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**ESTIMATED INVENTORY OF CHEMICALS ADDED
TO UNDERGROUND WASTE TANKS, 1944 THROUGH 1975**

G. K. Allen

March 1976

**PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT
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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	3
SUMMARY	3
DISCUSSION	4
WASTE GENERATION	4
The Bismuth Phosphate Process	5
The Uranium Recovery Process	5
The Redox Process	10
The Purex Process	11
The Waste Fractionization Process	14
WASTE MEASUREMENT	15
Sludges	15
Salt Cakes	15
Actinide Elements	19
RELATIVE CHEMICAL TOXICITY	20
REFERENCES	24
ACKNOWLEDGEMENTS	25

LIST OF TABLES

Table I, Total Estimated Hanford Waste Tank Chemicals	6,7
Table II, Theoretical Bismuth Phosphate Sludge	9
Table III, Theoretical Uranium Recovery Sludge	10
Table IV, Theoretical Redox Sludge	11
Table V, Total Consumed Chemicals of the Thorium Campaigns	12
Table VI, Theoretical Purex Sludge	14
Table VII, Redox Sludge Samples	16
Table VIII, Purex Sludge Samples	17
Table IX, 242-S Salt Cake Samples	18
Table X, ITS Salt Cake Samples	19
Table XI, Tank Farm Actinide Contents	20
Table XII, Toxicity of Chemicals	22
Table XIII, Relative Toxicity of Hanford Tank Farm Chemicals	23

LIST OF FIGURES

Figure 1, Bismuth Phosphate - Uranium Recovery Flow Diagram	8
Figure 2, Purex B-Plant Flow Diagram	13

ESTIMATED INVENTORY OF CHEMICALS ADDED TO UNDERGROUND WASTE TANKS, 1944 THROUGH 1975

INTRODUCTION

The objective of the salt cake and sludge characterization program is to define the quantities and concentrations of materials stored in the Hanford underground waste tanks. The current uses foreseen for this characterization information include: an evaluation of salt cake acceptability for interim storage; an inventory of the physical properties influencing waste solids retrieval and interstitial liquid removal, and a definition of feed materials for waste volume reduction and final solidification studies. Special equipment has been designed to allow sampling of the entire solids profile depth in a tank while preserving the physical properties of the sample. It is planned to extract at least one solid core sample, in several segments, from the entire solids depth of each underground storage tank. These core samples will be analyzed to determine the chemical composition and the physical properties of the solids.

An estimate of the expected chemical composition would assist effective utilization of analytical effort by allowing concentration of effort on those constituents of greatest importance. An anticipated solids chemical composition could save laboratory time trying to analyze trace chemicals and would give an expected concentration range of the solid chemicals. The relative chemical toxicity could be used in establishing a chemical analysis priority and the level of accuracy needed for analysis. This document presents the results of a study that estimates the total chemicals sent to underground storage.

SUMMARY

The five major chemical processes, the Bismuth Phosphate process, the Uranium Recovery process, the Redox process, the Purex process, and the Waste Fractionization process have each contributed to give the total Hanford waste chemicals. Each of these processes are studied to determine the total estimated chemicals stored in underground waste tanks. The chemical contents are derived mainly from flowsheet compositions and recorded waste volumes sent to underground storage. The major components and amounts of Hanford waste are sodium hydroxide - 230 million gram - moles (20 million pounds), sodium nitrate - 1400

million gram-moles (270 million pounds), sodium nitrite - 220 million gram-moles (34 million pounds), sodium aluminate - 400 million gram-moles (72 million pounds), and sodium phosphate - 87 million gram-moles (31 million pounds).

Sludges and salt cakes, the two types of solids contained in Hanford underground storage each have a characteristic chemical composition. Chemical analyses of the sludge and salt cake samples are tabulated to determine the chemical characteristics of the solids. Sludge analyses indicate Redox sludge to contain primarily iron, nitrate, and aluminum compounds. Purex sludge is composed primarily of iron and aluminum compounds. The salt cake samples taken from the in-tank solidification units, the 242-T atmospheric evaporator, and the 242-S Evaporator-Crystallizer are composed primarily of sodium nitrate with varying minor amounts of sodium phosphate, sodium carbonate, and sodium nitrite.

A relative chemical toxicity of the Hanford underground waste tank chemicals is developed from maximum permissible chemical concentrations in air and water. The amount of air or water required to dilute each tabulated chemical to the maximum permissible concentration is calculated as a percentage of the total amount of air or water required to dilute all tabulated chemicals to their maximum permissible concentrations. This system enables the reader to tell at a glance which Hanford waste chemicals are the most toxic in relationship to each other. If drinking water standards set toxic limits, the most toxic chemicals are sodium phosphate - 35 percent, sodium aluminate - 28 percent, and chromium hydroxide - 19 percent. If air standards set toxicity limits, the most toxic chemicals are bismuth - 41 percent, chromium hydroxide - 23 percent, and fluoride - 10 percent.

DISCUSSION

WASTE GENERATION

Five major processes have been operated at Hanford: The Bismuth Phosphate process, the Uranium Recovery process, the Redox process, the Purex process, and the Waste Fractionization process. The bulk of chemicals stored in underground tanks as radioactive waste are a result of one of these five processes. A total chemical inventory in underground storage is estimated by studying each of the five processes to determine the quantity and type of chemicals that were sent to underground storage. Chemical flowsheet compositions and recorded waste volumes comprise the main source of information. [REDACTED] Approximate gallons for planning purposes are used where recorded waste volumes were unavailable.

Other chemicals used nonroutinely and not included in flowsheet compositions are taken from essential material consumption records. This method gives a total estimated Hanford waste tank chemicals as shown in Table I.

The total waste solution found by the above outlined methods is then used to predict theoretical sludges formed from the processes. The results can be used to predict compositions and volumes of the different types of process sludges. When available, actual sludge samples and volumes are used to check the calculational method of the theoretical volumes and compositions.

The Bismuth Phosphate Process

The Bismuth Phosphate process operated between 1944 and 1956 in the 221-B and 221-T Buildings. Four major waste streams were sent to underground tanks: coating waste, metal waste, first cycle waste, and second cycle waste. A simplified flow diagram is shown in Figure 1. The metal waste chemicals, recovered from the tanks and processed in the Uranium Recovery Plant, are included in the discussion of the Uranium Recovery process. The total stored underground waste chemicals for the Bismuth Phosphate process is estimated from the flowsheet chemical compositions and recorded volumes.

No Bismuth Phosphate process solid samples are available, but an approximate volume and composition can be obtained from component solubility data. The sludge volume can be estimated from the assumption that the bulk density of the precipitate will be 50 percent of the particle density. It is also assumed that all silicon, chromium, iron, zirconium, bismuth, cerium, and phosphate compounds precipitate. As the exact precipitation point of sodium aluminate is not known in Hanford waste solution, it is assumed that the fraction of aluminum precipitated from Bismuth Phosphate process solutions was the same as the fraction of aluminum precipitated from Purex solutions.

Results of these calculations and their assumed sludge chemical species are shown in Table II.

Table II shows the major component of a Bismuth Phosphate process solid, 80 percent by volume, to be sodium phosphate with a theoretical solids volume of 1.3 million gallons. Total theoretical Bismuth Phosphate process solid volume is estimated at 1.5 million gallons.

The Uranium Recovery Process

The Uranium Recovery process operated between 1952 and 1957 in the 221-U Building. This process generated only one type of waste from the processing of the Bismuth Phosphate process metal waste solution.

TABLE IA⁽¹⁾

TOTAL ESTIMATED HANDED WASTE TANK CHEMICALS

COMPOUND NAME ⁽²⁾	10 ⁶ GM-MOLES				TOTAL
	EUPEX	REDOX	BIPPO ₄	U REC	
NaNO ₃	41	20	100	610	1400
NaAlO ₂	240	110	55	--	400
NaNO ₂	170	11	57	--	220
NaOH	--	NOT BROKEN DOWN BY GROUPS			200 ⁽³⁾
Na ₂ PO ₄	0.6	--	56	50	10
Na ₂ CO ₃	27 ⁽⁴⁾	24	7	19	54
Na ₂ SO ₄	19	--	--	--	19
Fe ³⁺	12	1	4	4.5	21
NaI	17	--	--	--	19
Na ₂ CO ₃ (b)	9	--	--	--	9
Na ₂ SiO ₃	--	0.03	1	--	11
Na ₂ C ₂ O ₄	--	5	--	--	5
Ca ²⁺	--	2.2	0.1	--	3
H ₂ SO ₄	--	--	.9	--	.9
Na ₂ CO ₃ (c)	3	--	--	--	3.5
Na ₂ CO ₃ (d)	2.3	0.41	0.04	--	2.7
Na ₂ CO ₃ (e)	2.7	--	--	--	2.7
Ca ²⁺	--	--	.4	--	2.1
CaCO ₃	0.75	--	--	1.	1.75
Na ₂ CO ₃	--	--	--	1.5	1.5
Na ₂ CO ₃ (f)	--	--	--	1.	1
BIPPO ₄	--	--	1.	--	1
Cl ⁻	--	--	--	1.	1
MnO ₂	1.7	--	--	--	1.7
EDTA (g)	0.57	--	--	--	0.57
Na ₂ CO ₃	--	--	--	0.12	0.12
Fe	0.1	0.10	--	--	0.2
Fe(NO ₃) ₃	--	--	--	0.16	0.16
Fe(NO ₃) ₂	0.04	--	--	--	0.04
Fe(NO ₃) ₃	0.03	--	--	--	0.03
Pb(NO ₃) ₂	NOT BROKEN DOWN BY GROUPS				4.2 x 10 ⁻³
AgNO ₃	NOT BROKEN DOWN BY GROUPS				7.3 x 10 ⁻³
Cd(NO ₃) ₂	1.9 x 10 ⁻³	--	--	--	1.9 x 10 ⁻³
P ₂ O ₅ .24H ₂ O.44H ₂ O ⁽⁵⁾	3.6 x 10 ⁻³	--	--	--	3.6 x 10 ⁻³
Hg(NO ₃) ₂	4.5 x 10 ⁻³	4.8 x 10 ⁻³	--	--	5 x 10 ⁻³

TOTAL TRANSURANIC ELEMENTS IN TANK FARM⁽⁵⁾ (Pg)

Pu	240,000
Am	5,200
Pu	240
Th	13,000
Np	38

(1) Refer to Table 1b for chemicals in pounds

(2) Compound may not be in tabulated form in waste tank

(3) 100% hydroxide taken from Reference 6

(4) Chemicals consumed in B Plant

(5) 6.1 x 10⁶ gm-moles consumed in B PlantHO.CH₂.CO₂H = Hydroxyacetic AcidH₃C₆H₅O₇ = Citric AcidP₂O₅.24H₂O.44H₂O = Phosphotungstic acid

TABLE 1B

TOTAL ESTIMATED HANFORD WASTE TANK CHEMICALS

$\longleftrightarrow 10^6 \text{ POUNDS} \longleftrightarrow$					
COMPOUND ⁽¹⁾	PUREX	REDOX	BiPO ₄	U REC	TOTAL
NaNO ₃	10	70	35	150	270
NaAlO ₂	43	19	9.5	--	72
NaNO ₂	26	1.7	5.6	--	34
NaOH	NOT BROKEN DOWN BY SOURCE				20 ⁽²⁾
Na ₃ PO ₄	0.21	--	13	18	31
Na ₂ SO ₄	8.5 ⁽⁴⁾	0.74	1.6	6.1	17
Na ₂ CO ₃	4.5	--	--	--	4.5
Fe ⁺³	1.4	0.15	0.42	0.6	2.6
NaF	1.6	0.20	--	--	1.8
HO·CH ₂ CO ₂ H ⁽³⁾	1.5	--	--	--	1.5
Na ₂ SiO ₃	2.4	0.01	0.49	--	2.8
Na ₂ Cr ₂ O ₇	--	2.9	--	--	2.9
Cr ⁺³	--	0.39	0.04	--	0.43
SiF ₆ ⁻²	--	--	1.2	--	1.2
H ₃ C ₆ H ₅ O ₇ ⁽³⁾	1.4	--	--	--	1.4
ZrO ₂ ·2H ₂ O	0.83	0.11	0.01	--	0.95
HEDTA ⁽³⁾	2.1	--	--	--	2.1
Ce ⁺³	--	--	0.73	--	0.73
CaCO ₃	0.17	--	--	0.41	0.57
NiSO ₄	--	--	--	0.50	0.50
Na ₄ Fe(CN) ₆	--	--	--	0.87	0.87
BiPO ₄	--	--	0.83	--	0.83
Cl ⁻	--	--	--	0.09	0.09
MnO ₂	0.32	--	--	--	0.32
EDTA ⁽³⁾	0.48	--	--	--	0.48
SrNO ₃	--	--	--	0.14	0.14
KF	0.02	0.02	--	--	0.04
K ₄ Fe(CN) ₆	--	--	--	0.13	0.13
Fe(NH ₂ SO ₃) ₆	0.02	--	--	--	0.02
KMnO ₄	0.01	--	--	--	0.01
Pb(NO ₃) ₂	NOT BROKEN DOWN BY SOURCE				0.31
AgNO ₃	NOT BROKEN DOWN BY SOURCE				0.03
Cd(NO ₃) ₂	0.01	--	--	--	0.01
P ₂ O ₅ ·24WO ₃ ·44H ₂ O ⁽³⁾	0.05	--	--	--	0.05
Hg(NO ₃) ₂	3.2×10^{-3}	3.5×10^{-4}	--	--	3.6×10^{-3}

TOTAL TRANSURANIC ELEMENTS IN TANK FARMS (LBS.)

U	1.8×10^6
²³⁵ U	1.2×10^4
Pu	540
Th	2.9×10^4
Np	84

(1) Compound may not be in tabulated form in waste tanks

(2) Total hydroxide taken from Reference 6

(3) Chemicals consumed in B Plant

(4) 1.9×10^5 pounds consumed in B PlantHO·CH₂·CO₂H = Hydroxyacetic AcidH₃C₆H₅O₇ = Citric AcidP₂O₅·24WO₃·44H₂O = Phosphotungstic Acid

Figure 1
Bismuth Phosphate - Uranium Recovery
Flow Diagram

TABLE II

THEORETICAL BISMUTH PHOSPHATE SLUDGE

COMPOUND	POUNDS	BULK DENSITY* (GM/CM ³)	GALLONS	AMOUNT ASSUMED PRECIPITATED, PERCENT
Na ₃ PO ₄	1.3 x 10 ⁷	1.27	1.2 x 10 ⁶	100
Na ₂ SiO ₃	1.7 x 10 ⁶	1.2	1.7 x 10 ⁵	100
Ce(OH) ₃	7.3 x 10 ⁵	2	4.4 x 10 ⁴	100
NaAlO ₂	1.9 x 10 ⁵	1.2	1.9 x 10 ⁴	2
Fe(OH) ₃	4.2 x 10 ⁵	1.7	3.0 x 10 ⁴	100
BiPO ₄	8.3 x 10 ⁵	3.16	3.1 x 10 ⁴	100
Cr(OH) ₃	4.0 x 10 ⁴	2	2.4 x 10 ³	100
ZrO ₂ .2H ₂ O	1.0 x 10 ⁴	1.63	7.4 x 10 ²	100
Total			1.5 x 10 ⁶	

*Assumed 50 percent solids voids.

The total Uranium Recovery process stored underground waste chemicals is estimated from flowsheet chemical compositions and recorded volumes. A scavenging process which precipitated strontium and cesium was used on most of the Uranium Recovery process waste solutions. Scavenging chemicals, not included in the flowsheet compositions, are included in the total chemicals for the process.

No Uranium Recovery process solid samples are available, but the same method used in calculating Bismuth Phosphate solids compositions previously is employed here also. Chemicals assumed to precipitate completely include: iron hydroxide, nickel hydroxide, nickel ferrocyanide, calcium carbonate, and sodium phosphate. Potassium ferrocyanide and sodium ferrocyanide, used in the scavenging process, reacted with nickel and precipitated as nickel ferrocyanide. Assuming the solids are 50 percent voids, the total volumes of each chemical and the total solid volume is shown in Table III.

TABLE III

THEORETICAL URANIUM RECOVERY SLUDGE

<u>COMPOUND</u>	<u>POUNDS</u>	<u>BULK DENSITY (GM/CM³)</u>	<u>GALLONS</u>	<u>AMOUNT ASSUMED PRECIPITATED, PERCENT</u>
Na ₃ PO ₄	1.8 x 10 ⁷	1.27	1.7 x 10 ⁶	100
Ni ₂ Fe(CN) ₆	1.1 x 10 ⁶	0.95	1.3 x 10 ⁵	100
Fe(OH) ₃	6.0 x 10 ⁵	1.7	4.2 x 10 ⁴	100
CaCO ₃	4.1 x 10 ⁵	1.47	3.3 x 10 ⁴	100
Total			1.9 x 10 ⁶	

*Assumed 50 percent solids voids.

Table III shows the major component of the Uranium Recovery sludge, 89 percent by volume, to be sodium phosphate with a theoretical solids volume of 1.7 million gallons. Total theoretical Uranium Recovery process solids volume is estimated at 1.9 million gallons. The actual volume of scavenged solids from BY Tank Farm is approximately two million gallons. The close agreement between the actual sludge volume and the theoretical sludge volume demonstrates the validity of this method of predicting solids.

The Redox Process

The Redox Process operated between 1952 and 1966 in the 202-S Building. Two types of waste were sent to underground storage; coating waste and Redox high level waste. The total stored underground waste chemicals for the Redox Process is estimated from chemical flowsheet compositions and recorded waste volumes.

A theoretical volume and composition of Redox sludge is calculated by methods similar to those used calculating Bismuth Phosphate and Uranium Recovery sludges. Virtually all chromium, zirconium, iron, and silicon compounds are expected to precipitate. The fraction of nitrate and aluminate compounds precipitated, a function of solution composition and storage conditions, cannot be predicted with great accuracy. But by using Redox sludge samples as a basis for establishing precipitation points of aluminum and nitrate compounds, a theoretical sludge is determined. It is assumed all iron hydroxide is precipitated from the Redox wastes. Iron to aluminate and iron to nitrate ratios from Redox sludge samples

(Table VII) were used to calculate the sodium aluminate and sodium nitrate that precipitated from the flowsheet composition. Chemicals assumed to precipitate fully include silicon, iron, chromium, and zirconium compounds. Approximately eight percent of the nitrate and five percent of the aluminate compounds are expected to precipitate. A summary of the type of solids calculated from flowsheet compositions is shown in Table IV.

TABLE IV

THEORETICAL REDOX SLUDGE

<u>COMPOUND</u>	<u>POUNDS</u>	<u>BULK DENSITY*</u> <u>(GM/CM³)</u>	<u>GALLONS</u>	<u>AMOUNT ASSUMED</u> <u>PRECIPITATED, PERCENT</u>
NaAlO ₂	9.5 x 10 ⁵	1.2	9.5 x 10 ⁴	5
NaNO ₃	5.6 x 10 ⁶	1.13	5.9 x 10 ⁵	8
Na ₂ SiO ₃	1.0 x 10 ⁴	1.2	1.0 x 10 ³	100
Cr(OH) ₃	6.2 x 10 ⁶	2	3.7 x 10 ⁵	100
Fe(OH) ₃	1.5 x 10 ⁵	1.7	1.1 x 10 ⁴	100
ZrO ₂ ·2H ₂ O	1.1 x 10 ⁵	1.63	8.1 x 10 ³	100
Total			1.1 x 10 ⁶	

*Assumed 50 percent solids voids.

Table IV shows the major component of a Redox process solid, 54 percent by volume, to be sodium nitrate with a theoretical solids volume of 590,000 gallons. Total theoretical Redox process solids volume is estimated at 1.1 million gallons. The actual volume of Redox sludge in S, SX, and U Farms, 3.5 million gallons, does not agree well with the theoretical 1.1 million gallons. Two possible explanations can be found for this discrepancy. The Redox high level waste was self boiling which would tend to precipitate additional solids. Also, a minor change in the iron to aluminum and iron to nitrate ratios from the Redox sludge samples will make a significant increase in the volume of predicted solids.

The Purex Process

The Purex process operated between 1957 and 1973 in the 202-A Building. Three types of waste were sent to underground storage; coating waste (CW), organic wash waste (OWW), and boiling waste (CAW or IWW). Two types of coating waste

were also discharged by the Purex process; aluminum and zirflex. A simplified flow chart of the process waste route is shown in Figure 2. The total stored underground waste chemicals is derived from several sources. The CW chemicals are taken from flowsheet compositions and recorded volumes. The OWW chemicals are derived from flowsheet compositions and approximate gallons OWW per gallon CW. The IWW chemicals are taken from flowsheet compositions and approximate gallons IWW per ton uranium processed. Various chemicals found in Purex sludge not included in IWW flowsheet compositions are also included in the total chemicals. Chemicals not appearing in flowsheet chemical compositions either because the concentration was so small or the chemical was only used for a short period of time are also included in the total. Mercuric nitrate, used for iodine suppression, and cadmium nitrate solution, used as a soluble neutron poison during the transfer of rework solutions are minor chemicals not included in flowsheets. Other nonflowsheet chemicals used include lead nitrate and silver nitrate. These chemical amounts are obtained from purchase or receiving orders.

Two major thorium campaigns ran during the Purex operation; the first in 1966 and the second in 1970. Although these campaigns are considered major, the amount of chemicals used is inconsequential when compared to the total Purex process chemicals. The total chemicals used, from essential material requirements, are shown in Table V (references 2, 3). They are also included in the total Purex chemicals in Table I.

TABLE V
TOTAL CONSUMED CHEMICALS OF THE
THORIUM CAMPAIGNS

<u>CHEMICAL</u>	<u>GRAM-MOLES USED</u>	<u>POUNDS USED</u>
NaNO_3	2.5×10^6	4.7×10^5
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}^*$	1.5×10^5	1.3×10^5
KF	1.8×10^5	2.3×10^4
$\text{Fe}(\text{NH}_2\text{SO}_3)_2$	3.9×10^4	2.1×10^4
H_3PO_4	1.3×10^5	2.8×10^4
KMnO_4	3.5×10^4	1.2×10^4
HNO_3	3.0×10^5	4.2×10^6
Na_2CO_3	7.0×10^6	1.6×10^6

*Shown as NaAlO_2 in Table I.

*Current acid wastes and 1WW wastes are the same, but reach B Plant through alternate routes.

Figure 2
Purex - B Plant Flow Diagram

A theoretical volume and composition of Purex sludge can be calculated by the same method used previously. All iron, manganese, silicon, zirconium, and phosphate compounds are assumed to precipitate completely. The fraction of sodium aluminate that precipitates is derived by using the Purex sludge analyses as a basis. Iron was assumed to precipitate completely. The iron to aluminum ratio in Purex sludge was then used to establish the theoretical amount of sodium aluminate that precipitates as sludge. A summary of the composition of Purex process solids expected from flowsheet compositions is shown in Table VI.

TABLE VI

THEORETICAL PUREX SLUDGE				
COMPOUND	POUNDS	BULK DENSITY* (GM/CM ³)	GALLONS	AMOUNT ASSUMED PRECIPITATED, PERCENT
Fe(OH) ₃	1.4 x 10 ⁶	1.7	1.0 x 10 ⁵	100
MnO ₂	3.3 x 10 ⁵	2.5	1.6 x 10 ⁴	100
Na ₂ SiO ₃	2.4 x 10 ⁶	1.2	2.3 x 10 ⁵	100
NaAlO ₂	1.5 x 10 ⁶	1.2	1.5 x 10 ⁵	2
ZrO ₂ ·2H ₂ O	8.3 x 10 ⁵	1.63	6.1 x 10 ⁴	100
Na ₃ PO ₄	2.1 x 10 ⁵	1.27	2.0 x 10 ⁴	100
Total			5.8 x 10 ⁵	

*Assuming 50 percent solids voids.

Table VI shows the major chemicals comprising a Purex process solid to be iron hydroxide, sodium silicate, and sodium aluminate with a total theoretical Purex process sludge of 586,000 gallons. The actual volume of Purex sludge before the sluicing program began was 686,000 gallons. The theoretical volume and actual volume and the theoretical composition and actual composition are in close agreement with each other which establishes the validity of the predictive method.

Waste Fractionization

The Waste Fractionization process, started in 1968, operates in the 271-B building. The cesium-strontium removal process does not significantly add chemicals to the processed wastes, but there are a few specialized chemicals used in B Plant which should be included in the total waste inventory. These chemicals, appearing under the Purex heading in Table I, include phosphotungstic acid, HEDTA, EDTA, hydroxyacetic acid, citric acid, and sodium sulfate. The chemical amounts were taken from B Plant consumption records.

WASTE MEASUREMENTS

Two basic types of solids are contained in Hanford waste tanks; sludge and salt cake. Sludge is formed when solids precipitated from liquid waste upon standing. Salt cake has been formed by three basic evaporation processes; the In-Tank Solidification (ITS) units, the 242-T Atmospheric Evaporator, and the 242-S Evaporator-Crystallizer. This section summarizes the present analytical data available for each of these types of solids.

Sludges

Each major separation process has an associated characteristic sludge. Sludge samples have been analyzed for Purex and Redox process sludges. No sludge samples have ever been analyzed from sludges formed from separation processes prior to the Redox process, i.e., the Bismuth Phosphate process and the Uranium Recovery process.

Redox sludge analyses are shown in Table VII. Average results from Table VII shows that the Redox sludge is primarily composed of iron, nitrate, and aluminate. There are also small amounts of phosphate and carbonate present. Nitrate salts are quite soluble in a Redox type waste, but due to the concentration by self boiling and the long period of time wastes have been contained in storage some nitrate salts did indeed precipitate.

Purex sludge analyses are shown in Table VIII. The Purex sludge composition, slightly different than the Redox sludge composition, is composed primarily of iron and aluminum compounds. No nitrate salts have precipitated from Purex waste solutions; all sludge nitrate concentrations can be accounted for through interstitial liquor and are not reported in the analytical results.

Salt Cakes

The majority of the salt cake samples came from the 242-S Evaporator-Crystallizer bottoms system. Table IX summarizes the results of the 242-S Evaporator-Crystallizer bottoms salt analyses. The major compound is nitrate salt with minor amounts of phosphate, carbonate, and nitrite salts.

Only one ITS sample is known to have been taken. Table X shows that ITS salt is also primarily composed of nitrate salts. Minor concentrations of carbonate, phosphate, and sulfate are also present.

TABLE VII
REDOX SLUDGE SAMPLES⁽¹⁾

Tank No	Percent	Moles/Liter										G./L.	μ Ci./L.	
	H ₂ O	Fe	Al	Si	Mg	Mn	NO ₂	NO ₃	SO ₄	PO ₄	CO ₃	²³⁹ Pu	⁸⁹⁺⁹⁰ Sr	¹³⁷ Cs
102-S ⁽²⁾ —Top	45	0.03	1.4	0.37	--	--	0.02	3.18	--	2.37	--	6.78×10^{-4}	2.5×10^4	2.25×10^4
102-S ⁽²⁾ —Bottom	10	0.27	25.9	0.18	--	--	0.02	0.0	--	0.09	--	1.14×10^{-3}	7.6×10^2	1.0×10^4
107-S	47.3	0.41	0.75	--	--	--	0.01	6.59	--	2.63	--	7.2×10^{-2}	4.84×10^4	4.19×10^4
110-S ⁽³⁾ —Top	36.1	0.28	8.02	--	--	--	0.008	10.0	0.124	0.059	4.52	1.04×10^{-2}	5.95×10^5	1.86×10^5
110-S ⁽³⁾ —Bottom	45.0	0.24	12.1	--	--	--	<0.07	4.16	0.098	0.015	0.95	1.52×10^{-2}	1.09×10^6	9.45×10^4
111-S	9.46	0.02	15.84	--	--	--	0.02	0.54	<0.01	<0.01	0.13	$<3 \times 10^{-4}$	3.87×10^3	9.83×10^3
102-SX ⁽⁴⁾ —Top	28.6	0.135	5.77	--	--	--	<0.3	7.47	0.037	0.004	--	1.95×10^{-3}	1.37×10^6	4.52×10^5
102-SX ⁽⁴⁾ —Bottom	14.3	1.26	5.12	--	--	--	<0.3	8.86	0.021	0.015	7.75	7.56×10^{-4}	7.98×10^5	2.22×10^5
103-SX	45.4	0.2	4.8	0.2	0.04	0.1	<0.2	17.3	--	0.01	--	9.73×10^{-3}	2.63×10^6	2.29×10^5
104-SX ⁽⁵⁾ —Top	--	--	--	--	--	--	--	21.2	--	--	--	--	99	8.5×10^3
104-SX ⁽⁵⁾ —Bottom	18.6	0.19	3.53	--	0.041	--	0.13	11.5	0.024	<0.07	<0.11	--	2.53×10^6	1.29×10^5
105-SX ⁽⁶⁾ —Top	15.6	0.1	14.3	--	--	--	--	4.18	0.09	0.07	0.65	4.89×10^{-3}	8.86×10^5	1.89×10^5
105-SX ⁽⁶⁾ —Bottom	17.8	0.56	13.6	--	--	0.11	<0.18	2.19	0.18	0.19	--	2.12×10^{-2}	5.68×10^6	5.12×10^4
115-SX	4.4	1.64	3.15	0.55	1.92	0.4	0.08	27.3	--	<0.19	--	0.2	4.68	7.06×10^4
107-U	50.0	0.09	0.30	--	--	0.01	<0.01	2.76	--	2.44	--	8.04×10^{-3}	7.06×10^{-4}	2.47×10^4
110-U	44.3	0.26	7.48	--	--	--	0.02	5.35	0.13	0.65	2.03	1.66×10^{-2}	9.3×10^5	5.71×10^4
111-SX	33.8	0.4	8.4	0.01	--	0.05	1.7	21.8	--	13.4	--	1.31×10^{-3}	3.38×10^6	2.15×10^5
101-S	37.4	0.08	4.8	0.4	--	0.08	<0.2	9.1	--	0.08	--	5.97×10^{-3}	1.01×10^6	2.95×10^5
Average	31.0	0.40	7.19	0.29	0.67	0.13	0.22	9.31	0.07	1.61	1.66	2.9×10^{-2}	1.32×10^6	1.48×10^5

(1) Analytical results from J. S. Buckingham, Chemical Technology Laboratory

(2) Sample contained two layers of equal volume.

(3) Sample contained two layers; the top layer was 10 volume percent of total.

(4) Sample contained two layers; the top layer was 25 volume percent of total.

(5) Sample contained two layers; the top layer was 15 volume percent of total.

(6) Sample contained two layers; the top layer was 15 volume percent of total.

TABLE VIII

PUREX SLUDGE SAMPLES⁽¹⁾

Tank No.	%H ₂ O	Moles/Liter							G./L.	Ci./L.	
		Fe	Al	Si	Mg	Mn	Ca	Ba	²³⁹ Pu	⁸⁹⁺⁹⁰ Sr	¹³⁷ Cs
102-A	31.5	3.61	<1.5	0.83	--	1.11	--	--	--	49.8	1.71
103-A	Soft ⁽²⁾	51.7	1.91	2.02	0.50	--	--	--	--	25.9	0.97
	Hard	9.3	3.06	<5	0.74	--	--	--	--	32.3	5.78
104-A	42.3	4.99	2.82	0.83	0.11	0.71	0.41	0.009	0.11	43.9	1.15
101-AX	47.6	3.3	3.8	0.74	0.07	0.3	0.4	0.01	0.062	28.2	4.51 x 10 ⁻⁴
102-AX	42.5	2.54	--	1.26	0.044	0.217	0.199	0.011	0.067	9.31	1.26
103-AX	60.7	1.94	1.05	0.283	0.056	0.298	0.240	0.027	0.0358	22.4	3.11
104-AX	44.2	6.69	--	1.3	--	--	--	--	0.143	93.5	2.02
106-C	--	1.78	1.95	0.136	0.09	0.55	0.20	<0.04	0.06	18.8	0.86
Average	43.1	3.41	2.41	0.75	0.07	0.42	0.29	0.02	0.08	36.84	1.89
										With 101-AX	5639

(1) Analytical results from J. S. Buckingham, Chemical Technology Laboratory

(2) Two different solids were received. The soft material was 55 volume percent of the total.

TABLE IX

242-S SALT CAKE SAMPLES⁽¹⁾

Tank No.	Weight Percent									Gm./Gm.	μ Ci./Gm.	
	H_2O	AlO_2^-	OH^-	NO_2^-	NO_3^-	CO_3^{2-}	PO_4^{3-}	Al_2O_3	FeO_2H	Pu	$^{89+90}Sr$	^{137}Cs
105-S	3.4	0.1	0.5	0.3	100.3	2.5	--	--	--	--	--	8.9
106-S	29.1	4.7	6.2	4.5	39.5	10.1	2.4	0.1	0.2	2.7×10^{-5}	0.69	200
106-S ⁽²⁾	4.2	0.6	1.0	<0.1	90.1	4.1	--	--	--	--	--	17.2
109-S	9.2	1.1	2.3	<0.1	86.1	2.7	--	--	--	--	2.08	56.0
110-S	19.3	2.5	3.2	3.1	57.8	2.9	<3.2	--	--	9.11×10^{-9}	81.1	108.8
111-S	18.4	2.3	6.6	2.7	69.9	10.8	1.2	--	--	--	7.54	9.6
112-S	15.8	2.5	4.4	3.1	58.7	14.6	0.8	0.1	--	1×10^{-8}	0.67	10.1
101-SX	3.2	1.1	0.7	0.5	87.9	3.6	<0.1	--	--	$<8 \times 10^{-9}$	0.23	24.8
Average	12.8	1.9	3.1	1.8	73.8	6.4	1.5	--	--	6.78×10^{-6}	15.4	54.4

(1) Analytical results from J. S. Buckingham, Chemical Technology Laboratory

(2) Two samples were taken from 106-S

TABLE XITS SALT CAKE SAMPLE⁽¹⁾

<u>COMPOUND</u>	<u>WEIGHT PERCENT</u> ⁽²⁾
Al	3.5
NO ₂	3.6
NO ₃	32.5
CO ₃	11.0
SO ₄	2.5
PO ₄	1.5
Na	43
Fe	1.2
Si	0.5
¹³⁷ Cs	0.28 Curies/liter

(1) Analytical results from J. S. Buckingham, Chemical Technology Laboratory

(2) The salt sample contained two layers. These compositions are the average of the two layers.

No reliable 242-T salt cake samples have been taken. Based on 242-S and ITS salt samples, the 242-T salt cake should be predominantly nitrate salts.

Actinide Elements

The total amount of radioactive actinides stored in tank farms [REDACTED] is compiled in Table XI, a tank farm summary of the radioactive actinide contents. The total actinides are also shown in Table I.

TABLE XI

TANK FARM ACTINIDE CONTENTS

TANK FARM	KILLOGRAMS				
	<u>U</u>	²³⁵ <u>U</u>	<u>Pu</u>	<u>Th</u>	<u>Np (Grams)</u>
B	47,000	310	20	--	--
BX	67,000	440	11	--	10
BY	150,000	1000	25	--	21
C	180,000	1200	69	13,000	38,000
T	52,000	340	32	--	--
TX	130,000	840	6	--	--
TY	32,000	210	7	--	3
U	90,000	590	3	--	--
S	40,000	270	27	--	--
SX	48,000	320	45	--	3
TOTAL	840,000	5500	240	13,000	38,000

RELATIVE CHEMICAL TOXICITY

A relative chemical toxicity analysis of the Hanford underground waste tank chemicals will help establish a chemical analysis priority by identifying the most toxic chemicals contained in underground storage. The chemicals that have the greatest hazard should have a corresponding high analysis priority.

A compilation of the maximum permissible concentration of the elements in various valence states for potable water, air, and aquatic life is found in [REDACTED]. These elemental concentration limits can also be used for chemical compounds of the same valence state. For example, the toxicity of

10 CFR 20

sodium nitrate is determined by the toxicity of pentavalent nitrogen. Based on reference 5, Table XII summarizes the toxicity of the chemicals found in Hanford waste. The volume of air or water required to dilute these chemicals to the permissible toxic limits is also shown in Table XII. A comparison of the relative toxicity of each chemical can be made by taking each diluent volume as a percentage of the total diluent volume in its category; i.e., potable water, aquatic life, or air. These results are summarized in Table XIII. If potable water is decided to be used as the basis for the relative toxicity rating system, the percentages in the potable water column are applicable and so forth for the other two categories. If all three categories are considered in the relative toxicity rating system, the total toxicity should be used. The total toxicity was derived by averaging the three separate toxicities. Note that it is important to decide on what basis the relative toxicity rating system is determined since the most toxic chemicals vary between the three separate toxicities and the total toxicity. It is interesting that nitrate, the most abundant chemical in Hanford waste tanks, is very insignificant in relative toxicity.

TABLE XII

TOXICITY OF CHEMICALS

	← MOLES/LITER →	← MOLES/M ³ →	← QUANTITY →	← LITERS REQUIRED TO DILUTE TO PERMISSIBLE LEVEL →	← M ³ REQUIRED TO DILUTE TO PERMISSIBLE LEVEL →		
CHEMICAL	PORTABLE WATER	AQUATIC LIFE	AIR	10 ⁶ GM-MOLES	POTABLE WATER	AQUATIC LIFE	AIR
Al ⁺³	1.9 x 10 ⁻⁵	5.6 x 10 ⁻⁵	5.6 x 10 ⁻⁶	390	2.1 x 10 ¹³	7.1 x 10 ¹²	7.1 x 10 ¹³
OH ⁻	--	--	5.0 x 10 ⁻⁵	230	--	--	4.6 x 10 ¹³
NO ₃ ⁻	2.1 x 10 ⁻⁴	7.1 x 10 ⁻²	--	1400	6.7 x 10 ¹²	2.0 x 10 ¹⁰	--
NO ₂ ⁻	--	--	6.4 x 10 ⁻⁶	220	--	--	3.4 x 10 ¹³
Si ⁺⁴	1.8 x 10 ⁻⁴	1.8 x 10 ⁻³	--	14	8.1 x 10 ¹⁰	8.1 x 10 ⁹	--
Zr ⁺²	1.1 x 10 ⁻⁵	1.1 x 10 ⁻⁴	5.5 x 10 ⁻⁷	3	2.5 x 10 ¹¹	2.5 x 10 ¹⁰	4.9 x 10 ¹²
F ⁻	7.9 x 10 ⁻⁵	7.9 x 10 ⁻⁵	1.3 x 10 ⁻⁷	43	5.4 x 10 ¹¹	5.4 x 10 ¹¹	3.2 x 10 ¹⁴
K ⁺	3.9 x 10 ⁻²	1.3 x 10 ⁻³	--	1.0	2.6 x 10 ⁷	7.9 x 10 ⁸	--
Fe ⁺³	8.9 x 10 ⁻⁶	3.6 x 10 ⁻⁶	1.8 x 10 ⁻⁷	21	2.4 x 10 ¹²	5.9 x 10 ¹²	1.2 x 10 ¹⁴
PO ₄ ⁻³	3.2 x 10 ⁻⁶	1.3 x 10 ⁻³	3.2 x 10 ⁻⁷	88	2.7 x 10 ¹³	6.9 x 10 ¹⁰	2.7 x 10 ¹⁴
Mn ⁺⁵	9.1 x 10 ⁻⁷	1.8 x 10 ⁻⁶	9.1 x 10 ⁻⁷	1.7	1.9 x 10 ¹²	9.3 x 10 ¹¹	1.9 x 10 ¹²
CO ₃ ⁻²	3.3 x 10 ⁻²	2.5 x 10 ⁻³	7.5 x 10 ⁻³	22	6.6 x 10 ⁸	8.8 x 10 ⁹	2.9 x 10 ⁹
Cr ⁺⁶	9.6 x 10 ⁻⁷	9.6 x 10 ⁻⁷	1.9 x 10 ⁻⁸	14	1.4 x 10 ¹³	1.4 x 10 ¹³	7.2 x 10 ¹⁴
SO ₄ ⁻²	7.8 x 10 ⁻³	4.4 x 10 ⁻²	3.1 x 10 ⁻⁷	56	7.1 x 10 ⁹	1.3 x 10 ⁹	1.8 x 10 ¹⁴
Cl ⁻	6.9 x 10 ⁻³	1.4 x 10 ⁻³	--	1.2	1.8 x 10 ⁸	8.9 x 10 ⁸	--
Bi ⁺³	2.4 x 10 ⁻⁶	--	9.6 x 10 ⁻¹⁰	1.2	5.2 x 10 ¹¹	--	1.3 x 10 ¹⁵
Ce ⁺³	1.4 x 10 ⁻⁵	1.4 x 10 ⁻⁷	--	2.4	1.7 x 10 ¹¹	1.7 x 10 ¹³	--
Ag ⁺	4.6 x 10 ⁻⁷	9.3 x 10 ⁻⁸	9.3 x 10 ⁻¹⁰	0.07	1.6 x 10 ¹¹	7.9 x 10 ¹¹	7.9 x 10 ¹³
Pb ⁺²	1.9 x 10 ⁻⁵	--	7.3 x 10 ⁻⁷	0.42	2.2 x 10 ¹⁰	--	5.8 x 10 ¹¹
Hg ⁺²	2.5 x 10 ⁻⁸	5.0 x 10 ⁻⁸	2.5 x 10 ⁻⁹	0.005	2.0 x 10 ¹¹	1.0 x 10 ¹¹	2.0 x 10 ¹²
Cd ⁺²	8.9 x 10 ⁻⁸	8.9 x 10 ⁻¹⁰	1.8 x 10 ⁻⁸	1.9	2.1 x 10 ¹¹	2.1 x 10 ⁻³	1.0 x 10 ¹²
Ni ⁺²	1.7 x 10 ⁻⁶	8.5 x 10 ⁻⁷	1.7 x 10 ⁻⁷	1.5	8.7 x 10 ¹¹	1.7 x 10 ¹²	8.7 x 10 ¹²
Sr ⁺²	1.1 x 10 ⁻⁴	2.3 x 10 ⁻³	--	0.42	3.7 x 10 ⁹	1.9 x 10 ⁸	--
W ⁺⁶	2.7 x 10 ⁻³	2.7 x 10 ⁻⁴	2.7 x 10 ⁻⁷	0.004	1.3 x 10 ⁶	1.3 x 10 ⁷	1.3 x 10 ¹⁰
Total					7.7 x 10 ¹³	6.9 x 10 ¹³	3.2 x 10 ¹⁵

TABLE XIII

RELATIVE TOXICITY OF HANFORD TANK FARM CHEMICALS

← Percent of Total Toxicity →

	<u>Potable Water</u>	<u>Aquatic Life</u>	<u>Air</u>	<u>Total*</u>
Al	28	10	2	13
OH	--	--	1	0.33
NO ₃	9	0.03	--	3
NO ₂	--	--	--	0.33
Si	0.10	0.01	--	0.04
Zr	0.32	0.04	0.16	0.17
F	0.70	0.78	10	4
K	--	--	--	--
Fe	3	9	4	5
PO ₄	35	0.10	9	15
Mn	2	1	0.06	1
CO ₃	--	0.01	--	--
Cr	19	21	23	21
SO ₄	0.01	--	6	2
Cl	--	--	--	--
Bi	0.67	--	41	14
Ce	0.22	24	--	8
Ag	0.21	1	33	1
Pb	0.03	--	0.02	0.02
Hg	0.26	0.14	0.064	0.15
Cd	0.27	30	0.03	10
Ni	1	3	0.28	1
Sr	--	--	--	--
W	--	--	--	--

*Results of averaging portable water, aquatic life, and air toxicity

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