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WTP-RPT-137, Rev. 0

Oxidative Alkaline Leaching of SX-101 and SY-102 and Its Impact on Immobilized High-Level Waste

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Prepared for Bechtel National Inc.
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Test specification: 24590-PTF-TSP-RT-03-003, Rev. 0
Test plan: Not applicable
Test exceptions: 24590-PTF-TEF-RT-05-00001 and
24590-PTF-TEF-RT-05-00004
R&T focus area: Pretreatment & Vitrification
Test Scoping Statement(s): B-89

6/23/05
for W. Tamosaitis

ACCEPTED FOR
WTP PROJECT USE

Battelle—Pacific Northwest Division
Richland, Washington 99352

Completeness of Testing

Work and testing had been previously performed under Test Specification 24590-PTF-TSP-03-003, Rev. 0 and Test Plan TP-RPP-WTP-275. This report describes additional data evaluation under Test Exceptions 24590-PTF-TEF-RT-05-00001 and 24590-PTF-TEF-RT-05-00004. The work followed the quality assurance requirements outlined in the Test Specifications and Test Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. The test results and this report have been reviewed and verified.

Approved:

DE Kurath for GHB
Gordon H. Beeman, Manager
WTP R&T Support Project

6/21/05
Date

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Abbreviations and Acronyms

AEA	alpha energy analysis
AES	atomic emission spectroscopy
BBI	best basis inventory
CL	Caustic Leach
CSREX	Cesium Strontium Rare Earth Extraction
CW	cladding waste
DOE	U.S. Department of Energy
DI	deionized (water)
EDS	energy-dispersive spectroscopy
FP	fission products
GEA	gamma energy analysis
HLW	high-level waste
IC	ion chromatography
ICP	inductively coupled plasma
IHLW	immobilized high-level waste
LANL	Los Alamos National Laboratory
LAW	low-activity waste
MS	mass spectrometry
MT	metric ton
OL	Oxidative Leach
ORNL	Oak Ridge National Laboratory
ORP	Office of River Protection
PAS	PUREX acidified sludge
PAW	PUREX acid waste
PNWD	Battelle—Pacific Northwest Division
PUREX	plutonium-uranium extraction
QC	quality control
REDOX	reduction/oxidation
SEM	scanning electron microscopy
SRTC	Savannah River Technology Center
TBP	tri-butylphosphate
TWINS	Tank Waste Information Network System
WTP	Waste Treatment Plant
XRD	X-ray diffraction

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Testing Summary

A recent Battelle—Pacific Northwest Division (PNWD) letter report (WTP-RPT-117, Rapko et al. 2004) described the impact of oxidative alkaline leaching on washed sludges from Hanford Tanks SX-101(1) and SY-102 as a function of the sequence of caustic leaching and oxidative alkaline leaching. The other variables examined were the temperature and the hydroxide concentration during oxidative alkaline leaching. However, the report did not address the effects of a simple *caustic* leach separate from those of the *oxidative* leach. Further, the literature review conducted before the testing focused only on chromium and plutonium. An additional assessment of oxidative leaching's impact on potentially high-level waste (HLW) limiting elements is needed. These elements would include chromium, aluminum, plutonium, sulfur, and any others identified as potentially limiting HLW loadings. This information will be used to complete the oxidative leaching process design to be implemented in ultrafiltration. An assessment is also needed to determine whether meaningful simulants can be developed to further optimize oxidative leaching test methods.

Objectives

Test Objective	Objective met (Y/N)	Discussion
Identify the leach factors for simple caustic leaching only and for oxidative leaching only for sludges SX-101 and SY-102 from previously published data (WTP-RPT-117).	Y	In Task 1, the impact of caustic leaching was determined as follows: the mass was calculated for each metal component from the caustic leach and oxidative leach step, along with their corresponding wash solutions and together with the total mass of the metal component in the residual solids. These masses were then summed to give the total mass of each metal component in the sludge. From this information, the percent of each component removed in each step can be calculated. To calculate the mass changes for the sludge during intermediate leaching steps, such as an initial caustic leach in test numbers 3 and 4 or an initial oxidative leach in test numbers 5 and 6(2) (this information is needed to calculate solids loading into immobilized HLW relative to washed sludge), the mass of each metal component as their stable oxide is calculated, and the masses of these oxides are summed to give the total oxide mass.

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(1) All Hanford waste tanks have a "241" prefix on the tank designation, but this common prefix will not be used in this report.

(2) Test numbers 3, 4, 5, and 6 were tests performed under Test Plan TP-RPP-WTP-275 and reported in report RP WTP-117.

Test Objective	Objective met (Y/N)	Discussion
Assess whether the impact of sulfur distribution by oxidative alkaline leaching and simple caustic leaching can be determined. This will involve the following activities: 1. Review alkaline leaching and oxidative leaching literature on Hanford sludges to cull information regarding the speciation of sulfur. There is likely little to no speciation information for sulfur available—and such a finding is a legitimate conclusion from this evaluation. Reviews of the literature regarding the origin of sulfur in the Hanford tanks will also assess possible speciation of sulfur from this information. 2. Assess the likely impact of oxidative alkaline leaching on the sulfur species based on literature precedent and basic chemical principles if speciation data for sulfur are available. 3. Forecast an evaluation of the distribution of any identified sulfur species in either simple caustic leaching or oxidative alkaline leaching.	Y	In Task 2, caustic leach studies from Hanford and other U.S. Department of Energy (DOE) sites were reviewed, particularly for information about sulfur speciation. Saltcake and sludge speciation data from Hanford and other DOE sites also were examined for information about identified sulfur species. Finally, processes performed at the Hanford site were reviewed to determine what sulfur-containing chemicals were added, and from that information, likely forms of sulfur in the waste tanks were surmised.
Evaluate the possibility of using an alternative approach for evaluating the impact of problematic glass components by testing these glass component's behaviors with a simulant, well designed (and preferentially validated) to respond as would actual Hanford sludge to the changing conditions. Specifically, in light of the available speciation information about Hanford tank waste, assess the usefulness of such a sludge simulant for performing such an evaluation.	Y	In Task 3, the information from Task 2, in addition to reviewing prior efforts on simulant formation, were used to determine the difficulty of preparing a simulant suitable for evaluating the performance of alternative pretreatments in the waste treatment plant.

Test Exceptions

List Test Exceptions	Describe Test Exceptions
24590-PTF-TEF-RT-05-00001	Prior work as described in WTP-RPT-117 did not address the effects of caustic leaching separate from those of oxidative leaching. Additional assessment of oxidative leaching's impact on potentially HLW limiting elements is need. This test exception outlines work to provide that additional assessment. First, those conditions reported in WTP-RPT-117 that involved an initial caustic leach followed by a subsequent oxidative leach will be evaluated to separate the impact of caustic leaching versus oxidative leaching. Second, the alkaline leach literature will be reviewed to ascertain the form and impact of oxidative leaching on sulfur removal. Third, the usefulness of simulants in lieu of actual Hanford tank sludge at supplying leach information will be evaluated.
24590-PTF-TEF-RT-05-00004	This test exception expands the analysis of the leaching literature in WTP-RPT-117 to include all testing that involved sequential oxidative alkaline leaching and caustic leaching. In addition, the use of radiological data to support the leach factors supplied by direct metal's analysis is specified.

Results and Performance Against Success Criteria

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
Identify simple caustic leach factors for washed SX-101 and SY-102 Hanford tank sludges.	The following tables S.1 through S.4 supply the leach factors for the major bulk metals and Pu for simple caustic leaching of washed SX-101 and SY-102 Hanford tank sludges. There are four conditions described in Tables S.1 through S.4. For Condition #3, an initial caustic leach at 3 M NaOH, 85°C, was performed followed by an oxidative leach with permanganate, at a 0.25 M initial concentration of NaOH at 25°C. Condition #4 is identical to Condition #3 except that the oxidative leach was performed at 85°C. Conditions #5 and #6 are identical to conditions #3 and #4, respectively, except that the order of the oxidative leach and caustic leach is reversed. From this information, it is clear that a simple caustic leach primarily removes Al from the sludge whereas the oxidative alkaline leach is required to remove any substantial amount of Cr from the sludges under likely Waste Treatment Plant (WTP)

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
	operating conditions. Further details with respect to component concentrations in the various streams and previously reported oxidative alkaline leach factors are summarized in the appendices.

Table S.1. Percent Removal of Metals from Washed SX-101 Sludge by a) an Initial Caustic Leach, b) a Subsequent Oxidative Alkaline Leach, and c) Total Removed

Component	SX-101-3, % Removed			SX-101-4, % Removed		
	CL	OL	Total	CL	OL	Total
Ag	0	0	0	0	0	0
Al	79	4	83	79	10	89
As	NA	NA	NA	NA	NA	NA
B	36	61	97	36	61	98
Ba	0	0	0	0	0	0
Be	100	0	100	NA	NA	NA
Bi	0	0	0	0	0	0
Ca	0	0	0	0	6	6
Cd	7	0	7	0	0	0
Ce	0	0	0	0	0	0
Co	NA	NA	NA	NA	NA	NA
Cr	6	82	87	5	89	94
Cu	0	0	0	0	0	0
Dy	0	0	0	0	0	0
Eu	0	100[(a)]	100[(a)]	0	100[(a)]	100[(a)]
Fe	0	0	0	0	0	0
K	NA	NA	NA	NA	NA	NA
La	0	0	0	0	0	0
Li	0	0	0	0	0	0
Mg	0	0	0	0	0	0
Mn	0	0	0	0	0	0
Mo	NA	NA	NA	NA	NA	NA

Table S.1. (cont'd)

Component	SX-101-3, % Removed			SX-101-4, % Removed		
	CL	**OL**	**Total**	**CL**	**OL**	**Total**
Na	83	14	97	81	16	97
Nd	0	0	0	0	0	0
Ni	NA	NA	NA	NA	NA	NA
P	62	0	62	23	63	86
Pb	3	35	38	4	0	4
Pd	NA	NA	NA	NA	NA	NA
Rh	NA	NA	NA	NA	NA	NA
Ru	NA	NA	NA	NA	NA	NA
Sb	NA	NA	NA	NA	NA	NA
Se	NA	NA	NA	NA	NA	NA
Si	19	27	46	19	32	50
Sn	0	0	0	0	0	0
Sr	0	0	0	0	0	0
Te	NA	NA	NA	NA	NA	NA
Th	0	0	0	0	0	0
Ti	0	0	0	0	0	0
Tl	76	24	100	NA	NA	NA
U	0	0	0	0	0	0
V	NA	NA	NA	0	100	100
W	0	100	100	0	100	100
Y	0	0	0	0	0	0
Zn	0	0	0	0	0	0
Zr	2	8	9	1	8	9
Pu	0	0	0	0	0	0

NA = not available. CL = Caustic Leach. OL = Oxidative Leach. Total = Total Removed

(a) Suspect data—see text for discussion.

Table S.2. Percent Removal of Metals from Washed SX-101 Sludge by a) an Initial Oxidative Leach, b) a Subsequent Caustic Leach, and c) Total Removed

Component	SX-101-5, % Removed[(a)]			SX-101-6, % Removed		
	OL	CL	Total	OL	CL	Total
Ag	0/49	0/0	0/49	0	0	0
Al	53/0	44/93	97/93	14	83	97
As	0/NA	100/NA	100/NA	0	100	100
B	95/NA	0/NA	95/NA	97	0	97
Ba	0/0	0/0	0/0	0	0	0
Be	58/NA	42/NA	100/NA	0	100	100
Bi	0/21	0/0	0/21	0	0	0
Ca	0/0	0/0	0/0	0	0	0
Cd	10/0	11/6	21/6	0	12	12
Ce	0/0	0/0	0/0	0	0	0
Co	NA/NA	NA/NA	NA/NA	NA	NA	NA
Cr	35/81	29/9	65/90	94	3	97
Cu	0/26	0/0	0/26	0	0	0
Dy	0/NA	0/NA	0/NA	0	0	0
Eu	NA/NA	NA/NA	NA/NA	NA	NA	NA
Fe	0/0	0/0	1/0	0	0	0
K	NA/NA	NA/NA	NA/NA	NA	NA	NA
La	0/0	0/0	0/0	0	0	0
Li	0/0	0/0	0/0	0	0	0
Mg	0/0	0/0	0/0	0	0	0
Mn	0/0	0/0	0/0	0	0	0
Mo	NA/NA	NA/NA	NA/NA	NA	NA	NA
Na	54/0	45/0	98/0	15	83	98
Nd	0/0	0/0	0/0	0	0	0
Ni	NA/NA	NA/NA	NA/NA	NA	NA	NA
P	41/43	34/33	75/78	0	44	44
Pb	25/0	22/6	47/6	0	15	15
Pd	NA/NA	NA/NA	NA/NA	100[(b)]	0[(b)]	100[(b)]

Table S.2. (cont'd)

Component	SX-101-5, % Removed			SX-101-6, % Removed		
	OL	**CL**	**Total**	**OL**	**CL**	**Total**
Rh	NA/NA	NA/NA	NA/NA	NA	NA	NA
Ru	NA/NA	NA/NA	NA/NA	NA	NA	NA
Sb	NA/NA	NA/NA	NA/NA	NA	NA	NA
Se	NA/NA	NA/NA	NA/NA	0	0	0
Si	29/0	26/10	55/10	41	25	67
Sn	0/39	0/0	0/39	0	0	0
Sr	0/0	0/0	0/0	0	0	0
Te	NA/NA	NA/NA	NA/NA	NA	NA	NA
Th	0/NA	0/NA	0/NA	0	0	0
Ti	0/NA	0/NA	0/NA	0	0	0
Tl	0/NA	100/NA	100/NA	0	0	0
U	0/0	0/0	0/0	0	0	0
V	NA/NA	NA/NA	NA/NA	NA	NA	NA
W	NA/NA	NA/NA	NA/NA	NA	NA	NA
Y	0/NA	0/NA	0/NA	0	0	0
Zn	0/58	0/0	0/58	0	0	0
Zr	2/0	2/0	4/0	8	2	10
Pu	0/29	1/1	1/30	0	3	3

NA = not available. CL = Caustic Leach. OL = Oxidative Leach. Total = Total Removed

(a) Left side of / calculated with the standard method; right side of / calculated with the following alternative method: OL% removed = 100*[Feed - (Residue+Caustic Leachate)]/Feed—see text in Section 2 for further discussion.

(b) Suspect data—see text for discussion.

Table S.3. Percent Removal of Metals from Washed SY-102 Sludge by a) an Initial Caustic Leach, b) a Subsequent Oxidative Alkaline Leach, and c) Total Removed

Component	**SY-102-3, % Removed**			**SY-102-4, % Removed**		
	CL	**OL**	**Total**	**CL**	**OL**	**Total**
Ag	0	0	0	0	0	0
Al	72	5	76	69	9	78
As	NA	NA	NA	NA	NA	NA
B	37	60	97	30	70	100
Ba	0	0	0	0	0	0
Be	100	0	100	100	0	100
Bi	2	0	2	2	0	2
Ca	0	0	0	0	0	0
Cd	0	0	0	0	0	0
Ce	0	0	0	0	0	0
Co	NA	NA	NA	NA	NA	NA
Cr	4	76	80	4	91	95
Cu	0	0	0	0	0	0
Dy	0	0	0	0	0	0
Eu	0	100(a)	100(a)	0	100(a)	100(a)
Fe	0	0	0	0	0	0
K	NA	NA	NA	NA	NA	NA
La	0	0	0	0	0	0
Li	0	0	0	0	0	0
Mg	0	0	0	0	0	0
Mn	0	63	63	0	0	0
Mo	NA	NA	NA	NA	NA	NA
Na	82	15	97	78	19	97
Nd	0	0	0	0	0	0
Ni	NA	NA	NA	NA	NA	NA
P	17	20	37	16	11	27
Pb	14	0	14	14	0	14
Pd	0(a)	100(a)	100(a)	0(a)	100(a)	100(a)
Rh	NA	NA	NA	NA	NA	NA

Table S.3. (cont'd)

Component	SY-102-3, % Removed			SY-102-4, % Removed		
	CL	**OL**	**Total**	**CL**	**OL**	**Total**
Ru	NA	NA	NA	NA	NA	NA
Sb	NA	NA	NA	NA	NA	NA
Se	NA	NA	NA	0	100	100
Si	15	17	31	13	23	36
Sn	0	0	0	0	0	0
Sr	0	0	0	0	0	0
Te	NA	NA	NA	NA	NA	NA
Th	0	0	0	0	0	0
Ti	0	0	0	0	0	0
Tl	0	100	100	NA	NA	NA
U	0	0	0	0	0	0
V	0	100	100	0	100	100
W	54	46	100	43	57	100
Y	0	0	0	0	0	0
Zn	0	0	0	0	0	0
Zr	1	8	9	1	21	22
Pu	0	0	0	0	0	0

NA = not available. CL = Caustic Leach. OL = Oxidative Leach. Total = Total Removed.

(a) Suspect data—see text for discussion.

Table S.4. Percent Removal of Metals from Washed SY-102 Sludge by a) an Initial Oxidative Leach, b) a Subsequent Caustic Leach, and c) Total Removed

Component	SY-102-5, % Removed[(a)]			SY-102-6, % Removed		
	OL	**CL**	**Total**	**OL**	**CL**	**Total**
Ag	0/0	0/0	0/0	5	0	5
Al	53/0	42/87	94/87	5	84	89
As	NA/NA	NA/NA	NA/NA	NA	NA	NA
B	54/0	43/38	97/38	56	39	95
Ba	0/0	0/0	0/0	0	0	0
Be	30/NA	24/NA	54/NA	0	25	25
Bi	3/0	2/0	5/0	0	1	1
Ca	0/0	0/0	0/0	1	0	1
Cd	2/0	2/0	4/0	0	1	1
Ce	0/NA	0/NA	0/NA	0	0	0
Co	NA/NA	NA/NA	NA/NA	NA	NA	NA
Cr	42/81	33/11	75/92	90	6	96
Cu	0/0	0/0	0/0	0	0	0
Dy	0/NA	0/NA	0/NA	0	0	0
Eu	NA/NA	NA/NA	NA/NA	100	0	100
Fe	0/0	0/0	0/0	0	0	0
K	NA/NA	NA/NA	NA/NA	NA	NA	NA
La	0/0	0/0	0/0	0	0	0
Li	0/0	0/0	0/0	0	0	0
Mg	0/0	0/0	0/0	0	0	0
Mn	0/0	0/0	0/0	0	0	0
Mo	NA/NA	NA/NA	NA/NA	100	0	100
Na	54/0	43/0	98/0	14	80	95
Nd	0/0	0/0	0/0	0	0	0
Ni	NA/NA	NA/NA	NA/NA	NA	NA	NA
P	11/27	9/7	19/34	13	6	19
Pb	17/0	14/0	31/0	0	16	16
Pd	NA/100[(b)]	NA/0[(b)]	NA/100[(b)]	100[(b)]	0[(b)]	100[(b)]

Table S.4. (cont'd)

Component	SY-102-5, % Removed			SY-102-6, % Removed		
	OL	**CL**	**Total**	**OL**	**CL**	**Total**
Rh	NA/NA	NA/NA	NA/NA	100	0	100
Ru	NA/NA	NA/NA	NA/NA	100	0	100
Sb	NA/NA	NA/NA	NA/NA	NA	NA	NA
Se	NA/NA	NA/NA	NA/NA	100	0	100
Si	17/0	14/0	31/0	16	12	28
Sn	0/5	0/0	0/5	0	0	0
Sr	0/0	0/0	0/0	0	0	0
Te	NA/NA	NA/NA	NA/NA	NA	NA	NA
Th	0/NA	0/NA	0/NA	0	0	0
Ti	0/0	0/0	0/0	0	0	0
Tl	NA/NA	NA/NA	NA/NA	100	0	100
U	0/27	0/0	0/27	0	0	0
V	NA/NA	NA/NA	NA/NA	100	0	100
W	55/NA	45/NA	100/NA	71	29	100
Y	0/NA	0/NA	0/NA	0	0	0
Zn	24/2	19/25	43/27	0	0	0
Zr	5/0	4/0	9/0	10	0	10
Pu	0/0	0/0	0/0	0	0	0

NA = not available. CL = Caustic Leach. OL = Oxidative Leach. Total = Total Removed

(a) Left side of / calculated with the standard method; right side of / calculated with the following alternative method: OL% removed = 100*[Feed - (Residue+Caustic Leachate)]/Feed—see text in Section 2 for further discussion.

(b) Suspect data—see text for discussion.

Quality Requirements

Battelle—Pacific Northwest Division's (PNWD's) Quality Assurance Program is based upon the requirements as defined in the U.S. Department of Energy (DOE) Order 414.1A, Quality Assurance and 10 CFR 830, Energy/Nuclear Safety Management, Subpart A—Quality Assurance Requirements (a.k.a. the Quality Rule). PNWD has chosen to implement the requirements of DOE Order 414.1A and 10 CFR 830, Subpart A by integrating them into the laboratory's management systems and daily operating processes. The procedures necessary to implement the requirements are documented through PNWD's Standards-Based Management System (SBMS).

PNWD implements the RPP-WTP quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. Work was performed to the quality requirements of

NQA-1-1989 Part I, Basic and Supplementary Requirements, NQA-2a-1990, Part 2.7 and DOE/RW-0333P, Rev 13, Quality Assurance Requirements and Descriptions (QARD). These quality requirements are implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual*. The analytical requirements are implemented through WTPSP's Statement of Work (WTPSP-SOW-005) with the Radiochemical Processing Laboratory (RPL) Analytical Service Operations (ASO).

The work described in this report used information provided by the Test Specification, "Ultrafiltration and Washing/Leaching of Hanford Tank 241-SY-102 Waste," 24590-PTF-TSP-RT-03-003, Rev. 0 (approved April 16, 2003). The analysis performed in this report addresses the scope covered by Bechtel National, Inc. (BNI) Test Exceptions 24590-PTF-TEF-RT-05-00001 and 24590-PTF-TEF-RT-05-00004. As no new experimental work was required, no new test plan was generated; all data used in this report were generated and controlled by the previous oxidative alkaline leach test plan, TP-RPP-WTP-275.

PNWD addressed internal verification and validation activities by conducting an independent technical review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verifies that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

R&T Test Conditions

No testing is described in this report.

Simulant Use

No new experimental work is reported so no simulants were used.

Discrepancies and Follow-on Tests

Instead of supplying an average of leach factors in the test, the individual leach factors are provided.

1.0 Introduction

Research is being conducted at the Hanford Site in southeastern Washington State to optimize tank waste composition to prepare the waste for vitrification. It has been determined that temperature and hydroxide concentration are the most important factors impacting washed sludges from Hanford Tanks SX-101 and SY-102 during caustic leaching and oxidative alkaline leaching.(3) However, further study is needed in the following areas: 1) the effects of a simple *caustic* leach with no oxidative alkaline leach, 2) the impact of oxidative leaching on potentially high-level waste (HLW) limiting elements (chromium, aluminum, plutonium, sulfur, and any others identified as potentially limiting HLW loadings) (these need to be determined to complete the oxidative leaching process design to be implemented in ultrafiltration), and 3) an assessment to determine whether meaningful simulants can be developed to further optimize oxidative leaching test methods.

This report describes the following three tasks designed to accomplish these objectives:

- Task 1. Identify the leach factors for simple caustic leaching only and for oxidative leaching only for sludges SX-101 and SY-102 from previously published data (WTP-RPT-117, Rapko et al. 2004).
- Task 2. Assess whether the impact of sulfur distribution by oxidative alkaline leaching and simple caustic leaching can be determined. This will involve the following activities:
  1. Review alkaline leaching and oxidative leaching literature on Hanford sludges to cull information regarding the speciation of sulfur. There is likely little to no speciation information for sulfur available—such a finding is a legitimate conclusion from this evaluation. Reviews of the literature regarding the origin of sulfur in the Hanford tanks will also assess possible speciation of sulfur from this information.
  2. Assess the likely impact of oxidative alkaline leaching on the sulfur species based on literature precedent and basic chemical principles if speciation data for sulfur are available.
  3. Forecast an evaluation of the distribution of any identified sulfur species in either simple caustic leaching or oxidative alkaline leaching.
- Task 3. Evaluate the possibility of using an alternative approach for evaluating the impact of problematic glass components by testing these glass component's behaviors with a simulant, well designed (and preferentially validated) to respond as would actual Hanford sludge to the changing conditions. Specifically, in light of the available speciation information about Hanford tank waste, assess the usefulness of such a sludge simulant for performing such an evaluation.

Section 2 evaluates the impact of an individual caustic leach or oxidative leach on washed tank solids from Tanks SY-102 and SX-101. Section 3 reviews caustic leaching data for removing sulfur, and Section 4 describes the impacts of using sulfur for sludge pretreatment testing.

1.1 Quality Requirement

Battelle—Pacific Northwest Division's (PNWD's) Quality Assurance Program is based upon the requirements as defined in the U.S. Department of Energy (DOE) Order 414.1A, Quality Assurance and

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(3) Battelle—Pacific Northwest Division (PNWD) letter report (WTP-RPT-117).

10 CFR 830, Energy/Nuclear Safety Management, Subpart A—Quality Assurance Requirements (a.k.a. the Quality Rule). PNWD has chosen to implement the requirements of DOE Order 414.1A and 10 CFR 830, Subpart A by integrating them into the laboratory's management systems and daily operating processes. The procedures necessary to implement the requirements are documented through PNWD's Standards-Based Management System (SBMS).

PNWD implements the RPP-WTP quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. Work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, NQA-2a-1990, Part 2.7 and DOE/RW-0333P, Rev 13, Quality Assurance Requirements and Descriptions (QARD). These quality requirements are implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual*. The analytical requirements are implemented through WTPSP's Statement of Work (WTPSP-SOW-005) with the Radiochemical Processing Laboratory (RPL) Analytical Service Operations (ASO).

The work reported in this report used information provided by the Test Specification, "Ultrafiltration and Washing/Leaching of Hanford Tank 241-SY-102 Waste," 24590-PTF-TSP-RT-03-003, Rev. 0 (approved April 16, 2003). The analysis performed in this report addresses the scope covered by Bechtel National, Inc. (BNI) Test Exceptions 24590-PTF-TEF-RT-05-00001 and 24590-PTF-TEF-RT-05-00004. As no new experimental work was required, no new test plan was generated; all data used in this report were generated and controlled by the previous oxidative alkaline leach test plan, TP-RPP-WTP-275.

PNWD addressed internal verification and validation activities by conducting an independent technical review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verifies that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

2.0 Evaluation of the Impact of an Individual Caustic Leach or Oxidative Leach on SY-102 and SX-101 Washed Tank Solids

A recent report (Rapko et al. 2004) described the impact of oxidative alkaline leaching as a function of various treatment conditions on SX-101 and SY-102 washed tank solids. In that study, no “blank” experiments were performed that described the impact of only a simple caustic leach or only a low hydroxide oxidative leach. However, four of the test conditions (#3, #4, #5 and #6 as labeled in the report RTP-WTP-117) involved treating the sludges with a baseline caustic leach treatment (3 M initial NaOH, 85 ± 5°C for 8 hours) in combination with a low hydroxide oxidative leach treatment. For Condition #3, following the initial caustic leach, an oxidative leach with permanganate was performed using a 0.25 M initial concentration of NaOH and a leach temperature of 25°C. Condition #4 is identical to Condition #3 except that the oxidative leach was performed at 85°C. Conditions #5 and #6 are identical to conditions #3 and #4, respectively, except the order of the oxidative alkaline leach and the caustic leach were reversed. In this section, the data from those tests are used to evaluate the impact of a simple caustic leach or a simple, low hydroxide, oxidative leach on these sludges in greater detail than in that previous report.

The methodology used to calculate the effect of the individual leach treatments parallels the approach described in the above-mentioned report and is briefly reviewed here. The data originally were collected in the following manner: a slurry with a known mass of water-insoluble sludge solids was introduced into a sample vial. Stock solutions of 10 M NaOH, $NaMnO_4$, and deionized (DI) water were added to achieve a nominal 3 M NaOH solution, in the case of the caustic leach, or 0.25 M NaOH, in the case of the oxidative leach, with a leachate to a settled solids ratio of 3:1 (v:v). The bottles were loosely capped and heated and shaken for 8 hours at the target temperature (± 5°C). The heating was then stopped and the samples cooled to room temperature overnight. The test suspensions were then centrifuged and the supernatants decanted into receiving bottles. The residual solids then were washed with 0.1 M NaOH until the washings were colorless. The washings were combined with the leachate solution, the combined leachate-washing solution was weighed, the solution was filtered, and aliquots were removed for analysis of metals by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and radionuclides by gamma energy analysis (GEA) and alpha energy analysis (AEA).

The impact of each leach step was determined as follows: the mass of each metal component from the caustic leach and oxidative leach step, along with their corresponding wash solutions, together with the total mass of the metal component in the residual solids, was calculated. These masses were then summed to give the total mass of each metal component in the sludge. From this information, the percent of each component removed in each step can be calculated. To calculate the mass loss for an intermediate leach step (needed to calculate solids loading into immobilized high-level waste [IHLW] relative to washed sludge), the mass of each metal component as its stable oxide is calculated, and the masses of these oxides are summed to give the total oxide concentration. This calculation of the sample mass following a leach and dilute hydroxide wash assumes that 1) the metals are present as these oxides, 2) there are no other anions present, such as chloride, fluorides, or nitrates, and 3) the metals not available by ICP-AES analysis of the solutions and leached residual solids (such as Ni, K due to the interferences from the KOH fusion in a Ni crucible used to prepared the leached solids for analysis) are not present in significant concentrations.

The agreement of the total mass calculated for each component by the summation method described above can be checked with the total mass for each component as calculated by multiplying the mass of water-insoluble sludge used in the test by the component concentration in the water-insoluble sludge. The results of such a calculation are given in Table 2.1. The NA in the tables above refers to components where quantities of the component were below the detection limit in the initial sample (denominator) or components that were not analyzed as noted above.

In general, the agreement for the major components is acceptable, especially considering the up to ±15% uncertainty associated with each of the four independent measurements used in this calculation. The exceptions are primarily either components where the added reagents themselves add mass to the system (Na, Mn) or components at concentrations close to their detection limits (Zr) where a corresponding increase in the uncertainty of the measurements exists. However, it should be noted that some of the results obtained by ICP-AES must be considered suspect. For example, it was previously reported (Rapko et al. 2004) that, by radiochemical analysis, no Eu or Am was leached from either SX-101 or SY-102 washed sludge. This contradicts the Eu ICP-AES data results for SX-101-3 and -4, which show complete removal by oxidative leaching. Since the ^{241}Am (which should show similarly performance to Eu) and the $^{155/154}$Eu measurements are much more sensitive, the ICP-AES results for SX-101 leaching must be considered suspect. Pd provides an example where the mass balances are particularly poor: around 50 to 60% for SY-102 and 0% for SX-101 (Table 2.1). Again, a consequence of possessing such an inexplicable mass balance is that the leach factors calculated for such elements must be considered suspect. More relevant examples are found for Pu, with 71% and 65% balances for SX-101-5 and SX-101-6, respectively; Al, with 226% and 239% balances for SX-101-5 and SY-102-5, respectively; and Cr, with 30%, 62%, and 33% for SX-101-5, SX 101-6, and SY-102-5, respectively.

Some of the poor mass balance agreements found in the -5 tests likely can be traced to an error in preparing and/or executing the analysis of the oxidative leach solutions. In general, if one examines the actual metal concentrations in the leach solution, it is discovered, as expected, that the Na concentrations in the 3 M NaOH caustic leach (and washes) are approximately an order of magnitude greater than in the 0.25 M NaOH oxidative leach (and washes). However, such a variance in the Na concentrations in the leach solutions is not reflected in oxidative leach versus caustic leach analytical data for SX-101-5 and SY-102-5. Here, the Na concentrations in both cases are typical for those seen in the caustic leach, not the oxidative leach. Furthermore, each of the individual metal components is almost identical for both the caustic leach and the low hydroxide oxidative leach. This result indicates that either the caustic leach solution was sampled twice for ICP-AES analysis, or it was analyzed in duplicate; in either case, the conclusion is that the component concentrations assigned to the oxidative leach solution are not those of the actual oxidative leach solution. This explains in part the magnitude and direction of the discrepancy in the mass balance for Cr (as Cr is expected to be present in higher concentrations in oxidative leach than in the caustic leach), the discrepancies in the chromate/chromium ratios, and the magnitude and extent of mass balance discrepancy for Al (expected to be present in lower concentrations in the lower hydroxide oxidative leach than in the caustic leach).

Given the questionable nature of the oxidative leach values for SX-101-5 and SY-102-5, an alternative analysis for these tests was explored. In the original approach, the measured masses from each leach solution and the residual solids were summed to obtain the total mass. The percent removed was simply the mass removed by an individual leach solution divided by the total mass removed, expressed as a percentage (Scheme 1). In the alternative analysis, the total amount of each component based on the calculated mass and measured component concentration in the initial test sample was calculated. Next, the mass of each component in the residual solids was calculated. The ratio of the residual to the initial solids was used to determine the percent removal of each component. The amount of each component removed during the caustic leach was then calculated, compared to the total amount removed, and expressed as a percentage; the difference was then assigned to the amount removed during the oxidative leach. This approach is illustrated in Scheme 2. The results obtained by the standard method are reported on the left hand side in Tables 2.3 and 2.5; the results obtained by this method are reported in the right hand side.

Scheme 1: Illustration of Standard Approach for Calculating Component Removals

For each component:

1) $\sum_{i} ([\text{component}]_i \text{ (g/ml)} * \text{volume}_i \text{ (ml)}) + [\text{component}]_{\text{residual solids}} \text{ (g/g)} * \text{mass}_{\text{residual solids}} \text{ (g)}$
$= \text{total component mass (g)}$

2) $\% \text{ component removal in solution}_i = 100 * (\text{mass solution}_i/\text{total component mass})$

Scheme 2: Illustration of Alternative Approach for Calculating Component Removals

For each component:

1) $[\text{component}]_{\text{initial solids}} \text{ (g/g)} * \text{mass}_{\text{initial solids}} \text{ (g)} = \text{initial component mass (g)}$

2) $[\text{component}]_{\text{residual solids}} \text{ (g/g)} * \text{mass}_{\text{residual solids}} \text{ (g)} = \text{residual component mass (g)}$

3) $\% \text{ component removal overall} = 100 * (\text{residual mass/initial component mass})$

4) $[\text{component}]_{\text{caustic leachate}} \text{ (g/ml)} * \text{volume}_{\text{caustic leachate}} \text{ (ml)}$
$= \text{component mass in caustic leachate (g)}$

5) $\% \text{ component removed}_{\text{caustic leach}} = 100 * (\text{mass component}_{\text{caustic leachate}}/\text{initial component mass})$

6) $\% \text{ component removed overall} - \% \text{ component removed}_{\text{caustic leach}}$
$= \% \text{ component removed}_{\text{oxidative leach}}$

Table 2.1. Mass Balances for SX-101-3, 4, 5, 6 and SY-102- 3, 4, 5, 6 Tests

	Mass Balance, %							
Component	**SX-101-3**	**SX-101-4**	**SX-101-5**	**SX-101-6**	**SY-102-3**	**SY-102-4**	**SY-102-5**	**SY-102-6**
Ag	51	52	51	33	97	97	100	103
Al	114	103	226	69	112	121	239	119
As	NA	NA	NA	NA	NA	NA	NA	NA
B	NA	NA	NA	NA	2100	2671	2049	2233
Ba	109	107	119	77	126	131	135	127
Be	NA	NA	NA	NA	NA	NA	NA	NA
Bi	80	77	79	58	112	114	122	120
Ca	117	118	123	73	117	120	121	128
Cd	96	86	119	60	113	112	117	116
Ce	95	105	112	68	NA	NA	NA	NA
Co	NA	NA	NA	NA	NA	NA	NA	NA
Cr	103	100	30	62	115	123	33	106
Cu	65	70	74	56	91	97	113	123
Dy	NA	NA	NA	NA	NA	NA	NA	NA
Eu	NA	NA	NA	NA	NA	NA	NA	NA
Fe	108	106	120	71	113	114	119	121
K	NA	NA	NA	NA	NA	NA	NA	NA
La	93	98	104	58	126	122	120	93
Li	114	113	139	89	110	109	134	153
Mg	162	175	175	127	142	142	149	152
Mn	433	471	476	384	1691	768	680	795
Mo	NA	NA	NA	NA	NA	NA	NA	NA
Na	3808	3972	9496	4532	3677	3933	7059	3479
Nd	95	98	106	63	108	100	108	94
Ni	NA	NA	NA	NA	NA	NA	NA	NA
P	90	205	97	36	96	105	82	110
Pb	195	123	178	82	128	131	163	137
Pd	0	0	0	29	49	66	0	58
Rh	NA	NA	NA	NA	NA	NA	NA	NA
Ru	NA	NA	NA	NA	NA	NA	NA	NA

Table 2.1. (cont'd)

Component	Mass Balance, %							
	SX-101-3	SX-101-4	SX-101-5	SX-101-6	SY-102-3	SY-102-4	SY-102-5	SY-102-6
Sb	NA	NA	NA	NA	NA	NA	NA	NA
Se	NA	NA	NA	NA	NA	NA	NA	NA
Si	166	179	201	171	152	181	169	180
Sn	64	64	61	46	99	91	95	115
Sr	114	111	125	73	122	125	128	127
Te	NA	NA	NA	NA	NA	NA	NA	NA
Th	NA	NA	NA	NA	NA	NA	NA	NA
Ti	NA	NA	NA	NA	102	114	126	131
Tl	NA	NA	NA	NA	NA	NA	NA	NA
U	101	98	110	66	78	62	73	72
V	NA	NA	NA	NA	NA	NA	NA	NA
W	NA	NA	NA	NA	NA	NA	NA	NA
Y	NA	NA	NA	NA	NA	NA	NA	NA
Zn	89	85	42	44	83	91	129	93
Zr	144	154	158	116	396	220	156	406
Pu	115	105	71	63	101	98	108	104

NA = not available.

By performing this analysis, one assumes a mass balance of 100%. In the cases where this is a poor approximation, one can obtain removals during the caustic leach with negative values or with values greater than 100%. In those cases, if over 100% removals were obtained, a value of 100% was used; if negative values were obtained, a value of 0% was assigned.

From the information summarized above, the amount of material removed during the caustic leach can be calculated and compared with the amount of material removed during a subsequent oxidative leach. These amounts are summarized in Tables 2.2 through 2.5. Note that in some instances, rounding to whole numbers for the percentages yields slightly different values for the total than is provided by simple addition of the caustic leach and oxidative leach values. The leach factors using the standard approach are given on the left side, and the alternative leach factors are supplied on the right side in the two sets of values given for SX-101-5 and SY-102-5.

Table 2.2. Percent Removal of Metals from Washed SX-101 Sludge by a) an Initial Caustic Leach, b) a Subsequent Oxidative Alkaline Leach, and c) Total Removed

Component	SX-101-3, % Removed			SX-101-4, % Removed		
	CL	**OL**	**Total**	**CL**	**OL**	**Total**
Ag	0	0	0	0	0	0
Al	79	4	83	79	10	89
As	NA	NA	NA	NA	NA	NA
B	36	61	97	36	61	98
Ba	0	0	0	0	0	0
Be	100	0	100	NA	NA	NA
Bi	0	0	0	0	0	0
Ca	0	0	0	0	6	6
Cd	7	0	7	0	0	0
Ce	0	0	0	0	0	0
Co	NA	NA	NA	NA	NA	NA
Cr	6	82	87	5	89	94
Cu	0	0	0	0	0	0
Dy	0	0	0	0	0	0
Eu	0	100(a)	100(a)	0	100(a)	100(a)
Fe	0	0	0	0	0	0
K	NA	NA	NA	NA	NA	NA
La	0	0	0	0	0	0
Li	0	0	0	0	0	0
Mg	0	0	0	0	0	0
Mn	0	0	0	0	0	0
Mo	NA	NA	NA	NA	NA	NA
Na	83	14	97	81	16	97
Nd	0	0	0	0	0	0
Ni	NA	NA	NA	NA	NA	NA
P	62	0	62	23	63	86
Pb	3	35	38	4	0	4
Pd	NA	NA	NA	NA	NA	NA
Rh	NA	NA	NA	NA	NA	NA
Ru	NA	NA	NA	NA	NA	NA

Table 2.2. (cont'd)

Component	SX-101-3, % Removed			SX-101-4, % Removed		
	CL	OL	Total	CL	OL	Total
Sb	NA	NA	NA	NA	NA	NA
Se	NA	NA	NA	NA	NA	NA
Si	19	27	46	19	32	50
Sn	0	0	0	0	0	0
Sr	0	0	0	0	0	0
Te	NA	NA	NA	NA	NA	NA
Th	0	0	0	0	0	0
Ti	0	0	0	0	0	0
Tl	76	24	100	NA	NA	NA
U	0	0	0	0	0	0
V	NA	NA	NA	0	100	100
W	0	100	100	0	100	100
Y	0	0	0	0	0	0
Zn	0	0	0	0	0	0
Zr	2	8	9	1	8	9
Pu	0	0	0	0	0	0

NA = not available. CL = Caustic Leach. OL = Oxidative Leach. Total = Total Removed

(a) Suspect Data—see text for discussion.

Table 2.3. Percent Removal of Metals from Washed SX-101 Sludge by a) an Initial Oxidative Leach, b) a Subsequent Caustic Leach, and c) Total Removed

Component	SX-101-5, % Removed[(a)]			SX-101-6, % Removed		
	OL	CL	Total	OL	CL	Total
Ag	0/49	0/0	0/49	0	0	0
Al	53/0	44/93	97/93	14	83	97
As	0/NA	100/NA	100/NA	0	100	100
B	95/NA	0/NA	95/NA	97	0	97
Ba	0/0	0/0	0/0	0	0	0
Be	58/NA	42/NA	100/NA	0	100	100
Bi	0/21	0/0	0/21	0	0	0

Table 2.3. (cont'd)

Component	SX-101-5, % Removed			SX-101-6, % Removed		
	OL	CL	Total	OL	CL	Total
Ca	0/0	0/0	0/0	0	0	0
Cd	10/0	11/6	21/6	0	12	12
Ce	0/0	0/0	0/0	0	0	0
Co	NA/NA	NA/NA	NA/NA	NA	NA	NA
Cr	35/81	29/9	65/90	94	3	97
Cu	0/26	0/0	0/26	0	0	0
Dy	0/NA	0/NA	0/NA	0	0	0
Eu	NA/NA	NA/NA	NA/NA	NA	NA	NA
Fe	0/0	0/0	1/0	0	0	0
K	NA/NA	NA/NA	NA/NA	NA	NA	NA
La	0/0	0/0	0/0	0	0	0
Li	0/0	0/0	0/0	0	0	0
Mg	0/0	0/0	0/0	0	0	0
Mn	0/0	0/0	0/0	0	0	0
Mo	NA/NA	NA/NA	NA/NA	NA	NA	NA
Na	54/0	45/0	98/0	15	83	98
Nd	0/0	0/0	0/0	0	0	0
Ni	NA/NA	NA/NA	NA/NA	NA	NA	NA
P	41/43	34/33	75/78	0	44	44
Pb	25/0	22/6	47/6	0	15	15
Pd	NA/NA	NA/NA	NA/NA	100	0	100
Rh	NA/NA	NA/NA	NA/NA	NA	NA	NA
Ru	NA/NA	NA/NA	NA/NA	NA	NA	NA
Sb	NA/NA	NA/NA	NA/NA	NA	NA	NA
Se	NA/NA	NA/NA	NA/NA	0	0	0
Si	29/0	26/10	55/10	41	25	67
Sn	0/39	0/0	0/39	0	0	0
Sr	0/0	0/0	0/0	0	0	0
Te	NA/NA	NA/NA	NA/NA	NA	NA	NA
Th	0/NA	0/NA	0/NA	0	0	0
Ti	0/NA	0/NA	0/NA	0	0	0
Tl	0/NA	100/NA	100/NA	0	0	0

Table 2.3. (cont'd)

Component	SX-101-5, % Removed			SX-101-6, % Removed		
	OL	**CL**	**Total**	**OL**	**CL**	**Total**
U	0/0	0/0	0/0	0	0	0
V	NA/NA	NA/NA	NA/NA	NA	NA	NA
W	NA/NA	NA/NA	NA/NA	NA	NA	NA
Y	0/NA	0/NA	0/NA	0	0	0
Zn	0/58	0/0	0/58	0	0	0
Zr	2/0	2/0	4/0	8	2	10
Pu	0/29(b)	1/1(b)	1/30(b)	0(b)	3(b)	3(b)

NA = not available. CL = Caustic Leach. OL = Oxidative Leach. Total = Total Removed

(a) Left side of / calculated with the standard method; right side of / calculated by the following alternative method: OL% removed = 100*[Feed - (Residue+Caustic Leachate)]/Feed—see text in Section 2 for further discussion.

(b) Suspect Data—see text for discussion.

Table 2.4. Percent Removal of Metals from Washed SY-102 Sludge by a) an Initial Caustic Leach, b) a Subsequent Oxidative Alkaline Leach, and c) Total Removed

Component	SY-102-3, % Removed			SY-102-4, % Removed		
	CL	**OL**	**Total**	**CL**	**OL**	**Total**
Ag	0	0	0	0	0	0
Al	72	5	76	69	9	78
As	NA	NA	NA	NA	NA	NA
B	37	60	97	30	70	100
Ba	0	0	0	0	0	0
Be	100	0	100	100	0	100
Bi	2	0	2	2	0	2
Ca	0	0	0	0	0	0
Cd	0	0	0	0	0	0
Ce	0	0	0	0	0	0
Co	NA	NA	NA	NA	NA	NA
Cr	4	76	80	4	91	95
Cu	0	0	0	0	0	0
Dy	0	0	0	0	0	0
Eu	0	100(a)	100(a)	0	100(a)	100(a)

Table 2.4. (cont'd)

Component	SY-102-3, % Removed			SY-102-4, % Removed		
	CL	**OL**	**Total**	**CL**	**OL**	**Total**
Fe	0	0	0	0	0	0
K	NA	NA	NA	NA	NA	NA
La	0	0	0	0	0	0
Li	0	0	0	0	0	0
Mg	0	0	0	0	0	0
Mn	0	63	63	0	0	0
Mo	NA	NA	NA	NA	NA	NA
Na	82	15	97	78	19	97
Nd	0	0	0	0	0	0
Ni	NA	NA	NA	NA	NA	NA
P	17	20	37	16	11	27
Pb	14	0	14	14	0	14
Pd	0	100	100	0	100	100
Rh	NA	NA	NA	NA	NA	NA
Ru	NA	NA	NA	NA	NA	NA
Sb	NA	NA	NA	NA	NA	NA
Se	NA	NA	NA	0	100	100
Si	15	17	31	13	23	36
Sn	0	0	0	0	0	0
Sr	0	0	0	0	0	0
Te	NA	NA	NA	NA	NA	NA
Th	0	0	0	0	0	0
Ti	0	0	0	0	0	0
Tl	0	100	100	NA	NA	NA
U	0	0	0	0	0	0
V	0	100	100	0	100	100
W	54	46	100	43	57	100
Y	0	0	0	0	0	0
Zn	0	0	0	0	0	0
Zr	1	8	9	1	21	22
Pu	0	0	0	0	0	0

NA = not available. CL = Caustic Leach. OL = Oxidative Leach. Total = Total Removed

(a) Suspect Data—see text for discussion.

Table 2.5. Percent Removal of Metals from Washed SY-102 Sludge by a) an Initial Oxidative Leach, b) a Subsequent Caustic Leach, and c) Total Removed

Component	SY-102-5, % Removed[(a)]			SY-102-6, % Removed		
	OL	**CL**	**Total**	**OL**	**CL**	**Total**
Ag	0/0	0/0	0/0	5	0	5
Al	53/0	42/87	94/87	5	84	89
As	NA/NA	NA/NA	NA/NA	NA	NA	NA
B	54/0	43/38	97/38	56	39	95
Ba	0/0	0/0	0/0	0	0	0
Be	30/NA	24/NA	54/NA	0	25	25
Bi	3/0	2/0	5/0	0	1	1
Ca	0/0	0/0	0/0	1	0	1
Cd	2/0	2/0	4/0	0	1	1
Ce	0/NA	0/NA	0/NA	0	0	0
Co	NA/NA	NA/NA	NA/NA	NA	NA	NA
Cr	42/81	33/11	75/92	90	6	96
Cu	0/0	0/0	0/0	0	0	0
Dy	0/NA	0/NA	0/NA	0	0	0
Eu	NA/NA	NA/NA	NA/NA	100	0	100
Fe	0/0	0/0	0/0	0	0	0
K	NA/NA	NA/NA	NA/NA	NA	NA	NA
La	0/0	0/0	0/0	0	0	0
Li	0/0	0/0	0/0	0	0	0
Mg	0/0	0/0	0/0	0	0	0
Mn	0/0	0/0	0/0	0	0	0
Mo	NA/NA	NA/NA	NA/NA	100	0	100
Na	54/0	43/0	98/0	14	80	95
Nd	0/0	0/0	0/0	0	0	0
Ni	NA/NA	NA/NA	NA/NA	NA	NA	NA
P	11/27	9/7	19/34	13	6	19
Pb	17/0	14/0	31/0	0	16	16
Pd	NA/100	NA/0	NA/100	100	0	100
Rh	NA/NA	NA/NA	NA/NA	100	0	100
Ru	NA/NA	NA/NA	NA/NA	100	0	100

Table 2.5. (cont'd)

Component	SY-102-5, % Removed			SY-102-6, % Removed		
	OL	**CL**	**Total**	**OL**	**CL**	**Total**
Sb	NA/NA	NA/NA	NA/NA	NA	NA	NA
Se	NA/NA	NA/NA	NA/NA	100	0	100
Si	17/0	14/0	31/0	16	12	28
Sn	0/5	0/0	0/5	0	0	0
Sr	0/0	0/0	0/0	0	0	0
Te	NA/NA	NA/NA	NA/NA	NA	NA	NA
Th	0/NA	0/NA	0/NA	0	0	0
Ti	0/0	0/0	0/0	0	0	0
Tl	NA/NA	NA/NA	NA/NA	100	0	100
U	0/27	0/0	0/27	0	0	0
V	NA/NA	NA/NA	NA/NA	100	0	100
W	55/NA	45/NA	100/NA	71	29	100
Y	0/NA	0/NA	0/NA	0	0	0
Zn	24/2	19/25	43/27	0	0	0
Zr	5/0	4/0	9/0	10	0	10
Pu	0/0	0/0	0/0	0	0	0

NA = not available. CL = Caustic Leach. OL = Oxidative Leach. Total = Total Removed

(a) Left side of / calculated with the standard method; right side of / calculated by the following alternative method: OL% removed = 100*[Feed - (Residue+Caustic Leachate)]/Feed—see text in Section 2 for further discussion.

As noted in the above-mentioned report on oxidative alkaline leaching of these sludges, the major components removed in this process were Al and Cr. However, the steps at which such removal occurs varied distinctly, as shown in Tables 2.6 and 2.7.

Table 2.6. Summary of Al and Cr Leach Behavior with SX-101 Washed Sludges

Component	SX-101-3, % Removed			SX-101-4, % Removed		
	CL	OL	Total	CL	OL	Total
Cr	6	82	87	5	89	94
Al	79	4	83	79	10	89
Component	SX-101-5, % Removed(a)			SX-101-6, % Removed		
	OL	CL	Total	OL	CL	Total
Cr	35/81	29/9	65/90	94	3	97
Al	53/0	44/93	97/93	14	83	97

(a) Left side of / calculated with the standard method; right side of / calculated with the following alternative method: OL% removed = 100*[Feed - (Residue+Caustic Leachate)]/Feed—see text in Section 2 for further discussion.

Table 2.7. Summary of Al and Cr Leach Behavior with SY-102 Washed Sludges

Component	SY-102-3, % Removed			SY-102-4, % Removed		
	CL	OL	Total	CL	OL	Total
Cr	4	76	80	4	91	95
Al	72	5	76	69	9	78
Component	SY-102-5, % Removed(a)			SY-102-6, % Removed		
	OL	CL	Total	OL	CL	Total
Cr	42/81	33/11	75/92	90	6	96
Al	53/0	42/87	94/87	5	84	89

(a) Left side of / calculated with the standard method; right side of / calculated with the following alternative method: OL% removed = 100*[Feed - (Residue+Caustic Leachate)]/Feed—see text in Section 2 for further discussion.

As expected with these 8-hour contact times, little Cr is removed by simple caustic leaching, with the bulk of the Cr being removed by oxidative alkaline leaching. Two exceptions are noted, the SY-102-5 and SX-101-5 tests; these exceptions have been discussed both above and in a previous report (Rapko et al. 2004), although it should be noted that in the alternative analysis, these exceptions again conform to the general trends observed. However, consistent with the rapid kinetic dissolution of identified Al-containing phases such as gibbsite (Rapko et al. 2004) in these washed sludges, if the initial leach is performed at high initial free hydroxide, the majority of the dissolved Al occurs during the initial leach. The slight additional amounts of dissolved Al found in subsequent oxidative alkaline leaching could be caused by several factors. For example, some of the Al could be incorporated into primarily Cr-containing phases and so not be in contact with the leachate solution until the extensive Cr removal found for oxidative alkaline leaching occurs. Alternatively, some material could have reprecipitated from a supersaturated leachate solution or have reprecipitated from the interstitial liquid when the hydroxide and ionic strength are dropped precipitously by contact with a wash solution. The unusual behavior of the -5 tests with respect to Al removal has already been commented upon above.

With simple caustic leaching, the effective removal of Al without adding Mn that results from oxidative alkaline leaching causes a substantial decrease in the mass of the sludge. Table 2.8 summarizes the initial masses used in these experiments as well as the calculated residual masses that would result after the initial leaching. The fraction of mass lost in the two tests generally is consistent, with only about 34% of the initial mass of dried solids remaining after a simple initial caustic leach for SX-101 and about 52% of the initial mass of dried solids remaining for SY-102. When the initial leach is a lower hydroxide oxidative leach with permanganate, the lesser removals of Al, coupled with the manganese replacement of Cr during oxidative leaching, lead to larger fractions of residual mass after the first leach.

To perform the analysis summarized in Table 2.8, the added mass caused by added Na as well as Na and Mn in the caustic leach and the oxidative leach, respectively, must be taken into account. This was done by assuming that the Na and Mn concentrations after an initial caustic leach maintained the same Na/Fe and Mn/Fe ratios as in the initial washed sludge solids. During an initial oxidative leach, it is only assumed that the Na/Fe ratio is maintained. In essence, this assumes that a washing of added Na equal to that of the initial washed solids after each leach is possible and that no Mn was removed by a simple caustic leach.

Table 2.8. Initial Masses and Calculated Final Masses after the Initial Leach

Test	Initial Leach Conditions	Initial Mass (g dried solids)	Final Mass (g dried solids)[(a)]
SX-101-3	3 M NaOH, 85°C	1.31	0.45
SX-101-4	3 M NaOH, 85°C	1.16	0.39
SX-101-5	0.25M NaOH, 30°C, 1.1 eq MnO_4^-	0.93	0.60/0.55
SX-101-6	0.25M NaOH, 85°C, 1.1 eq MnO_4^-	1.07	0.40
SY-102-3	3 M NaOH, 85°C	1.21	0.60
SY-102-4	3 M NaOH, 85°C	1.20	0.65
SY-102-5	0.25M NaOH, 30°C, 1.1 eq MnO_4^-	1.18	0.79/0.70
SY-102-6	0.25M NaOH, 85°C, 1.1 eq MnO_4^-	1.24	0.84

(a) Left hand column calculated with the standard method; right hand column calculated with the following alternative method: OL% removed = 100*[Feed - (Residue+Caustic Leachate)]/Feed—see text in Section 2 for further discussion.

The ultimate analysis of the impact of a simple caustic leach is to evaluate the consequences of such a leach on the capability to incorporate the leached materials into an IHLW form. Such a calculation was performed as described earlier (Rapko et al. 2004), and the results are summarized in Table 2.9.

The results are much as one might expect as to how much of the sludge can be loaded into IHLW given that the washed sludges are limited by their high Cr concentrations: little to no decrease in the glass volume will result from a simple caustic leach versus that obtainable through simple sludge washing. The slight decrease in IHLW by simple caustic leaching with SX-101 is comparable to the amount of Cr removed (5%) and, again, Cr is the glass-loading limiting component. The results for SY-102 actually suggest a slight increase in IHLW following a simple caustic leach, which is unreasonable. This result is likely an experimental artifact related to either analytical uncertainties or a flawed assumption that each aliquot of washed sludge suspension used to introduce the test material was identical in sludge composition and in the weight percent insoluble solids concentration.

Table 2.9. Calculated Effectiveness of Caustic Leaching on IHLW Volumes

	Units of Glass Produced/Unit Sludge pre-Leach Treatment (waste limiting component/condition)		
	TS-1.1[(a)]	**Current**	**Expanded**
SX-101 washed	15.0(Cr_2O_3 = 0.5)	15.0(Cr_2O_3 = 0.5)	7.5(Cr_2O_3 = 1.0)
SX-101-3 caustic leached	14.7(Cr_2O_3 = 0.5)	14.7(Cr_2O_3 = 0.5)	7.3(Cr_2O_3 = 1.0)
SX-101-4 caustic leached	14.4(Cr_2O_3 = 0.5)	14.4(Cr_2O_3 = 0.5)	7.2(Cr_2O_3 = 1.0)
SX-101-5 ox leached	3.7(Al_2O_3 = 11)	4.8(Al_2O_3 = 8.5)	2.7(Al_2O_3 = 15)
SX-101-5 ox leached (alt)	3.5(Al_2O_3 = 11)	4.6(Al_2O_3 = 8.5)	2.6(Al_2O_3 = 15)
SX-101-6 ox leached	2.0(Al_2O_3 = 11)	2.6(Al_2O_3 = 8.5)	1.5(Al_2O_3 = 15)
SY-102 washed	21.3(Cr_2O_3 = 0.5)	21.3(Cr_2O_3 = 0.5)	10.7(Cr_2O_3 = 1.0)
SY-102-3 caustic leached	23.7(Cr_2O_3 = 0.5)	23.7(Cr_2O_3 = 0.5)	11.8(Cr_2O_3 = 1.0)
SY-102-4 caustic leached	25.3(Cr_2O_3 = 0.5)	25.3(Cr_2O_3 = 0.5)	12.6(Cr_2O_3 = 1.0)
SY-102-5 ox leached	3.5(Cr_2O_3 = 0.5)	3.8(Al_2O_3 = 8.5)	2.5(T1%=950)[(b)]
SY-102-5 ox leached (alt)	3.5(Cr_2O_3 = 0.5)	3.5(Cr_2O_3 = 0.5)	2.4(T1%=950)[(b)]
SY-102-6 ox leached	2.8(Al_2O_3 = 11)	3.7(Al_2O_3 = 8.5)	2.2(T1%=950)[(b)]
(a) Technical Specification 1.1 of the WTP contract (DOE-ORP 2000). (b) Temperature at which the equilibrium volume in glass is 1% (on a quenched glass basis).			

Unlike the response to an initial caustic leach, performing an initial oxidative leach reaps the bulk of the benefits for reducing the amount of IHLW. In the optimum sequence of an initial 85°C oxidative leach, almost an order of magnitude reduction in IHLW can be achieved, and the limiting condition shifts from Cr to Al or, in selected cases, to a glass property constraint. Even in the 25°C oxidative leach, the oxidative leach is effective at removing Cr as the limiting component in most of the IHLW loading conditions examined. In short, despite that large amount of sludge mass that is removed from the sludge solids and transferred to the low activity waste (LAW) stream by either an initial oxidative leach or an initial caustic leach, it appears that little to no decrease in the amount of IHLW will result from performing a simple caustic leach on washed SX-101 and SY-102 sludge solids. Rather, an initial oxidative leach will reap most of the benefits observed by a sequential oxidative alkaline leach and caustic leach no matter what the order of the leach sequence.

Also worth noting in Tables 2.2 through 2.5 is the minimal Pu dissolution either in the simple caustic leach or in the oxidative leach. It may be that oxidative leaching did not dissolve Pu because of the low hydroxide concentration used in the oxidative leach. Budantseva and co-workers (Budantseva et al. 1997) have measured the oxidation potential of Pu(IV) to Pu(V) as a function of temperature and hydroxide concentration and have shown that the Pu(IV, V) redox potential increases markedly as the solution hydroxide concentration is decreased from about 7 M to 1 M hydroxide. Therefore, one explanation for poor Pu dissolution is that under the low hydroxide concentration of the oxidative leach, the Pu(IV, V) redox potential has increased to the point where oxidation by permanganate is not strongly favored thermodynamically. However, it should be noted that if the alternative analysis is used for SX-101-5, substantial Pu removal during the oxidative leach is indicated. But because of the lack of removal in SX-101-6, in which the same sequence is used but at a higher oxidative leach temperature, it seems more likely that this reflects a breakdown in the assumption of a 100% mass balance rather than any remarkable enhancement in Pu dissolution under these conditions. On the other hand, this leach behavior may be due to Pu being oxidized in all cases but reacting differently with the Mn oxides formed from permanganate reduction. The sorption of Pu onto Mn oxides produced by permanganate reduction has been reported previously (Peretrukin et Al. 1998). In any event, the system is probably complex, and, as with most complex systems, a variety of kinetic and thermodynamic factors are involved.

Finally, we can consider these leach data in light of the impact of oxidative alkaline leaching on problematic constituents with respect to the waste loading in IHLW. Table 2.10 describes the major problematic components that limit waste oxide loading.

If we limit the analysis to the question of how added permanganate may impact alkaline leaching, simple inspection of the list reveals that many of the components exist in their only stable, non-zero, oxidation states in aerated aqueous solution. This list includes the alkali (Na and K) and alkaline earth (Ca, Mg, Ba) metals. Therefore, speciation changes caused by oxidation by permanganate are not possible, and so no effect from any added permanganate can be expected. Other metals that only have non-accessible oxidation states include Cd, Zr, F, Ti and Th. This leaves Fe(III), U(IV), Ni(II), Pb(II), Bi(III), P(V), Cr(III), S(VI), Ag(I), Rh(III), Ru(III), and Pd(II) for further consideration. To facilitate this discussion, we will avoid all consideration of complexants, with the exception of hydroxide, and their possible impact on the oxidation/reduction potential. As noted previously, the primary reaction for permanganate will be reduction to MnO_2, which has a standard reduction potential of 0.58 V. Therefore, reductions with a standard reduction potential significantly greater than 0.58 V will not be oxidized by permanganate.

With the exception of Fe(VI) and Rh(IV), and likely Pd(IV), Ag(II) and Bi(V) as well, all of the components listed in Table 2.11 should prefer their more oxidized forms thermodynamically. This indicates that, besides the target of the permanganate oxidation, Cr, only the leaching behavior of U, Ni, Pb, and perhaps Ru and Pd remain of concern.

The data shown above indicates that no enhanced leaching of uranium occurs in the presence of permanganate, a result consistent with previous leaching and oxidative leaching studies. Examining the leaching behavior of Ni is problematic since Ni crucibles are used for the KOH fusions used to dissolve the solids before acidic dissolution and analysis. The remaining elements are not discussed in the oxidative alkaline leach literature with the exception of Pb and Pd above and Pb in an earlier report (Rapko 1998). As discussed earlier, the Pd data must be considered suspect because of the poor mass balances observed. The removal of Pb also shows mass balances that deviate from the ideal, particularly with one of the SX-101 tests, sufficiently so as to question the values calculated for the observed removals in the SX-101 and SY-102 tests. In addition, that SX-101 test is the only one where any dissolution during oxidative leaching was observed. In the earlier 1996 report, however, some enhanced in Pb dissolution at high hydroxide in the presence of permanganate is observed, with 53% of the Pb removed as opposed to 0% in a Ar-atmosphere blank, but, all in all, the results with respect to any enhanced Pb dissolution by permanganate treatment are ambiguous. To summarize, with the exception of Cr, none of the high or medium impact components will have their dissolution enhanced by the presence of permanganate, and data with respect to several of the low impact components is either lacking or contradictory.

Table 2.10. Candidate Species for Limiting Waste Loading in IHLW[(a)]

Component	Wt% (TS 1.1 Limit)	Likelihood of Waste-Loading Impact
Fe_2O_3	12.5	H
Al_2O_3	11	H
Na_2O+K_2O	15	M (inefficient washing)
ZrO_2	10	M
UO_2	8	L
ThO_2	4	H
CaO	7	L
MgO	5	L
BaO	4	L
CdO	3	L
NiO	3	M
PbO	1	L
TiO_2	1	L
Bi_2O_3	2	H (2% is hit often, > is tolerable in glass)
P_2O_5	3	M
F	1.7	M
$Al_2O_3+ZrO_2$	14	L
$Al_2O_3+ZrO_2+Fe_2O_3$	21	H
MgO+CaO	8	L
Cr_2O_3	0.5	H
SO_3	0.5	H
Ag_2O	0.25	L
$Rh_2O_3+Ru_2O_3+PdO$	0.25	L

H = High Probability, M = Medium Probability, L = Low Probability

(a) Taken from Office of River Protection (ORP). 2000. *Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant*. Contract Number: DE-AC27-01RV14136, as amended, U.S. Department of Energy, Richland, WA.

Table 2.11. Reduction Potential for Problematic Elements Affecting IHLW in Neutral or Alkaline Solution(a)

Oxidized Species	**Reduced Species**	**Reduction Potential (V vs NHE)**	**Comments**
Fe(VI)	Fe(III)	+0.72	
UO_2(II)	UO_2(I)	+0.062	
Ni(IV)	Ni(II)	+0.49	
Pb(IV)	Pb(II)	+0.28	
Bi(V)	Bi(III)	Not found	Bi(V) strong oxidant in acidic solution; $Bi_2O_4 + 4H^+ + 2e^- \rightarrow 2BiO^+ + 2H_2O$ is 1.59 V
P(V)	P(III)	-1.05	
Cr(VI)	Cr(III)	-0.12	
S(VI)	S(IV)	-0.92	
Ag(II)	Ag(I)	Not found	+1.98 V in acidic solution
Rh(IV)	Rh(III)	1.43	
Ru(IV)	Ru(III)	Not found	0.858 V in acidic solution
Pd(IV)	Pd(II)	Not found	1.29 V in acidic chloride solution
Mn(VII)	Mn(IV)	0.58	1.70 V in acidic solution
O_2	O_2^-	-0.56	

(a) Taken from Table 8.6 in Huheey (1978) and from Weast (1974, pp. D-120 through D-122).

3.0 Review of Caustic Leaching Data for Sulfur Removal

A number of caustic leaching and washing experiments have been performed using actual sludges from the Hanford tanks. Most of these studies were focused on determining the distribution of important sludge components (especially Al, Cr, and P) between the solid and liquid phases under a standard testing protocol. Several studies investigated the effects of parameters such as temperature, caustic concentration, and leaching time. Only a small subset of these investigations evaluated sulfur and/or sulfate distributions. This was primarily because of lack of the appropriate resources to analyze for sulfur in the sludge solids. In this section, we review the information regarding sulfur behavior that was generated during leaching tests with actual tank waste.

Measuring the total sulfur (e.g., by ICP-AES) in both the leached solids and in the leachate and washing solutions would be the best way to determine the distribution of sulfur during the caustic leaching of Hanford tank sludge solids. Unfortunately, such data were not generated during most of the caustic leaching tests performed with actual Hanford tank wastes. Thus, the following references contain no useful data concerning the distribution of sulfur or sulfate during caustic leaching (Beahm et al. 1997; Lumetta and Rapko 1994; Lumetta et al. 1996a, 1996b, 1997, 1998b, 2001, 2002; Rapko, Lumetta, and Wagner 1995; Temer and Villarreal 1997).

Hunt, Collins, and Chase (1998) performed caustic leaching experiments on Hanford Tank S-101 sludge in which total sulfur was determined in the caustic-leached solids. In this case, total sulfur was determined by inductively coupled plasma-mass spectrometry (ICP-MS) following a suitable digestion to dissolve the solids. Sulfate ion in the corresponding washing and leaching solutions was determined by ion chromatography (IC). This is the only example in which the total sulfur content in the leached solids was assessed. Following an initial washing of the sludge with dilute hydroxide solution, sub-samples of the washed sludge solids were leached for 168 hours under one of the following conditions: 1 M NaOH at 70°C, 1 M NaOH at 95°C, 3 M NaOH at 70°C, and 3 M NaOH at 95°C. In all cases, the sulfur in the leached solids was below the detection limit.

Temer and Villarreal (1995, 1996) performed IC analyses to determine sulfate in leached solids after the solids had been dissolved by acid digestion. These tests followed a general protocol in which the sludge solids were washed with inhibited water (0.01 M NaOH/0.01 M $NaNO_2$) followed by two successive caustic leaching steps (3.2 M NaOH for the first, 3.0 M NaOH for the second). Each leaching step was performed for 5 hours at 100°C. The leached solids were then washed with inhibited water. Table 3.1 summarizes the sulfate behavior in these experiments.

These data indicate variable behavior for sulfate in the different tank sludges. Good sulfate removal was observed for sludges from Tanks C-107, C-108, and TY-104. The initial concentrations of sulfate in these sludges were determined to be 0.013, 0.014, and 0.007 g/g dry sludge solids, respectively. Definitive values for sulfate removal from T-104 and T-107 sludges could not be determined because the residual sulfate was below the detection limit. However, for these two tanks, the removal was ~70% or higher. The initial sulfate concentrations in the T-104 and T-107 sludges were 0.012 and 0.028 g/g dry sludge solids, respectively. Only about 50% removal of sulfate was achieved for B-202 and S-104 sludges, which contained 0.013 and 0.004 g sulfate/g dried sludge solids, respectively.

Table 3.1. Summary of Sulfate Data from Caustic Leaching Experiments Performed at Los Alamos National Laboratory (LANL)

Tank	Sulfate Removed, %	Mass Recovery[(a)]	Reference
B-202	48	90%	Temer and Villarreal 1995
C-107	89	104%	Temer and Villarreal 1996
C-108	95	94%	Temer and Villarreal 1995
S-104	50	87%	Temer and Villarreal 1995
T-104	68 to 91	119%	Temer and Villarreal 1995
T-107	79 to 93	71%	Temer and Villarreal 1995
TY-104	94	121%	Temer and Villarreal 1996

(a) This represents the mass balance between the sulfate determined to be present in the as-received sludge and that found in the leaching and washing solutions and the leached solids.

Because of the relatively limited data set, sulfate removal should be correlated with waste type with caution. For informational purposes, the primary waste types contained in these tanks are listed in Table 3.2 along with a qualitative indication of sulfate removal based on the limited data listed in Table 3.1. It should be noted that like S-104, Tank S-101 contains reduction/oxidation (REDOX) waste, but the results of Hunt, Collins, and Chase (1998) indicated essentially complete removal of sulfate from S-101 sludge upon extended (one week) leaching.

Table 3.2. Primary Waste Types in Sludges Examined at LANL

Tank	Primary Waste	Secondary Waste	Relative SO_4^{2-} Removal
B-202	224	--	Poor
C-107	1C	CW	Good
C-108	TBP-F	1C	Good
S-104	R	--	Poor
T-104	1C	--	Fair to Good
T-107	1C	CW	Fair to Good
TY-104	TBP	1C-F	Good

224 = lanthanum fluoride decontamination cycle waste
1C = first bismuth phosphate decontamination cycle waste
CW = cladding waste
F = ferrocyanide scavenged waste
R = high-level reduction oxidation (REDOX) process waste
TBP = tri-butylphosphate process waste

In other work conducted at Oak Ridge National Laboratory (ORNL), the partitioning of sulfate was determined on leached and untreated Hanford Tank S-104 sludge by performing a water leach of the solids and determining sulfate in the water leachate using IC (Spencer, Chase, and Egan 1998). Although this methodology does not give definitive results because it cannot account for water-insoluble sulfur-containing species in the sludge solids, some useful information as to whether sulfate metathesis occurs during caustic leaching can be gleaned from the data. The key indicator for sulfate metathesis is the percent mass recovery, which is defined as the ratio of the sulfate determined by IC in the caustic leachate plus a water leach of the treated sludge solids to that determined in a water leach of the untreated sludge only. That is, if the sulfate mass recovery from caustic leaching solutions significantly exceeded that found by water leaching of the untreated sludge solids, this would suggest that some sulfate in the solids was metathesized to a more soluble form. Table 3.3 summarizes the sulfate mass recovery data reported by Spencer, Chase, and Egan (1998).

Table 3.3. Sulfate Mass Recovery in S-104 Caustic Leaching Tests as Determined by IC [(a)]

[NaOH]	T, °C	Soln-to-Solids, mL/g	Leaching Time, h	Sulfate Recovery, %[(b)]
3.8	67	9	4	98
3.8	67	9	24	59
4	70	6	21	145
4	70	12	21	158

(a) Data from Spencer, Chase, and Egan (1998).

(b) Sulfate Recovery = $100(S_{leach} + S_{residue})/S_{initial}$

where S_{leach} = amount of sulfate in the caustic leaching solution

$S_{residue}$ = amount of sulfate in a water leach of the leached solids

$S_{initial}$ = amount of sulfate in a water leach of the as-received sludge.

The results are mixed. When leached with 3.8 M NaOH at 67 °C, the sulfate mass recovery decreased upon going from 4 to 24 hours of leaching. This suggested that longer leaching times reduced the sulfate removal. However, this result was not supported by the subsequent tests done at 4 M NaOH and 70 °C. In the latter tests, the sulfate mass recovery was greater than 100%, suggesting the metathesis of insoluble sulfates to a more soluble form. The generally observed good removal of sulfate from S-104 in these tests contrasts to that reported by Temer and Villarreal (Table 3.1), but the leaching conditions in the two studies were different, so it may not be appropriate to directly compare the results.

Workers at ORNL also investigated caustic leaching of sludge from the Melton Valley storage tanks at ORNL (Collins et al. 1997). Unfortunately, the method used to determine sulfate is not explicitly given, although reference was given to another ORNL report. In that reference (Keller, Giaquinto, and Meeks 1996), the water leach method is discussed along with two additional sample preparation methods: 1) Parr bomb combustion of the sludge and 2) sodium peroxide/hydroxide fusion of the sludge. It is not clear if either of these methods was used in the Collins et al. (1997) work, so a rigorous interpretation of the results is difficult. Nevertheless, the results are summarized here.

When the Melton Valley sludge was sequentially leached at ambient temperature (3.1 M, 6.4 M, and then 0.16 M NaOH), 105% of sulfate was recovered. This result suggests that no significant increase (or decrease) in the amount of soluble sulfate at ambient temperature was observed and, therefore, no metathesis of metal sulfates with sodium hydroxide occurred. In contrast, when the Melton Valley sludge was leached with 1 M NaOH at 95°C for 4.2 hours, the amount of sulfate recovered in the leachate was only 56%. Similarly, sequential leaching of the Melton Valley sludge at 95°C (3.2 M NaOH for 4 hours; 6.3 M NaOH for 4 hours) resulted in low (30%) sulfate recovery. Low sulfate recovery (24%) was also obtained during leaching 3.2 M NaOH at 95°C for 8 hours. Slightly better recovery (29%) was obtained under similar conditions but at 75°C. These results suggest that leaching at elevated temperature adversely affects sulfate removal from the Melton Valley sludge. It is unknown whether such effects would also occur for Hanford tank sludges.

3.1 Review of Oxidative Leaching Data

The literature concerning oxidative leaching (and associated washing and caustic leaching operations) of Hanford tank sludge was reviewed to discern if any information was available on the distribution behavior of sulfur and/or sulfate. This review revealed no information concerning sulfur and/or sulfate behavior. The documents reviewed in this effort were Lumetta and Swanson (1993); Rapko, Lumetta, and Wagner (1996); Rapko (1998); Rapko et al. (2002), Rapko and Vienna (2002); Rapko et al. (2004).

3.2 Review of Tank Solids Speciation Data

There is a limited body of information regarding specific chemical species present in Hanford tank sludges. This information was summarized and tabulated by Rapko and Lumetta (2000). Very little information is available concerning the sulfur-containing species in the tank sludges. Indeed, only one sulfur-containing phase has been identified in the sludge solids—darapskite [$Na_3NO_3SO_4$-H_2O]—which was identified by X-ray diffraction (XRD) in Tank B-104 sludge. Based on the solubility of sodium nitrate and sodium sulfate, it would be expected that the sulfate in this phase would be readily removed by washing and caustic leaching. Indeed, this phase was not seen in the leached B-104 solids.

Fiskum et al. (2003) reported that Na_3FSO_4 was the dominant salt (57% by mass) formed during evaporative concentration of AZ-102 tank waste supernate. We also reviewed the work by Herting, Cooke, and Warrant (2002) to determine sulfur-containing phases that have been identified in Hanford tank salt cake. The following three sulfate-containing species have been detected in the examined salt cake samples:

- Na_3FSO_4 observed in salt cake from Tanks BY-102 and BY-109
- $Na_3NO_3SO_4$-H_2O observed in salt cake from TX-113
- $Na_6CO_3(SO_4)_2$ (burkeite), observed by XRD in saltcake from Tank S-112.

If present in tank sludges, all of these species should be sufficiently water-soluble that they should be removed during dilute hydroxide washing, and the sulfur therein would be routed to the LAW stream.

3.3 Sources of Sulfur in Hanford Tank Wastes

Given the relatively limited information described above concerning the behavior of sulfur in the caustic leaching and washing process, we examined historical documentation regarding the introduction of sulfur into the Hanford tank wastes. The goals were to 1) determine if information regarding the chemical form of the sulfur could be gleaned from the historical record and 2) provide an assessment of how sulfur would be expected to behave based on this information. Sources of sulfur in Hanford tank waste were investigated using a three-pronged approach: 1) reviewed current literature evaluating sulfate sources and inventory in the tanks, 2) evaluated source documents for other sulfur forms (non-sulfate) that may have been introduced to the tanks, and 3) queried the Tank Waste Information Network System (TWINS) database to compare total sulfur and sulfate results.

Boldt et al. (1999) reported an extensive inventory of sulfate sources and masses introduced into the Hanford tanks. The authors compared sulfate estimated from process records and purchases to estimates developed by Agnew et al. (1996) for tank waste composition. Although these estimates vary, they generally agree within the expected uncertainties of the records available. Tank waste inventories based on analysis were also briefly evaluated; however, these results were deemed to be biased low relative to the inventory/processing basis. The total tank inventory of sulfate is estimated to be 5,000 MT. The sulfate in the tanks came from the following compounds:

- Sulfuric acid (H_2SO_4)
- Ferrous sulfamate ($Fe(NH_2SO_3)_2$)
- Ferrous ammonium sulfamate ($Fe(NH_4)_2(SO_4)_2$)
- Sulfamic acid (NH_2SO_3H)
- Sodium sulfate (Na_2SO_4)
- Sodium bisulfate ($NaHSO_4$).

The ferrous sulfamate and sulfamic acid were considered to convert to sulfate through reactions with sodium nitrite and/or by hydrolysis (Irish and Reas 1957).

The sulfate source evaluation reported by Boldt et al. was not repeated; it is believed to stand well on its own merits. However, several of the resources were evaluated to confirm that the sulfur source types were indeed converted to sulfate. Byproduct and waste-stream processing were briefly reviewed to determine if additional sources of sulfur may have been sent to the tanks. The findings of this evaluation are presented in the following subsections.

3.3.1 Synopsis of Sulfate Origins

The origin of most sulfur is fairly well documented in Hanford plant operations. A summary of processing operations and process input sulfur forms is provided in Table 3.4. Synopses of the processes that created the waste are provided in this section.

3.3.1.1 Bismuth Phosphate Process

Initial plutonium production at Hanford used the bismuth phosphate precipitation process (Cleveland 1979; Lowroski 1955; Beaulieu 1954). Caustic was used to remove aluminum cladding, and the fuel was dissolved in nitric acid. The Pu valence state was adjusted to +4 with nitrite ion. Uranyl ion was complexed with sulfate (provided as sulfuric acid), and the tetravalent Pu was separated from hexavalent U by co-precipitation with bismuth phosphate leaving the U(VI) sulfate complex in solution. The $BiPO_4$, which contained the Pu, was dissolved in nitric acid, and the Pu valence was adjusted to +6 with $NaBiO_3$. The $BiPO_4$ precipitation was repeated, leaving Pu in the aqueous phase. The Pu valence was again adjusted with sodium nitrite and the precipitation repeated. (Note: Sulfuric acid would have presumably been added again for complexation of residual U, although this was not found in the process flowsheets.) The uranium from bismuth sulfate precipitation was reacted with carbonate and allowed to cool in underground storage tanks. The sulfate waste was presumably added to the tanks.

Table 3.4. Historical Sulfur Source Summary in Hanford Tank Wastes

Year	Plant	Operation	Identified Process Feed Containing Sulfur	Waste Storage Tanks
1944–1956	T	Bismuth phosphate precipitation	H_2SO_4	B, BX, BY, C, T, TX, U
1945–1952	B	Bismuth phosphate precipitation	H_2SO_4	B, BX, BY, C, T, TX, U
1952–x		Uranium recovery	$Fe(NH_2SO_3)_2$, NH_2SO_3H (possibly H_2SO_4 and Na_2SO_4)	
1952–1966	REDOX	REDOX process		
1956–1964	PUREX	Al clad U	$Fe(NH_2SO_3)_2$, NH_2SO_3H, $NaSO_4$	
1965–1984	B-plant	Sr purification	$NaHSO_4$, Na_2SO_4	
1965–1982	PUREX	Al and Zr-clad U and thoria	$Fe(NH_2SO_3)_2$, NH_2SO_3H, $NaSO_4$	
1983–1989	PUREX	zircaloy-clad fuel	$Fe(NH_2SO_3)_2$, NH_2SO_3H	AZ-101, AZ-102

3.3.1.2 Uranium Recovery Process

The uranium carbonate was retrieved, dissolved, and contacted with TBP for purification (Beaulieu 1954). There was no indication of the use of sulfur compounds in the recovery process.

3.3.1.3 REDOX Process

The REDOX process used plutonium valence state adjustments to aid in its separation from U using solvent extraction (Cleveland 1979; Lawroski and Levenson 1958). Sodium dichromate was added to dissolved Pu, U, and fission products (FP) to convert the Pu to the +6 oxidation state. Aluminum nitrate was added as a salting agent, and Pu and U were extracted into methyl isobutyl ketone (hexone), separating them from the FP, which remained in the aqueous phase. The U and Pu were stripped with water (containing $Na_2Cr_2O_7$). The Pu and U were concentrated and the extraction repeated. The Pu was then stripped into a solution containing $Al(NO_3)_3$ plus ferrous sulfamate to reduce Pu to +3. Both ferrous sulfamate and sulfamic acid were used as reductants in the REDOX process. After stripping the Pu, the U was stripped with dilute nitric acid.

Waste streams were reported to have been concentrated by evaporation and neutralized. The sulfamate has been assumed to be converted to sulfate through the Pu redox process. There was no indication in the process flowsheet that nitrite was added to complete the sulfamic acid oxidation according to Equation 1; however, the heating and hydrolysis would presumably have completed the conversion. It is probable that the sulfamic acid was converted during evaporation processes. At worst case, there could be $NH_2SO_3^-$ present in the tank waste, although, given the amount of nitrite in the tank waste, this seems unlikely.

$$NH_2SO_3^- + NO_2^- \rightarrow N_2 + SO_4^{2-} + H_2O \tag{3.1}$$

3.3.1.4 PUREX Process

The plutonium-uranium extraction (PUREX) process parallels the REDOX process except that it used TBP in kerosene instead of hexone and nitric acid in place of aluminum nitrate as the salting agent (Irish and Reas 1957; Cleveland 1979; Cooper and Walling 1961). The irradiated fuel was dissolved in nitric acid. Sodium nitrite was added to adjust Pu to the +4 oxidation state, and Pu and U were extracted into TBP/kerosene. An aqueous solution of ferrous sulfamate was used to strip the Pu as Pu^{3+} (a non-extractable form). Plutonium was reoxidized to Pu^{4+} with sodium nitrite (a large excess was required to overcome the sulfamate oxidation reaction) and then re-extracted, stripped with dilute HNO_3, and further purified by ion exchange. Alternative flowsheet processing allowed for the Pu-bearing solvent streams to be contacted with hydroxylamine sulfate (Irish and Reas 1957). The extent of the alternative flowsheet use was not discerned. Associated waste streams and byproducts were evaluated for sulfur materials, and none were found.

Flowsheets incorporating Np and Am purifications were also evaluated and were found not to result in any significant sulfur inventory. Americium recovery flowsheets indicated that low concentrations (0.05 M) of sulfate were present in initial extraction processing feeds (Szuliniski and Curtis 1963).

3.3.1.5 Other Processes Requiring Sulfur or Sulfate

Two other Hanford processes were identified that used sulfur-containing compounds:

- The Cesium Strontium Rare Earth Extraction (CSREX) process was used to purify Cs and Sr from PUREX acid waste (PAW) and PUREX acidified sludge (PAS). This process used sulfate and sulfamate for nitrite suppression. The PAS was prepared by lead sulfate co-precipitation (Richardson 1964).
- The Na_2SO_4 and/or $NaHSO_4$was used as a “sulfate strike” to remove ^{90}Sr fission product at either B-Plant and/or PUREX (Beard and Judson 1961).

In addition, the following indications of the use of sulfur compounds have been reported:

- Ruthenium volatilization was noted as a processing problem during Pu recovery. Research was conducted in 1951 on co-precipitation methods and optimization of ruthenium with copper as a sulfide (Hill and Leitz 1952). There was no evidence found that this process was incorporated into the process flowsheet. It is assumed that waste from this process was from analytical testing and is not a representative form of sulfur in the tanks.
- There was an indication that carbon disulfide was found in one of the U tanks (specific tank and concentration unknown, personal communication, E. Hoppe). A query into TWINS showed no detections for this analyte. Process flowsheet use for this chemical was not found.

- A TWINS query for Endosulfan I, Endosulfan II, and Endosulfan sulfate indicated no detection for these materials. Endosulfans are pesticides.
- A TWINS query for bis(3-tert-butyl-4-hydroxy-6-methyl-phenyl) sulfide (use unknown) was found at 12 μg/g in B-202; no other tank analyses for this analyte were provided in TWINS.

3.3.2 Analysis Comparisons Total Sulfur to Sulfate

A rather simple logic test for the accuracy of the evaluated input forms of sulfur (as sulfate) into the tanks is to compare total sulfur determination to the sulfate determination. If all sulfur was input as (or converted in-tank to) sulfate, than the two results will agree. The comparison will need to be used with caution, however, because the sulfate needs to be in a *water-soluble* form for measurement by IC, and the ICP-measured form of sulfur must not be lost through volatilization or lost by precipitation. Therefore, the comparison should only be used for indication.

The TWINS database was queried for total sulfur analysis determined by ICP-AES and for sulfate-specific determination by IC for all tanks. Tanks and tank samples were randomly selected to compare the total sulfur and sulfate determination. The samples used for the comparison had to meet the following minimum requirements:

- The evaluated results could not have quality control (QC) flags.
- Sulfur and sulfate results had to be above the instrument detection limit.
- Sample results had to be derived from splits of a common sub-sample (determined on the basis of same sample date, riser, depth, etc.).

The IC sulfate results were reported as μg/g or μg/mL sulfate, and the ICP results reported μg/g or μg/mL sulfur. Therefore, for comparison purposes, the IC sulfate results were converted to sulfur results by multiplying by 0.333 (mass fraction of sulfur in sulfate).

Table 3.5 shows the results of this TWINS query. For the most part, the total sulfur concentrations were equivalent (within ± 20%) to the sulfur measured as sulfate in both liquid and solid samples. This indicated the sulfate was the dominant form in the tank waste. There were discrepancies, however, and these are noted in boldface type. The largest variation was associated with the AN-104 solids sample analyzed at Savannah River Technology Center (SRTC) where 43% of the sulfur was sulfate. This may be related to a reporting problem because the AN-104 sample that was analyzed at the Hanford Site Building 222S resulted in good agreement between sulfur and sulfate.

Table 3.5. TWINS Reported Sulfur Data Evaluation

Tank Solids	Sampling Event	Sample ID (TWINS) Sulfur ICP Sulfate IC	Description	Total S (ICP) from Fusion or Acid Dissolution Step (µg/g)	Sulfur as Sulfate (IC) (µg/g)	Ratio Sulfate : Sulfur
A-101	Core 154: 6; Riser 15	S96T004743 S96T004721	Segment lower half, total	9980	10833	1.09
AN-102	2AN-0023; Riser 22, 76 in	S01T000517 S01T000516	Grab sample centrifuged solids	5480	4900	0.89
AN-103	Core 167; 2; Riser 21A	S96T005857 S96T005859	Segment Solids total	1040	590	**0.57**
AN-104	SRTC Composite; riser 22	AN-104 solids	Tank composite, filtered solids	11400	4933	**0.43**
AN-104	Core 163; 1; Riser 10A	S96T005287 S96T005290	Segment solids, total	3470	3733	1.08
AN-105	Core 153: 19; Riser 7B	S96T004446 S96T005326	Segment solids, total	2520	1893	**0.75**
AZ-101	C269: centrifuged solids; riser 15L	S00T000809 S00T000814	Core Composite centrifuged solids	9560	9567	1.00
AZ-102	C310: 19; Riser 59	S03T001676 S03T001675	Segment Solids; centrifuged solids	3060	3933	**1.29**
B107	Core 218: 2; Riser 2	S97T002120 S97T002121	Segment Solids total	56100	54000	0.96
B109	Core 170; 3; Riser 4	S96T005125 S96T005126	Sub-segment C; total	55100	63300	1.15
BX-109	Core 85: 3; Riser 2	S95T000840 S95T000998	Segment Upper half, total	6430	6170	0.96
SX-105	Core 229: 8 Riser 6	S98T001064 S98T001068	Segment Solids: total	13200	14000	1.06

Table 3.5. (cont'd)

Tank	Sampling Event	Sample ID (TWINS) Sulfur ICP Sulfate IC	Description	Total S (ICP) from Fusion or Acid Dissolution Step	Sulfur as Sulfate (IC)	Ratio Sulfate : Sulfur
Liquid				µg/mL	µg/mL	
AN-107	Core 304:01 Riser 19	S02T002156 S02T002155	Drainable liquid	2770	2710	0.98
AW-101	Core 295:8; Riser 22	S01T001986 S01T001986	Subsegment A; centrifuged liquid	974	701	**0.72**
AX-101	Core 228:7 Riser 9G	S98T000652 S98T000652	Drainable liquid, total	1090	1650	**1.51**
AZ-102	C262 CentLiquid 3: Riser 24A	S00T00206 S00T00206	Core composite; centrifuged liquid	6730	6200	0.92
BX-110	Core 198:2; Riser 3	S97T001323 S97T001323	Drainable liquid; total	1740	1003	**0.58**
BY-105	Core 246R:9R; Riser 11B	S98T002821 S98T002821	Drainable liquid; total	1480	1370	0.93
S-102	Core 125:11; Riser 11	S96T000634 S96T000634	Drainable liquid; total	718	1163	**1.62**
S-107	Core 111:1; Riser 16	S95T002601 S95T002601	Drainable liquid; total	1180	927	0.79
SY-103	Core 279:1; Riser 17	S00T001037 S00T001037	Drainable liquid; total	1070	807	**0.75**

3.4 Discussion

Based on the information presented above, it can reasonably be assumed that sulfur is largely present as sulfate ion in the Hanford tank sludges. Because of the limited amount of experimental data concerning the behavior of sulfate during caustic leaching and the rather scattered results indicated by that limited data set, accurate projections of the partitioning behavior of sulfate are currently difficult to make. However, some predictions concerning the behavior of sulfate during caustic leaching can be made based on the known solubilities of sulfate salts.

Removal of water-insoluble sulfate from the HLW sludges by caustic leaching relies upon the metathesis of the insoluble sulfate salt to the soluble sodium sulfate and the corresponding metal hydroxide. For example, the metathesis of lanthanum sulfate is given by the following reaction:

$$La_2(SO_4)_3(s) + 6NaOH(aq) \text{ to } 2La(OH)_3(s) + 3Na_2SO_4(aq)$$

For the metathesis reaction to proceed, the solubility of the metal hydroxide must be less than that of the metal sulfate salt. Table 3.6 is a compilation of the solubility products in water of sulfate salts that can reasonably be postulated to be present in Hanford tank sludges, along with the solubility products for the corresponding hydroxides. This list is not meant to be comprehensive, but should represent the major possible sulfates present. The solubility product data can be used to predict (qualitatively, anyway) the relative effectiveness of caustic leaching at removing sulfate from the tank sludges.

Generally speaking, only Sr^{2+} and Ba^{2+} hold the highest potential to retain sulfate in the HLW sludges. For the other listed metal ions, the hydroxides are less soluble than the sulfates; this is especially true for cations with +3 or greater charge. For these ions, metathesis to sodium sulfate and the corresponding hydroxide is thermodynamically favored. It should be noted that this analysis does not take into account the reaction kinetics. That is, a particular metathesis reaction may be so slow that caustic leaching does not efficiently remove the sulfate. Nevertheless, for the purposes of this discussion, we assume that the reaction kinetics is not a limiting factor.

If one assumes that Sr^{2+} and Ba^{2+} represent the thermodynamic sink for the sulfate in the tank wastes, one can predict the level of sulfate removal by caustic leaching. This prediction should be used with caution because it assumes 1) a simplified system in which all the tank wastes are homogenized, 2) that sulfate is present as simple sulfate salts, 3) that all of the Sr^{2+} and Ba^{2+} is converted to the sulfate salts, and 4) that reaction kinetics are not limiting. With these assumptions in mind, a query was made of the best basis inventory (BBI) in TWINS as to the total inventory of Sr and sulfate in the tank wastes (Ba was not listed in the BBI, so it is assumed to be of little importance). The total BBI (as of February 21, 2005) for sulfate was 3.63×10^6 kg (3.78×10^7 moles). The total BBI for Sr was 3.88×10^4 kg (4.43×10^5 moles). Thus, if all the Sr were converted to the sulfate, 4.43×10^5 moles of sulfate would remain in the HLW solids. On the other hand, 3.73×10^7 moles of sulfate would partition to the LAW stream. This represents ~99% of total sulfate inventory.

Based on the experimental results discussed above, 99% sulfate removal is probably an overly optimistic prediction. Nevertheless, it can be expected that caustic leaching will remove a significant fraction of the sulfate from the Hanford tank sludges. For planning purposes, removal of 70 to 80% of the sulfate from the tank solids is probably a reasonable estimate; however, this value should be verified by caustic leach testing on selected high-sulfate sludges.

Table 3.6. Solubility Products for Sulfate Salts Possibly in Hanford Tank Sludge and the Solubility Products for the Corresponding Hydroxide Salt

Metal Ion	**K_{sp} (Lange's Handbook [Dean 1973])**	
	Sulfate	**Hydroxide**
Al(III)	(a)	1.30E-33
Ba(II)	1.1E-10	5.0E-03
Bi(III)	(b)	4.0E-31
Ca(II)	9.1E-06	5.5E-06
Cr(III)	(a)	6.3E-31
Co(III)	(a)	1.3E-44
Fe(III)	(a)	4.0E-38
La(III)	3.2E-05	2.0E-19
Pb(II)	1.6E-08	1.2E-15
Mg(II)	(a)	1.8E-11
Mn(II)	(a)	1.9E-13
Ni(II)	(a)	2.0E-15
Ag(I)	1.4E-05	2.0E-08
Sr(II)	3.2E-07	(c)
Th(IV)	(a)	4.0E-45
U(VI)	(a)	1.1E-22
Zn(II)	(a)	1.20E-07
Zr(IV)	(a)	

(a) The hydrated sulfates (as would be expected in the Hanford tank wastes) for these ions are water soluble.

(b) Bismuth sulfate is unstable in aqueous media in which it is readily hydrolyzed (Greenwood and Earnshaw 1984, p. 689).

(c) The solubility of $Sr(OH)_2 \cdot 8H_2O$ is 0.9 g/100 mL cold water and 47.7 g/g hot water (Weast 1978, p. B-170).

4.0 On Using Simulants for Sludge Pretreatment Testing

It has occasionally been suggested that simulants should be used for sludge pretreatment testing. In this section, the technical feasibility of using sludge simulants for this purpose is discussed. To do so, one must first draw a distinction between simulants used to mimic physical properties versus those used to mimic chemical properties. Physical simulants would be used to test equipment and as such would primarily be designed to mimic the rheological and particle size properties of the waste. This discussion, is not concerned with physical simulants. Rather, the focus will be on chemical simulants, that is, simulants designed to mimic the partitioning of the chemical components between the various process streams.

Golcar et al. (2000a) performed a comprehensive compilation of Hanford tank waste simulants that have been prepared over the years. Only two sludge simulants were reported that were designed explicitly to mimic the chemical properties of the sludges during pretreatment processing, those from the extensively characterized single-shell tanks B-110 and U-110 (Elmore, Colton, and Jones 1992). Although the elemental composition of these simulated sludges compared favorably with the actual tank waste, the chemical phases identified in the simulants differed significantly from those observed in the actual waste material. Golcar et al. (2000b) described the preparation of an Envelope D sludge simulant. This however, was only meant to be a physical simulant used to test crossflow filtration equipment. Thus, experience with the comparative chemical behavior of sludge simulants to that of actual waste is very limited; and that which is available is not encouraging.

Mimicking the chemical behavior of Hanford tank sludges is a daunting challenge and would likely require an extensive simulant development effort. This is due in large part to the complexity of the sludge waste (in terms of the “ingredients” that formed the sludges) and to the variable “processing” conditions encountered in the various tanks. Indeed, at least 60 different chemical phases have been identified to be present in the Hanford tank sludges (Lumetta, Rapko, and Cho 2003). Based on this, it would be nearly impossible to develop comprehensive simulants, especially given the fact that the relative abundances of these various species are not known and are variable from tank to tank.

It could be argued that the caustic leaching and washing sludge pretreatment process is mainly directed at removing aluminum, chromium, phosphorus, and sulfur from the tank sludge solids, so the simulants would only need to account for the key species containing these elements.(a) To develop a realistic chemical sludge simulant, the following key information is needed:

- the specific chemically-important phases present
- the relative ratios of the different species for a given element (e.g., gibbsite, boehmite, aluminosilicates, etc. for the Al-containing phases)
- the morphology, especially the particle size distribution, of the leach-important phases.

(a) Data from tests with actual waste indicate that phosphorus is generally well removed by caustic leaching. This is also likely for sulfur (see separate discussion in this report), although data are lacking on sulfur. For this reason, these elements are omitted from the subsequent discussion.

The particle size will be an important parameter regarding dissolution kinetics because smaller particles would be expected to dissolve more rapidly than larger particles. This information would be required for each type of sludge waste to be simulated.

In the case of aluminum, the primary phases of interest are gibbsite, boehmite, and aluminosilicates. A number of aluminosilicate phases could exist in the Hanford tank sludges, and the currently available information does not provide detail as to which phases are actually present. Furthermore, the relative ratio of gibbsite/boehmite/aluminosilicates is not well established (and will be variable from tank-to-tank), and little information is available concerning the particle size of individual Al-containing phases. So in essence, further information as outlined above is required for the Al-containing phases in the Hanford sludges to properly design a simulant that would mimic the Al behavior in the actual tank waste.

The situation for Cr is even worse in that relatively little is known about the individual Cr-containing phases that are present in the water-insoluble sludge solids. A number of mixed metal oxides/hydroxides containing Cr have been identified. Examples of these mixed metal phases include $Bi_{38}CrO_{60}$, $Fe(Cr,Fe)_2O_4$ (donathite), $FeCr_2O_4$, Mn_2CrO_4, and amorphous $Al/Cr(OH)_3$ (Lumetta, Rapko, and Cho 2003). Removal of Cr from the mixed transition metal oxides by caustic leaching would be expected to be unfavorable because these phases are essentially insoluble in caustic solution; thus, only the Cr near the surface of the individual particles would be exposed to the leaching medium. On the other hand, Cr removal from the mixed Al/Cr phase would be more favorable because the Al would dissolve, exposing the Cr to the caustic leaching solution. The two “pure” Cr-containing phases identified are Cr(O)OH (grimaldite) and $CrPO_4$. The latter phase would likely be rapidly converted to $Cr(OH)_3$ in the caustic leaching process, which in turn would be expected to oxidize to the more soluble Cr(VI) form fairly rapidly.(a) On the other hand, grimaldite might be more refractory towards caustic leaching.

Accurately reproducing these phases in the laboratory for inclusion into simulants might be quite difficult. Yet it would be very important for Cr in the simulant to closely match the Cr in the actual sludge solids to produce meaningful caustic and oxidative leaching factors for Cr. The difficulty in preparing representative Cr-containing solids is further illustrated by recent experiments on sludge from Tank SX-101 (Rapko et al. 2004). In this work, a Cr-rich phase was examined by scanning electron microscopy (SEM) coupled with elemental mapping using energy-dispersive spectroscopy (EDS). Although this particle contained nearly 50-wt% Cr, the Cr was evenly dispersed with other elements, including Al, Mn, Fe, Si, U, and Pu (Figure 4.1). Similar examination of washed sludge solids from Tank U-108 revealed a broad distribution of Cr across the various solid phases, and they were often intermixed with Al (Rapko and Vienna 2002). Further research into how to synthesize these mixed phases would be required to develop realistic sludge simulants.

(a) Previous work in our laboratory has shown that the Cr in the caustic leachates is primarily Cr(VI); see Lumetta et al. (1998a, 1998b, 2001, 2002) and Rapko et al. (2004).

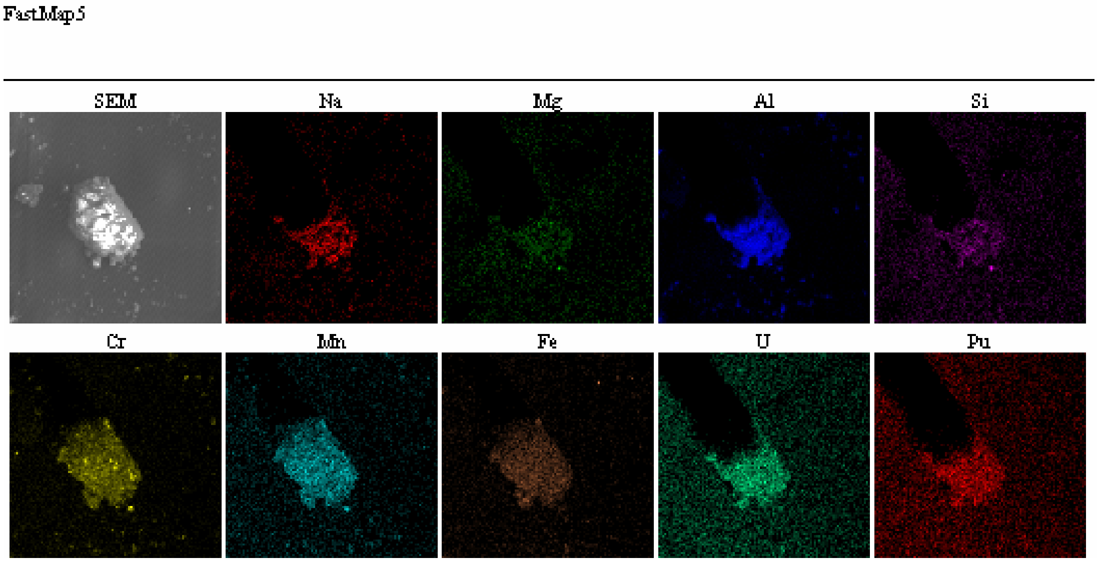

Figure 4.1. SEM/EDS Map of SX-101 Water-Insoluble Sludge Solids (Rapko et al. 2004)

One of the main reasons why it would be desirable to use sludge simulants in pretreatment testing would be to eliminate the radiological hazard associated with actual tank waste. However, in some cases, the behavior of the radioactive components is important. This is especially true for Pu in oxidative leaching tests because of the potential for Pu to be oxidized to the more soluble Pu(VI) form, which in turn could lead to unacceptable concentrations of Pu in the LAW stream. So there might be a need to develop simulants that contain Pu for oxidative leaching tests. The identification of Pu in Figure 4.1 is quite unusual. Typically, the Pu concentration is too low to detect by EDS in such examinations of sludge solids. For the particle shown in Figure 4.1, the Pu concentration is estimated to be ~ 0.4 wt%. This is two orders-of-magnitude higher than the Pu concentration for the bulk SX-101 solids—0.0017 wt% based on radiochemical analysis (Rapko et al. 2004) and assuming the Pu isotopic composition is 93% ^{239}Pu and 7 wt% ^{240}Pu)—so the Pu is particularly concentrated in this phase. Nevertheless, given the overall lack of information regarding the speciation of Pu (and Am) in the sludge solids, using a simulant to mimic the behavior of the TRU elements is not currently feasible.

In conclusion, it would be difficult to produce Hanford tank sludge simulants that would accurately mimic the behavior of the actual waste sludge solids in the caustic leaching and washing process. With some effort, a reasonable simulant to mimic the Al behavior could conceivably be developed because boehmite tends to be the phase that most influences the Al removal by caustic leaching. On the other hand, Cr simulants likely will be difficult to develop. An effort to better characterize the Cr-containing phases would be needed to better assess the feasibility of developing useful Cr simulants. Likewise, the inclusion of Pu in simulants for oxidative leaching tests would be quite challenging because characterization of the Pu species in actual tank sludge solids is difficult due to the low concentration of this element in the wastes.

5.0 Summary and Conclusions

Several disparate activities are described in this report. One activity involves analysis of the impact of the individual steps of caustic leaching and oxidative alkaline leaching at low hydroxide concentrations. Special attention was paid to the analytes Al, Cr, and Pu; the following table summarizes these component's responses to these tests.

Table 5.1. Key Components Leach Response to Sequential Caustic Leaching (CL)/Oxidative Alkaline Leaching (OL)

Test #	Al, % Removed		Cr, % Removed		Pu, % Removed	
	OL	**CL**	**OL**	**CL**	**OL**	**CL**
SX-101-3; CL, then OL, 30°C	4	79	82	6	0	0
SX-101-4; CL, then OL, 85°C	10	79	89	5	0	0
SX-101-5; OL, 30°C, then CL(a)	44/93	53/0	35/81	29/9	0/29(b)	1/1(b)
SX-101-6; OL, 85°C, then CL	14	83	94	3	0	3
SY-102-3; CL, then OL, 30°C	5	72	76	4	0	0
SY-102-4; CL, then OL, 85°C	9	69	91	4	0	0
SY-102-5; OL, 30°C, then CL(a)	53/0	42/87	42/81	33/11	0/0	0/0
SY-102-6; OL, 85°C, then CL	5	84	90	6	0	0

(a) Left hand column calculated with the standard method; right hand column calculated with the following alternative method: OL% removed = 100*[Feed - (Residue+Caustic Leachate)]/Feed—see text in Section 2 for further discussion.
(b) Suspect Data—see text for discussion.

Each step has its benefits for sludges SX-101 and SY-102, which are relatively high in Al and Cr. The oxidative leach step generally achieves the bulk of the benefits in minimizing the immobilized HLW volume per unit sludge, usually removing Cr as the IHLW-loading limiting component and generally leaving Al as the limiting component. The caustic leach step further reduces Al content and either reintroduces Cr as a loading limiting component or leads to other, non-leachable, metals, such as Mn (Rapko et al. 2004), limiting the sludge loading into IHLW.

The chemical properties of the potential IHLW-limiting components were briefly examined to evaluate any potential impact by oxidative alkaline leaching. Few elements are likely to be impacted, with the greatest potential for U, Ni, Pb and perhaps Ru and Pd. An examination of the literature related to caustic and oxidative leaching gave little information to support or refute leaching of these elements. But in general, little impact besides Cr removal and addition of Mn is likely to impact sludge loading in IHLW as a result of permanganate-based oxidative alkaline leaching.

The second subject examined in this work is the behavior of sulfur in the caustic leaching process. An examination of the sources of sulfur in Hanford tank waste, based on both analytical data and process information, led to the conclusion that sulfate is likely to be the predominant, if not exclusive, species in the tank wastes. Since sulfur as sulfate is in its highest oxidation state, it is concluded that oxidative alkaline leaching should have no impact on sulfur speciation or removal. Because of the limited amount of experimental data concerning the behavior of sulfate during caustic leaching and the rather scattered results indicated by that limited data set, it is difficult at present to accurately project the partitioning behavior of sulfate. However, consideration of the solubility products of sulfate salts likely to be present in the Hanford tank sludges suggests that good removal of sulfate via metathesis of these salts to the hydroxide can be expected. For planning purposes, removal of 70 to 80 percent of the sulfate from the tank solids is probably a reasonable estimate; however, this value should be verified by caustic leach testing on selected high-sulfate sludges.

Finally, the question as to whether simulants can be used to explore the response of Hanford tank sludges to alkaline leaching is addressed. Examination of this issue suggests it would be difficult to produce Hanford tank sludge simulants that would accurately mimic the partitioning behavior of the actual waste sludge solids in the caustic leaching and washing process. Realistic Al, Cr, and Pu simulants are of particular interest. Of these, simulating the behavior of Al is probably the most feasible because boehmite tends to be the phase that most influences Al removal by caustic leaching under WTP processing conditions. On the other hand, Cr simulants likely will be difficult to develop. An effort to better characterize the Cr-containing phases would be needed to better assess the feasibility of developing useful Cr simulants. Likewise, the inclusion of Pu in simulants for oxidative leaching tests would be quite challenging because characterization of the Pu species in actual tank sludge solids is difficult because of the low concentration of this element in the wastes. Valuable information could be obtained from the study of simple model systems and how they react under varying leach conditions should the challenges of identifying and synthesizing the appropriate chemical phases be overcome.

Appendix A: Calculated Metal Concentrations (μg/g dry solids) In Sludge After Initial Leaching

Metal	SX-101-3	SX-101-4	SX-101-5	SX-101-6	SY-102-3	SY-102-4	SY-102-5	SY-102-6
Ag	107	110	57	64	505	472	388	373
Al	158847	150572	377845	363980	109902	120449	288608	284599
As	0	0	1884	2521	0	0	0	0
B	3639	4210	115	122	2902	3842	1528	1601
Ba	378	384	221	246	381	365	301	281
Be	0	0	1	1	0	0	25	24
Bi	508	502	271	344	37315	35123	29774	29614
Ca	5914	6172	3337	3399	22504	21403	17291	17811
Cd	203	201	130	127	2021	1866	1524	1531
Ce	1241	1406	781	816	654	472	434	389
Co	0	0	0	0	0	0	0	0
Cr	145409	146299	15350	5524	162961	161143	20873	11589
Cu	147	161	89	117	533	527	488	526
Dy	632	703	359	513	574	626	457	522
Eu	20	25	0	0	23	28	0	0
Fe	77645	78031	45740	47077	134396	125224	104757	105258
K	0	0	0	0	0	0	0	0
La	632	683	380	367	735	659	520	398
Li	463	472	302	332	310	285	279	315
Mg	1806	2009	1041	1312	6166	5729	4800	4838
Mn	48685	48927	114532	159161	32118	29926	142678	164858
Mo	0	0	0	0	0	0	0	0
Na	78741	79132	46385	47742	64009	59641	49893	50131
Nd	2031	2159	1213	1248	1148	988	853	733
Ni	0	0	0	0	0	0	0	0
P	564	2655	501	543	6636	6757	4508	5840
Pb	5264	3384	1986	2112	8519	8067	7695	7723
Pd	0	0	0	0	1966	2447	0	0
Rh	0	0	0	0	0	0	0	0

Metal	SX-101-3	SX-101-4	SX-101-5	SX-101-6	SY-102-3	SY-102-4	SY-102-5	SY-102-6
Ru	0	0	0	0	0	0	0	0
Sb	0	0	0	0	0	0	0	0
Se	0	0	0	0	0	208	0	0
Si	28247	31388	0	309	38576	43559	0	0
Sn	2031	2109	15938	19422	2181	1866	30892	32937
Sr	5372	5373	1041	1341	612	585	1551	1864
Te	0	0	3139	3189	0	0	475	467
Th	3047	3515	0	0	2756	3073	0	0
Ti	113	110	1978	2099	287	296	2326	1947
Tl	33	0	62	70	110	0	264	269
U	81934	81446	80	641	11137	8232	0	0
V	0	41	47687	49614	34	42	7676	7539
W	161	218	0	0	231	353	0	0
Y	293	301	0	0	149	132	151	139
Zn	711	693	172	175	1481	1504	109	99
Zr	1689	1856	177	321	1580	809	1303	1222

Appendix B: Calculated Metal Concentrations (μg/g dry solids) for Washed SX-101 and SY-102 Sludges

Metal	SX-101	SY-102
Ag	72	260
Al	229,000	171,000
As	0	0
B	0	110
Ba	120	150
Be	0	0
Bi	220	16,800
Ca	1,750	9,600
Cd	79	897
Ce	450	0
Co	0	0
Cr	51,500	73,200
Cu	78	290
Dy	0	0
Eu	0	0
Fe	24,800	59,000
K	0	0
La	235	290
Li	140	140
Mg	385	2,160
Mn	15,550	14,100
Mo	0	0
Na	25,150	28,100
Nd	740	530
Ni	0	0
P	565	4,140
Pb	960	3,840
Pd	1,700	2,000
Rh	0	0

Metal	**SX-101**	**SY-102**
Ru	0	0
Sb	0	0
Se	0	0
Si	7,250	14,800
Sn	1,100	1,100
Sr	1,625	250
Te	0	0
Th	0	0
Ti	0	140
Tl	0	0
U	28,000	7,100
V	0	0
W	0	0
Y	0	0
Zn	275	890
Zr	410	200

Appendix C: Metal Concentrations (µg/ml)
In SX-101 Leach Solutions

Metal	SX-101-3 CL	SX-101-3 OL	SX-101-4 CL	SX-101-4 OL	SX-101-5 OL	SX-101-5 CL	SX-101-6 OL	SX-101-6 CL
Ag	-	-	-	-	-	-	-	-
Al	1,170	38.2	976	73.3	832	833	50.7	554
As	-	-	-	-	-	4.46	-	3.99
B	4.08	4.76	4.20	4.08	4.03	0	3.69	.00
Ba	-	-	-	-	-	-	-	-
Be	0.001	-	-	-	0.002	0.001	0	0.001
Bi	-	-	-	-	-	0	-	.00
Ca	-	-	-	0.37	0	-	0	-
Cd	0.028	-	-	-	0.029	0.037	0	0.025
Ce	-	-	-	-	-	-	-	-
Co	-	-	-	-	-	-	-	-
Cr	17.3	172	12.5	138	16.4	16.5	67.6	4.23
Cu	-	-	-	-	-	-	-	-
Dy	-	-	-	-	-	-	-	-
Eu	-	0.028	-	0.025	0	-	0	-
Fe	0.46	-	0.44	-	0.31	0.32	0	0.23
K	-	-	-	-	-	-	-	-
La	-	-	-	-	-	-	-	-
Li	-	-	-	-	-	-	-	-
Mg	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	0.293	-
Mo	-	-	-	-	-	-	-	-
Na	4,550	522	4,260	494	3,900	3,910	388	4,010
Nd	-	-	-	-	-	-	-	-
Ni	-	-	-	-	-	-	-	-
P	1.8	-	1.4	2.2	0.69	0.68	0	0.38
Pb	0.31	2.6	0.23	-	1.3	1.4	0	0.50
Pd	-	-	-	-	-	-	1.1	-
Rh	-	-	-	-	-	-	-	-

Metal	**SX-101-3 CL**	**SX-101-3 OL**	**SX-101-4 CL**	**SX-101-4 OL**	**SX-101-5 OL**	**SX-101-5 CL**	**SX-101-6 OL**	**SX-101-6 CL**
Ru	-	-	-	-	-	-	-	-
Sb	-	-	-	-	-	-	-	-
Se	-	-	-	-	-	-	-	-
Si	12.9	12.7	13.0	12.3	13.0	13.7	11.6	13.3
Sn	-	-	-	-	-	-	-	-
Sr	-	-	-	-	-	-	-	-
Te	-	-	-	-	-	-	-	-
Th	-	-	-	-	-	-	-	-
Ti	-	-	-	-	-	-	-	-
Tl	0.21	0.045	-	-	0	0.19	0	0
U	-	-	-	-	-	-	-	-
V	-	-	-	0.041	0	-	0	-
W	-	0.22	-	0.22	0	0	0	0
Y	-	-	-	-	-	-	-	-
Zn	-	-	-	-	-	-	-	-
Zr	0.053	0.18	0.039	0.15	0.039	0.043	0.083	0.045
- below detection limit. Note that sample diluted by a factor of approximately 10.5 (by weight) before analysis.								

Appendix D: Metal Concentrations (μg/ml) In SY-102 Leach Solutions

Metal	SY-102-3 CL	SY-102-3 OL	SY-102-4 CL	SY-102-4 OL	SY-102-5 OL	SY-102-5 CL	SY-102-6 OL	SY-102-6 CL
Ag	-	-	-	-	0	-	0	-
Al	660	32.6	678	38.2	766	757	34.5	813
As	-	-	-	-	-	.00	-	.00
B	4.16	4.78	4.16	4.24	4.38	4.24	4.47	4.59
Ba	-	-	-	-	-	-	-	-
Be	0.021	-	0.022	-	0.025	0	0	0
Bi	1.50	-	1.69	-	1.86	1.84	0	1.20
Ca	-	-	-	-	0	-	0.51	-
Cd	0.024	-	0	-	0.081	0.083	0	0.062
Ce	-	-	-	-	-	-	-	-
Co	-	-	-	-	-	-	-	-
Cr	15.6	223	16.7	169	35.7	35.3	229	22.20
Cu	-	-	-	-	-	-	-	-
Dy	-	-	-	-	-	-	-	-
Eu	-	0.039	-	0.031	0	-	0.046	-
Fe	0.32	0.11	0.28	0.11	0.23	0.23	0	0.16
K	-	-	-	-	-	-	-	-
La	-	-	-	-	-	-	-	-
Li	-	-	-	-	-	-	-	-
Mg	-	-	-	-	-	-	-	-
Mn	-	-	-	-	0.014	0.01	0	0.01
Mo	-	-	-	-	-	-	0.046	-
Na	4,070	523	4,070	431	3,850	3,800	462	3,740
Nd	-	-	-	-	-	-	-	-
Ni	-	-	-	-	-	-	-	-
P	3.26	2.70	3.35	0.94	1.3	1.30	1.9	1.30
Pb	3.19	3.4	3.32	2.7	3.89	3.88	0	3.88
Pd	-	-	-	-	0	-	3.8	-
Rh	-	-	-	-	-	-	0.34	-

Metal	**SY-102-3 CL**	**SY-102-3 OL**	**SY-102-4 CL**	**SY-102-4 OL**	**SY-102-5 OL**	**SY-102-5 CL**	**SY-102-6 OL**	**SY-102-6 CL**
Ru	-	-	-	-	-	-	0.14	-
Sb	-	-	-	-	-	-	-	-
Se	-	-	-	0.23	0	-	0.32	-
Si	15.8	13.1	16.0	12.7	15.2	15.3	13.7	15.3
Sn	-	-	-	-	-	-	-	-
Sr	-	-	-	-	-	-	-	-
Te	-	-	-	-	-	-	-	-
Th	-	-	-	-	-	-	-	-
Ti	-	-	-	-	-	-	-	-
Tl		0.19	-	0.16	0		0.27	0
U	-	-	-	-	-	-	-	-
V	-	0.058	-	0.046	0	-	0.072	-
W	0.65	0.40	0.67	0.39	0.45	0.45	0.76	0.45
Y	-	-	-	-	-	-	-	-
Zn	-	-	-	-	0.98	0.97	0	-
Zr	0.033	0.23	0.029	0.19	0.050	0.049	0.26	

\-   below detection limit. Note that sample diluted by a factor of approximately 10.5 (by weight) before analysis.

Appendix E: Measurements for Simple Caustic Leach Solutions

Leach Solution	Leach Density (g/ml)	Leach Mass (g)	Calculated Leach Volume (ml)
SX-101-3 CL	1.11	25.2	22.6
SX-101-3 OL	1.02	30.0	29.6
SX-101-4 CL	1.10	24.8	22.5
SX-101-4 OL	1.01	35.0	34.6
SX-101-5 OL	1.01	29.7	29.3
SX-101-5 CL	1.09	26.5	24.3
SX-101-6 OL	1.01	42.8	42.2
SX-101-6 CL	1.09	25.9	23.8
SY-102-3 CL	1.09	26.0	23.8
SY-102-3 OL	1.01	32.1	31.7
SY-102-4 CL	1.09	26.0	23.9
SY-102-4 OL	1.01	52.7	52.1
SY-102-5 OL	1.01	30.0	29.6
SY-102-5 CL	1.09	27.8	25.6
SY-102-6 OL	1.01	33.9	33.5
SY-102-6 CL	1.09	26.6	24.4

Appendix F: Leaching of Key, IHLW Components As Reported in PNL-8601

Element	Sample 102-SY-3T4J RT, 0.1M [OH], % Removed	Sample 34COMP RT, 0.1M [OH], % Removed	Sample 34COMP 100°C, 0.1M [OH], % Removed
Ag	NR	NR	NR
Al	12	9	30-49
Ba	NR	NR	NR
Bi	NR	NR	NR
Ca	1	19	0
Cd	NR	NR	NR
Cr	51	65	72
F	NR	NR	NR
Fe	0	0	0
K	NR	NR	NR
Mg	NR	NR	NR
Na	NR	NR	NR
Ni	NR	NR	NR
P	0	100	0
Pb	0	0	0
Pd	NR	NR	NR
Rh	NR	NR	NR
Ru	NR	NR	NR
S	NR	NR	NR
Th	0	0	0
Ti	NR	NR	NR
U	0	0	0
Zr	NR	NR	NR
NR = Not Reported			

Appendix G: Leaching of Key, IHLW Components As Reported in PNNL-11233

Element	Sample: Leached B-111 80°C, 0.01M [OH], % Removed	Sample: Leached SY-103 80°C, 0.01M [OH], % Removed
Ag	NR	NR
Al	2	1–2
Ba	NR	NR
Bi	NR	NR
Ca	3–4	7–13
Cd	NR	NR
Cr	18	90
F	NR	NR
Fe	0.01	<0.01–0.01
K	NR	NR
Mg	NR	NR
Na	NR	NR
Ni	NR	NR
P	<0.06	NR
Pb	NR	NR
Pd	NR	NR
Rh	NR	NR
Ru	NR	NR
S	NR	NR
Th	NR	NR
Ti	NR	NR
U	NR	NR
Zr	NR	NR

NR = Not Reported

Appendix H: Leaching of Key, IHLW Components
As Reported in PNNL-11571

Element	Sample: BY-110 80°C, 0.1M [OH], % Removed	Sample: BY-110 80°C, 3M [OH], % Removed	Sample: S-107 80°C, 0.1M [OH], % Removed	Sample: S-107 80°C, 3M [OH], % Removed	Sample: SX-108 80°C, 0.1M [OH], % Removed	Sample: SX-108 80°C, 3M [OH], % Removed
Ag	NR	NR	NR	NR	NR	NR
Al	41	52	11	36	8	18
Ba	NR	NR	NR	NR	NR	NR
Bi	<1	<1	<4	<16	<5	<5
Ca	1	1	8	27	6	8
Cd	1	1	NR	NR	NR	NR
Cr	83	94	58	80	22	45
F	NR	NR	NR	NR	NR	NR
Fe	1	1	<1	<1	<1	<1
K	NR	NR	NR	NR	NR	NR
Mg	NR	NR	NR	NR	NR	NR
Na	NR	NR	NR	NR	NR	NR
Ni	<1	<1	6	8	NR	NR
P	3	7	49	45	<4	<3
Pb	NR	NR	NR	NR	NR	NR
Pd	NR	NR	NR	NR	NR	NR
Rh	NR	NR	NR	NR	NR	NR
Ru	NR	NR	NR	NR	NR	NR
S	NR	NR	NR	NR	NR	NR
Th	NR	NR	NR	NR	NR	NR
Ti	NR	NR	NR	NR	NR	NR
U	3	6	<1	<5	<1	<1
Zr	NR	NR	NR	NR	NR	NR
NR = Not Reported						

Appendix I: Leaching of Key, IHLW Components As Reported in PNNL-11908

Element	Sample: U-108 80°C, 0.1M [OH], % Removed	Sample: U-108 80°C, 3M [OH], % Removed	Sample: U-109 80°C, 0.1M [OH], % Removed	Sample: U-109 80°C, 3M [OH], % Removed	Sample: Leached SX-108 80°C, 0.1M [OH], % Removed	Sample: Leached SX-108 80°C, 3M [OH], % Removed
Ag	NR	NR	NR	NR	NR	NR
Al	7	96	9	77	70	93
Ba	NR	NR	NR	NR	NR	NR
Bi	0	0	0	0	NR	NR
Ca	0	83	45	0	NR	NR
Cd	NR	NR	NR	NR	NR	NR
Cr	96.6	99.6	96.3	98.9	29	64
F	NR	NR	NR	NR	NR	NR
Fe	0	0	0	1.9	0.5	0.3
K	NR	NR	NR	NR	NR	NR
Mg	NR	NR	NR	NR	NR	NR
Na	NR	NR	NR	NR	NR	NR
Ni	NR	NR	NR	NR	NR	NR
P	NR	NR	NR	NR	NR	NR
Pb	0	0	0	53	NR	NR
Pd	NR	NR	NR	NR	NR	NR
Rh	NR	NR	NR	NR	NR	NR
Ru	NR	NR	NR	NR	NR	NR
S	NR	NR	NR	NR	NR	NR
Th	NR	NR	NR	NR	NR	NR
Ti	NR	NR	NR	NR	NR	NR
U	0	0	0	0	NR	NR
Zr	NR	NR	NR	NR	NR	NR
NR = Not Reported						

Appendix J: Leaching of Key, IHLW Components As Reported in PNNL-14018

Element	Sample: S-110 30°C, 0.1M [OH], % Removed	Sample: S-110 30°C, 3M [OH], % Removed	Sample: S-110 80°C, 0.1M [OH], % Removed	Sample: S-110 80°C, 3M [OH], % Removed
Ag	NR	NR	NR	NR
Al	3	15	12	49
Ba	NR	NR	NR	NR
Bi	NR	NR	NR	NR
Ca	NR	NR	NR	NR
Cd	NR	NR	NR	NR
Cr	87	93	90	95
F	NR	NR	NR	NR
Fe	NR	NR	NR	NR
K	NR	NR	NR	NR
Mg	NR	NR	NR	NR
Na	NR	NR	NR	NR
Ni	NR	NR	NR	NR
P	NR	NR	NR	NR
Pb	NR	NR	NR	NR
Pd	NR	NR	NR	NR
Rh	NR	NR	NR	NR
Ru	NR	NR	NR	NR
S	NR	NR	NR	NR
Th	NR	NR	NR	NR
Ti	NR	NR	NR	NR
U	NR	NR	NR	NR
Zr	NR	NR	NR	NR
NR = Not Reported				

Appendix K: Leaching of Key, IHLW Components As Reported in PNNL-14019

Element	**Sample: U-108 30°C, 0.1M [OH], % Removed**	**Sample: U-108 85°C, 0.1M [OH], % Removed**
Ag	NR	NR
Al	25	86
Ba	NR	NR
Bi	NR	NR
Ca	NR	NR
Cd	NR	NR
Cr	91	99
F	NR	NR
Fe	2.4	1.9
K	NR	NR
Mg	NR	NR
Na	NR	NR
Ni	NR	NR
P	NR	NR
Pb	NR	NR
Pd	NR	NR
Rh	NR	NR
Ru	NR	NR
S	NR	NR
Th	NR	NR
Ti	NR	NR
U	NR	NR
Zr	NR	NR
NR = Not Reported		

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