PNWD-3512
WTP-RPT-117, Rev 0

Oxidative-Alkaline Leaching of Washed 241-SY-102 and 241-SX-101 Tank Sludges

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October 2004

Prepared for Bechtel National, Inc.
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LEGAL NOTICE

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Test specification: 24590-PTF-TSP-RT-03-003, Rev 0
Test plan: TP-RPP-WTP-275, Rev. 0
Test exceptions: 24590-WTP-TEF-RT-03-079
24590-WTP-TEF-RT-04-00013
R&T focus area: Pretreatment & Vitrification
Test Scoping Statement(s): B-89

10/26/04
for W. Tamosaitis
ACCEPTED FOR
PROJECT USE

Battelle—Pacific Northwest Division
Richland, Washington 99352

Completeness of Testing

This report describes the results of work and testing specified by Test Specification 24590-PTF-TSP-RT-03-003, Rev 0 and Test Plan TP-RPP-WTP-275 Rev. 0 as modified by R&T Test Exception number 24590-WTP-TEF-RT-03-079 and 24590-WTP-TEF-RT-04-00013. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H Beeman

Gordon H. Beeman, Manager
WTP R&T Support Project

10/21/04
Date

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Acronyms

AEA	Alpha Energy Analysis
ALO	Analytical Laboratory Operations
ASTM	American Society for Testing and Materials
CCD	charge-coupled device
CI	confidence interval
CL	confidence level
CUF	cells unit filter
DOE	U.S. Department of Energy
EDS	Energy-Dispersive Spectroscopy
GEA	Gamma Energy Analysis
GFC	glass-forming chemical
HLRF	High-Level Radiochemistry Facility
HLW	high-level waste
ICDD	International Centre for Diffraction Data
ICP-AES	Inductively Coupled Plasma- Atomic Emission Spectroscopy
IHLW	immobilized high-level waste
LAW	low- activity waste
ORP	Office of River Protection
PCT	Product Consistency Test
PNWD	Battelle—Pacific Northwest Division
RCRA	Resource Conservation and Recovery Act
RMSE	root mean squared error
RPP	River Protection Project
RT	room temperature
SAL	Shielded Analytical Laboratory
SCI	simultaneous confidence interval
SEM	Scanning Electron Microscopy
SORWT	Sort on Radioactive Waste Type
TCLP	Toxicity Characteristic Leaching Procedure
TEM-ED	Transition Electron Microscopy-Electron Diffraction
TOC	total organic carbon
TRU	transuranic
UV-vis	ultraviolet-visible
WAPS	Waste Acceptance Product Specification
WL	waste loading
WTP	Waste Treatment Plant
XRD	X- Ray Diffraction

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Summary of Testing

Objectives

Significant experimental work has been conducted on the ultrafiltration process as part of the effort to immobilize waste at the Hanford Site in Washington State. This process includes the washing and caustic leaching of waste solids. Results of earlier testing have shown that caustic leaching does not remove enough chromium from the waste such that its presence in the sludges in certain tanks limits possible sludge loading in immobilized high-level waste (IHLW). Thus, there is a need to remove additional chromium from certain HLW sludges by an alternative method to improve waste loadings. The Waste Treatment Plant (WTP) contractor (Bechtel National Inc.) has been directed by the U.S. Department of Energy (DOE) to evaluate methods for oxidative leaching of chromium from sludge wastes. There is a need to determine feasibility, appropriate methodology, and specific implementation of the chromium leach process. A test specification was generated by Bechtel to address this need (Townson 2003).

This report describes activities covered under the Waste Treatment Support Project test plan TP-RPP-WTP-275, Rev. 0. These activities were designed to evaluate the process variables of time, temperature, and the sequence of caustic-leach/oxidative-alkaline leach contacts through bench scale testing of 241-SY-102 and 241-SX-101 (hereafter referred to as SY-102 and SX-101) sludges. The existing literature related to oxidative-alkaline leaching of chromium was initially reviewed to limit testing to those conditions that are the most likely to be successful for use in the WTP. Based on that review, permanganate was recommended as the reagent of choice for these tests. Also from the review, a side reaction was identified that might interfere with the permanganate reaction: consumption of permanganate by the oxidation of formate and residual organic species (complexants/extractant/solvents and aging/degradation products). The testing described in this report uses well-washed sludges and does not address any potential impact from such residual organic species.

The specific objectives of the work described in this report are to:

Test Objective	Objective Met (Y/N)	Discussion
1. Review available data in the literature and recommend a process for caustic and/or oxidative leaching of the high chromium bearing tank waste.	Y	Waste Treatment Support Project test plan TP-RPP-WTP-275, Rev. 0 provides a literature review and recommendation for testing of caustic and/or oxidative leaching of the high chromium-bearing tank wastes from washed SY-102 and SX-101 tank sludges. An update of that literature review of prior relevant research related to oxidative-alkaline leaching is located in the Introduction section.
2. Perform testing of alkaline oxidative leaching of the high chromium-bearing tank waste with permanganate as set forth in task plan TP-RPP-WTP-260. A literature review of alkaline and	Y	The bench scale testing of oxidative alkaline leaching was performed as described in TP-RPP-WTP-275 as modified by Test Exceptions 24590-WTP-TEF-RT-04-00013 and 24590-WTP-TEF-RT-03-079. Based on the literature review of alkaline and oxidative leaching previously mentioned and reported in the introduction section,

Test Objective	Objective Met (Y/N)	Discussion
oxidative leaching has been completed, and the recommended process is repeated in that task plan and will be repeated in the final report for this task. Evaluate and report the optimum conditions of time, temperature, sequence of caustic leaching and oxidative alkaline leaching, and oxidant.		experiments were performed to evaluate the conditions of time and temperature and leach sequence on oxidative-alkaline leaching of permanganate (the optimum oxidant based on the conclusion in the literature review) on washed SY-102 and SX-101 Hanford tank sludges. Specifically, the initial washed solids were analyzed for bulk metal concentrations by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and the concentrations of selected radionuclides were determined by gamma energy analysis (GEA) and alpha energy analysis (AEA). The identity of crystalline phases in these washed tank solids was evaluated by X-ray diffraction analysis, and the distribution of major elements in the sludge were evaluated by scanning electron microscopy-energy- dispersive spectroscopy (SEM-EDS) analysis. Table S.1 below summarizes the oxidative leach conditions tested. The results from the major non-radionuclides removed are summarized below in Table S.2, and radionuclide removal is summarized below in Table S.3. Analysis of the actual leachate solutions suggests that the bulk of the chromate formed during oxidative-alkaline leaching is formed within the first 6 hours. ICP-AES analysis and visible spectrophotometric analysis of the final combined leachate and wash solutions indicates that in almost all cases, all of the dissolved chromium is present as chromate. In only one of the 12 tests does the analyzed total chromium concentration exceed that of the analyzed chromate concentration. The 20% excess chromium to chromate is only slightly greater than the 15% uncertainty in the chromium concentration determined by ICP-AES. The plutonium concentration in the leachate solutions increased as a function of time, although the extent of plutonium removal is markedly less than that of either aluminum or chromium, and the absolute concentrations are such that no oxidative leach solution nor any immobilized low-activity waste (ILAW) generated from the leachate solutions themselves exceeded the transuranic (TRU) limit of 100 nCi/g. The effectiveness of the various leach conditions was evaluated by considering the amount of glass that would be required to immobilize a given amount of washed sludge

Test Objective	Objective Met (Y/N)	Discussion
		solids. Table S.4 below summarizes the results of those calculations.
3. Provide a recommendation for larger scale testing of oxidative-alkaline leaching in the Cells Unit Filter (CUF) device.	Y	Based on an evaluation of these experimental results as presented in Tables S.2 through S.4, it appears that performing the oxidative-alkaline leach at 85°C provides the best performance, both in the effectiveness of aluminum and chromium removal as well as maximizing waste loadings in IHLW glass. Indeed, these conditions are effective enough to alter the limiting component in waste loading from chromium in the washed solids to manganese. Consideration of Table S.3 allows for further refinement of the optimum oxidative-alkaline leach conditions. However, if the oxidative-alkaline leach is performed at high hydroxide concentrations, marked enhancement in plutonium dissolution is observed. This implies that a sequential caustic leach at 85°C, 3 M NaOH, together with a permanganate leach at low hydroxide, is a more robust approach. Although performing the caustic leach following the oxidative-alkaline leach provides slightly superior performance as measured by waste loading in IHLW glass, a slight enhancement in plutonium dissolution is also observed. The reason for this is not completely clear, but the data suggest that some plutonium precipitation occurs following consumption of the oxidant and/or cooling of the leachate solution. This freshly precipitated plutonium then may be more rapidly dissolved during a subsequent caustic leach. For these reasons, sequential leach contacts of 3 M NaOH/85°C followed by an oxidative-alkaline leach with stoichiometric or with a slight excess of permanganate provide the best compromise between minimizing plutonium dissolution and maximizing aluminum and chromium dissolution. However, should maximum aluminum and chromium removal be desired, reversing the order of the oxidative alkaline leach and caustic leach may prove to be superior – both leach sequences appear promising enough to be investigated in a larger scale demonstration.

Table S.1. Targeted Experimental Conditions for Oxidative-Alkaline Leach Testing

Sample Number	Prior NaOH Leach?	Post NaOH Leach?	Oxidative Leach $[NaOH]_{initial}$, M	Oxidative Leach Temp. °C	Oxidative Leach $[NaMnO_4]_{initial}/[Cr]$
Tank#-1	No	No	3	85	1.1
Tank#-2	No	No	5	85	5
Tank#-3	Yes	No	0.25	25	1.1
Tank#-4	Yes	No	0.25	85	1.1
Tank#-5	No	Yes	0.25	25	1.1
Tank#-6	No	Yes	0.25	85	1.1

Table S.2. Major Component Removal from SX-101 and SY-102 Washed-Sludges by Oxidative-Alkaline Leaching

Test #	% Component Removal					
	Al	Cr	Fe	Mn	Si	U
SX-101-1	96	96	< 0.1	0	42	0
SX-101-2	96	66	0.3	0	43	0
SX-101-3	83	87	0.3	0	46	0
SX-101-4	89	94	0.3	0	50	0
SX-101-5	97	65	0.6	0	55	0
SX-101-6	97	97	0.3	0.2	67	0
SY-102-1	86	94	< 0.1	0	17	0
SY-102-2	88	46	< 0.1	0	22	0
SY-102-3	76	80	0.1	0	32	0
SY-102-4	78	95	0.2	0	36	0
SY-102-5	94	75	0.2	0	31	0
SY-102-6	89	96	< 0.1	0	28	0

Table S.3. Radionuclide Removals from SX-101 and SY-102 Washed Sludges by Oxidative-Alkaline Leaching

Test	% Component Removal						
	^{239,240}Pu	^{241}Am	^{243,244}Cm	Total α	^{60}Co	^{137}Cs	^{154}Eu
SX-101-1	13	< 0.01	< 0.01	3.2	< 0.01	27	< 0.01
SX-101-2	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	33	< 0.01
SX-101-3	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	33(a)	< 0.01
SX-101-4	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	33(a)	< 0.01
SX-101-5	1.1(a)	< 0.01	< 0.01	0.3(a)	< 0.01	38	< 0.01
SX-101-6	2.8(a)	< 0.01	< 0.01	0.7(a)	< 0.01	29	< 0.01
SY-102-1	0.6	< 0.01	< 0.01	0.1	< 0.01	22	< 0.01
SY-102-2	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	37	< 0.01
SY-102-3	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	40(a)	< 0.01
SY-102-4	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	41(a)	< 0.01
SY-102-5	< 0.1 (a)	< 0.01	< 0.01	< 0.1(a)	< 0.01	41(a)	< 0.01
SY-102-6	0.2(a)	< 0.01	< 0.01	< 0.1(a)	< 0.01	37	< 0.01

(a) Component fraction removed during standard caustic leach greater than that removed during oxidative-alkaline leaching.

Table S.4. Calculated Effectiveness of Oxidative-Alkaline Leaching on IHLW Volumes

	Units of Glass Produced/Unit Treated Sludge (waste limiting component/condition)		
	TS-1.1	Current	Expanded
Washed SX-101	15.1(Cr_2O_3 = 0.5)	15.1(Cr_2O_3 = 0.5)	7.5(Cr_2O_3 = 1.0)
Caustic-Leached SX-101	17.4(Cr_2O_3 = 0.5)	17.4(Cr_2O_3 = 0.5)	8.7(Cr_2O_3 = 1.0)
SX-101-1	0.6(Cr_2O_3 = 0.5)	1.6(MnO = 7.0)	1.6(MnO = 7.0)
SX-101-2	5.3(Cr_2O_3 = 0.5)	5.3(Cr_2O_3 = 0.5)	2.7(Cr_2O_3 = 1.0)
SX-101-3	2.0(Cr_2O_3 = 0.5)	2.0(Cr_2O_3 = 0.5)	1.2(MnO = 7.0)
SX-101-4	0.9(Cr_2O_3 = 0.5)	1.3(MnO = 7.0)	1.3(MnO = 7.0)
SX-101-5	1.6(Cr_2O_3 = 0.5)	1.6(Cr_2O_3 = 0.5)	1.4(MnO = 7.0)
SX-101-6	0.3(Cr_2O_3 = 0.5)	1.1(MnO = 7.0)	1.1(MnO = 7.0)
Washed SY-102	21.4(Cr_2O_3 = 0.5)	21.4(Cr_2O_3 = 0.5)	10.7(Cr_2O_3 = 1.0)
Caustic-Leached SY-102	8.2(Cr_2O_3 = 0.5)	8.2(Cr_2O_3 = 0.5)	4.1(Cr_2O_3 = 1.0)
SY-102-1	1.1(Cr_2O_3 = 0.5)	1.9(MnO = 7.0)	1.9(MnO = 7.0)
SY-102-2	13.0(Cr_2O_3 = 0.5)	13.0(Cr_2O_3 = 0.5)	6.5(Cr_2O_3 = 1.0)
SY-102-3	4.9(Cr_2O_3 = 0.5)	4.9(Cr_2O_3 = 0.5)	2.5(Cr_2O_3 = 1.0)
SY-102-4	1.3(Cr_2O_3 = 0.5)	2.0(MnO = 7.0)	2.0(MnO = 7.0)
SY-102-5	1.8(Cr_2O_3 = 0.5)	1.8(MnO = 7.0)	1.8(MnO = 7.0)
SY-102-6	0.9(Cr_2O_3 = 0.5)	2.1(MnO = 7.0)	2.1(MnO = 7.0)

TS-1.1 = contract minimum loadings.
Current = WTP baseline.
Expanded = using an expanded region of validity for glass-properties models.

Test Exceptions

Two test exceptions were generated during testing. They are described below.

List Test Exceptions	Describe Test Exceptions
24590-WTP-TEF-RT-03-079	The high concentrations of Cr in the washed sludges suggested that the effective reaction of permanganate with Cr might result in leach solution becoming unacceptably acidic. In addition, the high concentrations of Al may saturate the solutions with Al, with potential interference in Cr dissolution. The test exception takes these factors into account and redefines the experimental conditions to be examined. More specifically, 1) examination of excess versus stoichiometric permanganate for each hydroxide concentration was reduced and instead the impact of a separate caustic leach before or after low hydroxide oxidative alkaline leaching was added, and 2) the initial hydroxide concentrations in the low hydroxide tests are increased from 0.1 M NaOH to 0.25 M NaOH. These changes rework the focus from predominantly a look at a single leach step to sequential steps involving caustic leach and oxidative alkaline leaching.
24590-WTP-TEF-RT-04-00013	This test exception clarifies the nature of the dissolution process for analysis of the leached solids and removes selected analytes not available because of interferences from the dissolution process. These changes have no impact on the task objectives.

Results and Performance Against Success Criterion

Success Criterion	Explain How the Tests Did or Did Not Meet the Success Criterion
Determination of leach factors for the oxidative leach process.	Tables S.2 and S.3 above provide the leach factors for the major bulk metals and major radionuclides for oxidative-alkaline leaching of washed SX-101 and SY-102 Hanford tank sludges in percentage form. Leach factors for metals of low concentration, despite being analytes of interest, even though available, are not reported in the body of the report but rather are available in an Appendix, since these components have no impact on the objective of this work, which is to provide a recommendation for oxidative alkaline leach conditions.

Quality Requirements

Application of RPP-WTP Quality Requirements:

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 organization. This work will be performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Part 2.7. 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 PNWD's *Conducting Analytical Work in Support of Regulatory Programs*. A matrix that cross-references the NQA-1 and 2a requirements with PNWD's procedures for this work is given in Appendix B of Test Plan TP-WTP-RPP-275. It includes justification for those requirements not implemented.

Conduct of Experimental and Analytical Work:

Experiments that are not method-specific shall be performed in accordance with PNWD's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration Control System," ensuring that sufficient data are taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

As specified by Townson (2003), BNI's QAPjP, PL-24590-QA00001, is not applicable since the work will not be performed in support of environmental/regulatory testing, and the data will not be used as such.

The applicable quality control (QC) parameters for chemical analysis are delineated in Tables A3 and A4 of Test Plan TP-WTP-RPP-275. The requirements for duplicate RPD were fulfilled with a replicate analysis for each analytical batch. Blank spike and/or lab control sample QC failures will result in re-analyzing the sample for the particular analyte for which the spike failed. Matrix spike and/or duplicate analysis QC failures will not result in reanalyzing the sample, but probable reasons for the failure will be discussed in the analytical report to be stored in the project files.

Additional equipment that was used included thermocouples and balances. The thermocouple was used to verify the heating block temperatures and was calibrated by PNWD Instrumentation Services and Technology. Balances are calibrated annually by a certified contractor, QC Services, Portland, Oregon.

Internal Data Verification and Validation:

PNWD addresses 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.*

The percent completeness for the analytes of interest will be calculated and reported according to the formula:

$$\%C = \left(\frac{N_p}{N_v}\right) X100 \tag{S.1}$$

where %C is the percentage completeness, N_p is the total number of planned measurements, and N_V is the number of valid measurements as defined by the project.

The percent completeness was 100%.

R&T Test Conditions

List R&T Test Conditions	Were Test Conditions Followed?
Battelle shall prepare a test plan containing detailed information needed to implement this test specification.	Yes, Test Plan TP-RPP-WTP-275 was prepared to implement the oxidative alkaline leaching bench scale test portion of the test specification. The client approved the test plan on 09/05/2003.

Simulant Use

No simulants were used during testing.

Discrepancies and Follow-on Tests

Small changes were made in the test plan procedure. First, the volume of settled solids instead of the volume of centrifuged solids was used to determine the leachate volume. This was done because while the volume of the settled solids was fairly consistent at 4 ml/test, the volume of the centrifuged solids appeared to be more variable (an estimated 2 – 3 ml). Second, samples were agitated by rotary shaking instead of magnetic stirring. This was done to avoid the possibility of magnetic particles attaching to the magnetic stir bar. Neither of these changes should adversely impact the conclusions in this report.

The results from this testing lead to the following recommendations for further study or implementation of oxidative-alkaline leaching:

1) That the possibility of selective precipitation of Pu from a permanganate-containing leach using standing caustic leach conditions be investigated. The leaching of Al and Cr is effective and if Pu can be selectivity precipitated under time effective and process-compatible conditions, adverse impacts due to the additional time required in successive leach contacts may be avoided.
2) That until a process and time-compatible Pu dissolution process is documented, further studies should focus on oxidative-alkaline leach conditions that combine a standard caustic leach (3 M, 85°C) with an independent oxidative-alkaline leach performed at a lower initial hydroxide concentration. Because of an observed discrepancy between the chromate concentration and total chromium by ICP-AES analysis, it remains unclear whether or not elevated temperatures are required for the oxidative-alkaline leach in an independent caustic leach/oxidative-alkaline leach sequence.
3) That any oxidative-alkaline leach be performed at temperature for at least 6 hours.
4) That a larger scale demonstration be performed to evaluate the order of the initial caustic leach and the oxidative-alkaline leach.
5) That this demonstration should monitor the chromate concentration in solution, the aluminum concentration, and the plutonium concentration as a function of leach contact times.
6) That the oxidation state of the dissolved plutonium should be evaluated.
7) That a further bench-scale test of test conditions #3, #4 , #5 and #6 be performed with the washed SX-101 and SY-102 sludge under the previous conditions characterized by larger solution:solids volumes. This will allow the chromium leach factors (% component removed values) reported in Table S.2 above to be correlated with the earlier oxidative-alkaline leach testing.

1.0 Introduction

Currently, there are approximately 200,000 m^3 of radioactive waste in the 177 underground storage tanks located at the U.S. Department of Energy's (DOE) Hanford Site. As part of the remediation efforts for these underground storage tanks, DOE plans to retrieve, pretreat, immobilize, and dispose of this radioactive waste. This tank waste is generally divided into three fractions: supernatant, saltcake, and sludge. The liquid supernatant is alkaline with high concentrations of salts such as sodium nitrate ($NaNO_3$), nitrite ($NaNO_2$), hydroxide (NaOH), carbonate (Na_2CO_3), phosphate (Na_3PO_4), and sulfate (Na_2SO_4). The saltcake is a solid phase consisting primarily of the above-mentioned components as precipitated salts. The sludge portion is a solid phase that consists primarily of precipitated metal oxides/hydroxides. The tank waste contains both mixed-fission products, such as ^{137}Cs, ^{90}Sr, and ^{99}Tc, and actinides, primarily uranium, plutonium, and americium. The actinides and ^{90}Sr are mostly found in the sludge layer while the ^{137}Cs and ^{99}Tc are partitioned amongst all three phases.

The tank wastes will be separated into high-level waste (HLW) and low-activity waste (LAW) fractions. The LAW will be processed to remove most of the dissolved radionuclides, with the remaining material being immobilized in a glass matrix. The HLW will be immobilized in a borosilicate glass and cast into stainless steel canisters. The stainless steel canisters will be ultimately disposed of by placement in a geologic repository (DOE/ORP 2001). Because of the expected high costs associated with HLW immobilization and disposal, pretreatment processes will be performed to reduce the volume of the immobilized HLW (IHLW).

Caustic leaching is the baseline method for pretreating Hanford tank sludges (Orme et al. 1996). Caustic leaching is expected to remove a large fraction of the aluminum, which is present in large quantities in Hanford tank sludges, by converting poorly soluble aluminum oxides/hydroxides to the more soluble sodium aluminate, $NaAl(OH)_4$. It is also expected that water-insoluble transition metal phosphates and sulfates will metathesize to their water-insoluble transition metal hydroxides and soluble Na_3PO_4 and Na_2SO_4. This will remove significant portions of phosphorus and sulfur, which are poorly tolerated in borosilicate glass, from these HLW solids.

Chromium too can interfere with the HLW immobilization process, in particular by increasing the liquidus temperature (T_L) of spinels ($[Fe,Mn,Ni][Fe,Cr,Mn]_2O_4$), by precipitating as eskolaite (Cr_2O_3), or by promoting molten salt (e.g., mixed alkali-sulfate, -chromate, -phosphate, -molybdate) segregation. For wastes with relatively high concentrations of Fe_2O_3 (> 5 mass% in glass) or NiO (> 0.5 mass% in glass), spinel precipitation is the most likely result. Spinel precipitation from the HLW glass could short the heating electrodes, clog the pour spout, or otherwise jeopardize the operation and life of the melter (Vienna et al. 2001). Relatively low concentrations of chromium in the HLW can promote spinel formation. Indeed, the chromium concentration in the high-level fraction of Hanford tank waste has the strongest influence on the volume of IHLW to be produced at Hanford (Certa et al. 2004; Perez et al. 2001; Hrma et al. 1994). For these reasons, minimizing the amount of residual chromium in selected Hanford tank sludges is an important pretreatment objective. This report describes work designed to examine pretreatment conditions for the selective removal of chromium from Hanford tank wastes from Tanks 241-SY-102 and 241-SX-101 (hereafter referred to as SY-102 and SX-101).

1.1 Background

The aqueous chemistry of chromium is dominated by species with the oxidation states Cr(III) and Cr(VI) (Greenwood and Earnshaw 1984). As illustrated by the Pourbaix diagram (Pourbaix 1974) below (Figure 1.1), in acidic solutions, the predominantly stable oxidation state is +3. In the absence of complexants, the +3 oxidation state for chromium exists as the aquo cation in acidic solution and as the tetrahydroxychromate(III) anion, $[Cr(OH)_4]^-$, in basic solution. In basic solution, chromium in the +6 oxidation state exists as the chromate anion, $[CrO_4]^{2-}$, and in acidic solution as the dichromate anion, $[Cr_2O_7]^{2-}$.

The simplest set of relationships that describe the equilibria between these oxidation states and the equilibrium between chromate and dichromate are given below by Equations 1.1 through 1.3 and are illustrated in Figure 1.2:

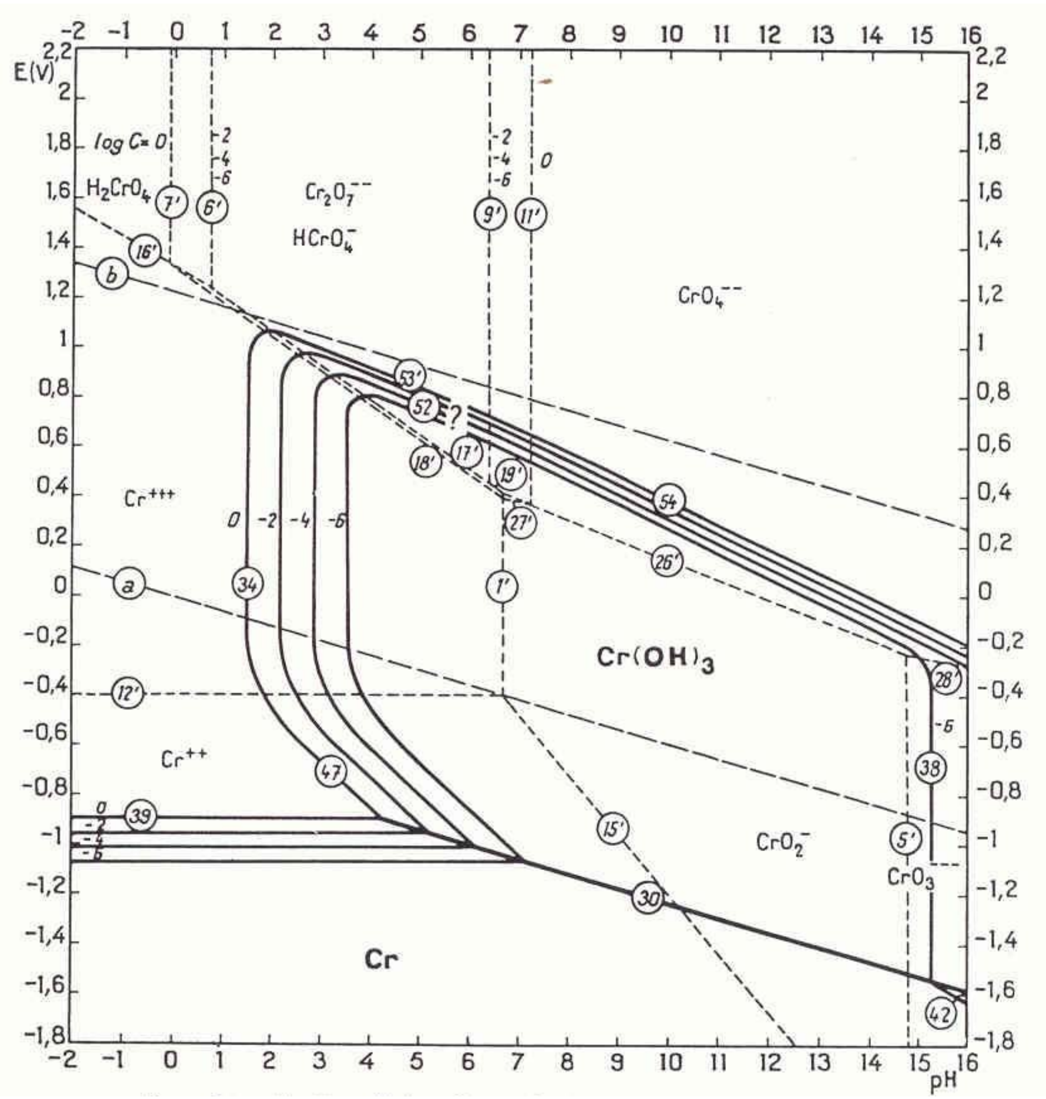

Figure 1.1. Pourbaix Diagram for Aqueous Chromium at 25°C Considering $Cr(OH)_3$. The a and b lines define the stability field for water itself.

$$CrO_4^{2-} + 3e^- + 8H^+ \rightleftharpoons Cr^{3+} + 4H_2O \tag{1.1}$$

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O \tag{1.2}$$

$$CrO_4^{2-} + 3e^- + 4H_2O \rightleftharpoons Cr(OH)_4^- + 4OH^- \tag{1.3}$$

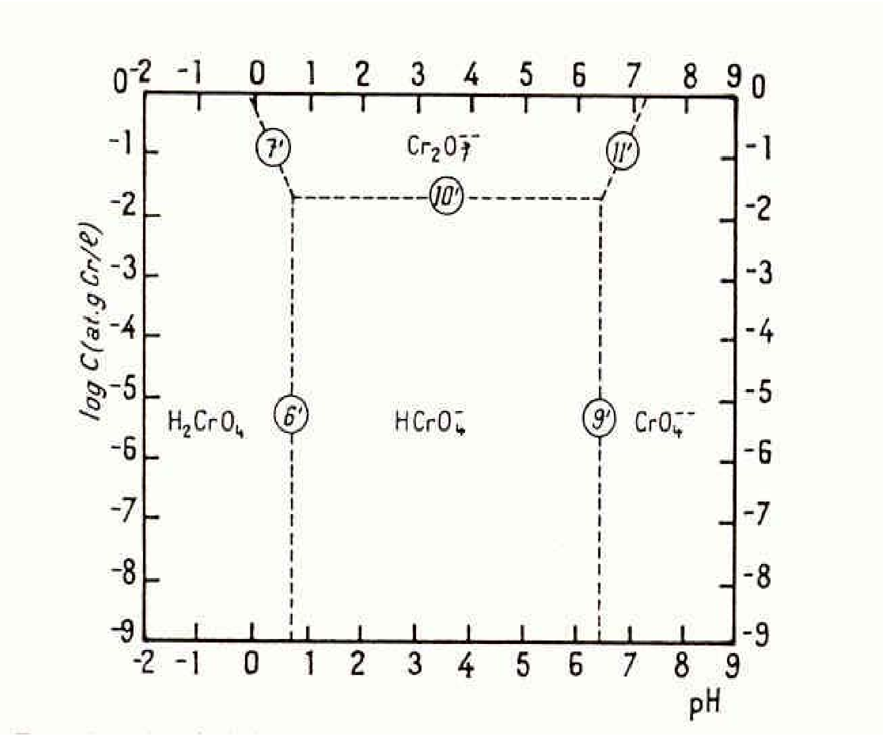

Figure 1.2. Cr(VI) Speciation in Aqueous Solution as a Function of pH and Chromium Concentration (Pourbaix 1974)

From these equations and Figure 1.1 and Figure 1.2, the following point emerges. The likely form of chromium is Cr(VI), i.e., chromate, at the alkaline pHs likely to be encountered in sludge washing and leaching (pH 12 and above). In alkaline solution, strongly reducing solution conditions are required to generate Cr(III). In neutral or acidic conditions, the most thermodynamically stable form is Cr(III). An alternative description of this speciation is that Cr(VI) becomes a weaker oxidant as the pH of the aqueous solution increases.

The solubilities of these Cr(III) and Cr(VI) species in alkaline solution are quite different. Sodium chromate/dichromate is quite soluble over a wide range of pH, with concentrations of greater than 1 M readily achievable. The solubility of Cr(III) in neutral and slightly alkaline solutions has been investigated by Rai et al. (1987). This investigation revealed relatively low solubility for tetrahydroxychromate(III), $[Cr(OH)_4]^-$, as compared to chromate, with no more than millimolar concentrations of chromium possible up to a pH of 14 (Figure 1.3). More recently, Rai et al. (2002) have investigated more concentrated hydroxide solutions and found that the Cr(III) concentrations in solution increase steadily as the hydroxide concentration increases and can reach concentrations of up to 0.01 to 0.1 M at very high hydroxide concentrations (Figure 1.4). In addition, it has been shown that at these

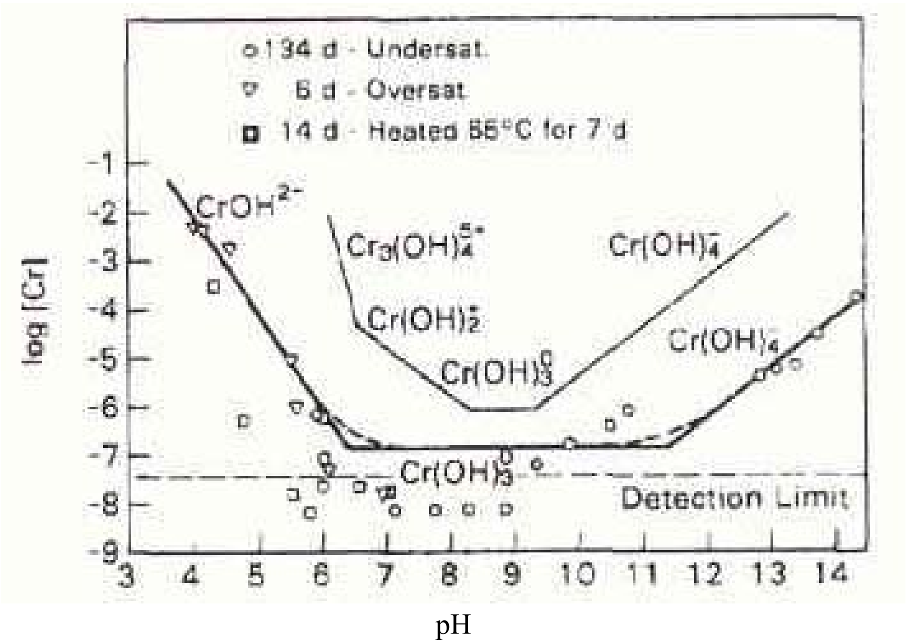

Figure 1.3. **Cr(III) Solubility and Speciation in Aqueous Solution (Rai et al. 1987)**

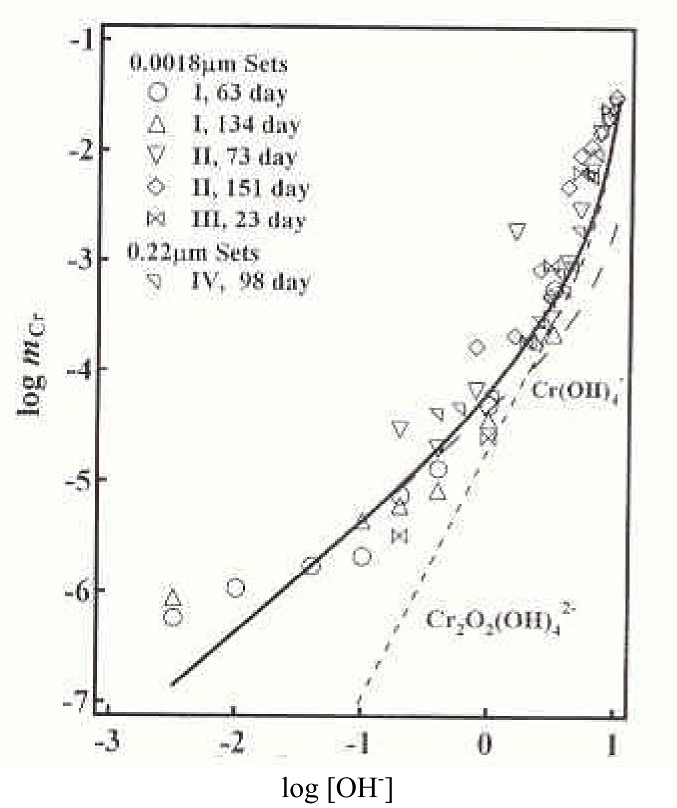

Figure 1.4. **Cr(III) Speciation in Aqueous Alkaline Solutions (Rai et al. 2002)**

higher hydroxide concentrations, Cr(III) was present both as mononuclear and polynuclear species (Freise et al. 2002), with the polynuclear species increasing in importance as the hydroxide concentration increased.

1.2 Recent Developments in Alkaline Chromium Chemistry Relevant to Hanford Tank Wastes

Studies on the speciation of chromium in actual Hanford tank sludges have indicated that chromium exists both in its +3 and +6 oxidation states, with the ratio of Cr(VI) to Cr(III) varying greatly depending on the sludge examined (Table 1.1). However, the dissolved chromium, regardless of its initial oxidation state in the sludge, was present in caustic-leach solutions (within experimental uncertainty) only in the +6 oxidation state (Rapko et al. 1996a; Blanchard et al. 1995; Blanchard et al. 1997). Furthermore, although the chromium remaining after caustic leaching is present only in the +3 oxidation state, the fraction of chromium removed often exceeds the amount initially present in the +6 oxidation state. These results imply that chromium initially present in the sludge in the +3 oxidation state underwent oxidation either during or after dissolution. The extent to which the Cr(III) fraction was removed during caustic leaching varied widely from sludge to sludge (Table 1.1). The observation that chromium present in solution during sludge washing and caustic leaching of Hanford tank wastes exists, within experimental error, in the +6 oxidation state has been supported by a large number of more recent sludge washing and caustic-leaching studies (Lumetta et al. 2003; Lumetta et al. 2002; Lumetta et al. 2001; Lumetta et al. 1998a; Lumetta et al. 1998b; Lumetta et al. 1997).

Some information also exists about the nature of chromium phases in Hanford tank sludge, mostly obtained by various physical methods, such as powder X-ray diffraction (XRD), transition electron microscopy coupled with electron diffraction (TEM/ED), or scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS). The first method gives information about the crystalline phases, and the second can give information about crystalline and non-crystalline phases, whereas the third method only supplies elemental information. It is important to note that the relative amounts of these phases are not quantified when multiple phases are observed. Table 1.2 summarizes the chromium-containing phases identified to date (Rapko and Lumetta 2000; Lumetta et al. 2003; Rapko et al. 2002). Table 1.2 can be summarized by noting that chromium generally has been found either as a pure oxide/hydroxide phase, is associated with aluminum, or exists in spinel phases.

Table 1.1. Cr(III)/Cr(VI) Compositions in Hanford Tank Sludges Before and After Caustic Leaching

	Untreated Sludge		**% Cr Removed by dilute $[OH^-]$ (wash)**	**After Caustic Leaching**		**% Removed**		
Tank	**Cr(III), %**	**Cr(VI), %**		**Cr(III), %**	**Cr(VI), %**	**Total Cr**	**Cr(III)**	**Cr(VI)**
B-111	73	27	27	> 95	< 5	41	18	> 95
BX-107	91	9	21	> 95	< 5	29	22	> 95
BY-110	69	31	47	> 95	< 5	48	2	> 95
S-104	< 5	> 95	90	Not Detected		96	Not Detected	
S-107	89	11	24	> 95	< 5	53	38	> 95
SX-108	13	87	71	> 95	< 5	78	24	> 95
SY-103	> 95	< 5	5	> 95	< 5	13	13	> 95
T-104	84	16	17	> 95	< 5	27	13	> 95
T-111	78	22	24	> 95	< 5	64	54	> 95

Table 1.2. Summary of Chromium Phase Information in Hanford Tank Sludges

Phase	Tank	Waste Type[(a)]		Present After Caustic Leaching?
		Primary	Secondary	
$Bi_{38}CrO_{60}$	B-111	2C	5-6	Yes
$Bi_{38}CrO_{60}$	T-104	1C	None	Yes
Cr(O)(OH) (grimaldite)	BY-110	TBP-F	EB-ITS	Yes
$CrPO_4$	T-104	1C	None	Yes
$Al/Cr(OH)_3$(am)[(b)]	SY-103	CC	None	Yes
$Al/Cr(OH)_3$(am)[(b)]	U-108	EB	CW	Not Determined
Cr(oxide/hydroxide)(am)[(c)]	U-108	EB	CW	Not Determined
$NaAlO_2/Cr(OH)_3$(am)[(d)]	AN-104	DSSF	None	Yes
Ca/Cr phase	AN-104	DSSF	None	Yes
$Fe(Cr,Fe)_2O_4$ (donathite)	BY-104	TBP-F	EB-ITS	Yes
$FeCr_2O_4$	S-111	R	EB	Yes
$CrMn_2O_4$	S-111	R	EB	Yes
$Cr_{1.5}Mn_{1.5}O_4$	S-111	R	EB	Yes

(a) Based on SORWT Model (Hill et al. 1995); R= high-level reduction oxidation waste, EB = evaporator bottoms, CC = complex concentrate, DSSF = double shell slurry feed, 1C = first decontamination cycle waste, 2C = second decontamination cycle waste, ITS = in-tank solidification, 5-6 = high-level B Plant waste from the bottom of Section 5, CW = cladding waste, TBP-F = tri-butyl phosphate ferrocyanide scavenged waste.

(b) Chromium and aluminum hydroxides associated with each other.

(c) Chromium in an oxide or hydroxide environment.

(d) Chromium associated with amorphous sodium aluminate.

Substantial dissolution of Cr(III) into alkaline solution as the tetrahydroxochromium(III) complex $[Cr(OH)_4]^-$ was anticipated in the early sludge washing and caustic-leaching experiments with Hanford tank sludges. This was based on the known amphoteric behavior for Cr(III) as illustrated in Figure 1.3 and discussed above. However, the results in Table 1.1, together with more recent results from caustic-leaching studies of actual Hanford tank sludges, indicate that the chromium behavior is more complex. While significant concentrations of Cr(III) hydroxide can exist in high-caustic solutions at room temperature (RT), it also has been shown that the heating of such solutions causes guyanaite, syn-(CrOOH), to precipitate. This precipitate does not readily redissolve in aqueous caustic media (Lumetta et al. 1998a,b). This observation is consistent with previous reports of an observed lowered solubility of (initially) amorphous $Cr(OH)_3$ in acidic and near-neutral solutions at elevated temperature (Lumetta et al. 1997; Rai et al. 1987); an example is shown in Figure 1.5. It is possible then that the elevated temperatures experienced in the tanks may have generated more poorly soluble Cr(III) phases than amorphous Cr(III) hydroxide.

This demonstration of the lowered solubility of Cr(III) hydroxide following heating in alkaline solution to temperatures often achieved in the Hanford tanks or during caustic leaching itself suggests that removing chromium as Cr(III) by simple alkaline sludge washing and/or caustic leaching is unlikely to be an effective and efficient strategy for chromium removal from Hanford tank sludges. A plausible alternative based on the above-described chemistry might be to add an oxidant and enhance the dissolution of water-insoluble chromium from Hanford tank sludge by facilitating the conversion from its relatively poorly alkaline-soluble +3 oxidation state to its more alkaline-soluble form as chromate, CrO_4^{2-} (Lumetta et al. 2000). Studies that have addressed this hypothesis are discussed in the next section.

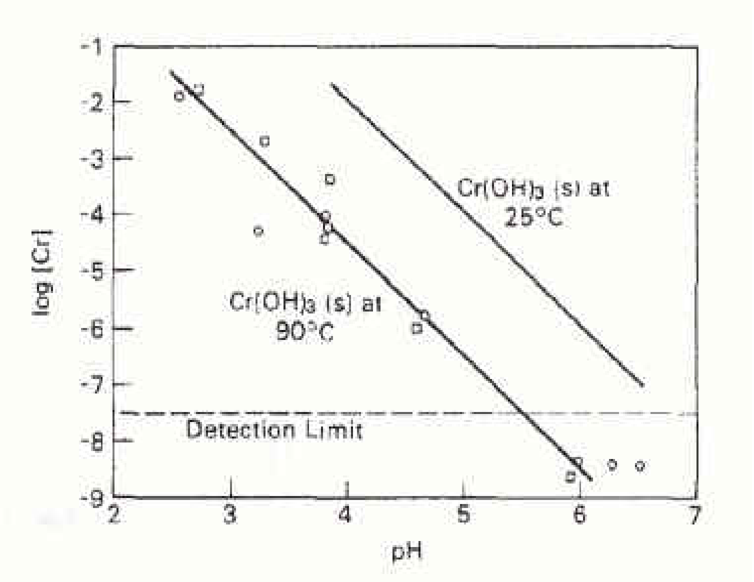

Figure 1.5. Chromium Hydroxide Solubility as Ambient and Elevated Temperature (Rai 1987)

1.3 Oxidative-Alkaline Leaching Studies with Hanford Tank Wastes

Studies over the last several years with Hanford tank sludge simulants and with actual Hanford tank sludges indicate that treating water-washed and caustic-leached solids with oxidizing agents indeed can significantly increase the effectiveness of chromium removal (Rapko et al. 1996b; Rapko et al. 1997; Rapko 1998; Delegard et al. 1993; Delegard 1995; Lumetta et al. 1995; Lumetta and Swanson 1993; Krot et al. 1999; Sylvester et al. 2001; Rapko et al. 2002; Rapko and Vienna 2002; Rapko and Vienna 2003). Tested oxidants to date include ozone, O_3 (Rapko et al. 1996b; Rapko et al. 1997; Delegard et al. 1993), hydrogen peroxide, H_2O_2 (Lumetta and Swanson 1993; Lumetta et al. 1995; Rapko et al. 1997; Lumetta et al. 1995; Delegard 1995; Krot et al. 1999), permanganate, MnO_4^- (Lumetta et al. 1995; Lumetta and Swanson 1993; Rapko et al. 1996b; Rapko et al. 1997; Rapko 1998; Rapko et al. 2002; Rapko and Vienna 2002; Rapko and Vienna 2003), oxygen, O_2 (Rapko 1998; Krot et al. 1999), persulfate, $S_2O_8^{2-}$ (Krot et al. 1999; Rapko et al. 2002), ferrate, FeO_4^{2-} (Sylvester et al. 2001; Rapko et al. 2002; Rapko and Vienna 2003) and peroxynitrite, $ONOO^-$ (Rapko and Vienna 2002). These tests and the primary relevant conclusions are reviewed below.

One of the earliest applications of oxidative-alkaline leaching to Hanford tank sludges was by Lumetta and Swanson (Lumetta et al. 1995; Lumetta and Swanson 1993), who examined alkaline hydrogen peroxide treatments and permanganate treatments of SY-102 Hanford tank sludge. Their qualitative observations were that severe foaming occurred upon treatment with hydrogen peroxide with no indication of any chromate formation. Permanganate treatment, however, led to the rapid formation of a yellow solution consistent with the presence of chromate. A qualitative test for alpha activity indicated no detectable alpha activity in the mildly alkaline (0.1 M hydroxide) leach solution following permanganate treatment.

Another early examination was performed by Delegard and co-workers (Delegard et al. 1993), who looked at the ozonolysis of both actual and simulated 241-SY-101 Hanford tank waste. The goal of this work was to investigate ozonolysis as a method for organic destruction. The key findings were (1) a rapid (complete after ca. 8 hour) destruction of total organic carbon (TOC) with concomitant decreases in americium and strontium solution concentrations, (2) a similarly rapid oxidation of nitrite to nitrate, and (3) a concomitant increase in dissolved chromium and plutonium once the TOC and nitrite were consumed. Figure 1.6 illustrates the changes in chromium and plutonium solution concentrations as a function of time.

A later examination involving oxidative-alkaline treatment of SY-101 simulant and SY-101 and SY-102 actual Hanford tank waste was also performed (Delegard 1995). Here the oxidant used was hydrogen peroxide. Although a significant enhancement of chromium dissolution (RT, 3 M NaOH, 2 days contact time) was observed (up to 50% of the water insoluble chromium) in tests with the SY-101 simulant, little to no change in the chromium concentration was observed when contacted with the actual SY-101 tank waste. Indeed, adding hydrogen peroxide to a 3 M NaOH solution in contact with actual SY-102 tank waste resulted in a slight decrease (16 from 21%) in the fraction of dissolved chromium as compared to contact of the tank waste with 3 M NaOH alone. With both actual SY-101 and SY-102, peroxide treatment led to about an order of magnitude increase in the amount of plutonium in solution, but in both cases, the fraction of plutonium that dissolved was low (< 5%).

A study of the rate of Cr(III) oxidation for various dissolved Cr(III) hydroxide species by hydrogen peroxide under alkaline conditions has been performed recently (Rao et al. 2002). The rate of Cr(III) oxidation to Cr(VI) was found to be first order in Cr(III), first order in hydrogen peroxide, and inverse first order in hydroxide. However, the oxidation rate constants differ for each species, with the rate constants increasing as the nuclearity of the Cr(III) species in solution decreases and with oxidation of the monomeric species tetrahydroxychromate(III) being the most rapid.

Krot and co-workers have examined the reactions of persulfate, oxygen, and hydrogen peroxide with chromium in a variety of solid forms under alkaline conditions (Krot et al. 1999). They found persulfate was the most effective, followed by oxygen (effective but slow for pure chromium phases and not effective when chromium exists in spinel phases), followed by hydrogen peroxide (compromised when

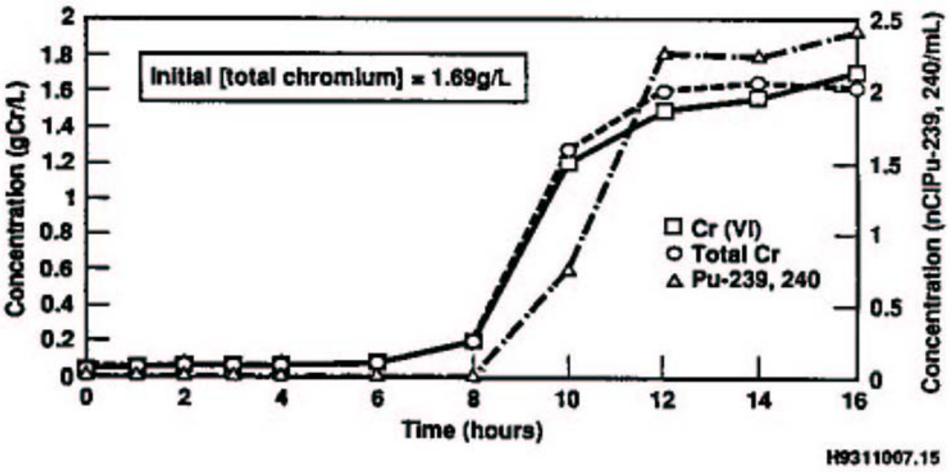

Figure 1.6. Dissolution of Chromium and ^{239,240}Pu from 241-SY-101 Tank Waste During Ozonolysis Under Alkaline Conditions (Delegard et al. 1993)

the solids contain iron or aged chromium). Persulfate also enhances plutonium dissolution, but it was found that subsequent treatment with hydrogen peroxide was effective at reprecipitating the dissolved plutonium.

The remaining studies of oxidative-alkaline leaching have been performed by Rapko and co-workers using a variety of oxidants and various washed Hanford tank sludges. These tests were designed to survey the effectiveness at oxidative-alkaline dissolution of chromium from Hanford tank sludges with relative high amounts of water insoluble chromium; it should be emphasized that they were not designed to mimic any proposed plant operations. These tests were generally characterized by high solution to solids ratios (typically 100:1) and typically explored temperature, time, oxidant, and hydroxide concentration as the variables. Contact times were typically 24 to 48 hours in duration. Table 1.3 summarizes the plutonium and chromium removals with the sludges tested, the initial hydroxide concentrations, the oxidant used, and the temperature of the leaching.

Table 1.3. Summary of PNNL Oxidative-Alkaline Leaching with Washed Hanford Tank Sludges. Samples are from washed sludge composites unless noted otherwise.

Tank	Oxidant	Initial [OH$^-$]	Temp (°C)	% Cr Removed	% Pu Removed	Reference
SY-103	$[MnO_4]^-$	0.01 M	RT, then 80°C	90	<0.01$^{(c)}$	Rapko et al. 1996b
	O_3	0.01 M	RT, then 80°C	89	5.3	Rapko et al. 1996b
	air	0.01 M	RT, then 80°C	34	0.02	Rapko et al. 1996b
B-111	$[MnO_4]^-$	0.01 M	RT, then 80°C	18	<0.02$^{(c)}$	Rapko et al. 1996b
	O_3	0.01 M	RT, then 80°C	12	<0.07$^{(c)}$	Rapko et al. 1996b
	air	0.01 M	RT, then 80°C	5	<0.07$^{(c)}$	Rapko et al. 1996b
BY-110	$[MnO_4]^-$	0.1 M	RT, then 80°C	83	0.01	Rapko et al. 1997
	O_3	0.1 M	RT, then 80°C	83	0	Rapko et al. 1997
	O_2	0.1 M	RT, then 80°C	2	<0.01	Rapko et al. 1997
	Ar	0.1 M	RT, then 80°C	8	<0.01	Rapko et al. 1997
	$[MnO_4]^-$	3 M	RT, then 80°C	94	13.4	Rapko et al. 1997
	O_3	3 M	RT, then 80°C	90	3.91	Rapko et al. 1997
	O_2	3 M	RT, then 80°C	11	0.19	Rapko et al. 1997
	Ar	3 M	RT, then 80°C	28	0.17	Rapko et al. 1997
SX-108	$[MnO_4]^-$	0.1 M	RT, then 80°C	22	0.09	Rapko et al. 1997
	O_3	0.1 M	RT, then 80°C	42	0.01	Rapko et al. 1997
	$[MnO_4]^-$	3 M	RT, then 80°C	45	2.09	Rapko et al. 1997
	O_3	3 M	RT, then 80°C	33	0.09	Rapko et al. 1997
S-107	$[MnO_4]^-$	0.1 M	RT, then 80°C	58	0.11	Rapko et al. 1997
	O_3	0.1 M	RT, then 80°C	84	0.01	Rapko et al. 1997
	O_2	0.1 M	RT, then 80°C	8	<0.01	Rapko et al. 1997
	Ar	0.1 M	RT, then 80°C	5	<0.01	Rapko et al. 1997
	$[MnO_4]^-$	3 M	RT, then 80°C	80	4.97	Rapko et al. 1997
	O_3	3 M	RT, then 80°C	87	0.13	Rapko et al. 1997
	O_2	3 M	RT, then 80°C	65	<0.01	Rapko et al. 1997
	Ar	3 M	RT, then 80°C	ND	ND	Rapko et al. 1997

Table 1.3 (Contd)

Tank	**Oxidant**	**Initial $[OH^-]$**	**Temp (°C)**	**% Cr Removed**	**% Pu Removed**	**Reference**
U-108(a)	$[MnO_4]^-$	0.1 M	RT, then 80°C	97	1	Rapko 1998
	O_2	0.1 M	RT, then 80°C	5	0	Rapko 1998
	Ar	0.1 M	RT, then 80°C	0.6	0.02	Rapko 1998
	$[MnO_4]^-$	3 M	RT, then 80°C	99.6	50	Rapko 1998
	O_2	3 M	RT, then 80°C	94	2	Rapko 1998
	Ar	3 M	RT, then 80°C	5	0.09	Rapko 1998
U-109(a)	$[MnO_4]^-$	0.1 M	RT, then 80°C	96	1	Rapko 1998
	O_2	0.1 M	RT, then 80°C	14	0	Rapko 1998
	Ar	0.1 M	RT, then 80°C	2	0	Rapko 1998
	$[MnO_4]^-$	3 M	RT, then 80°C	99	36	Rapko 1998
	O_2	3 M	RT, then 80°C	98	1	Rapko 1998
	Ar	3 M	RT, then 80°C	5	0.03	Rapko 1998
SX-108(b)	$[MnO_4]^-$	0.1 M	RT, then 80°C	29	0.53	Rapko 1998
	O_2	0.1 M	RT, then 80°C	5	0.0053	Rapko 1998
	$[MnO_4]^-$	3 M	RT, then 80°C	64	2	Rapko 1998
	O_2	3 M	RT, then 80°C	71	0.25	Rapko 1998
S-110	$[MnO_4]^-$	0.1 M	30°C	87	0.6	Rapko et al. 2002
	$[S_2O_8]^{2-}$	0.1 M	30°C	48	0.1	Rapko et al. 2002
	$[FeO_4]^{2-}$	1.1 M	30°C	88	9	Rapko et al. 2002
	air	0.1 M	30°C	5	0.01	Rapko et al. 2002
	$[MnO_4]^-$	0.1 M	80°C	90	1.5	Rapko et al. 2002
	$[S_2O_8]^{2-}$	0.1 M	80°C	89	5.3	Rapko et al. 2002
	$[FeO_4]^{2-}$	1.1 M	80°C	95	1.1	Rapko et al. 2002
	air	0.1 M	85°C	25	< 0.01	Rapko et al. 2002
	$[MnO_4]^-$	3 M	30°C	93	7	Rapko et al. 2002
	$[S_2O_8]^{2-}$	3 M	30°C	89	8	Rapko et al. 2002
	$[FeO_4]^{2-}$	3 M	30°C	90	8	Rapko et al. 2002
	air	3 M	30°C	10	0.5	Rapko et al. 2002
	$[MnO_4]^-$	3 M	80°C	95	11	Rapko et al. 2002
	$[S_2O_8]^{2-}$	3 M	80°C	94	10	Rapko et al. 2002
	$[FeO_4]^{2-}$	3 M	80°C	94	3	Rapko et al. 2002
	air	3 M	85°C	72	0.8	Rapko et al. 2002
U-108	$[MnO_4]^-$	0.1 M	30°C	91	0.2	Rapko and Vienna 2002
	$[ONOO]^-$	0.1 M	30°C	60	0.7	Rapko and Vienna 2002
	air	0.1 M	30°C	1	0.7	Rapko and Vienna 2002
	$[MnO_4]^-$	3 M	85°C	99	69	Rapko and Vienna 2002
	$[ONOO]^-$	3 M	85°C	58	0.5	Rapko and Vienna 2002
	air	3 M	85°C	13	1.8	Rapko and Vienna 2002

Table 1.3 (Contd)

(a) From washed saltcake.
(b) From caustic-leached sludge.
(c) Based on total alpha activity.
ND = Not Determined.
$[MnO_4]^-$ = leach solution contacted with permanganate.
O_3 = leach solution contacted with ozone.
O_2 = leach solution contacted with pure oxygen.
air = leach solution contacted with atmosphere.
$[ONOO]^-$ = leach solution contacted with peroxynitrite.
$[S_2O_8]^{2-}$ = leach solution contacted with persulfate.
$[FeO_4]^{2-}$ = leach solution contacted with ferrate.

In addition, there have been several caustic-leaching tests where air contact of Hanford tank sludges with alkaline solutions was performed with extended leach times and with contact by multiple, successive, leach solutions. These results are summarized in Table 1.4.

The results of these chromium-dissolution investigations can be summarized as follows, together with observations relevant to waste sludge processing:

- Hydrogen peroxide is ineffective when tested on actual tank solids, probably because of its catalytic decomposition by other waste components before reaction with chromium can occur.

Table 1.4. Alkaline Leaching in Air with Extended Contact Times

Sludge	Contact Time[(a)]	[NaOH], M	Leach Temperature (°C)	% Cr Removed[(a)]	% Pu Removed[(a)]	Reference
S-110	1 week	1	60	49	<1	Lumetta et al. 2001
	1 week	2.8	60	70	1	Lumetta et al. 2001
	1 week	4.8	60	81	2	Lumetta et al. 2001
	1 week	0.9	80	78	0.1	Lumetta et al. 2001
	1 week	2.7	80	89	1	Lumetta et al. 2001
	1 week	4.6	80	90	2	Lumetta et al. 2001
	1 week	0.8	100	83	0.3	Lumetta et al. 2001
	1 week	2.7	100	95	1	Lumetta et al. 2001
	1 week	4.5	100	99	3	Lumetta et al. 2001
S-104	211 hr	2.3	100	86	NM[(c)]	Lumetta et al. 1997
	76 (287) hr	2.9	100	13 (99)	NM[(c)]	Lumetta et al. 1997
S-101	5 hr	2.5	100	23	<2	Lumetta et al. 1997
	100 (105) hr	2.7	100	66 (89)[(b)]	<2	Lumetta et al. 1997
S-111	143 hr	1.9	100	81	<25	Lumetta et al. 1997
	60 (203) hr	2.5	100	17 (98)[(b)]	<25	Lumetta et al. 1997

(a) Cumulative totals in parenthesis.
(b) Includes final washes.
(c) NM = not measured.

- Ozone has been shown to be both rapid and effective in several tests. It also does not add to the mass of either the LAW or HLW streams. However, there is some evidence for significantly enhanced and concomitant dissolution of transuranic (TRU) elements. In addition, ozone is both toxic and highly corrosive. The reduced form of ozone, oxygen gas, may introduce flammability concerns as well.

- Persulfate is effective at oxidizing Cr(III) to chromate when found in the hydroxide form, the oxide form, and the oxyhydroxide form, and it also oxidizes Cr(III) in nickel and iron spinel phases to chromate. However, persulfate is also capable of oxidizing TRU elements to alkaline-soluble forms, which is undesirable. In addition, persulfate would add several equivalents of sulfur to the LAW waste stream for each equivalent of chromium removed from the HLW sludge, which also is undesirable.

- Ferrate is both rapid and effective, with chromium dissolution essentially completed within hours. The reduced form of ferrate is Fe(III) oxide, which will add mass to the HLW stream. The thermal stability of ferrate solutions under typical enhanced sludge-washing conditions is much less than permanganate solutions. Indeed, alkaline solutions of ferrate must be kept well below RT to remain stable, although at 5°C, alkaline solutions are stable for days to weeks. Some enhanced dissolution of TRU elements is observed.

- Peroxynitrite is not as rapid or effective as ferrate, ozone, or permanganate. In addition, the material is not readily available and, like ferrate, alkaline solutions of peroxynitrite must be kept cold. However, the reduced form, nitrate, should have negligible impact on the high-nitrate LAW stream.

- Oxygen (air) is selective and effective, and it adds no mass to either the LAW or HLW waste streams. However, the rate of chromium dissolution appears significantly slower than with the other oxidants examined and suggests that, at least with Hanford tank sludge and even under the optimum conditions of high temperature and strongly alkaline solution, several days to weeks may be required before the reaction with chromium is complete. Little to no enhanced dissolution of radionuclides is observed.

- Permanganate is both rapid and effective, with chromium dissolution effectively complete within hours. As discussed further below, at low hydroxide concentrations, the reduced form of permanganate is manganese dioxide, which will add mass to the HLW stream. With strongly alkaline solutions, the reduced form is manganate, which is quite soluble in these leach solutions. Aqueous solutions of permanganate, although somewhat light sensitive, are fairly stable thermally. A modest enhanced dissolution of TRU elements is observed at low hydroxide concentrations, although much greater dissolution of plutonium was observed occasionally when contacted with strongly alkaline leach solutions. It should also be noted that permanganate has been by far the most extensively tested of all added oxidants.

After examining the strengths and weaknesses of each of the oxidants, it appears that permanganate is the best choice for continued study. It is readily available, alkaline permanganate solutions are reasonably stable, and its oxidation of chromium from alkaline solutions is rapid and effective. At low hydroxide concentrations, the observed plutonium concentrations are not appreciably different than those found in simple caustic solutions at high hydroxide concentrations, so enhanced plutonium dissolution is unlikely to be problematic. Finally, other WTP plant operations, such as the Sr/TRU removal process, also use permanganate, so equipment compatibility should not be an issue. The major drawback of permanganate is added mass to the HLW waste stream, but the limited evidence from prior studies suggests that the added manganese is not the limiting component in HLW waste loadings after oxidative-alkaline leaching with permanganate (Rapko and Vienna 2002; Rapko and Vienna 2003). The next section focuses on permanganate oxidations in alkaline solution in greater detail.

1.4 Permanganate Oxidations of Hanford Tank Sludge

Some additional information regarding alkaline permanganate treatments of Hanford tank sludges is summarized in Table 1.5.

Table 1.5. Summary of Existing Experimental Results of Permanganate Leaching of Hanford Tank Sludges (Sederburg 2003)

Tank Sample	Waste Source Type	Conditions of [MnO_4^-] Treatment	$[Cr]_{initial}$ (µg/g dried solid)	$[Cr]_{final}$ (µg/g dried solid)	% Cr Removed	Reference Document
U-108	Washed sludge composite	0.1 M [OH], 30°C	200000	20108[(a)]	91	Rapko and Vienna 2002
U-108	Washed sludge composite	3 M [OH], 85°C	200000	3038	99	Rapko and Vienna 2002
S-110	Washed sludge composite	0.1 M [OH], 30°C	23050	3290	87	Rapko et al. 2002
S-110	Washed sludge composite	3 M [OH], 85°C	23050	2310	95	Rapko et al. 2002
U-108	Washed saltcake solids	0.1 M [OH], RT	112000	3775	96.6	Rapko 1998
U-108	Washed saltcake solids	3 M [OH], 80°C	112000	1200	99.6	Rapko 1998
U-109	Washed saltcake solids	0.1 M [OH], RT	255000	8870[(a)]	96.3	Rapko 1998
U-109	Washed saltcake solids	3 M [OH], 80°C	255000	2840	98.9	Rapko 1998
SX-108	Caustic-Leached sludge composite	0.1 M [OH], RT	1320	5240[(a)]	29	Rapko 1998
SX-108	Water-washed sludge composite	3 M [OH], 80°C	4270	4820	64	Rapko 1998
BY-110	Water-washed sludge composite	0.1 M [OH], RT/80°C	19250	3800	83	Rapko et al. 1997
BY-110	Water-washed sludge composite	3 M [OH], RT/80°C	19250	703	94	Rapko et al. 1997
S-107	Water-washed sludge composite	0.1 M [OH], RT/80°C	13100	3850	58	Rapko et al. 1997
S-107	Water-washed sludge composite	3 M [OH], RT/80°C	13100	1090	80	Rapko et al. 1997
SX-108	Water-washed sludge composite	0.1 M [OH], RT/80°C	5760	4205	22	Rapko et al. 1997
SX-108	Water-washed sludge composite	3 M [OH], RT/80°C	5760	1270	45	Rapko et al. 1997

Table 1.5 (contd)

Tank Sample	Waste Source Type	Conditions of $[MnO_4^-]$ Treatment	$[Cr]_{initial}$ (µg/g dried solid)	$[Cr]_{final}$ (µg/g dried solid)	% Cr Removed	Reference Document
SY-103	Caustic-Leached Sludge	0.01 M [OH], RT/80°C	220000	Not available	90	Rapko et al. 1996b
B-111	Caustic-Leached Sludge	0.01 M [OH], RT/80°C	7000	Not available	18	Rapko et al. 1996b
SY-102	Washed sludge	0.1 M [OH], RT	11600	Not available	65	Lumetta and Swanson 1993
SY-102	Washed sludge	0.1 M [OH], 100°C	11600	Not available	72	Lumetta and Swanson 1993
(a) Tests that exceed 5000 ppm residual chromium. RT = Room Temperature						

As can be seen from Table 1.5, for the vast majority of the samples, despite the initial chromium concentration in the sludge, permanganate treatment can reduce the residual chromium concentration to about 5000 ppm. Since this would meet the conservative Hanford Waste Vitrification Plant specification of 0.5% chromium oxide even at ca. 70% waste-oxide loading, it provides support to the hypothesis that permanganate treatments can remove chromium as the limiting component in the loading of waste oxide even in sludges with initially high chromium concentrations.

In Table 1.5, there are three exceptions to the 5000-ppm chromium residual: one condition with U-108, one condition with U-109, and one condition with SX-108. The SX-108 residual is within experimental error of 5000 ppm. The U-108 and U-109 tests were designed to be stoichiometric reactions with permanganate. Laboratory records indicate that all of the permanganate was consumed immediately, which suggests that a substoichiometric amount of permanganate to chromium may have been added. That other permanganate tests with these sludges easily reached 5000 ppm or less residual chromium also lends support to this hypothesis.

1.5 Permanganate Oxidations in Alkaline Solution

Figure 1.7 shows the Pourbaix diagram for manganese in contact with aqueous solution. Of particular interest to this discussion is the fate of the reduced manganese. At lower pH regions, the preferred form of any reduced permanganate is manganese dioxide, MnO_2, or even more reduced oxide forms of manganese. Under more basic conditions, the reduced form would be manganate ion, MnO_4^{2-}. Therefore, if a permanganate treatment were to be performed at high hydroxide, the reduced permanganate might well stay in solution and be transferred to the LAW stream with the leachate. If a permanganate treatment were to be done at low hydroxide concentrations, then the reduced manganese will precipitate as manganese dioxide and report to the HLW stream. According to Figure 1.7, the point at which the change in the permanganate-reduced form occurs is approximately pH 10.

Experience with leaching of Hanford tank sludges qualitatively confirms the conclusions reached from the Pourbaix diagram. Manganese dioxide precipitate is indeed generated with low hydroxide leach solutions while soluble manganese has been identified by ultraviolet-visible (UV-vis) spectroscopy with

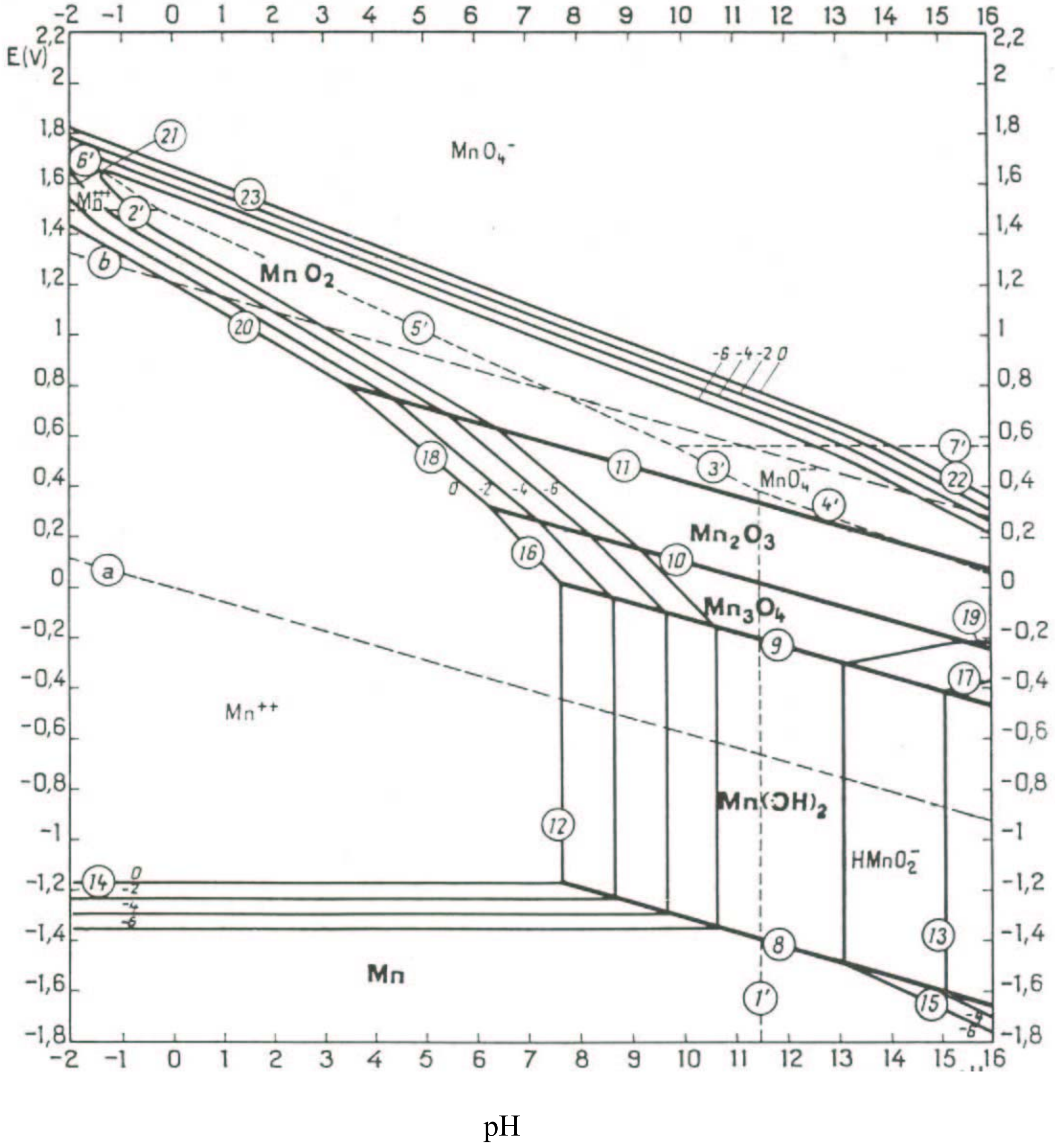

Figure 1.7. Pourbaix Diagram for Aqueous Manganese at 25°C (Pourbaix 1974). Lines a and b delineate the stability field for water.

high hydroxide leach solutions. However, the point at which the form of the reduced permanganate changes appears to occur at a much more alkaline condition than is indicated in Figure 1.7. Specifically, leach solutions of 0.1 M free hydroxide have been observed to generate manganese dioxide. Leach solutions have been > 1 M in free hydroxide before the sustained presence of manganate ion is observed.

The stoichiometries for the reaction of permanganate with chromium to form chromate and either manganese dioxide (4), manganate (5) or Mn(III) oxide (6) are shown below.

$$Cr(OH)_3 + MnO_4^- + OH^- \rightleftharpoons CrO_4^{2-} + MnO_2 + 2H_2O \qquad (1.4)$$

$$Cr(OH)_3 + 3MnO_4^- + 5OH^- \rightleftharpoons CrO_4^{2-} + 3MnO_4^{2-} + 4H_2O \qquad (1.5)$$

$$8Cr(OH)_3 + 6MnO_4^- + 10OH^- \rightleftharpoons 8CrO_4^{2-} + 3Mn_2O_3 + 17H_2O \qquad (1.6)$$

Regardless of the form of the reduced manganese, the oxidation of Cr(III) to Cr(VI) consumes hydroxide. The form of the reduced manganese has a substantial impact on the reaction stoichiometry. The formation of manganese dioxide, i.e., permanganate acting as a three-electron reductant, is most efficient in hydroxide and manganese consumption. If the reduced form is Mn(III) oxide, 25% more hydroxide is required (1.25 equivalents hydroxide/equivalent chromium). When the reduced form of permanganate is manganate, i.e., permanganate acting as a one-electron reductant, three equivalents of permanganate and five equivalents of hydroxide are required to oxidize one equivalent of chromium.

There are relatively few studies of the alkaline oxidation of Cr(III) either in solution or as a solid (a fact noted in a relatively recent study [Timmanagudar et al. 1997]). Three reports of note are discussed next. The first involved a study of permanganate oxidation of soluble Cr(III) in alkaline solutions ranging from $[OH^-] = 0.05$ to 0.5 M (Timmanagudar et al. 1997). The second looked at the kinetics of Cr(III) oxide dissolution by permanganate in alkaline solution (Segal and Williams 1986), and the third examined the dissolution of permanganate from chromium present in iron oxides (Manjanna and Venkateswaran 2002).

The oxidation of soluble Cr(III) by permanganate in alkaline solution was reported to be rate limiting by the formation of a Mn(VIII)-Cr(III) complex, probably through an oxo bridge (Timmanagudar et al. 1997). The rate equation is complex and dependent on both on the solution permanganate and Cr(III) concentrations.

In a study of the oxidation of Cr(III) oxide by permanganate in mildly alkaline solution (0.01 to 0.1 M hydroxide, [Segal and Williams 1986]) the rate was found to be dependent on (and favored by an increase in) both permanganate and hydroxide concentrations. The postulated mechanism is of hydroxide attack on the chromium oxide surface from a surface chromium-OH species, which in turn reacts with permanganate to form a surface Cr-O-Mn species, which then undergoes electron transfer with concomitant chromium dissolution. However, it is unclear to the authors why an alternative mechanism, involving hydroxide attack at the chromium oxide surface to form soluble $[Cr(OH)_4^-]$, followed by permanganate attack as described above, can be discounted.

In the study of chromium oxidation in chromium-substituted iron oxide by permanganate in mildly alkaline solutions (pH 11-13.2), pure chromium oxide was found to rapidly and completely dissolve under the reaction conditions (Manjanna and Venkateswaran 2002). However, with 20% chromium in Fe_2O_3, less than 10% of the total chromium dissolved. Permanganate does not oxidize iron oxide, so after the surface was depleted of chromium, the remaining chromium apparently became inaccessible to permanganate attack.

Studies related to the Sr/TRU precipitation process for Hanford tank supernatants provide further information relevant to alkaline oxidation of chromium from Hanford tank sludge (Gauger and Hallen 2001; Lilga et al. 2003). Recalling the above-mentioned ozonolysis study of SY-101 sludge, it was observed that both TOC and nitrite were oxidized before the oxidation of chromium began. Furthermore, at least in acidic solution, the oxalate reduction of permanganate is used for determining solution permanganate concentrations (Jeffrey et al. 1989). So the behavior of permanganate with these common tank waste constituents is of importance as it might consume permanganate in unwanted side reactions. This would increase the amount of permanganate required to effectively oxidize chromium and also might add additional manganese to the HLW stream. In contrast to ozone in alkaline solution or permanganate in acidic solution, Gauger and Hallen report that both nitrite and oxalate are unreactive towards permanganate in alkaline solution; thus, these species will not consume permanganate during oxidative-alkaline leaching. However, model studies of permanganate oxidation under alkaline conditions (Lilga et al. 2003) suggest that some organic oxidations may be kinetically competent to compete with chromium oxidation. Organic destruction, then, may be a permanganate-consuming side reaction to the oxidative-alkaline leaching of chromium. Fortunately, this potential side reaction likely can be avoided by first performing a solid-liquid separation step to remove the TOC. In short, studies related to Sr/TRU precipitation processing suggest that oxidative-alkaline leaching of chromium ought to be performed on washed sludges where the organic material has been separated from the sludge, rather than upon the as-received supernatant/solid slurry, at least for tank supernatants with high concentrations of organic material.

In conclusion, the review of aqueous chromium chemistry and prior oxidative-alkaline leaching studies provides several suggestions that should help focus further studies. These points can be summarized as follows:

- Permanganate appears to be the most compatible oxidant for use in the Waste Treatment Plant (WTP) for oxidative-alkaline leaching.

- The hydroxide concentration used for oxidative-alkaline leaching has several impacts. The oxidation of chromium by permanganate consumes hydroxide, so if too little hydroxide is in the system, the pH may drop to neutral from alkaline. Increased temperature and hydroxide concentration appear to slightly enhance chromium removal but occasionally also increases the extent of plutonium dissolution. It should be noted that while the rate of chromate formation has been monitored, the rate of plutonium dissolution has not. Therefore, examining the rate of plutonium dissolution to see if it, like with the ozone/SY-101 study, occurs concomitant with chromate formation is an important research objective. In general, modest hydroxide concentrations such as 0.1 M appear to be fairly efficient, but temperature and hydroxide concentrations are likely key variables for process optimization.

- To avoid potential side reactions with organic materials, oxidative-alkaline leaching of chromium from washed sludges is preferable.

- The permanganate to chromium stoichiometry may be an important variable. It has two impacts: the efficiency of the oxidant use (1:1 vs 3:1 permanganate: chromium) and the waste stream where the reduced permanganate reports. The information obtained to date indicates that adding manganese to the HLW will not be a limiting factor in glass loading, although this obviously depends on any specific waste's composition. Adding manganese as permanganate to the LAW stream may have downstream implications if further reaction with organic material occurs with resulting manganese precipitation. Another concern could be that any remaining excess permanganate may subsequently react with the organic ion exchange resins, with unknown consequences to processing. From these considerations, it appears that low hydroxide is likely to be preferred, but actual testing of this is probably still a worthwhile objective.

Applying these points, the following guidelines for testing on SY-102 and SX-101 Hanford tank sludges were developed:

- Use washed sludges.

- Investigate the impact of temperature (ambient and the elevated caustic-leach [85°C] conditions).

- Investigate the impact of permanganate stoichiometry (approximately 1:1 versus excess permanganate), and hydroxide concentration (but with the focus on low, 0.1 M, hydroxide leach solutions).

- Use relatively short contact times, given the historical rapid chromium dissolution observed previously.

- Monitor both of the rate of chromium dissolution (as chromate) and plutonium dissolution.

2.0 Experimental Testing Design and Procedure

This section describes the chromium leach reagent and the sludge samples from SY-102 and SX-101. The testing procedure includes the

- initial sludge washing
- subdivision of the washed SY-102 and SX-101 solids
- initial caustic leaching of washed SY-102 and SX-101 solids
- oxidative-alkaline leach testing of SY-102 and SX-101 solids
- final caustic leaching of washed SY-102 and SX-101 solids
- estimation of the glass volume
- calculations for glass formulation.

2.1 Chromium Leach Reagent Preparation and General Experimental Information

All reagents used in this work were of analytical grade purity or higher. The hydroxide concentrations of stock solutions were verified by titration with primary standard acid solutions. Hydroxide concentrations in the actual leach solutions were measured by titration with standardized solutions of hydrochloric acid using a Mettler Model DL 21 Autotitrator.

UV-vis measurements were made on a 400-series charge-coupled device array spectrophotometer (Spectral Instruments Inc.) with a 200- to 950-nm scanning range. The solutions were held in PLASTIBRAND® 1-cm cuvettes. UV-vis spectroscopic measurements were obtained as follows: sample aliquots were diluted as necessary with 0.1 M NaOH, and the spectra from 350 to 800 nm were recorded on a Spectral Instrument's 400 series charged-coupled device (CCD) array UV-vis spectrophotometer. The chromate concentrations were determined by measuring the test solution's absorbance at 372 nm, which is the wavelength of maximum absorbance for chromate in the visible spectrum. The instrument was calibrated at this wavelength using standards-grade potassium dichromate in 1 M NaOH in line with a published procedure (Gordon and Ford 1972). The results of the calibration are shown in Figure 2.1.

Samples for powder XRD measurements were prepared by slurrying a dried sludge sample with an amyl acetate-based, low X-ray background, glue, placing the slurry on a glass slide and drying the prepared sample before analysis. The XRD measurement was performed on a Sintag PAD V X-ray Powder diffractometer using Cu-Kα radiation and a solid-state detector. Measurement parameters include operation at 2 KW power, 0.02 degrees/step, and a 20 sec/step over a 2θ range of 5 to 65 degrees. The diffraction patterns were compared with known 2-theta/intensity data from the International Centre for Diffraction Data (ICDD) database 49 (through 1999) to identify crystalline phases. This measurement was performed according to the technical procedure PNL-ALO-268, Solids Analysis, X-ray Diffraction.

SEM-EDS measurements were performed using the model EDS2000 system with a 500 Digital processing unit and 5480 Imaging Interface (IXRF Systems Inc. Houston, Texas) connected to a 1610 Scanning Electron Microscope (Amray Microscopes Inc. Bedford, Massachusetts). Samples of

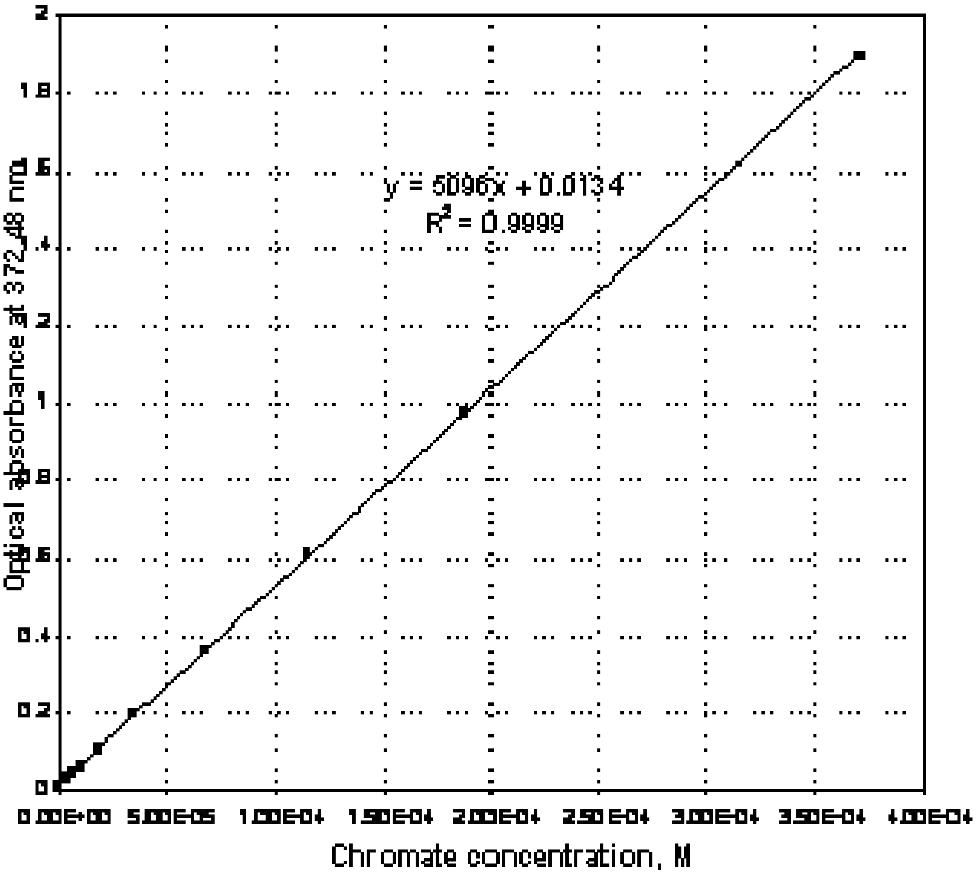

Figure 2.1. **Results from the Calibration of UV-vis Spectrometer at 372 nm Against Standard Chromate Solutions**

washed solids were fixed onto graphite tape and placed onto the SEM station stage, and the sample chamber was pumped down to 2E-07 to 4E-07 torr. The sample image then was brought into focus, and adjustments were made to system's KV and spot size control. A digital image was captured on the computer screen, and subsections of that image were examined by x-ray microanalysis.

The Analytical Services Organization at Battelle—Pacific Northwest Division (PNWD) performed all gamma energy analysis (GEA), alpha energy analysis (AEA), and inductively coupled plasma-alpha energy analysis (ICP-AEA) measurements using standard procedures.

2.2 Description of the SY-102 and SX-101 Sludge Samples

The Hanford tank SY-102 sample used for this testing is a composite of both liquid- and sludge-containing segments from two different core samples (Table 2.1). Several glass bottles, whose contents ranged from primarily solids to mostly liquids, were prepared at the Hanford 222-S Laboratory and shipped to PNWD in July 2003.

Table 2.1. Description of SY-102 Sludge Composite

Sample ID[a]	Core No.	Jar No.	Phase[b]	Amount Added, g
S03T001382	286	19506	S	44.7
S03T001383	286	19561	SL	48.1
S03T001376	284	19606	S	25.8
S03T001377	284	19607	S	45.9
S03T001375	284	19411	S	13.0
S03T001406	286	18982	S	6.9
S03T001381	286	18714	S	9.0
S03T001380	286	18599	S	34.1
S03T001374	284	18586	S	34.1
S03T001379	284	18528	L	135.5
S03T001385	286	19203	L	142.8
S03T001378	284	19213	L	171.4
S03T001405	284	19538	L	173.4
S03T001384	286	19209	L	166.3
S03T001404	286	19211	L	168.6

(a) Unique identifier associated with the 222-S Laboratory.
(b) S = Solid; SL = Slurry; L = Liquid

The Hanford tank sludge SX-101 sample used for this testing is a composite of SX-101 sludge-containing segments from Core 225. Approximately 75 grams of this black slurry (Sample ID S03T001373 in Jar #13998) were prepared at the Hanford 222-S Laboratory and were shipped to PNWD in July 2003.

2.3 Initial Sludge Washing

In the 325 Building's HLRF hot cell facilities, the contents of the SY-102 bottles were combined in a single 2-L jar. For both the SY-102 and SX-101 samples, the contents were mixed with a magnetic stirring bar, and a portion of each well-stirred suspension was transferred into a separate 50 ml centrifugation cone. The aliquots of the SY-102 and SX-101 samples individually were washed twice with enough 0.01 M NaOH so that the total volume of the suspension was 50 ml (an approximately 1:1 to 5:1 ratio [volume supernatant:volume centrifuge solids]). The solids were separated from the liquids by centrifugation after each wash. In the RPL hot cell facilities, the sludge-composite samples were transferred into 50-ml polyethylene centrifuge bottles and contacted repeatedly with fresh portions of 0.01 M NaOH at an initial solution-to-solids ratio of approximately 5:1. After each contact, the supernatant was decanted off and discarded. These washings were repeated until the bulk of the color was removed (typically 5 washes). Little color was observed in the final wash solution, although the yellow tinge imparted by the lead-glass windows made detection of any yellow color imparted by the presence of alkaline Cr(VI) somewhat speculative. The final slurry was prepared by adding a portion of 0.01 M NaOH to the washed, centrifuged solids. For each sludge sample, two weighed aliquots of the well-stirred (using a Teflon-coated magnetic stirring bar) suspension were removed and dried to a constant weight at 105°C. From this information, the amounts and concentrations of water-insoluble sludge were obtained. This information is summarized in Table 2.2.

Table 2.2. Initial Analytical Sampling of Washed Sludges

Sludge	SY-102		SX-101	
Wt slurry (g)	19.5191		27.6472	
Wt slurry aliquot (g)	1.1157	1.1120	0.7167	1.0313
Wt residual solids (g)	0.1887	0.1904	0.1717	0.2495
Wt% insoluble solids	16.91	17.12	24.00	24.19
Total insoluble solids (g)	3.32		6.66	

These SX-101 dried samples were used for subsequent SEM, XRD, AEA, GEA, and ICP-AES measurements. However, the amount of SY-102 solids isolated above was deemed insufficient for testing. So another sample of the SY-102 composite was taken and washed as above in the HLRF and SAL hot cells. These newly washed SY-102 solids were then combined with the previously washed SY-102 solids, and a second set of two weighed aliquots was removed from the well-stirred (using a Teflon-coated magnetic stirring bar) suspension and dried to a constant weight at 105°C. These new SY-102 data are summarized in Table 2.3.

Table 2.3. Second Analytical Sampling of Washed SY-102 Sludge

Sludge	SY-102	
Wt slurry (g)	109.2788	
Wt slurry aliquot (g)	1.1498	1.2100
Wt residual solids (g)	0.0870	0.0932
Wt% insoluble solids	7.57	7.70
Total insoluble solids (g)	8.35	

These SY-102 dried samples were used for subsequent SEM, XRD, AEA, GEA, and ICP-AES measurements. The concentrations of the major non-radioactive sludge components (defined here as >10,000 µg/g dried solids in either sludge) and the detected radionuclide components and concentrations are summarized in Table 2.4 and Table 2.5.

Table 2.4. ICP-AES Determined Composition of Major Components in Dilute Hydroxide-Washed SY-102 and SX-101 Solids

Component	SY-102 Concentration, µg/g Dried Solids	SX-101 Concentration, µg/g Dried Solids
Al	171000	229000
Cr	73200	51500
Fe	59000	24800
Mn	14100	15600
Na	28100	25200
Si	14800	7300[(a)]
U[(a)]	7100	28000
(a) Values above the minimum detectable quantity (MRQ) but above the EQL and so with an uncertainty above 15%		

Table 2.5. **Concentrations of the Major, Identified Radionuclides in Dilute Hydroxide-Washed SY-102 and SX-101 Solids**

Component	Analysis Method	SY-102 Concentration, µCi/g Dried Solids	SX-101 Concentration, µCi/g Dried Solids
^{239,240}Pu	AEA	3.71E+01	1.28E+00
^{243,244}Cm	AEA	7.18E-02	8.89E-02
^{238}Pu & ^{241}Am	AEA	1.29E+02	4.52E+00
Total α	Sum of AEA	1.66E+02	5.89E+00
^{137}Cs	GEA	7.10E+01	4.86E+01
^{60}Co	GEA	7.05E-02	7.11E-02
^{241}Am	GEA	1.36E+02	5.19E+00
^{154}Eu	GEA	2.17E+00	2.97E+00
^{155}Eu	GEA	1.10E+00	1.46E+00

2.4 Subdivision of the Washed SY-102 and SX-101 Solids

In the SAL hot cells, six aliquots were removed from the well-stirred sludge slurry, and each aliquot was transferred into a separate 30-ml plastic bottle. The targeted volumes were 4.6 ml of SX-101 slurry and 14.4 ml of SY-102 slurry. The masses of material transferred are summarized in Table 2.6.

Table 2.6. **Sub-Sampling of Washed SX-101 and SY-102 Solids for Oxidative-Alkaline Leach Testing**

Sample	Added Slurry (g)	Sample	Added Slurry (g)
SY-102-1	16.032	SX-101-1	4.668
SY-102-2	16.108	SX-101-2	4.610
SY-102-3	15.813	SX-101-3	5.402
SY-102-4	15.767	SX-101-4	4.823
SY-102-5	15.460	SX-101-5	3.851
SY-102-6	16.174	SX-101-6	1.370/9.963[(a)]
(a) Additional DI water added to slurry out all residual solids.			

The reaction bottles then were transferred from the SAL hot cells to a laboratory fume hood, and the reaction bottles were placed in a J-KEM heating/rotary aluminum shaker block into which holes, sized to securely hold the sample bottles, were cut. The depth of the holes kept the bulk of the test solution surrounded by the heating block. One position contained a blank solution of hydroxide into which a thermocouple was immersed. The thermocouple allowed the solution temperature to be maintained at temperature to within 1°C. Stock solutions of the oxidant, 10 M NaOH, deionized water, and sodium permanganate solution were added as needed to meet the targeted experimental conditions.

2.5 Initial Caustic Leaching of Washed SY-102 and SX-101 Solids

The initial amount of settled solids was estimated as about 4 ml for both SY-102 and SX-101. An initial caustic leaching on samples SX-101-3, SX-101-4, SY-102-3, and SY-102-4 was performed. A volume of 3:1 leachate:settled solids (v:v) was targeted for a total target volume of 16 ml. To achieve 16 ml of an initial 3 M NaOH leach solution, 4.8 ml of 10 M NaOH and 8.2 ml DI water were added to each system. These bottles were loosely capped and heated for 8 hours at 85 ± 5°C. The heating was then stopped and the system cooled to RT overnight. The test suspensions then were centrifuged and the supernatants decanted into 30-ml plastic vials. To the residual solids in each test container, 0.1 M NaOH was added at a 3:1 (v solution:v solids) ratio, the contents were mixed, the solids were again separated by centrifugation, and the solution was decanted into the sample container as the initial leachate solution. Washings were continued until the supernatant was colorless. Samples were then filtered through a 0.2-micron Nylon syringe filter, and a 1-ml aliquot was placed in a container with 10 ml of 1 M nitric acid for ICP-AES analysis. A portion of the filtered leachate was stored in a 7-ml glass vial for further analysis.

2.6 Oxidative-Alkaline Leach Testing of SY-102 and SX-101 Solids

Table 2.7 summarizes the experimental conditions targeted for the oxidative-alkaline leaching tests.

Table 2.7. Targeted Experimental Conditions for Oxidative-Alkaline Leach Testing

Sample Number	Prior NaOH Leach?	Post NaOH Leach?	Oxidative Leach $[NaOH]_{initial}$, M	Oxidative Leach Temp. °C	Oxidative Leach $[NaMnO_4]_{initial}/[Cr]$
Tank#-1	No	No	3	85	1.1
Tank#-2	No	No	5	85	5
Tank#-3	Yes	No	0.25	25	1.1
Tank#-4	Yes	No	0.25	85	1.1
Tank#-5	No	Yes	0.25	25	1.1
Tank#-6	No	Yes	0.25	85	1.1

Aliquots of the leach solutions were taken for analysis at approximately 2, 6, and 24 hours after the leach solutions were initially contacted with the sludge. Sampling involved tightly capping the vials and performing an initial centrifugation at 3000 rpm for 5 minutes to effect a preliminary solids/liquids separation. The caps were removed, and a solution aliquot was taken. These aliquots were passed through a 0.2-µm Nylon® syringe filter, and 0.1 ml was diluted into 2 ml of 0.25 M NaOH. A second 0.1-ml aliquot was added to a glass vial containing 1 ml of 0.67 M nitric acid for subsequent plutonium analysis; excess undiluted leach solution then was returned to the reaction vessel. The vials were then briefly agitated by vortex mixing to resuspend the solids and placed back into the heated rotary shaker.

After 24 hours, the test slurries were centrifuged (3000 rpm for a minimum of 5 minutes), and the supernatants were decanted from the residual solids. The residual solids were then washed three to four times with 0.1 M NaOH to remove any components present in the interstitial liquid. In all cases, the final wash solution appeared colorless. After each wash, the samples were centrifuged, and the supernatant was combined with the final leachate. A portion of the final leach solution was then filtered through a 0.2-µm Nylon® syringe filter, and a weighed aliquot of that filtered solution was added to a known amount of 1 M nitric acid to inhibit any precipitation before ICP-AES and radiochemical analysis.

Meanwhile, the 0.1 M NaOH-washed residual solids were dried to a constant weight at 105°C. These residual solids were subjected to a KOH fusion in a nickel crucible followed by dissolution into nitric acid. The content of the major metallic elements in both the acidified supernatants and dissolved residues was determined by ICP-AES as noted above for the initial washed solids. The radionuclide activities in both the acidified supernatants and dissolved residues were determined by alpha-energy analysis and gamma-energy analysis as described above for the washed solids.

2.7 Final Caustic Leaching of Washed SY-102 and SX-101 Solids

Following the oxidative-alkaline leaching and washing of the leached solids as described above, a final 3 M NaOH leach was performed on samples SX-101-5, SX-101-6, SY-102-5, and SY-102-6 as described previously for samples SX-101-3, SX-101-4, SY-102-3, and SY-102-4.

2.8 Glass Volume Estimation

The impact of various leaching techniques on glass volume was estimated using a systematic method that optimized waste loading in glass. A set of conditions, consistent with current River Protection Project-Waste Treatment and Immobilization Plant (RPP-WTP) vitrification process and compliance strategies, were met simultaneously. The glass-forming chemical (GFC) concentrations were varied until the waste loading was a maximum while meeting the full set of conditions. The various conditions are described in Section 2.8.1. Section 2.8.2 summarizes how these conditions were converted into numerical constraints, and Section 2.8.3 gives the details of how the optimization calculations were performed.

2.8.1 Compliance and Processing Conditions

The RPP-WTP compliance strategy for meeting Waste Acceptance Product Specification (WAPS) (DOE-EM 1996) and Contract (DOE-ORP 2000) specifications for IHLW is discussed by Nelson (2003). In addition to satisfying applicable compliance conditions, IHLW produced by the RPP-WTP must also satisfy several processing conditions. The following paragraphs describe each of the compliance and processing conditions considered in selecting optimized glass formulations.(a) In cases where uncertainties in the compliance or process variables are to be accounted for in the WTP IHLW compliance and process control strategies, they were accounted for in developing optimized glass formulations. For such cases, the type of statistical interval used to quantify the uncertainty in model predictions of compliance or processing properties is noted in the discussion. The types of statistical intervals are discussed further in Section 2.8.2.

2.8.1.1 Compliance Conditions

Three compliance conditions were factored into the glass composition optimization. These conditions are briefly described in the following paragraphs.

IHLW produced by the RPP-WTP must satisfy limits on product consistency test (PCT) (ASTM 1998) normalized releases of boron (r_B), lithium (r_{Li}), and sodium (r_{Na}). The PCT normalized releases

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(a) Many property and composition conditions/constraints are typically applied to the development of waste glass compositions. Only those key conditions/constraints critical to determining if a glass can be fabricated with uncertain and varying compositions were applied in this study.

must remain below the prescribed limits of 8.35 g/m^2 for r_B, 4.79 g/m^2 for r_{Li}, and 6.68 g/m^2 for r_{Na} (Jantzen et al. 1993). The uncertainty for models relating the natural logarithm of PCT normalized releases to HLW glass composition was calculated using 95% simultaneous confidence intervals (SCIs) (see Section 2.8.2).

To be compliant, IHLW produced by the RPP-WTP must have Toxicity Characteristic Leaching Procedure (TCLP) releases below the proposed delisting limits (Cook and Blumenkranz 2003). For the wastes evaluated in this study, cadmium (Cd) is the only Resource Conservation and Recovery Act of 1974 (RCRA) constituent present in high enough concentrations to be of concern (Kot et al. 2003). The proposed delisting limit for the TCLP Cd release, c_{Cd}, is 0.48 mg/L. The uncertainty in the model relating $\ln(c_{Cd})$ to glass composition was calculated using a 90% confidence interval (CI) (see Section 2.3), as specified by Cook and Blumenkranz (2003).

Compliance for waste loading (WL) is based on the constraints in Table TS-1.1 of the WTP Contract (DOE-ORP 2000). These constraints specify the minimum fraction of a component or sum of components in glass that must be from the waste for at least one such component or sum of components. Waste-loading compliance is achieved if the concentration of one of the waste components (set of components) is above the value listed in TS-1.1. According to the WTP Project compliance strategy for waste loading, composition uncertainty need not be accounted for in demonstrating waste-loading compliance.

2.8.1.2 Processing Conditions

Two processing conditions were factored into the glass composition optimization. These conditions are briefly described in the following paragraphs.

The processing condition for crystals in the WTP HLW melter is based on $T_{0.01}$, defined as the temperature at which the equilibrium volume fraction of crystals in glass is 0.01 (on a quenched glass basis). The condition is that $T_{0.01}$ should remain below the limit of 950˚C. This condition is imposed to avoid the accumulation of crystals in the melter, which may disrupt the power distribution in the melter or the capability to pour glass from the melter. According to the WTP HLW melter design basis document (Clarke 2003), the melter should be capable of continually operating with a glass melt that has a liquidus temperature (T_L) of less than or equal to 950°C.[a] In the design basis document, T_L is not defined; rather, it refers to the System Description (Peters and Casassa 2003). That document states that T_L is defined by Kot and Pegg (2001), in which T_L is defined as the temperature at which up to one volume percent of slow-settling crystals exist in equilibrium with the melt. This is effectively the same as $T_{0.01}$, used in this study. The model uncertainty for $T_{0.01}$ was calculated using 90% SCIs (see Section 2.8.2).

For the glass-optimization work discussed in this report, viscosity at 1150˚C (η_{1150}) was restricted to be between 25 and 60 poise. Also, viscosity at 1100˚C (η_{1100}) was restricted to be between 10 and 150 poise. The uncertainties for the models relating $\ln(\eta_{1150})$ and $\ln(\eta_{1100})$ to HLW glass composition were calculated using a 90% CI (see Section 2.8.2).

(a) The minimum melt-cavity temperature was estimated to 961°C during idling and normal operation. However, temperatures as low as 826°C were estimated in the pour region of the melter for periods of up to 473 minutes during normal operation.

2.8.2 Glass-Composition and Property Constraints

Several glass-composition and property constraints were assumed for the glass formulation optimization. Constraints were primarily lower and/or upper limits on single components, sums of components, and glass-property estimates from property-composition models. The property-composition models used to optimize glass formulation include:

- models for PCT normalized releases of boron, lithium, and sodium (r_B, r_{Li}, r_{Na}) vs. composition from Piepel and Cooley (2003)
- a model relating viscosity (η) to temperature and composition from Gan et al. (2004)
- a model relating TCLP Cd release concentration (c_{Cd}) to composition from Kot et al. (2003)
- a model relating temperature at 1% crystals ($T_{0.01}$) to composition from Vienna et al. (2003).

The models for spinel phase-field $T_{0.01}$, as well as PCT $\ln(r_B)$, $\ln(r_{Li})$, and $\ln(r_{Na})$, had the typical first-order mixture model form:

$$f(P) = \sum_{i=1}^{N} a_{P,i} g_i^N \tag{2.1}$$

where

$$g_i^N = \frac{g_i}{\sum_{i=1}^{N} g_i} \quad \text{where} \quad \sum_{i=1}^{N} g_i^N = 1 \tag{2.2}$$

where $f(P)$ = function of property P
$a_{P,i}$ = i^{th} component coefficient for the property P
g_i = mass fraction of i^{th} component in glass
N = number of components in glass for which the model was fit (dependent on property P)
g_i^N = normalized mass fraction of i^{th} model component.

In Equation 2.1, $f(T_{0.01}) = T_{0.01}$, and $f(r_i) = \ln(r_i)$ for i = B, Li, and Na.

The model used to estimate TCLP $\ln(c_{Cd})$ had the form:

$$\ln(c_{Cd}) = \sum_{i=1}^{N} a_{cCd,i} g_i^N + b_1 \ln(g_{CdO}) \tag{2.3}$$

where $a_{cCd,i}$ is the coefficient of the i^{th} normalized oxide component (g_i^N), and b_1 is the coefficient of the natural logarithm of unnormalized CdO (g_{CdO}) in the IHLW glass.

The model for viscosity as a function of temperature and composition was given as:

$$ln(\eta_T) = \frac{1}{T^2}\sum_i a_{\eta,i} g_i + b_0 \tag{2.4}$$

where T = absolute temperature

$a_{\eta,i}$ = i^{th} component coefficient

g_i = unnormalized mass fraction of the i^{th} component in glass

b_0 = a constant coefficient.

Note that the summation is over components *i* selected to appear in the model.

Table 2.8 lists the coefficients and goodness-of-fit statistics (R^2, R^2_A, and *s*) for the models used based on Equations (2.1), (2.3), and (2.4). R^2 is the fraction of variation in a modeled response property

Table 2.8. Summary of Model Coefficients Used to Estimate Constrained Glass Properties

Component	$a_{\eta,i}$ η **in poise**	$a_{T0.01,i}$ $T_{0.01}$ **in °C**	**PCT** $a_{rB,i}$ r **in g/m²**	**PCT** $a_{rLi,I}$ r **in g/m²**	**PCT** $a_{rNa,i}$ r **in g/m²**	**TCLP** $a_{cCd,i}$ c **in mg/L**
Al_2O_3	37891514.9	3391.671	-10.1923	-7.7581	-9.8577	0.3234
B_2O_3	-2159757.3	378.066	5.5843	3.2707	2.4722	8.6749
BaO	---	---	---	16.4840	---	---
CaO	---	---	-12.3992	-17.2629	-6.8451	---
CdO	15321023.8	---	---	---	---	21.6666
Cr_2O_3	75211455.7	27121.869	---	---	---	---
F	---	---	---	---	---	---
Fe_2O_3	6194895.3	3637.894	-1.9050	-4.6857	-2.6664	1.0137
K_2O	---	---	---	120.4309	---	---
Li_2O	-60583987.6	-2655.938	10.9736	11.5538	11.7138	9.4055
MgO	---	---	---	-25.1557	---	---
MnO	2628377.0	2852.645	---	---	---	6.4471
Na_2O	-10331075.2	-1786.463	12.9950	10.7807	16.8788	10.1264
NiO	19582478.7	13169.614	---	---	---	---
Sb_2O_3	-140193402.2	---	---	---	---	---
SeO_2	162438842.9	---	---	---	---	---
SiO_2	26918300.2	393.836	-4.4708	-3.0641	-4.8793	-0.9421
SrO	-8115167.1	-479.834	---	-3.3994	-11.1662	6.6293
ThO_2	---	---	-124.0320	---	-115.9263	-0.5965
TiO_2	---	---	---	-44.3963	---	---
Tl_2O_3	12149218.8	---	---	---	---	---
UO_2	---	---	---	4.1184	---	8.776
ZnO	---	---	---	-10.4650	---	14.3107
ZrO_2	21982480.7	4056.761	---	-7.7551	---	0.6811
b_0	-2.42258	---	---	---	---	---
b_1	---	---	---	---	---	0.9085
Observations (*n*)	240	41	42	41	44	101
Parameters (*p*)	16	11	8	15	9	14
R^2	0.961	0.869	0.854	0.907	0.877	0.981
Adjusted R^2	0.958	0.825	0.795	0.819	0.820	0.978
s	0.2790	53.492	0.4310	0.3156	0.4114	0.2049

[i.e., *f*(*P*)] accounted for by the model and can take values from 0 to 1. R^2_A is the fraction of variation in a modeled response property, adjusted for the number of fitted coefficients in the model. Finally, *s* is the root mean squared error (RMSE) of prediction errors, calculated from the data used to fit a model by (1) taking the sum-of-squares of differences in measured and predicted *f*(*P*) values, (2) dividing by the model degrees-of-freedom, $n - p$, where *n* is the number of data points used to fit the *p* coefficients in the model, and (3) taking the square root. If the model does not have a statistically significant lack-of-fit (LOF), then *s* = RMSE is an estimate of the experimental error standard deviation in fabricating glasses and measuring *f*(*P*).

Two types of model-uncertainty measures were used, both of which are uncertainties on the mean property response [i.e., *f*(*P*)] for composition ***x***. The first model-uncertainty measure is for the mean *f*(*P*) on a single composition ***x***, based on a confidence level (CL)% CI:

$$u_{CL\%CI} = t_{CL,n-p}\, s\sqrt{\mathbf{x}'\left(\mathbf{X}'\mathbf{X}\right)^{-1}\mathbf{x}} \tag{2.5}$$

The second model uncertainty measure is for the mean *f*(*P*) values corresponding to any set of compositions ***x***, based on a CL% SCI (a):

$$u_{CL\%SCI} = s\sqrt{p\, F_{CL,p,n-p}\;\mathbf{x}'\left(\mathbf{X}'\mathbf{X}\right)^{-1}\mathbf{x}} \tag{2.6}$$

In Equations (2.5) and (2.6),

$u_{CL\%\,CI}$ = uncertainty of a model prediction at composition ***x*** corresponding to the width of an upper CL% confidence interval on the mean transformed property *f*(*P*)
$u_{CL\%\,SCI}$ = uncertainty of a model prediction at composition ***x*** corresponding to the width of an upper CL% simultaneous confidence interval on the mean transformed property *f*(*P*) values for any set of compositions ***x***
CL = confidence level in percent (e.g., 90% or 95%)
$t_{CL,n-p}$ = CL^{th} percentile of a *t*-distribution with $n - p$ degrees-of-freedom (df) at the given confidence level
$F_{CL,p,n-p}$ = CL^{th} percentile of an *F*-distribution with *p* numerator df and $n - p$ denominator df at the given confidence level
s = root mean square error
p = number of fit parameters in the model
n = number of data points used to fit the model parameters
x = composition vector of the glass for which the property is being predicted
X = matrix of glass compositions used to fit the model
′ = a matrix or vector transpose
"-1" superscript = a matrix inverse.

(a) Based on the statistical theory, the set can contain an infinite number of compositions and provide the stated simultaneous confidence about the mean *f*(*P*) values for all such compositions.

In general, uncertainties based on SCIs are larger than uncertainties based on single CIs because an SCI provides the desired confidence level for the application of a model to any number of compositions, whereas a CI only provides the desired confidence for a single composition at a time. Hence, CIs are narrower than SCIs. However, there is a higher probability of one or more CIs not containing the mean $f(P)$ as the number of CIs for different $\boldsymbol{x}$ compositions increases.

Table 2.9 summarizes the constraints used for glass-optimization calculations, including their lower and upper limits and purposes. The glass-property constraints account for model uncertainties in

Table 2.9. Glass-Composition and Property Constraints Used for Glass-Formulation Optimization

Constraints	Lower Limit	Upper Limit	Purpose
Glass Property Constraints			
$T_{0.01} + u$ (90% SCI), °C	---(a)	950	Melter Processability
η (at 1150°C) - u (90% CI), poise	25	---	
η (at 1150°C) + u (90% CI), poise	---	60	
η (at 1100°C) - u (90% CI), poise	10	---	
η (at 1100°C) + u (90% CI), poise	---	150	
TCLP $c_{\mathrm{Cd}} + u$ (90% CI), mg/L	---	0.48	Delisting
PCT $r_{\mathrm{B}} + u$ (95% SCI), g/m^2	---	8.35	Waste Acceptance
PCT $r_{\mathrm{Li}} + u$ (95% SCI), g/m^2	---	4.79	
PCT $r_{\mathrm{Na}} + u$ (95% SCI), g/m^2	---	6.68	
Waste Loading Constraints (minimum mass fraction from waste for at least one constraint)			
Fe_2O_3	0.125	---	TS-1.1 (only the active constraints are listed).
Al_2O_3	0.11	---	
$Fe_2O_3 + Al_2O_3 + ZrO_2$	0.21	---	
$Al_2O_3 + ZrO_2$	0.14	---	
Single-Component Constraints (in mass fraction)			
Al_2O_3	0.03	---	Model Validity (only the active constraints are listed).
B_2O_3	0.05	---	
CdO	---	0.016	
Cr_2O_3	---	0.005 or 0.01(b)	
Fe_2O_3	---	0.14	
Li_2O	---	0.05	
MnO	---	0.07	
Na_2O	0.05	0.15	
SiO_2	0.35	0.53	
ZnO	0.02	---	

(a) --- denotes that no limit was imposed.

(b) Different variations for Cr_2O_3 concentration limits were considered. The 0.5% constraint is supported by current data. However, there is some indication that 1.0% may be possible with additional research efforts.

determining acceptable boundaries. Out of the 25 waste-loading constraints given in Table TS-1.1 of the WTP Contract (DOE-ORP 2000), the four that are relevant to the current evaluation(a) are given in Table 2.9.

The property-composition models, as empirical relationships, are only valid over fixed component concentration ranges. Model-validity constraints were added to ensure that the glass composition did not deviate from the ranges of model validity. Although there are some differences in the validity ranges between models, one set of the single-component ranges that are common for all the property models was used for the simplicity of glass-optimization calculations. Only single-component concentration constraints were used to define the model-validity range, although, in some cases, multi-component constraints were used to develop the glass-property data used for model fitting. Table 2.9 also lists these single-component constraints for model validity.

2.9 Glass Formulation Calculations

The glass composition is calculated from a mass balance:

$$g_i = W\, w_i + (1 - W)\, a_i \tag{2.7}$$

where g_i = mass fraction of the i^{th} component in glass
W = mass fraction of waste in glass (simply called “waste loading”)
w_i = mass fraction of the i^{th} component in waste
a_i = mass fraction of the i^{th} component in additives.

The initial optimization calculation involves finding the maximum W for each waste while satisfying all the constraints listed in Table 2.9. The W is always limited by more than one constraint after one of the Table TS-1.1 constraints is met. Stated in another way, other constraints must be satisfied in addition to satisfying one of the Table TS-1.1 limits for there to be an acceptable composition. For example, if one of the property constraints was met for a particular waste, the additive composition would be adjusted until at least one additional constraint was met, including model-validity constraints. For a glass limited by a single-component concentration constraint for components that come from waste, a unique optimum composition cannot be obtained.

Actual measured waste compositions were used as inputs for these calculations. Since a Ni crucible was used for solid sample fusions and Ni may influence $T_{0.01}$values, the starting concentrations for Ni were assumed to be present in all leached sludges. The set of RPP-WTP additives (a in equation 2.7) or GFCs, used in this optimization, are listed in Table 2.10. Also listed is the mass fraction of glass oxide components in each of the GFCs.

The initial optimization process revealed that each waste was limited only by single component constraints. Specifically, the loading of each waste in glass was determined by the allowable concentrations of either MnO (7 mass% in glass) or Cr_2O_3 (0.5 mass% in glass). Since there is some

---

(a) For the possible glass compositions corresponding to the waste compositions in this evaluation, only 4 of the 25 waste loading conditions have any chance of being violated.

Table 2.10. Mass Fractions and Uncertainty Ranges of Oxides in Each GFC

Oxide	Silica	Zincite	Borax	Sodium Carbonate	Lithium Carbonate
Al_2O_3	0.00135	0	0	0	0
B_2O_3	0	0	0.3750	0	0
CaO	0.00008	0	0	0	0
CdO	0	0.0001	0	0	0
Cl	0	0	0	0.0002	0.0001
Cr_2O_3	0	0	0	0	0.0001
Fe_2O_3	0.00016	0	0	0	0
K_2O	0	0	0	0	0
Li_2O	0	0	0	0	0.4020
MgO	0.00008	0	0	0	0.0001
MnO	0	0	0	0	0
Na_2O	0.00019	0	0.1670	0.5837	0.0008
NiO	0	0	0	0	0
P_2O_5	0	0	0	0	0
PbO	0	0	0	0	0
SiO_2	0.9970	0	0	0	0
SO_3	0	0	0	0.0001	0.0003
TiO_2	0.00008	0	0	0	0
UO_2	0	0	0	0	0
V_2O_5	0	0	0	0	0
ZnO	0	0.9990	0	0	0
ZrO_2	0	0	0	0	0
Total	0.99894	0.9991	0.5420	0.5842	0.4027

evidence that the concentration of Cr_2O_3 in glass may be increased with additional research (Vienna et al. 2002), a second set of calculations was performed using a Cr_2O_3 concentration constraint of 1 mass%.

3.0 Results and Discussion

This section discusses the analyses of washed SY-102 and SX-101 sludge solids with various techniques. It also discusses oxidative leach testing, the dissolution of non-radioactive and radioactive components, and the glass volumes resulting from immobilization of SX-101 and SY-102 sludge as a function of oxidative-alkaline leaching.

3.1 ICP-AES and Radiochemical Analysis of Washed SY-102 and SX-101 Sludge Solids

As noted in the introduction, to eliminate potential side reactions involving the oxidation of soluble organic compounds, the sludges were washed repeatedly with 0.1 M NaOH. In addition, this washing process removed all readily soluble chromium from the sludge, allowing the testing to focus on removing the dilute hydroxide-insoluble chromium. After each contact, the wash solution separated from the solids by centrifugation. At least five contacts, each at about a 5:1 solution to solids volume, were performed, after which it was assumed, based on previous experience, that the bulk of the water-soluble components had been removed from the interstitial liquid in the sludges. The residual solids were then suspended in dilute NaOH, and aliquots were taken for analysis.

Samples of the washed solids were dissolved by KOH fusion followed by nitric acid dissolution. The metals composition was determined by ICP-AES, and the radionuclide content was evaluated by AEA and GEA. Table 2.4 shows the concentrations of the major bulk components in the washed sludges. For both SX-101 and SY-102, aluminum is the primary metal present, followed by chromium. Substantial amounts of iron, sodium, manganese, and silicon (for SY-102) were also detected. The uranium content of the washed SX-101 solids was about a factor of four higher than that for the washed SY-102 solids.

Table 2.5 summarized the major radionuclide contents of the two washed sludges. Overall, the radionuclide concentrations in the washed sludges are similar: however, there is an order-of-magnitude greater plutonium and two orders of magnitude greater americium concentration in the washed SY-102 sludge than in the washed SX-101 sludge.

3.2 Analysis of the SY-102 and SX-101 Solids by XRD

The distribution and composition of the major sludge components was explored by X-ray powder diffraction to identify any crystalline phases and SEM/EDS to evaluate the distribution of the dominant metals present in the washed sludges.

The X-ray powder patterns obtained, as well as the patterns of the major identified phases, are shown in Figure 3.1 and Figure 3.2. For both sludges, the major crystalline material present is gibbsite, $Al(OH)_3$. For SX-101, a second phase was also identified, that of the uranium(VI) mineral, clarkeite, $Na[UO_2(O)(OH)]$. The presence of detectable quantities of a uranium-containing mineral in the washed SX-101 sludge is consistent with the greater concentrations of uranium found in that sludge.

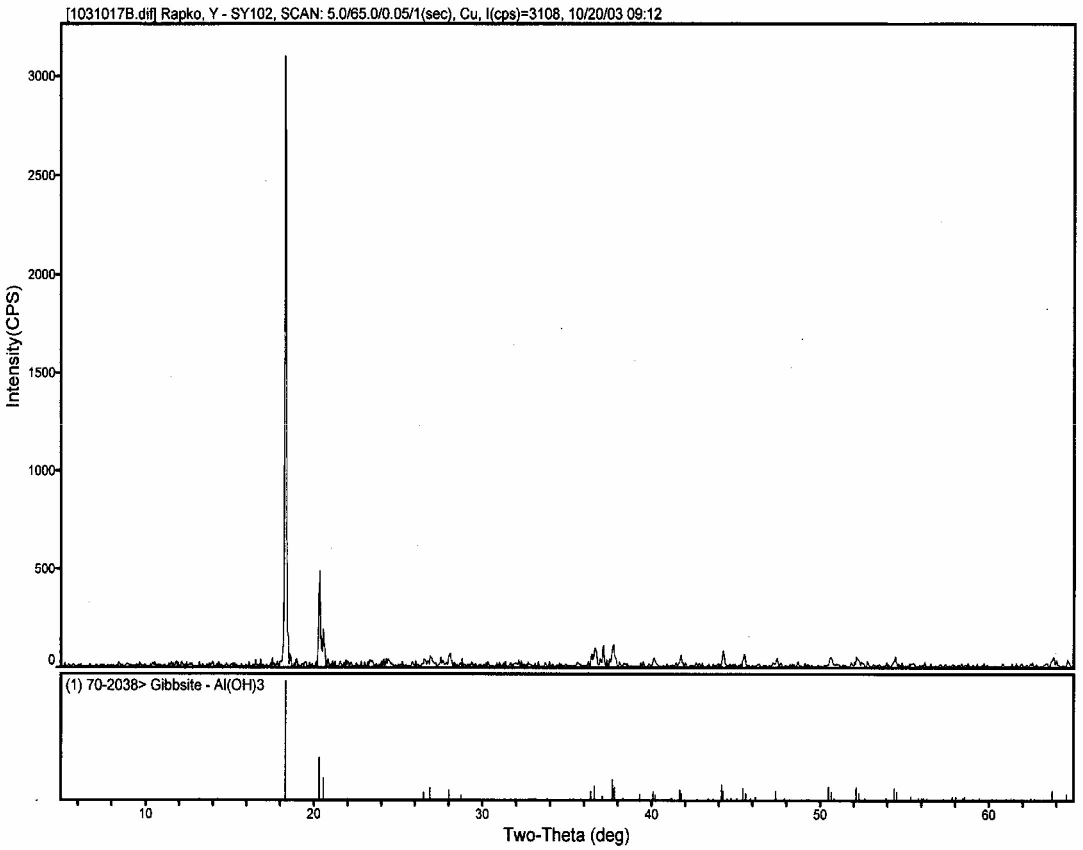


Figure 3.1. XRD Measurement (top) and Identified Pattern (bottom) for Washed SY-102 Sludge Solids

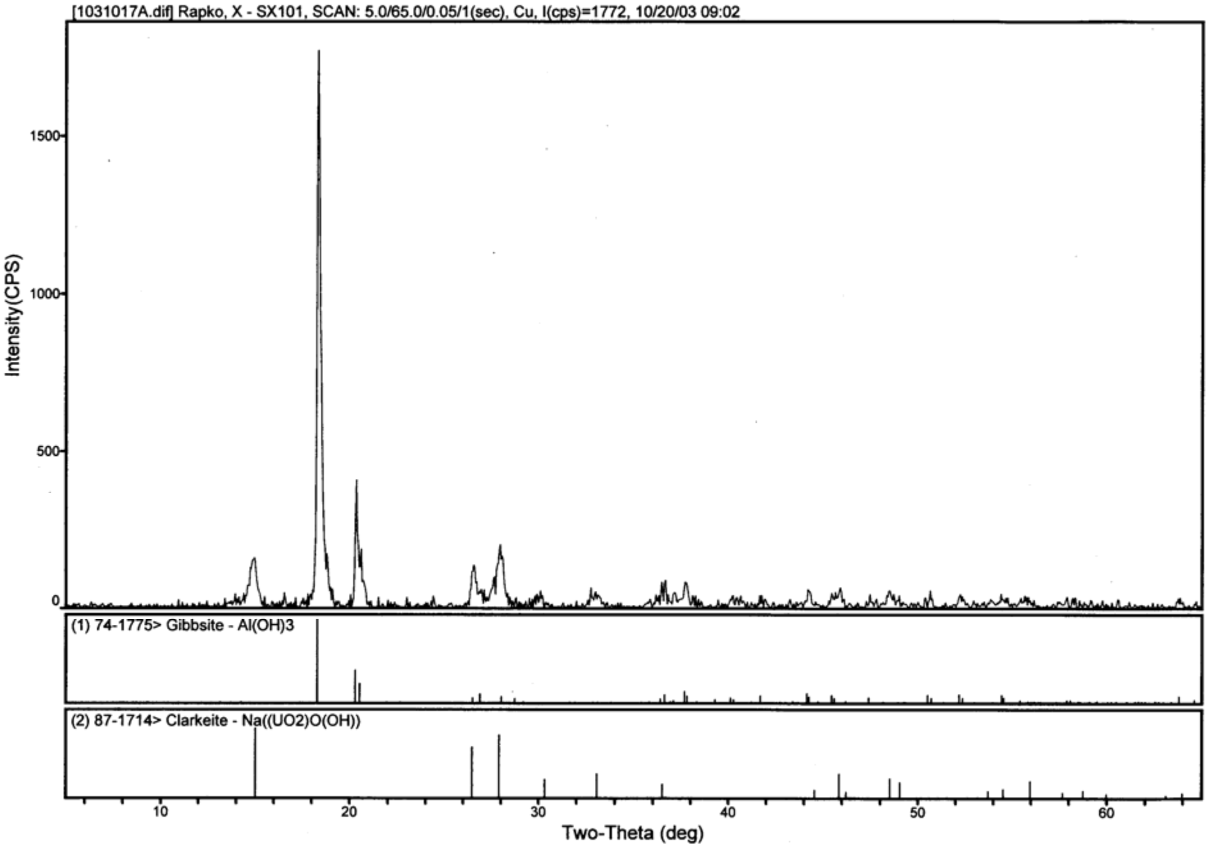


Figure 3.2. **XRD Measurement (top) and Identified Pattern (bottom) for Washed SX-101 Sludge Solids**

3.3 SEM/EDS Analysis of the SY-102 and SX-101 solids

3.3.1 SY-102 Washed Solids

The SEM-EDS analysis of washed SX-101 and SY-102 sludge solids reveals information about the distribution of the major metals in the sludge. A picture of the predominant solid particles observed for SY-102, together with a mapping of the major bulk components as indicated by EDS, the EDS spectrum itself and a magnified view are shown in Figure 3.3 through Figure 3.6, respectively. Table 3.1 reports the metals concentrations from the EDS analysis.

The majority of the particles found in the small SY-102 sludge samples examined were similar in size and shape to that shown in Figure 3.3 and Figure 3.5, namely irregularly-shaped solids with a “spongy” texture. A second type of particle was observed in the SY-102 washed solids. This particle appears to have a much better defined shape (Figure 3.7) and the EDS analysis indicates aluminum to be the primary metallic element present. The particle is likely that of the crystalline gibbsite revealed to be present by the XRD analysis.

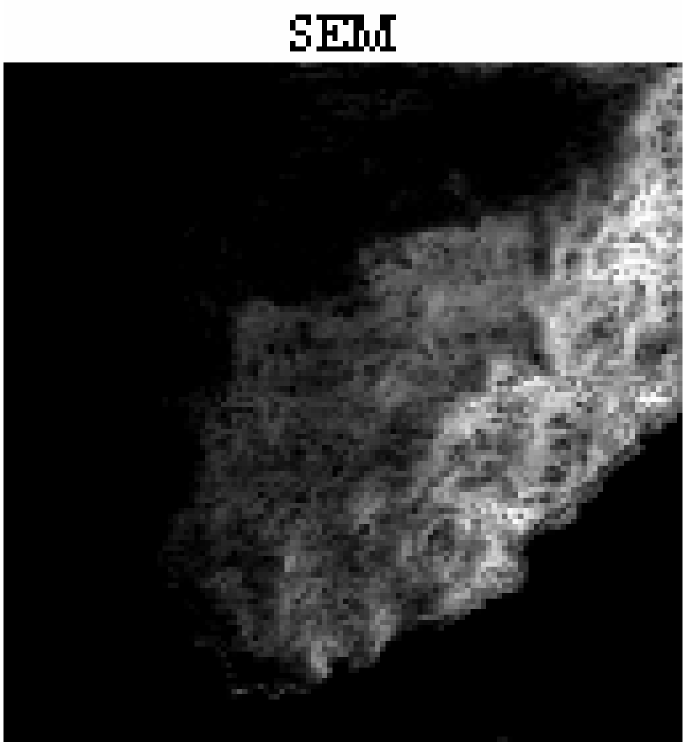


Figure 3.3. SEM Image of the SY-102 Particle Used for EDS Map

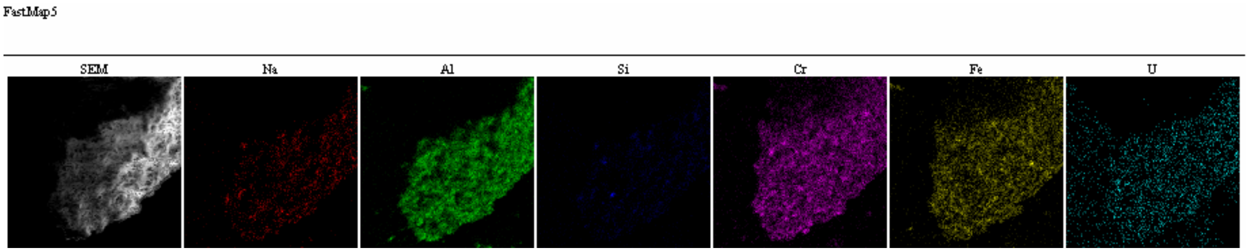


Figure 3.4. EDS Map of SY-102 Particle

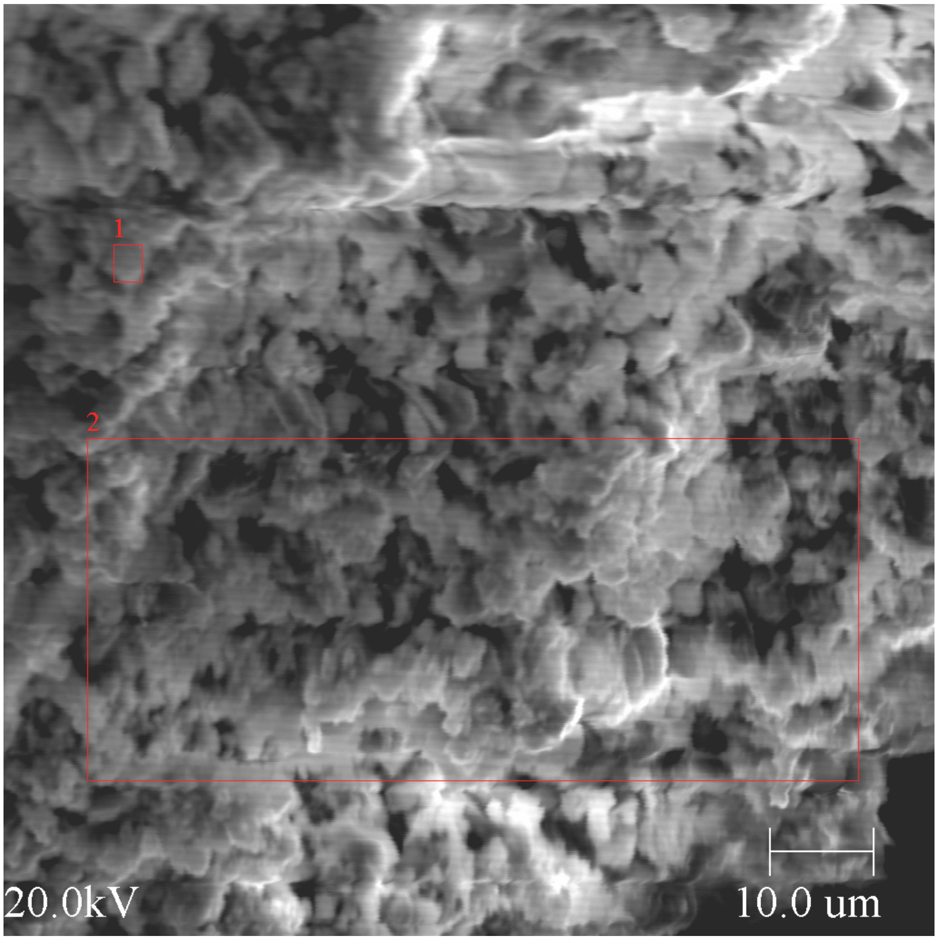


Figure 3.5. Expanded View of SY-102 Particle

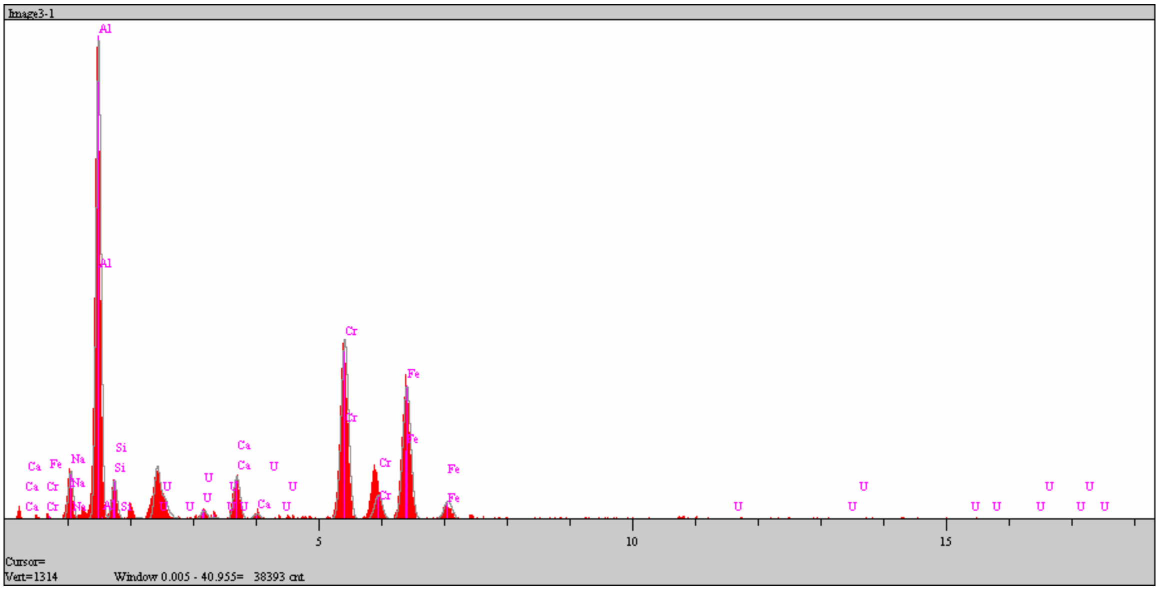
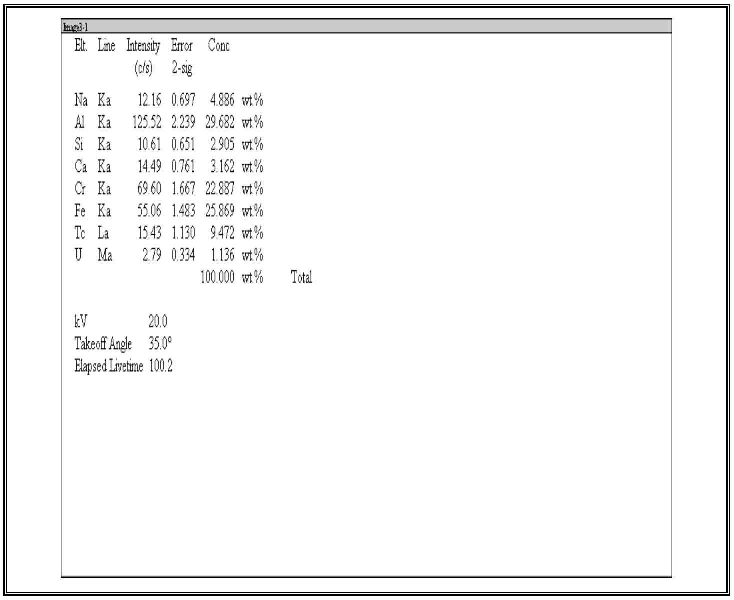


Figure 3.6. EDS Analysis of Figure 3.5 (Box 2)

Table 3.1. Data Output from EDS analysis of Figure 3.5 (Box 2)



```
Image3-1
 Elt.  Line  Intensity  Error    Conc
             (c/s)      2-sig

 Na    Ka      12.16   0.697    4.886  wt.%
 Al    Ka     125.52   2.239   29.682  wt.%
 Si    Ka      10.61   0.651    2.905  wt.%
 Ca    Ka      14.49   0.761    3.162  wt.%
 Cr    Ka      69.60   1.667   22.887  wt.%
 Fe    Ka      55.06   1.483   25.869  wt.%
 Tc    La      15.43   1.130    9.472  wt.%
 U     Ma       2.79   0.334    1.136  wt.%
                              100.000  wt.%       Total


 kV                20.0
 Takeoff Angle     35.0°
 Elapsed Livetime  100.2
```

In short, XRD and SEM analysis of SY-102 solids indicate that aluminum, iron, and chromium tend to be uniformly distributed in the bulk of the solids, with the exception of crystalline particles containing solely gibbsite. The presence of aluminum as gibbsite bodes well for the success of alkaline leaching at removing the bulk of the components from the tank sludge.

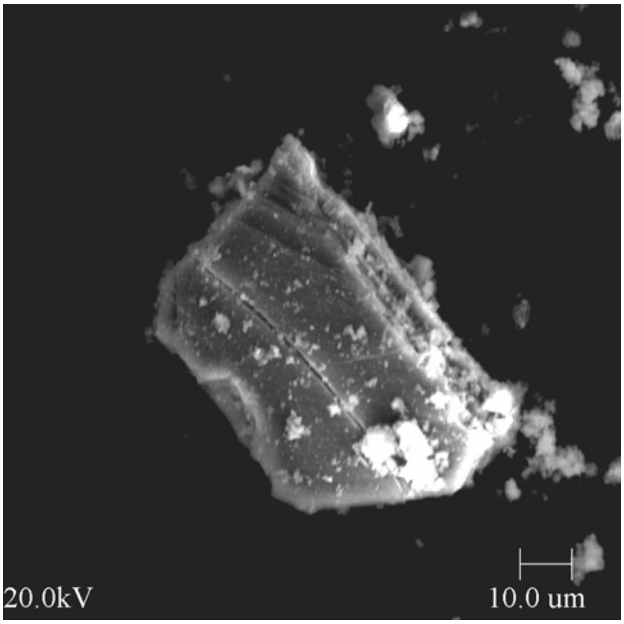


Figure 3.7. Aluminum-Rich Particle in Washed SY-102 Sludge

3.3.2 SX-101 Washed Solids

One major type of sludge particle was observed by SEM; the characteristics of that particle are summarized by the SEM image in Figure 3.8, by the EDS spectrum in Figure 3.9, by the relative metal concentrations in the area as determined by EDS analysis in Table 3.2, and by a EDS mapping of the distribution of the major observed metals in the washed SX-101 particle in Figure 3.10.

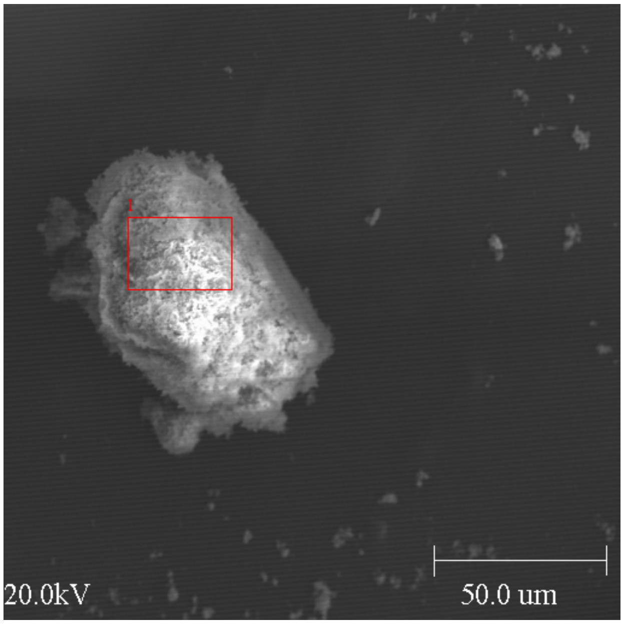


Figure 3.8. SEM of SX-101 Particle and Region Examined by EDS

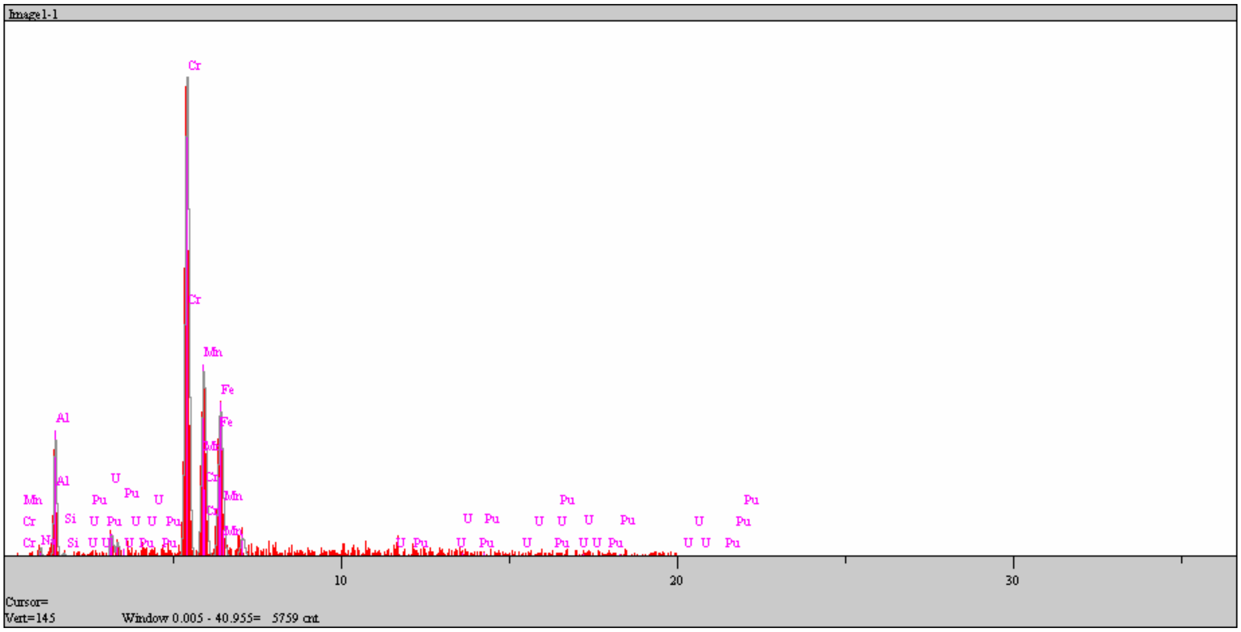
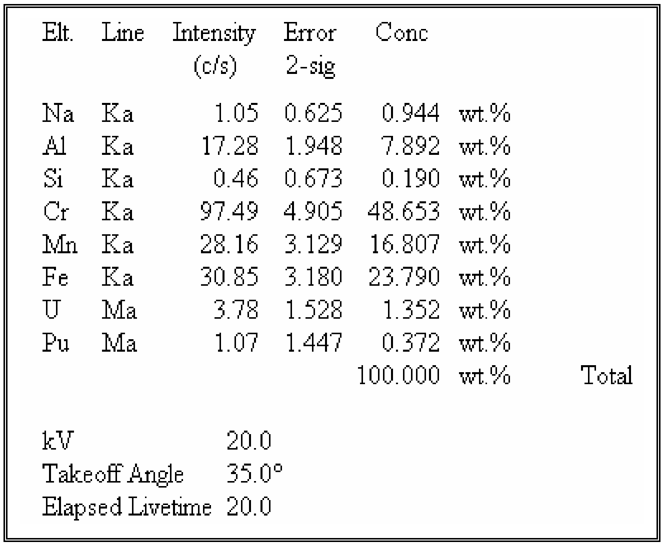


Figure 3.9. EDS Spectrum for SX-101 Particle

Table 3.2. Data for EDS of SX-101 Particle



```
Elt.  Line  Intensity  Error    Conc
             (c/s)     2-sig

Na    Ka       1.05    0.625     0.944  wt.%
Al    Ka      17.28    1.948     7.892  wt.%
Si    Ka       0.46    0.673     0.190  wt.%
Cr    Ka      97.49    4.905    48.653  wt.%
Mn    Ka      28.16    3.129    16.807  wt.%
Fe    Ka      30.85    3.180    23.790  wt.%
U     Ma       3.78    1.528     1.352  wt.%
Pu    Ma       1.07    1.447     0.372  wt.%
                               100.000  wt.%        Total

kV                 20.0
Takeoff Angle      35.0°
Elapsed Livetime   20.0
```

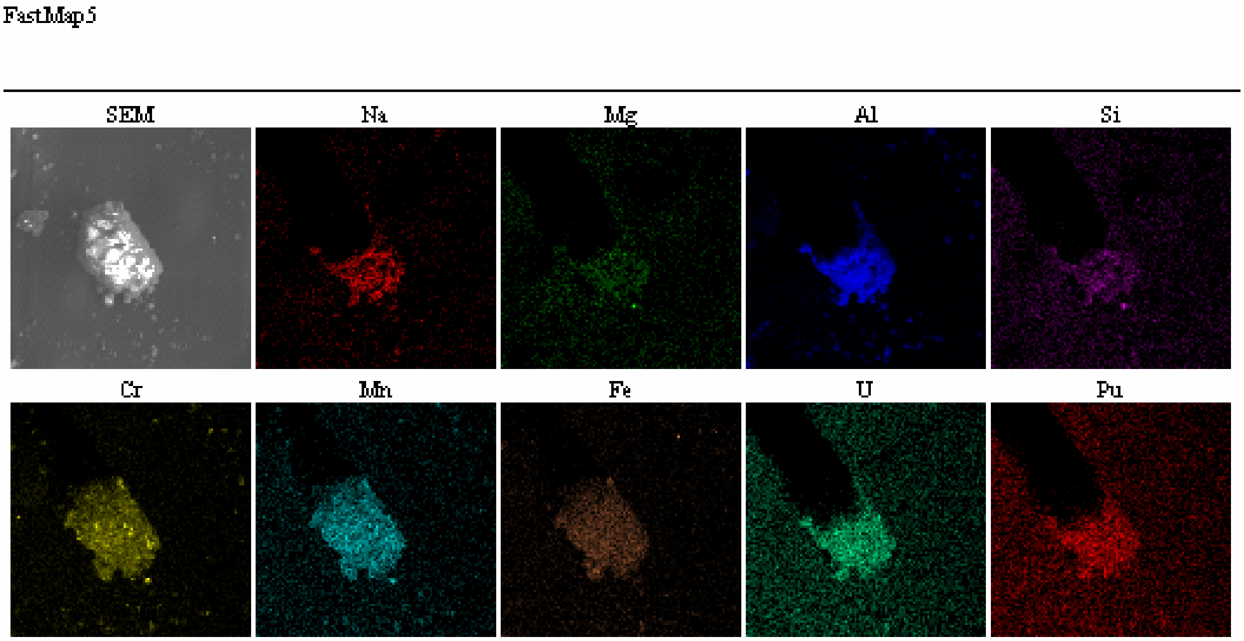


Figure 3.10. EDS Mapping of Major Observed Components in the SX-101 Particle

As with the SY-102 particle, the major observed components chromium, manganese, and iron seem to be broadly and evenly distributed throughout the particle. Aluminum, silica, and sodium are evenly distributed throughout much of the particle but appear to be less abundant towards the top. Finally, a broad view revealed some small irregular solids composed mostly of aluminum. Due to the irregular shape of this particle, some sort of amorphous $Al(OH)_3$ is postulated for its composition. No pure uranium crystalline phases were found, despite the identification of clarkeite by XRD.

In summary, both the washed SY-102 and SX-101 solids appear to be mostly composed of particles in which the major bulk components are evenly distributed. Of the crystalline material for SY-102, a single crystalline species, gibbsite, was identified by XRD, and the identification was supported by the SEM-EDS analysis. For SX-101, the XRD analysis also identified crystalline gibbsite as well as a crystalline uranium(VI) phase, clarkeite, but corresponding pure aluminum or uranium-containing particles were not found by SEM-EDS. As the SEM-EDS analysis involves examining only a few particles in a subsample of the washed solids, drawing conclusions by extrapolating these results to the entire system must be done with caution. Still, it does provide at least a qualitative insight as to the distribution of metals in the washed sludge solids.

3.4 Oxidative Leach Testing—Experimental Design and Execution

The conditions chosen for oxidative-alkaline leach testing have been summarized in Table 2.7 in the Experimental Section. These conditions were chosen to focus on three process variables: temperature, hydroxide concentration, and the order of alkaline leaching processes. In all cases, the initial solids volume to total leachate volume was kept constant at 1:4 (1 part settled sludge volume and three parts added solution volume). Tests 1 and 2 explore the possibility of combining a high hydroxide, high temperature, leach for aluminum removal with concomitant permanganate addition for chromium removal. Test 1 uses the standard caustic-leaching conditions (3 M NaOH, 85°C) while Test 2 explores the impact of a potential upset condition of excess permanganate and hydroxide at elevated temperature.

Tests 3 and 4 and Tests 5 and 6 explore the impact of temperature and the order of alkaline leach operations. In all cases, the targeted oxidative-alkaline leach conditions employ a targeted slight stoichiometric excess of permanganate and a low (0.25 M) initial hydroxide concentration in the leachate. Within the groups of tests (3 and 4 and also 5 and 6) the variable is that of temperature (ambient temperature, 25°C, or elevated temperature, 85°C). Between Tests 3 and 4 and Tests 5 and 6, the order of leaching is examined. For Tests 3 and 4, a caustic leach was performed before oxidative leaching, and for Tests 5 and 6, a standard caustic leach was performed following oxidative-alkaline leaching.

In previous oxidative-alkaline leach tests examining the effect of free hydroxide concentration, the lower initial hydroxide concentrations were typically lower than those targeted in this test. The reason for this lies in the lower leachate-to-solids ratio in these tests compared to those previously. Table 3.3 and Table 3.4 used the wt % insoluble solids in the initial washed solid slurries together with the amounts of slurry used for each test reported in Table 2.6 to calculate the mass of washed solids and using the chromium concentrations in the washed solids reported in Table 2.4 to calculate the total moles of chromium in the test samples. Table 3.3 and Table 3.4 indicate that approximately 1 mmol (SX-101) and 1.7 mmol (SY-102) of chromium were present for each test. As noted in the introduction section, the reaction of permanganate with Cr(III) hydroxide to form manganese dioxide and chromate consumes 1 equivalent of hydroxide, and if other reduced manganese species are formed, the hydroxide

Table 3.3. Sub-Sampling of Washed SY-102 Solids for Oxidative-Alkaline Leach Testing

Sample	Washed solids (g)	Mass Cr in Sample (g)	Mmol Cr in Sample
SY-102-1	1.22	0.09	1.72
SY-102-2	1.23	0.09	1.73
SY-102-3	1.21	0.09	1.70
SY-102-4	1.20	0.09	1.70
SY-102-5	1.18	0.09	1.66
SY-102-6	1.24	0.09	1.74

Table 3.4. Sub-Sampling of Washed SX-101 Solids for Oxidative-Alkaline Leach Testing

Sample	Washed solids (g)	Mass Cr in Sample (g)	Mmol Cr in Sample
SX-101-1	1.12	0.06	1.11
SX-101-2	1.11	0.06	1.10
SX-101-3	1.30	0.07	1.29
SX-101-4	1.16	0.06	1.15
SX-101-5	0.93	0.05	0.92
SX-101-6	1.03[a]	0.05	1.02

(a) Grams of washed solids calculated by subtracting total mass of slurry solids used from samples 1-5 from the total solids calculated to be present in the sample slurry.

consumption is even greater. This implies that at least 1 (SX-101) and 1.7 mmol (SY-102) of hydroxide from the oxidative-alkaline leach solution would be consumed during chromium oxidation. This corresponds to a decrease of about 0.063 to 0.106 M in the initial hydroxide concentration. So for these tests, the initial free hydroxide concentration was targeted so that chromium oxidation could go to completion while keeping a modest free hydroxide concentration in solution. It should be noted that aluminum dissolution would be expected to consume one equivalent of hydroxide. This implies that between 7.7 mmol (SY-102) and 9.4 mmol (SX-101) of hydroxide could be consumed by aluminum dissolution. This would correspond to an approximate decrease in free hydroxide concentration from 0.48 M (SY-102) to 0.59 M (SX-101) at the solid/solution ratios used. In short, the low hydroxide concentration experiments possess only enough free hydroxide for the chromium reaction. The high hydroxide tests possess enough hydroxide to oxidize chromium and dissolve aluminum. The separate caustic leaches associated with the low hydroxide oxidative leach supply enough hydroxide in this separate step to dissolve all aluminum not consumed by the oxidative-alkaline leach treatment.

As noted in the Experimental Section, two 0.1-ml sample aliquots were removed at 2, 6, and 24-hour contact times. Assuming no losses due to evaporation, this would remove 0.6/16 ml or about 4% of the leachate solution. No attempt to correct for these losses has been made in the analyses reported below, primarily due to an inability to account for any time dependence in the dissolution of most components together with the varying and unmonitored changes in leachate volume due to evaporation.

The general set-up procedure is described as follows: excess liquid was removed from the initial slurry by centrifugation/decantation. To the residual solids, DI water, 10 M NaOH, and 0.5 M $NaMnO_4$ in water were combined in this order as described in Table 3.5 to meet the test conditions as described in Table 2.7 above.

Because high volumes of reagent stock solutions were required to add sufficient equivalents of hydroxide and manganese in Test #2, a 4:1 total volume: slurry volume could not be achieved if the stock solution of 0.5 M sodium permanganate in water was used to introduce the permanganate; solid sodium permanganate was used instead. After the reagents were added, the vials were capped, and the centrifuged solids were resuspended by vortex mixing before being placed in an aluminum block on top of a rotary shaker to agitate the solids at temperature. This procedure represents a change in equipment from previous oxidative leach testing and avoids any artifacts due to a magnetic stirring bar being present in the system. The 25°C tests were capped tightly: the 85°C tests were capped loosely.

Table 3.5. Added Reagents in Oxidative-Alkaline Leaching Setup (assuming 4 ml sludge)

Test	Added 0.5 M $NaMnO_4$ (ml)	Added 10 M NaOH (ml)	Added DI Water (ml)
SX-101-1	2.5	4.8	4.7
SX-101-2	0.033*	6	6
SX-101-3	2.85	0.4	8.75
SX-101-4	2.5	0.4	9.1
SX-101-5	2.02	0.4	9.58
SX-101-6	2.4	0.4	9.2
SY-102-1	3.8	4.8	3.4
SY-102-2	0.055[(a)]	6	6
SY-102-3	3.74	0.4	7.86
SY-102-4	3.8	0.4	7.8
SY-102-5	3.66	0.4	7.94
SY-102-6	3.9	0.4	7.7
(a) Grams of solid $NaMnO_4$ added.			

After approximately 2 hours, 6 hours, and 24 hours of contact time, the vials were tightly capped and centrifuged, the supernatants were sampled, the centrifuged solids were resuspended by vortex mixing, and the vials were returned to the rotary shaker/heater as needed. For the 25°C tests, with the exception of the SY-102-5 test, the presence of permanganate/manganate could still be seen visually after 2 hours. For the SY-102-5 test, another 0.1 equivalent (0.36 ml) of 0.5 M sodium permanganate in water was added at this point. After 6 hours, the SY-102-5 test was again yellow, indicative of permanganate consumption, but no further permanganate was added.

For the 85°C oxidative leach tests, after 2 hours, all visual signs of permanganate had disappeared, with the exception of Test SX-101-6. For the samples with no visual presence of permanganate, 0.5 ml (approximately 0.1 to 0.2 equivalents additional permanganate) was added. After 6 hours, all of the SY-102 leachates and the SX-101-2 leachate showed no visual signs of permanganate; at this point, another 0.5 ml of 0.5 M sodium permanganate solution was added to these leachate solutions. After 24 hours of contact time, only the SX-101-6 test showed visual indications of the presence of permanganate in solution. In addition, a small but visually apparent decrease in the leachate solution volumes was apparent for Tests SX-101-2, SY-102-4, and SY-102-6. Larger decreases in the solution volume were apparent for the SX-101-4 and SX-101-6 tests.

One mishap occurred during the final solid-liquid separation washings with 0.1 M NaOH and analytical sampling. One pipette full of the first wash solution (estimated 2 to 2.5 ml) from Test SY-102-6 was added to the receipt container for SY-102-4. Because it was a wash solution instead of the actual leachate solution and because it was a relatively small amount of the wash solution, its impact on subsequent analysis is believed to be minor.

3.5 Dissolution of Non-Radioactive Components

Table 3.6 summarizes the overall removal of the major non-radioactive components present in the washed SX-101 and SY-102 solids as a function of the differing oxidative-alkaline leach methods tested.

Table 3.6. Major Component Removal from SX-101 and SY-102 Washed-Sludges by Oxidative-Alkaline Leaching

Test #	% Component Removal					
	Al	Cr	Fe	Mn	Si	U
SX-101-1	96	96	< 0.1	0	42	0
SX-101-2	96	66	0.3	0	43	0
SX-101-3	83	87	0.3	0	46	0
SX-101-4	89	94	0.3	0	50	0
SX-101-5	97	65	0.6	0	55	0
SX-101-6	97	97	0.3	0.2	67	0
SY-102-1	86	94	< 0.1	0	17	0
SY-102-2	88	46	< 0.1	0	22	0
SY-102-3	76	80	0.1	63	32	0
SY-102-4	78	95	0.2	0	36	0
SY-102-5	94	75	0.2	0	31	0
SY-102-6	89	96	< 0.1	0	28	0

These component removals were calculated by summing the total mass of each component found in all leach solutions together with the mass of the component in the residual solids and calculating the fraction of mass removed in the leachate from the calculated total mass.

As expected, the oxidative-alkaline leaching primarily dissolves both aluminum and chromium. Generally, aluminum removals are good to excellent (> 80%, often > 90%). Somewhat surprisingly, the combined 3 to 5 M NaOH/permanganate treatments seem to be somewhat more effective at aluminum removal (about 10% increased component removal) than sequential 3 M NaOH and dilute hydroxide/permanganate treatments.

Generally, removal of chromium also is high, but the dependence of chromium removals varies more with the leach conditions, ranging from > 50% to > 95%. Test conditions #2 (5 M NaOH, excess permanganate, 85°C) and #5 (25°C, 0.25 M NaOH followed by 3 M NaOH, 85°C) are markedly less effective at chromium removal. An inability to access and oxidize chromium because of the presence of undissolved aluminum in Test #5 could explain this behavior, but the reason for the poorer performance at chromium removal under conditions of 5 M NaOH/excess permanganate is unknown.

Significant amounts of Si are removed during leaching, but the amount appears to be independent of the leach conditions (but not the sludge type). Minor amounts of iron are removed, and the fractions removed appear to be independent of both the leach conditions and sludge type.

3.5.1 Chromium Dissolution and Chromate Formation

All oxidative leach solutions and subsequent washes were analyzed both by ICP-AES for the total chromium concentrations and by spectrophotometry for the chromate concentrations. In addition, the prior and subsequent 3 M NaOH/85°C leach and washes were analyzed in this manner as well. Table 3.7 compares the total chromium concentration of chromium measured in these leach solutions with the chromate concentrations.

Table 3.7. Chromate Versus Total Chromium Comparison in Washed SX-101 and SY-102 Alkaline Leach Solutions

Sample	$[CrO_4^{2-}]$, M[(a)]	$[Cr]_T$, M[(b)]	$[Cr]_T/[CrO_4^{2-}]$
SX-101-1 OL[(c)]	2.25E-02	2.26E-02	1.00E+00
SX-101-2 OL	1.87E-02	1.75E-02	9.36E-01
SX-101-3 OL	3.84E-02	3.69E-02	9.60E-01
SX-101-4 OL	2.92E-02	2.98E-02	1.02E+00
SX-101-5 OL	2.61E-02	3.29E-03	1.26E-01
SX-101-6 OL	1.52E-02	1.46E-02	9.57E-01
SX-101-3 IL	3.91E-03	3.44E-03	8.80E-01
SX-101-4 IL	2.68E-03	2.52E-03	9.42E-01
SX-101-5 FL	3.46E-03	3.31E-03	9.56E-01
SX-101-6 FL	8.74E-04	8.63E-04	9.88E-01
SY-102-1 OL	4.09E-02	3.79E-02	9.26E-01
SY-102-2 OL	1.88E-02	1.83E-02	9.73E-01
SY-102-3 OL	4.70E-02	4.68E-02	9.96E-01
SY-102-4 OL	3.59E-02	3.66E-02	1.02E+00
SY-102-5 OL	6.19E-02	7.17E-03	1.16E-01
SY-102-6 OL	5.18E-02	4.96E-02	9.58E-01
SY-102-3 IL	3.22E-03	3.17E-03	9.87E-01
SY-102-4 IL	3.54E-03	3.42E-03	9.66E-01
SY-102-5 FL	7.23E-03	7.08E-03	9.80E-01
SY-102-6 FL	3.77E-03	4.54E-03	1.20E+00

(a) As determined by visible spectroscopy.
(b) As determined by ICP-AES.
(c) OL = oxidative-alkaline leach solution
IL = caustic-leach solution before oxidative-alkaline leaching
FL = caustic-leach solution subsequent to oxidative-alkaline leaching.

Overall, the agreement between total chromium and chromate measurements is excellent, well within the 15% uncertainty claimed for the ICP-AES measurements of chromium. Three exceptions are noted: SY-102-5 oxidative leachate, SX-101-5 oxidative leachate, and the SY-102-6 final caustic leachate. In SY-102-5 and SX-101-5, the total chromium concentrations are less than the chromate concentrations by a significant quantity. It is impossible to have less chromium than chromate, but the source of the discrepancy is unknown. It may be that the ICP-AES analysis of the leachate solutions is low: not only are the measured chromate concentrations higher, but the overall mass balance is low for chromium specifically. The impact of this low ICP-AES value is significant; if the Cr concentrations based on chromate are used instead of the ICP-AES data, the removal of Cr increases from 65% to 90% for SX-101-5 and from 75% to 94% for SY-102-5. The SY-102-6 final leachate solution is the only solution that appears to have slightly more total chromium than chromate. No Cr(III) was detected by spectrophotometry, but the low extinction coefficients for Cr(III) compared to Cr(VI) indicate that such a low Cr(III) concentration suggested by the difference would be below detection limits.

The rate of chromate formation during oxidative leaching was monitored spectrophotometrically. The results are illustrated in Figure 3.11 and Figure 3.12.

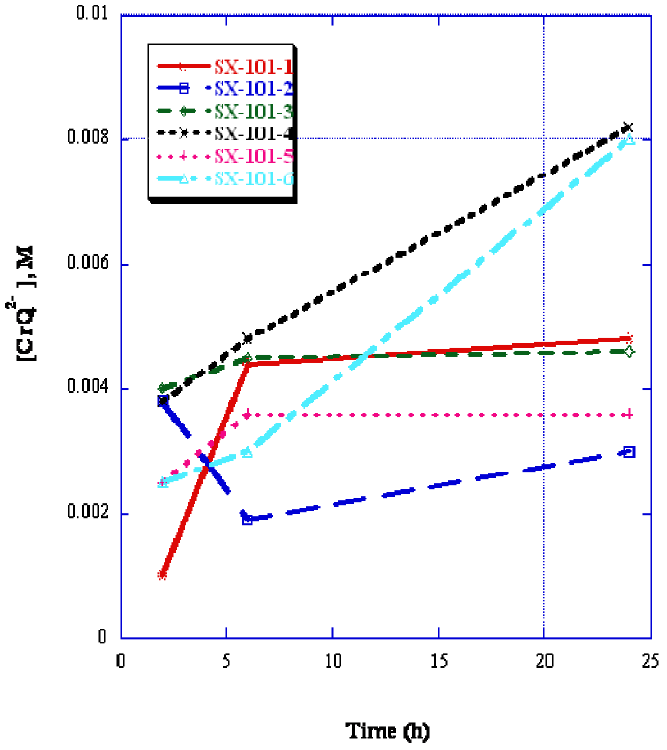


Figure 3.11. Chromate Formation During Oxidative-Alkaline Leaching of Washed SX-101 Sludge

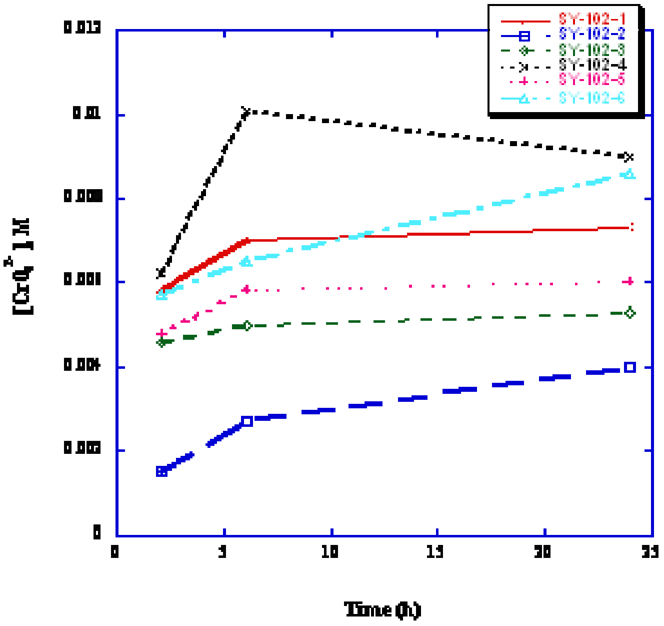


Figure 3.12. Chromate Formation During Oxidative Alkaline Leaching of Washed SY-102 Sludge

The results from the SX-101 testing appear more scattered than the results from the SY-102 testing; the reason for this is unknown. Overall, consistent with prior reports, it appears that most of the chromate formation occurs within the first 6 hours. Increases observed between 6 to 24 hours might be due in part to the evaporation losses noted previously, which would effectively increase the observed chromate concentration without increasing the amount of total dissolved chromium. Otherwise, the trends become difficult to interpret. For example, test conditions -4 and -6 differ from test conditions -3 and -5 only in the leach temperature (85°C versus 25°C, respectively). Yet in both cases, the 85°C contact shows further apparent increases in chromate concentration. With the reasonable assumption that increases in temperature should correspond to more rapid reaction, the 85°C should be complete sooner than the 25°C, which is not what is observed. On the other hand, if concentration due to evaporation is more prevalent, albeit variable, at 85°C than at 25°C, even if chromate formation were complete after 6 hours in both cases, consistent with these experimental findings, an apparent increase in the production of chromate would be observed.

3.6 Radionuclide Dissolution

One concern about employing oxidative-alkaline leaching is that concomitant oxidation of plutonium to Pu(VI) would lead to a problematic enhanced dissolution of plutonium. To evaluate this possibility, the radionuclide content of the leachate and wash solutions was measured by GEA and AEA to determine the extent of radionuclide dissolution, in particular actinide dissolution. The results are shown in Table 3.8.

The results for both the SY-102 and SX-101 sludges show similar trends. The only radionuclides that show any significant dissolution are plutonium and Cs. The Cs dissolution tends to be fairly constant at around 30 to 40% dissolution regardless of the sludge type or reaction conditions.

Table 3.8. Radionuclide Removals from SX-101 and SY-102 Washed Sludges by Oxidative-Alkaline Leaching

Test	% Component Removal						
	^{239,240}Pu	^{241}Am	^{243,244}Cm	Total α	^{60}Co	^{137}Cs	^{154}Eu
SX-101-1	13	< 0.01	< 0.01	3.2	< 0.01	27	< 0.01
SX-101-2	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	33	< 0.01
SX-101-3	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	33(a)	< 0.01
SX-101-4	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	33(a)	< 0.01
SX-101-5	1.1(a)	< 0.01	< 0.01	0.3(a)	< 0.01	38	< 0.01
SX-101-6	2.8(a)	< 0.01	< 0.01	0.7(a)	< 0.01	29	< 0.01
SY-102-1	0.6	< 0.01	< 0.01	0.1	< 0.01	22	< 0.01
SY-102-2	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	37	< 0.01
SY-102-3	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	40(a)	< 0.01
SY-102-4	< 0.1	< 0.01	< 0.01	< 0.1	< 0.01	41(a)	< 0.01
SY-102-5	< 0.1 (a)	< 0.01	< 0.01	< 0.1(a)	< 0.01	41(a)	< 0.01
SY-102-6	0.2(a)	< 0.01	< 0.01	< 0.1(a)	< 0.01	37	< 0.01

(a) Component fraction removed during standard caustic leach greater than that removed during oxidative-alkaline leaching.

With respect to plutonium dissolution, adding permanganate to a standard caustic-leach solution (i.e., condition number 1) results in the most enhanced plutonium dissolution of all the leach conditions tested. Interestingly, increasing the initial hydroxide concentration still further, from 3 to 5 M, in the presence of a greater excess of permanganate, causes a drop in the amount of plutonium dissolved. Performing a standard caustic leach following permanganate addition (i.e., conditions 5 and 6) results in more plutonium dissolution than reversing the order and performing an initial caustic leach followed by a low hydroxide oxidative leach (i.e., conditions 3 and 4). Notably, in these cases (conditions 5 and 6), the bulk of the plutonium dissolution is found during the subsequent caustic leach and not during the oxidative leach. The reasons for this are unclear, but perhaps it is a kinetic effect: additional plutonium dissolves during oxidative leaching but reprecipitates during cooling/washing. This freshly reprecipitated plutonium then more rapidly redissolves during the relatively short 8-hour contact times of the standard caustic leach. Finally, performing the oxidative leach at 85°C (conditions 4 and 6) results in a small enhancement in plutonium dissolution compared to performing a 25°C oxidative leach (conditions 3 and 5). In almost all cases, though, the extent of plutonium dissolution is relatively minor, especially when compared to the extent of aluminum and chromium removal described above.

Samples for plutonium analysis were collected of the oxidative-alkaline leachate solutions themselves after 2, 6, and 24 contact times, with the 2- and 24-hour contact times measured for plutonium. Soon after removal from the leachate, these samples were placed into a strongly acidic solution within a few seconds of removal to prevent plutonium hydrolysis and reprecipitation. This approach allows monitoring the extent of changes in dissolved plutonium, much like the rate of chromate formation was monitored. The results of this monitoring of plutonium dissolution are summarized in Figure 3.13 and Figure 3.14:

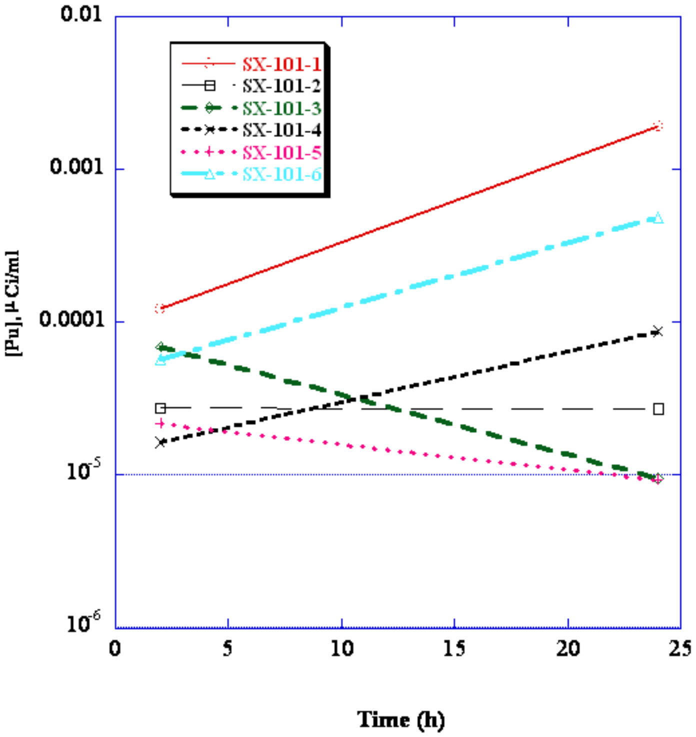


Figure 3.13. Rate of Plutonium Dissolution in Oxidative-Alkaline Leachate Solutions Contacted with Washed SX-101 Sludge Solids

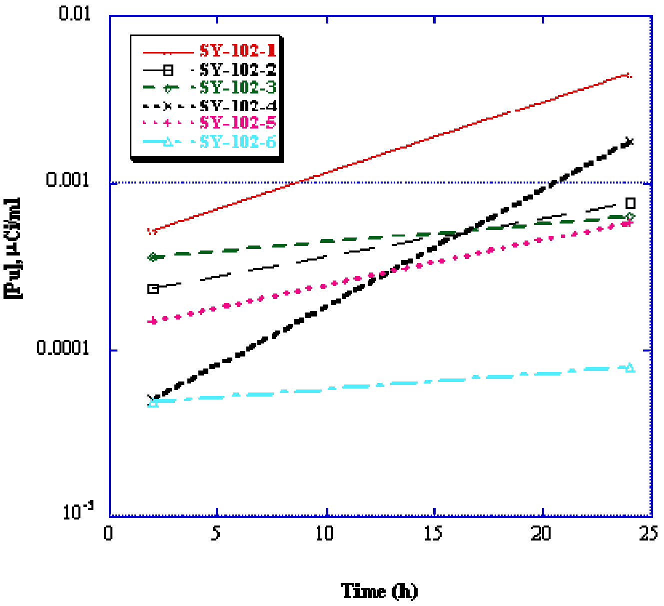


Figure 3.14. Rates of Plutonium Dissolution in Oxidative-Alkaline Leachate Solutions Contacted with Washed SY-102 Sludge Solids

In general, increases in the amount of dissolved plutonium are observed as a result of increased contact time, suggesting that optimal contact times may need to balance the extent of chromate formation with the extent of plutonium dissolution.

3.7 Glass Volumes or Immobilization of SX-101 and SY-102 Sludge as a Function of Oxidative-Alkaline Leaching

The ultimate goal of oxidative-alkaline leaching is to reduce the amount of IHLW produced while producing a leachate that can be made into acceptable immobilized low-activity waste (ILAW). In this section, we attempt to evaluate how effective the various test conditions were at achieving that goal. To evaluate the effectiveness of various leach conditions, we calculated the amount of glass required to immobilize one arbitrary unit of treated sludge. Three sets of loadings were calculated, one based on the DOE's minimum contract requirements (TS-1.1 in Table 3.9), one using the current WTP baseline model for IHLW, and one using an expanded model with a relaxed restriction on chromium concentration. Table 3.9 summarizes the results of the IHLW calculations as well as providing the limiting constituent to immobilizing the treated sludge.

The mass changes between the initial washed sludge used for testing and the actual metals content as determined by ICP-AES of the treated solids were used in the calculations summarized in Table 3.9. However, no test was performed only looking at the impact of a standard caustic leach; therefore, evaluating the loading of only a caustic leach required a different approach. From the data in tests -3 and

Table 3.9. Calculated Effectiveness of Oxidative-Alkaline Leaching on IHLW Volumes

	Units of Glass Produced/Unit Treated Sludge (waste limiting component/condition)		
	TS-1.1	**Current**	**Expanded**
Washed SX-101	15.1(Cr_2O_3 = 0.5)	15.1(Cr_2O_3 = 0.5)	7.5(Cr_2O_3 = 1.0)
Caustic-Leached SX-101	17.4(Cr_2O_3 = 0.5)	17.4(Cr_2O_3 = 0.5)	8.7(Cr_2O_3 = 1.0)
SX-101-1	0.6(Cr_2O_3 = 0.5)	1.6(MnO = 7.0)	1.6(MnO = 7.0)
SX-101-2	5.3(Cr_2O_3 = 0.5)	5.3(Cr_2O_3 = 0.5)	2.7(Cr_2O_3 = 1.0)
SX-101-3	2.0(Cr_2O_3 = 0.5)	2.0(Cr_2O_3 = 0.5)	1.2(MnO = 7.0)
SX-101-4	0.9(Cr_2O_3 = 0.5)	1.3(MnO = 7.0)	1.3(MnO = 7.0)
SX-101-5	1.6(Cr_2O_3 = 0.5)	1.6(Cr_2O_3 = 0.5)	1.4(MnO = 7.0)
SX-101-6	0.3(Cr_2O_3 = 0.5)	1.1(MnO = 7.0)	1.1(MnO = 7.0)
Washed SY-102	21.4(Cr_2O_3 = 0.5)	21.4(Cr_2O_3 = 0.5)	10.7(Cr_2O_3 = 1.0)
Caustic-Leached SY-102	8.2(Cr_2O_3 = 0.5)	8.2(Cr_2O_3 = 0.5)	4.1(Cr_2O_3 = 1.0)
SY-102-1	1.1(Cr_2O_3 = 0.5)	1.9(MnO = 7.0)	1.9(MnO = 7.0)
SY-102-2	13.0(Cr_2O_3 = 0.5)	13.0(Cr_2O_3 = 0.5)	6.5(Cr_2O_3 = 1.0)
SY-102-3	4.9(Cr_2O_3 = 0.5)	4.9(Cr_2O_3 = 0.5)	2.5(Cr_2O_3 = 1.0)
SY-102-4	1.3(Cr_2O_3 = 0.5)	2.0(MnO = 7.0)	2.0(MnO = 7.0)
SY-102-5	1.8(Cr_2O_3 = 0.5)	1.8(MnO = 7.0)	1.8(MnO = 7.0)
SY-102-6	0.9(Cr_2O_3 = 0.5)	2.1(MnO = 7.0)	2.1(MnO = 7.0)

TS-1.1 = contract minimum loadings.
Current = WTP baseline.
Expanded = using an expanded region of validity for glass properties models.

-4, where an initial 3 M NaOH/85°C caustic leach was performed, the total amount of each component was obtained. This was calculated from the initial estimate of sludge used in the test multiplied by the metals concentration in the washed sludge solids. The total mass of each metal component removed during caustic leaching was determined by the total volume of leachate multiplied by each metal component's concentration in the leachate. The total amount in the leachate was subtracted from the total amount initially present to give the total amount of each component in the caustic-leached solids. These values were then converted to metal oxide wt%, assuming only that the measured metal oxides were present in the caustic-leached solids and these amounts normalized to one gram of initial washed sludge. The resulting weight percent metal oxides then were used in the IHLW calculations.

Note that despite the very high aluminum concentrations (see Table 2.4) present in the washed SY-102 and SX-101 sludges, chromium remains the limiting component to sludge loading in IHLW. Performing a simple caustic leach yields little (SX-101) to a modest (SY-102) reduction in the amount of IHLW produced. The calculations actually show an increase in the amount of IHLW produced if a simple caustic leach is performed; we believe this to be an artifact of the indirect approach taken to obtain the composition of a caustic-leached sludge. The condition of 5 M NaOH/excess permanganate provides relatively poor removal of chromium and is the least effective condition for reducing the amount of IHLW. The most effective conditions are where the oxidative-alkaline leach is performed at 85°C

(Tests -1, -4, and -6), where greater than an order of magnitude reduction in IHLW is predicted. Indeed, in these cases, manganese now replaces chromium as the limiting component in the amount of sludge loaded into IHLW.

Since chromium is the limiting component, one might expect the percent removals to correlate well to the amount of IHLW generated. Figure 3.15 through Figure 3.18 examine this hypothesis. The first two figures compare the units of IHLW per unit of initial SX-101 or SY-102 washed sludge or per unit of leached SX-101 or SY-102 sludge. It should be noted that the % Cr removals used in these comparisons for tests SX-101-5 and SY-102-5 are based on the dissolved Cr present as determined by chromate analysis, not by ICP-AES analysis as discussed above in Section 3.5.1.

Generally, the correlation is good with the exception of the 0% Cr removal (initial sludge) data point. The next two plots expand the correlation by excluding the unleached-solids data points. Note that now good linear correlations are found with both sludges between the % Cr removals and the ratio of ILHW/unit sludge generated based on either per unit of leached sludge or, more surprisingly, per unit of washed solids.

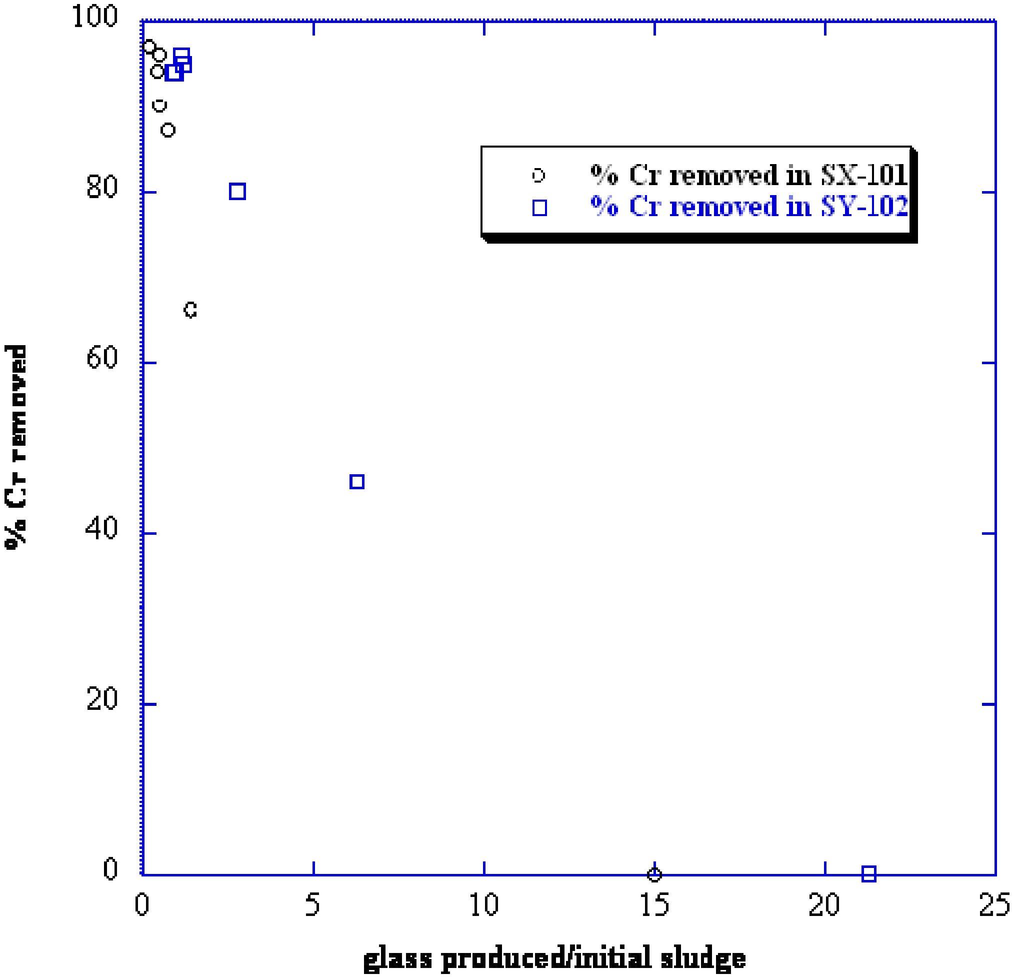


Figure 3.15. Comparison of % Cr Removal Versus Ratio of IHLW to Washed Sludge—All Data

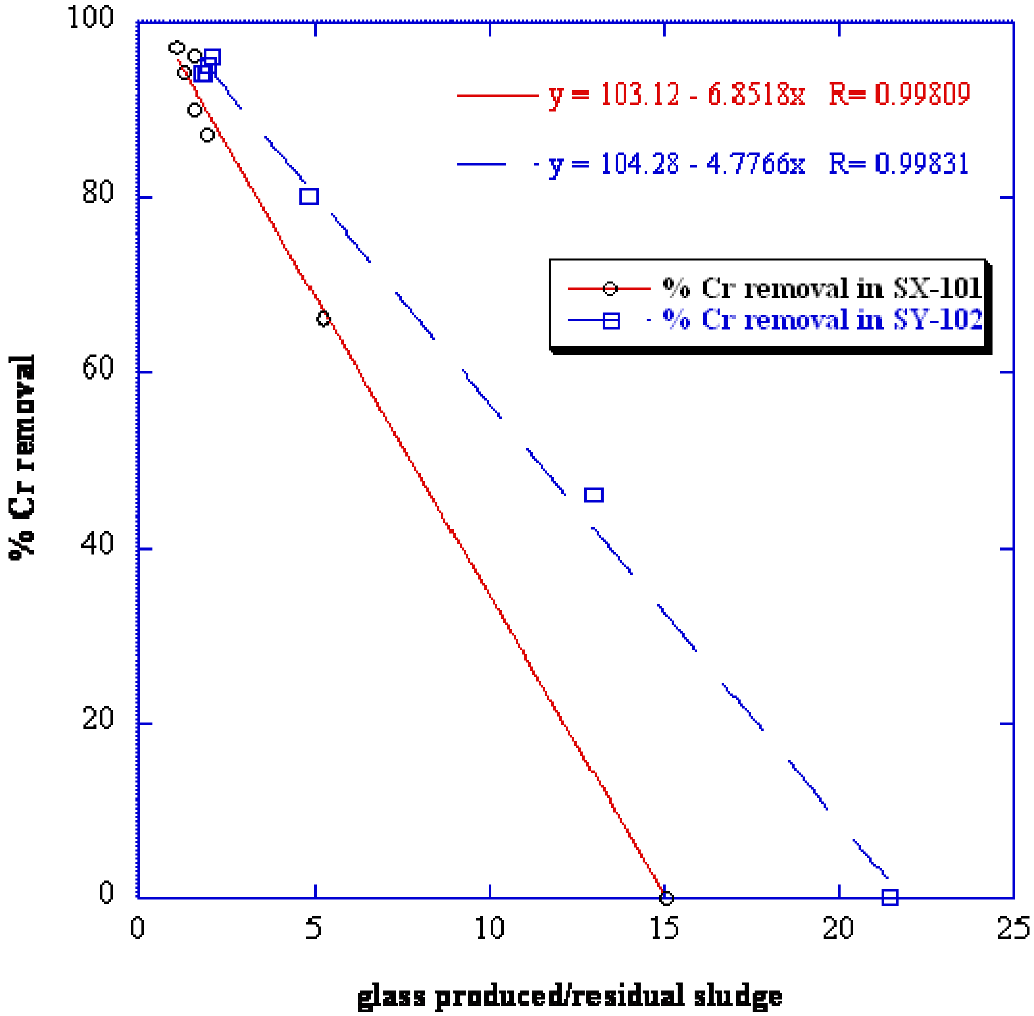


Figure 3.16. Comparison of % Cr Removal Versus Ratio of IHLW to Leached Sludge—All Data

The primary consideration with respect to producing ILAW from the leachates generated by oxidative alkaline leaching is whether the glass will be a TRU waste or not. Table 3.10 evaluates the TRU content of ILAW glass (assuming a leachate loading of 21.5 weight percent Na_2O [Muller et al. 2004]) derived by the various TRU leachates generated during each individual leach step or by the combined leach steps in Tests #3 through 6.

It should be noted that these leachates include not only the leach solutions but the low hydroxide washings designed to remove components that might be present in the interstitial liquid after the initial leachate/solids separation. These wash-to-leachate solution ratios may have little relation to those used in any actual process. Still, the relatively high TRU concentrations found for ILAW based on a concerted caustic leach/oxidative leach, while not a TRU waste, are significantly higher than alternative processes based on sequential caustic leach/oxidative leach steps.

To summarize the results from the immobilized waste calculations, 1) chromium is the component limiting washed SY-102 and SX-101 loading in IHLW, 2) a simple caustic leaching provides little or no (SX-101) to a modest (SY-102) decrease in the amount of IHLW produced, 3) performing an

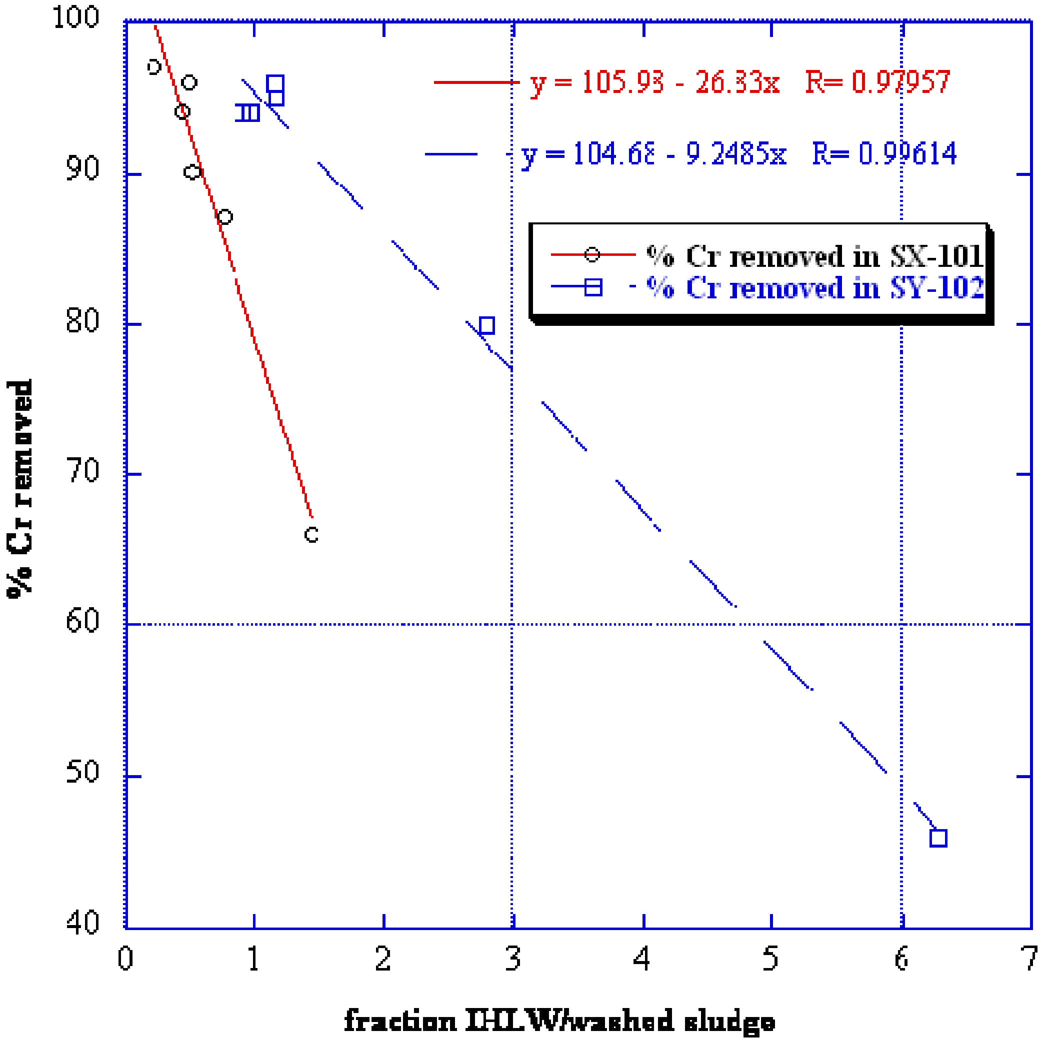


Figure 3.17. Comparison of % Cr Removal Versus Ratio of IHLW to Washed Sludge—Selected Data

oxidative-alkaline leach at 85°C either at low hydroxide in combination with a caustic leach or concomitant with a caustic leach can eliminate chromium as the limiting component to waste-oxide loading in IHLW, and 4) the TRU activity in ILAW glass is less than the TRU limits of 100 nCi/g in all cases, although the use of concomitant standard caustic leach with a permanganate-based oxidative alkaline leach results in a markedly higher TRU content in the glass.

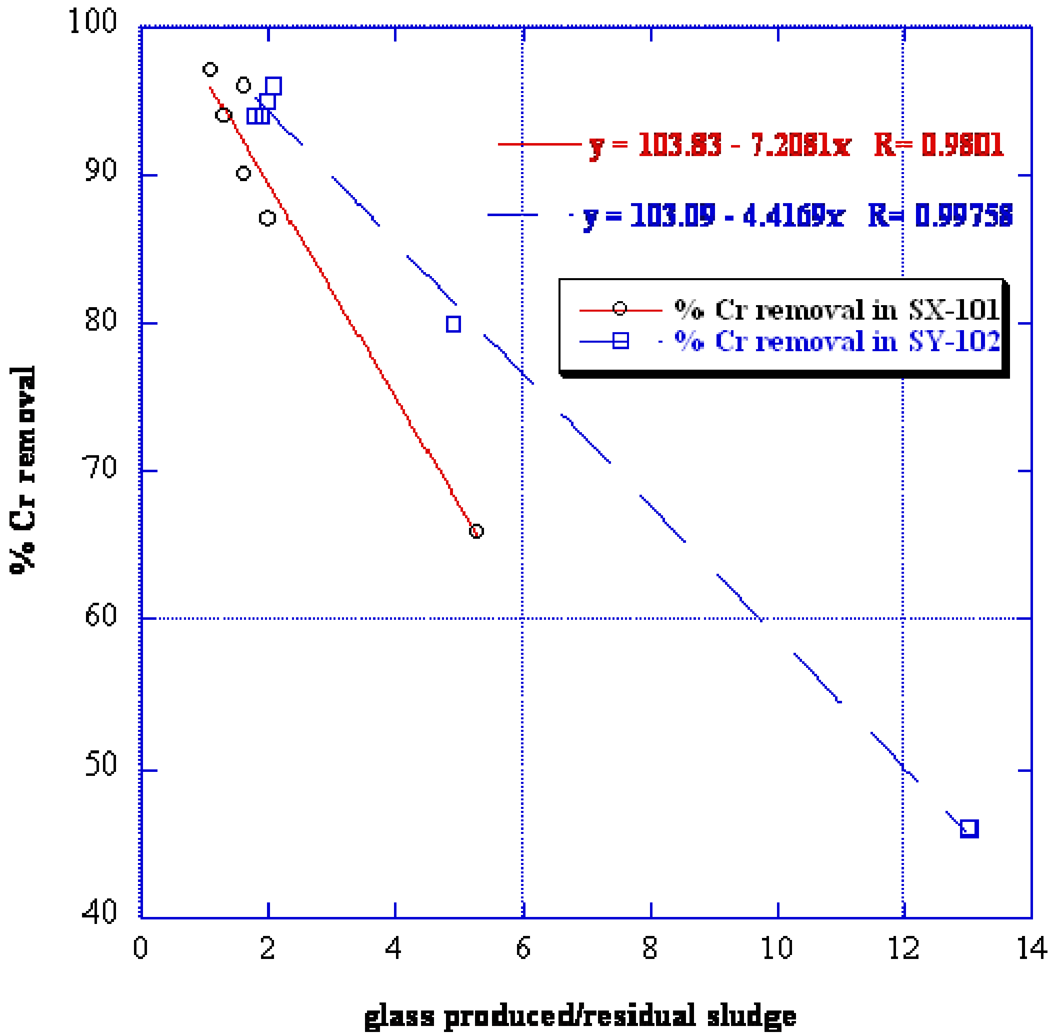


Figure 3.18. Comparison of % Cr Removal Versus Ratio of IHLW to Leached Sludge—Selected Data

Table 3.10. TRU Content of ILAW for Various Leachate Solutions

Leachate Solution	nCi TRU/g ILAW	Leachate Solution	nCi TRU/g ILAW
SX-101-1	37.4	SY-102-1	55.1
SX-101-2	0.1	SY-102-2	0.9
SX-101-3 ICL	0.1	SY-102-3 ICL	4.1
SX-101-3 OL	1.2	SY-102-3 OL	3.5
SX-101-3 C	0.3	SY-102-3 C	4.0
SX-101-4 ICL	0.2	SY-102-4 ICL	4.5
SX-101-4 OL	0.7	SY-102-4 OL	1.0
SX-101-4 C	0.3	SY-102-4 C	3.9
SX-101-5 OL	0.1	SY-102-5 OL	0.3
SX-101-5 FCL	1.7	SY-102-5 FCL	7.0
SX-101-5 C	0.8	SY-102-5 C	3.3
SX-101-6 OL	2.0	SY-102-6 OL	2.0
SX-101-6 FCL	4.2	SY-102-6 FCL	17.7
SX-101-6 C	4.0	SY-102-6 C	14.7

ICL = initial caustic leachate
OL = oxidative leachate
FCL = final caustic leachate
C = combined alkaline leachates

4.0 Summary and Conclusions

The focus of the work described in this report was to evaluate various alternative conditions for the selective removal of chromium through oxidative-alkaline leaching and then to provide recommendations for leach conditions to be used in the WTP. To accomplish this evaluation, previously reported chromium chemistry was reviewed as well as prior literature relevant to the oxidative-alkaline leaching of chromium from Hanford tank solids. From this review, a series of test conditions was chosen. These test conditions, unlike prior studies, were performed under leach conditions more closely resembling those likely to be used at the WTP.

From the literature review, permanganate was selected as the oxidant of choice. Six conditions were evaluated. The first leach condition involved contact of washed SX-101 and SY-102 tank solids with a slight stoichiometric excess of permanganate using the standard caustic-leach conditions of initial 3 M NaOH and a leach temperature of 85°C. The second leach condition involved contact of washed SX-101 and SY-102 tank solids with excess initial hydroxide (5 M) and excess permanganate. The third leach condition involved contact of washed SX-101 and SY-102 tank solids with an initial standard caustic leach followed by contact with a slight stoichiometric excess of permanganate at lower initial hydroxide concentration (0.25 M) at 25°C. The fourth leach condition was similar to the third leach condition except that the oxidative leaching step was conducted at 85°C. A fifth leach condition involved contact of washed SX-101 and SY-102 tank solids initially with permanganate at lower initial hydroxide concentration (0.25 M) at 25°C, followed by treatment with the standard caustic-leach conditions of 3 M NaOH and 85°C. The sixth leach condition was similar to the third leach condition except that the initial oxidative leaching step was conducted at 85°C. These leach tests were performed at a targeted 3:1 volume of leachate-to-volume of settled tank solids.

Various analyses were performed to evaluate the leaching process. The initial solids were examined for selected metals content by ICP-AES, for TRU elements by AEA, and for gamma-emitting isotopes by GEA. The distribution of the major bulk components within individual solid particles was evaluated by SEM/EDS, and crystalline phases present were evaluated by XRD. For both the SX-101 and SY-102 washed solids, the major crystalline phase was gibbsite, $Al(OH)_3$. For SX-101, an uranium-containing phase, clarkeite, $Na[(UO_2)(O)(OH)]$, was also observed. SEM-EDS analysis indicated that, with the exception of these phases, the major non-radioactive tank components tended to be evenly distributed throughout the solids, although some exceptions were noted.

In general, effective removal of chromium and aluminum was observed, with relatively little plutonium dissolution. Surprisingly, under the most extreme conditions of hydroxide, permanganate, and temperature, less effective aluminum, chromium, and plutonium removal is observed with respect to most of the other leach conditions.

Consistent with some earlier reports, adding permanganate under the standard caustic-leach conditions results in some enhancement in the fraction of dissolved plutonium. No significant amounts of any other TRU elements were detected in the leach solutions. Performing the oxidative leach at 85°C generally results in a slight enhancement of aluminum and chromium with little enhancement in dissolved plutonium. Generally, the kinetics of dissolution for chromium appear relatively rapid, with the bulk of the dissolved chromium present in solution within the first 6 hours. However, in particular for the SX-101 tests, there is considerable scatter in the data. Plutonium dissolution also appears to be enhanced as a function of contact time.

A comparison of dissolved chromate to total chromium dissolved indicates, consistent with prior reports, that the bulk of the dissolved chromium is present as chromate. The oxidation state of the dissolved plutonium was not determined. In general, the total concentrations of dissolved TRU elements in the leachate solution are low enough such that even the leach solutions themselves, as well as the ILAW that would be generated from these leach solutions, are less than the TRU limits of 100 nCi/g. There is some evidence suggesting that reprecipitation of some TRU elements (plutonium) occurs during the cooling of the leachate solutions and/or the low hydroxide washings.

Overall, testing indicates that effective removal of aluminum and chromium is possible, with greater than 95% removals achievable. This is a remarkable result in view of the nature of the sludge as revealed by SEM-EDS analysis. In previous washed sludges with large quantities of chromium, SEM-EDS analysis has indicated that the chromium is generally present either in a pure chromium oxide phase or together with aluminum, another element generally well removed by caustic leaching. However, with SX-101 and SY-102, substantial iron and manganese appears to be mixed with the leachable metals aluminum and chromium. Despite the possibility then that chromium removal might be inhibited by the presence of these unleachable metals passivating the particle surface and making the chromium in the bulk of the sample inaccessible to oxidant, excellent removal of chromium was observed. Unfortunately due to resource limitations, a SEM-EDS examination of the leached solids was not performed.

An analysis of the waste-oxide loading of the washed sludges indicates that greater than an order of magnitude increases in waste-oxide loading are possible following oxidative-alkaline leaching for both the washed SX-101 and SY-102 tank solids. The analysis also suggests that a simple caustic leach (under the baseline WTP conditions) is much less effective at increasing waste-oxide loadings in IHLW and that performing oxidative-alkaline leaching, under several of the tested leach conditions, can remove chromium as the waste-oxide limiting component.

A previous summary of oxidative-alkaline leach testing of Hanford tank sludges concluded that a reduction of chromium to 5000 ppm or less was a defensible target (Sederburg 2003). Table 4.1 examines the residual chromium concentrations of the oxidatively leached SY-102 and SX-101 sludges.

Table 4.1. Aluminum, Chromium and Iron Concentrations in Washed SX-101 and SY-102 Sludges Following Oxidative Alkaline Leaching

Treatment	[Al], μg/g		[Cr], μg/g		[Fe], μg/g	
	SX-101	SY-102	SX-101	SY-102	SX-101	SY-102
Washed	22900	171000	51500	73200	24800	59000
Oxidative Leach - 1	32400	37100	6680	6940	83000	129000
Oxidative Leach - 2	40500	48000	66600	91400	100000	141000
Oxidative Leach - 3	116000	79300	17400	29600	68800	117000
Oxidative Leach - 4	77500	78200	9310	7280	77700	114000
Oxidative Leach - 5	50000	43700	16100	11600	86700	135000
Oxidative Leach - 6	23900	40200	4890	5705	80500	127000

Only in one instance, test condition #6, do the residual chromium concentrations approach 5000 ppm for both sludges. Test conditions #1 and #4 are within a factor of two, with test condition #4 showing the higher residual concentrations of these leachable metals. Even so, the information provided in Table 3.9 indicates that the reductions in the aluminum and chromium concentrations found for test conditions #2, #4, and #6 are sufficient to remove both aluminum and chromium as the waste-oxide-limiting components.

These observations lead to the following recommendations for further study or implementation of oxidative-alkaline leaching:

1) That the possibility of selective precipitation of Pu from a permanganate-containing leach using standing caustic leach conditions be investigated. The leaching of Al and Cr is effective and if Pu can be selectivity precipitated under time effective and process-compatible conditions, adverse impacts due to the additional time required in successive leach contacts may be avoided.
2) That until a process and time-compatable Pu dissolution process is documented, further studies should focus on oxidative-alkaline leach conditions that combine a standard caustic leach (3 M, 85°C) with an independent oxidative-alkaline leach performed at a lower initial hydroxide concentration. Because of an observed discrepancy between the chromate concentration and total chromium by ICP-AES analysis, it remains unclear whether or not elevated temperatures are required for the oxidative-alkaline leach in an independent caustic leach/oxidative-alkaline leach sequence.
3) That any oxidative-alkaline leach be performed at temperature for at least 6 hours.
4) That a larger scale demonstration be performed to evaluate the order of the initial caustic leach and the oxidative-alkaline leach.
5) That this demonstration should monitor the chromate concentration in solution, the aluminum concentration, and the plutonium concentration as a function of leach contact times.
6) That the oxidation state of the dissolved plutonium should be evaluated.
7) That a further bench-scale test of test conditions #3, #4 , #5 and #6 be performed with the washed SX-101 and SY-102 sludge under the previous conditions characterized by larger solution:solids volumes. This will allow the chromium leach factors (% component removed values) reported in Table 3.6 to be correlated with the earlier oxidative-alkaline leach testing summarized in Sederburg (2003).

In summary, the results of the study indicate that oxidative-alkaline leaching of SX-101 and SY-102 sludges can be performed with extensive removal of the leachable metals aluminum and chromium with minimal concomitant dissolution of problematic radionuclides, specifically plutonium. The use of sequential standard caustic-leach conditions and an oxidative-alkaline leach of low hydroxide and elevated temperature yields a chromium leach factor of approximately 0.95 and can result in chromium no longer being the limiting component in waste-oxide loading into IHLW.

Appendix A

Leach Factors from SX-101 Testing

Appendix A: Leach Factors from SX-101 Testing

Component	SX-101-6	SX-101-5	SX-101-4	SX-101-3	SX-101-2	SX-101-1
Ag	0.0	0.0	0.0	0.0	0.0	0.0
Al	96.7	96.8	88.9	82.7	95.6	95.8
^{241}Am	0.0	0.0	0.0	0.0	0.0	0.0
Ba	0.0	0.0	0.0	0.0	0.0	0.0
Bi	0.0	0.0	0.0	0.0	0.0	0.0
Ca	0.0	0.0	5.9	0.0	0.0	3.9
^{137}Cs	28.9	37.9	32.7	32.5	33.2	26.9
Cd	12.5	21.0	0.0	6.6	0.0	6.0
^{60}Co	0.0	0.0	0.0	0.0	0.0	0.0
Cr	96.7	64.7	93.9	87.3	65.9	95.8
Cu	0.0	0.0	0.0	0.0	0.0	0.0
$^{154\&155}$Eu	0.0	0.0	0.0	0.0	0.0	0.0
Fe	0.3	0.6	0.3	0.3	0.3	0.1
La	0.0	0.0	0.0	0.0	0.0	0.0
Mg	0.0	0.0	0.0	0.0	0.0	0.0
Mn	0.2	0.0	0.0	0.0	0.0	0.0
Mo	ND	ND	ND	ND	ND	ND
Na	98.3	98.4	97.4	97.2	98.3	96.7
P	44.2	75.0	86.3	61.9	70.8	70.6
^{239,240}Pu	2.8	1.1	0.1	0.1	0.1	13.5
Si	66.8	55.0	50.5	45.5	43.4	41.9
Sn	0.0	0.0	0.0	0.0	0.0	0.0
Sr	0.0	0.0	0.0	0.0	0.0	0.0
Ti	0.0	0.0	0.0	0.0	0.0	0.0
U	0.0	0.0	0.0	0.0	0.0	0.0
Zn	0.0	0.0	0.0	0.0	0.0	0.0
Total α	0.7	0.3	0.0	0.0	0.0	3.2

Leach Factors are expressed here as a percentage.
ND = Component Not Detected in Either Leach Solutions or Residue

Appendix B

Leach Factors from SY-102 Testing

Appendix B: Leach Factors from SY-102 Testing

Component	SY-102-6	SY-102-5	SY-102-4	SY-102-3	SY-102-2	SY-102-1
Ag	5.5	0.0	0.0	0.0	0.0	8.8
Al	88.9	94.4	77.8	76.4	88.2	86.3
^{241}Am	0.0	0.0	0.0	0.0	0.0	0.0
Ba	0.0	0.0	0.0	0.0	0.0	0.0
Bi	1.3	4.6	1.9	1.7	1.9	0.5
Ca	1.3	0.0	0.0	0.0	0.0	0.0
^{137}Cs	36.6	41.0	41.0	40.0	37.3	22.4
Cd	1.3	4.0	0.0	0.5	1.1	0.8
^{60}Co	0.0	0.0	0.0	0.0	0.0	0.0
Cr	95.9	74.9	95.2	79.9	46.2	93.5
Cu	0.0	0.0	0.0	0.0	0.0	0.0
$^{154\&155}$Eu	0.0	0.0	0.0	0.0	0.0	0.0
Fe	0.0	0.2	0.2	0.1	0.1	0.0
La	0.0	0.0	0.0	0.0	0.0	0.0
Mg	0.0	0.0	0.0	0.0	0.0	0.0
Mn	0.0	0.0	0.0	63.1	0.0	0.0
Mo	100.0	ND	ND	ND	ND	ND
Na	94.9	97.7	96.6	96.0	97.6	94.0
P	18.8	19.4	26.9	36.6	13.1	5.4
^{239,240}Pu	0.2	0.1	0.0	0.0	0.0	0.6
Si	27.9	30.9	35.7	31.4	22.4	17.1
Sn	0.0	0.0	0.0	0.0	0.0	0.0
Sr	0.0	0.0	0.0	0.0	0.0	0.0
Ti	0.0	0.0	0.0	0.0	0.0	0.0
U	0.0	0.0	0.0	0.0	0.0	0.0
Zn	0.0	43.0	0.0	0.0	0.0	0.0
Total α	0.1	0.0	0.0	0.0	0.0	0.1
Leach Factors are expressed here as a percentage. ND = Component Not Detected in Either Leach Solutions or Residue						

The components listed above were selected in the following manner. The list of analytical requirements from Test Specification 24590-PTF-TSP-RT-03-003, Rev 0, “Ultrafiltration and Washing/Leaching of Hanford Tank 241-SY-102 Waste” was reviewed. Since both solution and solids data are required to measure a leach factor, components that were not required for both the solid and solution measurements were discarded. When the element’s leach factor could be evaluated by either radiochemical or chemical analysis, the more sensitive method (radiochemical except for uranium) is used. When an element’s leach factor was determined by radiochemical methods, the isotope information is supplied. When information is obtained for a combination of multiple isotopes (such as with ^{239,240}Pu), a comma is used to separate the isotopes present in the measurement. If independent measurements on several isotopes were made with identical results (such as with ^{154}Eu and ^{155}Eu) a "&" sign is used.

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