

12
9-19/95 JS ①

PNL-10712

UC-~~921~~ 2030

Washing and Caustic Leaching of Hanford Tank Sludges: Results of FY 1995 Studies

B. M. Rapko
G. J. Lumetta
M. J. Wagner

August 1995

Prepared for
the U.S. Department of Energy
Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute



PNL-10712

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any **warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161



The contents of this report is printed on recycled paper.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

**WASHING AND CAUSTIC LEACHING OF HANFORD
TANK SLUDGES: RESULTS OF FY 1995 STUDIES**

B. M. Rapko
G. J. Lumetta
M. J. Wagner

August 11, 1995

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

MASTER

Summary

This report describes the sludge washing and caustic leaching tests conducted at Pacific Northwest Laboratory in FY 1995 under the Sludge Treatment Technology Development Task of the Tank Waste Remediation System (TWRS) Pretreatment Technology Development Project. The highlights from this work were as follows.

- Sludge washing and caustic leaching tests were performed on sludge composites from six Hanford single-shell tanks (B-111, BX-107, C-103, S-104, T-104 and T-111) and one double-shell tank (SY-103). The studies, designed to evaluate the current baseline pretreatment flowsheet, involved contacting the sludges once with 0.01 M NaOH/0.01 M NaNO₂, followed by two contacts with ~3 M NaOH, and finally three washes with 0.01 M NaOH/0.01 M NaNO₂. Except for the final washes, each step was performed at 100°C. The settling behavior of the solids at each step, the elemental composition, radionuclide composition, and anion composition of the initial solids, the treated solids, and all aqueous solutions were measured to evaluate the effectiveness of the sludge washing and caustic leaching treatment.
- Particle sizes for the untreated sludges typically ranged around 1 μm according to the number distribution, or between 1 to 5 μm according to the volume distribution. In general, little change in particle size was observed as a result of sludge washing and caustic leaching.
- Solids settling behavior ranged widely from tank to tank. In general, the initial wash suspensions, containing ~2.3 wt% solids, settled well. But poor settling behavior was observed for the caustic leach and final wash step, which contained ~8 wt% solids.
- For the single-shell tank sludges, the only radionuclides removed to any great extent were ¹³⁷Cs and ⁹⁹Tc. Small fractions of the transuranic elements (TRUs) and ⁹⁰Sr were removed from the double-shell tank sludge SY-103.
- If the wash and leach solutions from a given tank were combined and concentrated to 20 M Na in the final low-level waste form, most of the resulting materials would be below the limits for Nuclear Regulatory Commission Class C low-level waste. An exception to this is seen for C-103 sludge, which (if no further pretreatment is performed) would have a transuranic concentration in the low-level waste near the 0.1 μg/g Class C limit.

- The removal of bulk nonradioactive sludge constituents varied widely from sludge to sludge as indicated in Table S.1.
- The washing and leaching results were compared to phenomenological assumptions commonly used to describe P and Al leaching from tank sludges. In general, on a tank-by-tank basis, these assumptions appear consistent with the observed behavior. Exceptions include the removal of Al from tanks C-103 and S-104, and the removal of P from Tank T-104.
- The concentrations of the treated tank sludges were combined with the total mass of the sludges in their respective tanks together with Hanford Waste Vitrification Plant feed specifications to calculate the number of high-level waste glass canisters (1650 kg/canister) that would result from treated and untreated sludges on a tank-by-tank basis. On this basis, caustic leaching will result in reductions ranging from 7% to 91% in the amount of glass required to immobilize the waste, when compared to sludge washing alone.
- Two sludges responded poorly to the sludge washing and caustic leaching tests. When considered on a tank-by-tank basis, the high concentration of Al in treated S-104 sludge and the high concentration of Cr in treated SY-103 sludge could lead to large volumes of high-level waste glass. Alternative pretreatment methods for these specific tank sludges are currently being investigated.

Reference

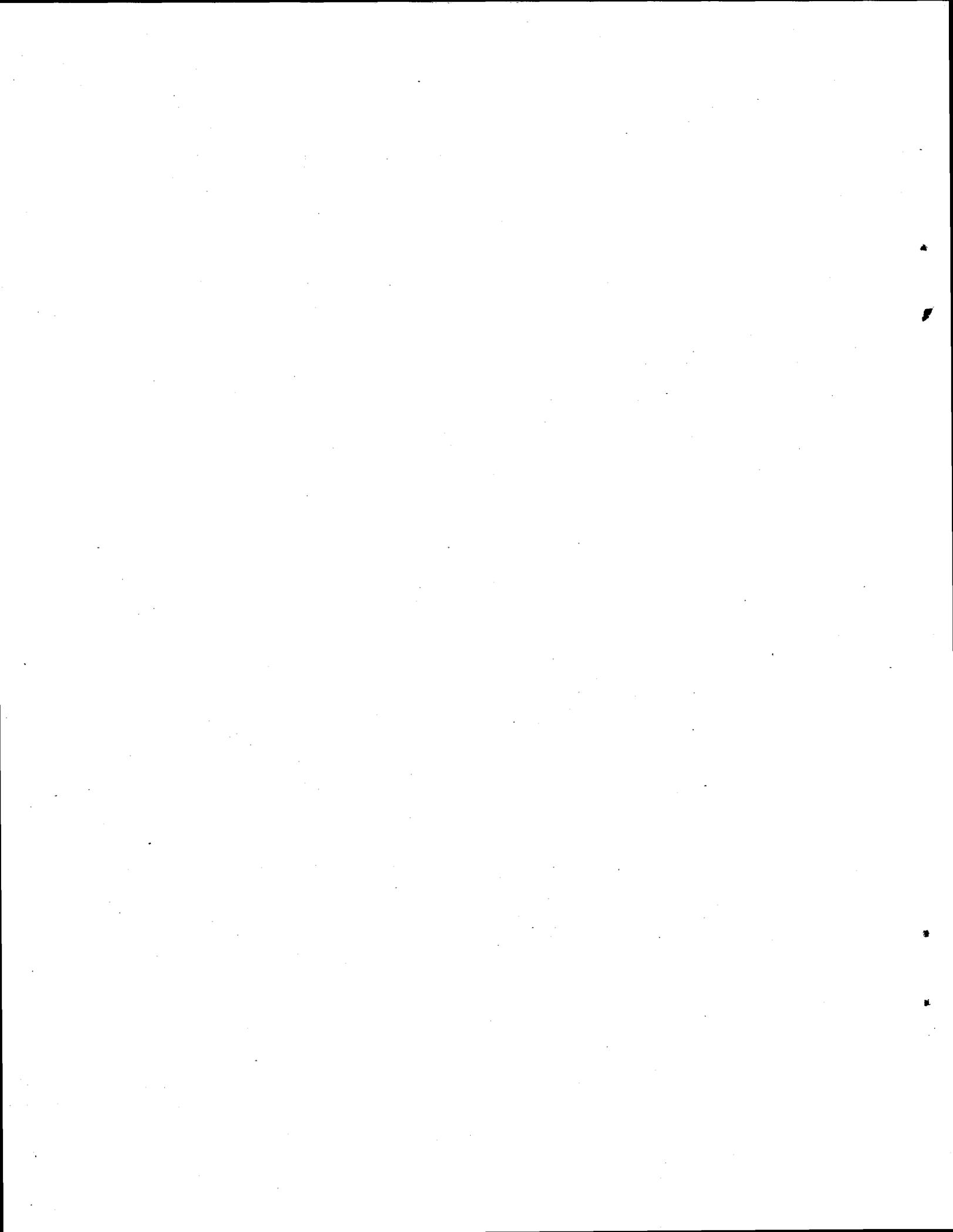
Colton, N. G. 1995. *Sludge Pretreatment Chemistry Evaluation: Enhanced Sludge Washing Separation Factors*. PNL-10512, Pacific Northwest Laboratory, Richland, Washington.

Table S.1. Summary of Sludge Components Removed by Sludge Washing and Caustic Leaching

Tank	Amount of Component Removed, %					
	Al	Cr	Fe	Na ^(a)	P	S
B-111	2	40	0	91	91	100
BX-107	68	29	0	91	93	95
C-103	48	11	0	24	66	^(b)
S-104	38	97	1	92	^(c)	100
SY-103	90	12	25	99	98	^(b)
T-104	62	27	0	40	55	100
T-111	13	63	0	85	72	67

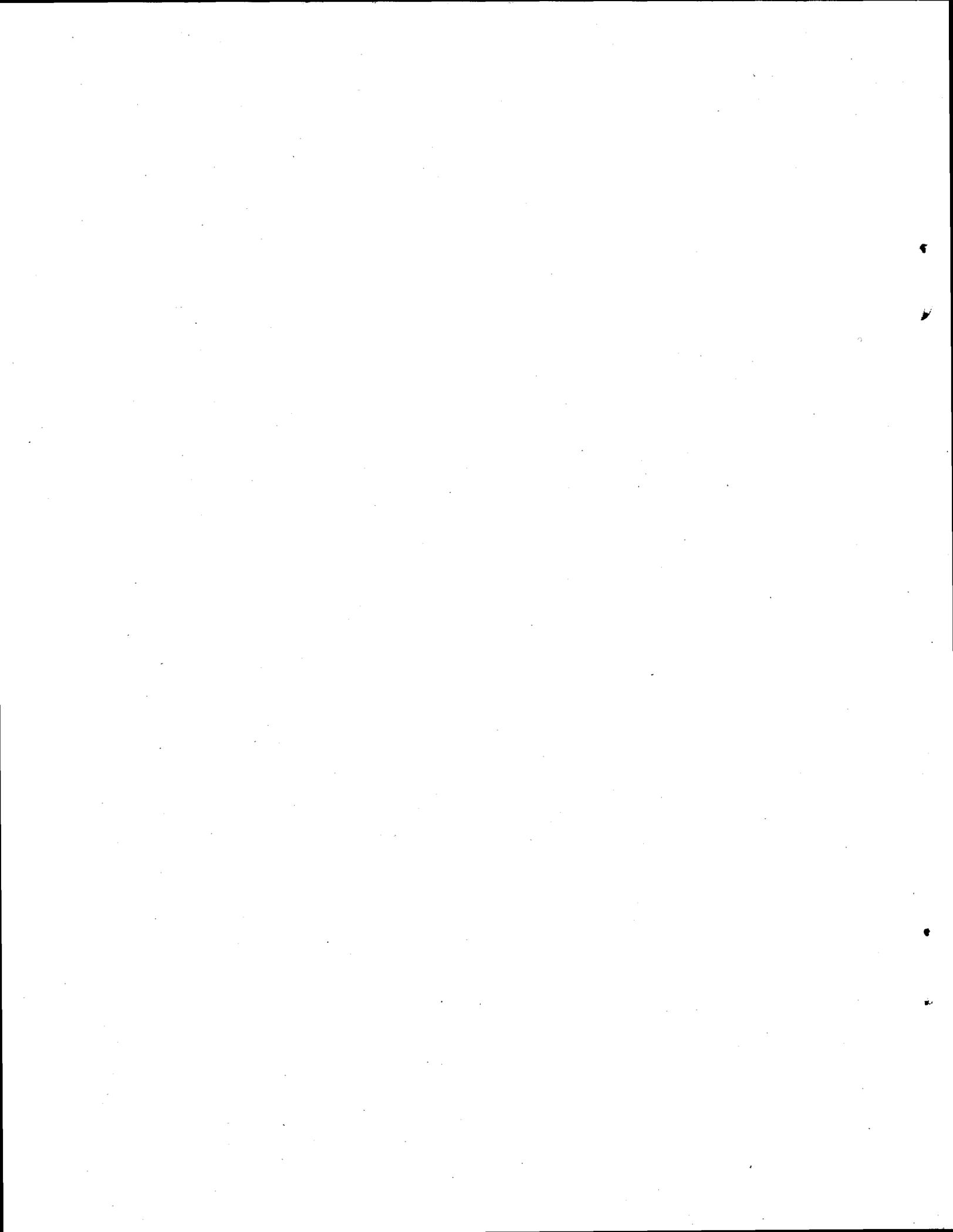
Tank	Concentration of Component in Untreated Sludge, g/g Dried Sludge					
	Al	Cr	Fe	Na	P	S
B-111	3.0E-03	3.1E-03	4.6E-02	2.4E-01 ^(d)	4.1E-02	1.3E-02
BX-107	3.5E-02	2.3E-03	2.8E-02	2.1E-01	5.6E-02	6.6E-03
C-103	1.4E-01	1.6E-03	2.0E-01	4.6E-02	5.0E-03	^(b)
S-104	1.5E-01	4.7E-03	3.4E-03	2.0E-01	^(c)	6.7E-03
SY-103	4.7E-02	1.3E-02	4.1E-03	2.8E-01	7.8E-03	^(b)
T-104	4.7E-02	3.1E-03	2.8E-02	1.9E-01	6.9E-02	1.0E-02
T-111	4.9E-03	4.5E-03	6.0E-02	3.7E-01	2.6E-02	5.7E-03

- (a) Because Na was added in the form of NaOH during the leaching process, the amount of Na removed from the sludge could not be determined per se. The value reported here is the amount of Na found in the dried, leached, residue relative to that in the untreated sludge, i.e., $100 \cdot [100(f/i)]$, where f is the amount of Na in the dried, washed, sludge and i is the amount in the dried, untreated, sludge.
- (b) Due to matrix effects, analyte could not be accurately determined.
- (c) No P was detected in this sludge sample.
- (d) Due to analytical difficulties, reliable data for Na are not available for these untreated sludges; the Na concentrations reported here were taken from Colton 1995.



Acknowledgments

The authors thank G. M. Richardson for assistance with performing the Tank C-103 sludge washing and caustic leaching test in the 325A Hot Cell facility. The authors also thank R. R. Odell, M. J. Lindberg, and A. L. Fishback of WHC for their assistance in performing the tests. The assistance of S. G. McKinley and other members of the Pacific Northwest Laboratory Analytical Chemistry Laboratory who contributed to this work is gratefully acknowledged. The authors thank W. C. Cosby, N. G. Colton, and J. L. Swanson for reviewing this document.



Contents

Summary	iii
Acknowledgments	vii
Contents	viii
Figures	x
Tables	xiii
1.0 Introduction	1.1
2.0 Experimental	2.1
2.1 Materials	2.1
2.2 Sludge Washing and Caustic Leaching Procedure	2.2
2.3 Analytical Methods	2.4
3.0 Results and Discussion	3.1
3.1 General Observations	3.1
3.2 Settling Behavior of the Sludge Solids	3.4
3.3 Particle Size Analysis of Sludges Before and After Washing and Leaching	3.9
3.4 Behavior of Nonradioactive Components During Sludge Washing and Caustic Leaching	3.11
3.5 Behavior of Anionic Components During Sludge Washing and Caustic Leaching	3.12
3.6 Radionuclide Behavior During Sludge Washing and Caustic Leaching	3.15
3.7 Comparison of the Sludge Washing and Caustic Leaching Results to the Tank Waste Remediation Studies Planning Assumptions	3.17
3.8 Impact on High-Level Waste Glass Volume	3.26

3.9 Conclusion 3.30

4.0 References 4.1

Appendix A Results from the Tank B-111 Sludge Washing and Caustic Leaching Test

Appendix B Results from the Tank BX-107 Sludge Washing and Caustic Leaching Test

Appendix C Results from the Tank C-103 Sludge Washing and Caustic Leaching Test

Appendix D Results from the Tank S-104 Sludge Washing and Caustic Leaching Test

Appendix E Results from the Tank SY-103 Sludge Washing and Caustic Leaching Test

Appendix F Results from the Tank T-104 Sludge Washing and Caustic Leaching Test

Appendix G Results from the Tank T-111 Sludge Washing and Caustic Leaching Test

Figures

Figure 2.1.	Titration of the First Caustic Leach Solution from the S-104 Sludge Washing and Caustic Leaching Test. (a) Titration curve: vertical line indicates the first equivalence point. (b) Gran plot.	2.7
Figure 3.1.	Settling of the Retrieval Wash Suspensions	3.5
Figure 3.2.	Properties of the Settled and Centrifuged Solids After the Retrieval Wash Step	3.6
Figure 3.3.	Properties of the Settled and Centrifuged Solids After the First Caustic Leach Step	3.7
Figure 3.4.	Properties of the Settled and Centrifuged Solids After the Second Caustic Leach Step	3.8
Figure 3.5.	Observed Aluminum Dissolution vs. Baseline Assumption	3.19
Figure 3.6.	Observed Phosphorus Removal Compared to the Unleachable Alkaline Earth Phosphate Hypothesis.	3.23
Figure A.1.	Schematic of the B-111 Sludge Washing and Caustic Leaching Test	A.1
Figure A.2.	Particle-Size Data for Untreated B-111 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph	A.9
Figure A.3.	Particle-Size Data for Treated B-111 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph	A.10
Figure B.1.	Schematic of the BX-107 Sludge Washing and Caustic Leaching Test	B.1
Figure B.2.	Particle-Size Data for Untreated BX-107 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph	B.9

Figure B.3.	Particle-Size Data for Treated BX-107 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph	B.10
Figure C.1.	Schematic of the C-103 Sludge Washing and Caustic Leaching Test	C.1
Figure C.2.	Particle-Size Data for Untreated C-103 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph	C.9
Figure C.3.	Particle-Size Data for Treated C-103 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph	C.10
Figure D.1.	Schematic of the S-104 Sludge Washing and Caustic Leaching Test	D.1
Figure D.2.	Particle-Size Data for Untreated S-104 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph	D.9
Figure D.3	Particle-Size Data for Treated S-104 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph	D.10
Figure E.1.	Schematic of the SY-103 Sludge Washing and Caustic Leaching Test	E.1
Figure E.2.	Particle-Size Data for Untreated SY-103 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph	E.9
Figure E.3	Particle-Size Data for Treated SY-103 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph	E.10
Figure F.1.	Schematic of the T-104 Sludge Washing and Caustic Leaching Test	F.1

Figure F.2. Particle-Size Data for Untreated T-104 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph F.9

Figure F.3. Particle-Size Data for Treated T-104 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph F.10

Figure G.1. Schematic of the T-111 Sludge Washing and Caustic Leaching Test G.1

Figure G.2. Particle-Size Data for Untreated T-111 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph G.9

Figure G.3. Particle-Size Data for Treated T-111 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph G.10

Tables

Table S.1.	Summary of Sludge Components Removed by Sludge Washing and Caustic Leaching	v
Table 1.1.	Primary and Secondary Waste Types Stored in the Tanks Investigated	1.2
Table 2.1.	Description of the Tank Samples Used	2.1
Table 2.2.	Comparison of Free Hydroxide Ion Concentrations Determined by Gran Plot Method and by First Equivalence Point Method	2.6
Table 3.1.	Summary of General Sludge Characteristics During Sludge Washing and Caustic Leaching	3.2
Table 3.2.	Number Distribution Summary for Particle-Size Analyses of Sludge Composites	3.10
Table 3.3.	Volume Distribution Summary for Particle-Size Analyses of Sludge Composites	3.11
Table 3.4.	Summary of the Effectiveness of Sludge Washing and Caustic Leaching in Removing Key Nonradioactive Components	3.13
Table 3.5.	Summary of Phosphate and Sulfate Removal by Sludge Washing and Caustic Leaching	3.14
Table 3.6.	Summary of Phosphate and Phosphorus Concentrations in Treated vs. Untreated Sludges	3.16
Table 3.7.	Summary of Radionuclide Removal by Sludge Washing and Caustic Leaching	3.17
Table 3.8.	Aluminum and Silicon Molar Concentrations in Treated Sludges	3.21
Table 3.9.	Water Insoluble Phosphorus Removed by Caustic Leaching	3.22

Table 3.10.	Calcium and Phosphorus Concentrations in Treated Sludges	3.25
Table 3.11.	Comparison of Sludge Washing and Caustic Leaching Results From Tanks In the Same SORWT Groups	3.27
Table 3.12.	Impact of Sludge Washing and Caustic Leaching on Glass Required for Sludge Vitrification	3.28
Table A.1.	Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the B-111 Test	A.3
Table A.2.	Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the B-111 Test	A.4
Table A.3.	Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the B-111 Test	A.5
Table A.4.	Mass Balance for Nonradioactive Sludge Components From the B-111 Test	A.6
Table A.5.	Concentrations of the Radioactive Sludge Components in the Various Process Streams From the B-111 Test	A.7
Table A.6.	Distribution of the Radioactive Sludge Components Between the Various Process Streams From the B-111 Test	A.8
Table A.7.	Mass Balance for Radioactive Sludge Components From the B-111 Test	A.8
Table B.1.	Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the BX-107 Test	B.3
Table B.2.	Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the BX-107 Test	B.4
Table B.3.	Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the BX-107 Test	B.5
Table B.4.	Mass Balance for Nonradioactive Sludge Components From the BX-107 Test	B.6
Table B.5.	Concentrations of the Radioactive Sludge Components in the Various Process Streams From the BX-107 Test	B.7

Table B.6.	Distribution of the Radioactive Sludge Components Between the Various Process Streams From the BX-107 Test	B.8
Table B.7.	Mass Balance for Radioactive Sludge Components From the BX-107 Test	B.8
Table C.1.	Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the C-103 Test	C.3
Table C.2.	Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the C-103 Test	C.4
Table C.3.	Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the C-103 Test	C.5
Table C.4.	Mass Balance for Nonradioactive Sludge Components From the C-103 Test	C.6
Table C.5.	Concentrations of the Radioactive Sludge Components in the Various Process Streams From the C-103 Test	C.7
Table C.6.	Distribution of the Radioactive Sludge Components Between the Various Process Streams From the C-103 Test	C.8
Table C.7.	Mass Balance for Radioactive Sludge Components From the C-103 Test	C.8
Table D.1.	Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the S-104 Test	D.3
Table D.2.	Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the S-104 Test	D.4
Table D.3.	Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the S-104 Test	D.5
Table D.4.	Mass Balance for Nonradioactive Sludge Components From the S-104 Test	D.6
Table D.5.	Concentrations of the Radioactive Sludge Components in the Various Process Streams From the S-104 Test	D.7

Table D.6.	Distribution of the Radioactive Sludge Components Between the Various Process Streams From the S-104 Test	D.8
Table D.7.	Mass Balance for Radioactive Sludge Components From the S-104 Test	D.8
Table E.1.	Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the SY-103 Test	E.3
Table E.2.	Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the SY-103 Test	E.4
Table E.3.	Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the SY-103 Test	E.5
Table E.4.	Mass Balance for Nonradioactive Sludge Components From the SY-103 Test	E.6
Table E.5.	Concentrations of the Radioactive Sludge Components in the Various Process Streams From the SY-103 Test	E.7
Table E.6.	Distribution of the Radioactive Sludge Components Between the Various Process Streams From the SY-103 Test	E.8
Table E.7.	Mass Balance for Radioactive Sludge Components From the SY-103 Test	E.8
Table F.1.	Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the T-104 Test	F.3
Table F.2.	Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the T-104 Test	F.4
Table F.3.	Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the T-104 Test	F.5
Table F.4.	Mass Balance for Nonradioactive Sludge Components From the T-104 Test	F.6
Table F.5.	Concentrations of the Radioactive Sludge Components in the Various Process Streams From the T-104 Test	F.7

Table F.6.	Distribution of the Radioactive Sludge Components Between the Various Process Streams From the T-104 Test	F.8
Table F.7.	Mass Balance for Radioactive Sludge Components From the T-104 Test	F.8
Table G.1.	Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the T-111 Test	G.3
Table G.2.	Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the T-111 Test	G.4
Table G.3.	Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the T-111 Test	G.5
Table G.4.	Mass Balance for Nonradioactive Sludge Components From the T-111 Test	G.6
Table G.5.	Concentrations of the Radioactive Sludge Components in the Various Process Streams From the T-111 Test	G.7
Table G.6.	Distribution of the Radioactive Sludge Components Between the Various Process Streams From the T-111 Test	G.8
Table G.7.	Mass Balance for Radioactive Sludge Components From the T-111 Test	G.8

1.0 Introduction

During the past few years, the primary mission at the U.S. Department of Energy's Hanford Site has changed from producing plutonium to environmental restoration. Large volumes of high-level radioactive wastes (HLW), generated during past Pu production and other operations, are stored in underground tanks on site. The current plan for remediating the Hanford tank farms consists of waste retrieval, pretreatment, treatment (immobilization), and disposal. The HLW will be immobilized in a borosilicate glass matrix; the resulting glass canisters will then be disposed of in a geologic repository. Because of the expected high cost of HLW immobilization and disposal, pretreatment processes will be implemented to reduce the volume of borosilicate glass produced in processing the tank wastes.

This document describes sludge washing and caustic leaching tests conducted in FY 1995 at the Pacific Northwest Laboratory (PNL)^(a) at the request of Westinghouse Hanford Company. These tests were performed using sludges from seven Hanford waste tanks—B-111, BX-107, C-103, S-104, SY-103, T-104, and T-111. The primary and secondary types of waste stored in each of these tanks are given in Table 1.1. The data collected in this effort will be used to support the March 1998 Tri-Party Agreement decision on the extent of pretreatment to be performed on the Hanford tank sludges (Ecology, EPA, and DOE 1994).

According to the baseline sludge pretreatment flowsheet, the sludge will be retrieved from the tanks by sluicing and pumping with inhibited water (0.01 M NaOH/0.01 M NaNO₂), leached with caustic (3 M NaOH), then washed with inhibited water to remove the added NaOH and the components dissolved during the caustic leaching step. The retrieval, leachate, and wash solutions will be combined and processed to remove ¹³⁷Cs (and possibly other radionuclides). The decontaminated solution will then be routed to the low-level waste (LLW) stream, where it will be immobilized in a glass matrix. The leached solids, which will contain the transuranic (TRU) elements and ⁹⁰Sr, will be handled as HLW (Orme 1994).

^(a) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

Table 1.1. Primary and Secondary Waste Types Stored in the Tanks Investigated^(a)

<u>Tank</u>	<u>Primary Waste</u>	<u>Secondary Waste</u>
B-111	2C	5-6
BX-107	1C	TBP
C-103	SRS	SR-WASH
S-104	R	(b)
SY-103	CC	(b)
T-104	1C	(b)
T-111	2C	224

(a) The waste types are defined as follows (Hill, Anderson, and Simpson 1995).

CC	Complexant concentrate
R	Reduction oxidation (REDOX) process high-level waste
SRS	Sludge feed for the Sr extraction process at B Plant
SR-WASH	Particulates from Sr wash of plutonium uranium extraction (PUREX) wastes in AR Vault
TBP	Waste from the tributyl phosphate (TBP) uranium extraction process at U Plant
1C	First-cycle decontamination waste from the bismuth-phosphate process
2C	Second-cycle decontamination waste from the bismuth-phosphate process
224	Lanthanum fluoride decontamination waste from the bismuth-phosphate process
5-6	High-level waste from Tank 5-6 at B Plant

(b) No major secondary waste type.

Caustic leaching is expected to remove a large fraction of the Al, which is present in large quantities in Hanford tank sludges (Weber 1982). A significant portion of the P is also expected to be removed from the sludge by metathesis of water-insoluble metal phosphate salts to insoluble hydroxide salts and soluble Na_3PO_4 . Removing Al and P from the sludge solids could have a large impact in reducing the volume of HLW glass produced during tank waste disposal operations.

Previous studies on leaching sludges with highly caustic solutions (both in the presence or absence of other Cr-solubilizing agents) suggest that Cr might also be removed from the sludges (Lumetta et al. 1994; Lumetta and Swanson 1993b). Enhanced Cr dissolution has been observed at highly caustic vs. mildly basic solutions and may be due to the increased solubility of Cr(III) at high-hydroxide concentrations (Rai, Sass, and Moore 1987). For certain sludges, leaching such key components should result in a greatly decreased volume of HLW glass produced without resorting to more aggressive dissolution and separation methods (Straalsund et al. 1992). For example, removal of Cr from Plutonium Finishing Plant (PFP) sludge alone is estimated to decrease the number of glass canisters from 2500 for washed-only sludge to 500 for Cr-free washed sludge (Lumetta, Swanson, and Barker 1995).^(a)

Previous studies of washing and caustic leaching of Hanford tank sludges have been reported (Lumetta and Rapko 1994; Lumetta, Rapko, and Colton 1994). Although the previous tests were not performed under conditions identical to those of the current baseline flowsheet, the results indicated 83% removal of Al, 62% removal of Cr, and 89% removal of P from the total quantities present in the five tanks investigated.

^(a) These HLW glass canister projections are based on 1650-kg glass logs and it is assumed that the PFP sludge is not blended with other wastes before immobilizing.

2.0 Experimental

The materials and methods used in the sludge washing and caustic leaching screening tests are discussed in this section.

2.1 Materials

Sludge washing and caustic leaching screening tests were performed on sludges from seven Hanford tanks. The seven tanks are listed in Table 2.1 along with the details of the individual samples investigated.

Table 2.1. Description of Tank Sludge Samples Used

<u>Tank</u>	<u>Core Number</u>	<u>Description</u>
B-111	29 and 30	Composite sample comprised of 2.65 g of Core 29 composite 1 {Analytical Laboratory Operations (ALO) Number 93-04314}, ^(a) 1.96 g of Core 29 composite 2 (ALO Number 93-04315), 2.64 g of Core 30 composite 1 (ALO Number 93-04322), and 2.57 g of Core 30 composite 2 (ALO Number 93-04323)
BX-107	41	Composite from Core 41 (222-S Jar Number J941) ^(b)
C-103	63	Composite sample of segments 2-4 from core 63 (222-S Jar Number 6770)
S-104	43	Composite of segments 4 and 5 from Core 43 (222-S Jar Number 6588)
SY-103	62	Composite of segments 10 through 14 from Core 62 (222-S Jar Number 6590)
T-104	46	Composite of segments 2, 3, and 4 from Core 46 (222-S Jar Number 6555)
T-111	33	Composite of segments 1 and 3 from Core 33 (222-S Jar Number 6591)

(a) The ALO Number is a unique identifying number used by the PNL Analytical Chemistry Laboratory to track samples.

(b) Identifying number used at the Westinghouse Hanford Company (WHC) 222-S laboratory for tracking samples.

Solutions were prepared using reagent grade NaOH, NaNO₃, and NaNO₂. The concentrations of the NaOH solutions were confirmed by titration with standard HCl.

2.2 Sludge Washing and Caustic Leaching Procedure

The same general procedure was used for each sludge washing and caustic leaching test; specific details for each test are given in schematic figures in the appendices (Figures A.1, B.1, C.1, D.1, E.1, F.1, and G.1). The procedure consisted of the following steps.

1. A portion of the sludge was placed in a high-density polyethylene (HDPE) or polymethylpentene bottle.
2. The sludge was slurried in water (4 g water/g sludge); then four aliquots of the slurry were removed.
3. One of the aliquots was dried to a constant weight at 80°C; this dried aliquot was submitted for analysis.
4. Two of the aliquots were saved. One was used for particle-size measurements; the second was dried and used for microscopy studies.
5. The fourth aliquot was washed with three 5-mL portions of 0.01 M NaOH/0.01 M NaNO₂ at room temperature, and was then dried to a constant weight at 80°C. This weight was assumed to represent the water-insoluble solids in the sludge, and was used to determine the weight percent of such solids in the sludge sample.
6. The weight percent of water-insoluble solids determined in step 5 was used to determine the total volume of "retrieval" solution needed to yield a slurry containing 2.3 wt% solids.^(a) Water, NaOH, and NaNO₂ were added to the sludge slurry to give the appropriate volume of 0.01 M NaOH/0.01 M NaNO₂ retrieval solution. The resulting mixture was stirred and heated at 100°C for 1 h.
7. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity.

^(a) The first step in the process was designed to mimic the retrieval process outlined in the baseline sludge treatment flowsheet (Orme 1994).

8. Once the sludge had stopped settling, the mixture was centrifuged, and the solution was decanted. Hereafter, this solution will be referred to as the "retrieval wash" solution.
9. The weight percent of water-insoluble solids determined in step 5 was used to determine the total volume of caustic leach solution needed to yield a slurry containing 8 wt% solids (assuming that 30% of the water-insoluble solids dissolve in the caustic leaching step).
10. At this point, the sludge was transferred to a smaller container that was more consistent with the volume of the caustic leach solution to be used. Typically this smaller container was a 20-mL HDPE vial or a 30-mL polypropylene Oak Ridge-type centrifuge tube. The sludge was transferred using portions of the retrieval wash solution that was collected in Step 8. Upon quantitative transfer of the sludge, the slurry was centrifuged; then the supernatant solution was decanted and combined with the rest of the retrieval wash solution.
11. Water and 10 M NaOH were added to the sludge to give a caustic leach mixture with the volume determined in Step 9, and an initial hydroxide concentration of nominally 3.2 M. The resulting mixture was stirred and heated at 100°C for 5 h.
12. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity.
13. Once the sludge had stopped settling, the mixture was centrifuged, and the solution was decanted. Hereafter, this solution will be referred to as the first caustic leach solution.
14. A second caustic leach step was performed by adding enough 3 M NaOH to give a total volume equal to that determined in Step 9. Again, the leach mixture was stirred and heated at 100°C for 5 h.
15. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity.
16. Once the sludge had stopped settling, the mixture was centrifuged, and the solution was decanted. Hereafter, this solution will be referred to as the second caustic leach solution.
17. The leached sludge was successively washed with three portions of 0.01 M NaOH/0.01 M NaNO₂; the volume of each portion of wash solution was equal to the volume of the second caustic leach solution decanted in Step 16. For the first two portions, mixing was stopped after mixing for at least 0.5 h at room temperature, and the solids were allowed to settle under the force of gravity. In the case of the third wash, two aliquots of the suspension were removed before the solids were allowed to settle. One aliquot was saved for a particle-size measurement; the second was dried and used for microscopy.

studies. In each case, after gravity settling the mixture was centrifuged then the wash liquor was decanted.

18. Finally, the remaining residue was dried to a constant weight at 80°C.

Some of the weights measured in the course of the tests had inconsistencies. This was especially true for the C-103 test, which was performed in a hot cell due to the high ⁹⁰Sr content of that material. For example, when a portion of the slurried sludge (C103-2B in Figure C.1) was dried to determine the wt% solids in the sludge, the amount of dry sludge solids (0.54 g) was greater than the amount of sludge expected to be in the slurry (0.47 g). This might have resulted from inadequate stirring of the slurry during sampling; that is, if the sludge solids were not homogeneously dispersed in the slurry, the portion withdrawn in C103-2B could have contained >0.47 g. During an earlier test with the same C-103 sludge sample, the sludge was found to consist of 43 wt% solids.^(a) Using the latter value, the dry weight of the solids leached was determined to be 6.3 g, which is the value given in Figure C.1.

The amount of retrieval wash solution obtained for the C-103 test was also inconsistent with the amount of materials added. Correcting for the mass of samples taken and the mass lost due to evaporation during heating, the mass of the retrieval wash slurry was 99.8 g. Yet only a total of 87.9 g of material (76.9 g of retrieval wash solution and 11.0 g of centrifuged solids) was recovered. The reason for this discrepancy is unknown.

2.3 Analytical Methods

Portions of the sludges were analyzed before and after the sludge washing/caustic leaching treatment. The solid samples were solubilized for analysis by a well established KOH fusion method.^(b) Samples of the retrieval wash, the first and second caustic leach, and the

^(a) This earlier test was aborted during the first caustic leaching step due to a suspected loss of containment of the vial being used.

^(b) Analytical Chemistry Laboratory Department. *Analytical Chemistry Laboratory (ACL) Procedure Compendium*. PNL-MA-599. Pacific Northwest Laboratory, Richland, Washington.

final wash solutions were analyzed after acidification with HNO_3 . The major metallic elements (Al, Bi, Cr, Fe, Na, etc.) as well as P and Si were determined by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). Ion chromatography (IC) was performed to determine the anions present. Alpha spectroscopy was used to determine the transuranic elements present, and gamma spectroscopy was used to measure the gamma-emitting radionuclides such as ^{137}Cs . Uranium concentrations were determined by laser fluorimetry. A proportional beta counter was used to determine ^{90}Sr and ^{99}Tc after chemical separation of these isotopes from the other radionuclides. Established procedures were used for all these analyses.^(a)

Particle-size measurements were made using a Brinkmann Instruments Model PSA 2010, which measures particle diameter based on the time required for a fixed-velocity scanning laser beam to traverse the particle. The samples were dispersed for the measurement in 1:1 (v:v) mixture of water and glycerin.

Free hydroxide concentrations in the caustic leach solutions were determined by titration with standard HCl. The titrations were performed potentiometrically using a Mettler DL21 automatic titrator equipped with a ROSS® combination pH electrode (Orion Research Inc., Boston, Massachusetts). Work by others at PNL using simulated Tank SY-101 simulant indicated that the free hydroxide concentration in complex matrices can be determined by the Gran plot method.^(a) In the course of this work, it was found that a simpler way to determine the free hydroxide concentration in the sludge leach solutions was to equate the first inflection point in the titration curve to the free hydroxide concentration. The latter method assumes that hydroxide ion is the strongest base in the leach solution and thus is consumed first by the HCl titrant. A typical titration curve and corresponding Gran plot are given in Figure 2.1. In this example, a 0.1-mL aliquot of the first caustic leach solution from the S-104 test was diluted with 10 mL of water and titrated with 0.103 M HCl. The first inflection point in the titration curve was at 3.70 mL, which corresponds to 3.8 M free hydroxide ion. The Gran plot reveals

^(a) Karl Pool. 1994. Unpublished data. Pacific Northwest Laboratory, Richland, Washington.

the equivalence point for free hydroxide ion to be 3.62 mL, giving 3.7 M OH⁻. Table 2.2 presents a comparison of free hydroxide ion concentrations determined by both methods. Clearly, the two methods are essentially equivalent.

Table 2.2. Comparison of Free Hydroxide Ion Concentrations Determined by Gran Plot Method and by First Equivalence Point Method

Solution	Free Hydroxide Concentration, M	
	Gran Plot	First Inflection Point
B-111 First Caustic Leach	2.2	2.3
B-111 Second Caustic Leach	4.0	4.3
BX-107 First Caustic Leach	2.0	2.0
BX-107 Second Caustic Leach	3.5	3.6
C-103 First Caustic Leach	0.61	0.60
C-103 Second Caustic Leach	1.0	1.0
S-104 First Caustic Leach	3.7	3.8
S-104 Second Caustic Leach	2.9	3.0
SY-103 First Caustic Leach	2.2	2.2
SY-103 Second Caustic Leach	2.7	2.8
T-104 First Caustic Leach	0.32	0.31
T-104 Second Caustic Leach	2.2	2.2
T-111 First Caustic Leach	3.3	3.5
T-111 Second Caustic Leach	3.2	3.4

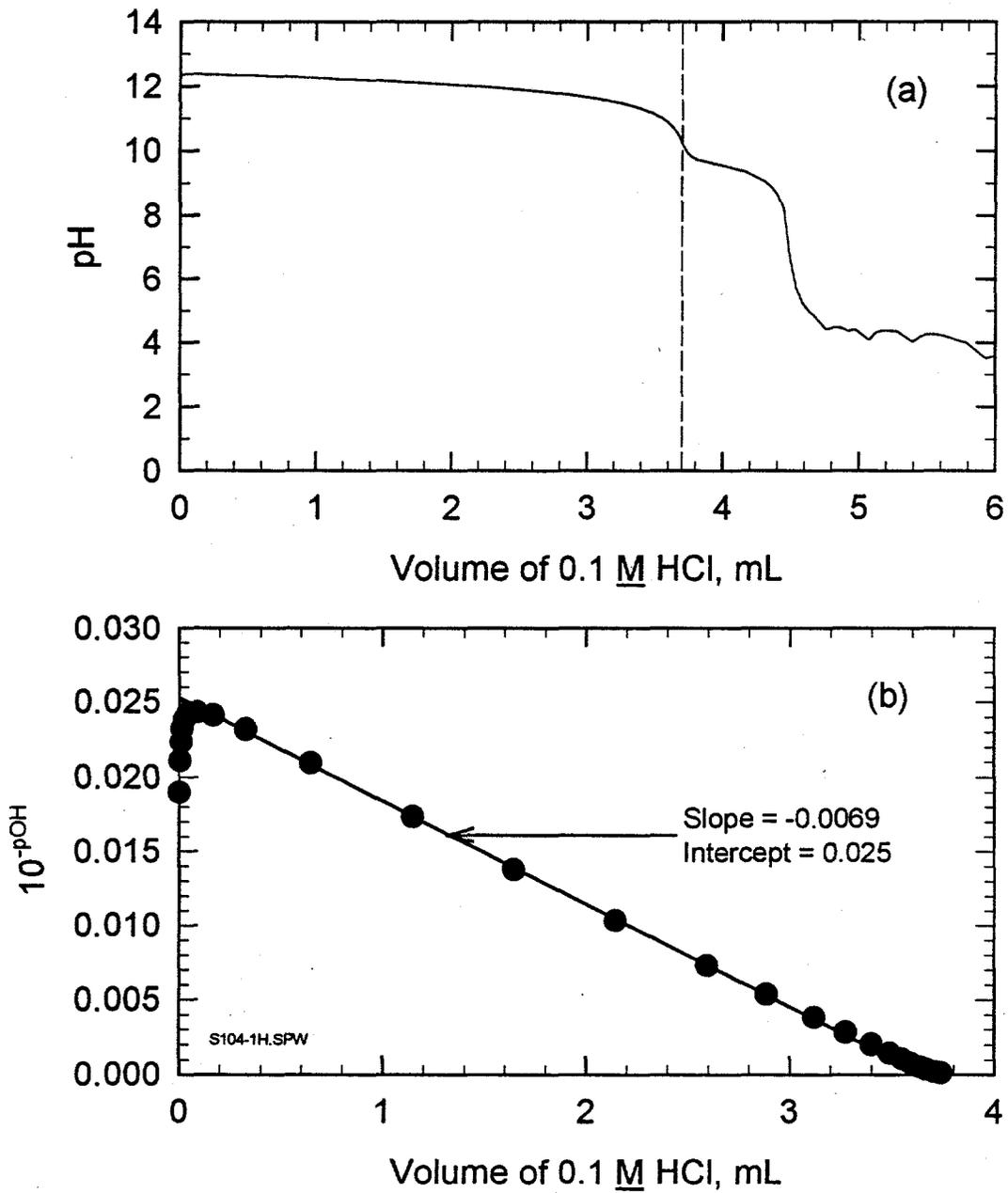


Figure 2.1. Titration of the First Caustic Leach Solution from the S-104 Sludge Washing and Caustic Leaching Test. (a) Titration curve: vertical line indicates the first equivalence point. (b) Gran plot.

3.0 Results and Discussion

Data obtained from the sludge washing and caustic leaching screening tests are discussed in this section. The presentation is organized according to the type of measurements performed; that is, the results of each type of measurement or observation are discussed regarding the entire series of sludges investigated. The following subjects are covered in this section: 1) general observations, 2) settling behavior of sludge solids, 3) particle size before and after leaching, 4) behavior of nonradioactive sludge components, 5) behavior of anionic components, 6) behavior of radionuclides, 7) impacts of the data on the planning assumptions, and 8) impact of sludge washing and caustic leaching on the HLW glass volume.

3.1 General Observations

This section describes basic changes that occurred during the sludge washing and caustic leaching tests. Table 3.1 summarizes such features as the pH of the retrieval wash solutions following contact with the sludges, weight percent insoluble solids found for each sludge, and the mass loss accompanying the sludge washing and caustic leaching pretreatment tests.

A tank-by-tank comparison of any of the features described in Table 3.1 indicates considerable variability—a common theme throughout this work and one that is not unexpected given the disparate processes by which these sludges were generated. The second column reports the percentage of the sludge mass attributed to the solids present in the as-received composites (including the mass of dissolved salts in the interstitial liquid) and compares this measured value to that reported during the initial sludge characterization. The sludge samples varied from very wet materials (e.g., T-104 and T-111) to fairly dry solids (e.g., S-104). These values correlate with the general appearance of the sludges: T-104 and T-111 sludges appeared as runny slurries, while S-104 appeared as more of a thick dry paste, or even as tar-like in consistency. Agreement with the tank characterization reports for these sludges was reasonably good, and the general trend appeared to be the same in that the tank characterization data also indicate T-104 and T-111 sludges have the highest water contents. Reasons for the lack of close agreement where discrepancies are apparent include possible

Table 3.1. Summary of General Sludge Characteristics During Sludge Washing and Caustic Leaching

Tank	Wt% Solids ^(a)	Wt% Water-Insoluble Solids ^(b)	Estimated Mass Loss During Leaching, %	pH of Retrieval Wash Solution (pH of sludge) ^(a)
B-111	45 (36)	22	0	9.7 (11)
BX-107	53 (43)	34	36	9.8 (9.7)
C-103	42 (39)	31	na	10.2(9.8)
S-104	87 (65)	49	33	12.2 (13)
SY-103	64 (na)	11	56	13.2 (na)
T-104	28 (29)	56	1	9.8 (10)
T-111	22 (24)	62	10	11.4 (10)

na = data not available

(a) Values in parentheses are taken from Colton (1995), which in turn were compiled from original tank characterization data.

(b) Based on the dry weight of the sludge solids.

differences in the composite used or, more likely, some drying of the materials during storage. The latter possibility is supported by the fact that in every case except T-104 and T-107, the weight percent solids measured in this work is greater than that measured in the tank characterization work.

The third column in Table 3.1 reports the weight percent water-insoluble solids, based on the dry weight of the sludge solids. The amount of insoluble material as a portion of the total solids ranged over a factor of ~6 for the sludges examined, with T-104, T-111, and S-104 having high portions of water-insoluble solids. Tank SY-103 contains complexant concentrate waste and thus would be expected to have some of the metallic elements present in a complexed water-soluble form. Indeed, the SY-103 sludge had the lowest fraction of water insoluble solids for the sludges investigated in this work.

The fourth column in Table 3.1 reports on the mass lost during the washing and caustic leaching steps. This was calculated by taking the final dried solids weight (after compensation

for the aliquots removed for particle-size determination and microscopy) and dividing by the calculated amount of initial water-insoluble solids present. To estimate the volume of leach solution required to give 8 wt% solids at the end of the caustic leach step, the test procedure assumed 30% of the water-insoluble solids would be removed during the caustic leach step. Table 3.1 indicates that while 30% appears as a reasonable median value, actual mass losses ranged from 0% (T-104 and B-111) to almost 60% (SY-103). The function of the caustic leach step is both to dissolve some major nonradioactive components (primarily Al), and to metathesize insoluble phosphate and sulfate salts to the corresponding insoluble hydroxides and soluble sodium phosphate and sodium sulfate. Qualitatively, the observed trends of mass loss during the caustic leach step were consistent. Sludges with relatively high amounts of Al (SY-103, S-104, BX-107) showed the most substantial mass losses during the sludge washing and caustic leaching tests.

The final column in Table 3.1 reports the pH of the retrieval wash solutions, as well as the reported approximate pH of the sludge (Colton 1995). With 0.01 M OH⁻ in the retrieval wash solutions, the initial expectation would be that the pH of the retrieval wash solution upon contact with the sludge solids should be a value between the sludge's reported pH and that of the retrieval wash solution (pH ~ 12). This expectation was borne out in all cases but B-111, where the observed pH of the retrieval wash solution (9.7) was much less than either the wash solution itself or the sludge. The reason for the unusual behavior for B-111 is unknown, but could be due to differences in the sample used in the previous characterization work to that used here. In all other cases, the pH of the retrieval wash solutions were indeed bounded by the sludge and the wash solution before sludge contact. In most cases, the sludges exhibited a substantial buffering effect as indicated by the retrieval wash solution's final pH being closest to the initial pH of the sludge, even at the relatively high volume/solids ratio of 2.3% insoluble solids used. However, for sludges T-111 and S-104 the impact of the sludge on the solution's final pH was markedly less.

3.2 Settling Behavior of the Sludge Solids

The settling behavior of the sludge solids during the retrieval wash step is summarized in Figure 3.1. Data for six sludges, B-111, BX-107, S-104, SY-103, T-104, and T-111 are included. The sludge washing and caustic leaching test with C-103 was performed in the hot cell. Poor visibility vitiated gathering settling data for this test. As Figure 3.1 illustrates, different sludges had very different settling characteristics, ranging from the rapid settling observed with SY-103, BX-107, and T-104 sludges to the very poor settling of S-104 sludge. For T-111 sludge, an induction period was observed before the onset of rapid settling; such behavior was not observed for the other sludges investigated in this work, but has been observed in other studies (Lumetta and Swanson 1993a). In general, these sludges settled to nearly their final sludge volumes within the first few hours, S-104 being a noticeable exception.

Figures 3.2 to 3.4 summarize the extent of the solids settling (generally, after 18 h), as well as the extent of solids compaction by centrifugation at up to 1700 G for 15 min. In selected cases, longer centrifugation times were employed with little, if any, additional decrease in the sludge height. The solids concentrations in the gravity-settled and centrifuged sludges (indicated at the bottom of the figures) were derived from the initial solids concentrations in the starting slurry (indicated in the middle of the figures) and the corresponding decrease in the solids volume (indicated at the top of figures). Figure 3.2 focuses on the final solids characteristics during the retrieval wash step. The centrifuged solids compacted to within a fairly narrow range of around 10% of the original volume of the retrieval wash slurry, giving a solids concentration of around 15 to 25 wt% in all cases. Very different values were found for the gravity settled solids in the retrieval wash solutions. While some sludges such as T-104 and SY-103 settled by gravity to 20% of the original volume, S-104 settled by gravity to only 70% of the original volume. This led to solids loading in the settled sludge ranging from around 3 to 15 wt% under the conditions employed here.

Figures 3.3 and 3.4 describe the final solids characteristics in the first and second caustic leach steps, respectively. The behavior was very similar between each leach step. In all

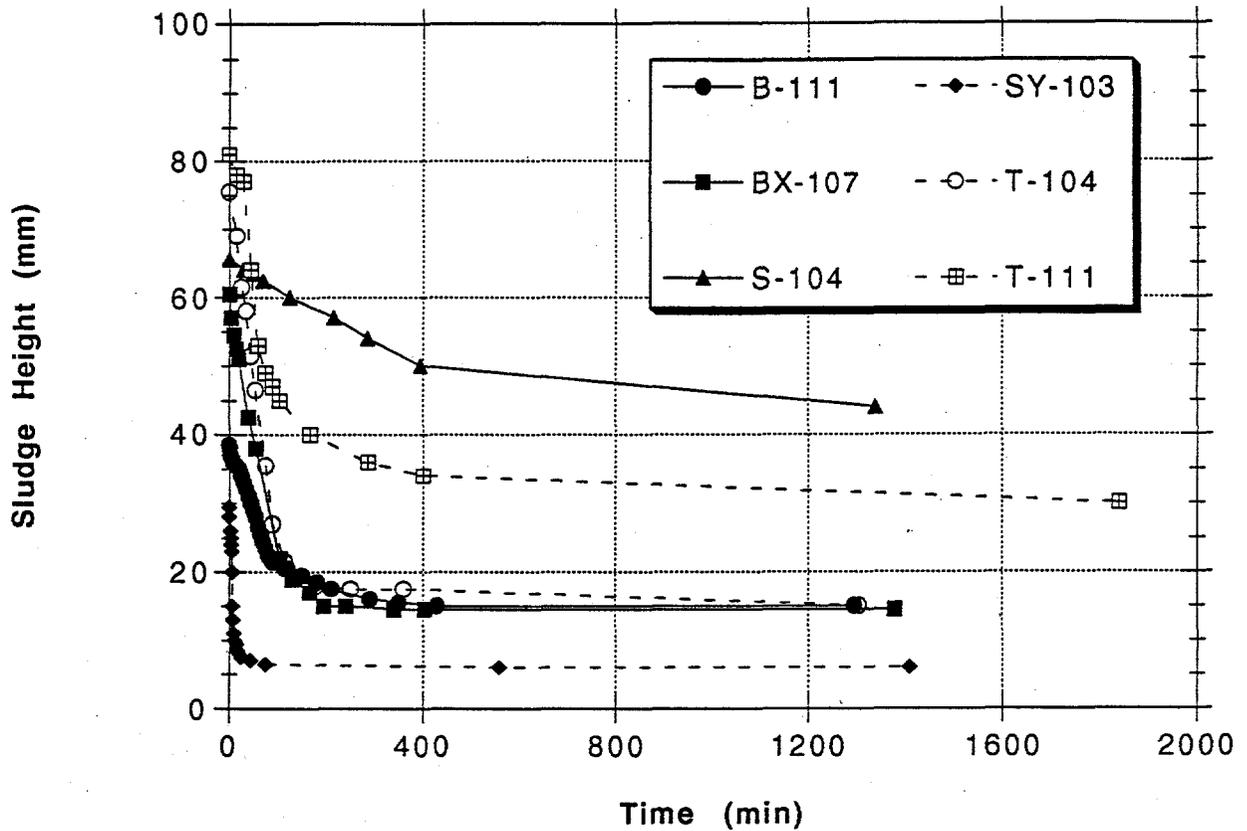


Figure 3.1. Settling of the Retrieval Wash Suspensions

cases, the solids compaction by gravity settling during the leaching step was much poorer than during the retrieval wash. Indeed, half of the sludge suspensions examined showed no clear liquid at all and the ones that did showed much less settling than in the retrieval wash step. In most cases, the solids concentrations in the centrifuged solids after the second caustic leaching step were similar to those in the centrifuged solids following the retrieval wash step. This suggests much of the settling difference observed for the retrieval wash and caustic leaching steps simply reflects the higher initial solids concentration used in the caustic leach steps.

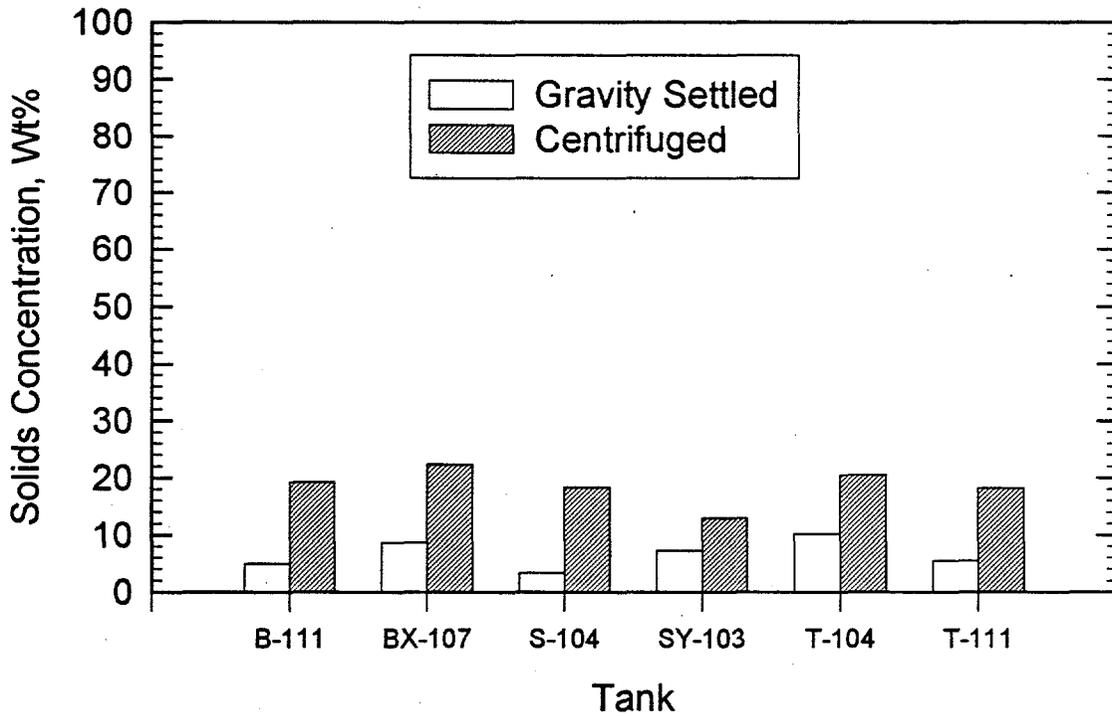
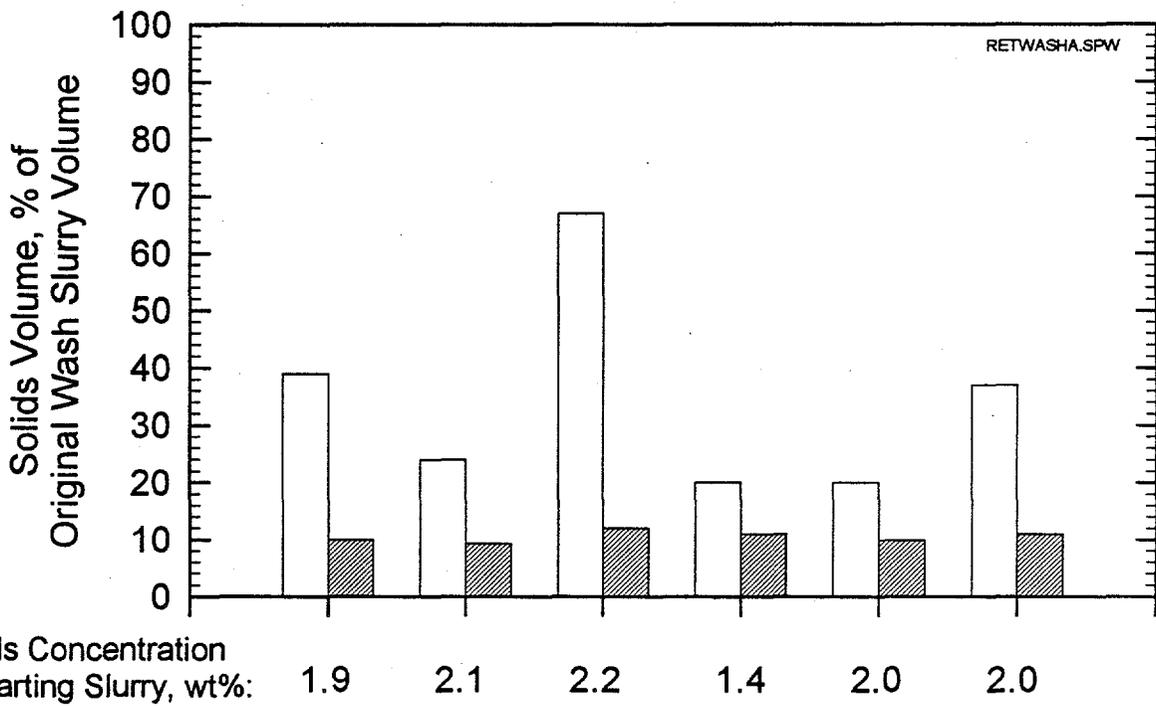
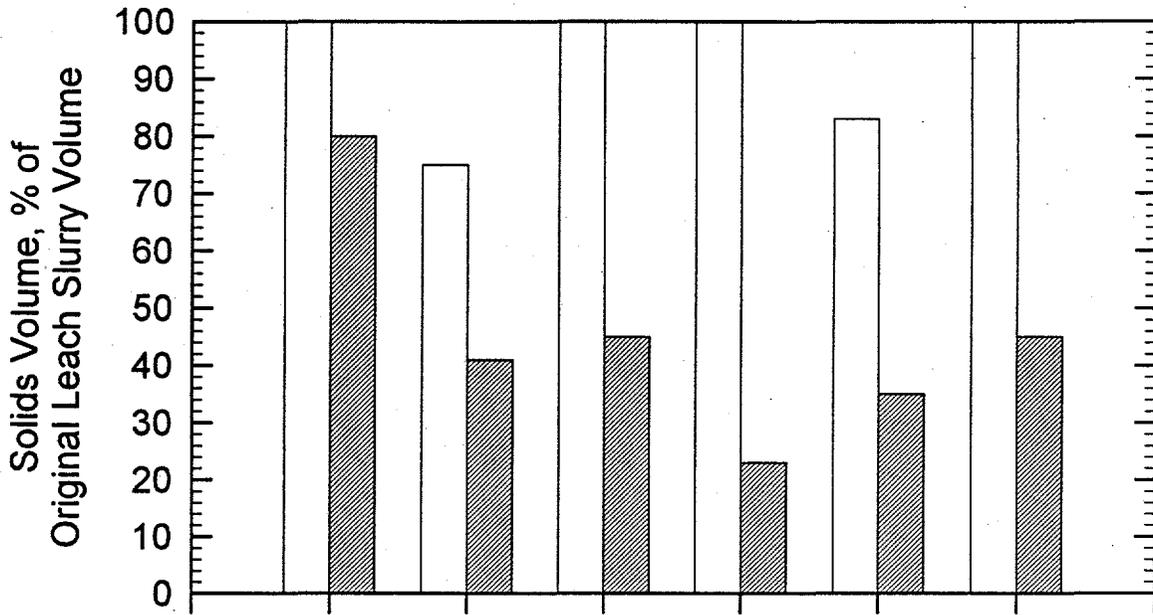


Figure 3.2. Properties of the Settled and Centrifuged Solids After the Retrieval Wash Step



Solids Concentration
in Starting Slurry, wt%:

11.3

6.9

12.2

5.4

13.0

11.9

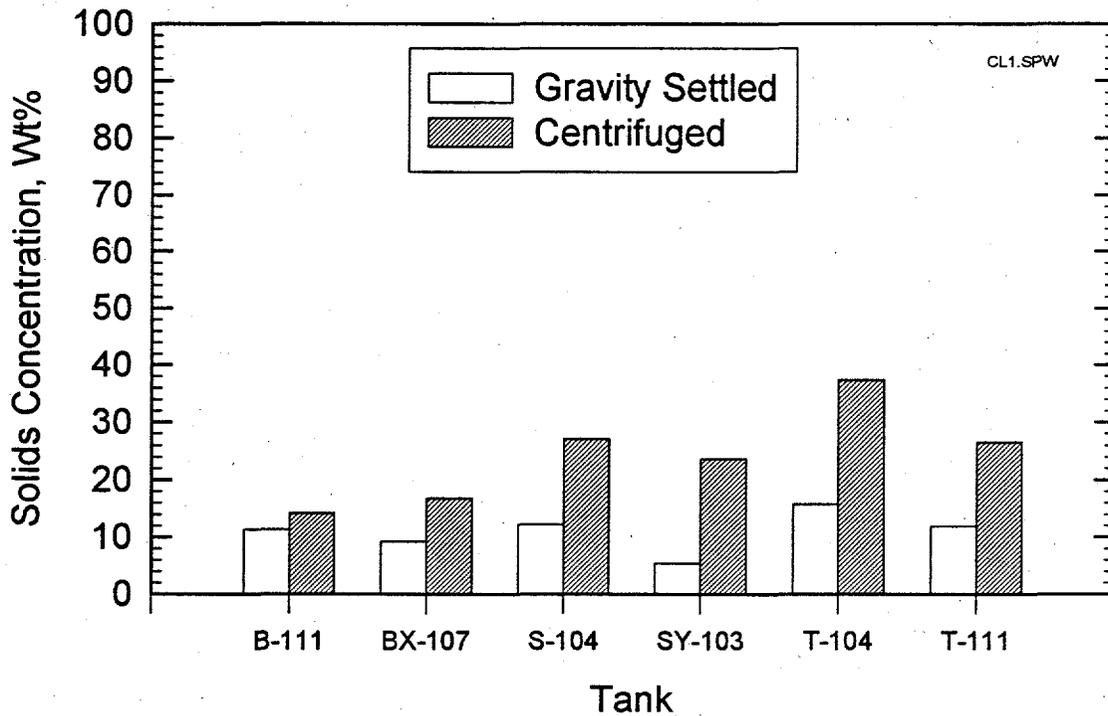


Figure 3.3. Properties of the Settled and Centrifuged Solids After the First Caustic Leach Step

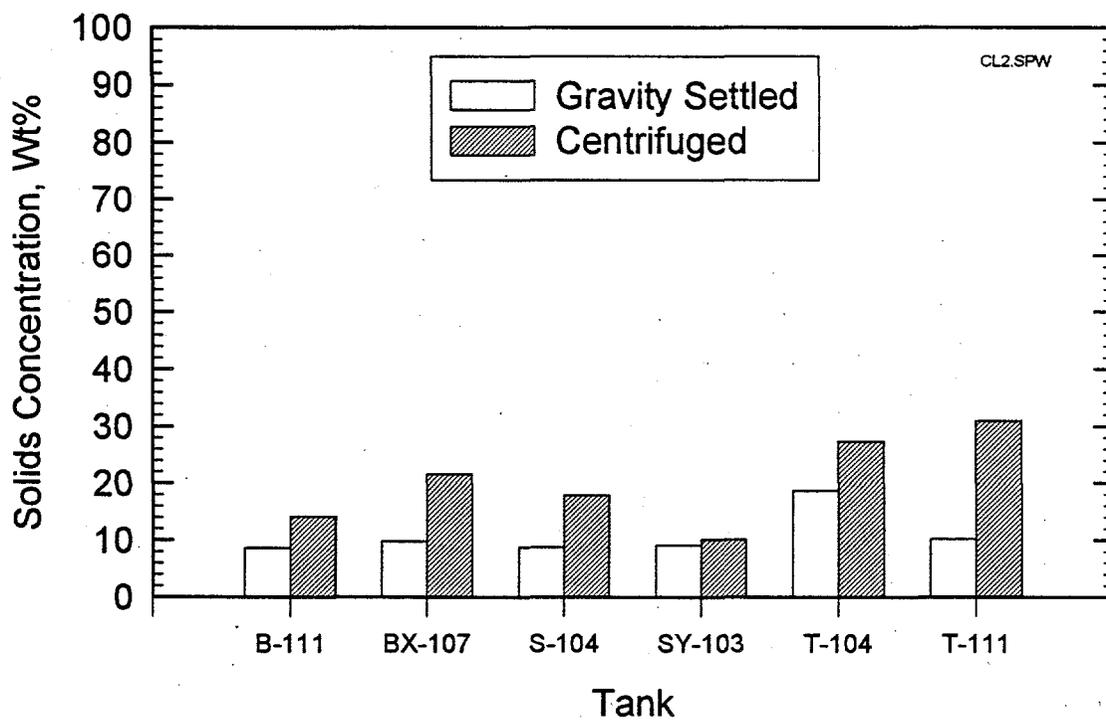
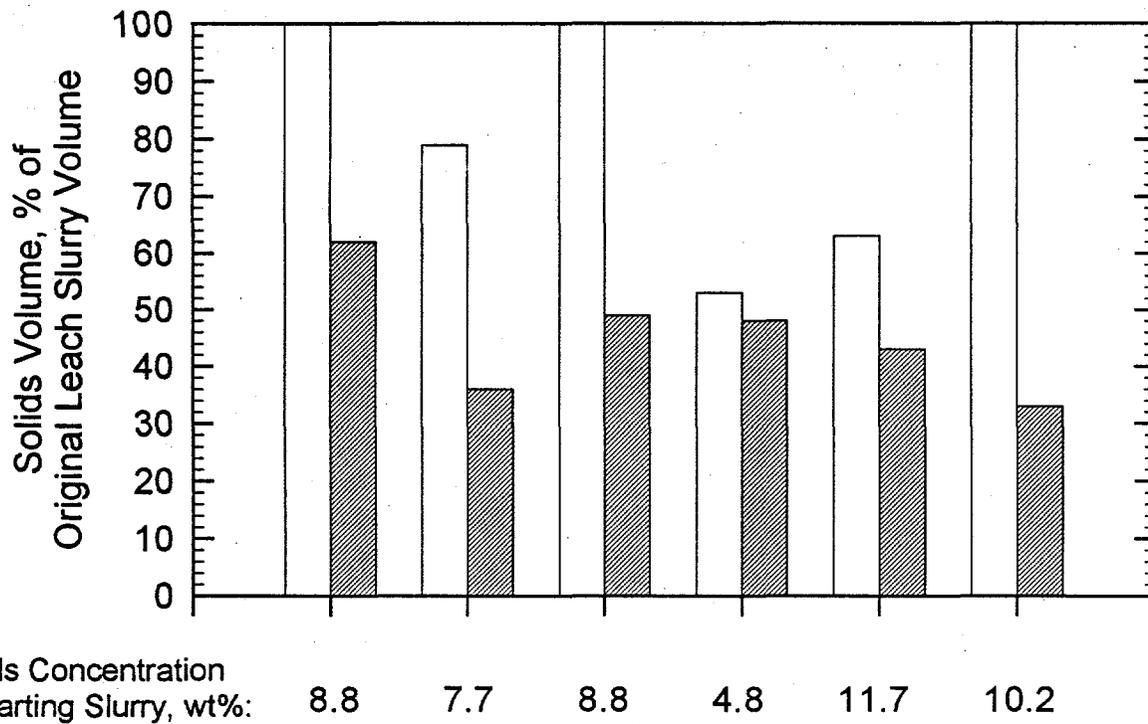


Figure 3.4. Properties of the Settled and Centrifuged Solids After the Second Caustic Leach Step

3.3 Particle-Size Analysis of Sludges Before and After Washing and Leaching

Particle-size distributions of the sludge solids were measured both before and after sludge washing and caustic leaching. Plots of the results, expressed as both a number and a volume percent distribution, are given in the Appendices. The samples were prepared for analysis by suspension in a 1:1 water/glycerin matrix, and it is unclear if this matrix yields an accurate measurement of the particle-size distributions that would be encountered in processing. Because of primary particle agglomeration phenomena, solution variables, such as ionic strength and hydroxide concentration, can dramatically affect the apparent particle-size distributions in these types of materials when measured in this manner. Furthermore, the methods of transferring and mixing the sludge will likely have significant effects on the particle size distribution. Thus, the values presented here should be used with caution, especially if attempting to extrapolated to behavior to try to predict particle size distributions during actual processing. A summary of the median particle-size, mean particle-size, and the standard deviation of the mean particle-size (which provides a sense of the width of the distribution) is provided in Tables 3.2 and 3.3. In most cases, the initial sludges appeared similar in size and distribution, with mean number distribution on the order of 1 μm . Values for the volume distributions were higher and over a larger range, with measured mean values of 1 to 6 μm .

Several types of changes in the particle-size distributions as a function of sludge washing and caustic leaching were seen. In some cases, sludge washing and caustic leaching caused little change in the measured distributions of particle-size; C-103 and T-104 are examples of this first type of behavior. On the other hand, SY-103 showed a decrease in the measured particle-size as indicated both by volume and by number. A third type of behavior was shown by B-111, which showed a modest increase in the distribution by number, but a major increase in the particle-size by volume. Tanks BX-107, S-104, and T-111 sludges were similar to B-111. In these cases, the most modest increase in the particle-size by number translated into a major change in the particle-size distribution by volume. Overall, under the conditions of the particle size measurements, little change in the particle-size was measured as a result of

Table 3.2. Number Distribution Summary for Particle-Size Analysis of Sludge Composites

<u>Sludge</u>	<u>Median (μm)</u>	<u>Mean (μm)</u>	<u>SD^(a)</u>
B-111 Untreated	0.86	1.03	0.77
B-111 Treated	0.92	1.43	2.48
BX-107 Untreated	0.74	0.93	0.77
BX-107 Treated	0.73	0.97	1.08
C-103 Untreated	0.84	0.86	0.25
C-103 Treated	0.88	0.90	0.27
S-104 Untreated	0.81	0.95	0.53
S-104 Treated	0.69	0.87	0.78
SY-103 Untreated	0.87	1.07	0.83
SY-103 Treated	0.76	0.82	0.27
T-104 Untreated	0.71	0.90	0.80
T-104 Treated	1.11	1.46	1.16
T-111 Untreated	1.03	1.52	1.30
T-111 Treated	0.84	0.97	0.67

(a) SD = Standard Deviation of the Mean

sludge washing and caustic leaching. An exception was SY-103, where some decrease in particle-size was found.

Table 3.3. Volume Distribution Summary for Particle-Size Analysis of Sludge Composites

Sludge	Median (μm)	Mean (μm)	SD ^(a)
B-111 Untreated	3.70	3.66	1.82
B-111 Treated	45.12	42.38	16.26
BX-107 Untreated	4.71	5.67	3.77
BX-107 Treated	22.22	20.70	11.60
C-103 Untreated	1.07	1.06	0.25
C-103 Treated	1.12	1.13	0.28
S-104 Untreated	3.37	2.78	1.28
S-104 Treated	26.98	23.18	15.80
SY-103 Untreated	5.73	9.71	8.35
SY-103 Treated	1.09	1.13	0.40
T-104 Untreated	4.48	4.85	2.64
T-104 Treated	4.69	4.82	2.11
T-111 Untreated	4.44	4.82	2.22
T-111 Treated	4.62	7.39	6.71

(a) SD = Standard Deviation of the Mean

3.4 Behavior of Nonradioactive Components During Sludge Washing and Caustic Leaching

Tables are provided in the appendices listing the concentrations of the nonradioactive sludge components in the process solutions, the concentrations of the nonradioactive sludge components in the leached sludges, and the distribution of the nonradioactive sludge components into the various process streams. Mass-balance between the nonradioactive sludge components found in the process solutions plus the leached solids and those found by direct

analysis of the untreated sludges are also given in the appendices. In general, the mass balance between the elemental composition of the untreated sludge and the elemental composition derived from the composition of the treated sludge together with the elemental composition of the wash solutions agreed well, typically within 20% and often within a few percent. Substantial deviations were found in selected cases: these usually involved elements present near their analytical detection limits, which added appreciably to the uncertainty of these values. Fortunately, such instances rarely include elements of most interest regarding the sludge washing and caustic leaching process (e.g., Al, Cr, P). In the case of BX-107, however, a general tendency existed towards lower elemental concentrations based on summation of the individual steps in the process as compared to the direct measurement of the elemental composition of the initial sludge. The reason for this is unknown, but incomplete drying of the final solid or the presence of a small amount of undissolved material in the analysis of the final solid are two possible explanations.

Table 3.4 summarizes how effectively several key nonradioactive elements were removed during sludge washing and caustic leaching for the seven sludges investigated. As expected for highly alkaline solutions, elements such as Bi and Fe did not generally dissolve. A significant fraction of the Fe was removed from SY-103 sludge. As noted previously, this complexant concentrate waste would be expected to contain chemical agents capable of solubilizing metal cations even in alkaline solutions, consistent with the observed result. Other key elements, such as Al, P, and Si, showed highly variable dissolution behavior in response to sludge washing and caustic leaching. The extent to which this variable behavior is consistent with the planning assumptions made in the baseline pretreatment flowsheet will be discussed in Section 3.7.

3.5 Behavior of Anionic Components During Sludge Washing and Caustic Leaching

Tables are provided in the appendices listing the concentrations of key anions in the process solutions, the concentrations of key anions in the leached sludges, and the distribution of key anions into the various process streams. Results of a mass balance calculation for key

Table 3.4. Summary of the Effectiveness of Sludge Washing and Caustic Leaching in Removing Key Nonradioactive Components

Tank	Amount of Component Removed, %						
	Al	Bi	Ca	Cr	Fe	P	Si
B-111	2	0	12	40	0	91	47
BX-107	68	0	27	29	0	93	2
C-103	48	^(a)	1	11	0	66	1
S-104	38	0	36	97	1	^(b)	0
SY-103	90	0	76	12	25	98	80
T-104	62	0	27	27	0	55	1
T-111	13	0	1	63	0	72	59

(a) Bismuth was present at less than its detection limits for both the initial and leached sludges and at close to its detection limits in the leach solutions.

(b) Phosphorus was not detected in this sample.

anions and its comparison to the directly measured concentrations in the untreated sludges are also provided in the appendices. The anions measured were NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , F^- , Cl^- , and Br^- . Table 3.5 summarizes these results for two anions of special importance, phosphate and sulfate. Quantification and mass-balance calculation for the other anions proved to be impractical for differing reasons. Nitrate, nitrite, and occasionally chloride could not be measured in the solids due to the overwhelming contributions of the HNO_3 and HCl required to dissolve the solids. Consequently, mass balance calculations could not be performed, and the percent removed in each process step could not be determined. Indeed, the analysis of all anions is affected by the dilutions required to keep the total anion concentrations low enough to avoid overwhelming the column's capacity. Fluoride in principle ought to have been detectable in the solids by IC, but is masked by the presence of elements such as Al. The IC results measure only free fluoride concentration, but Al, Zr, and some other metallic elements complex fluoride so strongly that fluoride will not be found by IC in their presence. However,

Table 3.5. Summary of Phosphate and Sulfate Removal by Sludge Washing and Caustic Leaching

Tank	Amount of Component Removed, %		
	Phosphate ^(a)	Phosphorus ^(b)	Sulfate ^(a)
B-111	96	91	100
BX-107	97	93	95
C-103	(c)	66	(c)
S-104	(d)	(d)	100
SY-103	(c)	98	(c)
T-104	89	55	100
T-111	76	72	67

(a) Determined by IC analysis.

(b) Determined by ICP/AES analysis.

(c) Due to matrix effects, accurate determination of these analytes could not be performed.

(d) The species was not detected in this sludge.

its presence in the sludges is indicated by its detection in the retrieval wash solutions. The metallic elements that mask fluoride generally are not soluble under such conditions. Finally, the amount of bromide in these samples appears to be so small that it was simply not detected.

Overall, the phosphate removal as measured by IC analysis agreed remarkably well with that indicated by ICP/AES analysis, especially considering the high detection limits of the IC method. The only significant deviation in the results obtained by these two methods was found in T-104; the reasons for this discrepancy are unknown. No such check is available on the sulfate analyses, but the close agreement in the P values lends confidence as to the validity of the sulfate values.

In general, the anion concentrations determined by direct IC analysis agreed (within 20%) with those determined by summing the components found in the treated sludge and in the wash and leach solutions. The major exceptions were the T-104 phosphate (55% recovery)

and sulfate (41 % recovery) analyses and the sulfate analyses for S-104 (9% recovery). The sulfate recovery for S-104 assumed no sulfate in the treated sludge because this component was below the detection limit. If the sulfate were present in the treated sludge at close to the detection limits, better agreement would be obtained. Even so, the high detection limit for sulfate in the treated sludge provided only a partial explanation: if the detection limit was used for the sulfate concentration in the treated sludge, the mass balance agreement increased only to 26%. The source for the discrepancy remains unknown.

Table 3.6 compares the concentrations obtained by IC for phosphate with those obtained for P by ICP/AES for the treated and untreated sludges. With the exception, as noted above, of the treated sludge of T-104, reasonable agreement between the two methods is seen. Such a result corroborates the assumption that the P measured in the ICP/AES is actually present in the sludges as phosphate.

3.6 Radionuclide Behavior During Sludge Washing and Caustic Leaching

Table 3.7 summarizes the behavior of the radiochemical components during the sludge washing and caustic leaching tests. Ideally, no radionuclides would be removed from the sludge because the sludge solids are to be routed to HLW disposal. Analysis of the total alpha content as well as the gamma-energy analysis confirm that the transuranic elements were not removed to any significant extent during sludge washing and caustic leaching. Analogous results were seen for ^{90}Sr . Tank SY-103 is a modest exception: it showed a small amount of TRU removal (1%) as well as a small amount of ^{90}Sr removal (4%), consistent with the presence of metal-solubilizing complexing agents in this complexant concentrate (CC) waste. As expected, ^{137}Cs and ^{99}Tc generally were readily removed by sludge washing and caustic leaching; perhaps the most interesting result is how much the removal of these radioelements varied. For example, ^{137}Cs removal ranged from quantitative for SY-103 to only 13% for T-104. Technetium-99 removal also varied from quantitative for S-104 and B-111 to 12% removal with T-111.

Table 3.6. Summary of Phosphate and Phosphorus Concentrations in Treated vs. Untreated Sludges

Tank	Equivalents P/g Dry Sludge			
	Untreated Sludge		Leached Sludge	
	By IC	By ICP/AES	By IC	By ICP/AES
B-111	1.3 E-03	1.3 E-03	2.1 E-04	5.2 E-04
BX-107	1.4 E-03	1.8 E-03	2.1 E-04	5.5 E-04
C-103	(a)	1.6 E-04	(a)	9.7 E-05
S-104	(b)	(b)	(b)	(b)
SY-103	(a)	2.5 E-04	(a)	2.3 E-05
T-104	2.5 E-03	2.2 E-03	3.2 E-04	2.0 E-03
T-111	5.3 E-04	8.4 E-04	3.2 E-04	4.6 E-04

(a) Due to matrix effects, accurate determination of these analytes could not be performed.

(b) Phosphorus and phosphate were not detected in this sample.

The radionuclide content of the wash and leach solutions is of interest regarding LLW disposal. Because the LLW form has not yet been defined, a rigorous assessment cannot be performed. However, for the purposes of this discussion, it is assumed that the LLW form will contain ~23 wt% Na₂O and have a density of 2.65 g/mL; i.e., the Na concentration will be 20 M. For most of the tanks examined in this work, if the wash and leach solutions were combined and concentrated to 20 M Na, the resulting mixtures could likely be classified as Nuclear Regulatory Commission (NRC) Class C LLW (10 CFR 61). An exception to this is seen for C-103 sludge, which would have a TRU concentration in the LLW stream close the the 0.1 μCi/g Class C limit.

Table 3.7. Summary of Radionuclide Removal by Sludge Washing and Caustic Leaching

Tank	Amount of Component Removed, %			
	Total Alpha ^(a)	⁹⁰ Sr	¹³⁷ Cs	⁹⁹ Tc
B-111	<0.1	<0.02	95	100
BX-107	<0.2	<0.2	94	99
C-103	<0.4	<0.2	73	68
S-104	<0.1	<0.08	98	100
SY-103	<0.9	<4	100	85
T-104	<0.1	<2	13	^(b)
T-111	<0.1	<0.05	56	12

(a) The total alpha behavior reflects the behavior of the TRU elements.

(b) Radionuclide not detected in this sludge.

3.7 Comparison of the Sludge Washing and Caustic Leaching Results to the Tank Waste Remediation System Planning Assumptions

In this section, the results of the sludge washing and caustic leaching tests are compared to the planning assumptions used to design the baseline sludge-treatment flowsheet (Orme 1994).

One of the planning assumptions in the current baseline flowsheet concerns the amount of Al removed by sludge washing and caustic leaching. The existing assumption is that Al and Si form an unleachable material (e.g., cancrinite) having a 1:1 molar composition. If there is a molar excess of Al over Si, then 85% of the excess Al will be removed by sludge washing and caustic leaching. Figure 3.5 compares the results of sludge wash and caustic leach testing of Hanford tank sludges to those expected based on this assumption using data not only from the work described in this report but also the results of previous studies (Lumetta and Rapko 1994)

and work conducted in FY 1995 at Los Alamos National Laboratory (LANL) (Temer and Villareal 1995).

In almost every instance, the measured removal of Al was more effective than that expected from the planning assumption. A striking exception was S-104, where only about one-half of the expected amount of Al was dissolved. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) characterization of S-104 sludge indicated that the aluminum oxides in this tank exist primarily as boehmite, unlike the other sludges, where the aluminum oxides generally exist as gibbsite.^(a) Boehmite is much more difficult to dissolve in alkaline solutions than gibbsite, which could explain the observed results (Weber 1982). Alternatively, it is possible that the low Al removal for S-104 sludge was due to saturation of the leach solutions with Al; that is, the Al removal might have been constrained by solubility rather than by kinetics. This explanation seems unlikely because significantly higher Al concentrations were achieved in leaching with other sludges (C-103 and SY-103) under similar conditions. A third possible explanation lies in the fact that the leach solutions were sampled at room temperature whereas the actual leaching step was performed at 100°C. It is possible that a fraction of the Al precipitated when the solution cooled, but before the solution was sampled. Three points can be put forth to refute the latter explanation. First, as mentioned above, leach solutions from other tests contained significantly higher Al concentrations than the S-104 sludge leach solutions. There is no reason to believe that Al would precipitate from the S-104 solution on cooling, but not from the others. Second, the Al mass balance between the amount of Al revealed by direct analysis of the sludge versus that obtained by summing the amount of Al found in the wash and leach solutions and that found in the leached sludge (Table D.4) was within 20%. Indeed the percent recovery of Al was greater than 100; if Al precipitated upon cooling, the Al mass recovery would be significantly below 100. Third, microscopy studies of the leached sludge indicated boehmite as the exclusive Al-containing species. If a fraction of the Al precipitated on cooling of the

^(a) J. P. Lafemina and others (1995). Report entitled *Tank Waste Treatment Science: Report for the Second Quarter FY 1995*. TWRSP-95-008. Pacific Northwest Laboratory, Richland, Washington.

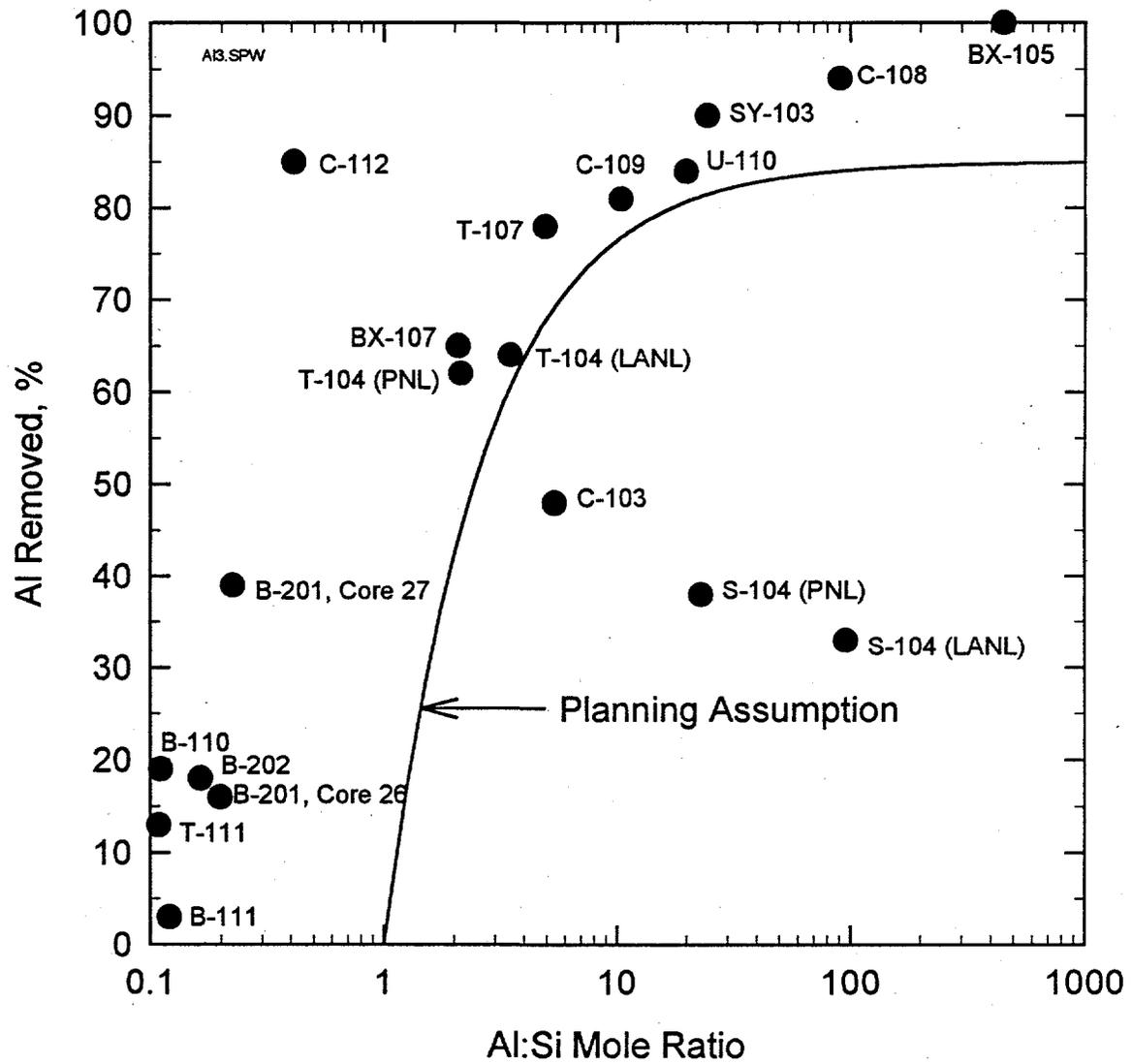


Figure 3.5 Observed Aluminum Dissolution vs. Baseline Assumption

leach mixture, that fraction of Al would not be present as boehmite because boehmite is formed under more harsh conditions. Thus, the most likely explanation for the low removal of Al from S-104 sludge is that the dissolution of boehmite is kinetically slow.

Another sludge that displayed low Al removal compared to the baseline assumption was C-103 sludge; however, in that case, the leach was performed at a free hydroxide concentration (1 M), well below the targeted value of 3 M (see Table 2.1). Presumably, at a higher hydroxide concentration, additional Al would be removed from the C-103 sludge. Also, the possibility that low Al removal was due to saturation limits cannot be ruled out for the C-103 test. The Al concentration in the second leach solution was greater than that in the first (refer to Table C.1), indicating that the solutions might have been Al-saturated.

The 85% removal of Al in molar excess of Si assumed in the baseline flowsheet is based on an idealized blend of the tank sludge wastes. Based on the current sludge inventories,^(a) if sludge from the twelve tanks investigated by PNL to date were blended, the resulting material would contain 1.50×10^7 moles of Al in excess of the number of moles of Si present. Using the Al removal factors from tank-to-tank, a total of 1.19×10^7 moles of Al would be removed by washing and leaching, which translates to 80% of the Al present in excess of Si. This value is 5% less than the assumed 85% removal, with the low S-104 Al removal having a large effect on the overall Al removal from this set of tanks. When all the Al is considered in these twelve tanks (1.84×10^7 moles), the cumulative Al removal would be 65%.

One caveat concerns the interpretation of Figure 3.5—the Al to Si molar ratio used in Figure 3.5 uses the initial Al:Si molar ratio, and no Si dissolution is assumed. Table 3.8 shows the mole ratio of Al:Si for the final washed and leached solids. If all of the Al and Si leaching behavior could be explained by formation of a 1:1 Al:Si species together with 85% dissolution of the excess Al, then the final Al/Si ratio in the treated solids should be around 1.2. A smaller value corresponds to more effective Al dissolution than anticipated in the baseline assumption while a higher value indicates less effective Al dissolution. Table 3.8

^(a) All tank-by-tank P inventories were taken from Colton 1995, except for Tank SY-103, which was taken from Hanlon 1995. In the latter document, only the volume is given for SY-103 sludge (573 kgal), the mass was estimated by assuming a sludge density of 1.5 g/mL.

Table 3.8. Aluminum and Silicon Molar Concentrations in Treated Sludges

Tank	Concentration in Leached Sludge, mole/g		Al/Si in Leached Sludge
	Al	Si	
B-111	6.7 E-04	2.3 E-03	0.29
BX-107	1.5 E-03	1.7 E-03	0.87
C-103	3.9 E-03	1.2 E-03	3.2
S-104	1.2 E-02	1.8 E-04	67
SY-103	3.1 E-03	4.3 E-04	7.2
T-104	1.2 E-03	1.3 E-03	0.9
T-111	2.1 E-04	1.2 E-03	0.18

shows that the dissolution behavior of Al and Si is poorly described by this simple model, with values both appreciably higher and lower than expected. Thus, it appears that the simple model used to estimate Al behavior in the planning assumption has little validity regarding the chemistry of the systems.

The planning assumption in the current baseline flowsheet regarding P removal can be stated as "70% of the water insoluble fraction of the P is removed by caustic leaching." Although this 70% removal factor is applied to an overall blend of the tank sludges in the flowsheet, it is illustrative to compare this assumption to the results for each tank studied to date. The percentage of the water insoluble P in each sludge removed by caustic leaching is presented in Table 3.9. As might be expected, the actual efficacy of caustic leaching in removing P varies greatly from tank to tank. However, when the entire P inventory (see footnote on page 3.20) is considered for the tanks investigated to date, the overall removal of the water insoluble fraction of the P is 65%, which is near the assumed value of 70%.

Table 3.9. Water Insoluble Phosphorus Removed by Caustic Leaching

<u>Tank</u>	<u>Water Insoluble P Removed by Caustic Leaching, %</u>
B-110 ^(a)	81
B-111 ^(b)	84
B-201 ^(a,c)	25
BX-107 ^(b)	91
C-103 ^(b)	54
C-109 ^(a)	13
C-112 ^(a)	69
SY-103 ^(b)	92
T-104 ^(b)	39
T-111 ^(b)	45
U-110 ^(c)	90

- (a) Data taken from Lumetta and Rapko (1994).
- (b) Data from this work.
- (c) Average values from tests on cores 26 and 27 used.

An alternative assumption for P removal by sludge washing and caustic leaching supposes that all of the P (presumed to be present as phosphate) will be removed except that portion that forms an insoluble and unleachable phase with alkaline earth metals. Unlike most water-insoluble phosphates, those of the alkaline earth elements are not expected (based on thermodynamics) to be metathesized to hydroxides (thus releasing the phosphate so that it can be washed away) in the caustic leach step.

The stoichiometry of simple alkaline earth phosphates requires a 3:2 molar ratio of alkaline-earth metal to P. In Hanford tank sludges, the amount of alkaline earth metal present is generally dominated by the amount of Ca and, in some cases, by the amount of Ca and Sr present. Figure 3.6 compares the results of sludge wash and caustic leach testing of Hanford tank sludges to that expected based on the unleachable alkaline earth phosphate hypothesis,

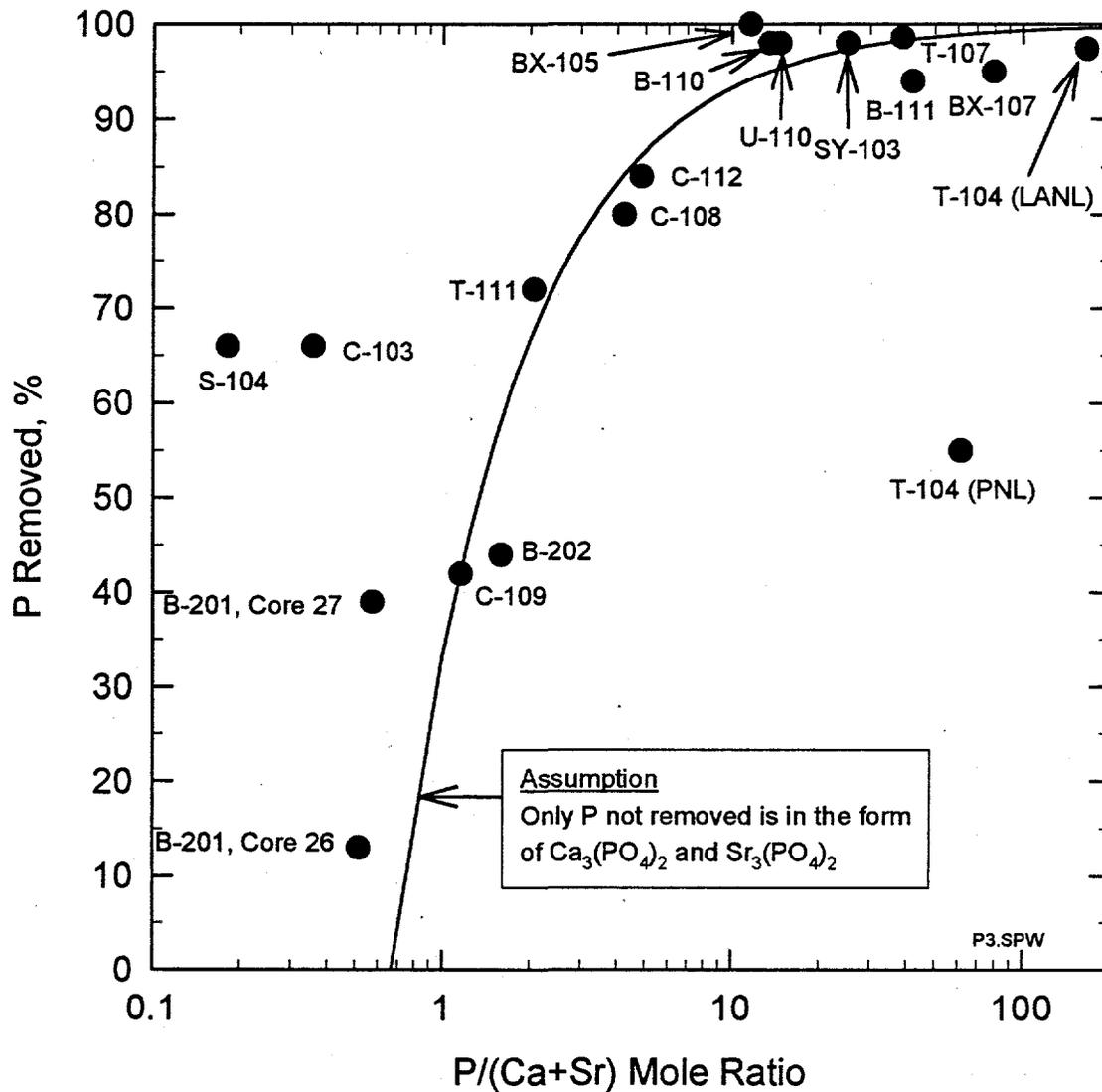


Figure 3.6. Observed Phosphorus Removal Compared to the Unleachable Alkaline-Earth Phosphate Hypothesis. The solid line represents the removal of P expected if only Ca and Sr phosphates were not leached from the sludge, using data from the tests conducted to date.

For the most part, the data fall near the curve associated with the hypothesis. Results from the B-111, B-202, BX-107, C-108, and C-112 tests show slightly poorer than expected removal of P based upon this hypothesis. The major discrepancy is found for the T-104 sludge.

Two additional concerns are associated with the test results from T-104. First, as revealed in Tables 3.5 and 3.6, comparing the amount of P removed (based on ICP/AES data for P) with the amount of phosphate removed (based on IC data) produced results that are very different for T-104. Only T-104 produced such differences, however, raising a cautionary note about these values. Figure 3.6 was generated using ICP/AES data in all instances. The P removal (89%) indicated by the IC data for T-104 was much closer the value expected by the unleachable alkaline-earth phosphate hypothesis. In addition, recent work at Los Alamos National Laboratory (Temer and Villarreal 1995), where the same test was performed on T-104, gave very different results. The LANL results are much more in line with the unleachable alkaline-earth phosphate hypothesis, although they too indicate slightly less effective P removal than expected from the hypothesis. The combination of the LANL T-104 results together with the phosphate/P discrepancy suggests that the T-104 values should be viewed with some caution. Be that as it may, quantitative material balance for P was achieved by the ICP/AES analysis whereas only a 55% recovery for PO_4^{3-} was achieved by IC analysis (see Table F.4). Thus, in the case of the work performed at PNL, the value of 55% removal of P from T-104 sludge seems to be the most reliable.

In an attempt to validate the hypothesis that only the alkaline-earth phosphates are not removed by washing and caustic leaching, the P/(Ca+Sr) mole ratio in the treated solids was considered (Table 3.10). If the only P-containing species in the leached residue are Ca and Sr phosphates, the P/(Ca+Sr) molar ratio in the residue should be 0.67. A lower value would indicate that the assumption is a conservative one, either because of insufficient P being initially present relative to Ca, or due to some additional P-removing processes occurring.

The results are clearly mixed regarding the insoluble alkaline-earth metal phosphate hypothesis. In two cases, with S-104 and SY-103, the P/(Ca+Sr) ratio is clearly lower than expected if all of the Ca and Sr complexed with the P to form the corresponding phosphates.

Table 3.10. Phosphorus, Calcium, and Strontium Concentrations in Treated Sludges

Tank	Concentration in Leached Sludge, mole/g			P/(Ca + Sr) in Leached Sludge
	P	Ca	Sr	
B-111	5.2E-04	1.8E-04	2.4E-05	2.7
BX-107	5.5E-04	3.7E-05	1.1E-05	11
C-103	9.7E-05	2.2E-04	2.3E-06	0.44
S-104	0	4.5E-05	2.5E-05	0
SY-103	2.3E-05	1.3E-04	1.1E-06	0.18
T-104	2.0E-03	4.5E-05	7.6E-06	38
T-111	4.2E-04	5.5E-04	1.5E-05	0.74

In the case of S-104, this is because the solids contained little or no P to begin with. The P/(Ca+Sr) ratio of 0.77 observed for the treated T-111 solid is very close to the 0.67 ratio expected. However, with B-111, BX-107, C-103, and T-104, the P:Ca ratio is just as clearly higher than expected, indicating that other P-containing species are present in the treated solids. Thus, the good correlation indicated in Figure 3.6 is likely based on coincidence rather than on chemical fact. Nevertheless, this hypothesis has thus far proved to be a remarkably good assumption, given the complexity of the systems examined.

One aspect of the current sludge pretreatment testing strategy is to divide the tanks into groups having similar waste types based on the sort on radioactive waste type (SORWT) model (Hill, Anderson, and Simpson 1995). It is commonly presumed that wastes from tanks within a given SORWT group will exhibit similar behavior in the sludge washing and caustic leaching pretreatment process. If this were the case, then it would not be necessary to perform tests on every tank within the SORWT group, but rather sludges from selected tanks could be tested and the results extrapolated to the other tanks in the same SORWT groups.

Several examples exist in which tanks in the same SORWT group have been tested. Table 3.11 summarizes these along with the observed removals of Al, Cr, and P. The general trends between SORWT groups is consistent. For example, removing Al from tanks in SORWT groups X and XIII is generally better than from tanks in groups VII and XVI. However, significant variability is seen for removing certain components within given SORWT groups. This is especially true for P removal from groups VII and XIII tanks, Al removal from group XVI tanks, and Cr removal from group VII tanks. Clearly, much more data are needed to validate the use of SORWT (or other models) for extrapolating test results to tanks that have not actually been tested.

3.8 Impact on High-Level Waste Glass Volume

This discussion concludes with the reduction in HLW glass volume achieved by sludge washing and caustic leaching. Table 3.12 illustrates the calculated amount of glass canisters (each canister containing 1650 kg of borosilicate glass) expected from vitrifying the sludge solids in the seven tanks investigated in this work. Three cases are considered: no pretreatment, washing with inhibited water, and caustic leaching plus washing with inhibited water. The vitrification feed specifications reported by Swanson (1993) were used to calculate the number of glass canisters resulting in each case. To determine the number of glass canisters, the total mass of each potential glass-limiting component in the untreated sludge was determined by multiplying the total amount of sludge (on a dry weight basis) by the concentration of each component in the untreated sludge as reported in the appendices. The total amount of sludge in each tank was taken from Colton (1995), except for SY-103, which was obtained from Hanlon (1995). For the "no pretreatment" case, these component masses were used directly. For the other two cases, the amount of each component in the HLW was obtained by multiplying the amount of that component originally in the waste by the fraction left after the individual treatment. The total mass of each element in the HLW stream was then compared to its allowable limits in the HLW vitrification feed (Swanson 1993) to determine the number of HLW glass canisters that would result from each component. The three

Table 3.11.

Comparison of Sludge Washing and Caustic Leaching Results from Tanks In the Same SORWT Groups

	SORWT Group	Cumulative Removal, %		
		Al	Cr	P
B-110 ^(a)	XVI	18	52	98
B-111	XVI	2	40	91
Mean		10	46	94
Std. Dev.		11	8	5
B-201 ^(a,b)	VII	27	56	26
B-202 ^(c)	VII	19	29	44
Mean		23	42	35
Std. Dev.		6	19	13
C-108 ^(c)	XIII	94	80	80
C-109 ^(a)	XIII	81	85	42
C-112 ^(a)	XIII	85	88	84
Mean		87	84	69
Std. Dev.		7	4	23
T-107 ^(c)	X	78	61	99
U-110 ^(a)	X	84	71	98
Mean		81	66	98
Std. Dev.		4	7	1

(a) Lumetta and Rapko 1994.

(b) Average of the results from two cores.

(c) Temer and Villarreal 1995.

Table 3.12. Impact of Sludge Washing and Caustic Leaching on Glass Required for Sludge Vitrification

<u>Tank^(a)</u>	<u>Largest Number of Glass Canisters (Limiting Component)</u>	<u>2nd Largest Number of Glass Canisters (Limiting Component)</u>	<u>3rd Largest Number of Glass Canisters (Limiting Component)</u>
B-111 (untreated)	2290 (P)	1600 (S)	1550 (Na)
B-111 (SW)	1300 (P)	160 (Cr)	130 (S)
B-111 (SW+CL)	210 (P)	170 (Na)	130 (Cr)
BX-107 (untreated)	5210 (P)	2260 (Na)	1430 (S)
BX-107 (SW)	4170 (P)	630 (F)	220 (Cr)
BX-107 (SW+CL)	370 (P)	350 (Na)	200 (Cr)
C-103 (untreated)	300 (Al)	120 (Fe)	90 (Na)
C-103 (SW)	300 (Al)	120 (Fe)	600 (P)
C-103 (SW+CL)	160 (Al)	120 (Fe)	80 (Na)
S-104 (untreated)	3460 (Na)	2900 (Al)	2300 (S)
S-104 (SW)	2810 (Al)	170 (Na)	100 (U)
S-104 (SW+CL)	1800 (Al)	250 (Na)	100 (U)
SY-103 (untreated)	14500 (Na)	7540 (Cr)	3500 (P)
SY-103 (SW)	7160 (Cr)	2480 (Al)	910 (P)
SY-103 (SW+CL)	6630 (Cr)	270 (Al)	90 (Na)
T-104 (untreated)	5370 (P)	1710 (Na)	1710 (S)
T-104 (SW)	3970 (P)	470 (Al)	260 (Cr)
T-104 (SW+CL) ^(b)	2420 (P)	980 (Na)	230 (Cr)

Table 3.12 contd.

T-111 (untreated)	2670 (Na)	1620 (P)	410 (S)
T-111 (SW)	810 (P)	410 (S)	280 (Cr)
<u>T-111 (SW+CL)</u>	450 (P)	410 (S)	190 (Na)

- (a) SW = washing with inhibited water only; SW+CL = caustic leaching plus sludge washing (i.e., the baseline process).
- (b) Using the value of 89% removal of P that was obtained by IC, the limiting component for T-104 would be Na, and 980 canisters would result. The next limiting component would be P (590 canisters), and the third limiting component would be Cr (230 canisters).

components that yield the maximum number of glass canisters are reported in Table 3.12 for each sludge.

Two caveats must be placed upon the canister numbers in Table 3.12. First, a certain set of glass specifications was used in the calculations; modified glass specifications could result in modifications to the values presented in Table 3.12. For example, the P limit used in a recent study (Lambert and Kim 1994) is threefold higher than that used by Swanson (1993); incorporation of this change would give a threefold reduction in the P-limited canister count values. Second, the canister numbers are based on processing on a tank-by-tank basis. Implementation of waste-blending schemes could likely reduce the number of glass canisters required.

Several trends are apparent from Table 3.12. The glass-volume-limiting components for the untreated sludges are primarily Na and P. Only in the case of C-103, which possesses an unusually low concentration of Na, is another element (Al) the limiting component. Sludge washing and caustic leaching are of wide and varying effectiveness in reducing the number of glass canisters formed upon vitrifying the treated solids. For some sludges, sludge washing and caustic leaching are very effective at reducing the amount of glass canisters that would be needed to vitrify the residual solids. For B-111 sludge, for example, the HLW volume should be decreased by a factor > 10 if the baseline process is implemented. Tank BX-107 and, to a lesser extent, T-111, should also experience large decreases in HLW volume. On the other

hand, with the four other sludges examined in this work, C-103, S-104, SY-103, and T-104, a decrease of only a factor of ~ 2 in the amount of HLW required after sludge washing and caustic leaching is indicated. However, the amount of HLW glass required for vitrifying the leached T-104 solids is dominated by the amount of P remaining in the residual solids. As noted above, that number is suspect, and if it is in fact sufficiently reduced such that Na becomes the limiting agent, a decrease in glass of between a factor of 4 and 5 would result.

The reasons for the relatively poor performance in glass reduction for the four sludges noted above are unique to each sludge type. The case of T-104 was described previously. In the case of C-103, the final limiting component is Al. However, more effective Al dissolution would have a relatively small impact, since the amount of Fe remaining in the residual solids results in almost the same number of glass canisters. Any large additional decreases in glass from vitrifying treated C-103 solids would require effective removal of Fe from the solids or solids dissolution coupled with a radionuclide separation scheme.

Tank S-104 and SY-103 sludges are both different from each other and from the other sludges in respect to what determines the amount of glass formed by vitrifying these solids. In the case of S-104, poor dissolution of Al determines both the poor reduction in glass volume and the relatively high total number of canisters required. More effective Al and Na removal could further reduce the number of glass canisters by an order of magnitude. With SY-103, more effective Cr dissolution could reduce the number of glass canisters by more than a factor of 20, and, if coupled with more effective Al dissolution, a further reduction of approximately two orders of magnitude might be possible.

3.9 Conclusion

The effectiveness of sludge washing and caustic leaching in reducing the number of HLW glass canisters required to immobilize the treated solids varies greatly from tank-to-tank. Transuranic and Sr dissolutions are minimal in all cases and particularly small, unless the sludge is likely to contain metal complexing agents. Enhanced Cr, P, Al, and perhaps Fe

dissolution, when waste immobilization is considered on a tank-by-tank basis, could have a major impact in the amount of glass produced over and above the current baseline sludge washing and caustic leaching scheme. Finally, the current planning assumptions regarding sludge washing and caustic leaching give values that are generally close to the experimental results to date, even though the planning assumptions appear to have relatively little chemical basis.

4.0 References

10 CFR 61. 1988. U.S. Nuclear Regulatory Commission, "Licensing Requirements for Land Disposal of Radioactive Waste." *U.S. Code of Federal Regulations*.

Colton, N. G. 1995. *Sludge Pretreatment Chemistry Evaluation: Enhanced Sludge Washing Separation Factors*. PNL-10512, Pacific Northwest Laboratory, Richland, Washington.

Ecology, EPA, and DOE. 1994. *Hanford Federal Facility Agreement and Consent Order*. Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.

Hanlon, B.M. 1995. *Tank Farm Surveillance and Waste Status Summary Report for May, 1995*. WHC-EP-0182-86, Westinghouse Hanford Company, Richland, Washington.

Hill, J. G., G. S. Anderson, and B. C. Simpson. 1995. *The Sort on Radioactive Waste Type Model: A Method to Sort Single-Shell Tanks into Characteristic Groups*. PNL-9814 Rev. 2, Pacific Northwest Laboratory, Richland, Washington.

Lambert, S. L., and D. S. Kim. 1994. *Tank Waste Remediation System High-Level Waste Feed Processability Assessment Report*. WHC-SP-1143, Westinghouse Hanford Company, Richland, Washington.

Lumetta, G. J., B. M. Rapko, and N. G. Colton. 1994. *Washing and Caustic Leaching of Hanford Tank Sludges*. PNL-SA-23598, Pacific Northwest Laboratory, Richland, Washington.

Lumetta, G. J., and J. L. Swanson. 1993a. *Pretreatment of Neutralized Cladding Removal Waste (NCRW) Sludge - Results of FY 1991 Studies*. PNL-8536. Pacific Northwest Laboratory, Richland, Washington.

Lumetta, G. J., and J. L. Swanson. 1993b. *Pretreatment of Plutonium Finishing Plant (PFP) Sludge: Report for the Period October 1990 - March 1992*. PNL-8601. Pacific Northwest Laboratory, Richland, Washington.

Lumetta, G. J., J. L. Swanson, and S. A. Barker. 1995. "Process Chemistry For The Pretreatment of Hanford Tank Wastes." *Chemical Pretreatment of Nuclear Waste for Disposal*. W. W. Schulz and E. P. Horwitz, eds., Plenum Press, New York.

Lumetta, G. J., and B. M. Rapko. 1994. *Washing and Alkaline Leaching of Hanford Tank Sludges: A Status Report*. PNL-10078. Pacific Northwest Laboratory, Richland, Washington.

Lumetta, G. J., B. M. Rapko, M. J. Wagner, C. D. Carlson, and R. J. Barrington. 1994. *Sludge Treatment and Extraction Technology Development: Results of FY 1993 Studies*. PNL-9387. Pacific Northwest Laboratory, Richland, Washington.

Orme, R. M. 1994. *TWRS Process Flowsheet*. WHC-SD-WM-TI-613, Westinghouse Hanford Company, Richland, Washington.

Rai, D., B. M. Sass, and D. A. Moore. 1987. "Chromium(III) Hydrolysis Constants and Solubility of Chromium(III) Hydroxide." *Inorg. Chem.*, Volume 26, pp. 345-349.

Straalsund, J. L., J. L. Swanson, E. G. Baker, J. J. Holmes, E. O. Jones, and W. L. Kuhn. 1992. *Clean Option: An Alternative Strategy for Hanford Tank Remediation. Volume 1. Overview*. PNL-8388 Vol. 1, Pacific Northwest Laboratory, Richland, Washington.

Swanson, J. L. 1993. *Clean Option: An Alternative Strategy for Hanford Tank Waste Remediation. Volume 2: Detailed Description of First Example Flowsheet*. PNL-8388 Vol 2, Pacific Northwest Laboratory, Richland, Washington.

Temer, D. J., and R. Villareal. 1995. *Sludge Washing and Alkaline Leaching Tests on Actual Hanford Tank Sludge: A Status Report*. LAUR-95-2070, Los Alamos National Laboratory, Los Alamos, New Mexico.

Weber, E. J. 1982. *Aluminum Hydroxide Dissolution in Synthetic Sludges*. DP-1617, Savannah River Laboratory, Aiken, South Carolina.

Appendix A

Results from the Tank B-111 Sludge Washing and Caustic Leaching Test

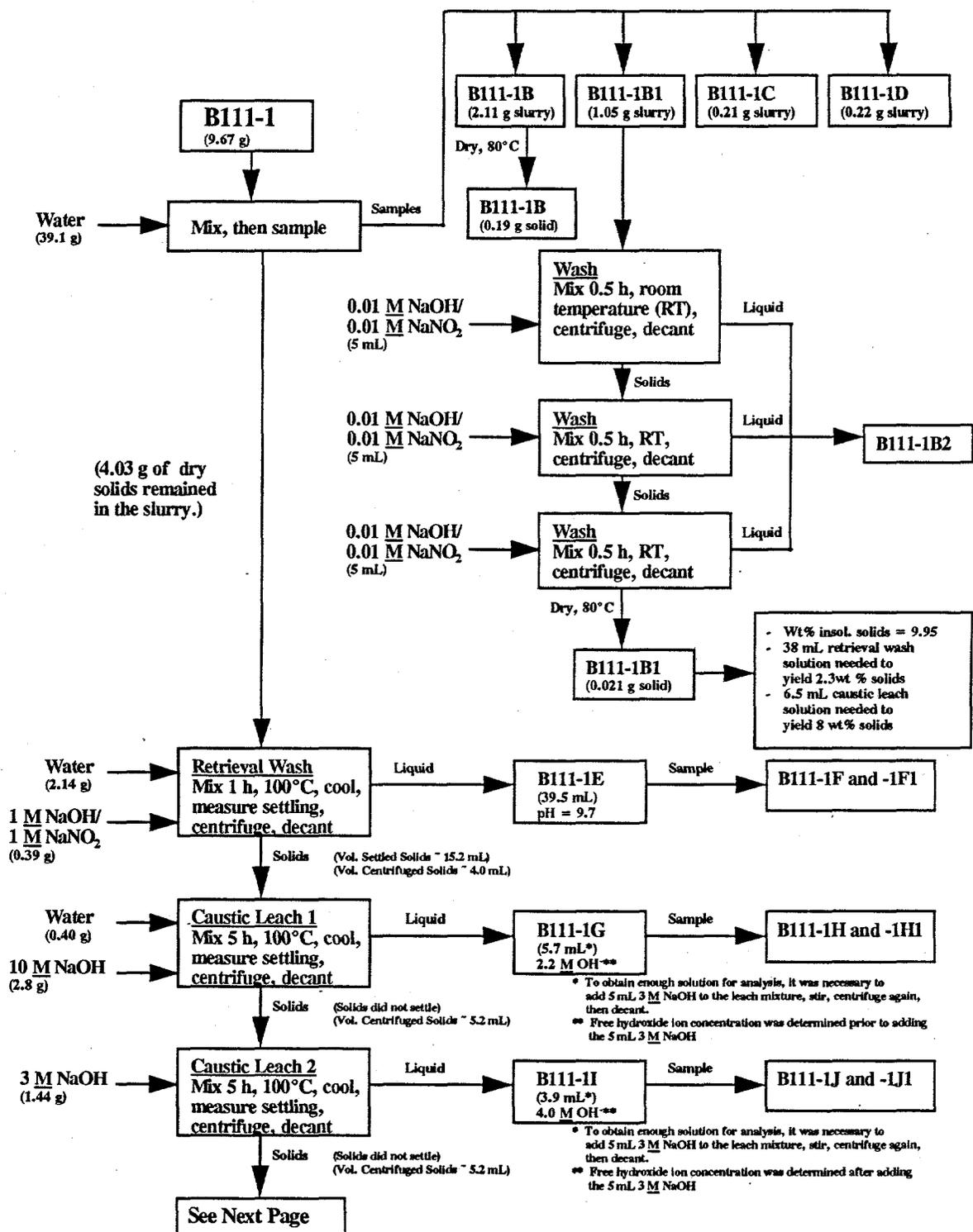
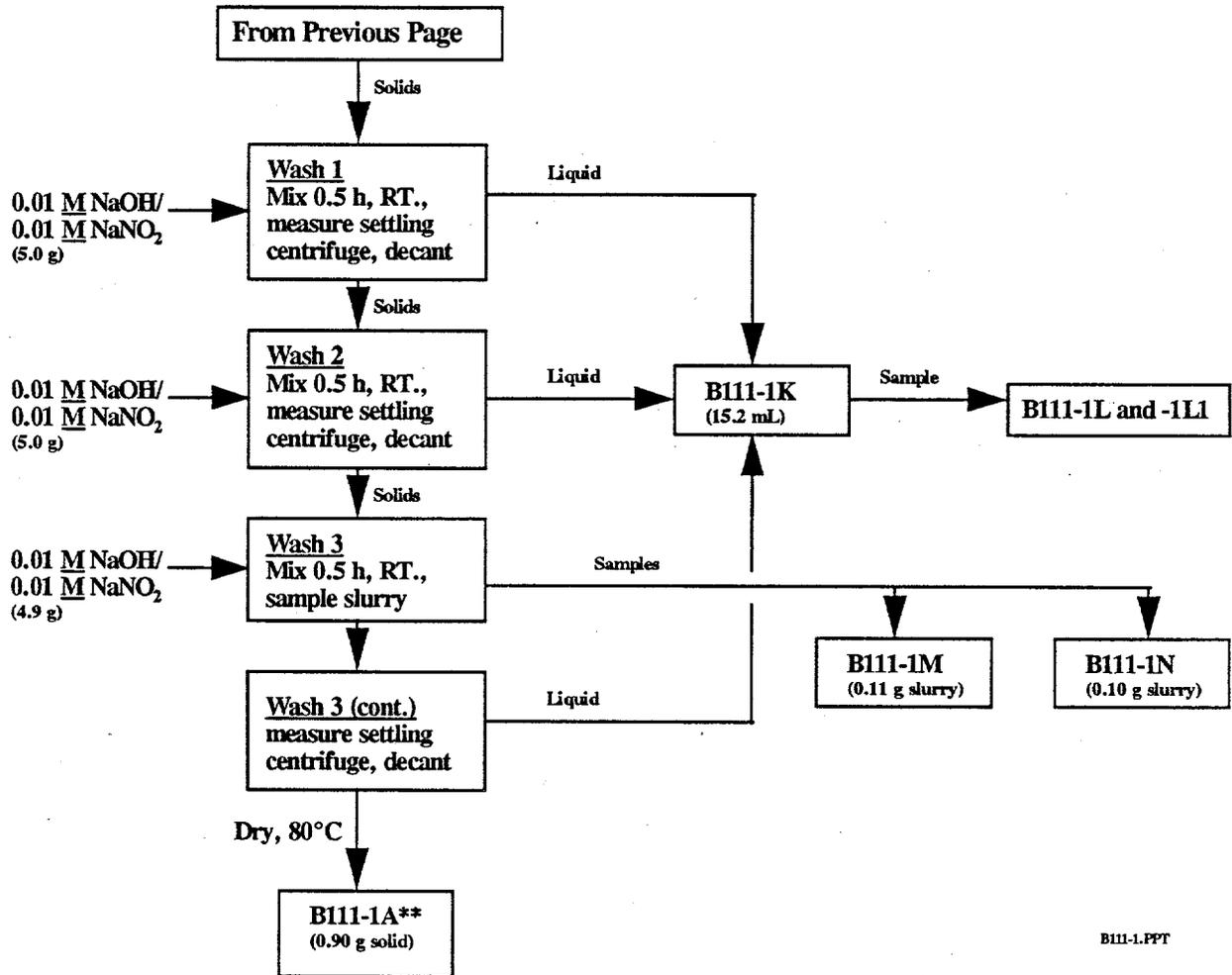


Figure A.1. Schematic of B-111 Sludge Washing and Caustic Leaching Test



B111-1.PPT

Figure A.1. (contd.)

Table A.1. Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the B-111 Test

Component	Detection Limit, $\mu\text{g/mL}$	Concentration, $\mu\text{g/mL}$ ^(a)			
		Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Ag	0.17	0	0	0	0
Al	0.85	0	17.85	16	8.5
As	1.7	0	0	0	0
B	0.34	3.4	4.76	3.2	0.60
Ba	0.17	0	0	0	0
Be	0.08	0	0	0	0
Bi	1.7	0	20.4	124.8	8.5
Ca	0.85	17.85	8.5	8	6.0
Cd	0.17	0	0	0	0
Ce	1.7	0	0	0	0
Co	0.17	0	0	0	0
Cr	0.34	71	31	176	41
Cu	0.17	0.77	9.35	54.40	2.13
Dy	0.34	0	0	0	0
Eu	0.17	0	0	0	0
Fe	0.17	0.43	16.15	28.80	2.47
Gd	3.4	0	0	0	0
K	25.5	85	170	80	0
La	0.51	0	0	0	0
Li	0.34	0	0	0	0
Mg	1.7	0	0	0	0
Mn	0.08	0	0	0	0
Mo	0.34	9.35	2.55	1.6	0
Na	17	21250	76500	107200	33150
Nd	0.51	0	0	0	0
Ni	0.51	0	0	0	3.4
P	1.7	1870	1785	1136	4420
Pb	0.85	0	29.75	120	7.65
Pd	2.55	0	0	0	0
Rh	1.7	0	0	0	0
Ru	1.7	0	0	0	0
Sb	0.85	0	0	0	0
Se	1.7	0	0	0	0
Si	0.85	74.8	3485	3840	935
Sn	17	0	0	0	0
Sr	0.08	0	0	0	0
Te	3.4	0	0	0	0
Th	17	0	0	0	0
Ti	0.08	0	0	0	0
Tl	8.5	0	0	0	0
U	0.00003	33.92	5.91	10.18	1.60
V	0.17	0	0.34	0	0
W	1.7	0	0	0	0
Y	0.17	0	0	0	0
Zn	0.34	0	23.8	48	6.97
Zr	0.17	0	0	0	0
NO ₃ ⁻	500	18900	5900	3500	680
NO ₂ ⁻	500	11900	4100	2500	800
PO ₄ ³⁻	100	5300	5700	3500	13000
SO ₄ ²⁻	50	2890	1000	590	130
F ⁻	25	270	0	0	0
Cl ⁻	25	300	100	60	0
Br ⁻	50	0	< 25	< 25	< 25

(a) Zero values indicate the analyte was below the detection limit.

Table A.2. Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the B-111 Test

<u>Component</u>	<u>Detection Limit, $\mu\text{g/g}$</u>	<u>Concentration, $\mu\text{g/g}$ ^(a)</u>
Ag	20	50
Al	100	18000
As	100	0
B	30	1100
Ba	20	290
Be	8	0
Bi	200	180000
Ca	80	7300
Cd	20	30
Ce	100	200
Co	20	40
Cr	30	7000
Cu	20	2300
Dy	30	0
Eu	20	0
Fe	20	180000
Gd	300	0
K	(b)	(b)
La	50	60
Li	30	0
Mg	100	2400
Mn	8	990
Mo	30	40
Na	100	100000
Nd	50	200
Ni	(c)	(c)
P	200	16000
Pb	100	14000
Pd	200	0
Rh	200	0
Ru	200	0
Sb	80	0
Se	100	300
Si	80	65000
Sn	2000	0
Sr	8	2100
Te	300	0
Th	1000	0
Ti	8	300
Tl	800	0
U	10000	1026
V	20	0
W	100	200
Y	20	0
Zn	30	770
Zr	20	100
NO ₃ ⁻	(d)	(d)
NO ₂ ⁻	(d)	(d)
PO ₄ ³⁻	21200	20000
SO ₄ ²⁻	8500	0
F ⁻	21200	0
Cl ⁻	(d)	(d)
Br ⁻	21200	0

(a) Zero values indicate the analyte was below the detection limit.

(b) Potassium values are not reported since the sample was dissolved using a KOH fusion method.

(c) Nickel values are not reported because a Ni crucible was used during the KOH fusion procedure.

(d) Measurement impractical due to method of sample preparation.

Table A.3. Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the B-111 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Ag	0	0	0	0	100
Al	0	1	0	1	98
As	(a)	(a)	(a)	(a)	(a)
B	11	2	1	1	84
Ba	0	0	0	0	100
Be	(a)	(a)	(a)	(a)	(a)
Bi	0	0	0	0	100
Ca	9	1	0	1	88
Cd	0	0	0	0	100
Ce	0	0	0	0	100
Co	0	0	0	0	100
Cr	27	2	6	6	60
Cu	1	2	9	1	86
Dy	(a)	(a)	(a)	(a)	(a)
Eu	(a)	(a)	(a)	(a)	(a)
Fe	0	0	0	0	100
Gd	(a)	(a)	(a)	(a)	(a)
K	(b)	(b)	(b)	(b)	(b)
La	0	0	0	0	100
Li	(a)	(a)	(a)	(a)	(a)
Mg	0	0	0	0	100
Mn	0	0	0	0	100
Mo	87	3	1	0	8
Na	(c)	(c)	(c)	(c)	(c)
Nd	0	0	0	0	100
Ni	(b)	(b)	(b)	(b)	(b)
P	43	6	3	39	9
Pb	0	1	3	1	94
Pd	(a)	(a)	(a)	(a)	(a)
Rh	(a)	(a)	(a)	(a)	(a)
Ru	(a)	(a)	(a)	(a)	(a)
Sb	(a)	(a)	(a)	(a)	(a)
Se	0	0	0	0	100
Si	3	18	14	13	53
Sn	(a)	(a)	(a)	(a)	(a)
Sr	0	0	0	0	100
Te	(a)	(a)	(a)	(a)	(a)
Th	(a)	(a)	(a)	(a)	(a)
Ti	0	0	0	0	100
Tl	(a)	(a)	(a)	(a)	(a)
U	57	1	2	1	39
V	0	100	0	0	0
W	0	0	0	0	100
Y	(a)	(a)	(a)	(a)	(a)
Zn	0	12	17	9	62
Zr	0	0	0	0	100
NO ₃ ⁻	93	4	2	1	(d)
NO ₂ ⁻	91	5	2	2	(d)
PO ₄ ³⁻	44	7	3	42	4
SO ₄ ²⁻	92 (87) ^(e)	5 (4) ^(e)	2	2 (1) ^(e)	0 (6) ^(e)
F ⁻	100 (34) ^(e)	0	0	0 (1) ^(e)	0 (64) ^(e)
Cl ⁻	94	5	2	0	(d)
Br ⁻	(a)	(a)	(a)	(a)	(a)

(a) Component was not detected.

(b) K and Ni values could not be determined due to the KOH fusion method used to prepare the leached sludge for analysis.

(c) Removal of the Na from the sludge cannot be reliably tracked because the Na from the sludge cannot be distinguished from the Na added in the washing and leaching steps.

(d) Measurement impractical due to method of sample preparation.

(e) Values in parentheses represent the values obtained if, for cases where the component was below the detection limit, the component concentration was assumed to be the detection limit.

Table A.4. Mass Balance for Nonradioactive Sludge Components From the B-111 Test

Component	Concentration in Dried Sludge, g/g Sludge		Recovery, %
	Direct Analysis	Summation Method	
Ag	< 9.00E-05	1.12E-05	
Al	3.00E-03	4.11E-03	137
As	< 7.00E-04		
B	2.00E-03	2.92E-04	15
Ba	< 9.00E-05	6.50E-05	
Be	< 4.00E-05		
Bi	5.20E-02	4.05E-02	78
Ca	1.00E-03	1.85E-03	185
Cd	< 9.00E-05	6.72E-06	
Ce	< 7.00E-04	4.48E-05	
Co	< 9.00E-05	8.97E-06	
Cr	3.10E-03	2.64E-03	85
Cu	4.00E-04	5.97E-04	149
Dy	< 2.00E-04		
Eu	< 9.00E-05		
Fe	4.60E-02	4.04E-02	88
Gd	< 2.00E-03		
K	(b)	(b)	
La	< 3.00E-04	1.34E-05	
Li	< 2.00E-04		
Mg	< 7.00E-04	5.38E-04	
Mn	4.00E-04	2.22E-04	55
Mo	< 2.00E-04	1.06E-04	
Na	(c)		
Nd	< 3.00E-04	4.48E-05	
Ni	(b)	(b)	
P	4.10E-02	4.22E-02	103
Pb	4.00E-03	3.33E-03	83
Pd	< 1.00E-03		
Rh	< 9.00E-04		
Ru	< 9.00E-04		
Sb	< 4.00E-04		
Se	< 7.00E-04	6.72E-05	
Si	2.60E-02	2.75E-02	106
Sn	< 9.00E-03		
Sr	5.80E-04	4.71E-04	81
Te	< 2.00E-03		
Th	< 7.00E-03		
Ti	9.00E-05	6.72E-05	75
Tl	< 4.00E-03		
U	6.00E-04	5.86E-04	98
V	< 9.00E-05	4.81E-07	
W	< 7.00E-04	4.48E-05	
Y	< 9.00E-05		
Zn	< 2.00E-04	2.79E-04	
Zr	< 9.00E-05	2.24E-05	
NO ₃ ⁻	(d)	1.99E-01	
NO ₂ ⁻	(d)	1.28E-01	
PO ₄ ³⁻	1.20E-01	1.17E-01	97
SO ₄ ²⁻	4.00E-02	3.08E-02	77
F ⁻	< 3.67E-02	2.64E-03	
Cl ⁻	(d)	3.14E-03	
Br ⁻			

(a) Blank spaces indicate values below the detection limits.

(b) K and Ni values could not be determined due to the KOH fusion method used to prepare the solids for analysis.

(c) Reliable value not available due to problems encountered in analytical procedure.

(d) Measurement impractical due to method of sample preparation.

Table A.5. Concentrations of the Radioactive Sludge Components in the Various Process Streams From the B-111 Test

Component	Concentration, $\mu\text{Ci/mL}$			
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Total Alpha	< 2.55E-05	< 2.55E-05	< 4.8E-05	< 2.55E-05
$^{239,240}\text{Pu}$	ND ^(a)	ND	ND	ND
$^{241}\text{Am} + ^{238}\text{Pu}$	ND	ND	ND	ND
$^{241}\text{Am}(\gamma)$	< 4.00E-04	< 6.00E-03	< 4.00E-04	< 3.00E-04
^{137}Cs	2.02E+01	6.84E+01	4.02E+01	8.76E+00
^{90}Sr	8.67E-04	6.32E-03	2.22E-02	1.14E-02
^{99}Tc	3.04E-02	9.18E-03	4.82E-03	1.16E-03

Component	Concentration, $\mu\text{Ci/g}$
	Residue
Total Alpha	2.90E+00
$^{239,240}\text{Pu}$	1.32E+00
$^{241}\text{Am} + ^{238}\text{Pu}$	7.74E-01
$^{241}\text{Am}(\gamma)$	1.01E+00
^{137}Cs	7.97E+01
^{90}Sr	3.03E+03
^{99}Tc	1.81E-03

(a) ND = Not Determined. The low total alpha activity made these separations impractical.

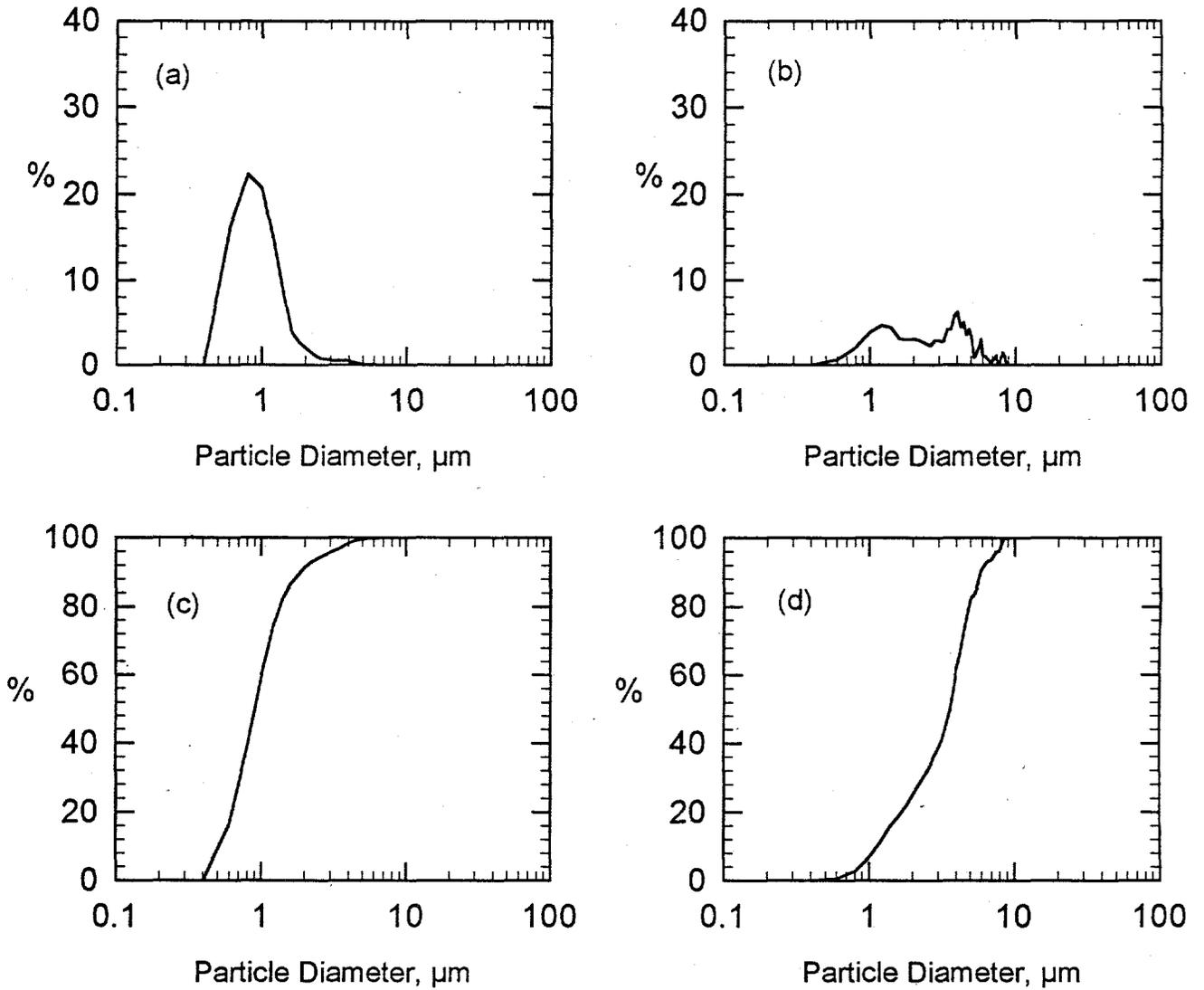
Table A.6. Distribution of the Radioactive Sludge Components Between the Various Process Streams From the B-111 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Total Alpha	0	0	0	0	100
^{239,240} Pu	(a)	(a)	(a)	(a)	100
²⁴¹ Am + ²³⁸ Pu	(a)	(a)	(a)	(a)	100
²⁴¹ Am(γ)	0	0	0	0	100
¹³⁷ Cs	52	25	10	9	5
⁹⁰ Sr	0	0	0	0	100
⁹⁹ Tc	93	4	1	1	0

(a) Not determined due to the low total alpha activity of the samples.

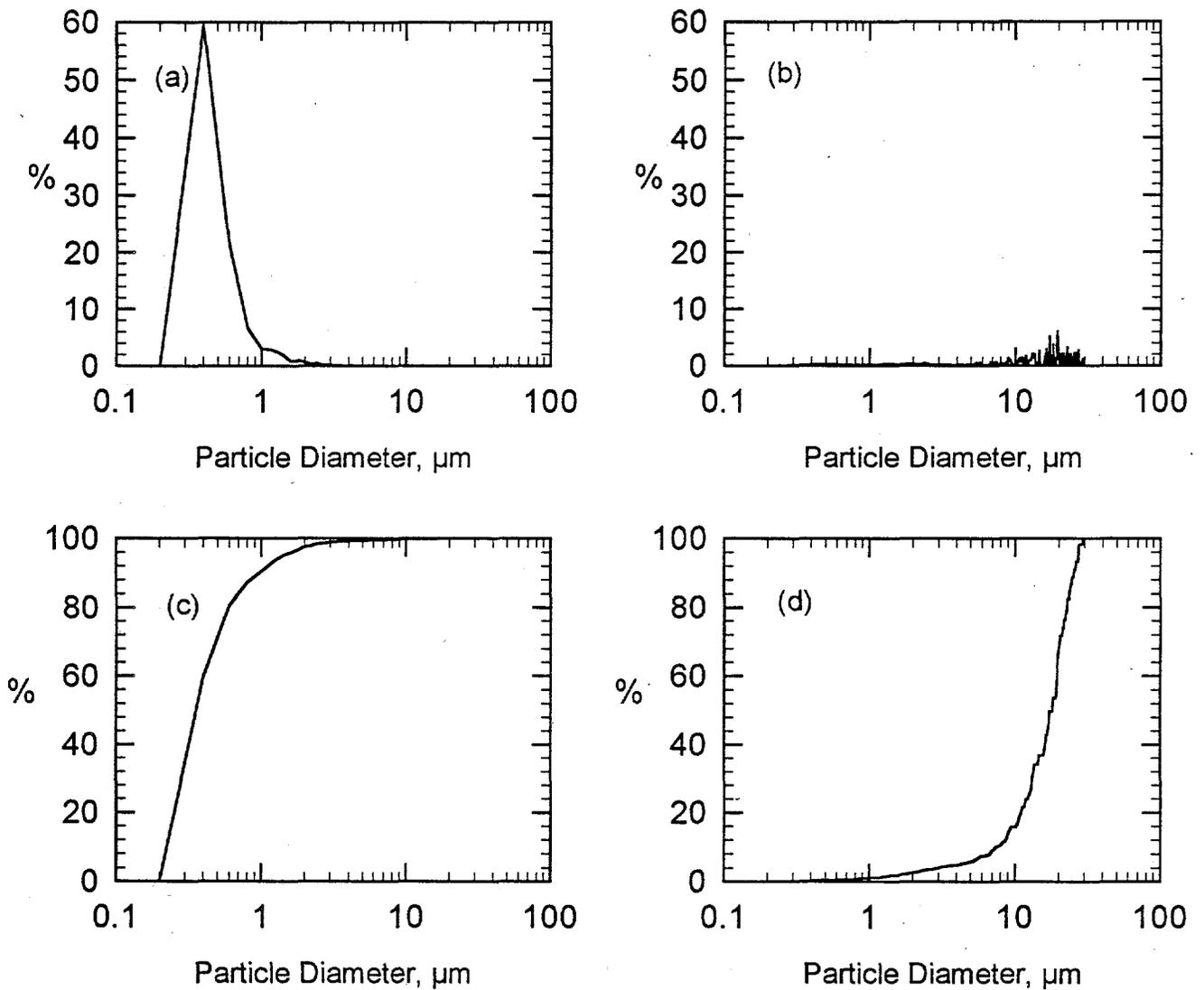
Table A.7. Mass Balance for Radioactive Sludge Components From the B-111 Test

Component	Concentration in Dried Sludge, $\mu\text{Ci/g}$		Recovery, %
	Direct Analysis	Summation Method	
Total Alpha	4.08E-01	6.50E-01	159
^{239,240} Pu	2.82E-01	2.95E-01	105
²⁴¹ Am + ²³⁸ Pu	1.26E-01	1.73E-01	138
²⁴¹ Am(γ)	2.65E-01	2.25E-01	85
¹³⁷ Cs	3.72E+02	3.85E+02	103
⁹⁰ Sr	6.46E+02	6.78E+02	105
⁹⁹ Tc	2.24E-01	3.20E-01	143



B111-C.SP.W

Figure A.2. Particle-Size Data for Untreated B-111 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.



B111-M.SPW

Figure A.3. Particle-Size Data for Treated B-111 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.

Appendix B

Results from the Tank BX-107 Sludge Washing and Caustic Leaching Test

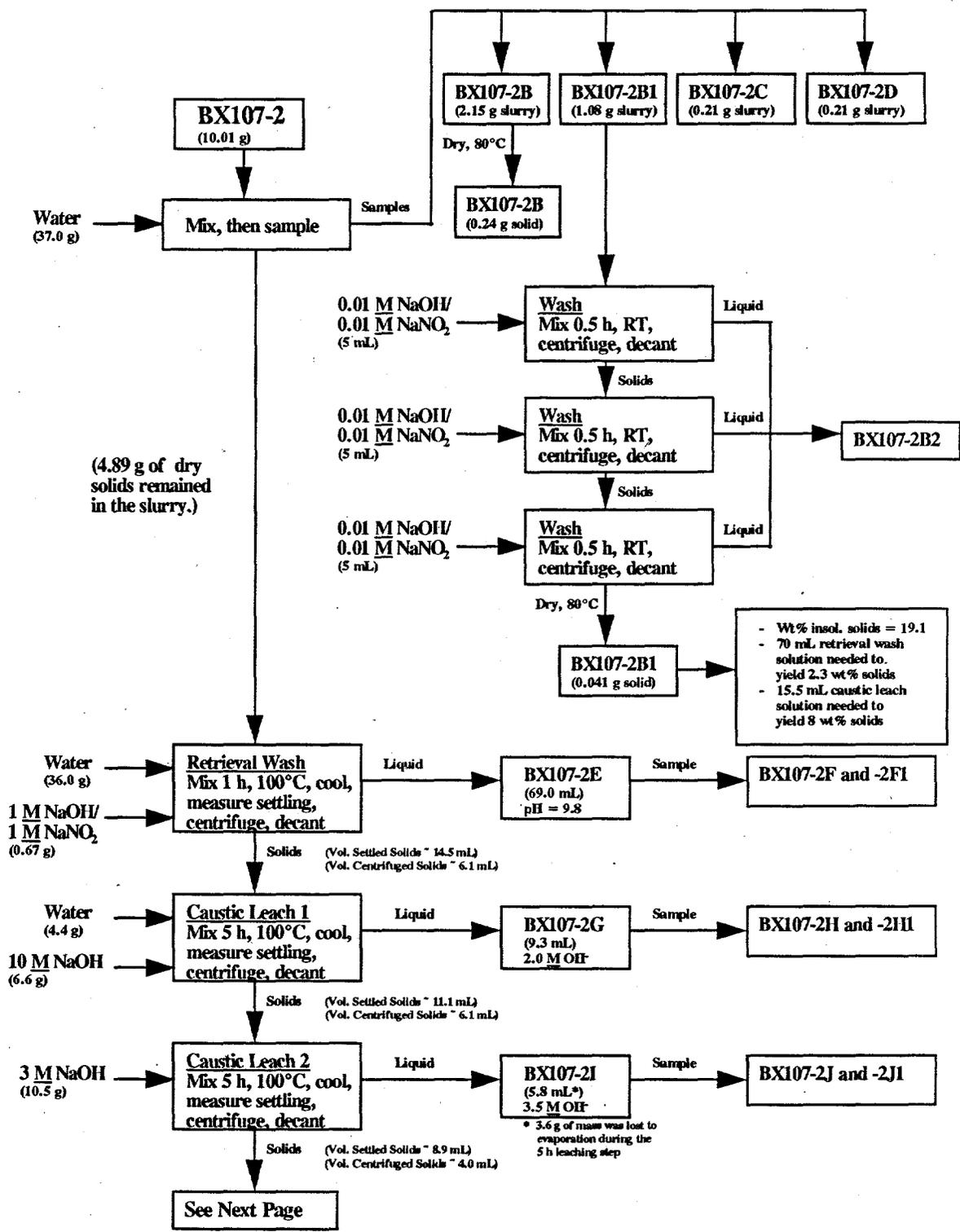
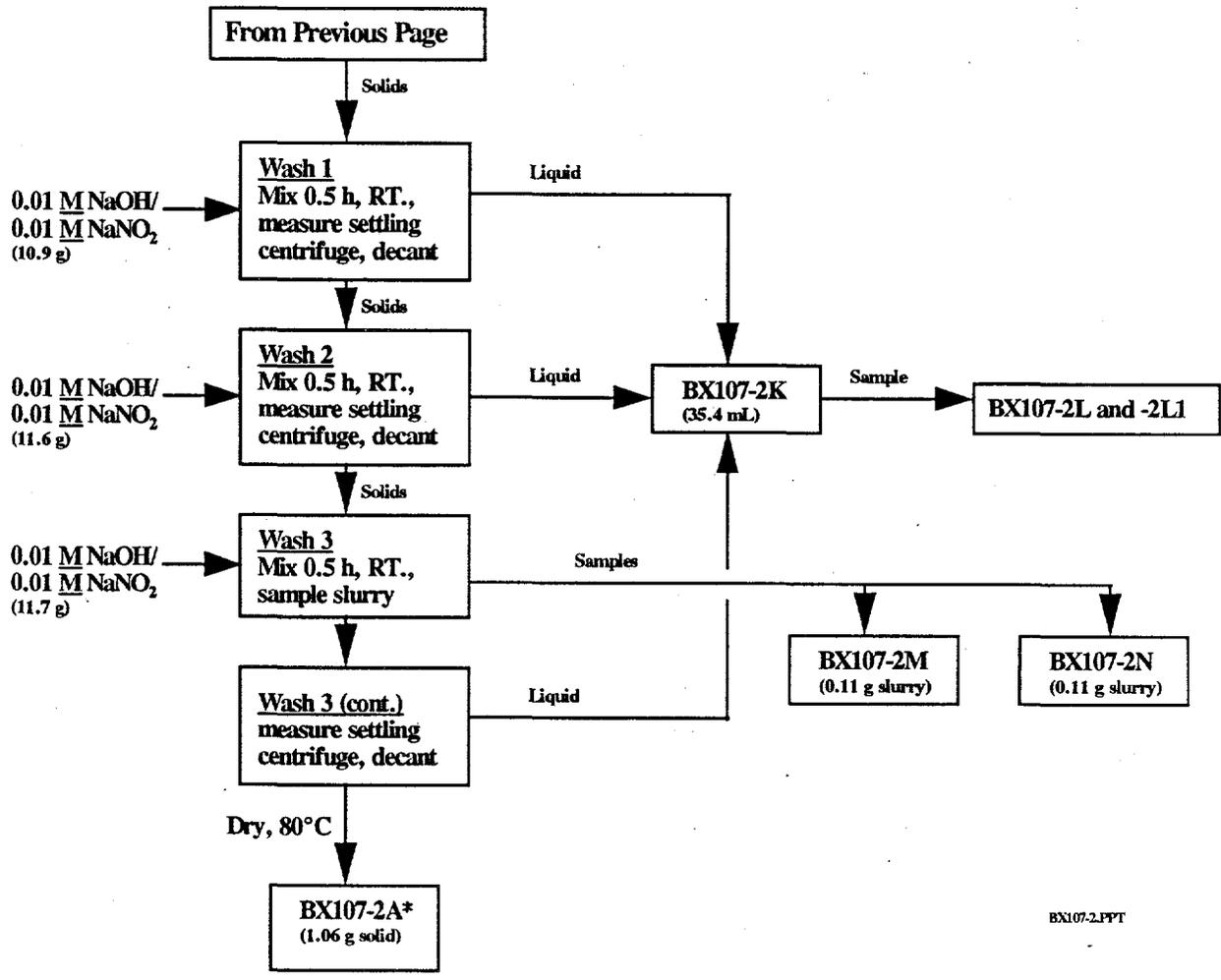


Figure B.1. Schematic of BX-107 Sludge Washing and Caustic Leaching Test



BX107-2.PPT

Figure B.1. (contd.)

Table B.1. Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the BX-107 Test

Component	Detection Limit, $\mu\text{g/mL}$	Concentration, $\mu\text{g/mL}$ ^(a)			
		Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Ag	0.43	0	0	0	0
Al	2.6	26.4	7225	2720	272
As	3.4	0	17	6	0
B	0.85	3.4	2.6	0	0
Ba	0.43	0	0	0	0
Be	0.26	0	0	0	0
Bi	4.3	0	17	34	0
Ca	2.6	4.3	8.5	0	6
Cd	0.43	0	0	0	0
Ce	3.4	0	0	0	0
Co	0.43	0	0	0	0
Cr	0.85	19.6	18.7	38.3	4.3
Cu	0.43	0	0	0.85	0
Dy	0.85	0	0	0	0
Eu	0.43	0	0	0	0
Fe	0.43	3.4	4.3	4.4	0
Gd	8.5	0	0	0	0
K	68	76.5	0	0	0
La	1.7	0	0	0	0
Li	0.85	0	0	0	0
Mg	3.4	0	0	0	0
Mn	0.26	0.6	0.43	0	0
Mo	0.85	1.7	0	0	0
Na	3.4	9350	66300	102000	22950
Nd	1.7	0	0	0	0
Ni	1.7	0	6.8	0	2.55
P	4.3	740	570	306	4930
Pb	2.6	0	0	0	0
Pd	6.8	0	0	0	0
Rh	4.3	0	0	0	0
Ru	4.3	0	0	0	0
Sb	2.6	0	0	0	0
Se	3.4	0	0	0	0
Si	2.6	0	29.8	119	8.5
Sn	43	0	0	0	0
Sr	0.26	0	0	0	0
Te	8.5	0	0	0	0
Th	34	0	0	0	0
Ti	0.26	0	0	0	0
Tl	26	0	0	0	0
U	0.00003	53.7	39.7	37.4	4.45
V	0.43	0	0	0	0
W	3.4	0	0	0	0
Y	0.43	0	0	0	0
Zn	0.85	0	23	15.3	3.4
Zr	0.43	0	0	0.85	0
NO ₃ ⁻	500	13900	4300	1810	150
NO ₂ ⁻	50	2530	790	290	420
PO ₄ ³⁻	50	2310	1920	790	14600
SO ₄ ²⁻	50	1440	500	70	20
F ⁻	25	550	5200	0	2200
Cl ⁻	25	140	50	20	0
Br ⁻	25	0	0	0	0

(a) Zero values indicate the analyte was below the detection limit.

Table B.2. Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the BX-107 Test

Component	Detection Limit, $\mu\text{g/g}$	Concentration, $\mu\text{g/g}$ ^(a)
Ag	20	0
Al	100	41000
As	100	0
B	40	4100
Ba	20	60
Be	9	0
Bi	200	350000
Ca	90	1500
Cd	20	30
Ce	100	900
Co	20	30
Cr	40	4400
Cu	20	100
Dy	40	0
Eu	20	0
Fe	20	72000
Gd	400	0
K	(b)	(b)
La	50	0
Li	40	0
Mg	100	900
Mn	9	360
Mo	40	50
Na	100	84000
Nd	50	0
Ni	(c)	(c)
P	200	17000
Pb	100	600
Pd	300	0
Rh	200	0
Ru	200	0
Sb	90	0
Se	100	200
Si	90	49000
Sn	2000	0
Sr	9	940
Te	400	0
Th	1000	0
Ti	9	70
Tl	900	0
U	0.00003	16900
V	20	0
W	100	0
Y	20	0
Zn	40	300
Zr	20	860
NO ₃ ⁻	(d)	(d)
NO ₂ ⁻	(d)	(d)
PO ₄ ³⁻	17900	20000
SO ₄ ²⁻	7175	4835
F ⁻	17900	0
Cl ⁻	(d)	(d)
Br ⁻	17900	0

(a) Zero values indicate the analyte was below the detection limit.

(b) Potassium values are not reported since the sample was dissolved using a KOH fusion method.

(c) Nickel values are not reported because a Ni crucible was used during the KOH fusion method.

(d) Measurement impractical due to method of sample preparation.

Table B.3. Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the BX-107 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Ag	(a)	(a)	(a)	(a)	(a)
Al	1	49	11	7	32
As	0	82	18	0	0
B	5	1	0	0	94
Ba	0	0	0	0	100
Be	(a)	(a)	(a)	(a)	(a)
Bi	0	0	0	0	100
Ca	14	4	0	10	73
Cd	0	0	0	0	100
Ce	0	0	0	0	100
Co	0	0	0	0	100
Cr	21	3	3	2	71
Cu	0	0	4	0	96
Dy	(a)	(a)	(a)	(a)	(a)
Eu	(a)	(a)	(a)	(a)	(a)
Fe	0	0	0	0	100
Gd	(a)	(a)	(a)	(a)	(a)
K	(b)	(b)	(b)	(b)	(b)
La	(a)	(a)	(a)	(a)	(a)
Li	(a)	(a)	(a)	(a)	(a)
Mg	0	0	0	0	100
Mn	10	1	0	0	89
Mo	69	0	0	0	31
Na	(c)	(c)	(c)	(c)	(c)
Nd	(a)	(a)	(a)	(a)	(a)
Ni	(b)	(b)	(b)	(b)	(b)
P	20	2	1	70	7
Pb	0	0	0	0	100
Pd	(a)	(a)	(a)	(a)	(a)
Rh	(a)	(a)	(a)	(a)	(a)
Ru	(a)	(a)	(a)	(a)	(a)
Sb	(a)	(a)	(a)	(a)	(a)
Se	0	0	0	0	100
Si	0	1	1	1	98
Sn	(a)	(a)	(a)	(a)	(a)
Sr	0	0	0	0	100
Te	(a)	(a)	(a)	(a)	(a)
Th	(a)	(a)	(a)	(a)	(a)
Ti	0	0	0	0	100
Tl	(a)	(a)	(a)	(a)	(a)
U	16	2	1	1	80
V	(a)	(a)	(a)	(a)	(a)
W	(a)	(a)	(a)	(a)	(a)
Y	(a)	(a)	(a)	(a)	(a)
Zn	0	29	12	16	43
Zr	0	0	1	0	99
NO ₃	95	4	1	1	(d)
NO ₂	88	4	1	7	(d)
PO ₄ ³⁻	22	2	1	72	3
SO ₄ ²⁻	90	4	0	1	5
F ⁻	23 (21) ^(e)	29 (26) ^(e)	0	47 (42) ^(e)	0 (10) ^(e)
Cl ⁻	94	5	1	0	(d)
Br ⁻	(a)	(a)	(a)	(a)	(a)

(a) Component was not detected.

(b) K and Ni values could not be determined due to the KOH fusion procedure used to prepare the leached sludge for analysis.

(c) Removal of Na from the sludge cannot be reliably tracked because the Na in the sludge cannot be distinguished from the Na added in the washing and leaching.

(d) Measurement impractical due to method of sample preparation.

(e) Values in parentheses represent the values obtained if, for cases where the component was below the detection limit, the component concentration was assumed to be the detection limit.

Table B.4. Mass Balance for Nonradioactive Sludge Components From the BX-107 Test

Component	Concentration in Dried Sludge, g/g Sludge		Recovery, %
	Direct Analysis	Summation Method	
Ag	< 4.00E-05		
Al	3.50E-02	2.83E-02	81
As	< 3.00E-04	3.94E-05	
B	3.50E-03	9.48E-04	27
Ba	< 4.00E-05	1.31E-05	
Be	< 2.00E-05		
Bi	4.80E-02	7.64E-02	159
Ca	2.00E-03	4.48E-04	22
Cd	< 4.00E-05	6.55E-06	
Ce	< 3.00E-04	1.96E-04	
Co	5.00E-05	6.55E-06	13
Cr	2.30E-03	1.35E-03	59
Cu	6.90E-04	2.28E-05	3
Dy	< 7.00E-05		
Eu	< 4.00E-05		
Fe	2.80E-02	1.58E-02	56
Gd	< 7.00E-04		
K	(b)	(b)	(b)
La	< 1.00E-04		
Li	< 7.00E-05		
Mg	4.00E-04	1.96E-04	49
Mn	4.40E-04	8.78E-05	20
Mo	< 7.00E-05	3.49E-05	
Na	2.10E-01		
Nd	< 1.00E-04		
Ni	(b)	(b)	(b)
P	5.60E-02	5.13E-02	92
Pb	< 2.00E-04	1.31E-04	
Pd	< 9.00E-04		
Rh	< 4.00E-04		
Ru	< 4.00E-04		
Sb	< 2.00E-04		
Se	< 3.00E-04	4.36E-05	
Si	2.00E-02	1.10E-02	55
Sn	< 4.00E-03		
Sr	3.70E-04	2.05E-04	55
Te	< 7.00E-04		
Th	< 3.00E-03		
Ti	4.00E-05	1.53E-05	38
Tl	< 2.00E-03		
U	1.42E-02	4.60E-03	32
V	< 4.00E-05		
W	< 3.00E-04		
Y	< 4.00E-05		
Zn	5.00E-04	1.52E-04	30
Zr	1.00E-04	1.89E-04	189
NO ₃ ⁻	(c)	2.08E-01	
NO ₂ ⁻	(c)	4.06E-02	
PO ₄ ³⁻	1.30E-01	1.47E-01	113
SO ₄ ²⁻	1.98E-02	2.26E-02	114
F ⁻		3.36E-02	
Cl ⁻	(c)	2.09E-03	
Br ⁻			

(a) Blank spaces indicate that the analyte was below the detection limit.

(b) K and Ni values could not be determined due to the KOH fusion method used to prepare the solids for analysis.

(c) Measurement impractical due to method of sample preparation.

Table B.5. Concentrations of the Radioactive Sludge Components in the Various Process Streams From the BX-107 Test

Component	Concentration, $\mu\text{Ci/mL}$			
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Total Alpha	< 2.55E-05	2.38E-05	1.00E-04	< 2.55E-05
^{239,240} Pu	ND ^(a)	ND	ND	ND
²⁴¹ Am + ²³⁸ Pu	ND	ND	ND	ND
²⁴¹ Am(γ)	< 5.00E-05	< 3.00E-04	< 2.00E-04	< 5.00E-05
¹³⁷ Cs	4.02E-01	9.01E+00	4.00E+00	4.38E-01
⁹⁰ Sr	7.49E-04	1.30E-03	3.94E-03	2.11E-03
⁹⁹ Tc	4.73E-03	1.88E-03	6.95E-04	5.29E-05

Component	Concentration, $\mu\text{Ci/g}$
	Residue
Total Alpha	1.41E+00
^{239,240} Pu	1.26E+00
²⁴¹ Am + ²³⁸ Pu	1.45E-01
²⁴¹ Am(γ)	1.25E-01
¹³⁷ Cs	9.25E+00
⁹⁰ Sr	7.57E+01
⁹⁹ Tc	4.18E-03

(a) ND = Not Determined. The low total alpha activity made these separations impractical.

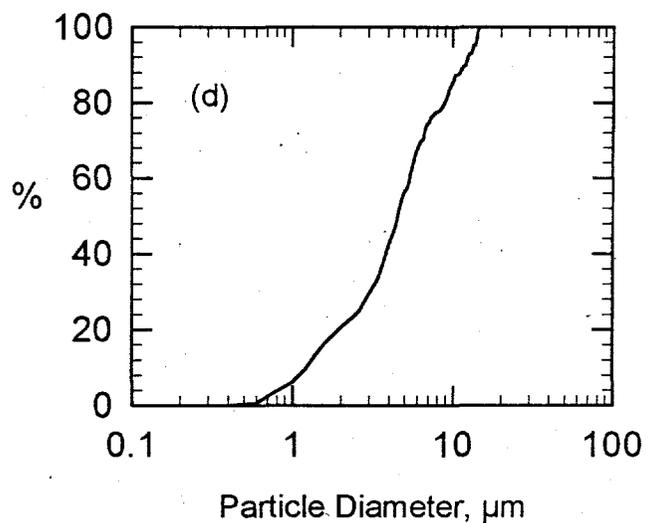
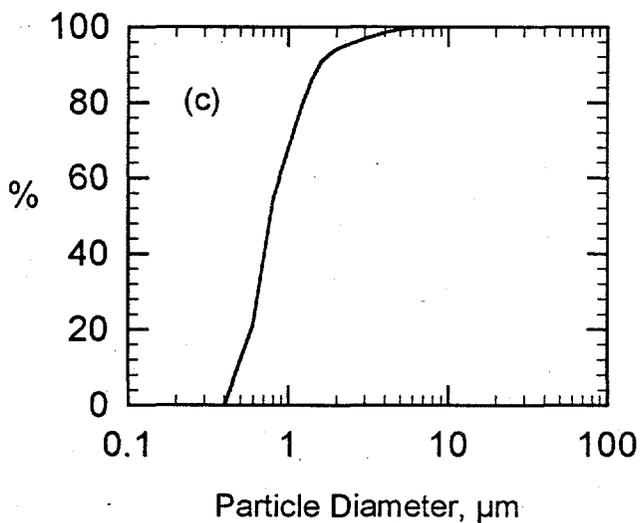
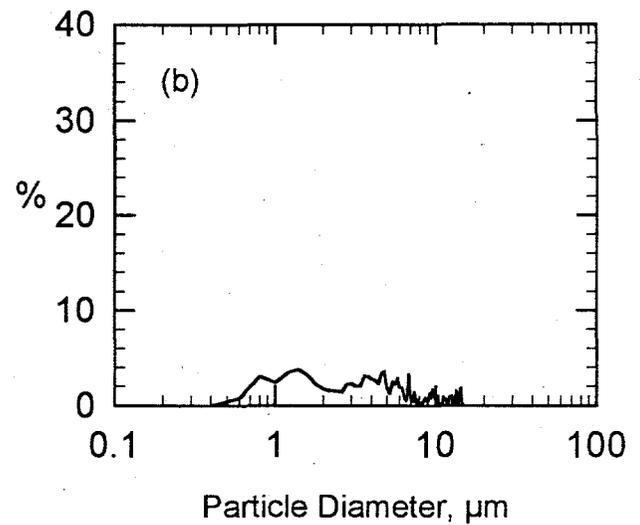
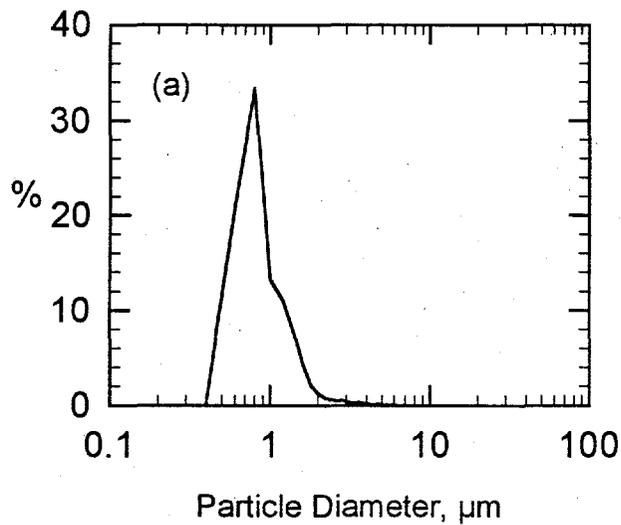
Table B.6. Distribution of the Radioactive Sludge Components Between the Various Process Streams From the BX-107 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Total Alpha	0	0	0	0	100
^{239,240} Pu	(a)	(a)	(a)	(a)	100
²⁴¹ Am + ²³⁸ Pu	(a)	(a)	(a)	(a)	100
²⁴¹ Am(γ)	0	0	0	0	100
¹³⁷ Cs	17	52	15	10	6
⁹⁰ Sr	0	0	0	0	100
⁹⁹ Tc	92	5	1	1	1

(a) Not determined due to a lack of alpha activity in some components.

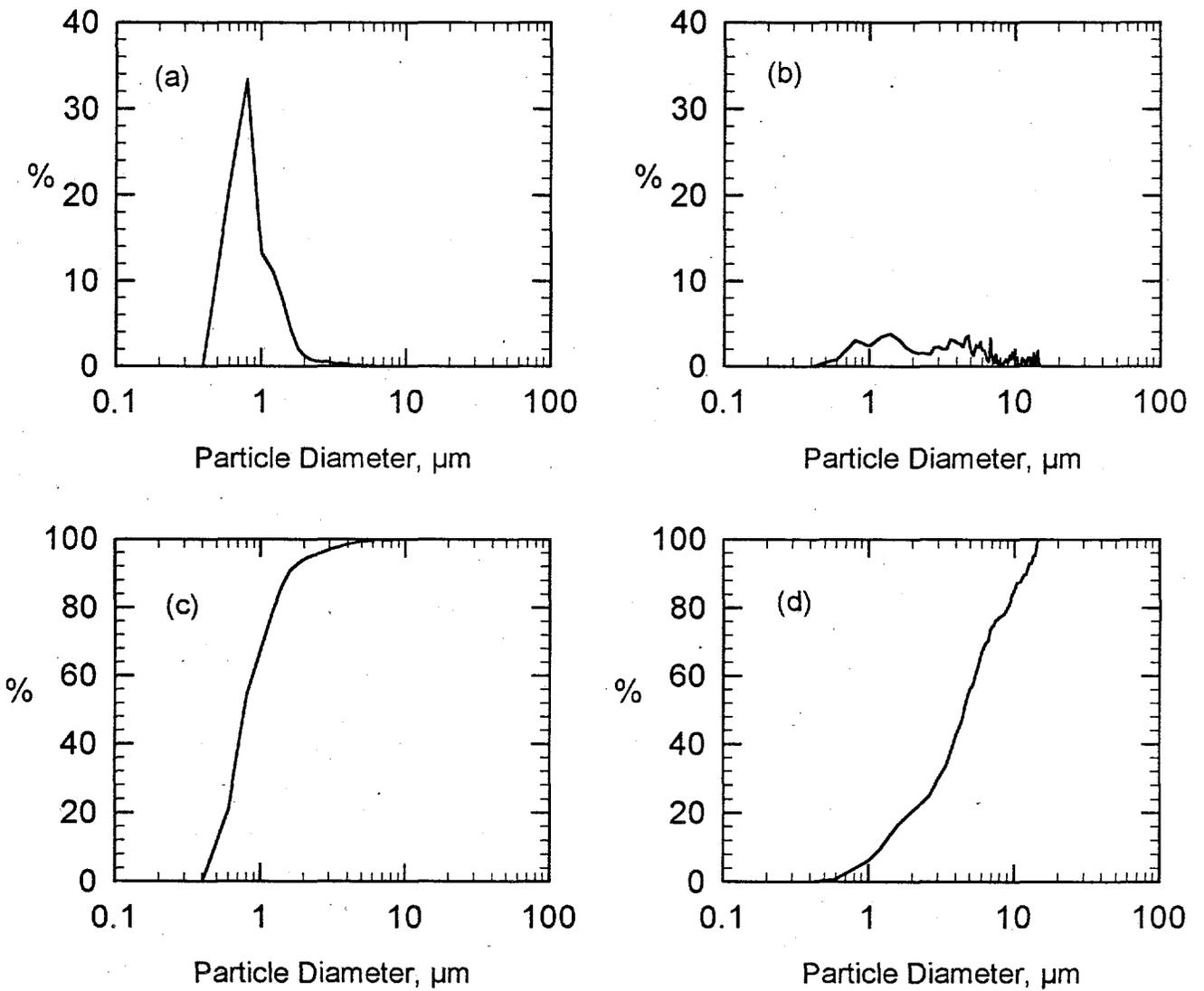
Table B.7. Mass Balance for Radioactive Sludge Components From the BX-107 Test

Component	Concentration in Dried Sludge, μCi/g		Recovery, %
	Direct Analysis	Summation Method	
Total Alpha	3.45E-01	3.08E-01	89
^{239,240} Pu	3.08E-01	2.75E-01	89
²⁴¹ Am + ²³⁸ Pu	3.24E-02	3.16E-02	98
²⁴¹ Am(γ)	< 2.08E-01	2.73E-02	
¹³⁷ Cs	3.81E+01	3.27E+01	86
⁹⁰ Sr	2.30E+01	1.66E+01	72
⁹⁹ Tc	5.16E-02	7.25E-02	140



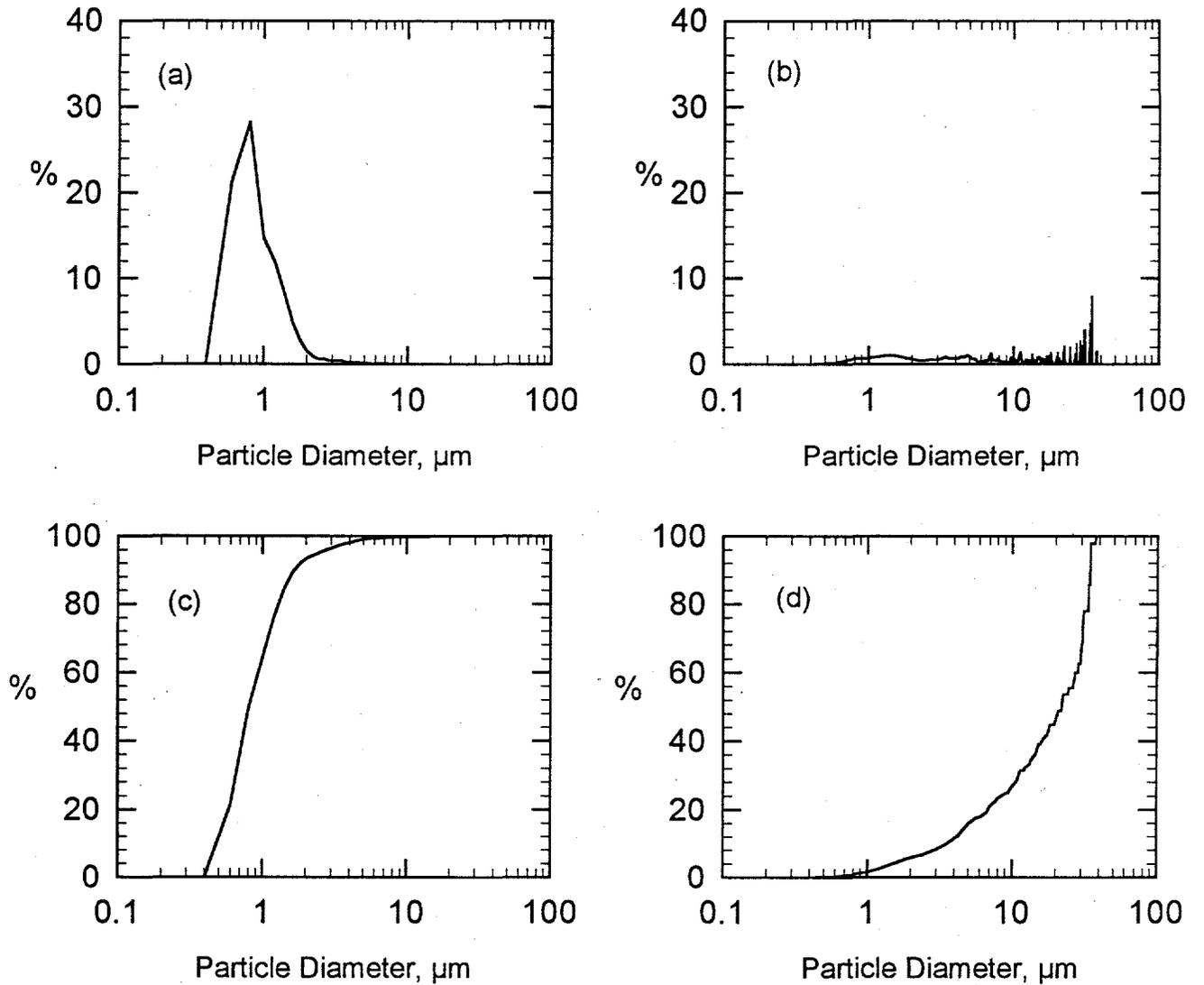
BX107-2C.SPW

Figure B.1. Particle-Size Data for Untreated BX-107 Sludge: a) Probability-Number Density Graph, b) Probability Volume-Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.



BX107-2C.SPW

Figure B.2. Particle-Size Data for Untreated BX-107 Sludge: a) Probability-Number Density Graph, b) Probability Volume-Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.



BX107-2M.SPW

Figure B.3. Particle-Size Data for Treated BX-107 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.

Appendix C

Results from the Tank C-103 Sludge Washing and Caustic Leaching Test

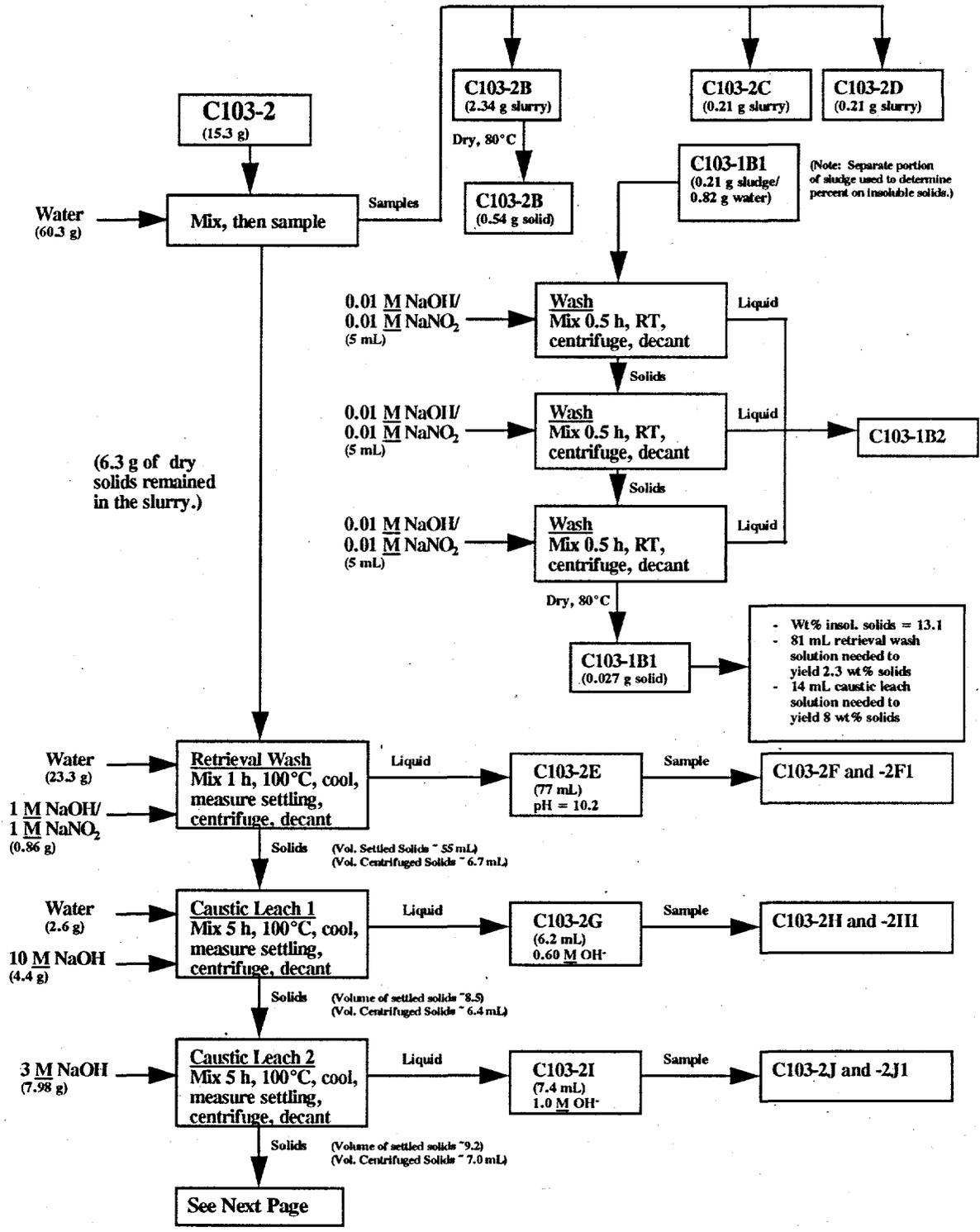
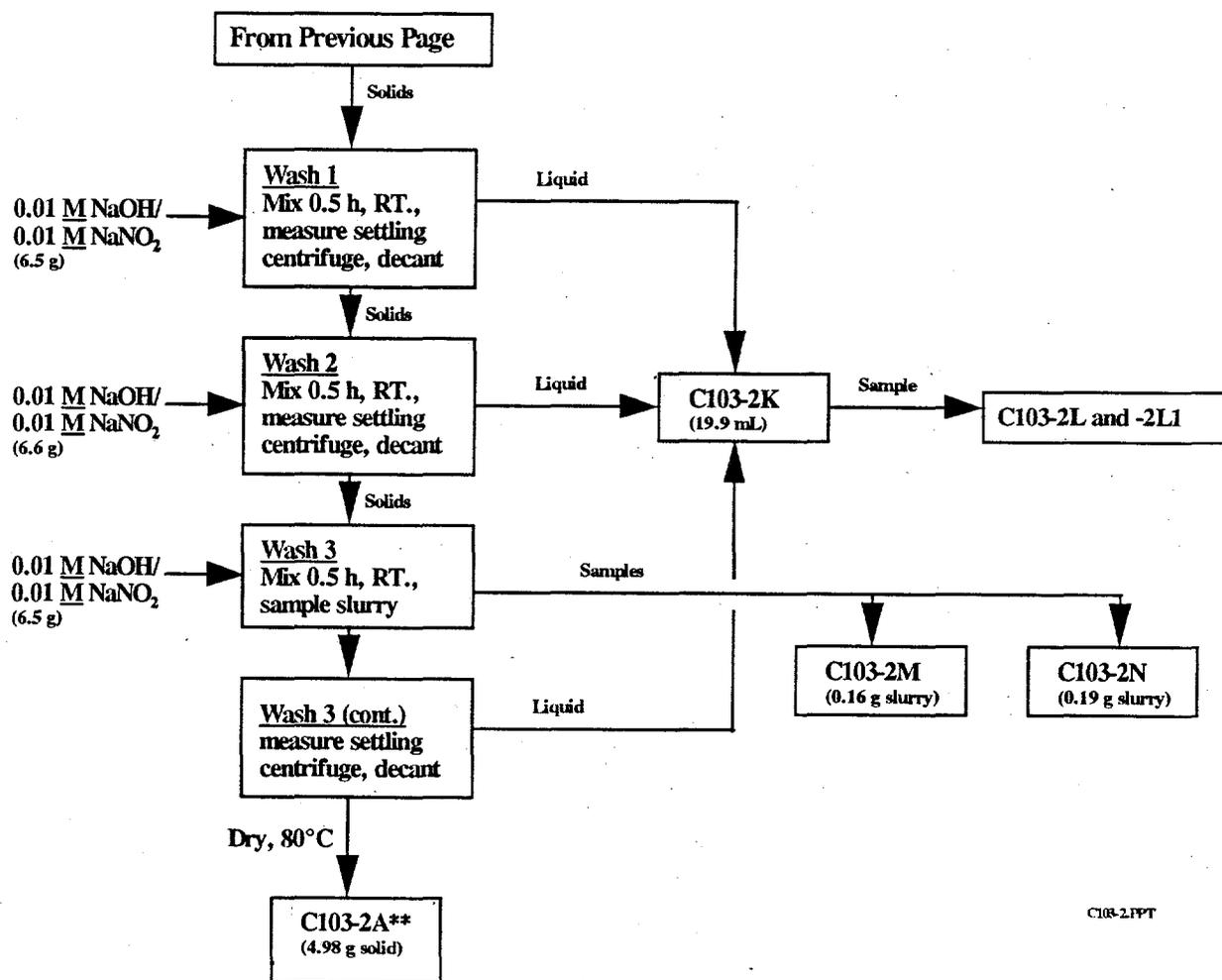


Figure C.1. Schematic of C-103 Sludge Washing and Caustic Leaching Test



C103-2.FPT

Figure C.1. (contd.)

Table C.1. Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the C-103 Test

Component	Detection Limit. μg/mL ^(a)	Concentration, μg/mL ^(b)			
		Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Ag	0.085	0.17	0	0	0
Al	0.51	7.23	25500	30600	4505
As	0.68	0	22.95	27.2	5.1
B	0.17	0	0.85	0.6	0
Ba	0.085	0.68	0	0	0
Be	0.043	0	0.17	0.17	0
Bi	0.85	0	2.55	2.55	0
Ca	0.43	3.4	5.95	5.1	9.35
Cd	0.085	0.34	0	0	0
Ce	0.68	0	0	0	0
Co	0.085	0	0.51	0.51	0
Cr	0.17	1.7	44.2	34.85	6.38
Cu	0.085	24.65	170	102	10.2
Dy	0.17	0	0	0	0
Eu	0.085	0	0	0	0
Fe	0.085	12.75	2.38	2.55	0.43
Gd	1.7	0	0	0	0
K	17	25.5	170	85	25.5
La	0.26	0	0	0	0
Li	0.17	0.85	0	0	0
Mg	0.68	1.7	0	0	0.85
Mn	0.043	0.94	0	0	0
Mo	0.17	0.85	0.85	0.43	0
Na	0.68	3995	69700	69700	11900
Nd	0.26	0	0	0	0
Ni	0.26	3.4	1.7	1.7	3.32
P	0.85	153	1530	697	145
Pb	0.51	1.7	0	0	0
Pd	1.7	0	0	0	0
Rh	0.85	0	0	0	0
Ru	0.85	0	0	0	0
Sb	0.43	0	0	0	0
Se	0.68	0	2.55	3.4	0
Si	0.43	4.93	55.25	47.6	1.7
Sn	8.5	0	42.5	25.5	0
Sr	0.043	0	0	0	0
Te	1.7	0	0	0	0
Th	6.8	0	0	0	0
Ti	0.043	0.05	0	0	0
Tl	0.43	0	42.5	51	8.5
U	0.00425	334	78.4	64.3	8.6
V	0.085	0	2.04	0.8	0.26
W	0.68	1.7	15.3	8.5	2.6
Y	0.085	0	0	0	0
Zn	0.17	0.6	31.45	23.8	3.91
Zr	0.085	19.55	2.55	2.38	0
NO ₃ ⁻	0.5	60	<50	<50	<50
NO ₂ ⁻	0.5	1100	440	160	330
PO ₄ ³⁻	0.5	290	2770	840	270
SO ₄ ²⁻	0.5	220	<50	<50	<50
F ⁻	0.25	(c)	(c)	(c)	(c)
Cl ⁻	0.25	30	(c)	(c)	(c)
Br ⁻	25	0	0	0	0

(a) The detection limits for two caustic leach solutions (G and I) solutions are twice the values reported in this column.

(b) Zero values indicate the analyte was below the detection limit.

(c) Analyte could not be accurately determined due to matrix effects.

Table C.2. Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the C-103 Test

<u>Component</u>	<u>Detection Limit, $\mu\text{g/g}$</u>	<u>Concentration, $\mu\text{g/g}$^(a)</u>
Ag	60	1200
Al	400	105000
As	500	0
B	100	1350
Ba	60	1500
Be	30	0
Bi	600	0
Ca	300	9000
Cd	60	760
Ce	500	550
Co	60	85
Cr	100	1300
Cu	60	4500
Dy	100	0
Eu	60	0
Fe	1000	210000
Gd	200	0
K	(b)	(b)
La	200	650
Li	100	0
Mg	500	850
Mn	30	5550
Mo	100	0
Na	500	42500
Nd	200	1500
Ni	(c)	(c)
P	600	3000
Pb	400	6450
Pd	1000	0
Rh	600	0
Ru	600	2000
Sb	300	0
Se	500	0
Si	300	34000
Sn	6000	0
Sr	30	200
Te	1000	0
Th	5000	0
Ti	30	420
Tl	3000	0
U	0.4	1720
V	60	0
W	500	0
Y	60	200
Zn	100	500
Zr	60	21500
NO ₃ ⁻	(d)	(d)
NO ₂ ⁻	(d)	(d)
PO ₄ ³⁻	(d)	(d)
SO ₄ ²⁻	(d)	(d)
F ⁻	(d)	(d)
Cl ⁻	(d)	(d)
Br ⁻	(d)	(d)

- (a) Zero values indicate the analyte was below the detection limit.
 (b) Potassium values are not reported because the sample was dissolved for analysis using a KOH fusion technique.
 (c) Nickel values are not reported because a Ni crucible was used during the KOH fusion procedure.
 (d) Analyte could not be accurately determined due to matrix effects.

Table C.3. Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the C-103 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Ag	0	0	0	0	100
Al	0	16	23	9	52
As	0	32	45	23	0
B	0	0	0	0	100
Ba	1	0	0	0	99
Be	0	46	54	0	0
Bi	0	46	54	0	0
Ca	1	0	0	0	99
Cd	1	0	0	0	99
Ce	0	0	0	0	100
Co	0	1	1	0	98
Cr	2	4	4	2	89
Cu	7	4	3	1	85
Dy	(a)	(a)	(a)	(a)	(a)
Eu	(a)	(a)	(a)	(a)	(a)
Fe	0	0	0	0	100
Gd	(a)	(a)	(a)	(a)	(a)
K	(b)	(b)	(b)	(b)	(b)
La	0	0	0	0	100
Li	100	0	0	0	0
Mg	3	0	0	0	97
Mn	0	0	0	0	100
Mo	89	7	4	0	0
Na	(c)	(c)	(c)	(c)	(c)
Nd	0	0	0	0	100
Ni	(b)	(b)	(b)	(b)	(b)
P	27	21	12	7	34
Pb	0	0	0	0	100
Pd	(a)	(a)	(a)	(a)	(a)
Rh	(a)	(a)	(a)	(a)	(a)
Ru	0	0	0	0	100
Sb	(a)	(a)	(a)	(a)	(a)
Se	0	39	61	0	0
Si	0	0	0	0	99
Sn	0	58	42	0	0
Sr	0	0	0	0	100
Te	(a)	(a)	(a)	(a)	(a)
Th	(a)	(a)	(a)	(a)	(a)
Ti	0	0	0	0	100
Tl	0	33	47	21	0
U	73	1	1	0	24
V	0	53	25	22	0
W	38	28	18	15	0
Y	0	0	0	0	100
Zn	2	7	6	3	83
Zr	1	0	0	0	99
NO ₃ ⁻	(d)	(d)	(d)	(d)	(d)
NO ₂ ⁻	(d)	(d)	(d)	(d)	(d)
PO ₄ ³⁻	(d)	(d)	(d)	(d)	(d)
SO ₄ ²⁻	(d)	(d)	(d)	(d)	(d)
F ⁻	(d)	(d)	(d)	(d)	(d)
Cl ⁻	(d)	(d)	(d)	(d)	(d)
Br ⁻	(d)	(d)	(d)	(d)	(d)

(a) Component was not detected.

(b) K and Ni values could not be determined due to the KOH fusion procedure used in the analysis of the residue.

(c) Removal of Na from the sludge cannot be reliably tracked because the Na in the sludge cannot be distinguished from the Na added in the washing and leaching steps.

(d) Values could not be determined because analysis of the leached sludge was unsuccessful.

Table C.4. Mass Balance for Nonradioactive Sludge Components From the C-103 Test

Component	Concentration in Dried Sludge, g/g Sludge ^(a)		Recovery, %
	Direct Analysis	Summation Method	
Ag	8.60E-04	9.49E-04	110
Al	1.40E-01	1.58E-01	113
As	< 6.00E-04	7.05E-05	
B	1.00E-03	1.07E-03	107
Ba	2.00E-03	1.19E-03	60
Be	< 4.00E-05	3.66E-07	
Bi	< 7.00E-04	5.50E-06	
Ca	1.80E-02	7.18E-03	40
Cd	8.90E-04	6.04E-04	68
Ce	9.00E-04	4.34E-04	48
Co	1.00E-04	6.81E-05	68
Cr	1.60E-03	1.15E-03	72
Cu	5.70E-03	4.17E-03	73
Dy	< 1.00E-04		
Eu	< 7.00E-05		
Fe	2.00E-01	1.66E-01	83
Gd	< 1.00E-03		
K	(b)	(b)	(b)
La	8.00E-04	5.13E-04	64
Li	< 1.00E-04	1.04E-05	
Mg	1.00E-03	6.94E-04	69
Mn	5.80E-03	4.39E-03	76
Mo	< 1.00E-04	1.17E-05	
Na	4.60E-02		
Nd	2.00E-03	1.18E-03	59
Ni	(b)	(b)	(b)
P	5.00E-03	7.01E-03	140
Pb	7.10E-03	5.11E-03	72
Pd	< 1.00E-03		
Rh	< 7.00E-04		
Ru	2.00E-03	1.58E-03	79
Sb	< 4.00E-04		
Se	< 5.00E-04	6.49E-06	
Si	2.70E-02	2.70E-02	100
Sn	< 7.00E-03	7.17E-05	
Sr	2.00E-04	1.58E-04	79
Te	< 1.00E-03		
Th	< 6.00E-03		
Ti	4.10E-04	3.32E-04	81
Tl	< 4.00E-03	1.28E-04	
U	3.05E-03	5.61E-03	184
V	< 7.00E-05	3.76E-06	
W	< 6.00E-04	5.39E-05	
Y	3.00E-04	1.58E-04	53
Zn	7.00E-04	4.73E-04	68
Zr	2.30E-02	1.72E-02	75
NO ₃ ⁻	(c)	(c)	(c)
NO ₂ ⁻	(c)	(c)	(c)
PO ₄ ³⁻	(c)	(c)	(c)
SO ₄ ²⁻	(c)	(c)	(c)
F ⁻	(c)	(c)	(c)
Cl ⁻	(c)	(c)	(c)
Br ⁻	(c)	(c)	(c)

(a) Blank spaces indicate that the analyte was below the detection limit.

(b) K and Ni values could not be determined due to the KOH fusion procedure used in the analysis of the residue.

(c) Analyte could not be accurately determined due to matrix effects.

Table C.5. Concentrations of the Radioactive Sludge Components in the Various Process Streams From the C-103 Test

Component	Concentration, $\mu\text{Ci/mL}$			
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Total Alpha	6.67E-03	< 2.55E-04	4.74E-04	1.84E-04
^{239,240} Pu	2.36E-03	< 2.55E-04	< 2.55E-04	1.09E-04
²⁴¹ Am + ²³⁸ Pu	4.31E-03	< 2.55E-04	4.74E-04	7.60E-05
²⁴¹ Am(γ)	3.37E-03	< 1.70E-02	< 3.40E-03	< 1.70E-03
¹³⁷ Cs	4.31E+00	2.80E+01	1.94E+01	4.39E+00
⁹⁰ Sr	9.27E-01	1.14E-01	1.25E-01	1.90E-02
⁹⁹ Tc	2.90E-03	1.26E-03	5.71E-04	1.21E-04

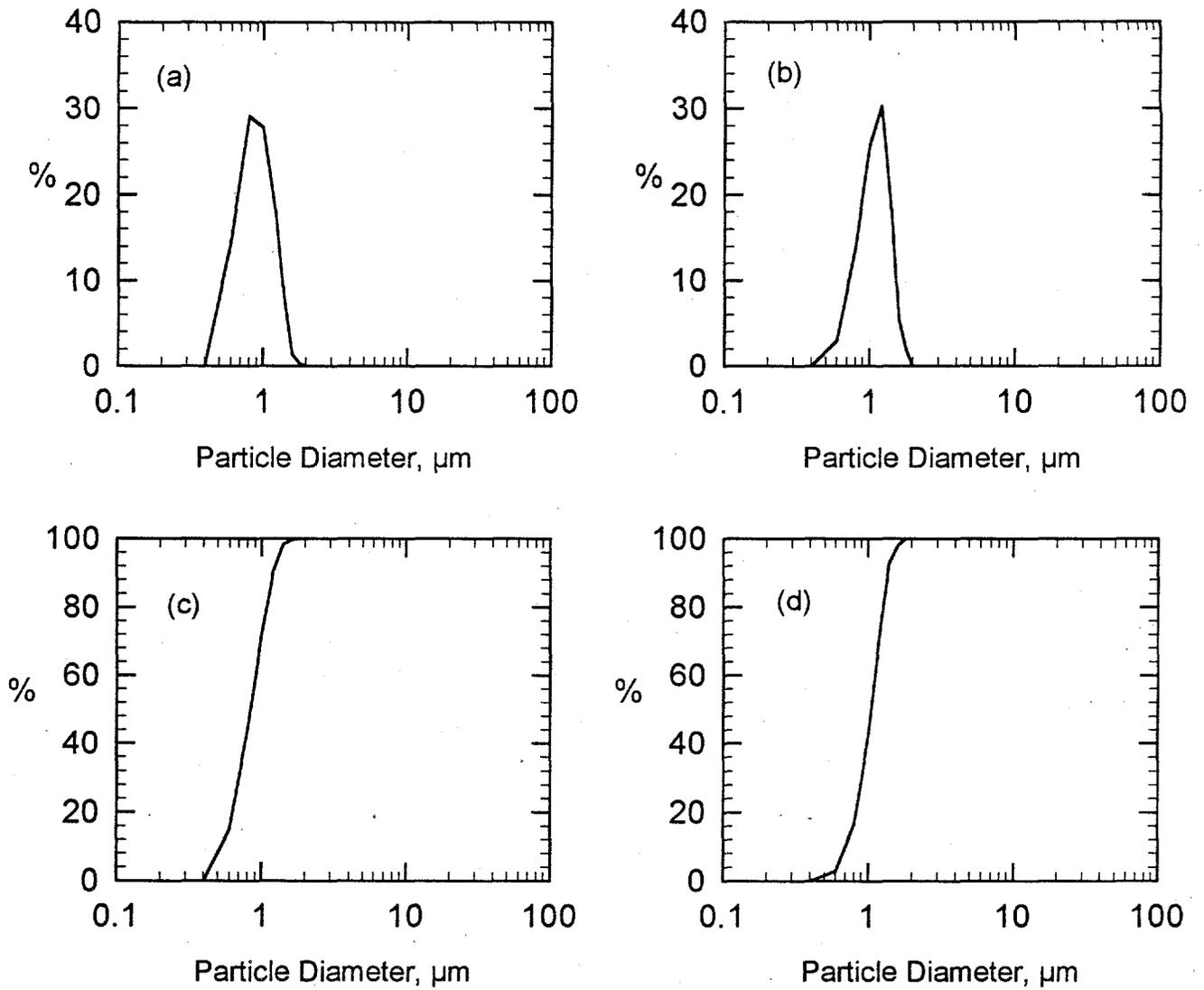
Component	Concentration, $\mu\text{Ci/g}$
	Residue
Total Alpha	2.53E+01
^{239,240} Pu	4.20E+00
²⁴¹ Am + ²³⁸ Pu	2.07E+01
²⁴¹ Am(γ)	1.95E+01
¹³⁷ Cs	1.88E+02
⁹⁰ Sr	9.91E+03
⁹⁹ Tc	6.27E-03

Table C.6. Distribution of the Radioactive Sludge Components Between the Various Process Streams From the C-103 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Total Alpha	0	0	0	0	100
^{239,240} Pu	1	0	0	0	99
²⁴¹ Am + ²³⁸ Pu	0	0	0	0	100
²⁴¹ Am(γ)	0	0	0	0	100
¹³⁷ Cs	20	10	9	5	56
⁹⁰ Sr	0	0	0	0	100
⁹⁹ Tc	83	3	2	1	12

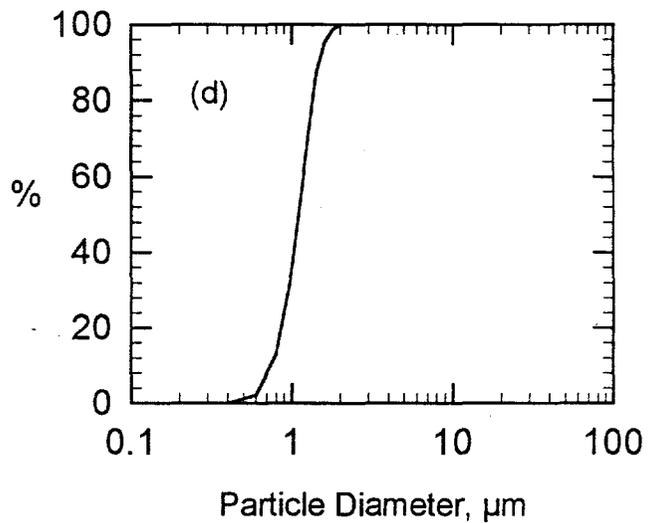
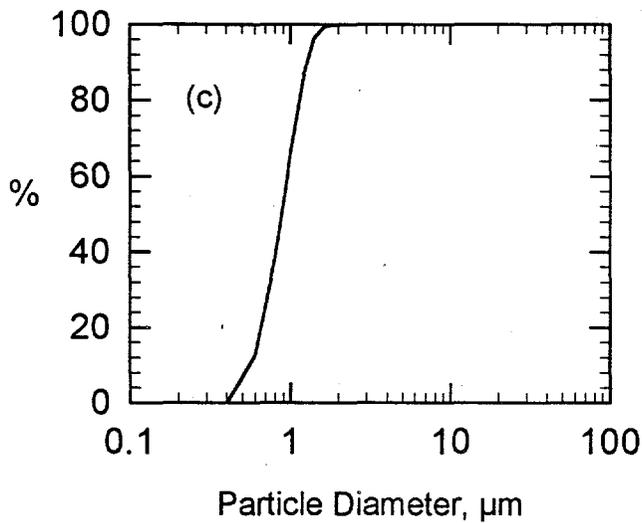
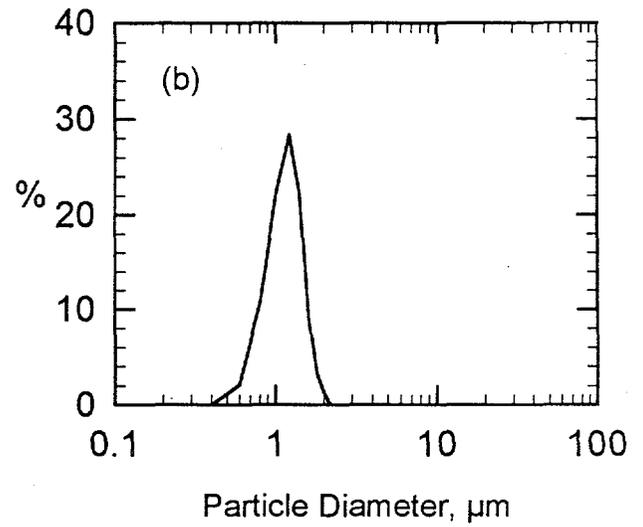
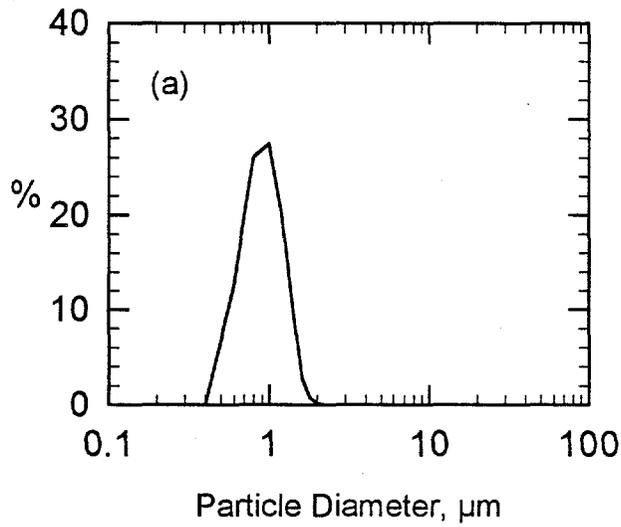
Table C.7. Mass Balance for Radioactive Sludge Components From the C-103 Test

Component	Concentration in Dried Sludge, $\mu\text{Ci/g}$		Recovery, %
	Direct Analysis	Summation Method	
Total Alpha	2.79E+01	2.00E+01	72
^{239,240} Pu	4.85E+00	3.34E+00	69
²⁴¹ Am + ²³⁸ Pu	2.27E+01	1.64E+01	72
²⁴¹ Am(γ)	2.19E+01	1.54E+01	70
¹³⁷ Cs	2.36E+02	2.65E+02	112
⁹⁰ Sr	9.86E+03	7.82E+03	79
⁹⁹ Tc	2.10E-02	4.26E-02	203



C103-2C.SPW

Figure C.2. Particle-Size Data for Untreated C-103 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.



C103-1M.SPW

Figure C.3. Particle-Size Data for Treated C-103 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.

Appendix D

**Results from the Tank S-104 Sludge
Washing and Caustic Leaching Test**

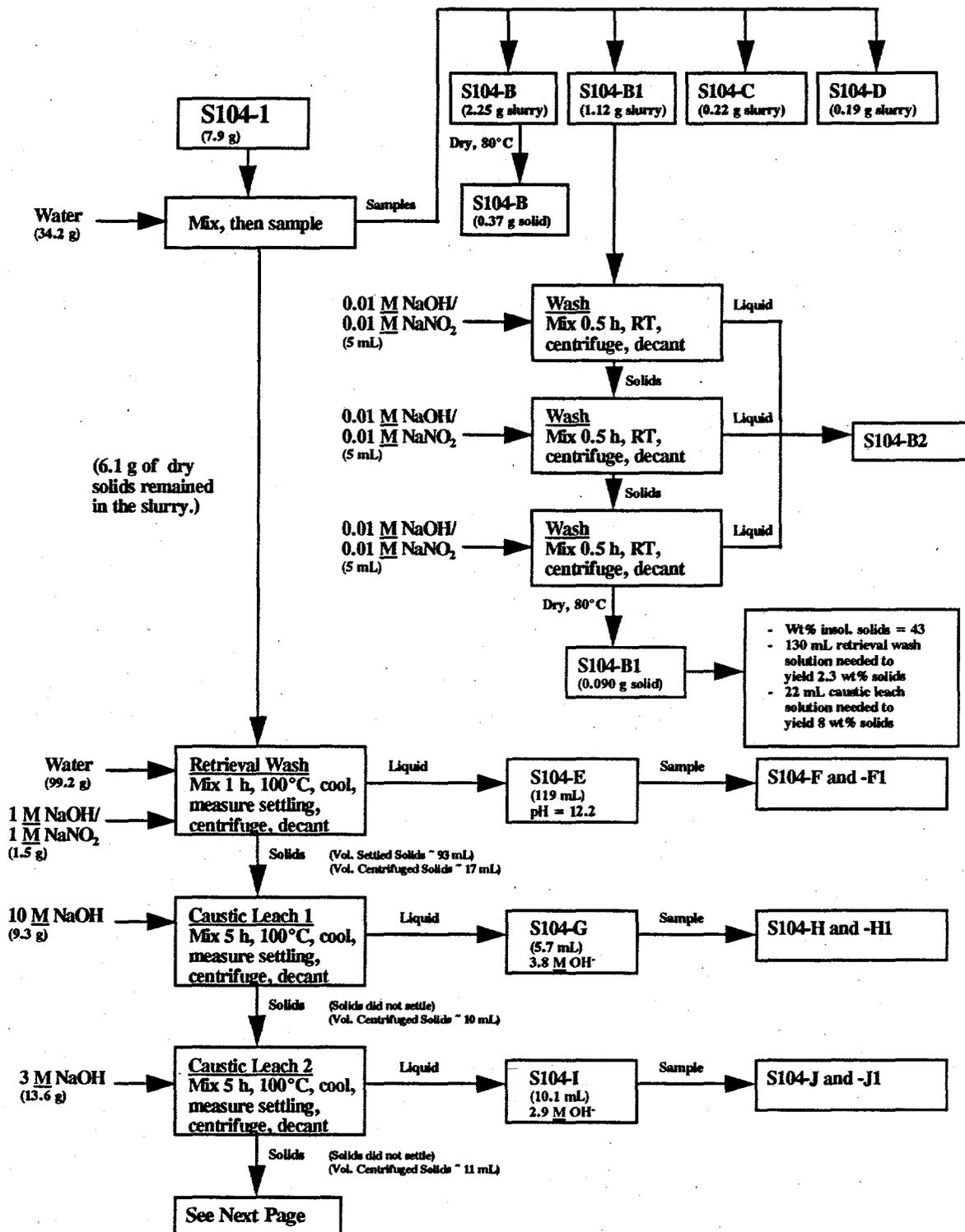
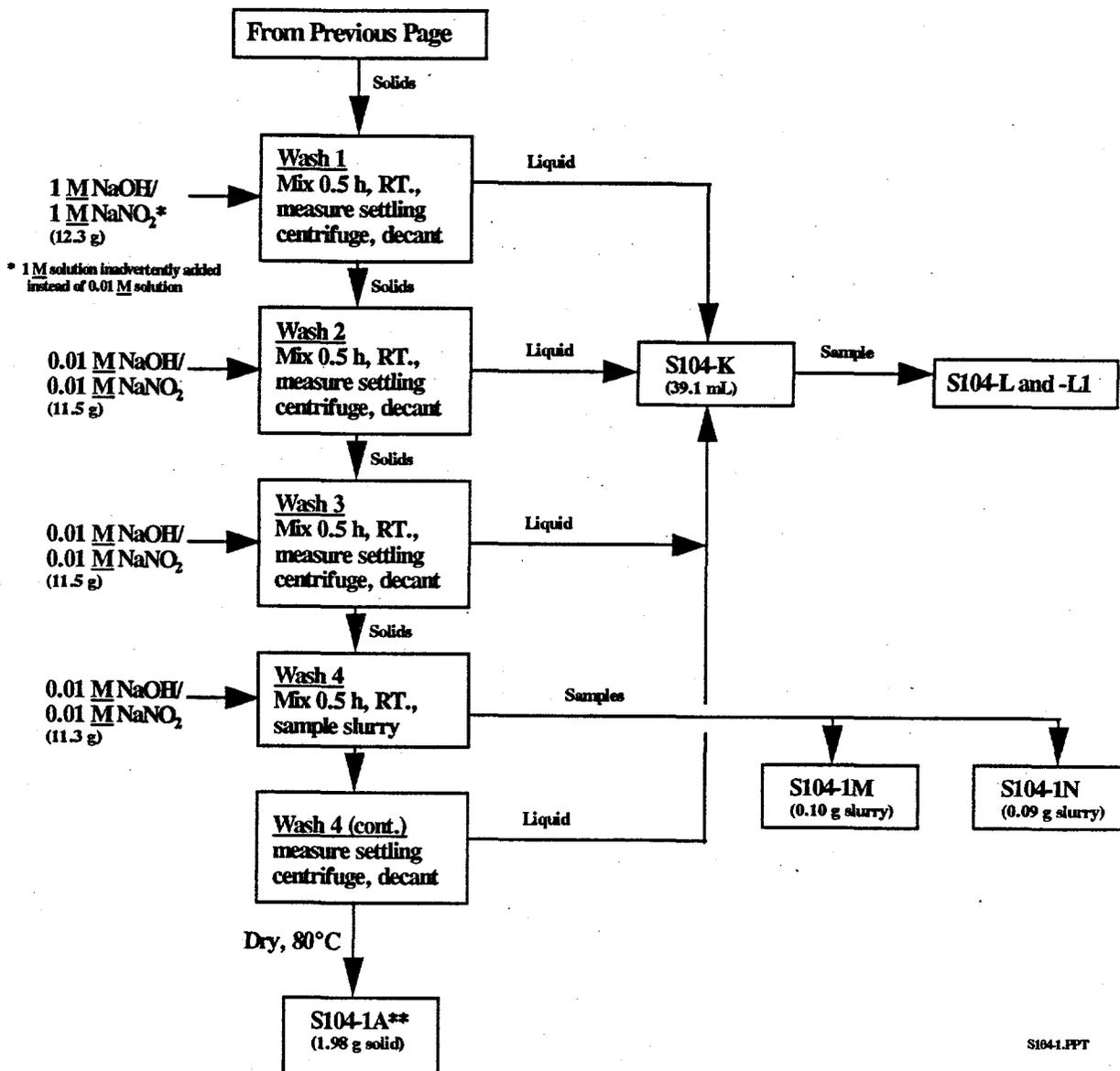


Figure D.1. Schematic of S-104 Sludge Washing and Caustic Leaching Test



S1041.PPT

Figure D.1. (contd.)

Table D.1. Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the S-104 Test

Component	Detection Limit, $\mu\text{g/mL}$	Concentration, $\mu\text{g/mL}$			
		Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Ag	0.17	0	0	0	0
Al	0.85	289	18700	13600	3060
As	1.7	0	42.5	27.2	6.8
B	0.34	0	0	0.425	0
Ba	0.17	0	0	0	0
Be	0.085	0	0	0	0
Bi	1.7	0	0	0	0
Ca	0.85	10.2	0	5.1	17.85
Cd	0.17	0	0	0	0
Ce	1.7	0	0	0	0
Co	0.17	0	0	0	0
Cr	0.34	195.5	110.5	47.6	11.9
Cu	0.17	0	0	0.85	0
Dy	0.34	0	0	0	0
Eu	0.17	0	0	0	0
Fe	0.17	0.425	17	5.61	0.85
Gd	3.4	0	0	0	0
K	25.5	0	0	0	0
La	0.51	0	0	0	0
Li	0.34	0	0	0	0
Mg	1.7	0	0	0	0
Mn	0.085	0	0	0	0
Mo	0.34	0	0	0.425	0
Na	1.7	8160	110500	85000	31450
Nd	0.51	0	0	0	0
Ni	0.51	0	0	0	0
P	1.7	0	0	0	0
Pb	0.85	0	0	0	0
Pd	2.55	0	0	0	0
Rh	1.7	0	0	0	0
Ru	1.7	0	0	0	0
Sb	0.85	0	0	0	0
Se	1.7	0	0	5.1	0
Si	0.85	0	0	0	0
Sn	17	0	0	0	0
Sr	0.085	0	0	0.17	0
Te	3.4	0	0	0	0
Th	17	0	0	0	0
Ti	0.085	0	0	0	0
Tl	8.5	0	0	25.5	0
U	0.00255	0.02618	0.80495	0.7004	0.2431
V	0.17	0	0	0	0
W	1.7	0	0	0	0
Y	0.17	0	0	0	0
Zn	0.34	4.25	4.25	2.55	3.4
Zr	0.17	0	0	0	0
NO ₃ ⁻	250	11700	6100	2540	580
NO ₂ ⁻	100	2600	1220	570	11200
PO ₄ ³⁻	25	0	0	0	0
SO ₄ ²⁻	25	100	0	0	0
F ⁻	12.5	0	0	0	0
Cl ⁻	12.5	190	60	30	30
Br ⁻	12.5	0	0	0	0

(a) The detection limit for the first caustic leach solution (G) was ten times the values reported in the column.

(b) Unless otherwise indicated, zero values indicate the analyte was below the detection limit.

Table D.2. Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the S-104 Test

<u>Component</u>	<u>Detection Limit, $\mu\text{g/g}$</u>	<u>Concentration, $\mu\text{g/g}$ ^(a)</u>
Ag	7	10
Al	40	330000
As	60	300
B	10	1000
Ba	7	180
Be	4	0
Bi	70	80
Ca	40	1800
Cd	7	0
Ce	60	90
Co	7	20
Cr	10	370
Cu	7	240
Dy	10	0
Eu	7	0
Fe	7	12000
Gd	100	0
K	(b)	(b)
La	20	60
Li	10	0
Mg	60	400
Mn	4	7200
Mo	10	0
Na	60	50000
Nd	20	100
Ni	(c)	(c)
P	70	0
Pb	40	0
Pd	200	0
Rh	70	0
Ru	70	0
Sb	40	0
Se	50	70
Si	40	5100
Sn	700	0
Sr	4	2200
Te	100	0
Th	600	0
Ti	4	65
Tl	400	700
U	90	35450
V	7	0
W	60	0
Y	7	20
Zn	10	100
Zr	7	160
NO ₃ ⁻	(d)	(d)
NO ₂ ⁻	(d)	(d)
PO ₄ ³⁻	25000	0
SO ₄ ²⁻	10000	0
F ⁻	25000	0
Cl ⁻	(d)	(d)
Br ⁻	25000	0

(a) Zero values indicate the analyte was below the detection limit.

(b) Potassium values are not reported since the sample was dissolved using a KOH fusion method.

(c) Nickel values are not reported because a Ni crucible was used during the KOH fusion method.

(d) Measurement impractical due to method of sample preparation.

Table D.3. Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the S-104 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Ag	0	0	0	0	100
Al	3	10	12	13	62
As	0	16	19	23	42
B	0	0	0	0	100
Ba	0	0	0	0	100
Be	(a)	(a)	(a)	(a)	(a)
Bi	0	0	0	0	100
Ca	21	0	1	15	64
Cd	(a)	(a)	(a)	(a)	(a)
Ce	0	0	0	0	100
Co	0	0	0	0	100
Cr	90	2	2	2	3
Cu	0	0	2	0	98
Dy	(a)	(a)	(a)	(a)	(a)
Eu	(a)	(a)	(a)	(a)	(a)
Fe	0	0	0	0	99
Gd	(a)	(a)	(a)	(a)	(a)
K	(b)	(b)	(b)	(b)	(b)
La	0	0	0	0	100
Li	(a)	(a)	(a)	(a)	(a)
Mg	0	0	0	0	100
Mn	0	0	0	0	100
Mo	0	0	100	0	0
Na	(c)	(c)	(c)	(c)	(c)
Nd	0	0	0	0	100
Ni	(b)	(b)	(b)	(b)	(b)
P	(a)	(a)	(a)	(a)	(a)
Pb	(a)	(a)	(a)	(a)	(a)
Pd	(a)	(a)	(a)	(a)	(a)
Rh	(a)	(a)	(a)	(a)	(a)
Ru	(a)	(a)	(a)	(a)	(a)
Sb	(a)	(a)	(a)	(a)	(a)
Se	0	0	26	0	74
Si	0	0	0	0	100
Sn	(a)	(a)	(a)	(a)	(a)
Sr	0	0	0	0	100
Te	(a)	(a)	(a)	(a)	(a)
Th	(a)	(a)	(a)	(a)	(a)
Ti	0	0	0	0	100
Tl	0	0	15	0	85
U	0	0	0	0	100
V	(a)	(a)	(a)	(a)	(a)
W	(a)	(a)	(a)	(a)	(a)
Y	0	0	0	0	100
Zn	54	3	3	18	22
Zr	0	0	0	0	100
NO ₃ ⁻	94	2	2	2	(d)
NO ₂ ⁻	36	1	1	63	(d)
PO ₄ ³⁻	(a)	(a)	(a)	(a)	(a)
SO ₄ ²⁻	100 (35) ^(e)	0	0 (1) ^(e)	0 (4) ^(e)	0 (61) ^(e)
F ⁻	(a)	(a)	(a)	(a)	(a)
Cl ⁻	91	1	1	6	(d)
Br ⁻	(a)	(a)	(a)	(a)	(a)

(a) Component was not detected.

(b) K and Ni values could not be determined due to the KOH fusion procedure used to prepare the leached sludge for analysis.

(c) Removal of Na from the sludge cannot be reliably tracked because the Na in the sludge cannot be distinguished from the Na added in the washing and leaching steps.

(d) Measurement impractical due to method of sample preparation.

(e) Values in parentheses represent the values obtained if, for cases where the component was below the detection limit, the component concentration was assumed to be the detection limit.

Table D.4. Mass Balance for Nonradioactive Sludge Components From the S-104 Test

Component	Concentration in Dried Sludge, g/g Sludge		Recovery, %
	Direct Analysis	Summation Method	
Ag	< 2.00E-05	3.30E-06	
Al	1.50E-01	1.77E-01	118
As	2.00E-04	2.34E-04	117
B	1.70E-03	3.31E-04	19
Ba	6.00E-05	5.94E-05	99
Be	< 8.00E-06		
Bi	< 2.00E-04	2.64E-05	
Ca	2.20E-03	9.35E-04	42
Cd	< 2.00E-05		
Ce	< 1.00E-04	2.97E-05	
Co	< 2.00E-05	6.60E-06	
Cr	4.70E-03	4.10E-03	87
Cu	2.10E-04	8.06E-05	38
Dy	< 3.00E-05		
Eu	< 2.00E-05		
Fe	3.40E-03	4.00E-03	118
Gd	< 3.00E-04		
K	(b)	(b)	(b)
La	< 5.00E-05	1.98E-05	
Li	< 3.00E-05		
Mg	2.00E-04	1.32E-04	66
Mn	2.20E-03	2.38E-03	108
Mo	< 3.00E-05	6.84E-07	
Na	2.00E-01		
Nd	< 5.00E-05	3.30E-05	
Ni	(b)	(b)	(b)
P	< 2.00E-04		
Pb	< 1.00E-04		
Pd	< 4.00E-04		
Rh	< 2.00E-04		
Ru	< 2.00E-04		
Sb	< 8.00E-05		
Se	< 1.00E-04	3.13E-05	
Si	6.80E-03	1.68E-03	25
Sn	< 2.00E-03		
Sr	6.10E-04	7.27E-04	119
Te	< 3.00E-04		
Th	< 1.00E-03		
Ti	3.00E-06	2.15E-05	715
Tl	< 8.00E-04	2.72E-04	
U	1.01E-02	1.17E-02	116
V	< 2.00E-05		
W	< 1.00E-04		
Y	< 2.00E-05	6.60E-06	
Zn	1.00E-04	1.48E-04	148
Zr	< 2.00E-05	5.28E-05	
NO ₃ ⁻	(c)	2.36E-01	(c)
NO ₂ ⁻	(c)	1.39E-01	(c)
PO ₄ ³⁻	< 3.96E-02		
SO ₄ ²⁻	2.00E-02	1.90E-03	9
F ⁻	< 3.96E-02		
Cl ⁻	(c)	3.94E-03	
Br ⁻			

- (a) Blank spaces indicate that the analyte was below the detection limit.
 (b) K and Ni values could not be determined due the KOH fusion method used to prepare the solids for analysis.
 (c) Measurement impractical due to method of sample preparation.

Table D.5. Concentrations of the Radioactive Sludge Components in the Various Process Streams From the S-104 Test

Component	Concentration, $\mu\text{Ci/mL}$			
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Total Alpha	< 1.7E-05	< 1.7E-05	< 2.55E-05	< 2.55E-05
$^{239,240}\text{Pu}$	ND ^(a)	ND	ND	ND
$^{241}\text{Am} + ^{238}\text{Pu}$	ND	ND	ND	ND
$^{241}\text{Am}(\gamma)$	< 2.00E-04	< 2.00E-04	< 9.00E-05	< 4.00E-05
^{137}Cs	4.16E+00	2.91E+00	1.23E+00	2.82E-01
^{90}Sr	2.13E-03	4.51E-02	9.35E-02	2.64E-02
^{99}Tc	1.59E-03	7.48E-04	3.13E-04	7.17E-05

Component	Concentration, $\mu\text{Ci/g}$
	Residue
Total Alpha	2.72E+00
$^{239,240}\text{Pu}$	2.02E+00
$^{241}\text{Am} + ^{238}\text{Pu}$	7.00E-01
$^{241}\text{Am}(\gamma)$	7.29E-01
^{137}Cs	6.01E+00
^{90}Sr	1.63E+03
^{99}Tc	< 5.00E-04

(a) ND = Not Determined. The low total alpha activity made these separations impractical.

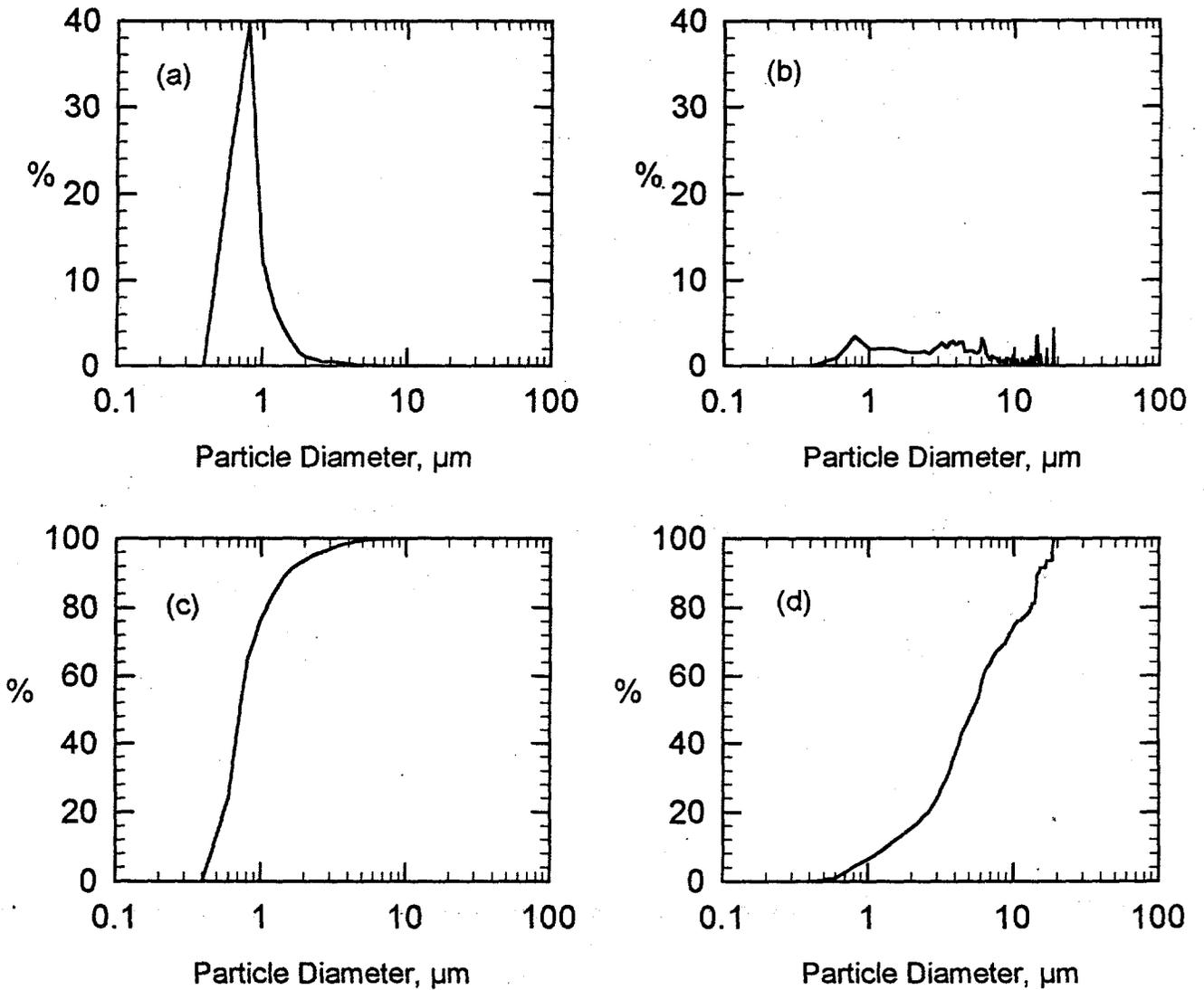
Table D.6. Distribution of the Radioactive Sludge Components Between the Various Process Streams From the S-104 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Total Alpha	0	0	0	0	100
^{239,240} Pu	(a)	(a)	(a)	(a)	100
²⁴¹ Am + ²³⁸ Pu	(a)	(a)	(a)	(a)	100
²⁴¹ Am(γ)	0	0	0	0	100
¹³⁷ Cs	90	3	2	3	2
⁹⁰ Sr	0	0	0	0	100
⁹⁹ Tc	95	2	2	2	0

(a) Not determined due to a lack of total alpha activity in the components

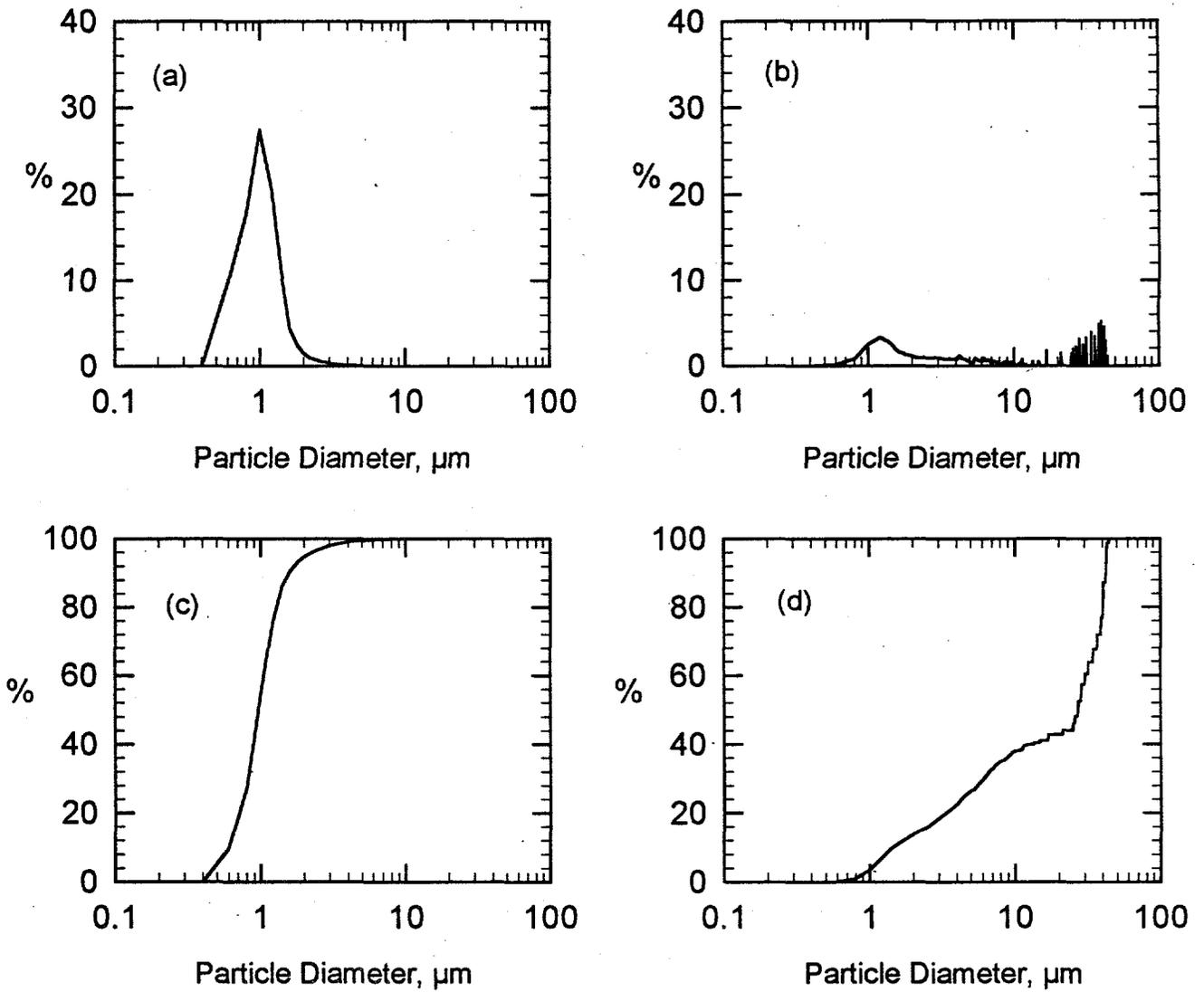
Table D.7. Mass Balance for Radioactive Sludge Components From the S-104 Test

Component	Concentration in Dried Sludge, μCi/g		Recovery, %
	Direct Analysis	Summation Method	
Total Alpha	7.29E-01	8.96E-01	123
^{239,240} Pu	5.45E-01	6.65E-01	122
²⁴¹ Am + ²³⁸ Pu	1.84E-01	2.31E-01	126
²⁴¹ Am(γ)	2.49E-01	2.41E-01	97
¹³⁷ Cs	9.16E+01	8.77E+01	96
⁹⁰ Sr	4.91E+02	5.39E+02	110
⁹⁹ Tc	2.70E-02	3.19E-02	118



S104-C02.SPW

Figure D.2. Particle-Size Data for Untreated S-104 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.



S104-M01.SPW

Figure D.3. Particle-Size Data for Treated S-104 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.

Appendix E

Results from the Tank SY-103 Sludge Washing and Caustic Leaching Test

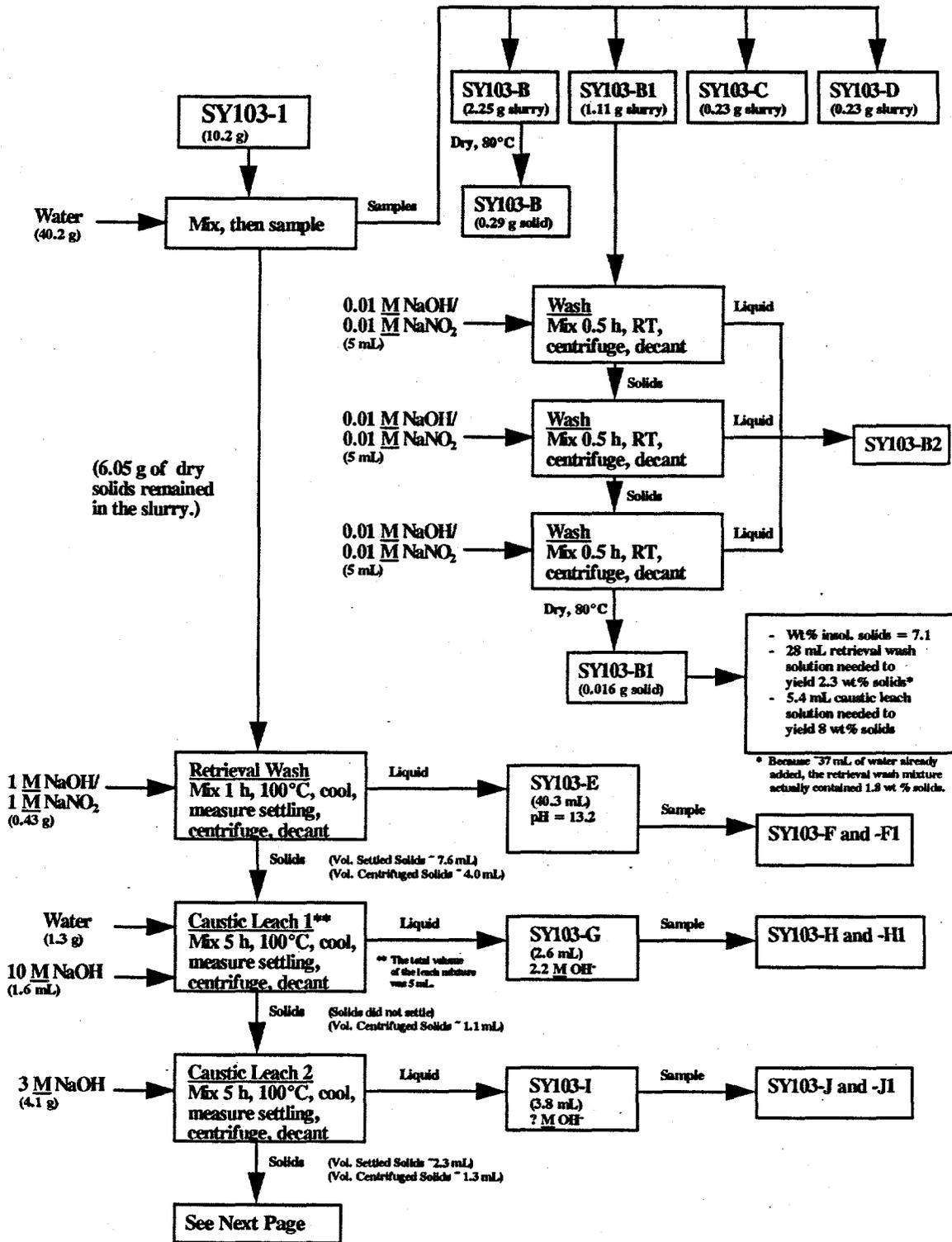


Figure E.1. Schematic of SY-103 Sludge Washing and Caustic Leaching Test

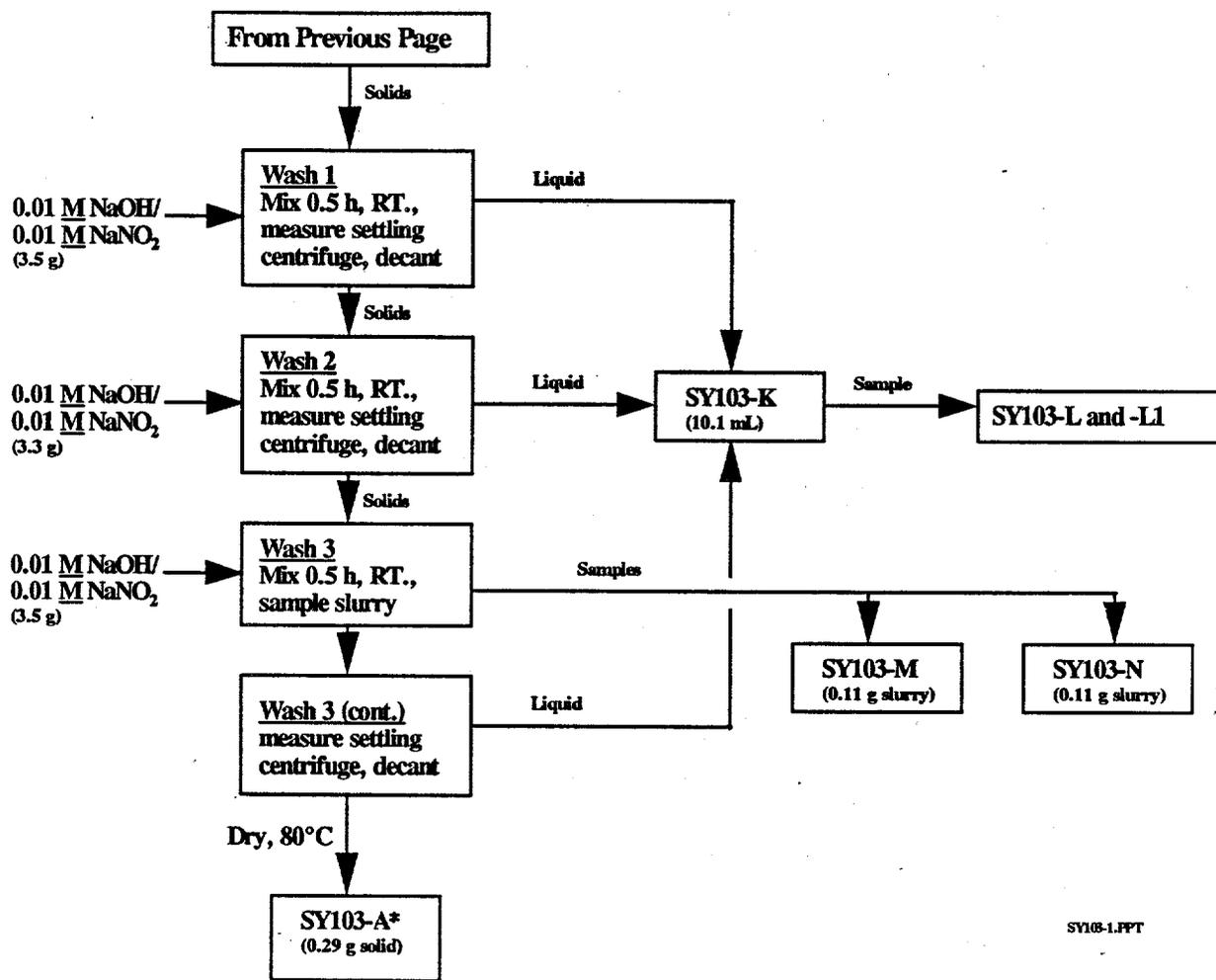


Figure E.1. (contd.)

Table E.1. Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the SY-103 Test

Component	Detection Limit, $\mu\text{g/mL}$	Concentration, $\mu\text{g/mL}$ ^(a)			
		Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Ag	0.17	0	0	0	0
Al	0.85	518.5	43350	15300	1615
As	0.34	3.4	0	15.3	0
B	0.34	11.05	76.5	1.7	0
Ba	0.17	0	25.5	0	0
Be	0.085	0	0	0	0
Bi	1.7	0	0	0	0
Ca	0.85	10.2	1683	5.1	3.4
Cd	0.17	0.255	0	0	0
Ce	1.7	0	0	0	0
Co	0.17	0	1249.5	0	0
Cr	0.34	85	739.5	646	136
Cu	0.17	0	0	0	0
Dy	0.34	0	0	0	0
Eu	0.17	0	0	0	0
Fe	0.17	0.85	2805	0.85	0.34
Gd	3.4	0	0	0	0
K	25.5	459	0	34	0
La	0.51	0	0	0	0
Li	0.34	0	0	0.51	0
Mg	1.7	0	0	0	0
Mn	0.085	0	0	0	0
Mo	0.34	16.15	0	0	0
Na	1.7	42500	163200	82450	9350
Nd	0.51	0	0	0	0
Ni	0.51	5.78	459	0	0
P	1.7	161.5	510	153	20.4
Pb	0.85	0	0	0	0
Pd	2.55	0	0	0	0
Rh	1.7	0	0	0	0
Ru	1.7	2.55	0	0	0
Sb	0.85	0	0	0	0
Se	1.7	0	0	2.55	0
Si	0.85	7.65	5355	0	0
Sn	17	0	0	0	0
Sr	0.085	0	0	0	0
Te	3.4	0	0	0	0
Th	17	0	0	0	0
Ti	0.085	0	0	0	0
Tl	8.5	0	0	25.5	0
U	0.00425	5.321	13.94085	17.935	2.9665
V	0.17	0.34	0	0.51	0
W	1.7	26.35	0	5.95	0
Y	0.17	0	0	0	0
Zn	0.34	0	127.5	0.85	0.425
Zr	0.17	0	0	0.51	0
NO ₃ ⁻	500	22200	130	1910	170
NO ₂ ⁻	500	13700	90	1200	350
PO ₄ ³⁻	20	1750	0	290	0
SO ₄ ²⁻	50	1240	0	110	0
F ⁻	(b)	(b)	(b)	(b)	(b)
Cl ⁻	250	1100	(b)	(b)	(b)
Br ⁻	250	0	0	0	0

(a) Unless otherwise indicated, zero values indicate the analyte was below the detection limit.

(b) Analyte could not be determined due to analytical difficulties.

(c) The detection limit was 50 $\mu\text{g/mL}$ for nitrate, nitrite, phosphate, and sulfate for the leach and final wash steps; the detection limit for bromide was 25 $\mu\text{g/mL}$ for the leach and wash steps.

Table E.2. Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the SY-103 Test

<u>Component</u>	<u>Detection Limit, $\mu\text{g/g}$</u>	<u>Concentration, $\mu\text{g/g}$ ^(a)</u>
Ag	20	200
Al	100	83000
As	200	500
B	50	2300
Ba	20	260
Be	10	0
Bi	200	2300
Ca	100	5100
Cd	20	580
Ce	60	1000
Co	20	30
Cr	200	220000
Cu	20	470
Dy	50	0
Eu	20	0
Fe	20	75000
Gd	500	0
K	(b)	(b)
La	70	1400
Li	50	200
Mg	200	1000
Mn	10	23000
Mo	50	0
Na	200	41000
Nd	70	2200
Ni	(c)	(c)
P	200	700
Pb	100	7400
Pd	300	2000
Rh	200	0
Ru	200	0
Sb	100	0
Se	200	300
Si	100	12000
Sn	2000	0
Sr	10	100
Te	500	0
Th	2000	0
Ti	10	170
Tl	1000	0
U	0.0005	31800
V	20	60
W	200	700
Y	20	300
Zn	50	860
Zr	20	1900
NO ₃ ⁻	(d)	(d)
NO ₂ ⁻	(d)	(d)
PO ₄ ³⁻	(d)	(d)
SO ₄ ²⁻	(d)	(d)
F ⁻	(d)	(d)
Cl ⁻	(d)	(d)
Br ⁻	(d)	(d)

- (a) Zero values indicate the analyte was below the detection limit.
 (b) Potassium values are not reported since the sample was dissolved using a KOH fusion method.
 (c) Nickel values are not reported because a Ni crucible was used during the KOH fusion method.
 (d) Due to matrix effects, analyte could not be determined accurately.

Table E.3. Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the SY-103 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Ag	0	0	0	0	100
Al	9	48	25	7	10
As	40	0	17	0	43
B	34	15	0	0	51
Ba	0	46	0	0	54
Be	(a)	(a)	(a)	(a)	(a)
Bi	0	0	0	0	100
Ca	6	69	0	1	24
Cd	6	0	0	0	94
Ce	0	0	0	0	100
Co	0	100	0	0	0
Cr	5	3	3	2	88
Cu	0	0	0	0	100
Dy	(a)	(a)	(a)	(a)	(a)
Eu	(a)	(a)	(a)	(a)	(a)
Fe	0	25	0	0	75
Gd	(a)	(a)	(a)	(a)	(a)
K	(b)	(b)	(b)	(b)	(b)
La	0	0	0	0	100
Li	0	0	3	0	97
Mg	0	0	0	0	100
Mn	0	0	0	0	100
Mo	100	0	0	0	0
Na	(c)	(c)	(c)	(c)	(c)
Nd	0	0	0	0	100
Ni	(b)	(b)	(b)	(b)	(b)
P	74	15	7	2	2
Pb	0	0	0	0	100
Pd	0	0	0	0	100
Rh	(a)	(a)	(a)	(a)	(a)
Ru	100	0	0	0	0
Sb	(a)	(a)	(a)	(a)	(a)
Se	0	0	10	0	90
Si	2	78	0	0	20
Sn	(a)	(a)	(a)	(a)	(a)
Sr	0	0	0	0	100
Te	(a)	(a)	(a)	(a)	(a)
Th	(a)	(a)	(a)	(a)	(a)
Ti	0	0	0	0	100
Tl	0	0	100	0	0
U	2	0	1	0	96
V	41	0	6	0	53
W	82	0	2	0	16
Y	0	0	0	0	100
Zn	0	56	1	1	43
Zr	0	0	0	0	100
NO ₃ ⁻	(d)	(d)	(d)	(d)	(d)
NO ₂ ⁻	(d)	(d)	(d)	(d)	(d)
PO ₄ ³⁻	(d)	(d)	(d)	(d)	(d)
SO ₄ ²⁻	(d)	(d)	(d)	(d)	(d)
F ⁻	(d)	(d)	(d)	(d)	(d)
Cl ⁻	(d)	(d)	(d)	(d)	(d)
Br ⁻	(d)	(d)	(d)	(d)	(d)

(a) Component was not detected.

(b) K and Ni values could not be determined due to the KOH fusion procedure used to prepare the leached sludge for analysis.

(c) Removal of Na from the sludge cannot be reliably tracked because the Na in the sludge cannot be distinguished from the Na added in the washing and leaching steps.

(d) Due to matrix effects, analyte could not be determined accurately.

Table E.4. Mass Balance for Nonradioactive Sludge Components From the SY-103 Test

Component	Concentration in Dried Sludge, g/g Sludge		Recovery, %
	Direct Analysis	Summation Method	
Ag	1.00E-05	9.72E-06	97
Al	4.70E-02	3.84E-02	82
As	1.00E-04	5.65E-05	57
B	1.00E-03	2.19E-04	22
Ba	2.00E-05	2.36E-05	118
Be	< 3.00E-06		
Bi	2.00E-04	1.12E-04	56
Ca	4.00E-04	1.05E-03	262
Cd	4.00E-05	2.99E-05	75
Ce	< 6.00E-05	4.86E-05	
Co	< 7.00E-06	5.38E-04	
Cr	1.30E-02	1.22E-02	94
Cu	4.00E-05	2.28E-05	57
Dy	< 1.00E-05		
Eu	< 7.00E-06		
Fe	4.10E-03	4.86E-03	118
Gd	< 1.00E-04		
K	(b)	(b)	(b)
La	6.00E-05	6.80E-05	113
Li	< 1.00E-05	1.00E-05	
Mg	8.00E-05	4.86E-05	61
Mn	1.40E-03	1.12E-03	80
Mo	9.00E-05	1.08E-04	120
Na	2.80E-01		
Nd	1.00E-04	1.07E-04	107
Ni	(b)	(b)	(b)
P	7.80E-03	1.46E-03	19
Pb	4.30E-04	3.60E-04	84
Pd	< 1.00E-04	9.72E-05	
Rh	< 7.00E-05		
Ru	< 7.00E-05	1.70E-05	
Sb	< 3.00E-05		
Se	< 5.00E-05	1.62E-05	
Si	2.00E-03	2.93E-03	147
Sa	< 7.00E-04		
Sr	8.00E-06	4.86E-06	61
Te	< 1.00E-04		
Th	< 6.00E-04		
Ti	1.00E-05	8.26E-06	83
Tl	< 3.00E-04	1.60E-05	
U	1.61E-03	1.60E-03	100
V	9.00E-06	5.50E-06	61
W	2.00E-04	2.13E-04	107
Y	2.00E-05	1.46E-05	73
Zn	7.00E-05	9.78E-05	140
Zr	1.00E-04	9.26E-05	93
NO ₃ ⁻	(c)	(c)	(c)
NO ₂ ⁻	(c)	(c)	(c)
PO ₄ ³⁻	(c)	(c)	(c)
SO ₄ ²⁻	(c)	(c)	(c)
F ⁻	(c)	(c)	(c)
Cl ⁻	(c)	(c)	(c)
Br ⁻	(c)	(c)	(c)

(a) Blank spaces indicate that the analyte was below the detection limit.

(b) K and Ni values could not be determined due to the KOH fusion method used to prepare the samples for analysis.

(c) Due to matrix effects, analyte could not be determined accurately.

Table E.5. Concentrations of the Radioactive Sludge Components in the Various Process Streams From the SY-103 Test

Component	Concentration, $\mu\text{Ci/mL}$			
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Total Alpha	1.78E-03	5.59E-04	1.79E-04	2.83E-05
^{239,240} Pu	1.33E-03	5.59E-04	6.94E-05	1.32E-05
²⁴¹ Am + ²³⁸ Pu	4.45E-04	< 3.57E-04	1.09E-04	1.51E-05
²⁴¹ Am(γ)	< 1.70E-02	< 1.25E-02	< 1.70E-03	< 5.10E-04
¹³⁷ Cs	5.73E+01	1.55E+01	5.33E+00	5.73E-01
⁹⁰ Sr	4.35E-01	1.67E-02	2.36E-02	3.30E-03
⁹⁹ Tc	1.72E-02	6.41E-03	5.26E-03	9.69E-04

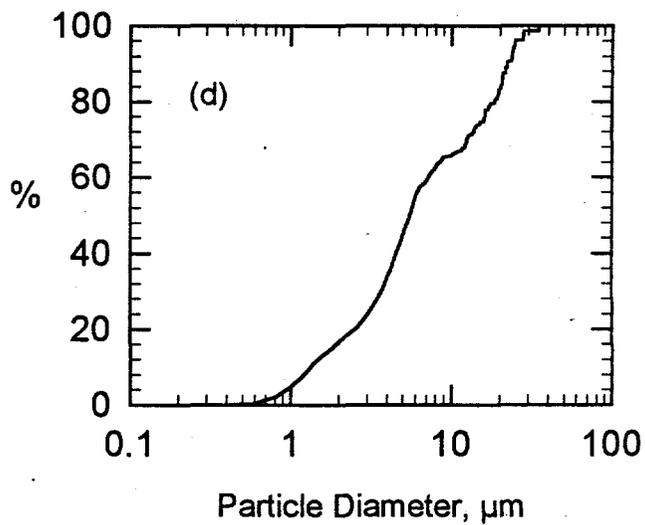
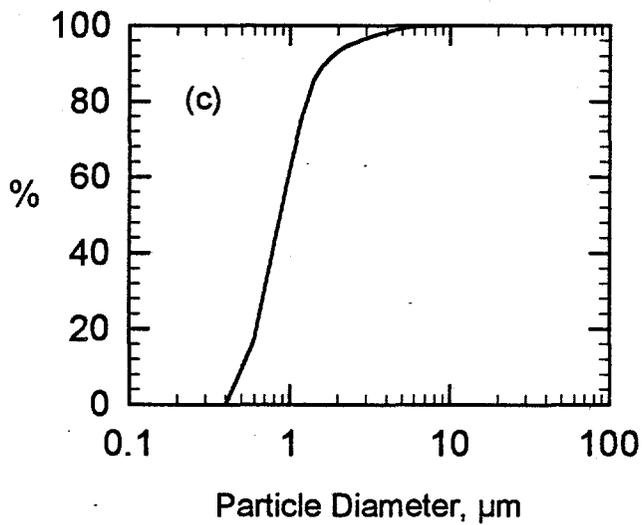
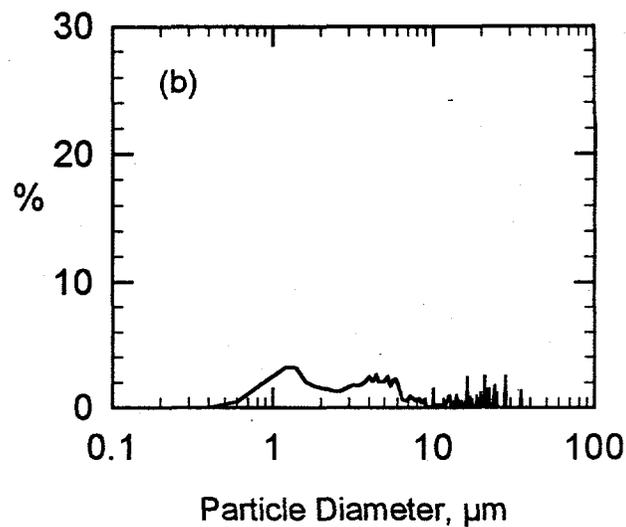
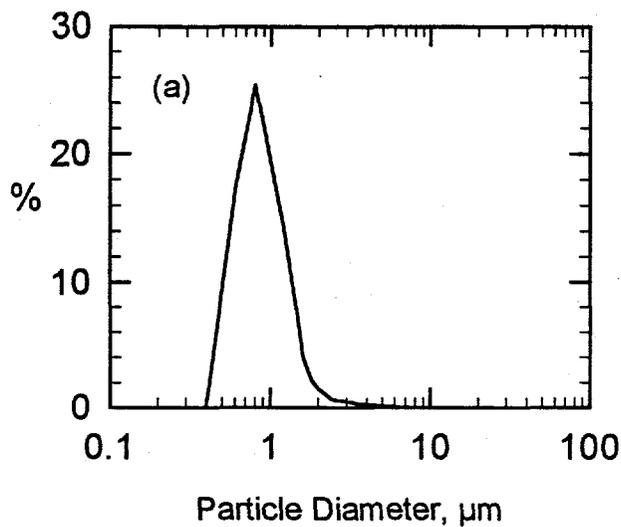
Component	Concentration, $\mu\text{Ci/g}$
	Residue
Total Alpha	2.75E+01
^{239,240} Pu	< 3.00E-01
²⁴¹ Am + ²³⁸ Pu	2.75E+01
²⁴¹ Am(γ)	2.49E+01
¹³⁷ Cs	1.91E+01
⁹⁰ Sr	1.48E+03
⁹⁹ Tc	4.42E-01

Table E.6. Distribution of the Radioactive Sludge Components Between the Various Process Streams From the SY-103 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Total Alpha	1	0	0	0	99
^{239,240} Pu	97	3	0	0	0
²⁴¹ Am + ²³⁸ Pu	0	0	0	0	100
²⁴¹ Am(γ)	0	0	0	0	100
¹³⁷ Cs	97	2	1	0	0
⁹⁰ Sr	4	0	0	0	96
⁹⁹ Tc	80	2	2	1	15

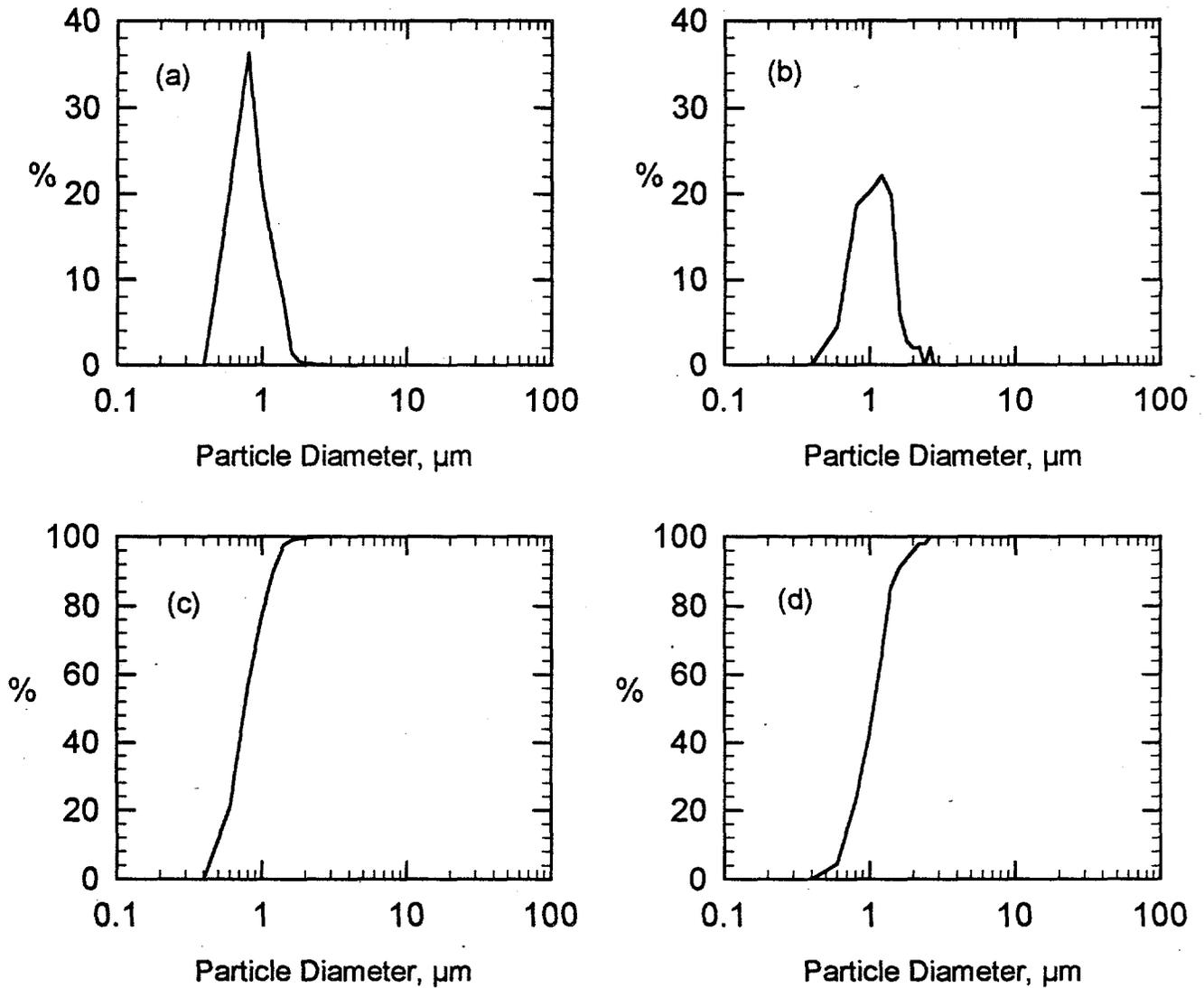
Table E.7. Mass Balance for Radioactive Sludge Components From the SY-103 Test

Component	Concentration in Dried Sludge, $\mu\text{Ci/g}$		Recovery, %
	Direct Analysis	Summation Method	
Total Alpha	1.47E+00	1.35E+00	92
^{239,240} Pu	< 4.00E-03	9.19E-03	
²⁴¹ Am + ²³⁸ Pu	1.47E+00	1.34E+00	91
²⁴¹ Am(γ)	1.31E+00	1.21E+00	92
¹³⁷ Cs	3.61E+02	3.93E+02	109
⁹⁰ Sr	8.30E+01	7.48E+01	90
⁹⁹ Tc	3.53E-01	1.44E-01	41



SY103-C.SPW

Figure E.2. Particle Size-Data for Untreated SY-103 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.



SY103-M.SP.W

Figure E.3. Particle-Size Data for Treated SY-103 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.

Appendix F

Results from the Tank T-104 Sludge Washing and Caustic Leaching Test

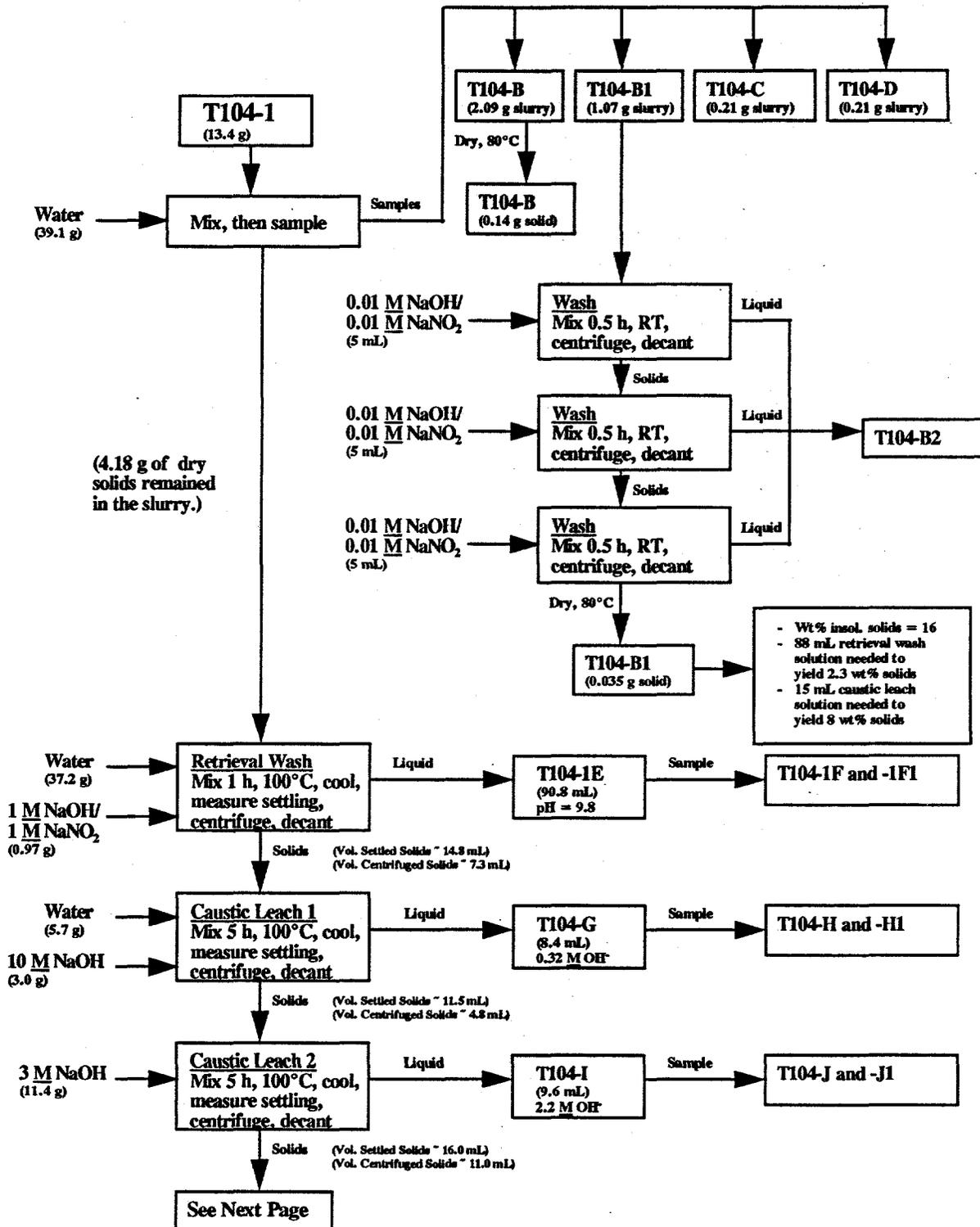
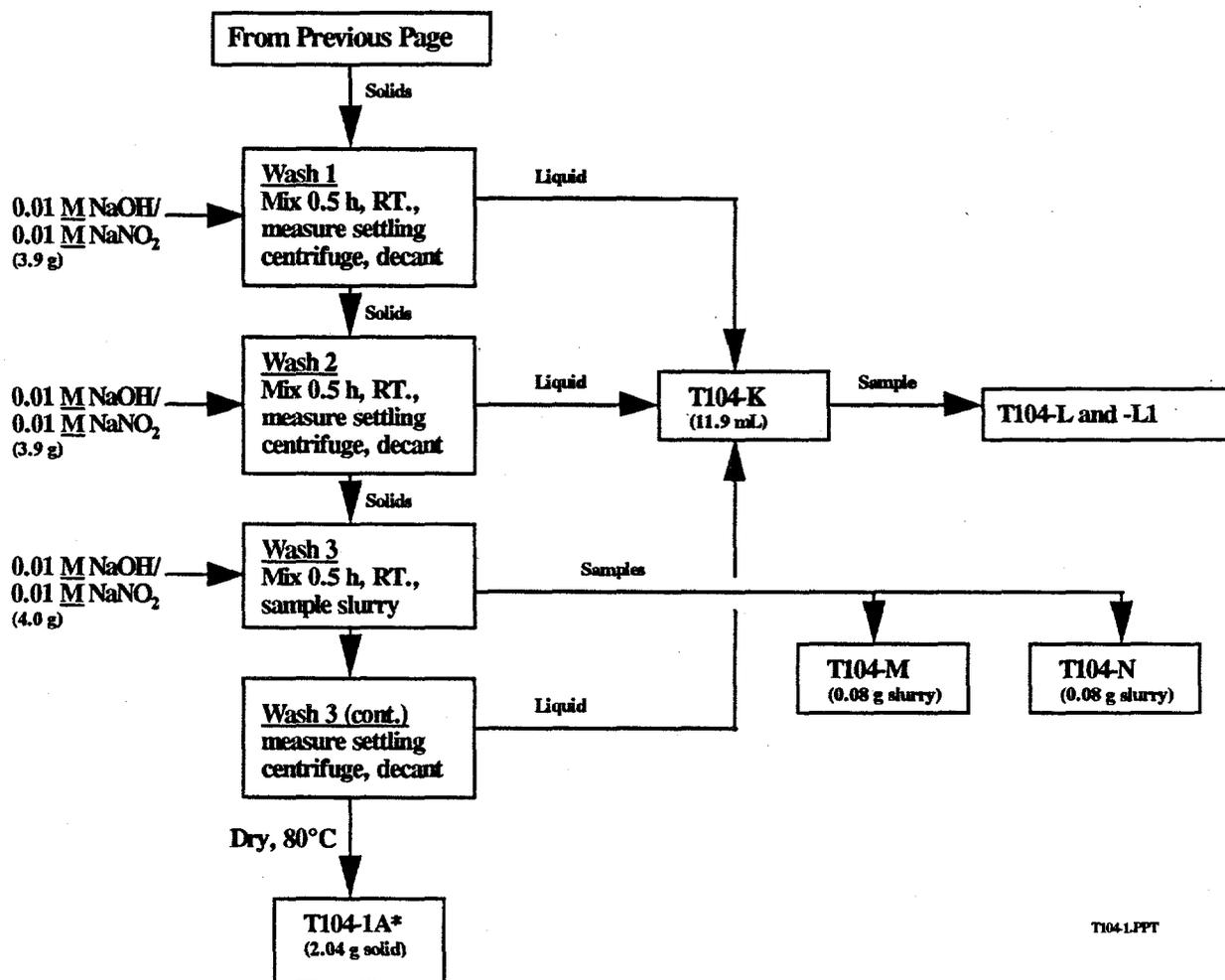


Figure F.1. Schematic of T-104 Sludge Washing and Caustic Leaching Test



T104-LPPT

Figure 2.6. (contd.)

Table F.1. Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the T-104 Test

Component	Detection Limit, $\mu\text{g/mL}$	Concentration, $\mu\text{g/mL}$ ^(a)			
		Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Ag	0.17	0	0	0	0
Al	0.85	24.65	5015	4845	1615
As	1.7	0	8.5	8.5	3.4
B	0.34	0.425	0.765	0	0
Ba	0.17	0	0	0	0
Be	0.085	0	0	0	0
Bi	1.7	0	2.55	18.7	5.95
Ca	0.85	12.75	5.95	5.1	7.65
Cd	0.17	0	0	0	0
Ce	1.7	0	0	0	0
Co	0.17	0	0	0	0
Cr	0.34	24.65	56.1	47.6	23.8
Cu	0.17	0	0	0	0
Dy	0.34	0	0	0	0
Eu	0.17	0	0	0	0
Fe	0.17	0.85	0.51	2.38	0.68
Gd	3.4	0	0	0	0
K	25.5	0	0	0	0
La	0.51	0	0	0	0
Li	0.34	0	0	0	0
Mg	1.7	0	0	0	0
Mn	0.085	0	0	0	0
Mo	0.34	0	0	0	0
Na	1.7	6205	24650	52700	34850
Nd	0.51	0	0	0	0
Ni	0.51	5.865	0	0	2.55
P	1.7	833	2975	850	4080
Pb	0.85	0	0	0	0
Pd	2.55	0	0	0	0
Rh	1.7	0	0	0	0
Ru	1.7	0	0	0	0
Sb	0.85	0	0	0	0
Se	1.7	0	0	0	0
Si	0.85	0	0	45.05	22.95
Sn	17	0	0	0	0
Sr	0.085	0	0	0	0
Te	3.4	0	0	0	0
Th	17	0	0	0	0
Ti	0.085	0	0	0	0
Tl	8.5	0	0	0	0
U	0.00255	1.258	18.19	96.05	28.9
V	0.17	0	0	0	0
W	1.7	0	0	0	0
Y	0.17	0	0	0	0
Zn	0.34	5.865	0.51	3.485	3.485
Zr	0.17	0	0	0.34	0
NO ₃	250	8400	4100	1000	260
NO ₂	100	1100	500	140	8800
PO ₄ ³⁻	100	2600	9000	3100	12400
SO ₄ ²⁻	100	500	500	100	30
F	50	630	3000	80	1480
Cl	50	120	120	< 25	15
Br	50	< 50	< 50	< 25	< 25

(a) Unless otherwise indicated, zero values indicate the analyte was below the detection limit.

Table F.2. Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the T-104 Test

<u>Component</u>	<u>Detection Limit, $\mu\text{g/g}$</u>	<u>Concentration, $\mu\text{g/g}$ ^(a)</u>
Ag	10	0
Al	60	33000
As	80	90
B	20	1100
Ba	10	70
Be	5	0
Bi	100	110000
Ca	50	1800
Cd	10	0
Ce	80	1400
Co	10	30
Cr	20	4600
Cu	10	460
Dy	20	0
Eu	10	0
Fe	10	59000
Gd	200	0
K	(b)	(b)
La	20	0
Li	20	0
Mg	80	500
Mn	5	440
Mo	20	0
Na	80	230000
Nd	30	0
Ni	(c)	(c)
P	100	62000
Pb	60	300
Pd	300	0
Rh	100	0
Ru	100	0
Sb	50	0
Se	80	100
Si	50	38000
Sn	1000	0
Sr	5	670
Te	200	0
Th	800	0
Ti	5	94
Tl	500	0
U	343	7470
V	10	0
W	80	0
Y	10	0
Zn	20	270
Zr	10	250
NO ₃	(d)	(d)
NO ₂	(d)	(d)
PO ₄ ³⁻	20800	30000
SO ₄ ²⁻	8330	0
F	20800	0
Cl	(d)	(d)
Br	20800	0

- (a) Zero values indicate the analyte was below the detection limit.
- (b) Potassium values are not reported since the sample was dissolved using a KOH fusion method.
- (c) Nickel values are not reported because a Ni crucible was used during the KOH fusion method.
- (d) Measurement impractical due to sample preparation method.

Table F.3. Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the T-104 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Ag	(a)	(a)	(a)	(a)	(a)
Al	1	24	26	11	38
As	0	19	21	11	49
B	2	0	0	0	98
Ba	0	0	0	0	100
Be	(a)	(a)	(a)	(a)	(a)
Bi	0	0	0	0	100
Ca	23	1	1	2	73
Cd	(a)	(a)	(a)	(a)	(a)
Ce	0	0	0	0	100
Co	0	0	0	0	100
Cr	17	4	4	2	73
Cu	0	0	0	0	100
Dy	(a)	(a)	(a)	(a)	(a)
Eu	(a)	(a)	(a)	(a)	(a)
Fe	0	0	0	0	100
Gd	(a)	(a)	(a)	(a)	(a)
K	(b)	(b)	(b)	(b)	(b)
La	(a)	(a)	(a)	(a)	(a)
Li	(a)	(a)	(a)	(a)	(a)
Mg	0	0	0	0	100
Mn	0	0	0	0	100
Mo	(a)	(a)	(a)	(a)	(a)
Na	(c)	(c)	(c)	(c)	(c)
Nd	(a)	(a)	(a)	(a)	(a)
Ni	(b)	(b)	(b)	(b)	(b)
P	26	9	3	17	45
Pb	0	0	0	0	100
Pd	(a)	(a)	(a)	(a)	(a)
Rh	(a)	(a)	(a)	(a)	(a)
Ru	(a)	(a)	(a)	(a)	(a)
Sb	(a)	(a)	(a)	(a)	(a)
Se	0	0	0	0	100
Si	0	0	1	0	99
Sn	(a)	(a)	(a)	(a)	(a)
Sr	0	0	0	0	100
Te	(a)	(a)	(a)	(a)	(a)
Th	(a)	(a)	(a)	(a)	(a)
Ti	0	0	0	0	100
Tl	(a)	(a)	(a)	(a)	(a)
U	1	1	5	2	91
V	(a)	(a)	(a)	(a)	(a)
W	(a)	(a)	(a)	(a)	(a)
Y	(a)	(a)	(a)	(a)	(a)
Zn	46	0	3	4	48
Zr	0	0	1	0	99
NO ₃ ⁻	(d)	(d)	(d)	(d)	(d)
NO ₂ ⁻	(d)	(d)	(d)	(d)	(d)
PO ₄ ³⁻	43	14	5	27	11
SO ₄ ²⁻	89 (67) ^(e)	8 (6) ^(e)	2 (1) ^(e)	1	0 (25) ^(e)
F ⁻	57 (40) ^(e)	25 (17) ^(e)	1	18 (12) ^(e)	0 (30) ^(e)
Cl ⁻	(d)	(d)	(d)	(d)	(d)
Br ⁻	(a)	(a)	(a)	(a)	(a)

(a) Component was not detected.

(b) K and Ni values could not be determined due to the KOH fusion procedure used to prepare the leached solid for analysis.

(c) Removal of Na from the sludge cannot be reliably tracked because the Na in the sludge cannot be distinguished from the Na added in the washing and leaching steps.

(d) Measurement impractical due to sample preparation method.

(e) Values in parentheses represent the values obtained if, for cases where the component was below the detection limit, the component concentration was assumed to be the detection limit.

Table F.4. Mass Balance for Nonradioactive Sludge Components From the T-104 Test

Component	Concentration in Dried Sludge, g/g Sludge		Recovery, %
	Direct Analysis	Summation Method	
Ag	< 2.00E-05		
Al	4.70E-02	4.29E-02	91
As	< 1.00E-04	9.12E-05	
B	2.20E-03	5.58E-04	25
Ba	< 2.00E-05	3.48E-05	
Be	< 8.00E-06		
Bi	5.20E-02	5.48E-02	105
Ca	1.30E-03	1.22E-03	94
Cd	< 2.00E-05		
Ce	4.00E-04	6.96E-04	174
Co	3.00E-05	1.49E-05	50
Cr	3.10E-03	3.12E-03	101
Cu	7.00E-05	2.29E-04	327
Dy	< 3.00E-05		
Eu	< 2.00E-05		
Fe	2.80E-02	2.94E-02	105
Gd	< 3.00E-04		
K	(b)	(b)	(b)
La	< 5.00E-05		
Li	< 3.00E-05		
Mg	3.00E-04	2.49E-04	83
Mn	3.60E-04	2.19E-04	61
Mo	< 3.00E-05		
Na	1.90E-01		
Nd	< 5.00E-05		
Ni	(b)	(b)	(b)
P	6.90E-02	6.87E-02	100
Pb	2.00E-04	1.49E-04	75
Pd	< 4.00E-04		
Rh	< 2.00E-04		
Ru	< 2.00E-04		
Sb	< 8.00E-05		
Se	< 1.00E-04	4.97E-05	
Si	2.30E-02	1.91E-02	83
Sn	< 2.00E-03		
Sr	3.30E-04	3.33E-04	101
Te	< 3.00E-04		
Th	< 1.00E-03		
Ti	4.00E-05	4.67E-05	117
Tl	< 8.00E-04		
U	2.60E-03	4.08E-03	157
V	< 2.00E-05		
W	< 1.00E-04		
Y	< 2.00E-05		
Zn	1.00E-04	2.81E-04	281
Zr	2.40E-04	1.25E-04	52
NO ₃ ⁻	(c)	(c)	(c)
NO ₂ ⁻	(c)	(c)	(c)
PO ₄ ³⁻	2.40E-01	1.33E-01	55
SO ₄ ²⁻	3.00E-02	1.22E-02	41
F ⁻	< 3.9E-02	2.42E-02	
Cl ⁻	(c)	2.91E-03	
Br ⁻	< 3.9E-02		

- (a) Blank spaces indicate the analyte was below the detection limit.
 (b) K and Ni values could not be determined due to the KOH fusion used to prepare the solids for analysis.
 (c) Measurement impractical due to sample preparation method.

Table F.5. Concentrations of the Radioactive Sludge Components in the Various Process Streams From the T-104 Test

Component	Concentration, $\mu\text{Ci/mL}$			
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Total Alpha	< 2.55E-05	< 1.70E-05	3.49E-05	< 2.55E-05
^{239,240} Pu	ND ^(a)	ND	ND	ND
²⁴¹ Am + ²³⁸ Pu	ND	ND	ND	ND
²⁴¹ Am(γ)	< 2.00E-05	< 3.00E-05	< 3.00E-05	< 2.00E-05
¹³⁷ Cs	1.07E-04	7.55E-02	8.07E-02	3.03E-02
⁹⁰ Sr	< 4.25E-04	9.54E-02	8.46E-04	1.11E-03
⁹⁹ Tc	< 7.65E-06	< 7.65E-06	< 7.65E-06	< 7.65E-06

Component	Concentration, $\mu\text{Ci/g}$
	Residue
Total Alpha	1.28E+00
^{239,240} Pu	1.09E+00
²⁴¹ Am + ²³⁸ Pu	1.85E-01
²⁴¹ Am(γ)	1.79E-01
¹³⁷ Cs	3.80E-01
⁹⁰ Sr	2.56E+01
⁹⁹ Tc	7.42E-04

(a) ND = Not Determined. The low alpha total alpha activity made these separations impractical.

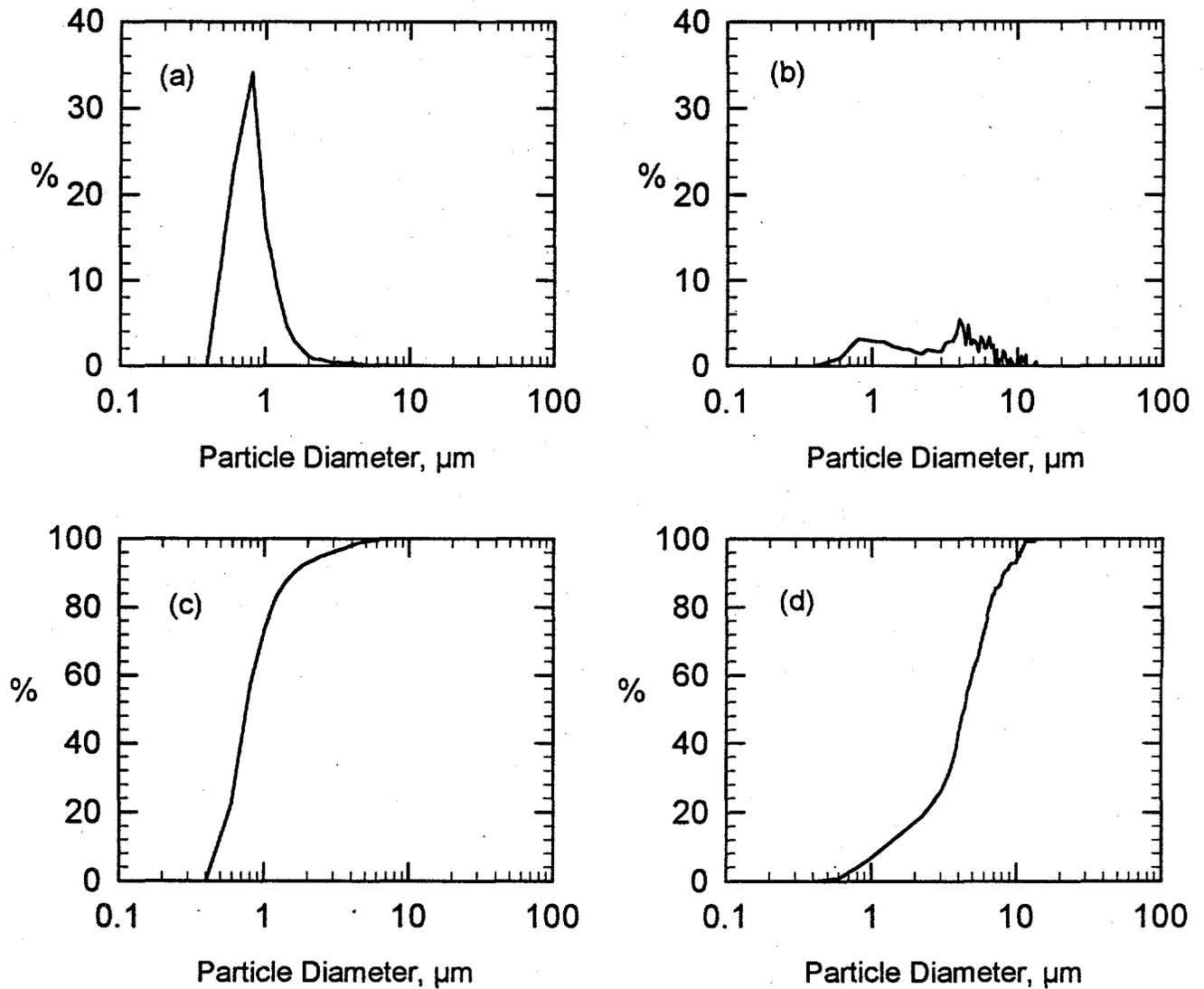
Table F.6. Distribution of the Radioactive Sludge Components Between the Various Process Streams From the T-104 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Total Alpha	0	0	0	0	100
^{239,240} Pu	(a)	(a)	(a)	(a)	100
²⁴¹ Am + ²³⁸ Pu	(a)	(a)	(a)	(a)	100
²⁴¹ Am(γ)	0	0	0	0	100
¹³⁷ Cs	0	25	30	14	31
⁹⁰ Sr	0	1	0	0	98
⁹⁹ Tc	0	0	0	0	100

(a) Not determined due to a lack of total activity in the sample.

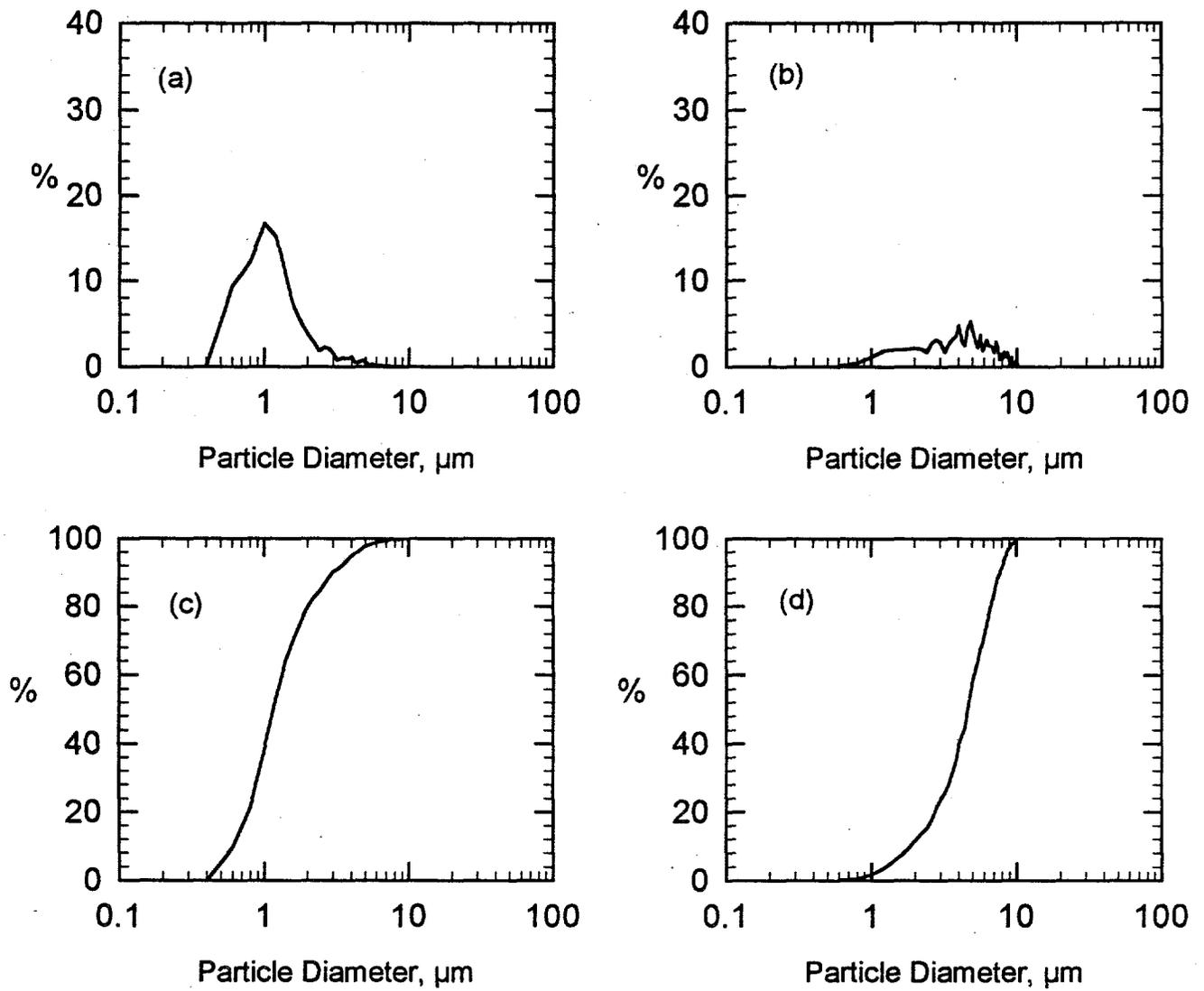
Table F.7. Mass Balance for Radioactive Sludge Components From the T-104 Test

Component	Concentration in Dried Sludge, $\mu\text{Ci/g}$		Recovery, %
	Direct Analysis	Summation Method	
Total Alpha	5.22E-01	6.37E-01	122
^{239,240} Pu	3.83E-01	5.42E-01	142
²⁴¹ Am + ²³⁸ Pu	1.39E-01	9.20E-02	66
²⁴¹ Am(γ)	7.18E-02	8.90E-02	124
¹³⁷ Cs	2.39E+00	6.17E-01	26
⁹⁰ Sr	1.25E+01	1.29E+01	103
⁹⁹ Tc	< 7.00E-04	3.69E-04	



T104-C.SPW

Figure F.2. Particle-Size Data for Untreated T-104 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.



T104-M02.SPW

Figure F.3. Particle-Size Data for Treated T-104 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.

Appendix G

Results from the Tank T-111 Sludge Washing and Caustic Leaching Test

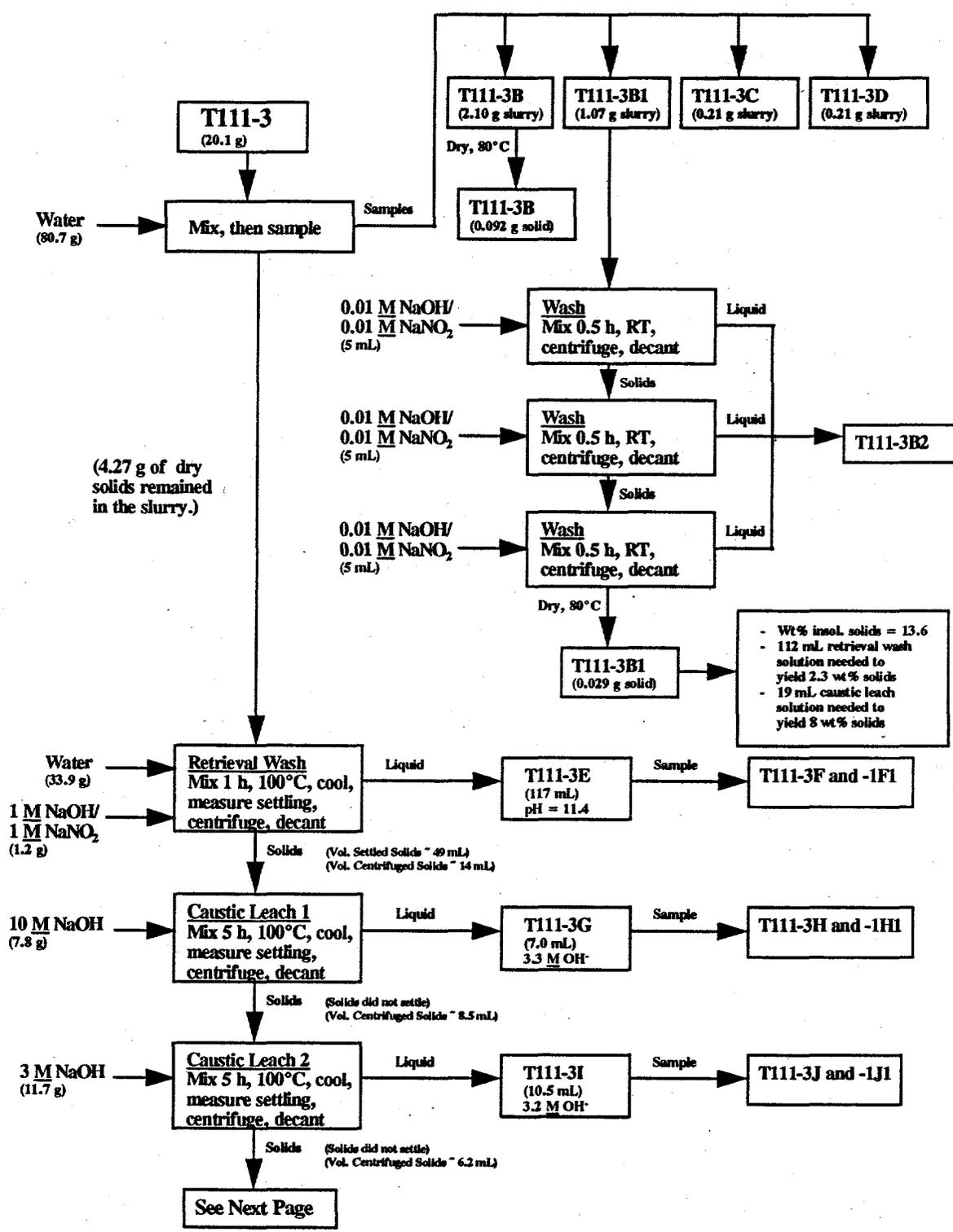


Figure G.1. Schematic of T-111 Sludge Washing and Caustic Leaching Test

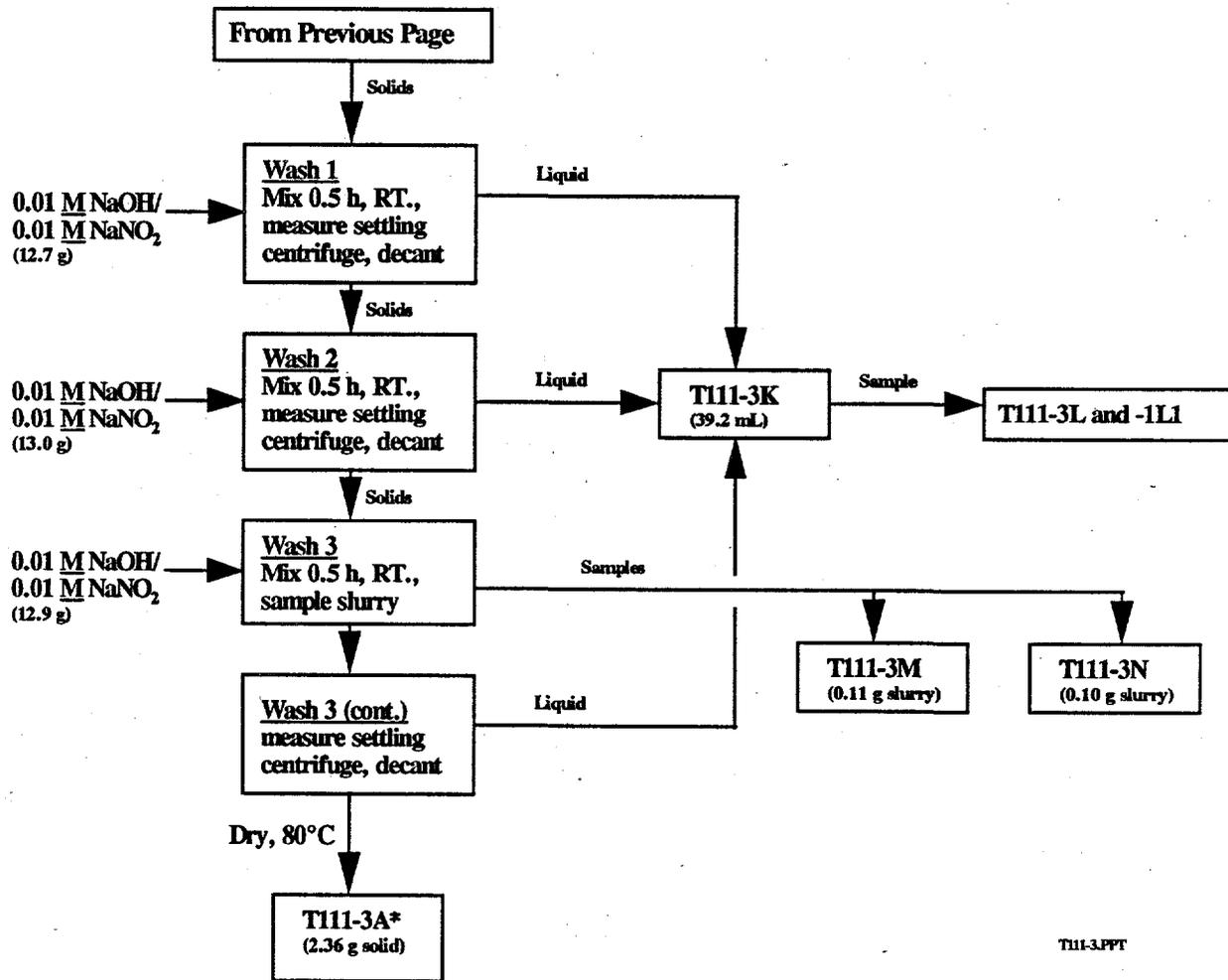


Figure G.1. (contd.)

Table G.1. Concentrations of the Nonradioactive Sludge Components in the Various Process Solutions From the T-111 Test

Component	Detection Limit,	Concentration, $\mu\text{g/mL}^{(a)}$			
		Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Ag	0.085	0.17	0	0	0
Al	0.51	0	79.9	78.2	17
As	0.68	0	0	0	0
B	0.17	39.95	29.75	15.3	3.06
Ba	0.085	0	0	0	0
Be	0.0425	0	0	0	0
Bi	0.85	0	25.5	25.5	1.7
Ca	0.425	0.765	0	0	7.905
Cd	0.085	0	0	0	0
Ce	0.68	0	0	0	0
Co	0.085	0	0	0	0
Cr	0.17	41.65	442	280.5	56.1
Cu	0.085	0	1.7	1.7	0
Dy	0.17	0	0	0	0
Eu	0.085	0	0	0	0
Fe	0.085	0	14.45	10.2	1.275
Gd	1.7	0	0	0	0
K	17	153	935	510	85
La	0.255	0	0	0	0
Li	0.17	0	0	0	0
Mg	0.68	0	0	0	0.85
Mn	0.0425	0	0.51	0.425	0.17
Mo	0.17	0	0	0	0
Na	3.4	4335	85000	85000	18700
Nd	0.255	0	0	0	0
Ni	0.255	0	0	0	3.145
P	0.85	476	1360	833	161.5
Pb	0.51	0	6.8	6.8	0
Pd	1.7	0	0	0	0
Rh	0.85	0	0	0	0
Ru	0.85	0	0	0	0
Sb	0.425	0	0	0	0
Se	0.68	0	0	0	0
Si	0.425	331.5	4250	2720	544
Sn	8.5	0	0	0	0
Sr	0.0425	0	0	0	0
Te	1.7	0	0	0	0
Th	6.8	0	0	0	0
Tl	0.0425	0	0	0	0
Tl	4.25	0	0	0	0
U	0.0255	0.1292	88.4	69.615	11.9
V	0.085	0	0.595	0	0
W	0.68	0	0	0	0
Y	0.085	0	0	0	0
Zn	0.17	0	33.15	26.35	5.27
Zr	0.085	0	0	0	0
NO ₃ ⁻	250	4500	2900	1030	160
NO ₂ ⁻	250	700	500	130	260
PO ₄ ³⁻	250 ^(d)	1500	3900	1790	240
SO ₄ ²⁻	250 ^(d)	400	200	70	0
F ⁻	125	300	(c)	(c)	(c)
Cl ⁻	125	0	(c)	(c)	(c)
Br ⁻	25	0	0	0	0

(a) The detection limits for the two caustic leach solutions (G and I) are five times the values reported in this column.

(b) Zero values indicate the analyte was below the detection limit.

(c) Measurement not performed.

(d) Phosphate and sulfate detection limits are 50 $\mu\text{g/ml}$ for 2nd leach and final wash steps.

Table G.2. Concentrations of the Nonradioactive Sludge Components in the Leached Sludge From the T-111 Test

<u>Component</u>	<u>Detection Limit, $\mu\text{g/g}$</u>	<u>Concentration, $\mu\text{g/g}$^(a)</u>
Ag	9	420
Al	60	5700
As	200	200
B	20	1100
Ba	9	330
Be	5	0
Bi	90	110000
Ca	50	22000
Cd	9	60
Ce	80	200
Co	9	60
Cr	20	3200
Cu	9	240
Dy	20	0
Eu	9	10
Fe	9	130000
Gd	200	400
K	(b)	(b)
La	30	20000
Li	20	0
Mg	80	4200
Mn	5	96000
Mo	20	40
Na	200	56000
Nd	30	300
Ni	(c)	(c)
P	90	13000
Pb	60	3500
Pd	200	0
Rh	90	100
Ru	90	0
Sb	50	0
Se	70	400
Si	50	34000
Sn	900	1000
Sr	5	1300
Te	200	0
Th	800	0
Ti	5	1100
Tl	500	0
U	1585	39600
V	9	0
W	80	100
Y	9	0
Zn	20	820
Zr	9	120
NO ₃ ⁻	(d)	(d)
NO ₂ ⁻	(d)	(d)
PO ₄ ³⁻	24100	30000
SO ₄ ²⁻	9600	10000
F	24100	0
Cl	(d)	(d)
Br	(d)	(d)

- (a) Zero values indicate the analyte was below the detection limit.
 (b) Potassium values are not reported since the sample was dissolved for analysis using a KOH fusion method.
 (c) Nickel values are not reported because a Ni crucible was used during the KOH fusion method.
 (d) Measurement impractical due to sample preparation method.

Table G.3. Distribution of the Nonradioactive Sludge Components Between the Various Process Streams From the T-111 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Ag	2	0	0	0	98
Al	0	4	5	4	87
As	0	0	0	0	100
B	60	3	2	2	34
Ba	0	0	0	0	100
Be	(a)	(a)	(a)	(a)	(a)
Bi	0	0	0	0	100
Ca	0	0	0	1	99
Cd	0	0	0	0	100
Ce	0	0	0	0	100
Co	0	0	0	0	100
Cr	24	15	14	11	37
Cu	0	2	3	0	95
Dy	(a)	(a)	(a)	(a)	(a)
Eu	0	0	0	0	100
Fe	0	0	0	0	100
Gd	0	0	0	0	100
K	(b)	(b)	(b)	(b)	(b)
La	0	0	0	0	100
Li	(a)	(a)	(a)	(a)	(a)
Mg	0	0	0	0	100
Mn	0	0	0	0	100
Mo	0	0	0	0	100
Na	(c)	(c)	(c)	(c)	(c)
Nd	0	0	0	0	100
Ni	(b)	(b)	(b)	(b)	(b)
P	50	9	8	6	28
Pb	0	1	1	0	99
Pd	(a)	(a)	(a)	(a)	(a)
Rh	0	0	0	0	100
Ru	(a)	(a)	(a)	(a)	(a)
Sb	(a)	(a)	(a)	(a)	(a)
Se	0	0	0	0	100
Si	20	15	14	11	41
Sn	0	0	0	0	100
Sr	0	0	0	0	100
Te	(a)	(a)	(a)	(a)	(a)
Th	(a)	(a)	(a)	(a)	(a)
Ti	0	0	0	0	100
Tl	(a)	(a)	(a)	(a)	(a)
U	0	1	1	0	98
V	0	100	0	0	0
W	0	0	0	0	100
Y	(a)	(a)	(a)	(a)	(a)
Zn	0	9	10	8	73
Zr	0	0	0	0	100
NO ₃ ⁻	(d)	(d)	(d)	(d)	(d)
NO ₂ ⁻	(d)	(d)	(d)	(d)	(d)
PO ₄ ³⁻	58	9	6	3	24
SO ₄ ²⁻	64	2	1	0	33
F ⁻	(d)	(d)	(d)	(d)	(e)
Cl ⁻	(d)	(d)	(d)	(d)	(d)
Br ⁻	(a)	(a)	(a)	(a)	(a)

(a) Component was not detected.

(b) K and Ni values could not be determined due to the KOH fusion procedure used to prepare the leached solid for analysis.

(c) Removal of Na from the sludge cannot be reliably tracked because the Na in the sludge cannot be distinguished from the Na added in the washing and leaching steps.

(d) Analyte could not be accurately determined due to matrix effects.

Table G.4. Mass Balance for Nonradioactive Sludge Components From the T-111 Test

Component	Concentration in Dried Sludge, g/g Sludge ^(a)		Recovery, %
	Direct Analysis	Summation Method	
Ag	2.00E-04	2.40E-04	120
Al	4.90E-03	3.68E-03	75
As	< 3.00E-04	1.12E-04	
B	7.50E-03	1.84E-03	25
Ba	2.00E-04	1.85E-04	93
Be	< 2.00E-05		
Bi	6.30E-02	6.18E-02	98
Ca	1.60E-02	1.24E-02	78
Cd	5.00E-05	3.36E-05	67
Ce	< 3.00E-04	1.12E-04	
Co	1.00E-04	3.36E-05	34
Cr	4.50E-03	4.90E-03	109
Cu	3.30E-03	1.42E-04	4
Dy	< 9.00E-05		
Eu	< 4.00E-05	5.61E-06	
Fe	6.00E-02	7.30E-02	122
Gd	< 9.00E-04	2.24E-04	
K	(b)	(b)	(b)
La	9.20E-03	1.12E-02	122
Li	< 9.00E-05		
Mg	2.00E-03	2.36E-03	118
Mn	5.30E-02	5.38E-02	102
Mo	< 9.00E-05	2.24E-05	
Na	3.70E-01		
Nd	3.00E-04	1.68E-04	56
Ni	(b)	(b)	(b)
P	2.60E-02	2.63E-02	101
Pb	2.00E-03	1.99E-03	100
Pd	< 1.00E-03		
Rh	< 4.00E-04	5.61E-05	
Ru	< 4.00E-04		
Sb	< 2.00E-04		
Se	< 3.00E-04	2.24E-04	
Si	4.70E-02	4.71E-02	100
Sn	< 5.00E-03	5.61E-04	
Sr	6.80E-04	7.29E-04	107
Te	< 9.00E-04		
Th	< 3.00E-03		
Ti	3.60E-04	6.17E-04	171
Tl	< 2.00E-03		
U	2.26E-02	2.26E-02	100
V	< 4.00E-05	9.87E-07	
W	< 3.00E-04	5.61E-05	
Y	< 4.00E-05		
Zn	1.30E-03	6.29E-04	48
Zr	< 4.00E-05	6.73E-05	
NO ₃ ⁻	(c)	(c)	(c)
NO ₂ ⁻	(c)	(c)	(c)
PO ₄ ³⁻	5.00E-02	7.15E-02	143
SO ₄ ²⁻	2.00E-02	1.72E-02	86
F ⁻	< 3.7E-02	(d)	(d)
Cl ⁻	(c)	(c)	(c)
Br ⁻	(d)	(d)	(d)

(a) Blank spaces indicate that the analyte was below the detection limit.

(b) K and Ni values could not be determined due to the KOH fusion used to prepare the solids for analysis.

(c) Measurement not performed.

(d) Analyte could not be accurately determined due to matrix effects.

Table G.5. Concentrations of the Radioactive Sludge Components in the Various Process Streams From the T-111 Test

Component	Concentration, $\mu\text{Ci/mL}$			
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)
Total Alpha	< 2.55E-5	2.21E-05	2.10E-05	< 2.55E-5
^{239,240} Pu	(a)	(a)	(a)	(a)
²⁴¹ Am + ²³⁸ Pu	(a)	(a)	(a)	(a)
²⁴¹ Am(γ)	< 2.00 E-05	< 3.00 E-05	< 3.00 E-05	< 2.00 E-05
¹³⁷ Cs	1.23E-02	9.78E-02	6.04E-02	1.16E-02
⁹⁰ Sr	< 4.25E-04	< 4.25E-04	1.69E-03	< 4.25E-04
⁹⁹ Tc	5.61E-06	< 7.65E-06	< 7.65E-06	< 7.65E-06

Component	Concentration, $\mu\text{Ci/g}$
	Residue
Total Alpha	3.12E+00
^{239,240} Pu	2.85E+00
²⁴¹ Am + ²³⁸ Pu	2.67E-01
²⁴¹ Am(γ)	4.74E-01
¹³⁷ Cs	1.08E+00
⁹⁰ Sr	7.99E+01
⁹⁹ Tc	1.95E-03

(a) ND = Not Determined. The low total alpha activity made these separations impractical.

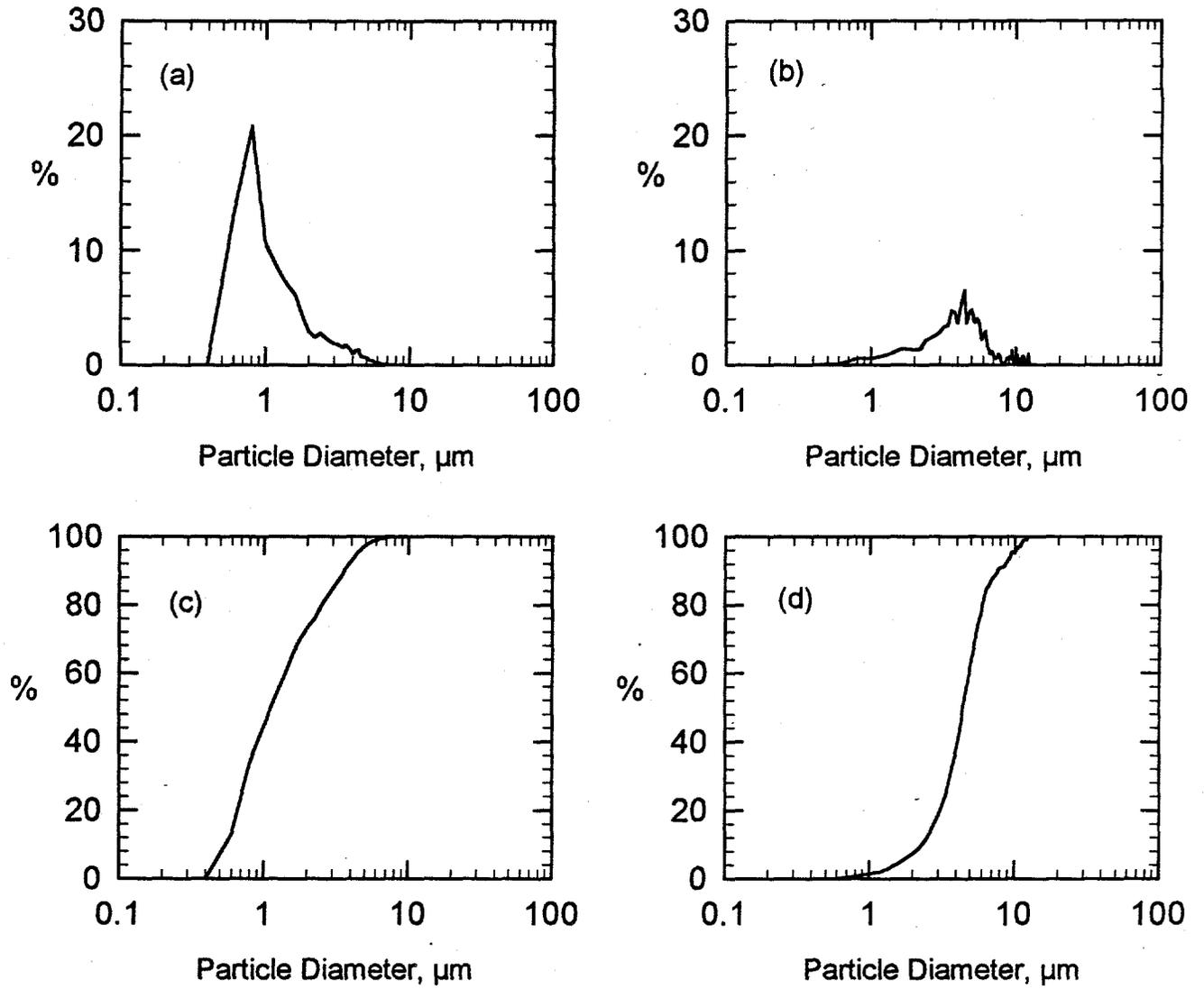
Table G.6. Distribution of the Radioactive Sludge Components Between the Various Process Streams From the T-111 Test

Component	Amount of Component Found, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Total Alpha	0	0	0	0	100
^{239,240} Pu	(a)	(a)	(a)	(a)	100
²⁴¹ Am + ²³⁸ Pu	(a)	(a)	(a)	(a)	100
²⁴¹ Am(γ)	0	0	0	0	100
¹³⁷ Cs	25	12	11	8	44
⁹⁰ Sr	0	0	0	0	100
⁹⁹ Tc	12	0	0	0	88

a) Not determined due to a lack of total activity in the sample.

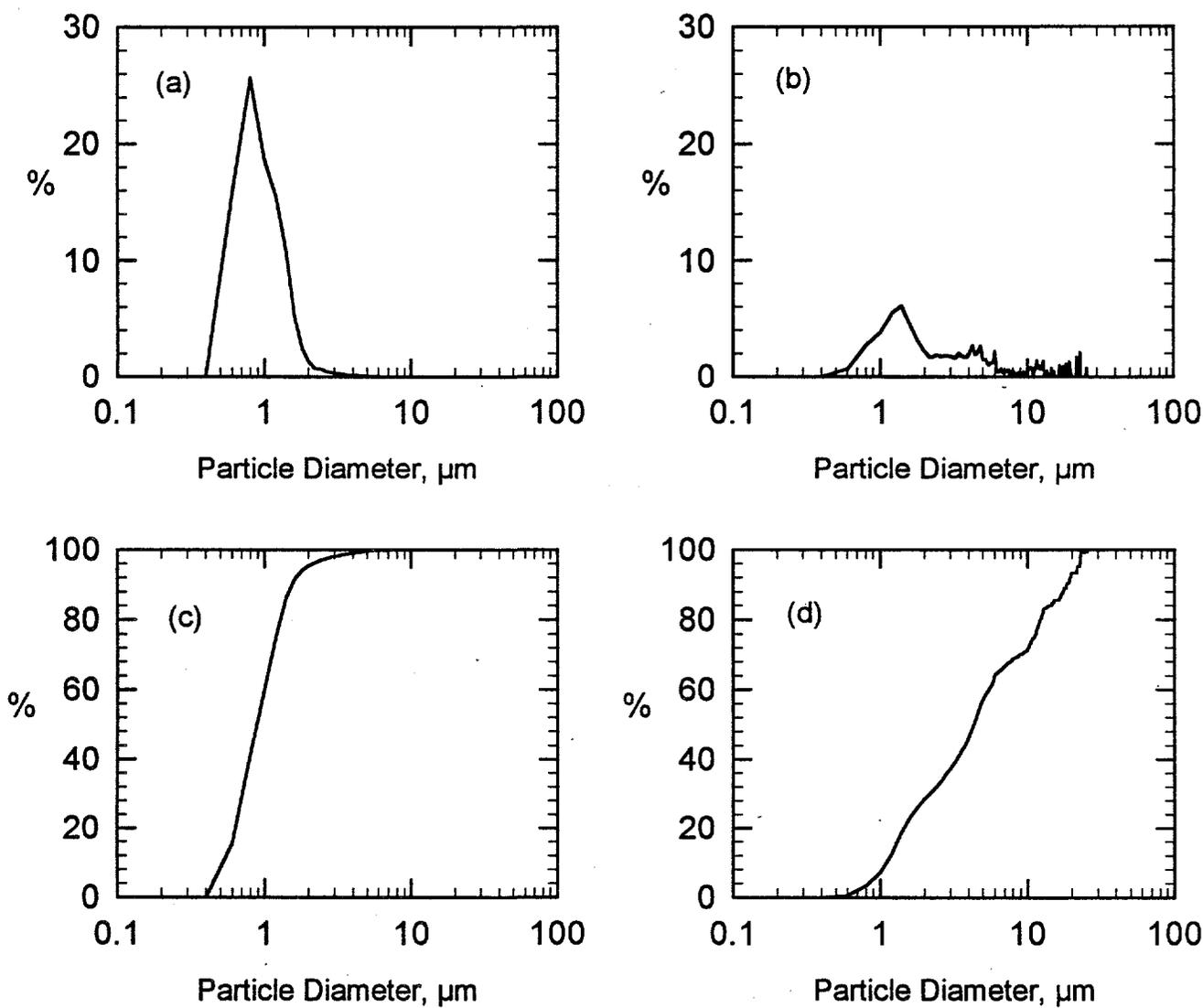
Table G.7. Mass Balance for Radioactive Sludge Components From the T-111 Test

Component	Concentration in Dried Sludge, μCi/g		Recovery, %
	Direct Analysis	Summation Method	
Total Alpha	1.70E+00	1.75E+00	103
^{239,240} Pu	1.49E+00	1.60E+00	107
²⁴¹ Am + ²³⁸ Pu	2.31E-01	1.49E-01	65
²⁴¹ Am(γ)	2.55E-01	2.66E-01	104
¹³⁷ Cs	1.16E+00	1.36E+00	118
⁹⁰ Sr	4.11E+01	4.48E+01	109
⁹⁹ Tc	< 7E-04	1.25E-03	



T111-3C.SPW

Figure G.2. Particle-Size Data for Untreated T-111 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.



T111-3M.SPW

Figure G.3. Particle-Size Data for Treated T-111 Sludge: a) Probability-Number Density Graph, b) Probability-Volume Density Graph, c) Probability-Number Distribution Graph, and d) Probability-Volume Distribution Graph.

Distribution

No. of Copies	No. of Copies
Offsite	Onsite
<p>12 DOE/Office of Scientific and Technical Information</p> <p>Dennis Wynne EM-361, Trevion II U.S. Department of Energy 12800 Middlebrook Road Germantown, MD 20874</p> <p>Robert King Washington Department of Ecology P.O. Box 47600 Olympia, WA 98594-7600</p> <p>Donald Temer Los Alamos National Laboratory P.O. Box 1663 Mail Stop G740 Los Alamos, NM 87545</p> <p>Steven Agnew Los Alamos National Laboratory P.O. Box 1663 Mail Stop J586 Los Alamos, NM 87545</p> <p>Phil McGinnis Oak Ridge National Laboratory P.O. Box 2008 Oak Ridge, TN 37831-6273</p> <p>Zane Egan Oak Ridge National Laboratory P.O. Box 2008 Oak Ridge, TN 37831-6223</p> <p>Samuel D. Fink Bldg. 773-A Rm. B-112 Westinghouse Savannah River Company P. O. Box 616 Aiken, SC 29802</p> <p>Dr. Denis Strachan Argonne National Laboratory 9700 S. Cass Avenue Argonne, IL 60439</p>	<p>3 DOE Richland Operations Office</p> <p>S. T. Burnum P. E. Lamont C. S. Louie</p> <p>17 Westinghouse Hanford Company</p> <p>J. N. Appel H. Babad G. R. Bloom A. L. Boldt S. J. Eberlein K. A. Gasper M. J. Klem R. A. Kirkbride M. J. Kupfer S. L. Lambert G. T. MacLean R. M. Orme I. E. Reep D. A. Reynolds B. C. Simpson J. P. Sloughter D. J. Washenfelder</p> <p>ICF Kaiser Hanford</p> <p>C. H. Brevick</p> <p>70 Pacific Northwest Laboratory</p> <p>G. H. Beeman D. L. Blanchard K. P. Brooks G. H. Bryan N. G. Colton W. C. Cosby A. R. Felmy J. G. Hill L. K. Holton (26) D. E. Kurath J. P. LaFemina G. J. Lumetta (20) B. M. Rapko (5) B. A. Reynolds R. D. Scheele G. J. Sevigny M. J. Wagner Technical Report Files (5)</p>