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PHYSICAL AND CHEMICAL
CHARACTERISTICS
OF
CANDIDATE WASTES
FOR
TAILORED CERAMICS

DOE Research and Development Report

*Prepared for the United States
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Rockwell International

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PHYSICAL AND CHEMICAL
CHARACTERISTICS
OF
CANDIDATE WASTES
FOR
TAILORED CERAMICS

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I. INTRODUCTION

Tailored Ceramics offer a potential alternative to glass as an immobilization form for nuclear waste disposal. The form is applicable to the wide variety of existing wastes and may be tailored to suit the diverse environments being considered as disposal sites.

Consideration of any waste product form, however, requires extensive knowledge of the waste to be incorporated. A variety of waste types are under consideration for incorporation into a Tailored Ceramic form. This report integrates and summarizes chemical and physical characteristics of the candidate wastes. Included here are data on Savannah River Purex Process waste; Hanford bismuth phosphate, uranium recovery, redox, Purex, evaporator and residual liquid wastes; Idaho Falls calcine; Nuclear Fuel Services Purex and Thorex wastes and miscellaneous waste including estimated waste stream compositions produced by possible future commercial fuel reprocessing.

II. CANDIDATE WASTES

A. SAVANNAH RIVER PLANT

Nuclear fuels reprocessing by the Savannah River Plant (SRP) over a span of 25 years has produced $\sim 90 \times 10^3 \text{ m}^3$ of alkaline high-level radioactive wastes. This waste consists of liquid (58 vol %), salt cake (29 vol %) and sludge (13 vol %).

The stored SRP wastes are mainly the product of two processing schemes: a Purex process waste stored in F Area tank farms and a modified Purex process (HM) waste stored in H Area tank farms. These, as well as secondary processes (^{233}U , ^{237}Np and thorium recovery, the separation of heavier actinides from plutonium, etc.) are thought to have created a diverse, inhomogeneous tanked waste.

Efforts to characterize the waste are underway at Savannah River Laboratory. Currently the main emphasis is on a sludge sampling and characterization program. Samples are taken in 3 to 55 liters and no effort is made to maintain configurational integrity. Surface or subsurface sampling is employed.

SRP waste can be roughly grouped into high aluminum and high iron wastes. Most of the Purex process waste stored in F Area farms contain large concentrations of iron. Coating waste, obtained from decladding targets that are processed in F area, contains high concentrations of aluminum. Because aluminum cladding and the uranium are co-dissolved in H Area, the HAW waste from the HM process in H Area contains high aluminum concentration while the LAW from the HM process is similar to Purex waste and high in iron.

To date, 3-liter sludge samples obtained from the surface of the sludge layer in Tanks 4, 5, 6, and 7 in F Area and Tanks 12, 13, 15, and 16 in H Area have been analyzed.^(1,6) Samples of Tanks 11, 13, and 15 sludge have been obtained from near the bottom of the sludge layer using the new 25-liter sampler. Analysis is complete on the Tank 15 sample and comparison to earlier results from 3-liter samples from Tank 15 confirms that the sludge layer is chemically inhomogeneous. Samples of supernate from Tanks 1 through 8 and 18 in F Area and 9 through 15, 21, and 24 in H area have also been analyzed.⁽²⁾

Detailed chemical analyses of SRP wastes have been previously published.⁽¹⁻⁴⁾ It is the intent here to integrate these data and compile them in an easily accessed, summary form. Table 1 contains the ranges of concentrations for the major components and radionuclides of sludges stored at the SRP. Table 2 contains the ranges of concentrations of minor sludge constituents. The analytical data were derived from analyses performed on washed and dried sludges. The data are expressed as ranges since any immobilization process designed should be capable of accommodating a widely varying waste stream. Additionally, these ranges begin to give a feel for inhomogeneity between tanks. Chemical compositions of supernates stored in the two areas are shown in Table 3.⁽²⁻⁴⁾ These are expressed as ranges and are broken out by tank farm area to reflect known dissimilarities between the stored wastes.

Analytical data on sludge and supernate samples have been reported without uncertainty limits. Waste tank analysis requires redetermination of detection and uncertainty limits due to the complicated sample matrix. Most detection and uncertainty limits are derived from analysis of water solutions. To date determination of these limits has not been accomplished at the SRP. Additionally, many of the analyses have been performed by spark-source mass spectroscopy, a method which is qualitatively excellent, but is somewhat suspect when accurate and precise determinations of trace elements are required. For this reason the data given should be taken to be no more accurate than $\pm 15\%$ for the major constituents and $\pm 50\%$ for the trace elements.

B. HANFORD WASTES

Waste from a variety of processing, solidification and fractionization schemes is stored at Hanford. This waste, sludge, salt cake and liquid are contained in 156 tanks in 15 tank farms. Approximately 24% of the total $186.5 \times 10^3 \text{ m}^3$ is residual liquid, 50% salt cake and 26% sludge.

Each of the processing schemes is assumed to have created a characteristic waste. Repeated transfer of tank contents has begun to level the concentrations of the separate ions; however, many differences are still expected to be seen among the separate waste types. Solid waste sludges stored at Hanford were

TABLE 1
MAJOR COMPONENTS OF SRP HIGH-LEVEL
SLUDGES(1-5)*

Constituent	Concentration Range (wt %)	
	F Area	H Area
Al	1.5 - 2.5	7.1 - 33.5
Ca	0.6 - 2.3	0.2 - 2.9
Fe	8.9 - 32.8	3.1 - 27.9
Hg	0.1 - 0.7	0.9 - 2.8
Mn	2.0 - 10.8	1.7 - 8.8
Na	2.8 - 6.1	1.0 - 3.1
Ni	2.1 - 6.3	0.3 - 0.7
NO ₃	0.12 - 1.2	0.2 - 0.4
NO ₂	0.02 - 0.12	0.01 - 0.2
SO ₄	<0.5	<0.05
U	3.3 - 15.4	0.9 - 4.5
Radionuclide	Activity Range (mCi/g)	
	F Area	H Area
¹⁴⁴ Ce	0.21 - 30.5	0.3 - 17.4
⁶⁰ Co	1 - 1	0.01 - 0.06
¹³⁴ Cs	0.01 - <0.02	<0.01 - 0.03
¹³⁷ Cs	0.7 - 1.30	0.05 - 0.30
¹⁵⁴ Eu	<0.01 - 0.6	0.08 - 1.18
⁹⁵ Nb	<0.01 - <0.03	≤0.02
¹⁰³ Ru	<0.01 - <0.02	<0.01
¹⁰⁶ Ru	1.3 - 11.4	0.08 - 1.74
¹²⁵ Sb	0.43	0.12 - 1.27
⁹⁰ Sr	27.03 - 177.5	15.49 - 55.0

*Data represent content of washed and dried sludge

TABLE 2
MINOR CONSTITUENTS OF SRP HIGH-LEVEL
SLUDGES(1-4)*

Species Composite	Concentration Ranges (wt %)	
	F Area	H Area
Ag	0.04 - 03	<0.1
B	<0.003 - <0.05	0.005 - 0.3
Ba	0.13 - 0.25	0.10 - 0.15
Ce	0.2 - 0.25	1.0 - 0.05
Cl	0.1 - 2.0	1.0
Cr	0.3 - 0.45	0.09 - 0.45
Eu	0.013 - 0.02	0.013
F	0.007 - 0.15	0.002 - <0.005
K	0.14 - 0.3	0.08 - 0.15
La	0.09 - 0.15	0.04 - 0.3
Mg	0.06 - 0.08	0.14 - 0.3
Mo	<0.01	-
Nb	0.05	<0.02 - <0.1
Nd	0.5 - 1.0	0.3 - <0.6
Np	<0.008	
P	0.03 - 0.07	0.03 - 0.3
Pb	0.04 - 0.25	0.01 - 0.5
Pm	0.04	-
Pr	0.09 - 0.15	0.04 - 0.2
Pu	<0.01	<0.005
Rh	0.01 - 0.05	0.007
Ru	0.3 - 0.5	0.03
S	0.08 - 0.5	<0.02 - <0.04
Si	0.4 - 3.2	0.22 - <0.4
Sm	<0.04 - 0.05	0.01
Sr	0.1 - 0.15	0.04
Th	0.007 - 0.07	0.11 - 0.18
Ti	0.04	<0.02 - <0.1
V	<0.005 - 0.01	<0.0007 - <0.007
Y	0.04 - 0.05	0.01 - 0.05
Zn	0.07 - 0.5	<0.04 - <0.2
Zr	0.04 - 0.5	0.11 - 0.4

*Data represent trace content of washed and dried sludge

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TABLE 3.
CONSTITUENTS OF SRP HIGH-LEVEL SUPERNATE (2-4)

Constituent	F Area	H Area
	Molarity Ranges	
Na ⁺	4.0 - 12.5	5.7 - 12.5
NO ₃ ⁻	1.6 - 2.5	1.9 - 6.4
NO ₂ ⁻	0.5 - 3.1	0.2 - 3.2
Al(OH) ₄ ⁻	0.4 - 0.8	0.4 - 1.6
OH ⁻	1.1 - 6.3	0.8 - 3.8
CO ₃ ⁻²	<0.1 - 0.3	<0.1 - 0.3
SO ₄ ⁻²	0.02 - 0.18	0.02 - 0.08
PO ₄ ⁻³	0.02 - 0.08	<0.01 - 0.05
Cl ⁻	0.03 - 0.11	0.005 - 0.029
CrO ₄ ⁻²	0.004 - 0.009	0.001 - 0.005
F ⁻	0.002 - 0.004	0.001 - 0.004
Fe	7 - 50 x 10 ⁻⁵	0.2 - 6 x 10 ⁻⁵
Hg	<20 - 320 µg/ml	60 - 340 µg/ml
NH ₄ ⁺	7 - 8 µg/ml	<1 - 67 µg/ml
Ag	<0.04 - 3 µg/ml	0.1 - 4 µg/ml
Pb	<0.02 µg/ml	2 - 58 µg/ml
U	4 - 16 µg/ml	0.4 - 6 µg/ml
Reducing Normality	0.005 - 0.28 N	<0.01 - 0.3 N
Density	1.20 - 1.41 g/ml	1.20 - 1.41 g/ml
Total Activity (d/m/ml)		
²⁴³ Am	<2 x 10 ⁴ - 12 x 10 ⁴	<0.1 x 10 ⁴ - 0.2 x 10 ⁴
¹⁴¹ Ce	ND	<1 x 10 ³ - <26 x 10 ³
¹⁴⁴ Ce	ND - <15 x 10 ⁴	<0.5 x 10 ⁴ - <26 x 10 ⁴
⁶⁰ Co	-	<2 x 10 ³ - 7 x 10 ³
¹³⁴ Cs	1 x 10 ⁸ - 27 x 10 ⁸	0.9 x 10 ⁸ - 10 x 10 ⁸
¹³⁷ Cs	4 x 10 ⁹ - 26 x 10 ⁹	1 x 10 ⁹ - 8 x 10 ⁹
¹⁵⁴ Eu	ND - 1 x 10 ⁴	<0.2 x 10 ⁴ - 0.3 x 10 ⁴
⁹⁵ Nb	ND - 98 x 10 ³	<0.9 x 10 ³ - 1 x 10 ³
¹⁰³ Ru	ND - 10.8 x 10 ⁷	<0.01 x 10 ⁷ - 0.29 x 10 ⁷
¹⁰⁶ Ru	3 x 10 ⁷ - 67 x 10 ⁷	0.09 x 10 ⁷ - 0.4 x 10 ⁷
⁸⁹ Sr	<0.2 x 10 ⁴ - <1 x 10 ⁴	<0.02 x 10 ⁴ - <2 x 10 ⁴
⁹⁰ Sr	1 x 10 ⁵ - 12 x 10 ⁵	0.2 x 10 ⁵ - 21 x 10 ⁵
⁹⁵ Zr	ND - 35 x 10 ⁴	0.3 x 10 ⁴ - <0.6 x 10 ⁴
Gross Alpha	<0.5 x 10 ⁴ - 1 x 10 ⁴	0.5 x 10 ⁴ - 40 x 10 ⁴
Total Pu	<0.01 x 10 ⁴ - 0.5 x 10 ⁴	0.001 x 10 ⁴ - 14 x 10 ⁴

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created by alkaline precipitation from saturated solutions of bismuth phosphate, redox, uranium recovery, Purex and waste solidification (liquid volume reduction) processes. These solids exist as a gelatinous sludge composed of varying concentrations of hydrous metal oxides contaminated interstitially with supernatant liquid and a predominantly sodium nitrate salt cake. The salt cake was created by precipitation from saturation solutions of residual liquid which had undergone partial evaporation. Stored residual liquid, while being a by-product of the same processing schemes, is much more uniform in concentration because of repeated recycling and transfer operations.

Solid waste in Hanford tanks is sampled using a core drilling technique. The contents of each tank are vertically drilled. An effort is made to maintain vertical integrity. Although most of the samples are blended prior to chemical analysis, physical and visual characterization of each separate core segment allows an estimation of vertical inhomogeneity. Chemical inhomogeneity can be determined when there is no sample compositing done. Core drilling provides the opportunity to determine vertical and horizontal inhomogeneity. Blending the sample prior to analysis provides a good "representative" sample of the tank concentration.

The waste sampling and analysis program at Hanford has thus far analyzed solids from 11 tanks. These tanks contain solids from various processing schemes with many of the tanks containing more than one type of waste.

Estimates of the concentrations of the constituents of each waste type have been previously published⁽⁷⁻⁹⁾ and a report detailing the actual analyses of the tanks is being prepared for publication later in FY 1980. It is the purpose of this section to present a comparison between estimates and actual tanked Hanford wastes, to summarize the work to date and to detail to the extent feasible the differences between estimates and actual waste. The inclusion of the estimated tanked wastes serves as a point of comparison. Most immobilization work has been done using synthetic waste which differs significantly from actual tanked wastes.

Table 4 compares the estimated composition of bismuth phosphate waste with compositions obtained for a few bismuth phosphate waste samples. Note that the

TABLE 4

ACTUAL AND ESTIMATED CONSTITUENT CONCENTRATION IN HANFORD BISMUTH PHOSPHATE SLUDGE

Constituent	Estimated BiPO ₄ Concentrations (wt %)(9)*						Actual Concentration Ranges, 1st Cycle (wt %)	
	1st Cycle		2nd Cycle		3rd Cycle		H ₂ O Soluble	H ₂ O Insoluble
	H ₂ O Soluble	H ₂ O Insoluble	Soluble	Insoluble	Soluble	Insoluble		
Al								1.6 - 3.9
Bi		6.4		4.2		4.2		1.6 - 3.8
Cd								
Cl								
CO ₃ ²⁻							0.1	
Cr		0.4		0.3		0.6	0.007 - 0.01	0.2 - 0.5
Fe		8.6					0.05	0.6 - 1.4
F ⁻		3.4		9.4		18.9	0.03 - 0.2	0.3 - 1.8
Hg								0.01 - 0.1
La						1.6		0.02 - 0.04
Mn						1.1		0.005 - 0.02
Na	7.3	0.9	7.6	3.9	4.1	0.5	5.4 - 17.0	5.8
Ni								0.5 - 4.4
NO ₃	7.5	0.4	6.5	0.9	9.0	0.5	9.2 - 20.0	1.3 - 5.0
Pb								1.3
PO ₄	4.3	6.5	5.0	7.3	0.9	1.1	1.5 - 6.2	4.8 - 9.8
Si		2.1		1.4			0.02 - 0.2	0.3 - 1.9
SO ₄	0.8	1.2	0.9	2.3	0.1	0.1	0.6 - 1.2	0.12
Zr		0.1						
²⁴¹ Am								3 ⁻⁹ - 2 ⁻⁸ g/g
¹³⁷ Cs							2.7 - 11.8 µCi/g	8.4 - 59.9 µCi/g
⁸⁹⁻⁹⁰ Sr							5.7 ⁻⁴ - 4.0 ⁻³ µCi/g	7.8 - 20.5 µCi/g
U							7.9 ⁻⁷ - 5.5 ⁻³ g/g	8.0 ⁻⁵ - 1.4 ⁻³ g/g
Total Organic Carbon								7.3 ⁻⁴ - 8.9 ³ g/g

*Based on a water content of 50 wt %

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process generated three separate waste streams of varying constituent concentrations. The bismuth phosphate tanks analyzed by the program to date have all been first cycle. Again, the measured concentrations in the actual tanks are expressed as ranges.

Tables 5, 6, and 7 contain the data for the uranium recovery, Purex, and waste solidification process wastes, respectively. Where a single tank containing waste from a specific process has been sampled, the table reflects the result of the analysis of one set of samples. To date no sample has been taken from a tank containing redox waste. Table 8 contains the estimated ion concentrations in the two types of redox waste. Tanks containing both types are scheduled to be sampled in FY 1981.

The estimates contained in Tables 5 through 8 are unwashed sludge assuming a water content of 50%. The analytical results quoted are from analyses performed on wet, as-received sludge.

While it can be seen that the estimated ion concentrations fall within the actual measured range reasonably often, careful note should be taken of the occasions where they do not. Based on comparison with actual analytical results, the estimates of major constituents may be in error. Any process designed to immobilize the waste must be capable of handling large variations in waste composition such as is found in the Hanford waste sludges.

Such a wide variation in liquid waste stored at Hanford is not expected. Analytical data regarding the composition of these residual liquids have been published previously,⁽¹⁰⁾ and Table 9 contains a summary of these analyses.

Average waste compositions are generally not prepared because there is no average sludge. However, for immobilization purposes Table 10 contains a composition derived from assuming the sludge and salt cake are slurried with residual liquid and estimating the composition of the composite.

TABLE 5
ESTIMATED AND ACTUAL CONSTITUENT CONCENTRATION
IN HANFORD URANIUM RECOVERY SLUDGE

Constituent	Estimated Concentration* (wt %)(g)		Actual Concentration (wt %)	
	H ₂ O Soluble	H ₂ O Insoluble	H ₂ O Soluble	H ₂ O Insoluble
Al				1.20 - 2.81
B			0.03	1.1 - 5.5
Cd				
Cl		1.8	1.8	
CO ₃ ²⁻	0.9	2.5	1.3 - 2.4	
Cr			0.004 - 0.04	0.08 - 0.2
Fe		4.4		
F ⁻			0.002 - 0.09	1.1 - 12.4
Hg				2.1 - 2.6
La				0.5 - 2.8
Mn				0.1 - 0.3
Na	6.9	1.6	0.5 - 20.2	1.1 - 8.1
Ni		0.5	0.003 - 0.01	0.3 - 13.9
NO ₃ ⁻	7.5	0.8	1.4 - 21.4	
OH				
Pb			0.1	
PO ₄ ³⁻	1.9	5.4	0.9 - 7.6	0.5 - 7.0
Si			0.02 - 0.1	0.4 - 11.4
SO ₄ ²⁻	2.7	7.6		
Zr				
¹³⁹ Cs			0.6 - 16.7 μ Ci/g	2.11 - 74.8 μ Ci/g
Pu			2 ⁻⁸ - 4 ⁻⁴ g/g	3.0 ⁻⁶ - 8.0 ⁻⁶ g/g
⁸⁹⁻⁹⁰ Sr			0.08 - 1.2 μ Ci/g	2.61 - 1.2 ³ μ Ci/g
U			5.4 ⁻⁶ - 1.4 ⁻⁴ g/g	1.7 ⁻³ - 0.1 g/g
Total Organic Carbon	0.1	0.6		

*Based on a water content of 50%

TABLE 6
ESTIMATED AND ACTUAL CONSTITUENT CONCENTRATION
IN HANFORD PUREX SLUDGE

Constituent	Estimated Concentration* (wt %)(g)		Actual Concentration (wt %)	
	H ₂ O Soluble	H ₂ O Insoluble	H ₂ O Soluble	H ₂ O Insoluble
Al	1.4	1.5		9.8
Bi			0.2	0.3
Cd				0.1
Cl				
CO ₃ ²⁻	2.5	1.3	9.2	
Cr				0.4
Fe		2.1		21.0
F ⁻		4.2	0.01	0.03
Hg		0.01		
La				2.0
Mn		0.6		4.6
Na	5.4	0.2	7.8	11.8
Ni			0.1	
NO ₂	5.2	0.1		
NO ₃	1.9	0.03		
OH				
Pb				
PO ₄ ³⁻	0.1	0.06	1.1	30.6
Si				6.7
SO ₄ ²⁻	3.5	1.7	0.26	
Zr		1.4		
¹³⁷ Cs			97.8 μ Ci/g	6.9 ² μ Ci/g
Pu				
89-90Sr			132.6 μ Ci/g	2.1 ⁴ μ Ci/g
U			1.6 ⁻⁴ g/g	2.9 ⁻⁷ g/g
Total Organic Carbon		16.5		

*Based on a water content of 50%

TABLE 7
ESTIMATED AND ACTUAL CONSTITUENT CONCENTRATION
IN HANFORD WASTE SOLIDIFICATION SALT CAKE

Constituent	Estimated Concentration* (wt %)(9)		Actual Concentration (wt %)	
	H ₂ O Soluble	H ₂ O Insoluble	H ₂ O Soluble	H ₂ O Insoluble
Al	1.0			
Bi				
Cd				
Cl ⁻				
CO ₃ ²⁻	1.5		0.5	
Cr				
Fe				0.2
F ⁻			0.04	4.7 ⁻⁵
Hg				
La				
Mn				
Na	15.5		26.3	1.8
Ni				
NO ₂ ⁻	1.0			
NO ₃ ⁻	31.0		36.3	
OH				
Pb				
PO ₄ ³⁻			33.3	3.8
Si			0.1	1.7
SO ₄ ²⁻			7.2	
Zr				
¹³⁷ Cs			5.6 μ Ci/g	6.3 μ Ci/g
Pu			5.4 ⁻⁹ g/g	1.2 ⁻⁷ g/g
89-90Sr			0.06 μ Ci/g	9.9 μ Ci/g
U			2.1 ⁻⁶ g/g	3.5 ⁻⁵ g/g
Total Organic Carbon			2.4 ⁻³ g/g	

*Based on a water content of 50%

TABLE 8
ESTIMATED CONSTITUENT CONCENTRATION
IN HANFORD REDOX SLUDGE

Constituent	Estimated Concentration* (wt. %)(9)	
	H ₂ O Soluble	H ₂ O Insoluble
Al	1.9 - 3.0	7.5 - 20.0
Bi		
Cd		
Cl ⁻		
CO ₃ ²⁻		
Cr	0.1	5.5 - 12.3
F ⁻		
Fe		1.5 - 3.4
Hg		
La		
Mn		
Na	4.6 - 5.0	2.1
Ni		
NO ₂		
NO ₃	11.9 - 13.0	1.2 - 2.7
OH		
Pb		
PO ₄ ³⁻		
Si		
SO ₄ ²⁻	0.3 - 0.4	0.8 - 1.9
Zr		
¹³⁷ Cs		
Pu		
89-90Sr		
U		
Total Organic Carbon		

*Based on a water content of 50%

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TABLE 9
CHEMICAL CONSTITUENT CONCENTRATIONS
IN HANFORD RESIDUAL LIQUID*

Constituents	Concentration (wt.%) [†]	Constituents	Concentration (wt.%) [†]
NaNO ₃	31.3	Na ₂ CrO ₄	4.2
NaNO ₂	23.6	Na ₃ PO ₄	1.0
NaOH	13.1	Na ₂ SO ₄	0.4
NaAlO ₂	17.7	Organics	5.5
Na ₂ CO ₃	3.1	Fe (complexed)	0.1

*Includes residual liquid, double-shell slurry and complexed concentrations

†Does not include water

TABLE 10
ESTIMATED CONSTITUENT CONCENTRATIONS IN BLENDED
DRIED (20°C) HANFORD WASTE

Constituent	Concentration (wt.%)	Constituents	Concentration (wt.%)
Al	14.4	Bi	2.8
Ca	0.8	Ce	-
Cr	2.5	Fe	9.8
La	0.2	Mn	0.7
Na	15.6	Ni	0.6
Si	3.2	Sr	2.0
Ti	1.7	U	0.5
Zr	2.8	CH	0.8
F	0.7	NO ₅	0.5
PO ₄	3.1	SO ₄	0.4
Volatiles*	19.6	O ₂ [†]	17.3

*Includes waters of hydration and all compounds lost by firing at 750°C

†Calculated by difference

The physical characteristics of the stored wastes are relevant to any immobilization scheme. Density and particle size give indications of the ability of a waste to be centrifuged, an important step in any processing scheme. Variations in physical characteristics can also give a projection of vertical stratification within the tank through percent water and density analyses. Table 11 contains the physical data on the four core segments from a tank containing uranium recovery waste. The data indicate a general lowering in water content as the depth from which the sample was taken increases. Table 11 also contains a summary of the physical characterization data from each tank type analyzed to date. These are expressed as ranges where possible.

TABLE 11
PHYSICAL CHARACTERISTICS OF HANFORD URANIUM
RECOVERY WASTE FROM TANK 105-TY

Characteristic	Analytical Values			
	Segment 1	Segment 2	Segment 3	Segment 4
Moisture (%)	45.4	15.8	19.4	13.2
Bulk Density (gm/cm ³)	1.44	1.37	1.45	1.52
Particle Density (gm/cm ³)	2.16	1.48	1.39	1.36
Characteristic	Solid Waste Ranges			
	Analytical Value Ranges			
Moisture (%)	13 - 64			
Bulk Density (gm/cm ³)	1.27 - 1.74			
Particle Density (gm/cm ³)	1.28 - 3.16			

A laboratory quality assurance and data validation program is currently in the initial phases of implementation for the waste characterization program at Hanford. This will allow accuracy and precision determinations to be made for Hanford wastes. The validation program is also designed to monitor for loss of analytical control on a continual basis.⁽¹¹⁾

C. NUCLEAR FUELS SERVICES

The Nuclear Fuels Services commercial fuel reprocessing facility in West Valley, New York has $\sim 2.3 \times 10^3 \text{ m}^3$ of high-level waste stored in two tanks. One tank contains between 2.1 and $2.3 \times 10^3 \text{ m}^3$ of neutralized Purex process waste, which is ~ 5 to 10% sludge.⁽¹²⁾ The second tank contains $\sim 45.4 \text{ m}^3$ of acidic Thorex process waste.

The Purex process used by Nuclear Fuels Services resulted in a high iron, high sodium waste stream.⁽¹²⁾ The sludge in the tank containing this neutralized waste has not been sampled so data contained here can only be estimations. Additionally, there is some indication that the sludge consists of two distinct layers. The top layer would be hydrous ferric and aluminum hydroxides with the more dense second layer containing the majority of the fission products but less aluminum and iron.⁽¹²⁾ Estimates of the sludge contents are contained in Table 12. These data are approximations of the total sludge contents. They do not reflect the inhomogenities anticipated to be present as a result of varying sludge density.

TABLE 12
ESTIMATED CHEMICAL CONSTITUENT CONCENTRATIONS IN
NUCLEAR FUEL SERVICES SLUDGE (12)

Constituents	Concentration (wt %)	Constituents	Concentration (wt %)
Fe(OH)_3	50.0	$\text{NaPO}_4 - 12 \text{ MoO}_3$	0.99
FePO_4	29.8	MnO_2	2.22
Cr(OH)_3	3.9	PuO_2	0.04
Ni(OH)_2	1.7	NaU_2O_7	6.77
Al(OH)_3	0.84	Actinides	0.02
Rare Earth	1.64		
Fission Products			
SO_4	1.25		
$(\text{OH})_4$	1.60		
O_3	0.21		
O_x^{-1}			

The alkaline supernate is routinely sampled and analyzed for the presence of major constituents. Table 13 reflects the results of these analyses.⁽¹²⁾ From the results of the analyses, it can be presumed that the oxalate ions have decomposed.

TABLE 13
CHEMICAL CONSTITUENT CONCENTRATIONS IN NUCLEAR FUEL SERVICES PUREX SUPERNATE⁽¹²⁾

Constituent	Concentration (M)	Constituent	Concentration (M)
Na + K	5.4	Al	<0.0093
Fe	0.0045	P	<0.008
Ni	<0.0043	C ₂ O ₄	<0.05
Cr	0.01	Cl	0.054
F	-	SO ₄	0.20
Mo	0.002	OH (excess)	0.236

Cesium is the only fission product analyzed in this waste. Based on process material balances, however, calculations estimate the tank to contain ~3300 kg of fission products, most of which are now in nonradioactive form. The estimated radionuclide constituents of interest are contained in Table 14.⁽¹²⁾

TABLE 14
ESTIMATED RADIONUCLIDE CONCENTRATIONS IN
NUCLEAR FUEL SERVICES WASTE⁽¹²⁾

Constituent	Sludge (Ci)	Supernate (Ci)
⁹⁰ Sr	8.2 x 10 ⁶	8.3 x 10 ⁴
⁹⁵ Zr	250	<1
⁹⁹ Tc		1.9 x 10 ³
¹⁰⁶ Ru	5.4 x 10 ⁴	5.5 x 10 ²
¹³⁷ Cs		1.1 x 10 ⁷
²³⁷ Np	23	
²³⁹ Pu	1.8 x 10 ³	
²⁴⁰ Pu	970	

TABLE 15
CHEMICAL CONSTITUENT CONCENTRATIONS IN NUCLEAR FUEL
SERVICES ACID THOREX WASTE⁽¹²⁾

Constituent	Concentration (wt %)	Constituent	Concentration (wt %)
Al	2.1	Ni	2.2
As	0.003	P	0.07
B	0.1	Pd	0.03
Ba	0.2	Pm	0.01
Ca	0.05	Pr	0.06
Ce	0.1	Rb	0.02
Cl	0.4	Rh	0.04
Co	0.01	Ru	0.1
Cr	3.9	S	0.2
Cs	0.2	Se	0.02
Cu	0.02	Sm	0.06
F	0.01	Sr	0.06
Fe	15.0	Tc	0.06
K	1.0	Th	70.2
La	0.06	Ti	0.05
Mn	0.2	V	0.01
Mo	0.2	Y	0.02
Na	2.1	Zn	0.02
Nd	0.3	Zr	0.04

Radionuclide	Total Intank Activity (Ci)
⁶⁰ Co	4.88×10^3
¹³⁴ Cs	1.11×10^4
¹³⁷ Cs	8.47×10^5
¹⁵⁴ Er	9.00×10^3
⁹⁰ Sr	8.02×10^5

The second tank at NFS contains the waste from processing a single batch of thorium-uranium commercial fuel. The waste in this tank is ~13 years old and is maintained as an acid to prevent thorium precipitation. The fuel was dissolved in nitric acid in the presence of fluoride and boric acid. The fluoride is likely to have caused the dissolution of some of the aluminum fuel cladding. The liquid has a density of ~1.8 gm/cm³ and is assumed to be all one phase.

Oak Ridge National Laboratory (ORNL) has done a detailed analysis of the Thorex waste.⁽¹²⁾ Table 15 contains the results of the analysis.

The analytical data for the NFS waste are generally assumed to have an accuracy of ±20% for the analyses performed by NFS. There is no statement of accuracy or precision associated with the work performed by ORNL.

D. IDAHO FALLS CALCINE

High- and intermediate-level defense wastes are processed by the Idaho Chemical Processing Plant (ICPP) located at the Idaho National Engineering Laboratory. Waste streams from a variety of processes are combined and calcined to yield powdered or granular products which are stored in stainless steel bins at the site. Calcined waste stored at ICPP falls into one of four general categories.^(13,14) Alumina waste is a product of the dissolution of aluminum clad fuel in nitric acid in the presence of mercuric nitrate. This dissolution is followed by tributyl phosphate (TBP) extraction of uranium. (Approximately 5000 m³ of waste calcine has been produced.)

Zirconia waste is generated by the dissolution of zirconium clad fuel in hydrofluoric acid. Currently, the zirconium solution from this process is combined with the stream generated by the dissolution of aluminum containing fuel in nitric acid (the process formerly creating alumina waste). This is the major waste produced and calcined by ICPP.

Sodium-bearing waste is generated by processes other than first cycle uranium recovery. These are aqueous wastes consisting of such things as second and third cycle wastes, laboratory wastes, decontamination wastes and washing wastes. These

streams are blended with zirconia wastes prior to calcining to reduce the sodium concentration in batches of calcine.

The final major waste calcine is produced from the electrolytic decomposition of stainless steel reactor waste in nitric acid. This waste is mixed with alumina and other low fluoride waste calcines. This is a high iron waste but it constitutes <5% of the total calcined waste.

Table 16 contains the major constituents for all four types of waste described.⁽¹⁴⁾ Any Tailored Ceramic must be able to encompass the range of concentrations seen here. Table 17 gives a brief idea of the physical properties of one of the calcines. These data are referenced without uncertainty limits and without knowledge of analytical methods.

TABLE 16
ICPP CALCINED WASTE COMPOSITIONS^(13,14)

Composition (wt %)	Waste Type			
	Alumina	Zirconia	Zr-Na Blend	Electrolytic
Fe ₂ O ₃				10 - 17
Al ₂ O ₃	82 - 95	13 - 17	10 - 16	57 - 85
Na ₂ O	1 - 3		6 - 8	1.4 - 2.7
ZrO ₂		21 - 27	16 - 19	
CaF ₂		50 - 56	33 - 39	
Gd ₂ O ₃				6 - 23
CaO		2 - 4	13 - 17	
NO ₃	5 - 9	0.5 - 2	7 - 9.5	1 - 5
B ₂ O ₃	0.5 - 2	3 - 4	2 - 3	2 - 6
Fission Product and Actinides	0.2 - 1	0.2 - 1	0.2 - 1	0.2 - 1
Miscellaneous	0.5 - 1.5	0.5 - 1.5	0.5 - 1.5	1 - 4

TABLE 17
PHYSICAL PROPERTIES OF ICPP ZIRCONIA WASTE^(13,14)

Density	g/cm ³	1.2 - 1.6
Particle Size	Bed (mm diameter)	0.1 - 0.6
	Fines (mm diameter)	0.01 - 0.1
Thermal Conductivity	W/m ² -°K	0.2 - 0.28

TABLE 18
ESTIMATED CONSTITUENT CONCENTRATIONS IN CONCENTRATED HIGH-LEVEL
WASTE FROM AGNS REPROCESSING PLANT⁽¹⁵⁾

Component (Simulant)	Concentration (M)	Component (Simulant)	Concentration (M)
Rb	0.09	Cr	0.01
Cs		PO ₄	0.06
Sr	0.02	Y	
Zr	0.11	La	
Mo	0.12	Ce	
Tc	0.12	Pr	0.20
Ru	0.11	Nd	
Fe		Sm	
Rh	0.01	Eu	
Pd	0.04	U	0.12
Cd	0.003	Np	
Te	0.001	Pu	
Ba	0.03	Am	
Gd	0.15	H	
Na	0.57	RE*	

*RE - Rare Earth

TABLE 19
ESTIMATED CONSTITUENT CONCENTRATIONS IN COMBINED WASTE
FROM AGNS REPROCESSING PLANT⁽¹⁵⁾

Component	Concentration (M)	Component	Concentration (M)
Rb	0.04	La	
Cs		Ce	
Sr	0.01	Pr	0.09
Zr	0.05	Nd	
Ru	0.05	Sm	
Fe		Eu	
Rh	0.01	U	0.11
Pd	0.02	Pu	
Cd	0.001	Np	
Te	0.005	Am	
Ba	0.01	SO ₄	0.002
Gd	0.07	Cl	0.01
Na	0.26	Hg	0.01
Cr	0.004	I	0.002
PO ₄	0.11	H	
Y			

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III. MISCELLANEOUS

No commercial nuclear fuel is currently undergoing reprocessing in the United States. Ceramic forms chosen for waste immobilization, however, must be capable of incorporating waste generated as a result of future reprocessing of this type. The majority of commercial fuel reprocessing would be done using Purex or a modified Purex process.

The waste generated from these processes will differ from those seen previously. They will be lower in iron and higher in rare earth content. Differences will also occur in radionuclide content and concentration. In commercial waste the concentrations of all fission products will be significantly higher than they are in defense waste, since commercial fuel is a higher burn than defense fuel.

Estimates of the concentrations of waste from the AGNS reprocessing plant in Barnwell, SC are contained in Table 18. The data included in this table are those anticipated from concentrated, high-level waste.⁽¹⁵⁾ Table 19 contains the anticipated concentrations of a combined high-level and low-level waste. The differences noted between waste produced by reprocessing commercial spent fuel are significant to any waste immobilization form under consideration. The higher levels of radionuclides present possible heat generation and waste loading problems. It is anticipated that commercial spent fuel reprocessing will be undertaken at some time within the United States. Therefore, the waste products generated by such reprocessing must be considered when analyzing any waste immobilization form.

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