

Pacific Northwest National Laboratory

Operated by Battelle for the
U.S. Department of Energy

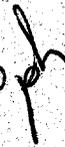
Oxidative Alkaline Dissolution of Chromium from Hanford Tank Sludges: Results of FY 98 Studies

B. M. Rapko

August 1998

RECEIVED
AUG 17 1998
OSTI

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 

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

DISCLAIMER

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

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

Printed in the United States of America

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

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



This document was printed on recycled paper.

DISCLAIMER

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

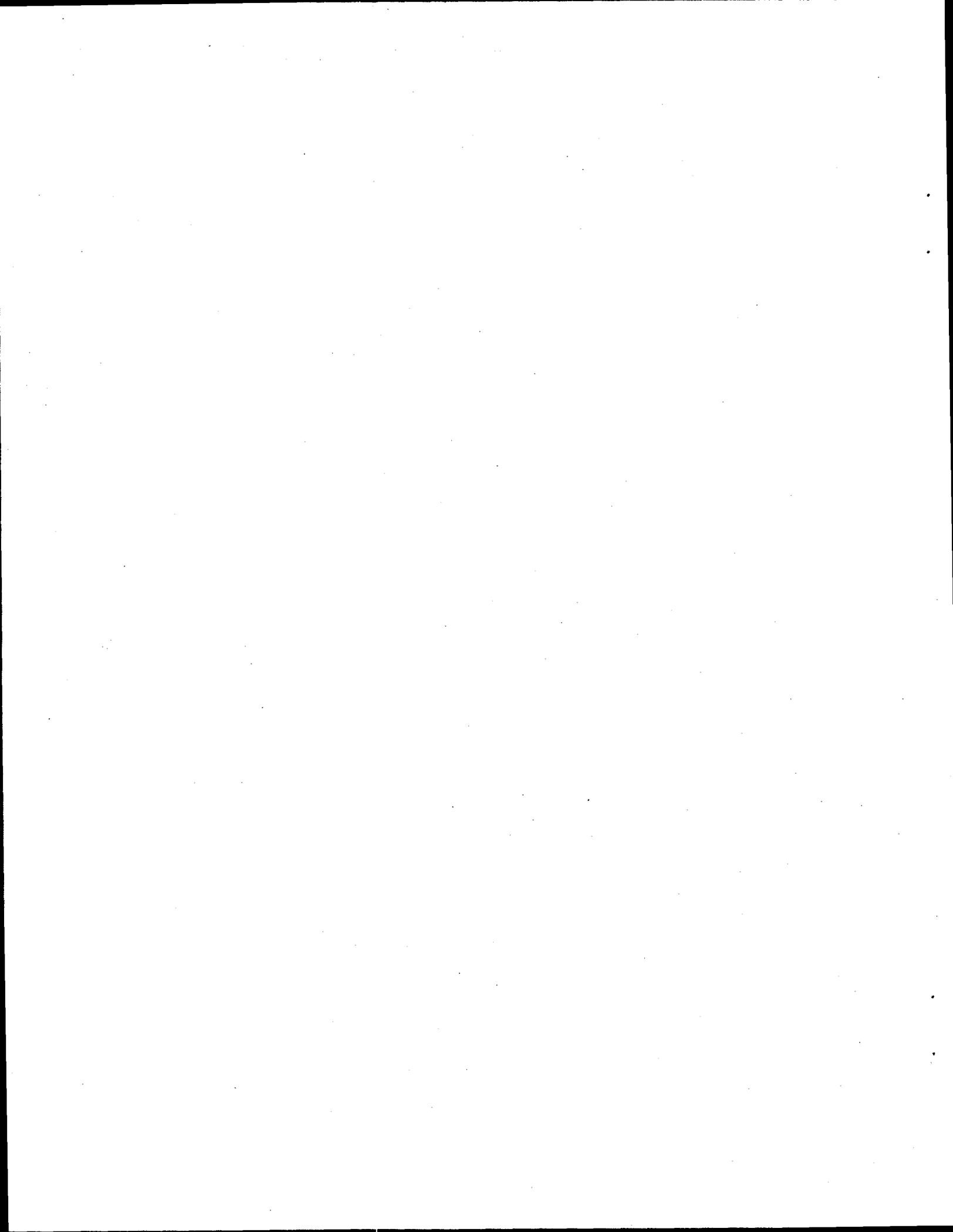
**Oxidative Alkaline Dissolution of
Chromium from Hanford Tank Sludges:
Results of FY-98 Studies**

B. M. Rapko

August 1998

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

Pacific Northwest National Laboratory
Richland, Washington 99352



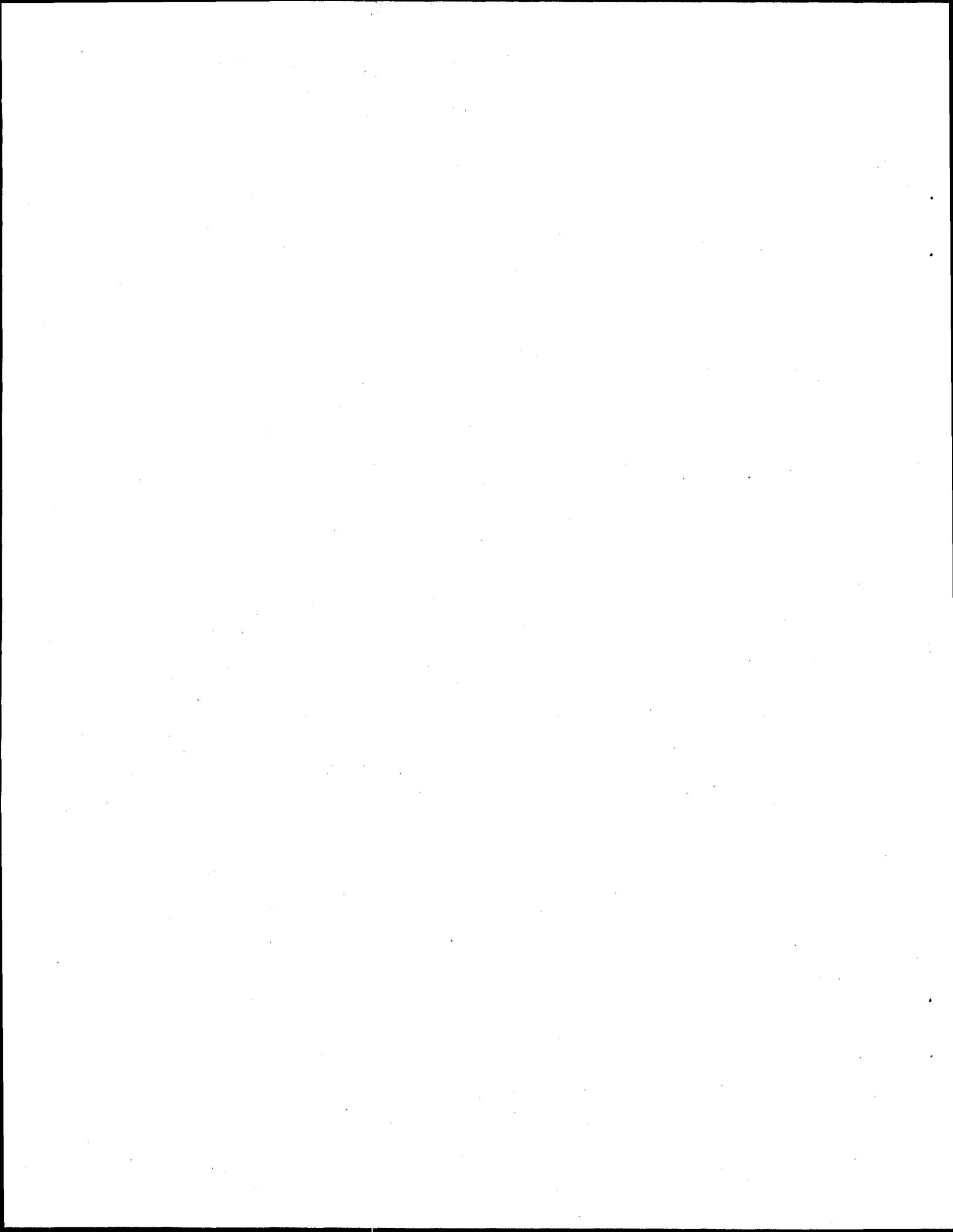
Summary

Plans for disposing of the high-level radioactive wastes at the Hanford Site call for retrieving, pretreating, and finally immobilizing the wastes in a glass matrix. Since the cost for vitrifying and disposing of high-level wastes will be very great, pretreatment processes are being developed to reduce their volume. The baseline method for pretreating Hanford tank sludges is caustic leaching.

Earlier studies with Hanford tank-sludge simulants and with actual Hanford tank sludges have indicated that treating water-washed and caustic-leached solids with oxidants can significantly increase the removal of Cr. Permanganate and ozone have been shown to be generally the most rapid and effective chemical agents for this purpose. The work described in this report continues to examine the effectiveness of solubilizing additional Cr from Hanford tank wastes by oxidation of the water-insoluble solids from tanks U-108, U-109, and SX-108 under alkaline conditions.

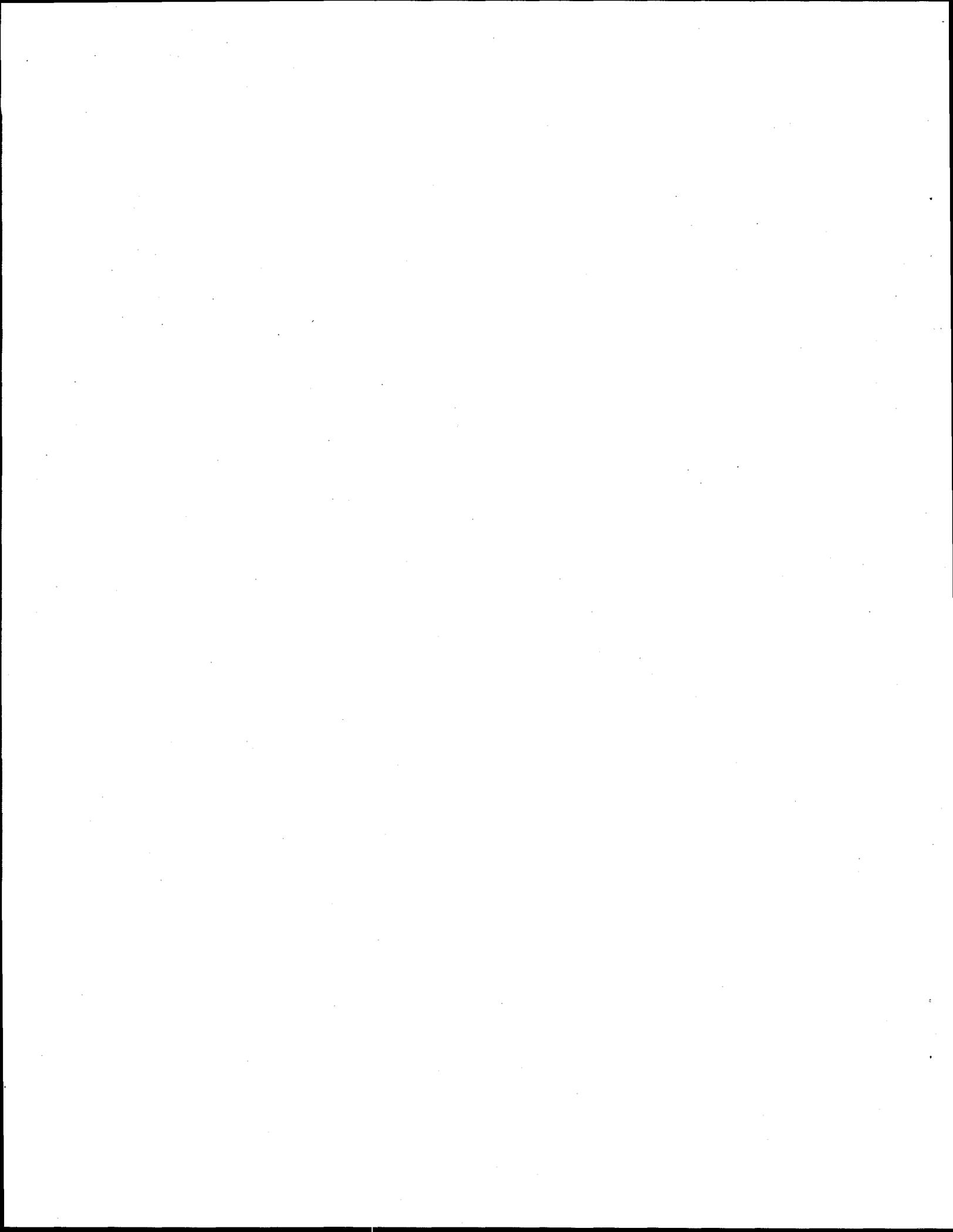
The current study confirms that permanganate is highly effective at removing chromium from waste solids under alkaline conditions, with Cr removals of up to 99+%. Elemental oxygen can also be highly effective, with removals up to 97+%. As in previous studies, all dissolved chromium was shown to be present as chromate in these leachates. However, unlike the results from previous studies, permanganate contacts were the most effective at increasing the transuranic (TRU) activity of the leachate solution. With permanganate, the TRU activity of the leachate was primarily due to the presence of Pu. However, even for the leachate solutions with the highest TRU activity, if the solutions were concentrated and vitrified to a loading of 20 wt.% sodium oxide, the glass still would be classified as a low-level waste.

The test results, especially those results indicating that oxygen can be an effective agent for the oxidative dissolution of chromium, are encouraging. The reagent is benign, no material is added to the residual tank solids, and the process is easily implemented. These conditions all point to oxidative alkaline leaching as a promising approach for solubilizing and removing chromium from high-chromium Hanford tank solids. Since oxygen is present in air at 20 wt.%, it may be possible that simple CO₂-free air sparging during baseline caustic leaching would remove chromium. This possibility should be pursued in future research.



Contents

Summary.....	iii
1.0 Introduction.....	1.1
2.0 Experimental.....	2.1
2.1 Sample Preparation.....	2.1
2.2 Testing Procedure.....	2.2
2.3 Description of Test Samples.....	2.7
3.0 Results and Discussion.....	3.1
3.1 General.....	3.1
3.2 Chromate Formation During Leaching of U-108, U-109, and SX-108 Solids.....	3.2
3.2.1 U-108 and U-109.....	3.2
3.2.2 SX-108.....	3.5
3.3 Dissolution of Bulk Components From U-108, U-109, and SX-108 Solids by Alkaline Oxidative Leaching.....	3.5
3.3.1 U-108 and U-109.....	3.5
3.3.2 SX-108.....	3.11
3.4 Radionuclide Dissolution During Alkaline Oxidative Leaching.....	3.15
3.4.1 U-108 and U-109.....	3.15
3.4.2 SX-108.....	3.17
4.0 Summary and Recommendations.....	4.1
5.0 References.....	5.1



Figures

Figure 2.1. Schematic Representation of the Preparation of U-108 Sludge for the Cr Leach Tests..	2.3
Figure 2.2. Schematic Representation of the Preparation of U-109 Sludge for the Cr Leach Tests..	2.4
Figure 2.3. Schematic Representation of the Preparation of SX-108 Sludge for the Cr Leach Tests..	2.5
Figure 3.1. Chromate Formation from U-108 Sludge as a Function of Time.....	3.3
Figure 3.2. Chromate Formation from U-109 Sludge as a Function of Time.....	3.4
Figure 3.3. Chromate Formation from SX-108 Sludge as a Function of Time.....	3.6

Tables

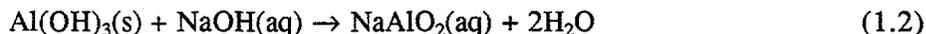
Table 2.1. Summary of Cr Leaching Conditions.....	2.7
Table 2.2. Summary of Sludges Used in Cr Leach Tests	2.8
Table 2.3. Concentrations ($\mu\text{g/g}$ dry solids) of Major Sludge Constituents as Determined by ICP-AES Analysis After Acid Dissolution of Solids.....	2.9
Table 3.1. Initial and Final Leachate Hydroxide Concentrations	3.2
Table 3.2. Summary of the Removal of Bulk Nonradioactive Components	3.7
Table 3.3. Summary of the Removal of Bulk Nonradioactive Components from U-109 Sludge By Oxidative Alkaline Leaching	3.8
Table 3.4. Concentrations ($\mu\text{g/g}$) of the Initial and Final, Leached U-108 Sludges.....	3.9
Table 3.5. Concentrations ($\mu\text{g/g}$) of the Initial and Final, Leached U-109 Sludges.....	3.9
Table 3.6. Initial and Final Sludge Masses in U-108 and U-109 Testing	3.10
Table 3.7. Comparison of Chromium Concentrations as Determined by ICP-AES and Chromate Concentrations as Determined by UV-vis Spectroscopy for U-108 and U-109 Final Leachate Solutions.....	3.11
Table 3.8. Major Bulk Component Removal by Alkaline Oxidative Leaching With SX-108 Solids (% Rem = % Removal MB = Mass Balance)	3.12
Table 3.9. Major Bulk Component Concentrations in SX-108 Solids (μg component/g solids)	3.13
Table 3.10. Al/Fe, Cr/Fe, and Al/Cr Molar Ratios in SX-108 Solids.....	3.13
Table 3.11. Radionuclide Removal by Alkaline Oxidative Leaching With U-108 Solids.....	3.16
Table 3.12. Radionuclide Removal by Alkaline Oxidative Leaching With U-109 Solids.....	3.16
Table 3.13. Radionuclide Removal by Alkaline Oxidative Leaching With SX-108 Solids.....	3.17
Table 3.14. Radionuclide Removal by Alkaline Oxidative Leaching With SX-108 Solids.....	3.17
Table 3.15. TRU Activity ($\mu\text{Ci/mL}$) in SX-108 Leachates	3.18
Table 3.16. TRU Activity of Oxidative Alkaline Leachate Solutions in Glass at 20 wt.% Na_2O ^(a)	3.18

1.0 Introduction

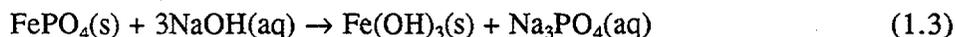
During the past few years, the primary mission at the U.S. Department of Energy's Hanford Site has changed from producing plutonium to restoring the environment. Large volumes of high-level radioactive wastes (HLW), generated during past Pu production and other operations, are stored in underground tanks onsite. The current plan for remediating the Hanford tank farms consists of waste retrieval, pretreatment, treatment (immobilization), and disposal. The tank wastes will be partitioned into high-level and low-level fractions. The low-level waste (LLW) will be processed to remove ^{137}Cs (and possibly other radionuclides), and then it will be immobilized in a glass matrix and disposed of by shallow burial onsite. The HLW will be immobilized in a borosilicate glass matrix; the resulting glass canisters will then be disposed of in a geologic repository (Orme et al. 1996). Because of the expected high cost of HLW vitrification and geologic disposal, pretreatment processes will be implemented to reduce the volume of immobilized high-level waste (IHLW).

Dilute hydroxide washing is the minimum pretreatment that would be performed on Hanford tank sludges. This method simply involves mixing the sludge with dilute (0.1 M or less) NaOH, then performing a solid/liquid separation. The function of this operation is to remove water-soluble sludge components (mainly sodium salts) from the HLW stream.

Caustic leaching (sometimes referred to as enhanced sludge washing or ESW) represents the baseline method for pretreating Hanford tank sludges. Caustic leaching is expected to remove a large fraction of the Al, which is present in large quantities in Hanford tank sludges. The Al will be removed by converting aluminum oxides/hydroxides to sodium aluminate. For example, boehmite and gibbsite, respectively, are dissolved according to the following equations (Weber 1982).



A significant portion of the P should also be removed from the sludge by metathesis of water-insoluble metal phosphates to insoluble hydroxides and soluble Na_3PO_4 . An example of this is shown for iron(III) phosphate in the following equation.



Similar metathesis reactions can occur for insoluble sulfate salts, allowing the removal of sulfate from the HLW stream.

The removal of Cr from certain Hanford tank sludges might be important due to the relatively low tolerance for Cr in the HLW immobilization process. Based on its known amphoteric behavior (Rai et al. 1987), Cr(III) might be expected to be removable by caustic leaching according to the following equation:



However, recent studies conducted at the Pacific Northwest National Laboratory (PNNL)^a have suggested that the behavior of Cr in the caustic leaching process is more complex (Lumetta et al. 1997). Significant dissolution of Cr(III) hydroxide does occur in high caustic solutions at room

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

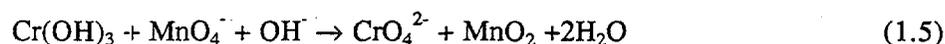
temperature, but heating such solutions causes precipitation of guyanaite, syn (CrOOH), which does not readily redissolve in aqueous caustic media. This observation is consistent with previous reports of the low solubility of Cr(OH)₃ in acidic and near-neutral solutions at elevated temperature (Rai et al. 1987). The precipitation of CrOOH also might explain the low Cr removal efficiencies observed during caustic leaching tests with certain tank waste sludges and the failure to observe any Cr(III) in the leachates (Lumetta et al. 1997). Earlier studies with Hanford tank sludge simulants and with actual Hanford tank sludges have indicated that treating water-washed and caustic-leached solids with oxidants can significantly increase the effectiveness of Cr removal from the sludges. For example, treatment with KMnO₄ was found to be effective at removing Cr from washed SY-102 sludge. Indeed, a combination of dilute hydroxide leaching and KMnO₄ removed 96% of the Cr from SY-102 sludge (Lumetta et al. 1995). Treating a water-washed, SY-101 sludge simulant with permanganate removed more than 90% of the water-insoluble Cr, and treating the actual, water-washed, SY-101 sludge increased the soluble Cr concentration between 5 and 50 fold (Orth et al. 1995).

Previous studies have also examined the consequences of contacting tank sludges with ozone under alkaline conditions. In one instance, ozone was contacted with sludge from SY-101 at 0.6 to 0.3 M hydroxide. Quantitative dissolution of Cr was observed; however, ~80% of the total Pu dissolved also (Delegard et al. 1993).

Other investigations of oxidative alkaline leaching of Cr on a number of Hanford tank sludges have occurred during the last 2 years. Treating caustic-leached sludge from SY-103 at low (< 0.01 M) free hydroxide with either ozone (O₃) or potassium permanganate (KMnO₄) removed ~90% of the residual Cr. However, treating the caustic-leached sludge from B-111 was less effective, with only an additional ~30% of its residual Cr being dissolved by alkaline oxidation (Rapko et al. 1996). With either sludge, air contact by itself under these experimental conditions of time, temperature, and hydroxide concentration was ineffective at Cr removal.

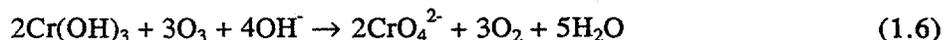
More recently, permanganate and ozone were shown to be generally the most rapid and effective chemical agents tested for additional Cr dissolution from previously caustic-leached sludges under alkaline conditions (0.1 or 3 M free hydroxide). Dissolution of 83 to 94% was found with BY-110 and 58 to 87% with S-107, but only 22 to 45% was found with SX-108 (Rapko et al. 1997). The extent of transuranic (TRU) dissolution was significantly less than that observed with SY-101 sludge as described above and, for the most part, could be explained by the solubility of Pu(IV) under the experimental conditions. Generally, in the absence of added oxidant, the presence or absence of oxygen itself was ineffective for enhanced Cr dissolution under the experimental conditions (up to 8 hours at 80°C). At that time, it was proposed that the relatively low Cr dissolution observed with SX-108 might be related to the relatively large amounts of residual Al present; in other sludges, Cr(III) has been found associated with Al and so may passivate the solids and inhibit additional Cr dissolution. If this hypothesis is correct, then more effective Al removal should result in enhanced Cr dissolution. A test of this hypothesis is a goal for this work.

Chromium(III) dissolves in the presence of permanganate when the poorly soluble Cr(III) oxidizes to Cr(VI), which is highly soluble in alkaline media. This oxidation proceeds with the following stoichiometry:



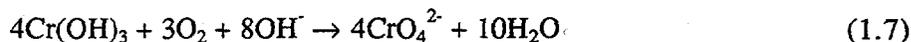
For every mole of Cr leached from the sludge, one mole of Mn is added in the form of MnO₂. Adding Mn to the sludge should not cause a major problem because the Mn limit in the HLW glass feed is expected to be much higher than that for Cr, although the Mn limit in the HLW glass feed has not been defined.

Chromium(III) oxidation by ozone to alkaline-soluble chromate proceeds with the following stoichiometry:



Unlike permanganate, which has a reduced form (MnO_2) that leaves an insoluble residue, the reduced form of ozone is gaseous oxygen, which obviously will add no mass to the residual sludge.

Elemental oxygen oxidation of Cr(III) proceeds with the following stoichiometry:



Here, the reduced form of the oxidant is water, which again adds no additional mass to the residual sludge solids. Oxygen (or air) would clearly be the oxidant of choice because of its ready availability as well as the benign nature of the reagent and its by-products. Although previous results have suggested that elemental oxygen is not as rapid as permanganate or ozone at oxidation of Cr(III)-containing solids, a goal of this work was to test the effectiveness of oxygen at the oxidation of the Cr(III) in tank solids by contact at longer times at elevated temperature. Such experiments should help ascertain whether elemental oxygen could be a practical alternative to ozone or permanganate.

The work described in this report continues an examination of the effectiveness of solubilizing additional Cr from Hanford tank wastes by oxidation under alkaline conditions. The solids examined came from Tank SX-108 and water-insoluble solids present in saltcakes from tanks U-108 and U-109. The oxidants examined were permanganate (MnO_4^-) and elemental oxygen (O_2).

2.0 Experimental

2.1 Sample Preparation

Samples from three tank sludges were tested: solids from Tank SX-108 that have been washed with dilute hydroxide and leached with high hydroxide and the residual solids from dilute hydroxide washing of U-108 and U-109 salt cakes, respectively. For the U-108 and U-109 solids, the solids were further washed with 0.1 M NaOH until the initially yellow supernatant was colorless, indicating that all of the Cr initially present in the +6 oxidation state (as chromate) had been removed. The SX-108 solid was prepared differently than the U-108 and U-109 solids. For the SX-108 tank sludge, the goal was to remove as much Al as possible from the sample and so ensure that the maximum amount of Cr-containing material would be exposed to the leach solution.

This Al dissolution was done in two ways. Half of the sample was designated for material to be used for contacts with low-hydroxide Cr-leach solutions. Here, poor Al dissolution was expected either because of kinetic reasons or Al solubility constraints. Therefore, the solids were subject to an initial high caustic leach to remove the bulk of the Al. Previous work (Lumetta et al. 1997) has indicated that leach times beyond approximately 1 week with 3 M NaOH at 100°C show little additional Al dissolution. Consequently, this material was first washed with dilute (0.1 M) NaOH, then leached with 3 M sodium hydroxide for 1 week, and then washed again thrice with 0.1 M NaOH to remove the bulk of the components remaining in the interstitial liquid.

With the samples to be subjected to the high (3 M) sodium hydroxide Cr-leach solutions, Al dissolution should occur anyway during the course of the testing. These samples therefore were prepared only by a simple dilute hydroxide washing to remove any chromate that might be initially present in the sample. The contact conditions with the high-hydroxide Cr-leach solutions (1 week at 80°C) are approximately the same (1 week at ~100°C) as the caustic leach before contact with the low-hydroxide Cr-leach solutions. The extent of Al dissolution from all of the SX-108 sludge samples at the conclusion of testing therefore should be approximately constant and so remove a potential variable from the interpretation of the results. Following sludge washing (U-108, U-109 and high-hydroxide targeted SX-108 samples) or low-hydroxide washing, high-hydroxide leaching and subsequent low-hydroxide washing (for the low-hydroxide SX-108 leach contact samples), the sludges were treated similarly, as illustrated in Figures 2.1 through 2.3.

A suspension of each of these solids was next divided into several portions. A small fraction of a suspension of the prepared sludge was removed, weighed, and dried to a constant weight at 105°C. The weight fraction of sludge in the suspension can be determined from this measurement. The Cr concentration in the washed SX-108 has been previously measured (Lumetta et al. 1996). The Cr concentration in the leached SX-108 sample was estimated by assuming complete Al dissolution with no further dissolution of Cr. The Al, Fe, and Cr concentrations of the water-washed U-108 and U-109 solids have been measured. Based on the previously measured or estimated concentrations of Cr in these solids, the amount of sludge required to allow detection of 5% of the available Cr as chromate by visible spectroscopy was calculated and targeted as an absolute minimum amount of material for each test. An additional constraint on the targeted amount of caustic-leached sludge was, after assuming complete Al dissolution, that the residue would contain at least 0.25 grams of solid. This was done to ensure that there would be sufficient material to analyze the residue at the end of each Cr leach test. One consequence of these limitations was that there was only sufficient SX-108 solids to perform four leach tests instead of the six performed on the U-108 and U-109 solids. Figures 2.1 through 2.3 summarize the operations used for sample preparation.

2.2 Testing Procedure

Once the desired quantity of sample for testing had been determined, the targeted aliquot of well stirred sludge suspension was transferred in the 325 Building hot cells to tared, 60-mL plastic bottles (U-108 and U-109) or to tared 125-mL plastic bottles (SX-108) and reweighed. These weights, coupled with the Cr concentration reported for the leached sludges (Lumetta et. al. 1996), were used to calculate the amount of permanganate needed to achieve at least a 1:1 ratio of permanganate to Cr. The bottles were transferred from the hot cells into the laboratory and centrifuged, and the supernatant was decanted off. The solids were suspended in either 0.1 M NaOH or 3 M NaOH as appropriate, and the oxidant was introduced. The total suspension volume in these Cr leach tests was 50 mL for the U-108 and U-109 tests and 100 mL for the SX-108 tests.

The flowrate of the gases introduced was monitored with a flowmeter and set at approximately 5 cc/min. Bottles of high-purity oxygen and high-purity argon were used to introduce these gases. Both the oxygen and argon gas lines were split in the hood using T-connections, allowing the gas to be sent to both the high- and low-hydroxide leach solutions simultaneously. However, the flowrate through each line was independently monitored.

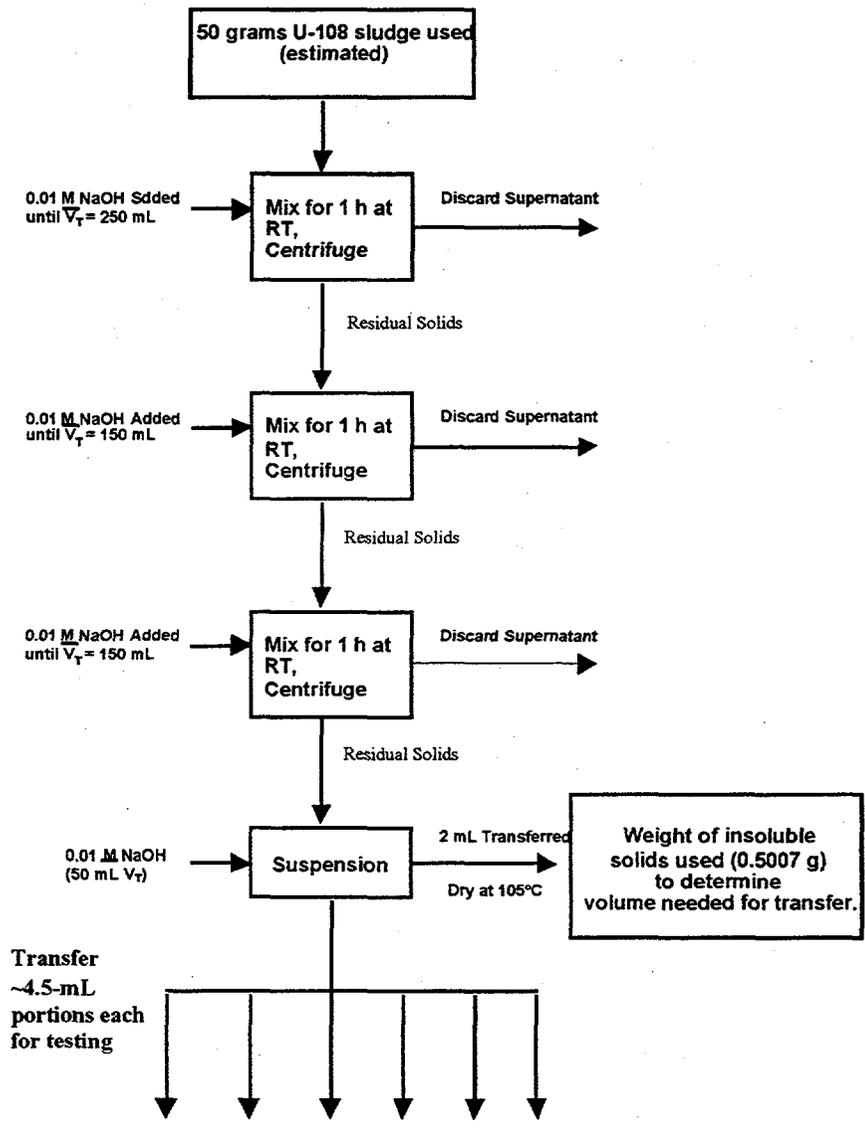


Figure 2.1. Schematic Representation of the Preparation of U-108 Sludge for the Cr Leach Tests

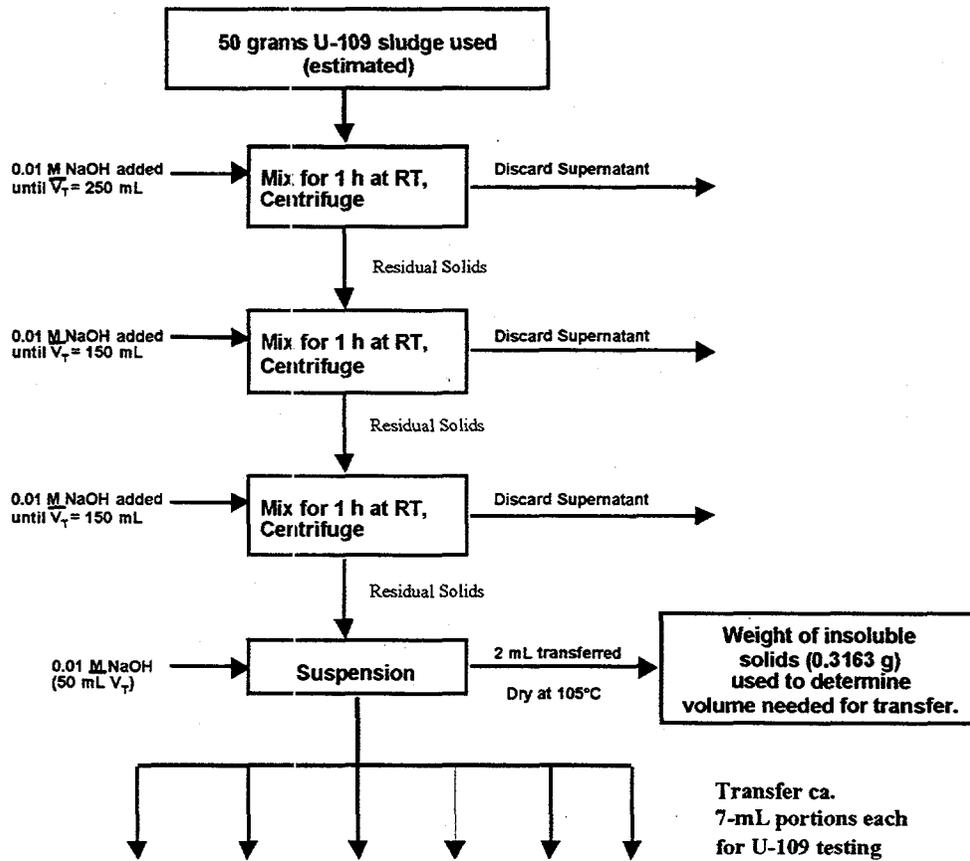
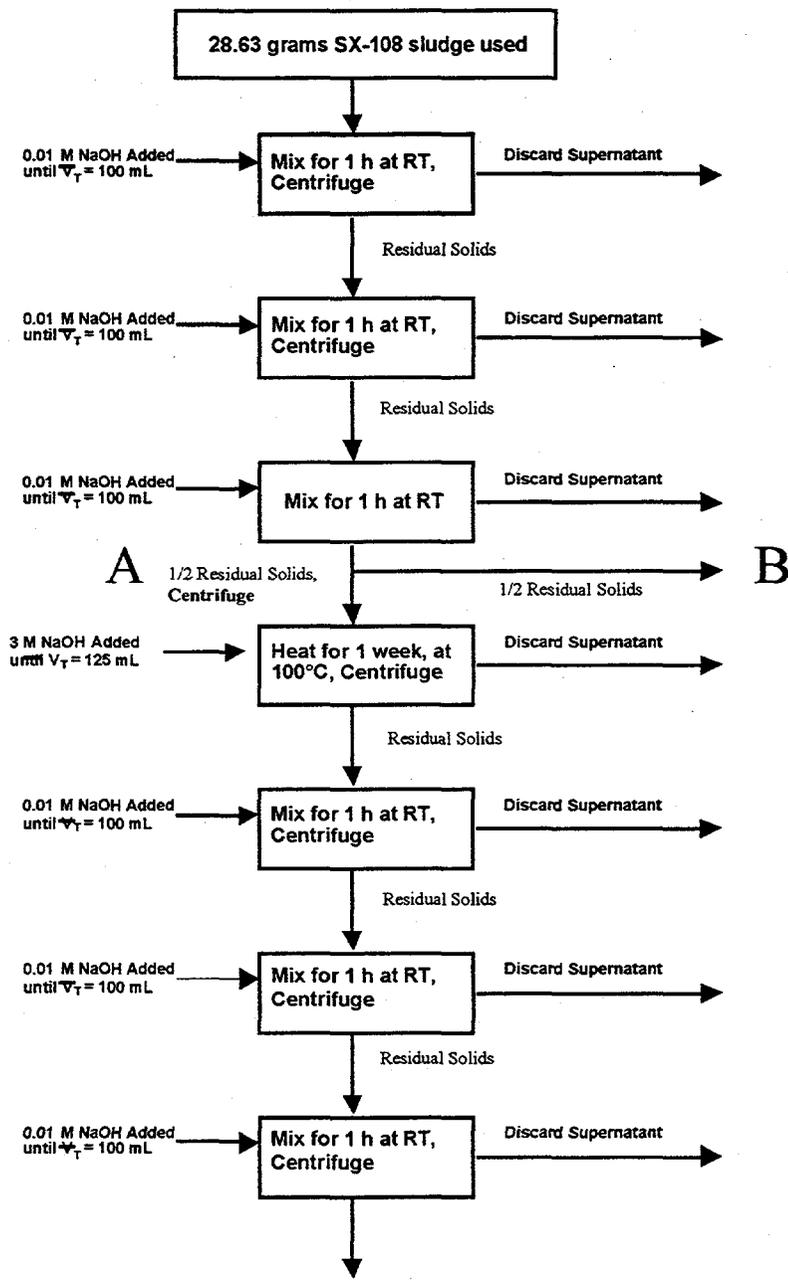


Figure 2.2. Schematic Representation of the Preparation of U-109 Sludge for the Cr Leach Tests



Continued on next page

Figure 2.3. Schematic Representation of the Preparation of SX-108 Sludge for the Cr Leach Tests (Path A: Dilute Hydroxide Rinse and Caustic Leach; Path B: Dilute Hydroxide Rinse Only)

Continued from previous page

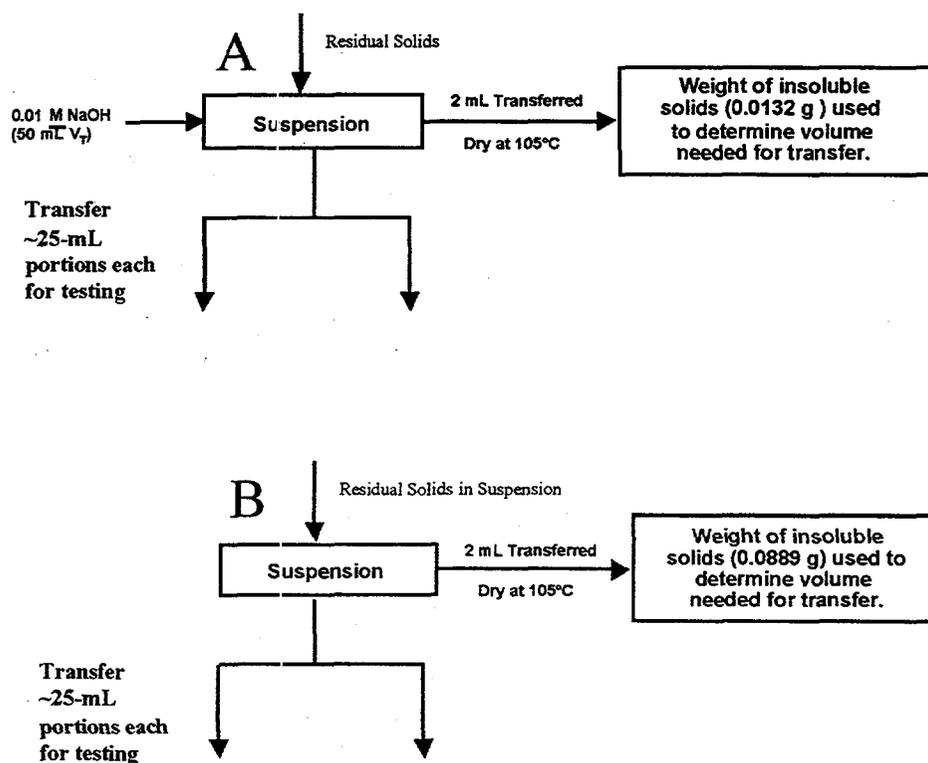


Figure 2.3. (contd)

The reaction bottles were placed in an Al heating block in which five holes, sized to securely hold the sample bottles, were cut. This Al block was placed on top of the five-place heater/stirrer. The depth of the holes kept the test solution entirely surrounded by the Al heating block. Four test samples were examined at one time; the fifth position contained a blank solution of hydroxide and contained a thermocouple. The thermocouple allowed the temperature to be monitored and controlled to within 1°C.

As summarized in Table 2.1, six tests were performed with U-108 and U-109 sludge; because of sample limitations, only the first four tests were performed with SX-108 sludge. In the first test, enough solid sodium permanganate was added to the sludge suspended in 0.1 M NaOH to obtain a 1:1 permanganate to chromium stoichiometry. In the second test, enough solid sodium was added to the sludge suspended in 3 M NaOH permanganate to obtain a 1:1 permanganate to chromium stoichiometry. In the third test, the sludge, suspended in 0.1 M NaOH, was contacted solely with oxygen. In the fourth test solution, oxygen was added to sludge suspended in 3 M NaOH. The fifth and sixth tests were designed as controls; argon gas was bubbled through sludge suspended in 0.1 and 3 M NaOH, respectively.

As with prior Cr leach tests, the samples were stirred at room temperature for the first 24 hours. The solutions then were heated at 80°C for the remainder of the experiment. The test containers were weighed following each sampling and then before the subsequent sampling.

Table 2.1. Summary of Cr Leaching Conditions

Experiment No.	Conditions	Targeted Oxidant:Cr Stoichiometry
1	Permanganate in 0.1 M NaOH	1
2	Permanganate in 3 M NaOH	1
3	Oxygen in 0.1 M NaOH	Large Excess
4	Oxygen in 3 M NaOH	Large Excess
5	Argon in 0.1 M NaOH	Not Applicable
6	Argon in 3 M NaOH	Not Applicable

Deionized water was added at this point to replenish evaporated water and the slurries were then briefly resuspended and allowed to resettle before sampling. Test samples were taken as soon as possible after the leach solution was introduced (0 hours), and then intermittently for the remainder of the experiment. The aliquots were passed through a 0.2-micron filter before analysis by ultraviolet visible (UV-vis) spectroscopy and by HCl titration for free [OH].

The test slurries were centrifuged, and the supernatants were decanted after the tests were completed. Aliquots were again taken for UV-vis spectroscopy and free [OH] measurement. The residual solids were then thrice washed with 0.1 M NaOH to remove any components present in the interstitial liquid. After each wash, the samples were centrifuged, and the supernatant was added to the final leachate. The washed residual solids were then dried to a constant weight at 105°C. These residual solids were taken to the hot cells and dissolved by KOH fusion in a Ni crucible. The content of the major metallic elements in both the supernatants and dissolved residues was determined by ICP-AES, and the activity due to TRU elements in both the supernatants and dissolved residues was determined by alpha energy analysis and gamma energy analysis. Established procedures were used for these analyses.^a

For the UV-vis spectroscopic measurements, portions of the 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 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 using standards-grade potassium dichromate in 0.05 M KOH according to standard procedures (Gordon and Ford 1972). The instrument showed good linearity from 2.05 to 0.04 absorbance units with a slope of 4833 L/mol-cm and a correlation coefficient of better than 0.999, as compared to the expected slope of 4845 L/mol-cm and correlation coefficient of 1. The calibration curve was then used to calculate a sample's Cr concentration from its measured 372-nm absorbance. A 0.1-mL aliquot was placed into 10 mL of deionized water. This sample was used to measure the free hydroxide concentration of the leachate, which was performed by leachate titration with a standard HCl solution using a Mettler DL21 automatic titrator equipped with a Ross combination pH electrode (Orion Research Inc., Boston, Massachusetts).

2.3 Description of Test Samples

As noted in Table 2.2, SX-108 belongs to SORWT (Sort on Radioactive Waste Type) group IV (Hill et al. 1995). The ten group IV tanks are estimated to contain 1228 kgal of sludge. The waste stored in these tanks originated from the REDOX process. Table 2.3 presents the major components

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

found after a 5-hour contact with 2 M NaOH at 100°C and a 5-hour contact with 3 M NaOH at 100°C (Lumetta et al. 1996). Extended leach times are expected remove almost all of the Al, although its impact on additional Cr removal is uncertain, since, in some cases, extended leach times have led to significant additional Cr dissolution. For example, the [Cr] in a S-101 caustic leach solution increased from 105 mg/mL after 5 hours at 100°C to 155 mg/mL after 100 hours at 100°C. Similarly, the [Cr] in S-111 increased from 185 mg/mL after 10 hours at 100°C to 1215 mg/mL after 143 hours at 100°C (Lumetta et al. 1997).

The remaining two samples are solids from tanks U-108 and U-109 following extended washing of the saltcakes with dilute hydroxide. Both of these are from SOWRT group VI and are primarily evaporator bottom and cladding waste. Although there is relatively little (314 kgal) sludge, there is substantially more (1877 kgal) saltcake in this waste type (Hill et al. 1995). Indeed, these two tanks comprise about 40% of the saltcake present in this SOWRT group. Previous work with these saltcakes indicates approximately 10% of the saltcake mass is composed of water insoluble solids, a mass roughly equal to the amount of sludge present in the U-108 and U-109 tanks.* Table 2.3 presents the major components found from dissolving the residue that remained following three 1-hour washes with 0.01 M NaOH at room temperature (leaving a colorless filtrate by the third wash) with approximately 2 M HNO₃ and 1 M HF. Clearly, both U-108 and U-109 contain substantial amounts of water-insoluble chromium.

Table 2.2. Summary of Sludges Used in Cr Leach Tests

Tank	SOWRT Group	Primary Waste Type ^(a)	Secondary Waste Type ^(a)	[Cr] in Prepared Sludge (µg/g solids)
U-108	VI	EB	CW	19,250 ^(b)
U-109	VI	EB	CW	13,100 ^(b)
SX-108	IV	R	None	5,760 ^(c)

(a) The waste types are defined as follows (Hill et al. 1995).
 EB Evaporator bottoms
 CW Cladding waste
 R High-level Reduction Oxidation (REDOX) process waste
 (b) As determined by ICP-AES.
 (c) As reported in Lumetta et al. (1996).

* D. L. Blanchard, Jr., W. E. Lawrence, G. R. Colcar, and D. E. Kurath. *Technecium Removal from Hanford Tank Wastes: Results of FY 1997 Studies*, Pacific Northwest National Laboratory, Richland, Washington (to be published).

Table 2.3. Concentrations ($\mu\text{g/g}$ dry solids) of Major Sludge Constituents as Determined by ICP-AES Analysis After Acid Dissolution of Solids

Component	U-108 ^(a)	U-109 ^(a)	SX-108 ^(b)
Al	42,600	75,100	270,000
Ca	10,900	5,100	11,200
Cr	126,000	205,000	5,760
Fe	14,300	7,180	71,700
Mn	2,390	2,880	21,200
Na	48,400	82,200	21,800
Si	191,000	242,000	10,670
U	12,500	<11,000	21,200

(a) Values are for material washed with dilute (0.01 M) hydroxide.
 (b) Values are for material leached with caustic (3 M NaOH).

3.0 Results and Discussion

3.1 General

Experimental work involving oxidative alkaline leaching has been performed on solids from tanks U-108, U-109, and SX-108. In addition, EXAFS studies have been performed on the solids from water-washed U-108 and U-109 saltcake, as well as water washed solids from tank BX-112. The EXAFS results will be presented in a separate report.

Two laboratory mishaps occurred during the leach testing that impact subsequent data interpretation. As noted in Section 2.2, the first mishap occurred when the gas flow was split in the hood via a T-adapter and from there into the sample bottles. Unfortunately, when the gas flow was stopped for sampling during the testing, some of the 3 M NaOH/Ar U-109 suspension siphoned into the 0.1 M NaOH/Ar U109 suspension, which had the effect of adding significant amounts of the latter test sample into the former. The second mishap occurred when the initial SX-108 sample aliquots were added. Stir bars were then added to the test samples, but the impact of this additional weight was not recorded. These unrecorded changes correspond to a change in the previously measured tare weights and result in an inability to directly ascertain the weights of the final leached residues. However, these weights can be estimated indirectly and so allow calculation of the percent component removed and mass balances. The specific means to estimate these values is discussed in detail below.

Hydroxide concentrations were monitored throughout the testing. Table 3.1 shows the initial and final hydroxide concentration for the U-108 and U-109 tests as determined by HCl titration of supernatant aliquots. In several instances, plots of the pH vs. added HCl show multiple breakpoints due to the presence of at least three species in solution that consume added hydrogen ion. As shown in Equations 3.1-3.3, neutralization of tetrahydroxyaluminate and condensation of chromate to form dichromate will compete with hydroxide neutralization for hydronium ion consumption. The contribution of hydronium ion consumption due to the neutralization of free [OH] was determined by evaluating the HCl consumption to the first breakpoint in the titration curve. This approach has previously been shown to yield reliable values for free hydroxide in similar tank leachates (Rapko et al. 1995).

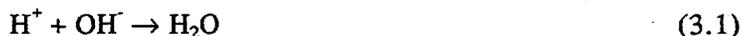


Table 3.1. Initial and Final Leachate Hydroxide Concentrations

Sample	U-108		U-109		SX-108	
	[OH ⁻]-initial, M	[OH ⁻]-final, M	[OH ⁻]-initial, M	[OH ⁻]-final, M	[OH ⁻]-initial, M	[OH ⁻]-final, M
0.1 M NaOH, MnO ₄ ⁻	0.10	0.13	0.09	0.11	0.11	0.05
3 M NaOH, MnO ₄ ⁻	2.98	2.77	2.80	2.98	2.9	0.95
0.1 M NaOH, O ₂	0.11	0.11	0.11	0.11	0.11	0.06
3 M NaOH, O ₂	2.97	3.02	2.77	2.65	2.6	0.59
0.1 M NaOH, Ar	0.09	0.10	0.10	0.12	(a)	(a)
3 M NaOH, Ar	2.92	2.89	2.90	2.53	(a)	(a)

(a) Test not performed

As revealed in Table 3.1, the leachate solutions for the U-108 and U-109 tests remained fairly close to their targeted free-hydroxide concentrations throughout the experiment. Consumption of free hydroxide during the conversion of Cr(III) to chromate, errors in replenishing evaporated water, and uncertainties in sample and in the titration itself can account for the small deviations observed between the initial and final values in Table 3.1. The transfer of 3 M NaOH/Ar U-109 sample to the 0.1 M NaOH/Ar U-109 sample may account for the slight increase in the final [OH⁻] concentration in the 0.1 M NaOH leachate and the slight decrease in the final [OH⁻] concentration in the approximately 3 M NaOH leachate.

Changes in the hydroxide concentrations during the SX-108 testing are more puzzling. Even complete dissolution of all likely major components, e.g., Al, Cr, and P, would have decreased the free hydroxide concentration by only ~10%. The reason behind for the additional consumed hydroxide is unknown.

3.2 Chromate Formation During Leaching of U-108, U-109 and SX-108 Solids

3.2.1 U-108 and U-109

Changes in the amount of Cr present in the leachate solutions were monitored by visible spectroscopy and are illustrated in Figures 3.1 (U-108) and 3.2 (U-109). As has been previously noted (Rapko et al. 1997), visible spectroscopy provides two pieces of information: the Cr concentration in solution and the Cr oxidation state. If Cr is present in the +6 oxidation state, i.e., as CrO₄²⁻, maximum absorbance occurs at ~372 nm. If Cr is present in the +3 oxidation state, i.e., as Cr(OH)₄⁻, a maximum absorbance at ~600 nm is observed. In all cases, only absorbances at 372 nm were observed, indicating that the dissolved Cr was present as chromate.

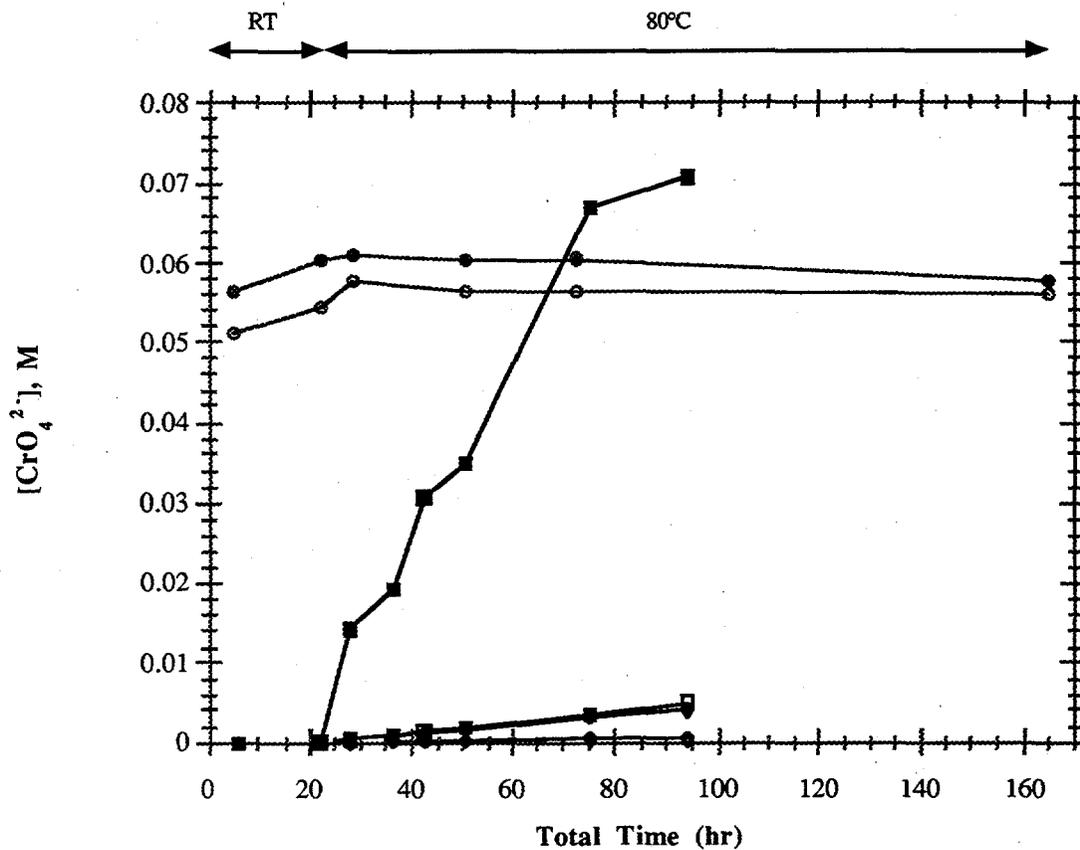


Figure 3.1. Chromate Formation from U-108 Sludge as a Function of Time

- Red Open Circles: Permanganate at 0.1 M NaOH
- Red Filled Circles: Permanganate at 3 M NaOH
- Blue Open Squares: Oxygen at 0.1 M NaOH
- Blue Filled Squares: Oxygen at 3 M NaOH
- Black Open Diamonds: Argon at 0.1 M NaOH
- Black Filled Diamonds: Argon at 3 M NaOH

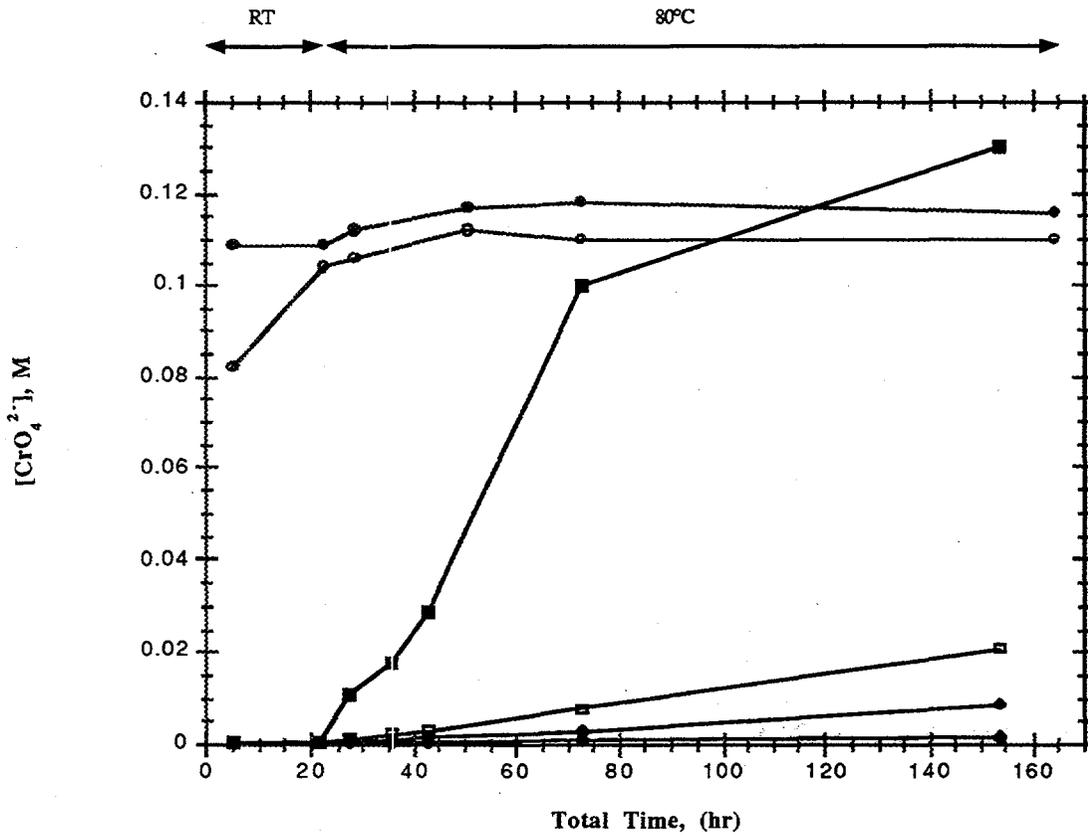


Figure 3.2. Chromate Formation from U-109 Sludge as a Function of Time

- Red Open Circles: Permanganate at 0.1 M NaOH
- Red Filled Circles: Permanganate at 3 M NaOH
- Blue Open Squares: Oxygen at 0.1 M NaOH
- Blue Filled Squares: Oxygen at 3 M NaOH
- Black Open Diamonds: Argon at 0.1 M NaOH
- Black Filled Diamonds: Argon at 3 M NaOH

Both U-108 and U-109 sludges showed similar responses to the alkaline oxidative leaching solutions. Permanganate, consistent with previous studies, rapidly formed chromate under mild conditions, with the reaction being essentially complete within a few hours at room temperature. Indeed, after 24 hours at room temperature, all added permanganate had been consumed. At this point, a small amount of additional permanganate was introduced to maintain the presence of excess free permanganate. Even so, subsequent contact at 80°C resulted in only a minor, if any, increase in the amount of chromate present in the leachate. The leachate's hydroxide concentration has no apparent influence on chromate formation using permanganate.

Chromate formation from oxygenated leachate solutions showed a dramatic effect by both temperature and hydroxide concentration. Essentially no formation of chromate was observed at either hydroxide concentration at room temperature. With low (0.1 M)-hydroxide leachates, chromate formation, even at elevated temperatures, was slow. However, with the higher (3 M)-hydroxide leachate solutions at 80°C, appreciable and rapid chromate formation was observed. Chromate concentrations in the leachate solutions increased steadily over the first 2 days at 80°C, eventually reaching concentrations comparable to those observed using permanganate. Since further, albeit smaller, increases were observed during the final two measurements, it is uncertain whether longer contact times would have resulted in still additional chromate formation.

Chromate formation in the absence of an added oxidant (Ar purge) was minimal at either hydroxide concentration, even after elevated heating for several days. The small amount of chromate that was formed is likely due to small amounts of oxygen in the leachate present despite the use of an Ar purge.

3.2.2 SX-108

Changes in the amount of chromate in the SX-108 leachate solutions were monitored by visible spectroscopy and are illustrated in Figure 3.3. Due to the relative low concentrations of Cr in these SX-108 solids, the chromate concentrations observed were much less than those found during U-108 and U-109 testing.

Like U-108 and U-109, the SX-108 leach tests at high hydroxide show that, while permanganate more quickly reaches its maximum concentration, both permanganate and oxygen leachate solutions reach similar final concentrations in chromate. Unlike the U-108 and U-109 samples, very different results are obtained with permanganate at low-hydroxide concentrations vs high-hydroxide concentrations. This can be explained by the differing Cr concentration in the starting materials in the low-hydroxide samples vs the high-hydroxide samples as discussed below.

3.3 Dissolution of Bulk Components From U-108, U-109, and SX-108 Solids by Alkaline Oxidative Leaching

3.3.1 U-108 and U-109

Tables 3.2 and 3.3 summarize the effect of oxidative alkaline leaching on removal of the major bulk components from U-108 and U-109 sludge, respectively. Tables 3.4 and 3.5 report on the concentrations of the major bulk components in the initial washed sludge and final, leached, U-108 and U-109 sludges, respectively. Finally, Table 3.6 summarizes the mass changes in the U-108 and U-109 sludges that occurred during oxidative alkaline leaching.

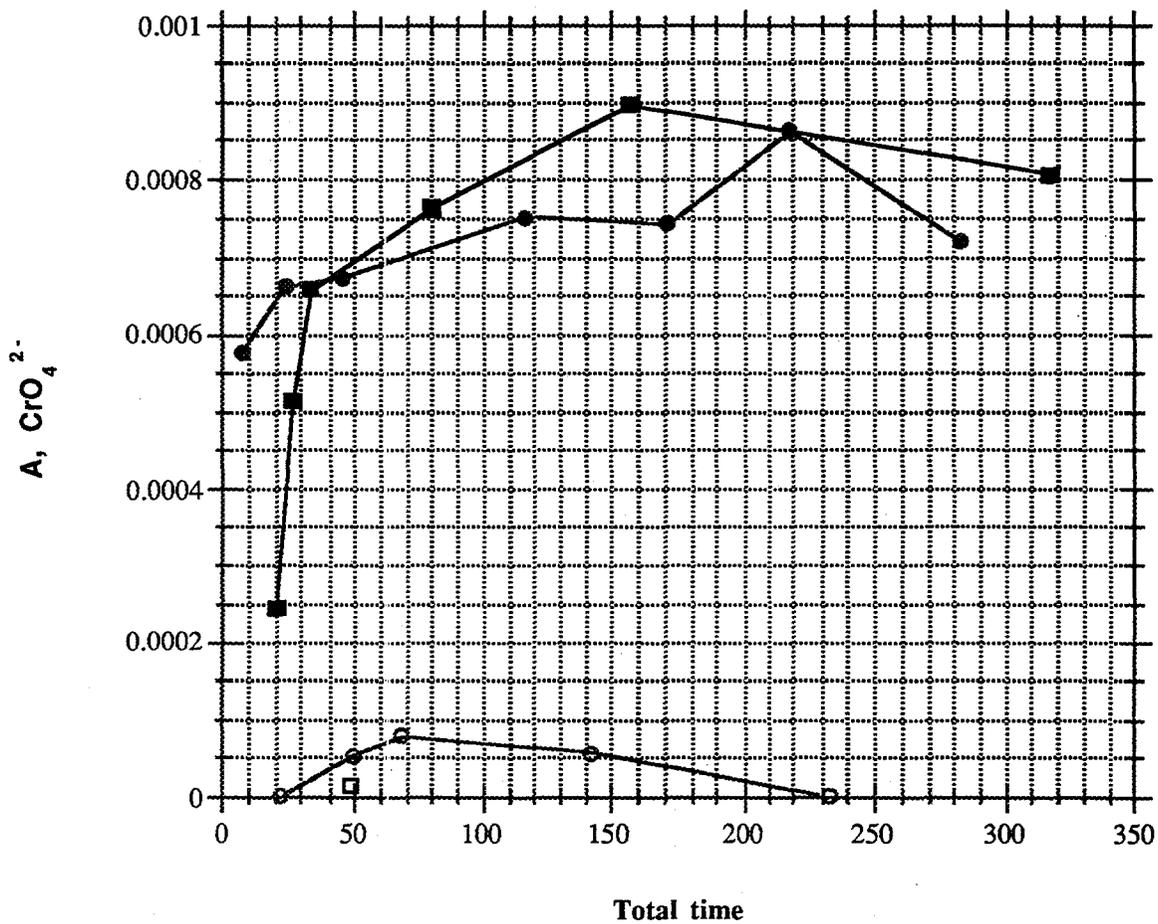


Figure 3.3. Chromate Formation from SX-108 Sludge as a Function of Time

- | | |
|----------------------|----------------------------|
| Red Open Circles: | Permanganate at 0.1 M NaOH |
| Red Filled Circles: | Permanganate at 3 M NaOH |
| Blue Open Squares: | Oxygen at 0.1 M NaOH |
| Blue Filled Squares: | Oxygen at 3 M NaOH |

Table 3.2. Summary of the Removal of Bulk Nonradioactive Components from U-108 Sludge By Oxidative Alkaline Leaching^(a)

Element	0.1 M NaOH/MnO ₄ ⁻		3 M NaOH/MnO ₄ ⁻		0.1 M NaOH/O ₂		3 M NaOH/O ₂		0.1 M NaOH/Ar		3 M NaOH/Ar	
	% Rem	MB	% Rem	MB	% Rem	MB	% Rem	MB	% Rem	MB	% Rem	MB
Al	6.5	98	96.4	100	12	74	94.7	95	10	88	81	91
Bi	0	85	0	72	0	117	0	66	0	103	0	93
Ca	0	103	83	614	0	137	43	336	0	125	0	117
Cr	96.6	100	99.6	96	4.9	155	94.4	106	0.57	117	5.1	124
Fe	0	112	0	91	3.3	116	4.8	172	3.8	92	3.4	107
Mn	NA	NA	NA	NA	0	138	0	157	0	44	0.3	100
Na ^(b)	-39	NA	-35	NA	15	NA	60	NA	16	NA	38	NA
Pb	0	90	0	40	0	96	75	100	0	97	8.5	90
Si	46	186	48	158	33	182	45	170	34	155	70	135
U	0	106	0	97	0	96	0	123	0	93	0	73

(a) % Rem = Percent Removed; MB = Mass Balance; NA = not appropriate due to added amounts of added component.

(b) % Sodium removal calculated as $100 - [(Na)_{residual\ solids} / (Na)_{initial\ solids}] \times 100$.

Table 3.3. Summary of the Removal of Bulk Nonradioactive Components from U-109 Sludge By Oxidative Alkaline Leaching

Element	0.1 M NaOH/MnO ₄ ⁻			3 M NaOH/MnO ₄ ⁻			0.1 M NaOH/O ₂			3 M NaOH/O ₂			0.1 M NaOH/Ar			3 M NaOH/Ar		
	% Rem.	MB		% Rem.	MB		% Rem.	MB		% Rem.	MB		% Rem.	MB		% Rem.	MB	
Al	9.2	98		77	99		17	105		80	100		24	72		54	136	
Bi	0	83		0	91		0	114		0	64		0	84		0	138	
Ca	45	117		0	87		0	73		0	79		0	49		66	268	
Cr	96.3	97		98.9	87		13.7	109		97.5	96.7		1.6	73		5.2	140	
Fe	0	110		1.9	115		2	118		0	115		3.1	74		0	149	
Mn	NA	NA		NA	NA		0	112		0	114		0	70		0	138	
Na ^(a)	-47	NA		-110	NA		26	NA		62	NA		40	NA		-16	NA	
Pb	0	101		53	117		0	123		0	23		0	76		0	137	
Si	37	143		31	137		14	103		22	93		22	78		21	142	
U	0	109		0	108		0	96		0	93		0	64		0	109	

(a) % Sodium removal calculated as $100 - [(mass\ residual\ solids^* [Na]_{residual\ solids}) / (mass\ initial\ solids^* [Na]_{initial\ solids})]$.

Comparison of Table 2.3 with 3.4 and 3.5 show that the acid dissolution method indicates an appreciably different solids composition than do the analytical results obtained following sludge dissolution by KOH fusion. Of the two sets of results, sludge dissolution by the KOH fusion method is much more likely to have been complete and so leading to a more reliable analysis of the true sludge composition. In any event, for the targeted analyte (Cr) of the acid-dissolution analysis, reasonable agreement between the two approaches was observed.

Table 3.4. Concentrations ($\mu\text{g/g}$) of the Initial and Final, Leached U-108 Sludges

Element	Initial Sample	0.1 M NaOH, NaMnO ₄	3 M NaOH, MnO ₄ NaMnO ₄	0.1 M NaOH, O ₂	3 M NaOH, O ₂	0.1 M NaOH, Ar	3 M NaOH, Ar
Al	202,000	183,500	18,100	149,000	66,500	179,000	81,500
Bi	460	390	830	610	2,000	530	970
Ca	2,500	2,550	6,400	3,890	31,900	3,500	6,670
Cr	112,000	3,775	1,200	187,000	44,200	146,000	300,000
Fe	4,690	5215	10,700	5,980	50,800	4,630	11,000
Mn	1,930	130,500	344,000	3,010	20,100	947	4,360
Na	32,700	45,250	110,000	31,400	85,500	30,900	46,400
Si	9,930	9,935	20,600	13,700	61,600	11,400	9,110
U	8,500	9,000	20,000	9,200	69,200	8,900	14,000

Table 3.5. Concentrations ($\mu\text{g/g}$) of the Initial and Final, Leached U-109 Sludges

Element	Initial Sample	0.1 M NaOH, NaMnO ₄	3 M NaOH, NaMnO ₄	0.1 M NaOH, O ₂	3 M NaOH, O ₂	0.1 M NaOH, Ar	3 M NaOH, Ar
Al	86,800	76,600	22,300	90,200	82,900	77,150	49,500
Bi	1,100	900	1,200	1,500	3,300	1,500	1,400
Ca	8,790	5,600	8,570	7,680	33,000	7,045	7,520
Cr	255,000	8,870	2,840	287,000	29,700	297,500	310,000
Fe	7,260	7,880	9,200	10,000	39,400	8,515	9,920
Mn	3,440	262,000	365,000	4,600	18,600	3,930	4,370
Na	55,700	66,400	117,000	49,400	99,300	54,450	59,100
Si	22,600	20,100	24,400	23,800	77,500	22,400	23,200
U	14,000	15,000	17,000	16,000	61,700	14,500	14,000

Of the major bulk constituents, Tables 3.2 and 3.3 reveal that Bi, Fe, Mn, Pb, and U are not significantly dissolved during alkaline oxidative leaching. The responses of silicon and calcium to the experimental variables of oxidant and hydroxide concentration are, in general, modest but erratic, and the responses of Al and Cr markedly change as the experimental variables are changed. In general, the mass balances, defined as the sum of the component mass found in the leachate and residual divided by the mass of the component in the initial sludge, are good, although the mass balances for silicon and calcium are often high. The reason for these poor mass balances is unknown. The solids transfer, previously described from the 0.1 M NaOH/Ar U-109 test to the 3 M NaOH/Ar U-109 test, is reflected by the universally low mass balances found in the 0.1 M NaOH/Ar U-109 test and the universally high mass balances found in the 3 M NaOH/Ar U-109 test. Since this transfer of material occurred towards the end of the test, the interpretation of component removal is also affected. Because of the artificially low amount of residual solids, the low-hydroxide leachate

results should be considered as maximum estimates for component removal. Because of the artificially high amount of residual solids, the high-hydroxide leachate results should be considered as minimum estimates for component removal.

Table 3.6. Initial and Final Sludge Masses in U-108 and U-109 Testing

Sample	Mass U-108 Sludge (g)	Mass U-109 Sludge (g)
0.1 M NaOH, MnO ₄ , initial	1.178	1.104
0.1 M NaOH, MnO ₄ , final	1.185	1.119
3 M NaOH, MnO ₄ , initial	1.172	1.130
3 M NaOH, MnO ₄ , final	0.469	1.005
0.1 M NaOH, O ₂ , initial	1.179	1.130
0.1 M NaOH, O ₂ , final	1.041	0.947
3 M NaOH, O ₂ , initial	1.178	1.122
3 M NaOH, O ₂ , final	0.178	0.237
0.1 M NaOH, Ar, initial	1.161	1.135
0.1 M NaOH, Ar, final	1.036	0.697
3 M NaOH, Ar, initial	1.174	1.129
3 M NaOH, Ar, final	0.517	1.229

The amount of sodium present in the U-108 and U-109 sludges at the end of the alkaline oxidative leach tests was generally greater than the amount initially present. This is because the initial samples were washed with 0.01 M NaOH, while the final washes were with 0.1 M NaOH. Therefore, the amount of sodium present in the interstitial liquid at the end of each test was greater than that present initially. Unless the mass reduction by alkaline oxidative leaching is sufficient to reduce the amount of interstitial liquid present in the sample at the conclusion of the test, one should expect that the test design will introduce additional sodium. Indeed, only in cases where significant mass loss was in fact observed, such as that found during leaching with 3 M NaOH/O₂, was a net decrease found in the amount of sodium present in the solids at the conclusion of the test.

Aluminum dissolution follows the trends typically observed during caustic leaching of Hanford tank sludges (Rapko et al. 1995; Lumetta et al. 1996; Lumetta et al. 1997), with greatly enhanced dissolution from high-hydroxide leachate solutions compared to low-hydroxide leachate solutions. As expected, there is no effect of added oxidant on Al dissolution. However, U-108 and U-109 sludges do respond differently. Despite the higher Al concentrations present in U-108 sludge, contact with high caustic is more effective at dissolving Al, with an average of 91% removal observed for the U-108 tests. Ignoring the 3 M NaOH/Ar results for the reasons mentioned above, the average removal of U-109 sludge after contact with 3 M NaOH was only 79%.

Chromium dissolution by permanganate is excellent, with 96.6% removed from U-108 sludge by the 0.1 M NaOH/permanganate leachate, and 96.3% removed from U-109 sludge by the 0.1 M NaOH/permanganate leachate. Permanganate leaching at high hydroxide appears even more effective, albeit only slightly, with 99.6% of the Cr removed from U-108 sludge by a 3 M NaOH/permanganate leachate, and 98.9% of the Cr removed from U-109 sludge by a 3 M NaOH/permanganate leachate. Chromium dissolution by hydroxide leachates in the absence of added oxidant is universally poor, with no better than 5% dissolution observed in any instance. As noted in

more detail below, even this small dissolution is likely due to the presence of a small amount of oxygen in the leachate solution.

Chromium dissolution in the oxygen-sparged leachate solutions shows a dramatic dependence on hydroxide concentration. With the low-hydroxide leachates, Cr removal is as good or better than any of the argon leachates, with approximately 5% removed from U-108 and approximately 14% from U-109 sludge, but it is notably poorer than the removals found with permanganate at comparable hydroxide concentrations. At 3 M hydroxide, however, after approximately 1 week at 80°C, oxygen is almost as effective as permanganate at Cr dissolution, with 94.4% removal from U-108 sludge and 97.5% removal from U-109 sludge observed. Given the increasing chromate concentrations found even at the end of the approximately 1-week contact, however, it is likely that a small extension in contact times would increase Cr removals to the values observed during the permanganate contacts.

One question always present in such tests, but especially so in the case of the argon-purged leachate solutions where no obvious oxidant is present for Cr(III), is whether the dissolved Cr is actually present as chromate or whether some of the dissolved Cr is present in the +3 oxidation state. This question can be addressed by comparing the chromate concentration in the leachate as determined by UV-vis spectroscopy with the total amount of Cr present in the leachate as determined by ICP-AES. Table 3.7 compares the Cr concentrations found by these two methods. In all cases, the agreement is within the experimental uncertainty of the ICP-AES measurement and, in many instances, the agreement is exceptionally good. These results reinforce the previous conclusion (Lumetta et al. 1996; Rapko et al. 1996; Lumetta et al. 1997; Rapko et al. 1997) that all Cr(III) dissolution found during the caustic leaching of tank sludge occurs via oxidation of Cr(III) to Cr(VI). Since most potential oxidants present in the tanks, such as nitrate or nitrite, would have been removed by the dilute hydroxide washes performed before these leach tests, adventitious atmospheric oxygen appears to be the most likely oxidant source for the observed Cr(III) to Cr(VI) conversion during these argon purges.

Table 3.7. Comparison of Cr Concentrations as Determined by ICP-AES and Chromate Concentrations as Determined by UV-vis Spectroscopy for U-108 and U-109 Final Leachate Solutions

Sample	U-108 Leachate Solutions		U-109 Leachate Solutions	
	[Cr], M, as Chromate	[Cr], M, by ICP-AES	[Cr], M, as Chromate	[Cr], M, by ICP-AES
0.1 M NaOH, MnO ₄	2.56 x 10 ⁻²	2.57 x 10 ⁻²	4.87 x 10 ⁻²	5.19 x 10 ⁻²
3 M NaOH, MnO ₄	2.73 x 10 ⁻²	2.52 x 10 ⁻²	5.26 x 10 ⁻²	5.06 x 10 ⁻²
0.1 M NaOH, O ₂	1.98 x 10 ⁻³	1.98 x 10 ⁻³	8.30 x 10 ⁻³	8.46 x 10 ⁻³
3 M NaOH, O ₂	2.70 x 10 ⁻³	2.70 x 10 ⁻³	5.39 x 10 ⁻³	5.09 x 10 ⁻³
0.1 M NaOH, Ar	1.82 x 10 ⁻⁴	1.81 x 10 ⁻⁴	6.85 x 10 ⁻⁴	6.34 x 10 ⁻⁴
3 M NaOH, Ar	1.72 x 10 ⁻³	1.65 x 10 ⁻³	4.02 x 10 ⁻³	3.92 x 10 ⁻³

3.3.2 SX-108

Table 3.8 reports on the concentrations of the major bulk components in the initial washed SX-108 sludge used in the 3 M NaOH oxidative leach tests, the initial 3 M NaOH leached sludge used in the 0.1 M NaOH oxidative leach tests and the final, oxidatively leached sludges. Table 3.9 summarizes the effect of oxidative alkaline leaching on removal of the major bulk components from

SX-108 sludges. Finally, Table 3.10 summarizes the changes in the Al, Cr and Fe molar ratios that were found in the initial and final sludges.

Table 3.8. Major Bulk Component Removal by Alkaline Oxidative Leaching With SX-108 Solids
 (% Rem = % Removal
 MB = Mass Balance)

Element	0.1 M [OH]; MnO ₄ ⁻		3 M [OH]; MnO ₄ ⁻		0.1 M [OH]; O ₂		3 M [OH]; O ₂	
	% Rem	MB	% Rem	MB	% Rem	MB	% Rem	MB
Al	70	26	93	90	63	21	89	139
Cr	29	73	64	93	4.5	63	71	136
Fe ^(a)	0.5	100	0.3	100	0.6	100	1.7	100
Mn	0	317	4	260	0	98	0	98
Na ^(b)	99	NA	57	NA	99	NA	78	NA
Si	95	66	91	241	95	60	73	412
U	0	42	0	95	0	41	0	87

(a) Mass balance for Fe is defined as 100%. See text for explanation.
 (b) % Removed calculated as $[\text{Na}]_{\text{final}} \cdot \text{assumed final mass} / ([\text{Na}]_{\text{initial}} \cdot \text{initial mass}) \cdot 100$
 NA = Not applicable

As was noted in the experimental section, the SX-108 samples subject to oxidative leaching at low hydroxide were initially leached with 3 M NaOH for one week at 100°C to remove most of the Al, while the samples subjected to oxidative alkaline leaching at high hydroxide were simply washed at room temperature with 0.1 M NaOH. The composition of the SX-108 solids used for testing reflect this pretreatment. The material subjected to an initial hydroxide leach showed a marked decrease in the Al present, although the very high residual Na concentration indicate that the subsequent low hydroxide washes intended to reduce the Na concentration were fairly unsuccessful. The samples subjected only to a simple low hydroxide wash show the high Al concentrations found during previous caustic leach tests (Lumetta 1996). The Cr concentration of both samples were lower than expected, especially with the material destined for low oxidative leach testing. Here, the likely explanation for the low Cr concentrations in this material is a combination a dilution effect from the very high residual Na concentrations as well as the the recently documented enhanced Cr dissolution that occurs during extended times at elevated temperatures in air (Lumetta 1997, Lumetta 1998). The very low Cr concentrations present in these samples suggest that the standard caustic leaching in and of itself would remove sufficient Cr from SX-108 sludge.

As mentioned in the Experimental section above, the lack of proper tare weights prevented calculation of the amount of residual solids after oxidative leaching. These values were estimated using the following method. First note that iron is present in good quantities in both the initial and leached solids. These Fe concentrations are conveniently measured by ICP-AES in the initial and final solids. Since the amount of initial solids is known as a result of the direct measurement of the amount of initial slurry added and the weight % solids present in this slurry, the amount of iron initially present in the leachate samples can be calculated. Since the concentrations of iron in the residual solids have also been measured, the mass of residual solid necessary to achieve mass balance for Fe can be readily calculated. This calculated value for the residual sludge is then used for all calculations based on ICP data. Small amounts of Fe were often detected in the leachate; the portion of Fe transferred to this waste stream is accounted for in the calculations.

Table 3.9. Major Bulk Component Concentrations in SX-108 Solids (μg component/g solids)

Element	0.1 M Oxidatively Leached Solids - Initial	3 M Oxidatively Leached Solids - Initial	0.1 M OH; MnO_4 ; residue	3 M OH; MnO_4 ; residue	0.1 M OH; O_2 ; residue	3 M OH; O_2 ; residue
Al	22900	235000	13300	50500	10900	116000
Cr	1320	4270	5240	4820	4940	5200
Fe	23000	48100	175000	163500	142000	148000
Mn	7600	13800	184000	117507	46200	43400
Na	449000	39400	49100	58100	30300	27500
Si	49500	14400	12000	11000	9360	50600
U	15000	14000	47500	45500	38500	38200

Table 3.10. Al/Fe, Cr/Fe, and Al/Cr Molar Ratios in SX-108 Solids

Element	0.1 M Oxidatively Leached Solids - Initial	3 M Oxidatively Leached Solids - Initial	0.1 M OH; MnO_4 ; residue	3 M OH; MnO_4 ; residue	0.1 M OH; O_2 ; residue	3 M OH; O_2 ; residue
Al/Fe	2.06	10.11	0.16	0.64	0.16	1.62
Cr/Fe	0.06	0.10	0.03	0.03	0.04	0.04
Al/Cr	33.44	106.07	4.89	20.19	4.25	42.99

Using this approach, the mass balances and % components were calculated. The behavior of the major constituents is summarized in Table 3.8. In general, mass balances are poor for most of the constituents in the 0.1 M hydroxide oxidative leach experiments, while the mass balances for the 3 M hydroxide oxidative leach experiments are similar to those found in the U-108 and U-109 tests. The mass balances for Al and U are low in the low hydroxide oxidative leach tests, but within typical experimental errors for the high oxidative leach tests. Silicon mass balances, like Al and U, are low for the low hydroxide leach tests but high for the high hydroxide oxidative leach tests. The reasons for the varying behavior of these constituents are unknown. Fortunately, the constituent with the best overall mass balance behavior in both low and high hydroxide leach tests is Cr, the focus of these tests.

The results indicate that, as expected based on previous studies, constituents such as Fe and U are not significantly dissolved during alkaline oxidative leaching. Based on the experiments performed in the absence of added manganese, no dissolution of the manganese initially present in the sludges occurs. On the whole, most of the silicon appears to dissolve, and the responses of Al and Cr markedly change as the experimental variables are changed.

As expected, there is no effect of type of oxidant added on Al dissolution. In general, the % of Al removed is excellent, ~90%, in the higher hydroxide leach solutions, despite the decrease in free hydroxide concentration observed during the experiment. This increase is much higher than the 29% previously observed using two, 5 hr, leach times at 100°C (Lumetta 1996). Such increases in Al dissolution with longer leach times for boehmite-containing sludges such as SX-108 have been documented recently (Lumetta 1997, Lumetta 1998). Although Al removal resulting from oxidative leaching at high hydroxide and 80°C was good, the lower Al concentrations found in the initial, low hydroxide sample compared to either of the two high, hydroxide oxidative leach residues indicates that 1 week leaching with 3 M NaOH at 100°C is even more effective.

The removal of Al coupled with the longer reaction times does appear to have led to improved dissolution of Cr by oxidative alkaline leaching. In previous studies with SX-108 sludge, the maximum percentage of Cr removed was 45%. In this study, the high hydroxide alkaline leach tests (which used a similarly prepared SX-108 sludge) removed from 64-71% of the Cr. Removals with the low hydroxide oxidative leach conditions were significantly lower, ranging from 29% with permanganate to 4.5% with oxygen. The poor Cr removal by oxygen at low hydroxide is consistent with the U-108 and U-109 results. The poor Cr removal by permanganate at low hydroxide is probably related to the removal of most of the accessible Cr by the initial caustic leach. While this material remained and so could be dissolved during the high hydroxide oxidative leach tests, its absence limited the amount of leachable Cr present in the low hydroxide tests and so led to poor Cr removals even when using a rapid and effective oxidant such as permanganate. The Cr/Fe, Al/Fe and Cr/Al ratios for the initial and final sludge samples shown in Table 3.10 lend support to this explanation. No matter what the starting point, with the markedly varying Al/Fe or Cr/Fe ratios, the final Cr/Fe ratio is remarkably consistent at 0.03-0.04. This suggests that there is some Cr associated with Fe that is not amenable to oxidative leaching, while all of the remaining Cr can be dissolved. It should be noted that a previous TEM study of SX-108 sludge (Lumetta 1996) indicated that some Cr was indeed associated with Fe.

As summarized in Table 3.8, the amount of sodium remaining at the end of the oxidative leach tests is fairly constant, within a factor of two despite the varying initial Na concentrations. Unlike with the U-108 and U-109 sludges, where the initial sample was washed with a liquid with a lower Na content than the final wash solutions, which led to a net increase in Na as a result of the oxidative leaching, the initial preparation of the SX-108 samples were with solutions of equal or substantially greater Na concentration. Where the initial sample had been prepared by contact with 3 M NaOH, Na removal by the 0.1 M NaOH leach solutions followed by extensive 0.1 M NaOH washing removed ~99% of the Na initially present. Where the initial sludge preparation was by contact with 0.1 M NaOH, the final washes using 0.1 M NaOH lead to modest Na removals.

3.4 Radionuclide Dissolution During Alkaline Oxidative Leaching

3.4.1 U-108 and U-109

Tables 3.11 and 3.12 describe the extent to which radionuclides dissolve during oxidative alkaline leaching from U-108 and U-109 solids, respectively. Table 3.13 shows the TRU activity of the leachate solutions as determined by alpha energy analysis. Overall, the type and extent of radionuclide dissolution is remarkably similar between the two sludges. In general, the mass balance appears satisfactory, although the mass balance for the 3 M NaOH/oxygen test with U-108 is uniformly high, and the consequences of material transfer, as noted above, between the U-109/Ar leach experiments are again apparent. Cesium-137 is removed with moderate success from both U-108 and U-109 solids, with percent removals typically ranging from 60 to 80%. There does not appear to be any hydroxide dependence associated with cesium removal from U-109 solids. With U-108 solids, removal appears to be slightly more effective at high-hydroxide concentrations.

No americium was detected by gamma emission spectroscopy (GEA) in any of the leachate solutions. The alpha activity of the leachate solutions depends primarily upon $^{239,240}\text{Pu}$ and $^{238,233,234}\text{U}$ activities as detected by alpha emission spectroscopy (AEA). Both the U-108 and U-109 sludges show similar trends and magnitudes in actinide dissolution. These results are consistent with a recent study that found increases in dissolved Pu following contact of Pu(IV) with potassium permanganate in alkaline (0.5 to 14 M NaOH) solutions. On the other hand, contact of Pu(IV) with either oxygen or chromate resulted in no enhanced dissolution of Pu (Shilov et al. 1997).

Plutonium dissolution appears to occur to a somewhat greater extent with the high-hydroxide leachates compared to the low-hydroxide leachates, consistent with the trends in Pu(IV) solubility in alkaline solution. The rough similarities in removal found when comparing the Ar and oxygen leachate solutions also support the idea that Pu dissolution is being controlled by the solubility of Pu(IV). However, contact with permanganate markedly increases the amount of Pu in the solution, suggesting that some oxidation of Pu by permanganate has occurred.

No U dissolution was observed by ICP-AES. However, the more sensitive radiochemical methods do detect substantial amounts of U dissolution. Indeed, especially with the non-permanganate leachates, the activity due to $^{233,234}\text{U}$ can be a substantial, even the predominant, contributor to the alpha activity in these leachates. All of the leachate solutions show comparable U concentrations, indicating that the extent of U dissolution is relatively independent of hydroxide concentration. However, the actual percent of the components removed depends on the U isotope examined; the extent of U dissolution is calculated to be typically about a factor of three greater if the $^{233,234}\text{U}$ isotope is considered than if the ^{238}U isotope is examined. The cause for this discrepancy is unknown but may reflect the somewhat higher uncertainties associated with the ^{238}U measurements.

Table 3.11. Radionuclide Removal by Alkaline Oxidative Leaching With U-108 Solids

Com- ponent	0.1 M [OH]/MnO ₄		3 M [OH]/MnO ₄		0.1 M [OH]/O ₂		3 M [OH]/O ₂		0.1 M [OH]/Ar		3 M [OH]/Ar	
	% Removed	Mass Balance	% Removed	Mass Balance	% Removed	Mass Balance	% Removed	Mass Balance	% Removed	Mass Balance	% Removed	Mass Balance
¹³⁷ Cs	61	86	70	80	65	81	81	77	67	71	94	72
¹⁵⁴ Eu	0	94	0	121	0	155	0	264	0	96	0	122
¹⁵⁵ Eu	0	81	0	84	0	120	0	189	0	80	0	88
²⁴¹ Am()	0	89	0	53	0	86	0	147	0	77	0	72
²³⁹ Pu	1	109	50	86	0	128	2	196	0.02	95	0.08	119
²⁴⁰ Pu												
²³⁵ U	2	98	11	79	6	61	6	140	4	67	9	83
²³³ U												
²³⁴ U	16	124	35	96	18	99	13	206	18	106	23	104

Table 3.12. Radionuclide Removal by Alkaline Oxidative Leaching With U-109 Solids

Com- ponent	0.1 M [OH]/MnO ₄		3 M [OH]/MnO ₄		0.1 M [OH]/O ₂		3 M [OH]/O ₂		0.1 M [OH]/Ar		3 M [OH]/Ar	
	% Removed	Mass Balance	% Removed	Mass Balance	% Removed	Mass Balance	% Removed	Mass Balance	% Removed	Mass Balance	% Removed	Mass Balance
¹³⁷ Cs	60	96	56	94	69	92	70	96	74	64	68	124
¹⁵⁴ Eu	0	105	0	114	0	108	0	136	0	77	0	146
¹⁵⁵ Eu	0	134	0	170	0	176	0	183	0	106	0	243
²⁴¹ Am()	0	53	0	60	0	70	0	69	0	45	0	87
²³⁹ Pu	1	95	36	98	0	109	1	117	0	70	0.03	138
²⁴⁰ Pu												
²³⁸ U	7	99	6	137	2	118	4	149	5	61	7	107
²³³ U												
²³⁴ U	20	143	18	171	12	145	12	164	15	99	13	168

Table 3.13. TRU Activity ($\mu\text{Ci}/\text{mL}$) in U-108 and U-109 Leachates

Leachate	$^{239,240}\text{Pu}$	$^{238}\text{Pu} + ^{241}\text{Am}$	$^{236}\text{Pu} + ^{243,244}\text{Cm}$
U-108; 0.1 M [OH]; MnO_4^-	2.42E-05	1.92E-06	3.57E-07
U-108; 3 M [OH]; MnO_4^-	1.21E-03	1.73E-04	5.00E-07
U-108; 0.1 M [OH]; O_2	< 2.08E-06	< 2.08E-6	< 2.08E-06
U-108; 3 M [OH]; O_2	8.59E-05	1.06E-05	ND
U-108; 0.1 M [OH]; Ar	4.91E-07	2.41E-06	ND
U-108; 3 M [OH]; Ar	2.59E-06	4.76E-06	ND
U-109; 0.1 M [OH]; MnO_4^-	7.06E-05	6.58E-06	ND
U-109; 3 M [OH]; MnO_4^-	2.18E-03	2.74E-04	ND
U-109; 0.1 M [OH]; O_2	< 2.12E-07	< 8.48E-07	< 3.18E-07
U-109; 3 M [OH]; O_2	7.28E-05	7.19E-06	< 3.17E-07
U-109; 0.1 M [OH]; Ar	< 5.20E-07	1.52E-06	< 3.12E-07
U-109; 3 M [OH]; Ar	2.16E-06	6.96E-06	4.30E-07

3.4.2. SX-108

Table 3.14 describes the extent to which radionuclides dissolve during oxidative alkaline leaching from SX-108 solids. Table 3.15 shows the TRU activity of the leachate solutions as determined by alpha energy analysis. As with the analysis of the bulk components, the samples were normalized to a specific radionuclide for purposes of the mass balance calculations. In this instance, the radionuclide used was ^{241}Am as measured by gamma spectroscopy. Americium-241, like Fe, has no history of significant dissolution in alkaline oxidative leach solutions. As with the ICP-AES results, the mass balances for the low-hydroxide leach solutions were poor, especially for ^{137}Cs , while the mass balances for the high-hydroxide contacts were comparable to the U-108 and U-109 results. Fortunately, the mass balances for Pu were good in both instances; Pu is the major radionuclide of interest in terms of its potential dissolutions by oxidative alkaline leaching.

Table 3.14. Radionuclide Removal by Alkaline Oxidative Leaching With SX-108 Solids

Radio-nuclide	0.1 M [OH]; MnO_4^-		3 M [OH]; MnO_4^-		0.1 M [OH]; O_2		3 M [OH]; O_2	
	% Rem	MB	% Rem	MB	% Rem	MB	% Rem	MB
^{137}Cs	57	10.1	96	44	59	7.5	95	88
^{155}Eu	0	216	0	160	0	210	0	168
^{154}Eu	0	217	0	181	0	192	0	202
$^{241}\text{Am}(\gamma)$	0	100	0	100	0	100	0	100
$^{239,240}\text{Pu}$	0.53	107	2.0	75	0.0053	97	0.25	93

As with the U-108 and U-109 samples, no dissolution of ^{241}Am was observed. Cesium-137 dissolution following contact with 3 M NaOH was improved (95% vs 23%) over the previous caustic leaching study (Lumetta 1996). As with the U-108 and U-109 samples, treatment with permanganate at either low or high hydroxide leads to slightly increased removals of Pu compared to treatment with oxygen (0.53 vs 0.005% at low hydroxide and 2.0 vs. 0.25% at high hydroxide. Unlike the U-108

and U-109 samples, the concentrations the ^{235}U and ^{238}U provided a negligible contribution to the overall alpha activity of the leachates.

Table 3.15. TRU Activity ($\mu\text{Ci}/\text{mL}$) in SX-108 Leachates

Leachate	$^{239,240}\text{Pu}$	$^{238}\text{Pu} + ^{241}\text{Am}$	$^{236}\text{Pu} + ^{243,244}\text{Cm}$
SX-108; 0.1 M [OH]; MnO_4^-	6.29E-06	3.45E-07	ND
SX-108; 3 M [OH]; MnO_4^-	5.76E-05	2.14E-05	ND
SX-108; 0.1 M [OH]; O_2	6.30E-07	< 3.00E-07	ND
SX-108; 3 M [OH]; O_2	6.85E-05	6.93E-06	ND
ND = not determined			

An important question, related to the applicability of oxidative alkaline leaching of tank solids is whether the resulting leach solutions will be a low-level or a high level (TRU) waste. Table 3.16 attempts to address this question by considering the TRU concentration of a glass derived from the leachate solutions when loaded with the leachate components to 20 weight percent sodium oxide composition. Even with the elevated Pu concentrations found with the permanganate leachates, all of the leachate solutions will make a LLW waste. Indeed, only for the case where the most extensive Pu dissolution is observed (3 M NaOH/permanganate with U-109 sludge) would the TRU concentration exceed the NRC Class A LLW limit of 10 nCi/gram.

Table 3.16. TRU Activity of Oxidative Alkaline Leachate Solutions in Glass at 20 wt.% Na_2O ^{(a),(b)}

Sample	[TRU] (nCi/g) in 20 wt% Na_2O Glass
U-108 with 0.1 M NaOH/ MnO_4^-	1.16
U-108 with 3 M NaOH/ MnO_4^-	6.54
U-108 with 0.1 M NaOH/ O_2	0.35
U-108 with 3 M NaOH/ O_2	0.49
U-108 with 0.1 M NaOH/Ar	0.16
U-108 with 3 M NaOH/Ar	0.04 ^(c)
U-109 with 0.1 M NaOH/ MnO_4^-	0.28
U-109 with 3 M NaOH/ MnO_4^-	11.26
U-109 with 0.1 M NaOH/ O_2	0.13
U-109 with 3 M NaOH/ O_2	0.51
U-109 with 0.1 M NaOH/Ar	0.08
U-109 with 3 M NaOH/Ar	0.05
SX-108 with 0.1 M NaOH/ MnO_4^-	3.48
SX-108 with 3 M NaOH/ MnO_4^-	2.92
SX-108 with 0.1 M NaOH/ O_2	0.03
SX-108 with 3 M NaOH/ O_2	0.28
(a) Calculation performed as previously described (Lumetta 1997).	
(a) Based on total measured alpha activity of Pu, Am and Cm.	
(c) Assumed [Na] leachate of ~30000 $\mu\text{g}/\text{mL}$.	

4.0. Summary and Recommendations

Sludge samples from the following types of Hanford tank wastes, water-washed solids from U-108 saltcake, and water-washed solids from U-109 saltcake and from SX-108 sludge have been subjected to oxidative alkaline leaching in an attempt to achieve a selective, oxidative dissolution of chromium. Leaching was performed either using the oxidants sodium permanganate or oxygen or a blank (argon). The effect of varying the oxidant, of varying the free-hydroxide concentrations between 0.1 and 3 molar, and the effect of varying temperature between ambient and 80°C have been evaluated for their impact on Cr dissolution. Key findings include

- Permanganate is highly effective at chromium removal from both U-108 and U-109 solids under alkaline conditions, with Cr removals ranging from 96 to 99+%.
 - Dissolution of chromium using permanganate was rapid, with chromate formation essentially complete within 24 hours at room temperature.
 - Dissolution of chromium using permanganate is insensitive to free-hydroxide concentration.
- Oxygen can be highly effective at chromium removal from both U-108 and U-109 solids under alkaline conditions, with up to 97+% removals being obtained.
 - Substantial dissolution at reasonable (1-week) contact times occurs only with high (3 molar) hydroxide concentrations and elevated temperature (80°C).
 - Low hydroxide and lower temperature greatly reduced the extent of chromium dissolution.
- In the absence of added oxidant, chromium dissolution is negligible (< 5%).
- Permanganate is moderately effective at chromium removal from dilute hydroxide-washed SX-108 solids, with Cr removal ranging from 29% to 71%.
 - Dissolution of chromium using permanganate was rapid, with chromate formation essentially complete within 24 hours at room temperature.
 - Dissolution of chromium using permanganate was much more effective with high free-hydroxide leachate (64%) than low free-hydroxide leachates (29%). This likely reflects the initial chromium concentrations of the specific test samples.
- Under leachate conditions of high free hydroxide, elevated temperature, and extended contact times, oxygen was as effective as permanganate at chromium removal from SX-108 solids.
- In all instances, dissolved chromium was found to be present in the +6 oxidation state, i.e., as chromate (CrO_4^{2-}), and not in the +3 oxidation state, i.e., as tetrahydroxochromium(III) $\text{Cr}(\text{OH})_4^-$.
- With SX-108 sludge, indications are that a small (< 10%) fraction of water insoluble Cr cannot be dissolved by alkaline oxidative leaching. Previous caustic leaching studies suggest that this Cr may be associated with Fe.
- Only the radionuclides ^{137}Cs , uranium, and plutonium were detected in the leach solutions. No evidence exists for americium dissolution during oxidative alkaline leaching.

- The Pu activity of the leachates tends to be greater at high hydroxide than at low hydroxide, consistent with the dissolution Pu(IV).
 - In contrast to the results from previous studies, a substantial fraction of Pu is dissolved by contact of U-108, U-109, and SX-108 with alkaline permanganate solutions. The extent of this enhanced dissolution is greater at high hydroxide than at low hydroxide.
 - Contact with oxygen at high hydroxide increases the Pu activity of the leachate solutions only slightly.
 - With U-108 and U-108 samples, in those instances where the Pu activity of the leachate is not enhanced, a significant portion of the overall alpha activity in the leachate is due to the presence of ^{233,234}U. The uranium activity in these leachates appears to be independent of the free-hydroxide concentration of the leachate as well as the presence or absence of added oxidant.
 - With SX-108, uranium dissolution contributes only a minor portion of the total alpha activity of the leachates.
- Even with enhanced Pu activity in the leachate, if the leach solutions were concentrated and vitrified to a loading of 20 wt.% sodium oxide, the glass still would be classified as a LLW. In all cases but one, the activity of the glass would be below the NRC Class A limit.

The test results using oxygen-sparged leaching of the water-insoluble solids from the U-108 and U-109 saltcakes and the SX-108 sludge solids are encouraging. The benign nature of the oxidant, the lack of any added material to the residual tank solids, and the accessible conditions (1 week at 80°C with a 3 M NaOH leachate), all point to oxidative alkaline leaching as a promising solution for chromium removal from high-chromium Hanford tank solids. Any future work should seek to 1) re-evaluate elemental oxygen as an oxidant with other Hanford tank solids containing high Cr(III) concentrations, 2) examine the effectiveness of added oxygen under baseline caustic leaching conditions, and 3) examine whether the oxygen concentrations present in air will be sufficient to achieve effective Cr dissolution under reasonable conditions of time and temperature. Perhaps the last point may provide the greatest potential impact, since, if successful, the implication is that simple air sparging during baseline caustic leaching may provide a satisfactory solution to the problem of high concentrations of residual Cr following the baseline caustic leaching of Hanford tank solids.

5.0 References

Delegard, C. H., A. M. Stubbs, and S. D. Boiling. 1993. *Laboratory Testing of Ozone Oxidation of Hanford Site Waste from Tank 241-SY-101*. WHC-EP-0701, Westinghouse Hanford Company, Richland, Washington.

Gordon, A. J., and R.A. Ford. 1992. *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*. John Wiley & Sons, Inc.

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

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

Lumetta, G. J., B. M. Rapko, M. J. Wagner, J. Liu, and Y. L. Chen. 1996. *Washing and Caustic Leaching of Hanford Tank Sludges: Results of FY 1996 Studies*. PNNL-11278, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Lumetta, G. J., I. E. Burgesson, M. J. Wagner, J. Liu, and Y. L. Chen. 1997. *Washing and Caustic Leaching of Hanford Tank Sludges: Results of FY 1997 Studies*. PNNL-11636, Pacific Northwest National Laboratory, Richland, Washington.

Orme, R. M., A. F. Manuel, L. W. Shelton, and E. J. Slaathaug. 1996. *Tank Waste Remediation System Privatization Process Technical Baseline*. WHC-SD-WM-TI-774, Westinghouse Hanford Company, Richland, Washington.

Orth, R. J., A. H. Zacher, A. J. Schmidt, M. R. Elmore, K. R. Elliot, G. G. Neuenschwander, and S. R. Gano. 1995. *Removal of Strontium and Transuranics from Hanford Tank Waste via Addition of Metal Cations and Chemical Oxidants - FY 1995 Test Results*, PNNL-10766, Pacific Northwest National Laboratory, Richland, Washington.

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

Rapko, B. M., G. J. Lumetta, and M. J. Wagner. 1995. *Washing and Caustic Leaching of Hanford Tank Sludges: Results of FY 1995 Studies*, PNL-10712, Pacific Northwest Laboratory, Richland, Washington.

Rapko, B. M., G. J. Lumetta, and M. J. Wagner. 1996. *Oxidative Dissolution of Chromium from Hanford Tank Sludges Under Alkaline Conditions*, PNNL-11233, Pacific Northwest National Laboratory, Richland, Washington.

Rapko, B. M., C. H. Delegard, and M. J. Wagner. 1997. *Oxidative Dissolution of Chromium from Hanford Tank Sludges Under Alkaline Conditions*, PNNL-11571, Pacific Northwest National Laboratory, Richland, Washington.

Shilov, V. P., L. N. Astafurova, A. Yu. Garnov, A. B. Yusov, and N. N. Krot. 1997. "Oxidation of Neptunium(IV) and Plutonium(IV) in Alkaline Solutions," *Radiochemistry*, Vol. 39, 438-442.

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

Distribution

<u>No. of Copies</u>	<u>No. of Copies</u>
OFFSITE	ONSITE
2 DOE/Office of Scientific and Technical Information Phil McGinnis Oak Ridge National Laboratory Bldg. 4500N, MS-6273 P.O. Box 2008 Oak Ridge, Tennessee 37381-6273 Don Temer Los Alamos National Laboratory P.O. Box 1663, MS-G740 Los Alamos, New Mexico 87545 Rodney Hunt Oak Ridge National Laboratory P.O. Box 2008 Oak Ridge, Tennessee 37381-6223 Ed Beahm Oak Ridge National Laboratory P.O. Box 2008 Oak Ridge, Tennessee 37381-6223 Harry Babad 2540 Cordova Ct. Richland, WA 99352 John Swanson 1318 Cottonwood Dr. Richland, WA 99352 George Vandergrift Argonne National Laboratory 9700 South Cass Avenue, Bldg. 205 Argonne, IL 60439 Steven J. Buelow Los Alamos National Laboratory CST-6, MS J567 Los Alamos, New Mexico 87545	2 <u>Numatec Hanford Company</u> R. A. Kirkbride H5-27 R. M. Orme H5-27 2 <u>DOE Richland Operations Office</u> Tank Focus Area Field Lead C/O J. A. Frey K8-50 C. S. Louie A6-54 <u>Lockheed Martin Hanford Corporation</u> J. O. Honeyman G3-21 27 <u>Pacific Northwest National Laboratory</u> TFA Technical Team Office (8) C/O G. C. Notch MSIN K9-69 Pacific Northwest National Laboratory P.O. Box 999 Richland, WA 99352 D. L. Blanchard P7-25 W. F. Bonner K9-14 C. H. Delegard P7-25 G. J. Lumetta P7-25 B. M. Rapko (10) P7-25 Technical Report Files (5)