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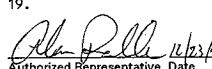
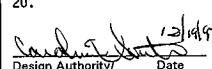
Page 1 of 1  
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## Tank 241-Z-361 Process and Characterization History

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Abstract: The history of the Plutonium Finishing Plant processes that sent waste to Tank 241-Z-361 is summarized. Documents reviewed include engineering files, laboratory notebooks from characterization efforts, and interviews of people. Records of transfers to the tank, past characterization efforts, and speculation were used to estimate the current condition of Tank 241-Z-361 and its contents.

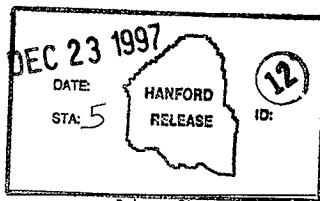
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## Tank 241-Z-361 Process and Characterization History

S. A. Jones

### Introduction

An Unreviewed Safety Question (Wagoner, 1977) was declared Tank 241-Z-361 in the 200W Area at Hanford. This document is a summary of the history of Tank 241-Z-361 through December 1997. Documents reviewed include engineering files, laboratory notebooks from characterization efforts, waste facility process procedures, supporting documents and interviews of people's recollections of 20 plus years ago. Records of transfers into the tank, past characterization efforts, and speculation will be used to estimate the current condition of Tank 241-Z-361 and its contents.

The Plutonium Finishing Plant was built in 1948 and began processing plutonium in mid-1949. The Incinerator (232-Z) operated from December 1961 until May 1973. The Plutonium Reclamation Facility (PRF, 236-Z) began operation in May 1964. The Waste Treatment Facility (242-Z) (Kasper, 1980) operated from August 1964 until August 1976. Waste from some processes went through transfer lines to 241-Z sump tanks. High salt and organic waste under normal operation were sent to Z-9 or Z-18 cribs.

The transfer lines to 241-Z were numbered D-4 to D-6. The 241-Z sump tanks were numbered D-4 through D-8. The D-4, 5, and 6 drains went to the D-6 sump tank. When D-6 tank was full it was transferred to D-7 tank. Prior to transfer to cribs, the D-7 tank contents were sampled. If the plutonium content was analyzed to be more than 10 g per batch, the material was (generally) sent to be reprocessed. Below the discard limit, caustic was added and the material was sent to the cribs via the 241-Z-361 settling tank where solids settled out and the liquid overflowed by gravity to the cribs.

Waste liquids that passed through the 241-Z-361 settling tank flowed from PFP to ground in the following sequence:

Processes → D-4, D-5, D-6 Drains → D-6 Sump Tank → D-7 or D-8 Sump Tank → 241-Z-361  
Settling Tank → Cribs

Each is discussed below.

### Processes

Waste going through 241-Z-361 was called "low-salt" waste consisted of large volumes of water containing relatively low concentrations of chemicals compared to the "high-salt" waste that went to Z-9 or Z-18. Process streams contributing to the low-salt waste are listed in Table 1.

Table 1. Low-salt Aqueous Process Streams in the Plutonium Finishing Plant

Stream	Source	Thousands of Gallons/Year	Plutonium Grams/Year	Chemical Contaminant
Uncontaminated lab wastes	Cooling equipment in labs	127	0	None
Contaminated lab wastes	Lab sink drains	174	100	Miscellaneous lab chemicals
Waste treatment aqueous waste	Ion exchange	86	60	Principally Al, Ca, Mg, nitrate
Incinerator scrubber solution	Spent caustic from scrubber	6	600	Considerable Na
Reclamation condensate	Process concentrators	54	12	Slight
Fluorinator off-gas jet	Water for vacuum jet	1906	100	hydrogen fluoride
total		2353	872	

Cooling water was simply sanitary water in closed lines that did not come in contact with chemicals or radioactive material.

Laboratory wastes constituted a very small portion of the total volume of wastes. While there may have been almost anything in that waste stream and there is virtually no information about it, the small volume coupled with large dilutions with the process streams make it unlikely to contain enough material to be of concern.

The incinerator burned a variety of materials including organic chemicals, paper and plastic. A caustic off-gas scrub solution was used to trap acid fumes, combustion products and fine particles. The incinerator operated intermittently from December 1961 to May 1973. In 1969, it was estimated that 600 grams of the 870 grams of plutonium sent to Z-12 were from the incinerator.

There is little known about reclamation condensate except that the chemical contaminants were considered "slight".

Fluorinator off-gas from hood HC-9B on the "Button Lines" contributed the largest volume of waste to D-6. It was also responsible for failure of D-6 due to corrosion. The HF concentration was approximately 0.06 M.

An estimate of the chemicals in the low salt waste from all sources in 1969 is given in Table 2.

Table 2. Chemicals from processes that discharged to low-salt waste in 1969.

Chemical	Weight/year	Chemical	Weight/year
Plutonium	870 g	Aluminum	96 kg
Calcium	320 kg	Sodium	7,394 kg
Magnesium	128 kg	Fluoride	6,100 kg
Manganese	13 kg	Nitrate	19,904 kg

## Drains

Table 3. Drains that fed into the D-6 tank in 241-Z (Rodgers 1991).

Drain	Area serviced
D4	Plutonium Chemistry Laboratory
D5	Analytical Laboratory - including film washing
D6	232-Z Incinerator
	234-5 Process - hood 9-B fluorinator off-gas
	236-Z PRF
	242-Z Waste treatment

## 241-Z Sump tanks

Neutralization of the acid wastes was initially accomplished by the addition of soda ash. Later sodium hydroxide was used to bring the pH up to 10. Still later it was found that a pH of 8 was better for immobilizing Pu in soil and the waste process was changed accordingly. Kasper stated in RHO-ST-44 "Occasionally, the wastes were only partially neutralized and were discharged slightly acidic."

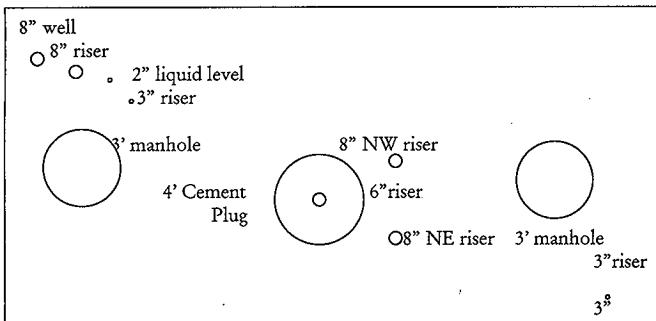
Procedures in the waste treatment facility manual called for addition of caustic to the D-7 tank, checking with alkoacid paper. If the paper was still red, more caustic was added. If the paper turned blue, tank contents were jettied to the settling tank and crib. In 1962, the sump tanks were assayed for plutonium hold up. The D-7 tank contained approximately 300 g of plutonium, which was removed by flushing the tank with nitric acid coupled with some mechanical scraping. Apparently, the acid flushes were sent directly to the settling tank.

## 241-Z-361 Settling Tank

The 241-Z-361 settling tank is 13' by 26' rectangular structure that is 17" deep at the influent end and 18" deep at the effluent end. Liquid entered 241-Z-361 through a baffled opening on the north end of the tank. The overflow to the cribs is at the south end at the 15' depth. The tank was constructed with 12" thick concrete walls, a layer of waterproofing, and a 3/8" thick carbon steel liner. Removal of all but about 800 liters of the supernate was completed May 1975. Photographs of the tank taken in 1975 showed that in the lower half of the tank the steel liner appears to have been corroded away with the waterproofing and concrete visible. This will contribute to the chemistry of the tank by adding iron from the dissolved liner. In addition, any concrete that reacts with the tank contents will raise the pH of acidic sludge.

There are eight penetrations into the tank visible from above ground. In addition, there is a 4' cement in the center of the tank cover, a 3' manhole at the north end, and a 3' manhole at the south end of the tank. These are illustrated in Figure 1.

Figure 1. 241-Z-361 Settling Tank Top View.



In March 1975, samples were taken through the north manhole. The liquid was analyzed as 0.0002 g/L Pu and pH 4 at the 14'3" level, 0.0006 g/L Pu and pH 4 at the 16'3" level, and sludge contained 0.91 g/L Pu and pH was very acid at the 18'3" level (Lundgren). All measurements were from the top of the riser.

The sludge in the tank was sampled five times in 1975 to 1977. The nonradioactive components that were analyzed are summarized in Table 4.

Table 4. Average Nonradioactive Elements in 241-Z-361 Sludge.

Chemical	Wt%	G/L
Al	11.99	0.222
Ca	18.11	0.335
Cd	0.05	0.001
Fe	12.50	0.232
Na	3.59	0.066
Si	0.45	0.008
O	5.94	0.110
H	1.64	0.030
C	3.60	0.067
Cl	1.85	0.034
F	0.21	0.004

Carbon analysis results have not been found except for a few samples. The carbon concentration

was as high as 6% of the sample. This could be as carbon from fly ash in the incinerator scrubber solution, carbonate from neutralization and absorption in to caustic solution, or from organic compounds. Most likely it is from a combination of all of these sources.

The bulk of the plutonium processed was weapons grade with an isotopic composition of approximately 93%  $^{239}\text{Pu}$ , 6%  $^{240}\text{Pu}$ , and 0.6%  $^{241}\text{Pu}$ . In the late 1960's, limited processing of fuel elements from power reactors occurred. The plutonium recovered from this fuel had a different isotopic composition estimated at 55%  $^{239}\text{Pu}$ , 25%  $^{240}\text{Pu}$ , and 15%  $^{241}\text{Pu}$ . The amount of  $^{241}\text{Pu}$  is directly related to the amount of  $^{241}\text{Am}$  that will be found in the tank. In cores drilled in the Z-12 crib, the nCi/g of  $^{239}\text{Pu}$  was approximated 4 times the nCi/g of  $^{241}\text{Am}$  in the mid-1970's. Stated another way, on average the plutonium contains approximately 0.45%  $^{241}\text{Am}$  by weight.

A sample of sludge taken from the settling tank in 1977 had the following isotopic distribution (Bouse 1977a): Isotope, Wt%,  $^{239}\text{Pu}$  0.00874%,  $^{239}\text{Pu}$  93.7%,  $^{240}\text{Pu}$  6.023%,  $^{241}\text{Pu}$  0.2335%,  $^{241}\text{Am}$ , 0.4758%. The sample was identified as NW-5 and was selected because it was the core segment with the highest plutonium concentration. Section 5 was at the 60 inch from bottom of tank level in a 90-inch segment. These values are consistent with the types of material that was processed in PFP.

Dressen (1976) and Dodd (1976) reported plutonium concentration from samples taken in 1975. The results are shown in Tables 5 and 6. The numbers reported by Dodd were corrected and reported again to be consistent with the calculation method used by Dressen. Examination of raw data in Dodd's notebook (Dodd 1975b) when compared to data later collected by Bouse indicates an error. Dodd filtered the sludge and measured the volume of liquid collected. This volume combined with a volume for solids calculated assuming a solid density of 2 g/cc was used to report a percent solids in the sludge. When Bouse measured the filtered liquid volume and the additional weight lost by the filtered solids upon drying, it was found that approximately an equal volume of liquid was trapped as was separated by filtration. Another corrected plutonium concentration was calculated and is presented in Table 6 with the results reported by Dodd (1976).

Table 5. Solids and Plutonium measurements in 241-Z-361 Sludge (Dressen).

Section #	Vol % solids	Pu Concentration g/L	
		in Solids	in Sludge
2	19.2	2.18	0.42
4	12.8	3.37	0.43
6	19.5	1.89	0.37
8	28.4	0.89	0.25
10	15.8	1.97	0.31
12	18.7	1.11	0.21
	avg.	1.90	0.33
	std dev	0.88	0.09

Table 6. Solids and Plutonium measurements in 241-Z-361 Sludge (Dodd).

Sample ID 361-Z-	Vol ml Filtrate	wt solids	Corrected vol% solids	Pu g/L dry solids	Corrected Pu in situ g/L	PPSL corrected vol % solids	PPSL corrected Pu in sludge g/L
3"-1-4	62	28.7	27.2	3.1	0.84	10.4	0.32
6"-1-2	32	22.8	27.0	1.9	0.52	15.1	0.29
6"-1-3	46	30.5	24.8			14.2	
6"-1-5	57	27.7	19.4	1.9	0.37	10.8	0.21
6"-1-6	45	25.1	21.9			12.2	0.00
6"-1-8	55	26.5	19.4	2.6	0.50	10.8	0.28
6"-1-9	48	31.8	24.9	3.0	0.75	14.2	0.43
6"-1-9 rerun	48	31.8	16.4	4.1	0.67	14.2	0.58
6"-1-11	50	19.6	16.4	2.6	0.43	8.9	0.23
6"-1-13	66	15.3	10.3			5.5	0.00
6"-1-16	37	14.8	16.7	2.4	0.41	9.1	0.22
1-3(10")	55	24.4	18.2	2.9	0.53	10.0	0.29
2-2(6")	128	86.0	25.1	1.5	0.38	14.4	0.22
2-4 (10")	110	62.8	22.2	2.8	0.62	12.5	0.35
3-3(10")	90	57.5	24.2	1.0	0.24	13.8	0.14
1-2	61	20.0	14.1			7.6	
1-5 (valve)	76	38.4	20.2	1.6	0.32	11.2	0.18
3-2	71	47.2	24.9			14.2	
3-5 (valve)	84	84.3	22.4	1.4	0.31	20.1	0.28
2-6 (valve)	73	48.7	25.0	2.6	0.65	14.3	0.37
4-2	85	63.9	27.4	1.6	0.43	15.8	0.25
4-3	64	37.1	22.5			12.7	
4-5 (valve)	86	85.3	33.4	0.5	0.15	19.9	0.09
3-5 (valve)	36	34.3	32.3	1.8	0.58	19.2	0.35
4-3	43	40.6	32.1	0.8	0.24	19.1	0.14
4-5 (valve)	45	75.3	45.5	1.2	0.56	29.5	0.37
4-4	42	39.4	31.9			19.0	
3-1	52	16.6	13.8			7.4	
3-3	43	41.0	32.3	1.1	0.37	19.2	0.22
3-4	42	15.7	15.7			8.6	0.00
4-1	43	16.2	15.9			8.6	0.00
3 B	48	28.5	22.8	2.7	0.62	12.9	0.35
3 B rerun	48	28.5	22.8	2.4	0.54	12.9	0.31
5 B	48	29.0	23.2	2.9	0.67	13.1	0.38
7 B	56	28.0	20.0	3.0	0.61	11.1	0.34
7 B rerun	56	28.0	20.0	8.6	1.71	11.1	0.95
7 B rerun	56	28.0	20.0	10.5	2.10	11.1	1.17
13B	72	29.8	17.1	2.8	0.47	9.4	0.26
15 B	64	18.4	11.1	1.9	0.21	6.7	0.12
avg.			22.58		0.58	13.10	0.29

Table 6. Sludge sample results from 1977 North West sampling (Bouse).

	Dried Solids Density (g/L)	Pu Solids (g/L)	Volume % Solids in Sample	Pu in Sludge (g/L) based on dried	Pu g/L sludge (NDA)	Wet analysis/NDA
NW-1	2.08	1.02	9%	0.09	0.27	0.32
NW-2	1.86	0.84	11%	0.10	0.29	0.33
NW-3	2.17	0.86	13%	0.12	0.35	0.33
NW-4	2.50	1.00	13%	0.13	0.25	0.54
NW-5	1.69	0.87	36%	0.32	0.60	0.52
NW-6	1.63	1.20	27%	0.32	0.23	1.44
NW-7	1.79	1.15	15%	0.18	0.59	0.30
NW-8	2.17	1.27	11%	0.14	0.18	0.77
NW-9	1.56	0.62	35%	0.22	0.37	0.59
NW-10	1.50	0.74	32%	0.24	0.28	0.84
NW-11	1.56	0.41	31%	0.13	0.20	0.63
NW-12	1.71	0.54	31%	0.17	0.17	0.99

The sludge contained layers of different material. These are described for the 1977 sludge samples in Table 7.

Table 7. Sample descriptions for 1977 Sludge sample.

	Sample Description
NW-1	Dark Brown -almost Black - loose -wet
NW-2	Color of Sample 1 - thicker
NW-3	Small amount of free liquid on top Color of sample 1 - thicker than 2
NW-4	Dark brown -lighter than 2- thinner
NW-5	Lighter color than 4 - very watery - thin soup
NW-6	Thicker than 5 - lighter color than 5 - gritty - sandy
NW-7	Thicker than 6 - dark tank color - pasty, creamy consistency
NW-8	same a 7 except lighter color
NW-9	Free liquid on top - only slightly darker color than 8 - same consistency
NW-10	same as 9
NW-11	tan-brown Same at 10 - slightly a darker
NW-12	Lot of liquid on top. Lt. brown darker than 5 above samples

**Crib**s

When the settling tank was filled to the overflow level, the liquid flowed by gravity to one of the cribs. Composition of the material in the settling tank can be inferred from descriptions of material being sent to the cribs. Routing to Z-1A appears to have changed between 1959 and 1964. Up until 1959, the overflow from Z-1, 2, and 3 went to Z-1A. When those cribs were taken out of service, Z-1A was not used for 5 years. When Z-1A was extended and put back in service in 1964, it is believed there was a waste route that did not include the 241-Z-361 settling tank.

Table 8. Cribs receiving waste from 241-Z (Knight).

Number	Description	Use From	Use To	Status
216-Z-1	231-Z, 234-5 Cooling Water Ditch	12/44	3/59	Terminated - Backfilled
216-Z-1	D-6 Waste	6/49	4/69	Terminated
	U	3/68	5/68	
216-Z-1A	Overflow from Z- 1, 2 and 3	6/49	3/59	Replaced by Z-12
	Reclamation Waste	6/64	3/69	Replaced by Z-18
216-Z-2	D-6 Waste	4/49	6/52	Replaced by Z-3
	Reclamation Waste	6/52	5/66	Terminated
	CAW	5/66	6/66	Temporary routing
216-Z-12	D-6 Waste	6/52	5/73	Inactive

## Conclusions

The tank carbon steel liner has been dissolved through corrosion. This was evident from photographs in 1975.

Some degradation of the concrete tank has occurred, but is most of the concrete remains in tact.

There is no separate organic phase in the tank. Organic compounds in the waste possibly include carbon tetrachloride (CCl<sub>4</sub>), tributyl phosphate (TBP), lard oil (triolein), and various complexants and solvents from the laboratories. The volatile compounds such as CCl<sub>4</sub> may have been steam distilled from the waste during the steam jetting transfer from the 241-Z sump tanks to the cribs. Folklore has it that steam rose from the settling tank during the transfers. Nonvolatile organic compounds were a very small portion of a large volume of waste. These would likely be distributed through the waste. A separate organic phase is not expected.

The plutonium in the tank has not migrated or segregated

Layers that were observed in samples of the sludge will still be stratified. There is no mechanism for mixing in the tank. The solids settled over many years and are expected to remain in the layered configuration.

Some drying of the sludge has occurred, but the volume of the sludge has not decreased significantly. The tank was blanketed off in 1973. Supernate liquid was pumped from the tank and the tank was sealed. There is no active ventilation. The tank is expected to breathe through loose-fitting covers. The contents are not generating much heat, so the sludge is not expected to be dry.

The tanks sludge may contain some or all of the components listed in Table 9. This list is based on the processes that were known or suspected to send waste to 241-Z-361 and analyses of the nonradioactive components in the tank.

Table 9. Known and Probable Components of 241-Z-361 Tank Sludge.

Type of Component	Component	Probable Source
Known Metals	Al	Waste Treatment
	Na	Incinerator Off-gas Treatment
	Ca	Waste Treatment
	Si	Incinerator Off-gas Treatment
	Cd	Most likely Analytical Artifact
Known Non-Metals	F	Hydrogen Fluorinator
	Cl <sup>-</sup>	Waste Treatment
	C (organic or total?)	Incinerator Off-gas Treatment
	H <sub>2</sub> O	All
	H <sup>+</sup>	All
Probable Metals	Pb	Incinerator Off-gas Treatment
	Mg	Waste Treatment
	Mn	Waste Treatment
	Cr	Corrosion of SS Equipment
	Ni	Corrosion of SS Equipment
	Ag	Lab Film Processing
Probable Non-Metals	NO <sub>3</sub> <sup>-</sup>	Waste Treatment
	NO <sub>2</sub> <sup>-</sup>	Radiolysis of NO <sub>3</sub> <sup>-</sup>
	SO <sub>4</sub> <sup>2-</sup>	Waste Treatment
	PO <sub>4</sub> <sup>3-</sup>	Degradation of TBP
	CO <sub>3</sub> <sup>2-</sup>	Incinerator Off-gas Treatment
Probable Organics	CCl <sub>4</sub>	Waste Treatment
	DBBP	Waste Treatment
	TBP	Waste Treatment
	DBP	Degradation of TBP
	MBP	Degradation of TBP
	Butanol	Degradation of TBP
	Urea	Incinerator Off-gas Treatment
	Lard Oil (Triolein)	Waste Treatment
	Oxalic Acid	Waste Treatment
	Acetic Acid	Incinerator Off-gas Treatment
Known Radionuclides	Benzene	Incinerator Off-gas Treatment
	Phthalic Acid	Incinerator Off-gas Treatment
	Pu	All
	Am	Decay of Pu <sup>241</sup>
	U	Waste Treatment

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