ND	ND	below detection limits
TOTAL U, ug/g,	18.37	20.70	
Isotopic composition	Atom%	Atom%	
234U	0.019%	0.018%	

235U	3.02%	2.96%	
236U	0.13%	0.13%	
238U	96.83%	96.89%	
241Am, ug/g	0.164	0.162	

Summary

Activity in the samples determined by counting methods was mainly from plutonium with very low levels from Am-241, and U-235. The TIMS results show that plutonium in all samples in 98.4 atom percent Pu-239 and 1.4 atom percent Pu-240 with very little (at detection limits) Pu-238 and Pu-241 (Tables 11 and 12). This is consistent with the data obtained by alpha spectrometry which determined that the samples were mostly Pu-239 with very little activity from Pu-238. Plutonium concentrations in two subsamples from 21GTW11-4948 were very different with values of 156 and 410ug/g (ppm). This indicates that the sample was not homogenized during transport and retained a heterogeneity that is likely present in the tank at this location. Subsamples from the east tank show consistent Pu concentrations consistent with observations that this sample appeared homogenized during transport.

Acid leaching and counting using liquid scintillation counting

Sludge samples from the east and West tanks were acid leached using 6.0 M nitric acid (HNO_3) and their radiological content determined by liquid scintillation counting. The acid leaching procedure was similar for all samples and each leach experiment was performed in triplicate or greater. The samples were equilibrated for times varying from 24 hours to 1 week. After equilibration the samples were centrifuged and aliquots from the supernatant were counted using Liquid Scintillation Counting (LSC) to determine total activity. Samples were sequentially leached three times using equal amounts of 6.0 M nitric acid, which resulted in essentially 100% Pu dissolution. The total activity was determined by addition of the activity released from each acid leach experiment.

Results

The data in Figure 2 show that the samples are very heterogeneous. The activity in individual samples varied from 0.3×10^6 CPM/g to 1.3×10^6 CPM/g. For all samples, the first acid leach experiment released most of the activity (average of 77% of the total activity); acid leach 2 released and average of 21% of the total activity and acid leach 3 released on average 2% of the activity. The weight loss resulting from the acid leach was minimal (0.035g/g) and did not correlate with the activity released from the sludge samples.

Ten samples from sludge sample 21-GTW (west tank) were sequentially leached three times using 6.0 M nitric acid. The activity released after each acid leach and the sludge weight loss were determined. The results are shown in Figure 3.

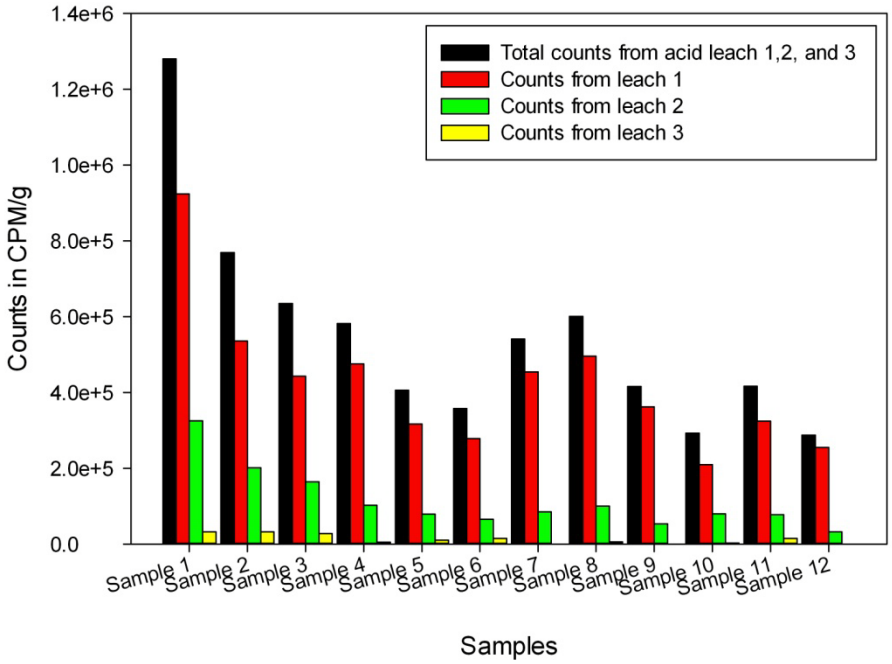


Figure 2. Data show the total activity released from the west tank (sample 4951) following three sequential acid leaching experiment using 6.0 M nitric acid along with the activity released from each individual leach experiment. The data were normalized to a per gram basis to allow comparison.

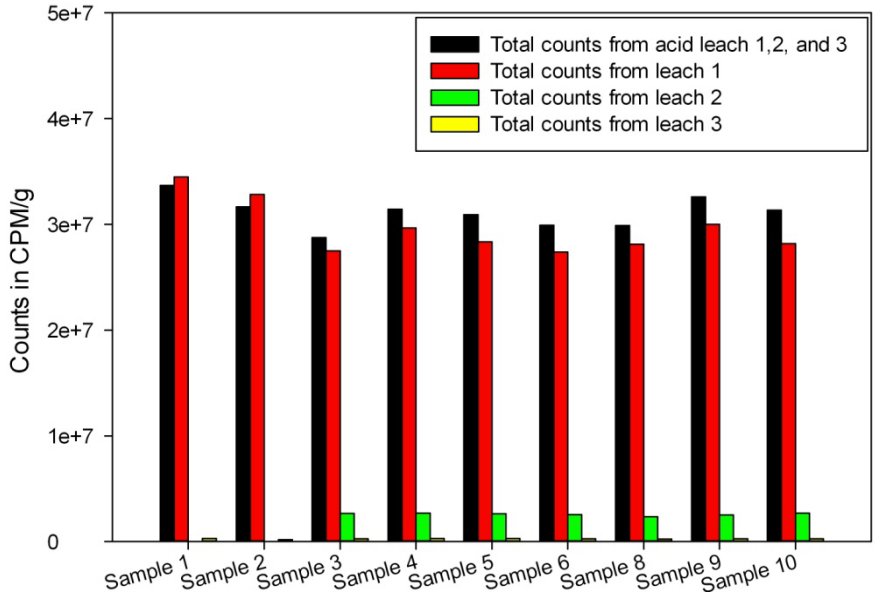


Figure 3. Plot of total activity released from the sample 21GTW (west tank) following three sequential acid leaching experiment using 6.0 M nitric acid. The plot also shows the activity released from each individual leach experiment. The data were normalized to a per gram basis to allow comparison.

The data show that the activity per gram is about two orders of magnitude greater than that from sample 4951 and all subsamples released similar activity with an average of about 3.1E7 cpm/g. Most of the activity was released in the first acid leach experiment. The weight loss resulting from the acid leach is more than 30% of original leached sludge.

Summary of Analytical Results

Our data show that most of the activity in the sludge samples is from Pu-239 (98.6 %) and Pu-240 (1.4%). Additional activity from ^{241}Am, ^{90}Sr, and ^{235}U is also present but does not contribute significantly to the total inventory. The plutonium concentration from samples analyzed by TIMS and in leaching studies is summarized in Table 13. Data presented in Figures 2 and 3 show concentrations in cpm/g for fully-saturated samples. These data were converted from cpm/g to Ci/g assuming 100% counting efficiency for the LSC measurements. The data are then corrected to Ci/g assuming an atom ratio of 98.6% ^{239}Pu and 1.4% ^{240}Pu. Finally, because the data presented in Figures 2 and 3 are for *fully-saturated* samples they are corrected to a dry mass basis; i.e. plutonium mass to mass of dry sample, by dividing by 0.64, which is the percentage of the solid mass in a saturated sample.

Table 13. Summary of all plutonium concentration data.

Sample ID	Plutonium concentration ug/g
4950	0.38*
4951	6.3*
4952	0.50*
4941	0.42*
21GTW	339* 156# 410#
21GTE	306#

*By LSC counting, #By Mass spectrometry

Plutonium is not distributed evenly in the samples. Samples 4950, 4951, 4952, and 4941 from the west tank all have lower plutonium concentrations compared to samples 21GTW and 21GTE. The sludge samples 21GTE and 21GTW have also the highest weight loss following acid digestion. We observed up to 30% weight loss in 6.0M nitric acid compared to 3.5 % or less obtained for sample 4951 and other samples with lower activity. Visually the samples with lower activity also contain higher percentages of soil grains. This is consistent with the weight loss measured during leaching experiments as the soil grains (quartz, feldspar, and clay) would not be readily soluble in 6.0M nitric acid, whereas a chemical precipitate would likely be readily dissolved. These data indicate that plutonium concentrations of samples from the west tank are impacted by dilution of sludge by soil material. Low plutonium concentrations in samples 4950, 4951, 4952, and 4941 are due to dilution by soil material. In contrast plutonium concentration data from 21GTW are considerably higher. This sample was taken by digging down below the soil material to get to fine-grained sludge material. Plutonium concentrations determined by

TIMS in this sample are still variable, likely reflecting some dilution by soil material. In contrast, the leaching data for this samples show relatively consistent concentrations. This method effectively leaches 100% of the plutonium in the sample, while leaving most of the soil grains undissolved, thus this the method targets the sludge material. The consistency of our data for 10 sample splits suggests that the value of 339ug/g represents a good average for plutonium concentration of the sludge. This value is in reasonable agreement with that from the east tank (21GTE) at 306ug/g, which does not appear to be contaminated with soil a contention that is also supported by the consistency of the plutonium concentrations from the two subsamples. We therefore believe that 339ug/g represents the best single value for plutonium concentration in the west tank.

VI. Inventory Estimation

Analysis of the plutonium concentration in the samples obtained during the 2010 sampling campaign shows a great distribution of activities for samples from the west tank between the different samples and also from splits of the same sample. Concentrations varied from no detect to 410 ug/g for the hottest samples. The east tank samples have relatively consistent plutonium concentrations. As discussed above, samples with lower plutonium concentrations are known to have been diluted with non-contaminated soil. The single sample (21GTW) with higher plutonium concentrations is considered to best represent the bulk of the sludge in the tank. Consistency of plutonium concentrations among 10 replicates in leaching experiments suggest that the average value of 339 ug/g best represents that average plutonium concentration in the west tank and is used to calculate the preferred inventory estimate (Table 14). Table 14 also presents an upper bound estimate of the west tank inventory using the highest plutonium concentration measured from the west tank (410 ug/g, Table 11). The sample 21GTE has relatively consistent plutonium concentrations and we use the average of these values to calculate the plutonium inventory for the east tank. These calculations assume that plutonium concentrations, density and porosity determined for samples 21GTE and 21GTW are representative of the entire sludge present in the tanks. The plutonium inventory calculation is performed as follows:

[Pu](ug/g) x sludge volume (cc) x sludge density (g/cc) x (1-porosity) x 0.000001g/ug

The total inventory for uranium and americium calculated using the formula above and using uranium and americium concentration data from Tables 11 and 12. The average value of splits 1 and 2 is used for the east tank. Results are given in Table 15.

Table 14. Plutonium inventory estimates in the General's Tanks. Density and porosity values are from Table 4.

	Sludge Volume (gal)	Sludge Volume (cc)	Sludge Mass (g)	Sludge Density (g/cc)	Sludge Porosity (%)	[Pu] (ug/g)	Total Pu (g)
East tank	640 327	2422656 1237826	2558102 1307030	1.84	43	306	783 397
West tank	1846	6987848	7224021	2.5	59	339 410	2428 2937

Table 15. Uranium and Americium inventory estimates in the General's Tanks.

	Sludge Volume (gal)	Sludge Volume (cc)	Sludge Mass (g)	[U] (ug/g)	Total U (g)	[Am] (ug/g)	Total Am (g)
East tank	640 327	2422656 1237826	2558102 1307030	19.5	50 25	0.163	0.414 0.212
West tank	1846	6987848	7224021	9.10 15.49	65 111	0.076 0.208	0.544 1.490

VII. Discussion of Uncertainties

Visual examination along with plutonium concentration data of samples obtained from the east tank suggest that the sludge in the tank is homogeneous and that the samples collected are representative of the average tank sludge. Porosity and density measurements made on east tank samples are relatively consistent and also support this contention. Combined errors from concentration, porosity and density measurements are all negligible compared to the error in the sludge volume, which vary by nearly 100%. This imparts the single greatest uncertainty in the estimate calculation for the east tank.

In contrast to samples from the east tank, samples from the west tank are heterogeneous and contain variable amounts of non-contaminated soil that flowed into the tanks from the surface during periods when the top was open. Although attempts were made to isolate the sludge in samples from the west tank it is likely that much of the variability in plutonium concentration, and density and porosity data is due to sample heterogeneity. If we make the assumption the two highest plutonium concentrations obtained (339 ug/g from leaching studies and 410 ug/g from TIMS) bracket concentrations for the west tank, then an average value of 375+/-19% ug/g (2 sigma) is obtained. No uncertainty is given in the sludge volume for the west tank (LANL 2011), yet there must be uncertainty in this value. For this calculation, a 10% (2 sigma) error is assumed for the sludge volume. Combining all uncertainties, a total uncertainty of approximately 27% (2 sigma) is obtained. We consider this as a minimum uncertainty of plutonium inventory in the west tank. Additional sampling of areas away from the existing opening is necessary to reduce this uncertainty.

VIII. References

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