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Pacific Northwest National Laboratory
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Selective Leaching of Chromium from Hanford Tank Sludge 241-U-108

B.M. Rapko
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Prepared for the U.S. Department of Energy
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Summary

Pretreatment approaches are planned to improve the effectiveness of vitrifying Hanford tank wastes. The presence of chromium in Hanford waste tank solids can interfere with the efficient vitrification of this waste. Therefore, an important pretreatment objective is to remove excess chromium from Hanford tank sludges. A proposed approach to increase the effectiveness of chromium removal from Hanford tank sludge is through oxidative alkaline leaching.

Chromium in tank sludge exists in both the +3 and +6 oxidation states. Chromium, when initially present in the +6 oxidation state, is effectively removed from the Hanford tank sludge solids by alkaline washing and caustic leaching. When present in the +3 oxidation state, however, chromium often dissolves poorly in simple alkaline-wash and caustic-leach solutions. Even when initially present in its +3 oxidation state, prior studies have shown that chromium exists only in caustic-leach solutions in its +6 oxidation state. Therefore, adding an oxidant to the sludge might be expected to facilitate conversion of chromium(III) to its more alkaline-soluble form (chromate [CrO_4^{2-}]) and so enhance its leaching from the sludge.

This study evaluated the oxidants permanganate, MnO_4^-, and peroxynitrite, $ONOO^-$, as selective chromium-leaching agents from washed 241-U-108 tank sludge under varying conditions of hydroxide concentration, temperature, and time. Table S.1 summarizes the extent of chromium removal under the various test conditions. Contacting the sludge at either 0.1 M [OH^-] and 30°C or 3 M [OH^-] and 85°C in the absence of any added oxidant generated relatively low amounts of chromate in solution by the end of the 24-h contact time. Contacting the sludge with peroxynitrite under conditions of low-hydroxide concentration and low temperature generated chromate more rapidly than in the absence of added oxidant and also did not appear to be complete at the end of the 24-h contact time. Under conditions of high hydroxide and high temperature, peroxynitrite generated a rapid initial formation of chromate followed by a slower increase in the solution's chromate concentration. Permanganate solutions appear to generate chromate extremely rapidly, both under high temperature/high hydroxide and low temperature/low hydroxide leach conditions, with chromate formation complete within 2 hours.

The total chromium concentrations in the leach solutions as measured by inductively couple plasma-atomic emission spectroscopy (ICP-AES) were compared with the chromate generated as measured by ultraviolet-visible (UV-vis) spectroscopy. Chromate and total chromium concentrations in the leachates were found to be identical within the reported ± 15% experimental error for the ICP-AES measurements.

It is also desirable that transuranic elements not be leached out of the sludge, so the effectiveness of the oxidants at dissolving transuranic elements was also examined. Only the leach solution with added permanganate at 3 M [OH^-] and 85°C showed a dramatic increase in plutonium dissolution. No evidence for either americium or curium in any leach solution was detected.

Finally, the mass changes and final sludge compositions were evaluated using glass-property models to ascertain the relative impacts of the various oxidative alkaline leach conditions on the amount of borosilicate glass required to immobilize a given amount of washed 241-U-108 Hanford tank sludge. Table S.2 summarizes the results. Only permanganate leaching removes sufficient chromium to make the chromium concentration in the oxidatively alkaline leached solids non-limiting. In the absence of added oxidants, continued washing or caustic leaching have no beneficial effects. Peroxynitrite addition reduces

the amount of glass required to immobilize a given amount of washed 241-U-108 tank sludge by approximately a factor of two. Depending on the leach conditions and the exact chromium concentration limits, contact with alkaline permanganate solutions reduces the amount of immobilized high-level waste glass by a factor of 10 to 30.

Table S.1. **Major* Bulk Component Removal from Oxidative Alkaline Leaching of Washed U-108 Sludge Solids**

			% Component Removal				
Initial [OH^-], M	**Temp, °C**	**Oxidant**	**Al**	**Cr**	**Fe**	**Si**	**U**
0.1	30	None	11	1	2.4	52	0
3	85	None	73	13	0	80	22
0.1	30	MnO_4^-	25	91	2.4	43	0
3	85	MnO_4^-	86	99	1.9	62	24
0.2	30	$ONOO^-$	17	60	3.3	51	34
3	85	$ONOO^-$	75	58	3.8	48	24

* A major bulk component is defined here as any metal present in a concentration greater than 10000 µg/g dried washed U-108 tank sludge.

Table S.2. Predicted U-108 Oxide Loadings in Borosilicate Glass as a Function of Pretreatment

Leach Conditions	**None**	**0.1 M $[OH^-]$, 30°C**	**3 M $[OH^-]$, 85°C**	**0.1 M $[OH^-]$, $[MnO_4^-]$, 30°C**	**3 M $[OH^-]$, $[MnO_4^-]$, 85°C**	**0.1 M $[OH^-]$, $[ONOO^-]$, 30°C**	**3 M $[OH^-]$, $[ONOO^-]$, 85°C**
% Waste Loading – 1.5 Wt % Cr	4.0	3.5	2.6	34.5	53.2	4.9	3.9
Oxide Loading Limiting Condition	Cr	Cr	Cr	T_L, V, Alk	T_L, B, V	Cr	Cr
Glass Canisters/1000 Kg Waste Oxide	8.23	8.24	8.94	0.83	0.41	4.64	4.35
% Waste Loading – 1.0 Wt % Cr	2.6	2.4	1.7	34.5	53.2	3.3	2.6
Oxide Loading Limiting Condition	Cr	Cr	Cr	T_L, V, Alk	T_L, B, V	Cr	Cr
Glass Canisters/1000 Kg Waste Oxide	12.34	12.37	13.42	0.83	0.41	6.95	6.52

Cr = chromium concentration limit. T_L = liquidus temperature of 1000°C constraint. Alk = 23 mass percent total alkali constraint.
V = lower viscosity limit of 2 Pa-s. B = 5 mass percent minimum B_2O_3 limit.

Glossary

AEA	alpha energy analysis
BNL	Brookhaven National Laboratory
CCD	charged-coupled device
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
GEA	gamma energy analysis
HLW	high-level waste
ICDD	International Centre for Diffraction Data
ICP-AES	inductively couple plasma-atomic emission spectroscopy
IHLW	immobilized high-level waste
LAW	low-activity waste
ORP	Office of River Protection
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
PP	polypropylene
SAL	Shielded Analytical Laboratory
SEM-EDS	scanning electron microscopy-energy-dispersive spectroscopy
SOWRT	Sort On Radioactive Waste Type
TRU	transuranic
UV-vis	ultraviolet-visible
WTP	Waste Treatment Plant
WVDP	West Valley Demonstration Project
XRD	X-ray diffraction

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1.0 Introduction

1.1 Selective Chromium Removal Under Alkaline Conditions

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 U, Pu, and Am. 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 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 Al, which is present in large quantities in Hanford tank sludges, by converting poorly soluble Al 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 precipitation as eskolaite (Cr_2O_3), or by promoting molten salt (mixed alkali-sulfate, -chromate, -phosphate, -molybdate, etc.) 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 (Perez 2001; Hrma 1994). For these reasons, minimizing the amount of residual chromium in Hanford tank sludges is an important pretreatment objective.

Based on the known amphoteric behavior (Rai et al. 1987), the dissolution of Cr(III) into alkaline solution as the tetrahydroxochromium(III) complex [$Cr(OH)_4$] was anticipated. However, prior caustic leaching studies indicate that the Cr behavior is more complex. While substantial concentrations of Cr(III) hydroxide can exist in high-caustic solutions at room temperature, the heating of such solutions causes guyanaite, syn-(CrOOH), to precipitate. This precipitate does not readily redissolve in aqueous caustic media (Lumetta et al. 1998). This observation is consistent with previous reports of low solubility of $Cr(OH)_3$ in acidic and near-neutral solutions at elevated temperature (Lumetta et al. 1997).

Other studies have indicated that Cr exists both in its +3 and +6 oxidation states in Hanford tank sludges. However, the dissolved Cr, regardless of its initial oxidation state in the sludge, is present in caustic leach solutions only in its +6 oxidation state (Rapko et al. 1996). This result implies that Cr initially in the +3 oxidation state requires oxidation for dissolution. It follows that adding an oxidant might enhance the dissolution of water-insoluble Cr from Hanford tank sludge by facilitating conversion from its poorly alkaline soluble +3 oxidation state to its more alkaline soluble form as chromate, CrO_4^{2-} (Lumetta et al. 2000).

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 oxidants indeed can significantly increase the effectiveness of Cr removal (Rapko et al. 1996; Rapko et al. 1997; Rapko 1998; Delegard et al. 1993; Lumetta et al. 1995; Krot et al. 1999; Sylvester et al. 2001, Rapko et al. 2002). Tested oxidants to date include ozone, O_3 (Rapko et al. 1996; Rapko et al. 1997; Delegard et al. 1993), hydrogen peroxide, H_2O_2 (Rapko et al. 1997; Lumetta et al. 1995; Krot et al. 1999), permanganate, MnO_4^- (Rapko et al. 1996; Rapko et al. 1997; Rapko 1998; Rapko et al. 2002; Lumetta et al. 1995), oxygen, O_2 (Rapko 1998; Krot et al. 1999), persulfate, $S_2O_8^{2-}$ (Krot et al. 1999), and ferrate, FeO_4^{2-} (Sylvester et al. 2001; Rapko and Vienna 2002). The results of these Cr-dissolution investigations can be summarized as follows:

- Hydrogen peroxide is ineffective when tested on actual tank solids, probably because of its catalytic decomposition by other waste components before reaction with Cr can occur.
- Ozone has been shown to be both rapid and effective in several tests. There is some evidence for significantly enhanced and concomitant dissolution of transuranic (TRU) elements.
- Oxygen is both selective and effective. However, the kinetics are slow and suggest that, at least with Hanford tank sludge and even under the optimum conditions of high temperature and strongly alkaline solution, days to weeks will be required before the reaction with Cr is complete. Little to no enhanced dissolution of radionuclides is observed.
- 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 Ni and Fe spinel phases to chromate. However, persulfate is also capable of oxidizing TRU elements to alkaline-soluble forms, which is undesirable.
- Permanganate is both rapid and effective, with Cr dissolution effectively complete within hours. Little enhanced dissolution of TRU elements is observed at low hydroxide concentrations.

- Ferrate is both rapid and effective, with Cr dissolution effectively complete within hours. The stability of ferrate solutions under typical enhanced sludge-washing conditions is much less than permanganate solutions. Little enhanced dissolution of TRU elements is observed.

It should be emphasized that each oxidative leaching agent described above has its strengths and weaknesses. Oxidation agents, such as hydrogen peroxide, oxygen, or ozone, are attractive because no solids would be added to the HLW stream. However, hydrogen peroxide is ineffective, ozone is a highly corrosive and hazardous reagent, and the kinetics of reaction with oxygen may prevent practical application. Persulfate also would not be expected to add any mass to the residual solids since both the oxidant itself and its reduced form, sulfate, are quite soluble in alkaline solution. In addition, persulfate may be capable of attacking Cr in forms inert to oxidants, such as permanganate or ferrate. However, persulfate will add several molar equivalents of sulfate to the LAW stream for each mole of chromate dissolved and, as one of the most potent of the oxidants considered, may be more likely to render the leach solution a HLW stream because of enhanced TRU dissolution. There is already great concern about sulfur being the component that defines the volume of immobilized low-activity glass mass; adding more sulfur would exacerbate the situation. Permanganate and ferrate, while rapid and generally effective at enhancing the dissolution of water-insoluble Cr, will add Mn and Fe, respectively, to the HLW sludge. Evaluating all such aspects in any proposed oxidative alkaline leach process is required to determine its suitability for HLW solids pretreatment.

This report describes contacting washed 241-U-108 Hanford tank sludge with dilute alkaline (approximately 0.1 M [OH^-]) and strongly alkaline (3 M [OH^-]) solutions, alone and in the presence of an added oxidant, either permanganate, MnO_4^-, or a previously untested candidate, peroxynitrite, $ONOO^-$. Peroxynitrite has been reported to be a strong oxidant (reported E^o from 0.83 to 0.9 V, depending on the experimental method used to make the measurement). This value is comparable to that of permanganate, with a reported E^o of 0.60 V (Lide 2000). Peroxynitrite anion will dominate in alkaline tank waste solutions since the pK_a of the conjugate acid is 6.8 (Goldstein et al. 1998 and references therein). It can be readily generated by reaction of nitrite anion with hydrogen peroxide and shows good stability in alkaline solution, especially at low temperature (Lymar and Hurst 1998). Its decomposition products, nitrate, nitrite, and NO_x, depending on the specific solution conditions, are attractive, as no insoluble solids should report to the HLW stream. For these reasons, peroxynitrite was chosen for evaluation, along with permanganate, the most extensively tested oxidant to date.

The goal of this study is to evaluate peroxynitrite and permanganate as selective, Cr-leaching agents for washed 241-U-108 Hanford tank sludge. This evaluation includes documenting both the effectiveness at Cr dissolution and the selectivity with respect to TRU dissolution of each oxidant under varying conditions of hydroxide concentration and temperature. The effectiveness of the Cr oxidation will be ultimately be measured by the decrease in the amount of borosilicate glass required to immobilize a given amount of washed 241-U-108 Hanford tank sludge; such an evaluation is also a goal for this study.

2.0 Experimental Testing Design and Procedure

2.1 Chromium Leach Reagent Preparation and General Experimental Information

All reagents used in this work were of analytical grade purity or higher. Dr. Sergei Lymar of Brookhaven National Laboratory (BNL) prepared the peroxynitrite solution as previously described, albeit with the minor substitution of hydrochloric acid for perchloric acid (Goldstein et al. 1998). The peroxynitrite solution was shipped here frozen in a solid, carbon dioxide-cooled, insulated container and stored at Pacific Northwest National Laboratory (PNNL) in a -80°C freezer until needed. Analysis at BNL indicated a peroxynitrite concentration of 0.178 M and a free hydroxide concentration of 0.291 M. From the quantities of reagents used, the peroxynitrite stock solution was calculated to have a NaCl concentration of 0.312 M, and the sum of the $NaNO_3$ and $NaNO_2$ concentrations was calculated as 0.062 M. Hydroxide concentrations measured at PNNL were determined by titration with a standard HCl solution. The stock solution's permangante concentration was measured by titration with a standard oxalic acid solution (Jeffery et al. 1989). The as-received peroxynitrite concentration in the stock solution was determined at PNNL by measuring the absorbance at 302 nm using the instrumentation described below and using the known peroxynitrite extinction coefficient of $\varepsilon_{302} = 1670\ M^{-1}cm^{-1}$. The PNNL measured concentration agreed with the BML reported concentration within experimental error.

Ultraviolet-visible (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 0.05 M KOH according to standard procedures (Gordon and Ford 1972). A plot of absorbance versus chromate concentration possessed a slope of 4937. This slope corresponds to the product of the solution pathlength and chromate's extinction coefficient. Using the known extinction coefficient for chromate of 4855 $M^{-1}\ cm^{-1}$ at 372 nm, this measurement indicates a solution pathlength of 1.017 cm.

A powder X-ray diffraction (XRD) measurement on the washed S-110 solids was 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.

Scanning electron microscopy-energy-dispersive spectroscopy (SEM-EDS) measurements were performed using the model EDS2000 system with a 500 Digital processing unit and 5480 Imaging Interface (IXRF Systems Inc. Houston, TX) connected to a1610 Scanning Electron Microscope (Amray

Microscopes Inc. Bedford, MA). Samples of washed U-108 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.

2.2 Description of the 241-U-108 Sludge Sample

Hanford tank sludge 241-U-108 (referred to henceforth as U-108) is from the tank waste group 17 (Hendrickson 1998). A description of this sludge based on the Sort On Radioactive Waste Type (SOWRT) model was provided in a previous oxidative alkaline leach study (Rapko 1998). This U-108 sludge sample was a composite of U-108 sludge-containing segments from three different core samples (Table 2.1). The composite sample was prepared at the Hanford 222-S Laboratory and shipped to PNNL in March 2001.

Table 2.1. Description of U-108 Sludge Composite

Sample ID[(a)]	Core No.	Segment No.	Amount Added, g
S96T002249	141	1	25.0
S96T002237	141	4A	25.0
S96T002602	141	6	25.0
S96T002870	145	5	25.0
S96T002907	145	9	25.0
S96T002950	146	3A	25.0
S96T003142	146	9	25.0
(a) Unique identifier associated with the 222-S Laboratory.			

2.3 Initial Washing of the U-108 Sludge Solids

In the 325 building's Shielded Analytical Laboratory (SAL) hot cell facilities, the U-108 composite sample was transferred into 200-mL high-density polyethylene centrifuge bottles and contacted four times with fresh portions of 0.01 M NaOH at an initial solution-to-solids ratio of 3:1 to 4:1. After each contact, the supernatant was decanted off and discarded. Little color was observed in the final wash solution. A slurry was prepared by adding a final portion of 0.01 M NaOH to the washed solids. Three weighed aliquots of the well-stirred suspension were removed and dried to a constant weight at 105°C. From this information, the remaining 47.9 g of slurry were determined to contain 7.57 wt% insoluble solids and a total quantity of 3.63 g of insoluble solids. The metal content of the dried solids was determined by ICP-AES. The metals most prevalent in the washed U-108 sludge are reported in Table 2.2. The radionuclide concentration of the washed U-108 solids (Table 2.3) was determined by alpha energy analysis (AEA), gamma energy analysis (GEA), and total beta analysis using procedures PNL-ALO-422, PNL-ALO-450 and PNL-ALO-4001/408, respectively.

Table 2.2. ICP-AES Determined Composition of Major Components in Dilute Hydroxide-Washed U-108 Solids

Component	Concentration, μg/g dried solids
Al	126440
Cr	200000
Fe	15560
Na	61720
Si	32200
U	26000

Table 2.3. Major Radionuclide Concentrations in Dilute Hydroxide-Washed U-108 Solids

Component	Analysis Method	Concentration, μCi/g dried solids
^{238}U	AEA	1.43E-02
^{239,240}Pu	AEA	1.19E+00
^{243,244}Cm	AEA	1.22E-01
Total α	Sum of AEA	4.59E+00
Total β	-	1.29E+02
^{137}Cs	GEA	1.75E+02
^{241}Am	GEA	3.06E+00
^{154}Eu	GEA	2.05E+00
^{155}Eu	GEA	1.03E+00

2.4 Division of the Washed U-108 Solids and the Chromium-Leach Experimental Details

In the SAL hot cells, seven aliquots, each containing nominally 7 g of slurry and approximately 0.5 g of insoluble U-108 solids, were transferred to 60-mL polypropylene (PP) bottles using a disposable polyethylene pipette. The PP reaction bottles then were transferred from the SAL hot cells to a laboratory fume hood, and 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 bulk of the test solution surrounded by the heating block. Up to four test samples were examined at one time; the fifth position contained a blank solution of hydroxide into which a thermocouple was immersed. The thermocouple allowed the solution temperature to be monitored, typically to within 1°C. Stock solutions of the oxidant, 10 M NaOH, and deionized water were added as needed to meet the targeted experimental conditions and an approximately 50-mL total slurry volume.

Table 2.4 summarizes the experimental conditions targeted for the oxidative alkaline leaching tests. It should be noted that because of the basic conditions under which the peroxynitrite solution is generated, a low (0.1 M) hydroxide target could not be met while keeping the solution to a solids target ratio of 100 and providing the desired excess of oxidant. Therefore, the low-hydroxide peroxynitrite-containing solutions were prepared by adding only the peroxynitrite stock solution to generate approximately 50 mL of total slurry volume, i.e., no further hydroxide or water was added. For the high-hydroxide peroxynitrite solution, only the peroxynitrite stock solution and sufficient 10 M NaOH stock solution were combined to generate a 3 M test solution. Adding the 10 M NaOH stock solution meant that less peroxynitrite could be introduced relative to the low hydroxide test solution, and this results in a lower oxidant:Cr ratio for the high-hydroxide peroxynitrite test compared to the low-hydroxide peroxynitrite test.

Table 2.4. Experimental Conditions for Oxidative Alkaline Leach Testing of U-108 Solids

Oxidant	$[NaOH]_{initial}$, M	Temperature, °C	$[Cr]/[Oxidant]_{initial}$
None	0.1	30	NA
None	3	85	NA
$NaMnO_4$	0.1	30	1.00
$NaMnO_4$	3	85	1.01
$ONOO^*$	0.3	30	3.85
$ONOO^*$	3	85	2.56
NA = not applicable			

Aliquots of the leach solutions were taken for analysis by UV-vis spectroscopy at approximately 2, 4, 6, and 24 h after the leach solutions were initially contacted with the sludge. These aliquots were passed through a 0.2-µm Nylon® syringe filter and diluted as required with 0.1 M NaOH before collecting the UV-vis spectra; excess undiluted leach solution was returned to the reaction vessel.

After 24 h, 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 two to three times with 0.01 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 0.01 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 Ni 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 U-108 solids. The radionuclide activities in both the acidified supernatants and dissolved residues were determined by alpha-energy analysis, gamma-energy analysis, and total-beta analysis as described above for the washed-U-108 solids.

2.5 Immobilized High-Level Waste Glass Calculations

The method chosen to determine the sensitivity of glass volume to differences in leaching procedure was to calculate an optimized glass composition for each resulting waste composition that has properties estimated to fit within the acceptable bounds for processability and product quality of a typical HLW glass. The reference set of constraints was adopted from the West Valley Demonstration Project

(WVDP), the Defense Waste Processing Facility (DWPF), and those planned for the Waste Treatment Plant (WTP). These constraints were applied to glass compositions by the use of glass-property models. Hrma et al. (2001) recently compiled an expansive database of key properties of HLW glasses. First-order expansions of product consistency test (PCT) response, viscosity temperature data, and T_L were fitted to this database. These expansions or first-order mixture models are given by:

$$\ln[r_\alpha] = \sum_{i=1}^{N} r_{\alpha,i} x_i \tag{1}$$

$$\ln[\eta] = \sum_{i=1}^{N} \left(a_i + \frac{b_i}{T} \right) x_i \tag{2}$$

$$T_{L,\beta} = \sum_{i=1}^{N} T_{\beta,i} x_i \tag{3}$$

where

x_i = ith component normalized mole fraction in glass
N = number of components for which the model was fit
r_α = normalized release of α (B, Na, and Li) from a PCT
$T_{L,\beta}$ = liquidus temperature in the β primary phase field (spinel and zircon)
T = absolute temperature
$r_{\alpha i}$, a_i, b_i, and $T_{\beta,i}$ = fitted model coefficients for the ith component.

Model coefficients from Hrma et al. (2001) were used for viscosity, T_L, in the zircon primary phase field, and PCT releases. For T_L in the spinel primary phase field, coefficients from Vienna et al. (2001) were used, and for electrical conductivity (ε), and density (ρ), coefficients from Hrma et al. (1994) were used in the glass-property calculations. The property models, as empirical or semi-empirical functions, are only valid over fixed component-concentration ranges. Model validity constraints were added to the calculations to assure that the glass composition did not significantly deviate from the ranges of model validity. Of particular interest is the concentration limit for MnO. For validity of the spinel T_L model, the MnO concentration must remain below roughly 4 mass%. The allowable concentration of MnO is significantly higher. Recent unpublished results suggest that MnO concentrations as high as 10 mass% are allowable. However, at concentrations above 4 mass%, MnO increases T_L to an extent significantly greater than that predicted by current models.

The glass property and composition constraint set used in glass optimization is summarized in Table 2.5. With waste compositions from each set of oxidative leaching experiments (plus untreated waste) and the property-composition models, glass compositions were optimized for maximum waste loading while maintaining properties and compositions within the constraints listed. Calculations were performed by an iterative solution method while allowing glass formers (or frit) components (including SiO_2, Na_2O, Li_2O, B_2O_3, and occasionally Fe_2O_3) to be added. This glass optimization technique is described in more detail elsewhere (Perez et al. 2001).

Table 2.5. Glass Property and Composition Constraints

Constraint	Value	Unit	Purpose
Melter Operating Temperature (T_M)	1150	°C	Processability
T_L (sp)	≤1000	ºC	Processability
T_L (zr)	≤1000	ºC	Processability
η	2–10	Pa·s	Processability
ε	10–100	S/m	Processability
r_B	≤2	g/m^2	WAPS
r_{Li}	≤2	g/m^2	WAPS
r_{Na}	≤2	g/m^2	WAPS
[B_2O_3]	5–15	Mass%	Model Validity
[Fe_2O_3]	≤20	Mass%	Model validity
[MnO]	≤4	Mass%	Model Validity
[Li_2O]	≤4	Mass%	Model Validity
[Na_2O]	≤20	Mass%	Model Validity
[SiO_2]	≥35	Mass%	Model Validity
[Na_2O]+[Li_2O]+[K_2O]=[Alk]	≤22	Mass%	Model Validity
[Cr_2O_3]	≤1	Mass%	Eskolaite T_L/Cr_2O_3 Solubility
[P_2O_5]	≤2.5	Mass%	Immiscibility/P_2O_5 Solubility
[F]	≤2	Mass%	Immiscibility/Opalescence
[SO_3]	≤0.8	Mass%	Immiscibility/Salt Formation
[RuO_2]+[Rh_2O_3]	≤0.10	Mass%	Noble Metal Solubility/Settling
[SiO_2]/([SiO_2]+[Na_2O]+[Al_2O_3])	≥0.62		Nepheline Formation On Cooling
[Alk]/([Alk]+[SiO_2]+[B_2O_3])	≥0.12		Immiscibility

3.0 Results and Discussion

3.1 Phase Identification in Washed U-108 Tank Sludge

Figure 3.1 shows the results of the XRD analysis of the washed U-108 tank sludge. The observed diffraction pattern is presented, along with the line pattern for the identified species. The analysis indicates that the observed pattern can be satisfactory described by two crystalline species, an Al phase, gibbsite, $Al(OH)_3$, and an aluminosilicate, hydroxycancrinite, $(Na_2O)_{1.06}(Al_2O_3)(SiO_2)_{1.60}(H_2O)_{1.60}$. Despite special attention in searching the database for possible candidates, no crystalline Cr-containing phases could be identified.

Figure 3.2 and Figure 3.3 show a typical small-particle SEM image for washed U-108 tank sludge. Figure 3.4 shows an image of a larger particle found in the washed U-108 tank sludge. The experimental apparatus allows for an elemental analysis either for the entire image or on subsections in the image. Figure 3.5 shows visually the distribution of the major non-radioactive elements Al, Cr, Fe, Na, Si, and U for Figure 3.2 and Figure 3.3. Figure 3.6 shows visually the distribution of the major non-radioactive elements Al, Ca, Cr, Na, Si, and U for Figure 3.4. The actual spectrum for the spot noted in Figure 3.2 is shown in Figure 3.7. The actual spectra for the spots labeled 1 to 3 in Figure 3.3 are shown in Figure 3.8 through Figure 3.10, respectively. Finally, the spectrum for the image in Figure 3.4 is shown in Figure 3.11. The weight percentages for the various identified elements are given in Table 3.1.

Table 3.1. EDS Elemental Analysis of U-108 Tank Sludge

	Relative Elemental Weight % Concentration (2 σ error)					
Element	**Figure 3.2 & 3.3 (Total)**	**Figure 3.2, Spot 1**	**Figure 3.3, Spot 1**	**Figure 3.3, Spot 2**	**Figure 3.3, Spot 3**	**Figure 3.4, (Total)**
Al	24.6(1.1)	29.3(1.5)	13.1(2.4)	88.4(3.7)	71.5(2.1)	21.2(0.8)
Ca	ND	ND	ND	ND	ND	3.9(0.3)
Cr	56.8(1.1)	8.2(0.4)	59.2(3.4)	11.6(0.7)	22.3(0.6)	43.3(0.7)
Fe	4.0(0.2)	ND	9.3(1.1)	ND	ND	ND
Na	4.4(0.4)	15.1(1.1)	ND	ND	2.0(0.3)	12.4(0.6)
Si	5.7(0.5)	47.5(1.7)	2.8(1.1)	ND	3.3(0.3)	16.9(0.7)
U	4.6(0.3)	ND	15.4(2.0)	ND	ND	2.3(0.2)
ND = not detected						

In general, the SEM study agrees well with the results obtained by ICP-AES for the entire washed U-108 sludge sample. For example, comparison of the weight % concentrations (relative to Cr) for the major non-radioactive tank components observed in the sludge material shown in Figure 3.2 and Figure 3.3 as determined by EDS and the relative weight % concentration for the total U-108 solids as determined by ICP-AES is shown in Table 3.2. The relative weight percentages agree fairly well, suggesting that this image may capture a fairly representative sludge sample.

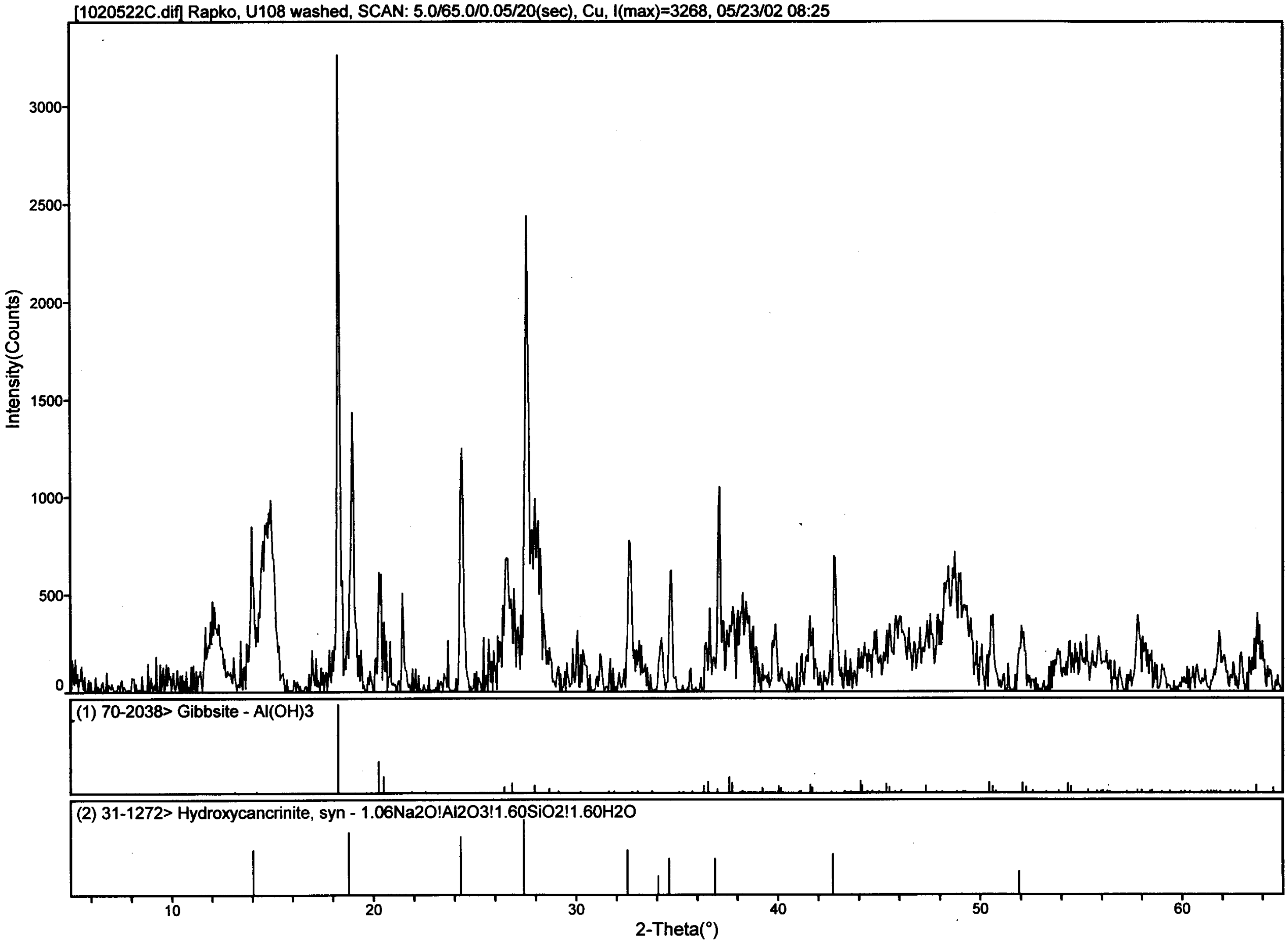

Figure 3.1. XRD of Washed U-108 Tank Sludge

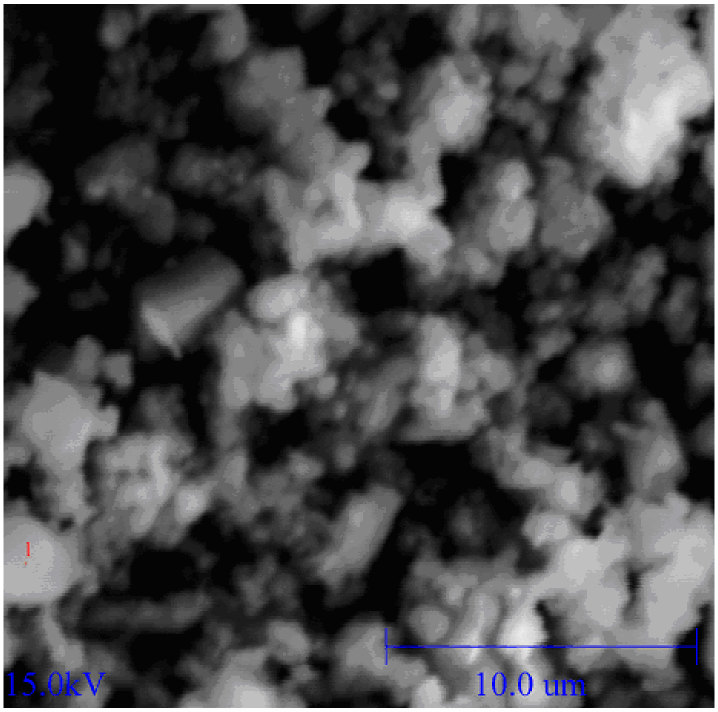

Figure 3.2. SEM Picture of Washed U-108 Tank Sludge (View 1). Subsample analysis performed at Spot 1.

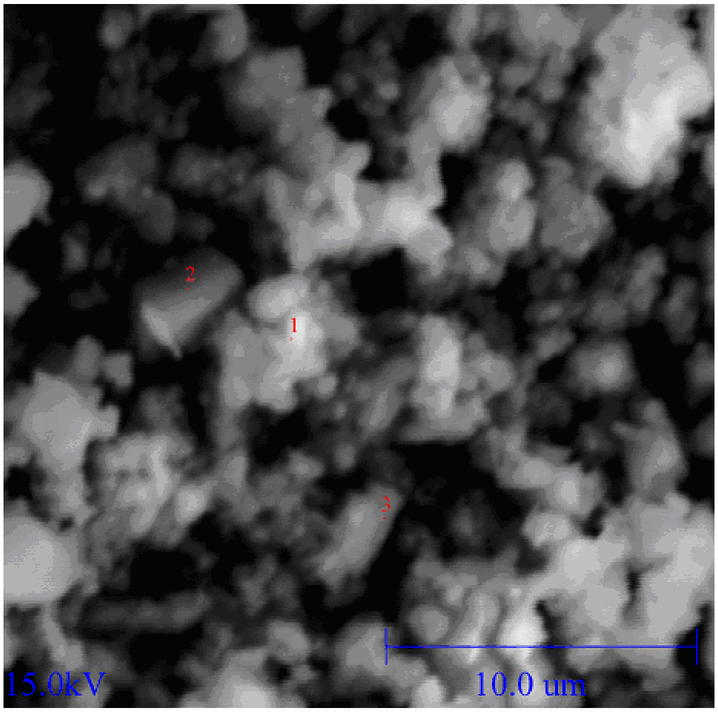

Figure 3.3. SEM Picture of Washed U-108 Tank Sludge (View 1 cont.). Subsample analysis performed at Spots 1-3.

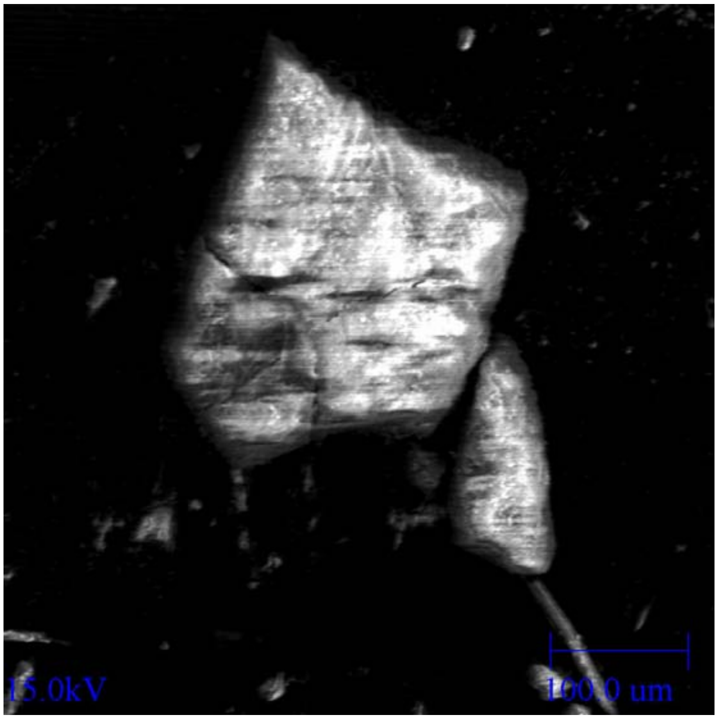

Figure 3.4. SEM Picture of Washed U-108 Tank Sludge (View 2)

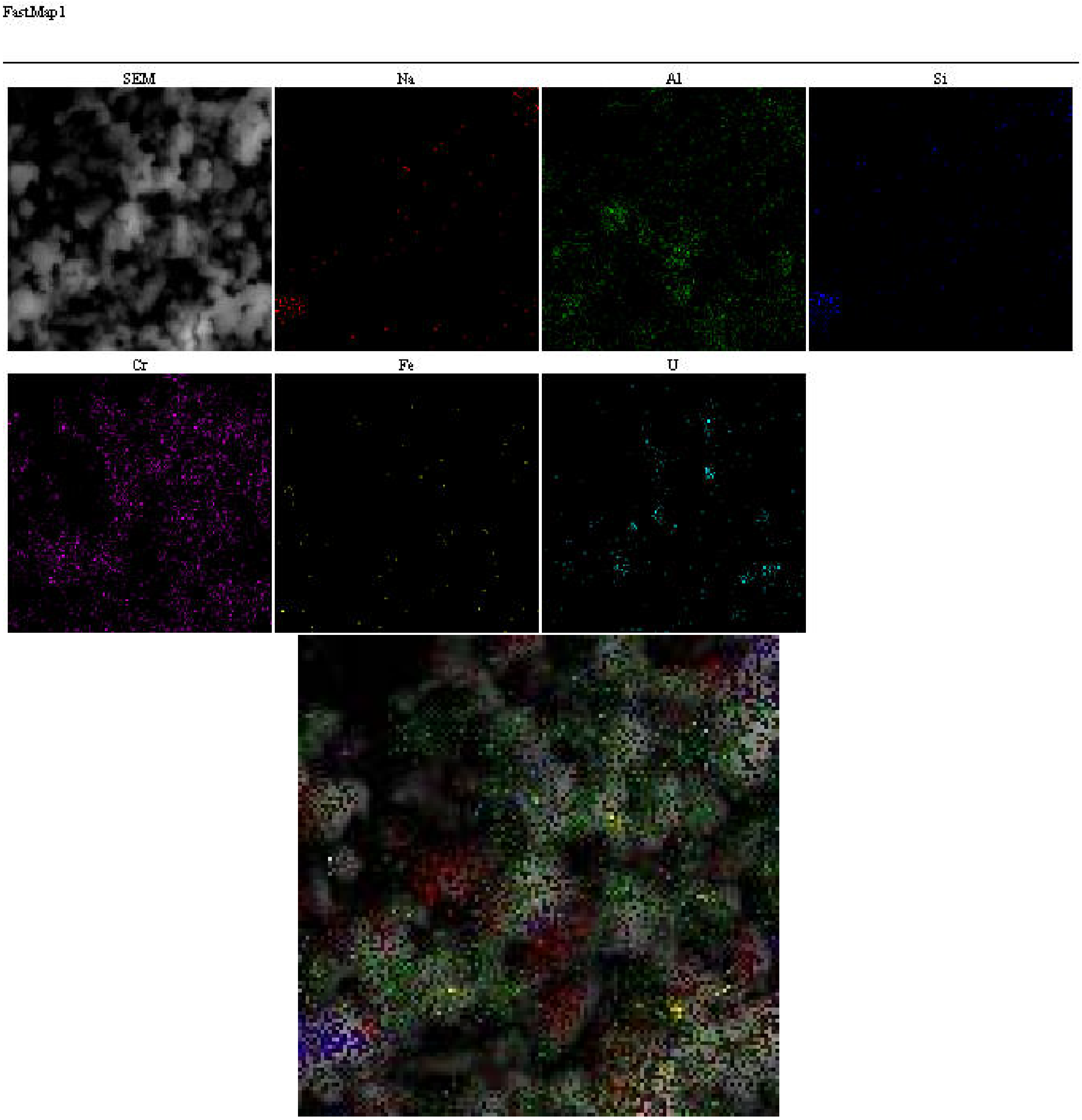

Figure 3.5. EDS Map for Major Bulk Tank Components (Figure 3.2 and Figure 3.3). Individual components are shown at the top and an overlay on the bottom. Color code: SEM image – gray; Al – red; Cr – green; Fe – pink; Na – blue; Si – orange; U – yellow.

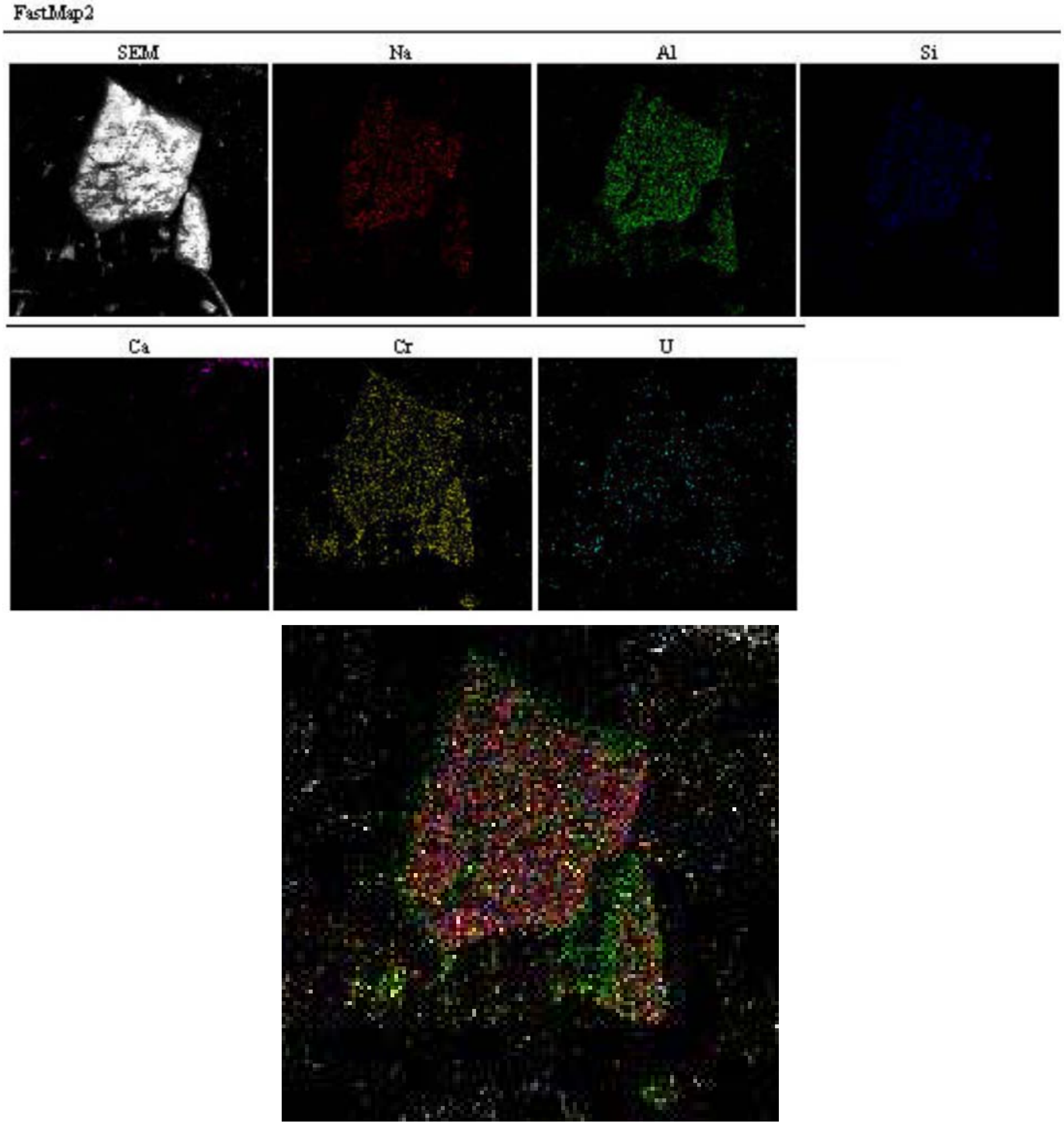

Figure 3.6. EDS Map for Major Bulk Tank Components (Figure 3.4). Individual components are shown at the top and an overlay on the bottom. Color code: SEM image – gray; Al – red; Cr – green; Fe – pink; Na – blue; Si – orange; U – yellow.

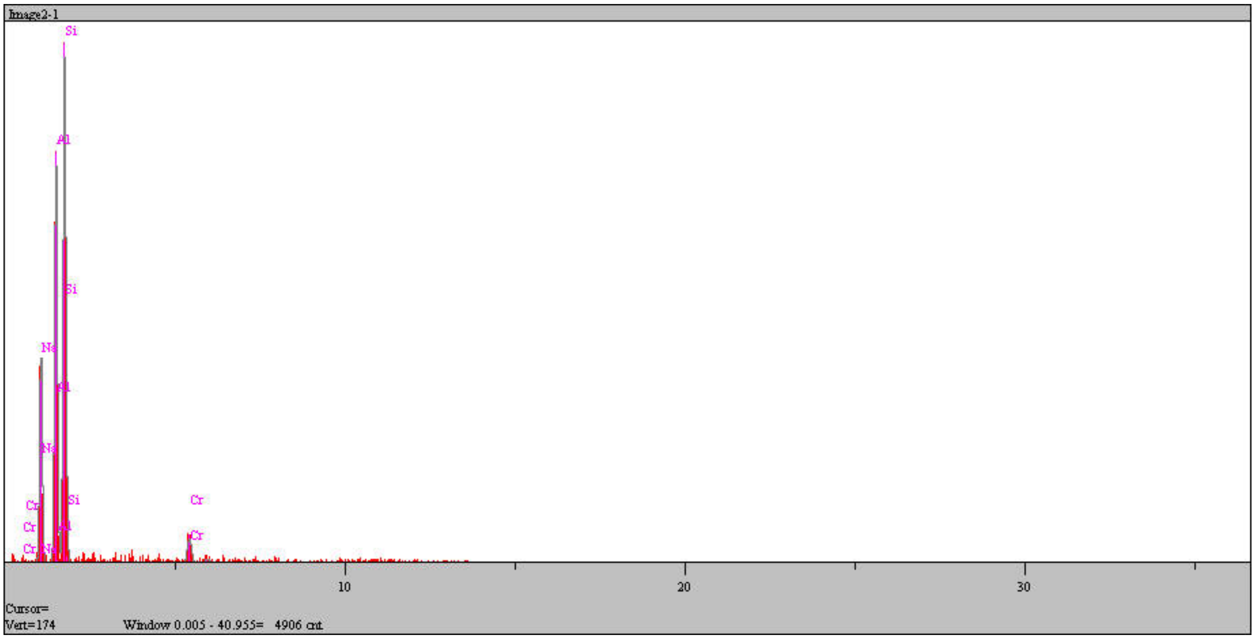

Figure 3.7. EDS Spectrum for Spot 1, Figure 3.2

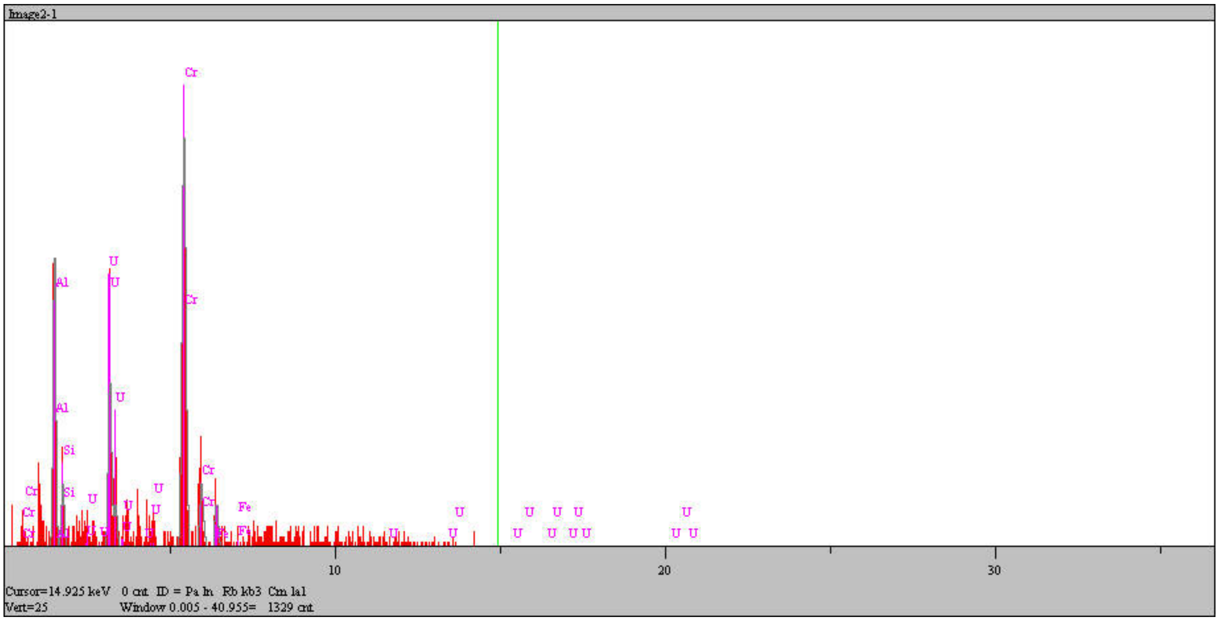

Figure 3.8. EDS Spectrum for Spot 1, Figure 3.3

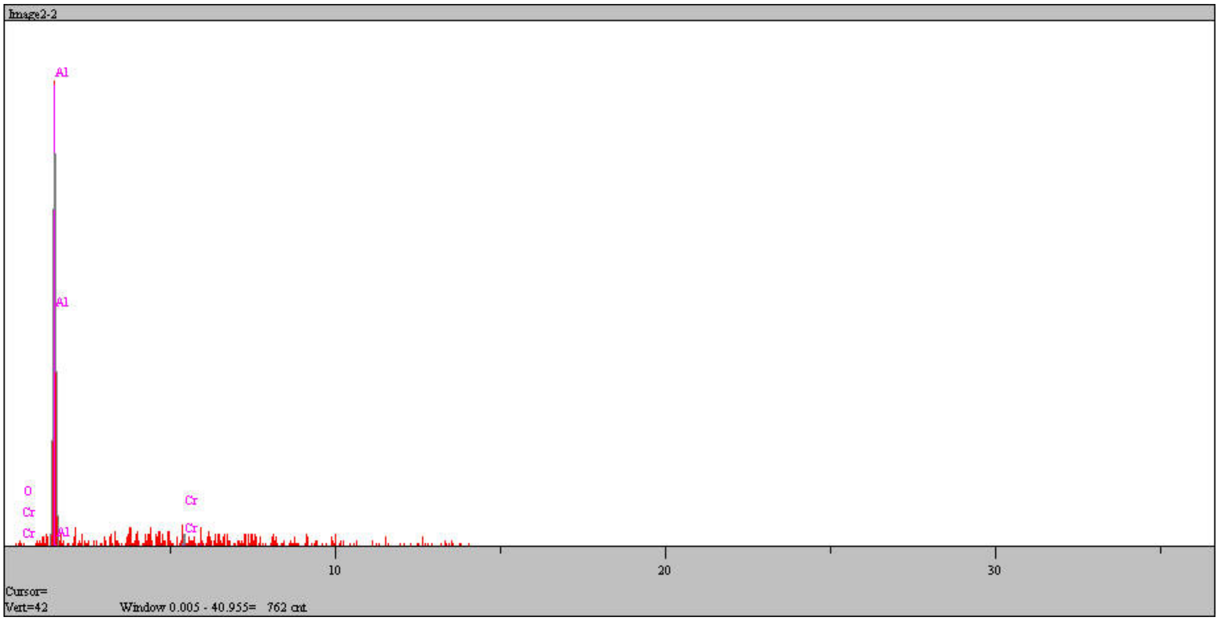

Figure 3.9. EDS Spectrum for Spot 2, Figure 3.3

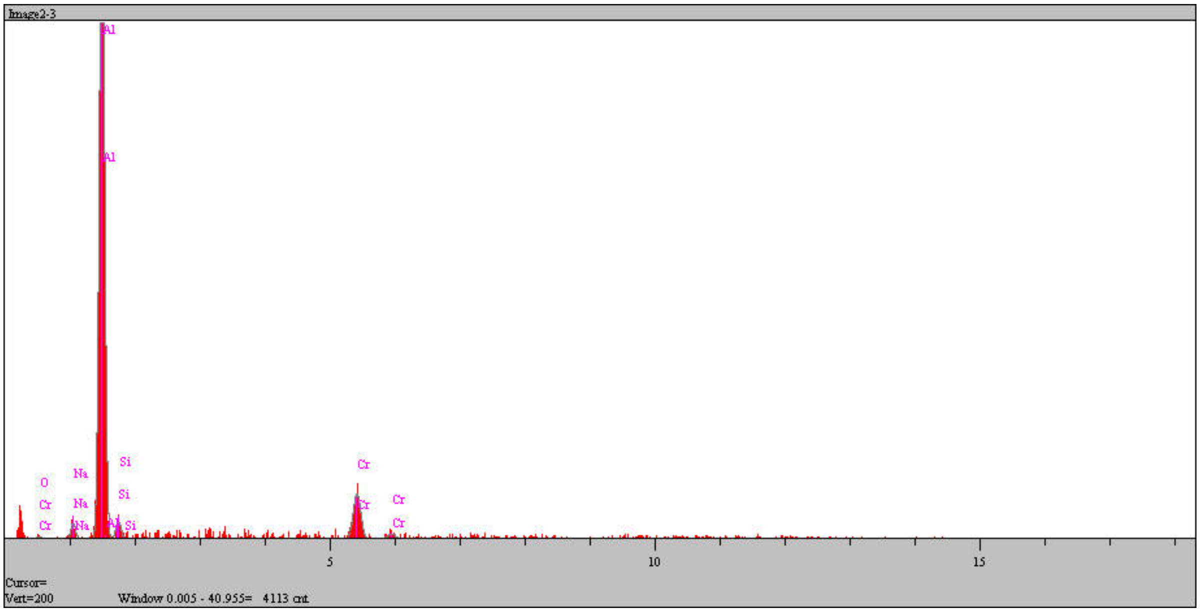

Figure 3.10. EDS Spectrum for Spot 3, Figure 3.3

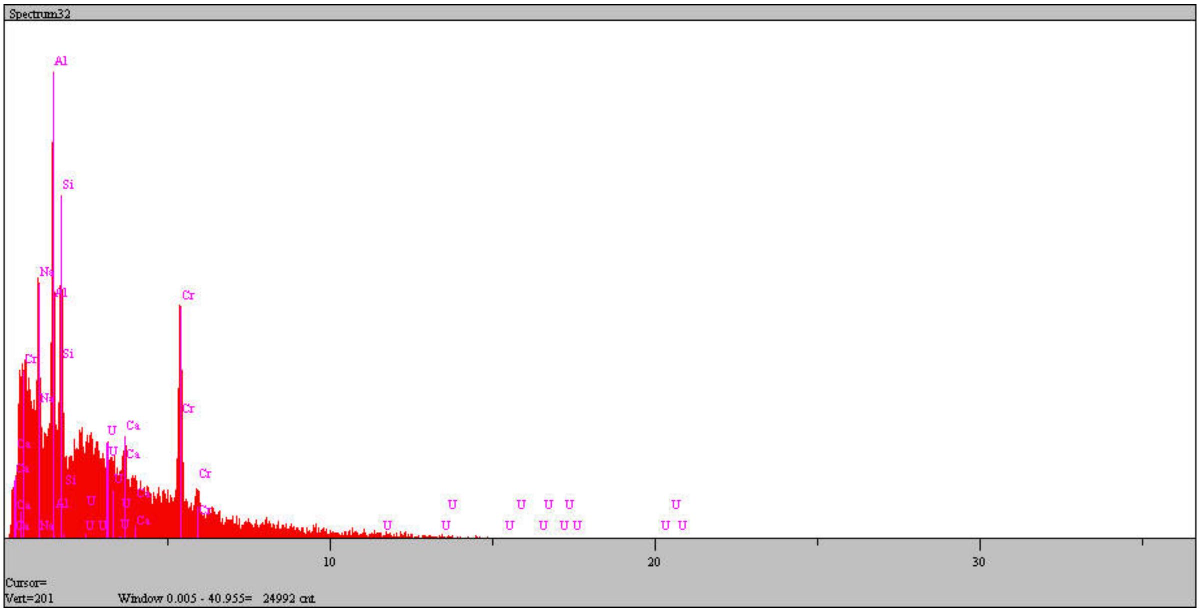

Figure 3.11. EDS Spectrum for Figure 3.4

Table 3.2. Percent Weight Compositions (relative to Cr) for U-108 Tank Sludge as Determined by EDS for the Figure 3.2 and Figure 3.3 Samples and the Composite U-108 Sludge as Determined by ICP-AES

Element	Weight Percentages Relative to Cr (EDS)	Weight Percentages Relative to Cr (ICP-AES)
Al	0.43	0.63
Cr	1.00	1.00
Fe	0.07	0.08
Na	0.08	0.31
Si	0.10	0.16
U	0.08	0.13

The elemental maps shed some insight into the phase composition of the U-108 tank sludge. Consider Figure 3.5. The Cr seems to be evenly dispersed over most of the particles. Aluminum is highly concentrated in a few particles, broadly distributed in others, and is completely absent in other areas. Uranium seems to be located in a few selected regions, although, despite considerable effort, no pure or even primarily U-containing particles could be located. Iron, consistent with its relatively low abundance in the sludge, appears here to be only a minor component broadly distributed.

Silicon and Na, on the other hand, are found in one concentrated area. Figure 3.7 shows an elemental map focusing on that area (Figure 3.2), and Table 3.1 reveals a particle composed of Na, Al, and Si, with a minor amount of Cr. Sodium, Si, and Al are components in hydroxycancrinite, which was identified in the XRD analysis of the washed U-108 sludge. However, the weight percent ratios of Na:Al:Si in hydroxycancrinite, roughly 1:1:2, differ from the observed ratios of 1:2:3 reported in Table 3.1. This suggests the presence of either an aluminosilicate of different composition or a mixture of materials, with the other phase rich in Si and Al compared to hydroxycancrinite.

The elemental compositions for the spots shown in Figure 3.3 were also examined as shown in Table 3.1 and Figure 3.8 through Figure 3.10. The amorphous material of Spot 1 is composed of smaller amounts of the other major components also present. Spot 2 appears to have a better-defined shape and consists predominantly of Al with a lesser amount of Cr. This is consistent with the XRD spectrum that reveals the presence of crystalline gibbsite. Spot 2 then may be a particle of crystalline gibbsite with either a small amount of amorphous Cr or a small fraction of Cr substituting for Al in the gibbsite crystal. Spot 3 also looks like Spot 2 in composition but with lesser amounts of other major tank constituents also present.

The map of the larger particle indicates a rather uniform distribution of the major sludge components throughout, in amounts that roughly correspond to their presence in the bulk solid. With the exception of Cr, there appear to be no regions dominated by any single bulk tank constituent.

In summary, XRD and SEM analyses of the U-108 tank solids suggest the presence of crystalline and amorphous aluminosilicates and a crystalline Al phase, gibbsite, as well as amorphous and primarily Al-containing particles. Chromium is broadly present throughout the sample in a non-crystalline form.

Particles whose only major tank constituent is Cr are occasionally found through the washed U-108 solids, but often Cr is associated with Al. No specific pure U-containing solids were identified.

3.2 Chromate Formation During Oxidative Alkaline Leaching of Washed U-108 Sludge

The original test design called for 12 batch contacts, 0.1 M NaOH at 30°C and 85°C, 3 M NaOH at 30°C and 85°C, 0.1 M NaOH/peroxynitrite at 30°C and 85°C, 3 M NaOH/peroxynitrite at 30°C and 85°C, 0.1 M NaOH/permanganate at 30°C and 85°C, and 3 M NaOH/permanganate at 30°C and 85°C. Previous testing was performed at a solution-to-solids ratio of 100 so that sample aliquots could be taken periodically during the test without appreciably disturbing the total oxidant-to-Cr ratio. It was decided that 0.5 g would be the minimum amount of water-insoluble, washed U-108 solids for each test. Although, because of the high concentration of Cr in these solids, much smaller quantities of washed U-108 sludge would still provide sufficient Cr so even if small fractions of the total Cr present were oxidized to chromate, it could be detected easily by UV-vis spectrometry. However, it was judged that testing with lesser amounts of washed U-108 solids might not leave sufficient residual material for analysis should effective removal of Cr and other major bulk constituents be achieved. Unfortunately, the amount of residual solid present after washing of the as-received U-108 sludge composite was markedly less than anticipated. Only about 2% of the initial U-108 sludge remained after dilute hydroxide washes, leaving only 3.5 g of water-insoluble U-108 available for testing. Since implementing the original test matrix required a minimum of 5 g, the number of tests was reduced. It was decided to limit testing to the extremes, i.e., high hydroxide at 85°C and low hydroxide at 30°C. This reduced the test matrix to six samples and the requirement for washed U-108 solids to 3 g for all testing, leaving one 0.5-g sample available in case a process upset occurred during a test, and a replacement was needed.

Figure 3.12 summarizes the rate of chromate formation under these various test conditions. Since the amounts of solids and solution-to-solids ratios used for each test were similar, the relative chromate concentrations (assuming all dissolved Cr is present as chromate) will roughly parallel the effectiveness of Cr removal.

Several features are immediately apparent upon examining Figure 3.12. Consistent with all previous studies, little chromate formation is observed after 24-h contacts with dilute hydroxide in air. Contact with 3 M hydroxide at 85°C increases the amount of chromate found in solution, but the chromate concentration is much less than would be expected if the majority of the Cr present in the U-108 tank solids were to dissolve as chromate.

As has been observed previously, Cr rapidly oxidizes with permanganate. Chromate formation appears to be complete after 2 h. However, no residual permanganate was observed in the UV-vis spectra after 2 h, so it is unclear whether further enhancements in chromate formation would have been possible. Although one equivalent was targeted, if the U-108 solids had slightly more Cr than expected, a sub-stoichiometric permanganate-to-Cr ratio could have been present in these tests.

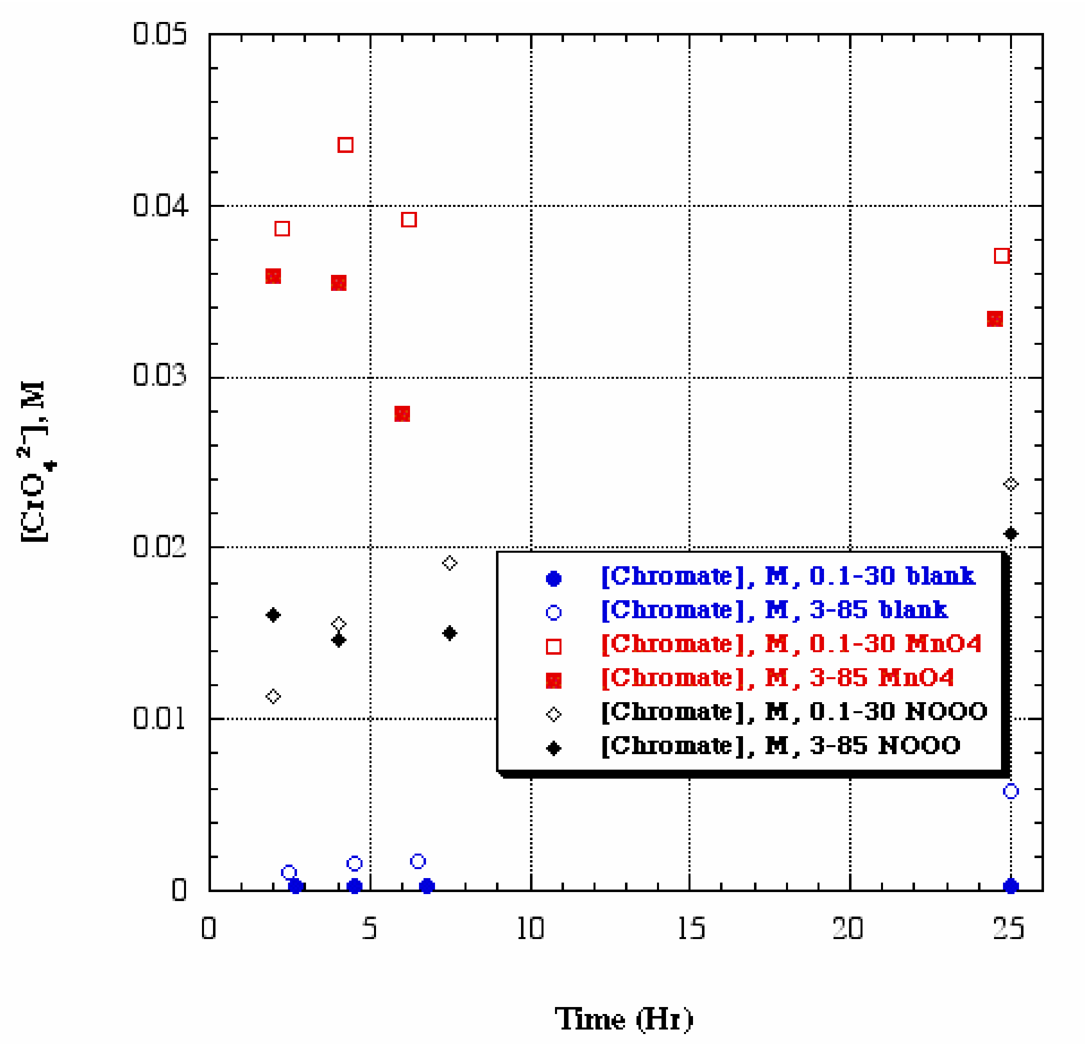

Figure 3.12. Rates of Chromate Formation in Leach Solutions Contacted with Washed U-108 Tank Sludge

Since the mechanism of Cr oxidation by peroxynitrite under these test conditions is not known with certainty, it is unclear whether a stoichiometric amount of peroxynitrite was present during these tests. If peroxynitrite acts only as a one-electron oxidant, then it is the limiting reagent in the high-hydroxide/high-temperature test. However, if it acts as has been previously suggested (Goldstein et al. 1998 and references therein) as a two-electron oxidant through homolysis of the peroxy bond and generation of a hydroxy radical and a NO_2 radical, then it is present in stoichiometric excess for Cr oxidation.

In any event, the peroxynitrite response at low hydroxide/low temperature appears to be slightly different than the response observed at high hydroxide/high temperature. The high hydroxide/high temperature contact initially enhanced Cr dissolution substantially over that observed by hydroxide alone. However, after that rapid initial enhancement, the trends in chromate formation with the high-temperature/high-hydroxide peroxynitrite leach solution parallel that of the high-temperature/high-hydroxide leach solution in the absence of added oxidant. Little change in the 302-nm absorbance, where peroxynitrite absorbs strongly, is observed from 2 h (A = 0.58) through 24 h (A = 0.71). Chromate formation, when contacted with the low-temperature/low-hydroxide peroxynitrite leach solution, on the other hand, appears to steadily increase through the 24-h contact time. In addition, the absorbance at 302 nm steadily decreases from the 2-h measurement (A = 1.82) through the 24-h measurement (A = 0.74). A more quantitative analysis of the changes in peroxynitrite concentration was not performed because of potential interferences at 302 nm by chromate and by possible peroxynitrite decomposition products such as nitrite.

One possibility for the observed rates of chromate formation with peroxynitrite consistent with these experimental observations is that the peroxynitrite rapidly oxidized Cr under high-hydroxide/high-temperature leach conditions. However, rapid decomposition of the peroxynitrite reduced the amount of peroxynitrite available for Cr oxidation to a sub-stoichiometric quantity and so prevented further Cr dissolution. Under conditions of low hydroxide/low temperature, the peroxynitrite's solution stability is enhanced, and oxidation proceeded, albeit more slowly, throughout the contact time. From the collected data, it is unclear whether further oxidation of Cr would have continued at longer times under the low-temperature/low-hydroxide test conditions.

The extent of chromate formation is of interest. Under all conditions, chromate formation upon contact of U-108 solids with peroxynitrite-containing leach solutions appears substantially less extensive than contact with permanganate leach solutions. After 24 h, the chromate concentrations in either leach solution are almost identical. This could be a coincidence, but it is intriguing to speculate that the Cr may exist in multiple forms—one amenable to oxidation only by permanganate and the other amenable to oxidation by both permangante and peroxynitrite. However, no definite conclusion can be drawn from the existing measurements.

3.3 Dissolution of Major, Bulk Sludge Components by Oxidative Alkaline Leaching of Washed U-108 Sludge

In this section, the mass changes in the U-108 solids and the distribution of the bulk constituents between the solid and leach solutions upon oxidative alkaline leaching is examined. In Table 3.3, the mass changes found for the U-108 solids following a 24-h leach contact and subsequent dilute hydroxide washes are summarized.

Table 3.3. Mass Changes in U-108 Tank Solids Following Oxidative Alkaline Leaching

Initial [OH^-], M	Temp, °C	Oxidant	Estimated Initial Solids Mass (g)	Final Solids Mass (g)	% Decrease
0.1	30	None	0.527	0.470	11
3	85	None	0.530	0.375	29
0.1	30	MnO_4^-	0.529	0.464	12
3	85	MnO_4^-	0.523	0.345	34
0.2	30	$ONOO^-$	0.531	0.372	30
3	85	$ONOO^-$	0.530	0.375	29

The trends are roughly consistent with the changes expected for the two major bulk components, Al and Cr, upon contact with these leach solutions. The changes in low-hydroxide contacts only reflect Al dissolution for the "no added oxidant" and "permanganate" tests. Little chromate was formed in the absence of added oxidant and with added permanganate, removal of 1 eq of Cr is compensated by adding 1 eq of Mn. The mass removal from the low-hydroxide peroxynitrite contact is enhanced since no there is no compensating mass added upon Cr oxidation/dissolution. Similarly, the mass decreases with the high-hydroxide/high-temperature contacts are in general greater than the low-hydroxide/low-temperature contacts due to the expected enhanced Al removals. The peroxynitrite leach solutions appear anomalous in that no enhancement is observed at high hydroxide/high temperature over low hydroxide/low temperature.

As shown in Table 3.4, large variances in the Cr and Al removal were discovered as the oxidative alkaline leach conditions were varied. As expected, contact with dilute hydroxide solutions at 30°C for 24 h results in little (11 to 25%) dissolution of Al, whereas contact at 85°C with more concentrated hydroxide solutions markedly increases (73 to 86%) Al removal. Dissolution of gibbsite by alkaline leaching at elevated temperatures tends to be rapid (Weber 1982), so it is likely that this portion of dissolved Al was obtained from either gibbsite or amorphous Al hydroxide. Previous studies on alkaline dissolution of Hanford tank sludges (Rapko et al. 1996) suggest that the leach conditions used in these tests are not sufficient to extensively dissolve Al from aluminosilicate phases.

As expected, the extent of Cr dissolution parallels the extent of chromate formation in the leach solutions. In the absence of added oxidant, Cr removal is low (1 to 13%), despite the use of high-hydroxide concentration and elevated temperatures. Adding 1 eq of permanganate generated extensive to almost complete (91 to 99%) Cr removal from the U-108 solids, suggesting that despite complete consumption of permanganate, the targeted Cr-to-permanganate ratio was close to the targeted 1:1 Mn:Cr stoichiometric ratio. Dissolution of Si varied significantly as the leach conditions were changed but with no obvious correlation to either temperature or hydroxide concentration.

The dissolution of U and Fe are puzzling. Dissolution is observed both in the presence and absence of oxidants and at both high and low hydroxide concentrations and temperatures, although in all cases, the solutions' concentrations are close to the ICP-AES detection limit. In previous studies, Fe and U dissolution by caustic leaching or oxidative alkaline leaching is rare and episodic—there is no obvious explanation for their presence in these leach solutions under these test conditions.

Table 3.4. Major* Bulk Component Removal from Oxidative Alkaline Leaching of Washed U-108 Sludge Solids

			% Component Removal				
Initial [OH$^-$], M	**Temp, °C**	**Oxidant**	**Al**	**Cr**	**Fe**	**Si**	**U**
0.1	30	None	11	1	2.4	52	0
3	85	None	73	13	0	80	22
0.1	30	MnO_4^-	25	91	2.4	43	0
3	85	MnO_4^-	86	99	1.9	62	24
0.2	30	$ONOO^-$	17	60	3.3	51	34
3	85	$ONOO^-$	75	58	3.8	48	24

* A major bulk component is defined here as any metal present in a concentration greater than 10000 μg/g dried washed U-108 tank sludge.

Table 3.5 describes the final compositions of the major sludge components. These reinforce the conclusion drawn from the percent dissolution results in Table 3.4. Contact with 3 M hydroxide at 85°C results in residual solids markedly less concentrated in Al. The use of permanganate generates residual solids that are greatly increased in Mn, consistent with the generation of insoluble Mn oxide/hydroxides. The use of permanganate also generates residual solids that are markedly depleted in Cr. The 3 M hydroxide/85°C/permanganate leach left residual solids with a much lower concentration of Cr than the 0.1 M hydroxide/30°C/permanganate leach. This decrease cannot be explained by dilution effects due to precipitated Mn since the Cr/Fe concentration ratio also changes (Fe being considered here as an internal standard since it remains almost exclusively with the solids during all of these leach tests). In the dilute hydroxide permanganate leach the Cr/Fe concentration ratio remains above 1, while the Cr/Fe concentration ratio in the high hydroxide permanganate leach is much less than 1. Clearly, high hydroxide and high temperature led to a more effective depletion of Cr from the U-108 solids, as noted in the percent-removal discussion above. However, it is unclear from this test whether this decreased removal is due to the presence of insufficient oxidant or whether an alternative reason (such as increased removal of Al in the high-hydroxide leach allowing access to additional Cr by the oxidant) is responsible. However, should the latter explanation be correct, small amounts of unreacted permanganate should have been observed in the UV-vis spectrum, contrary to the experimental result. Therefore, it is likely that further increases in Cr removal would have been possible in the low-hydroxide/low-temperature leach if additional permanganate had been present.

Table 3.5. Major or Key Elemental Concentrations in Treated U-108 Sludge

			Element Concentration, μg/g							
Temp, °C	**[OH$^-$], M**	**Oxidant**	**Al**	**Cr**	**Fe**	**Mn**	**Na**	**P**	**Si**	**U**
None	None	None	126440	200000	15560	9020	61700	2200	32200	26000
30	0.1	None	102630	182908	16100	9270	31220	1200	20900	24000
85	3	None	51300	277908	23100	13200	42600	240	13400	31000
30	0.1	MnO_4^-	92830	20108	15400	223000	78720	350	30700	24000
85	3	MnO_4^-	23630	3038	21200	325000	95620	0	26400	25000
30	0.2	$ONOO^-$	140630	143908	22200	12800	36720	750	29600	26000
85	3	$ONOO^-$	63330	180908	29300	16800	56020	330	41300	39000

3.4 Evaluating the Form of Chromium in Oxidative Alkaline Leach Solutions Contacted with U-108 Tank Sludge

In previous studies, the form of Cr in alkaline-leach solutions was evaluated by assuming two possibilities, Cr being present in the +6 oxidation state as chromate, CrO_4^{2}, and Cr being in the +3 oxidation state as tetrahydroxochromium(III), $Cr(OH)_4^-$. The chromate concentration can be determined with some sensitivity since chromate has a maximum in the visible spectrum at 372 nm with an extinction coefficient of almost 5000. Unfortunately, the direct detection of tetrahydroxochromium(III) is much more difficult by visible spectroscopy since the extinction coefficient at its maximum, ca. 600 nm, is more than two orders of magnitude lower (Lumetta et al. 1998). However, the total Cr concentration in solution can be determined with good sensitivity by ICP-AES, so the ratio of chromate to total Cr can be effectively measured. Table 3.6 shows the molar ratio of the chromate concentration in the final leachate + washes solution as determined by visible spectroscopy with the total Cr concentration as determined by ICP-AES. Clearly, within the 15% uncertainty of the ICP-AES measurement, the chromate and total Cr concentrations were identical. The lack of any systematic ratio under 1 also suggests that the ± 13% variance is due to analytical uncertainty rather than a contribution by non-chromate Cr species to the amount of dissolved Cr present in these leach tests.

Table 3.6. $[CrO_4^{2-}]/[Cr]$ Ratio in the Leachate + Final Wash Solutions

Leach Conditions	$[CrO_4^{2-}]/[Cr]_T$
0.1 M $[OH^-]$, 30°C	0.87
3 M $[OH^-]$, 85°C	0.95
0.1 M $[OH^-]$, 30°C, MnO_4^-	1.09
3 M $[OH^-]$, 85°C, MnO_4^-	1.09
0.2 M $[OH^-]$, 30°C, $ONOO^-$	1.11
3 M $[OH^-]$, 85°C, $ONOO^-$	0.87

3.5 Dissolution of Key Radionuclides From Washed U-108 Sludge by Oxidative Alkaline Leaching

The purpose of the oxidative alkaline leaching is to remove Cr from the HLW stream and divert it to the LAW stream. It follows that, to be successful, the oxidant must not only be effective at enhancing Cr dissolution; it also must be selective, especially with respect to radionuclides and in particular the TRU elements, as the limits on the concentrations of the TRU elements are the most restrictive (< 100 nCi/g). Attention to enhanced TRU dissolution is also important since oxidants could also act on these radionuclides and oxidize these radionuclides, as well as Cr, to more soluble forms, whereas the bulk of the non-TRU radionuclides are generally present in their highest accessible oxidation state. Therefore, the distribution of radionuclides was examined by GEA (focusing on ^{241}Am behavior) and AEA (to evaluate both potential enhanced Pu dissolution as well as the total TRU concentration) and total beta analysis. Table 3.7 summarizes the extent to which these components dissolved.

Table 3.7. Radionuclide Dissolution in Oxidative Alkaline Leachate Solutions

			% Removed					
Temp, °C	**$[OH^-]$, M**	**Oxidant**	**Total α**	**Total β**	**^{137}Cs**	**^{239,240}Pu**	**^{241}Am**	**^{243,244}Cm**
30	0.1	None	1.3	43	96	0.7	0	0
85	3	None	2.2	54	94	1.8	0	0
30	0.1	MnO_4^-	0.5	30	87	0.2	0	0
85	3	MnO_4^-	34	45	97	69	0	0
30	0.2	$ONOO^-$	2.5	27	88	0.7	0	0
85	3	$ONOO^-$	4.1	43	95	0.5	0	0

Examination of Table 3.7 shows several clear trends in the distribution of radionuclides in washed U-108 sludge when subjected to oxidative alkaline leaching. All solution contacts, regardless of the presence of oxidant, hydroxide concentration, or temperature, are effective at removing the bulk of the Cs. On the other hand, under these alkaline conditions, the poorly soluble and difficult-to-oxidize TRUs, such as Am and Cm, have no detectable presence in any leach solution. The amount of total beta removed from the sludge tends to increase at higher hydroxide/temperature leach solutions but does not appear to be influenced by the presence of added oxidant.

The major impact of added oxidant should be reflected in changes in Pu dissolution. Table 3.8 summarizes the ^{239,240}Pu concentrations in the final leachate and washes as well as the mass balance (total activity in the initial solids/[total activity in the final leach & washes solution + activity in the final solids]) for the % removal calculation.

The enhancements in the Pu concentration in the leachate (or leachate and washes solutions) of 1 to 3 orders of magnitude when comparing 0.1 M hydroxide versus 3 M hydroxide solutions in general and permanganate alkaline leach solutions in particular have been observed in previous studies. The poor mass balance for the 3 M hydroxide/permanganate leach data calls the apparently extensive amount of leached Pu calculated into question. However, the magnitudes of the observed Pu concentrations are not unusual, and these results suggest that the advantage of increased Cr removal with high-hydroxide/high-temperature leaching is offset by the enhancement in Pu dissolution. It is of interest that the Pu concentrations in the peroxynitrite contacts are almost identical to the hydroxide solutions themselves without added oxidant, suggesting that enhancement in Cr dissolution can be achieved with good selectivity using peroxynitrite.

Table 3.8. ^{239,240}Pu Final Leachate and Washes Solution Activity and % Removed Mass Balance

Temp, °C	[OH$^-$], M	Oxidant	[^{239,240}Pu], µCi/mL	Mass balance, %
30	0.1	None	3.75E-06	102
85	3	None	1.12E-05	86
30	0.1	MnO_4^-	1.18E-06	110
85	3	MnO_4^-	8.62E-04	41
30	0.2	$ONOO^-$	3.34E-06	92
85	3	$ONOO^-$	3.17E-05	86

3.6 Impact of Oxidative Alkaline Leaching on HLW Glass Immobilization of U-108 Sludge

The goal of oxidative alkaline leaching is to eliminate Cr as a limiting sludge component and so increase the amount of sludge that can be vitrified in a given amount of HLW glass. How successful were the addition of the chemical oxidants permanganate or peroxynitrite in achieving this task? In this section, we attempt to address this question.

Table 3.9 summarizes the maximum amount of Hanford tank sludge that current models predict can be loading into a borosilicate-glass waste canister. Two restrictions are considered: one is the current 1-weight percent Cr limit; the other, applicable to low Fe and Ni materials such as the U-108 washed and leached sludges, has a 1.5-weight percent Cr limit.

As previously mentioned, the smaller the number of glass canisters/1000 Kg waste oxide compared to the simple leached sludge, the more effective oxidative alkaline leaching is at reducing the amount of IHLW. The results summarized in Table 3.9 indicate that, surprisingly, further washing or caustic leaching adversely impacts the amount of glass required to immobilize washed U-108 sludge.

Peroxynitrite treatment, either at 30°C or 85°C, results in about half the amount of glass being required to immobilize treated U-108 sludge compared to simple dilute hydroxide washing. Permanganate treatment is much more effective; indeed, only permanganate treatments are effective at removing sufficient Cr so that it no longer limits waste immobilization. Depending on the Cr limit and the temperature/caustic concentration used, permanganate treatment reduces the amount of glass required to immobilize washed U-108 sludge by about a factor of 10 to 30.

Table 3.9. Predicted U-108 Oxide Loadings in Borosilicate Glass as a Function of Pretreatment

Leach Conditions	**None**	**0.1 M $[OH^-]$, 30°C**	**3 M $[OH^-]$, 85°C**	**0.1 M $[OH^-]$, $[MnO_4^-]$, 30°C**	**3 M $[OH^-]$, $[MnO_4^-]$, 30°C**	**0.1 M $[OH^-]$, $[ONOO^-]$, 30°C**	**3 M $[OH^-]$, $[ONOO^-]$, 30°C**
% Waste Loading – 1.5 Wt % Cr	4.0	3.5	2.6	34.5	53.2	4.9	3.9
Oxide Loading Limiting Condition	Cr	Cr	Cr	T_L, V, Alk	T_L, B, V	Cr	Cr
Glass Canisters/1000 Kg Waste Oxide	8.23	8.24	8.94	0.83	0.41	4.64	4.35
% Waste Loading – 1.0 Wt % Cr	2.6	2.4	1.7	34.5	53.2	3.3	2.6
Oxide Loading Limiting Condition	Cr	Cr	Cr	T_L, V, Alk	T_L, B, V	Cr	Cr
Glass Canisters/1000 Kg Waste Oxide	12.34	12.37	13.42	0.83	0.41	6.95	6.52

Cr = chromium concentration limit
T_L = liquidus temperature of 1000°C constraint
Alk = 23 mass percent total alkali constraint
V = lower viscosity limit of 2 Pa-s
B = 5 mass percent minimum B_2O_3 limit

4.0 Summary and Conclusions

In this report, the response of a composite sludge sample of U-108 tank sludge, washed with dilute hydroxide, to contact with alkaline solutions in the absence of added oxidant or in the presence of either permanganate or peroxynitrite was examined. The solids were leached either at low hydroxide/low temperature (0.1 M or 0.2 M [OH^-]/30°C) or high hydroxide/high temperature (3 M [OH^-]/85°C). The rate of chromate formation in the leachate solution was measured, and the distribution of major bulk components and key radionuclides between the leachate solution and residual solids was measured. The major findings of this work include:

- The composition of washed U-108 sludge composite, following KOH fusion, acid dissolution, and ICP-AES analysis, was found to be primarily Cr and Al, with lesser amounts of Na, Si, U, and Fe. The composition of the residual solids from washed U-108 saltcake was determined previously (Rapko 1998). Although solids from both U-108 tank sources are predominately Cr, the U-108 washed saltcake solids have a relatively low Al concentration and a much greater Si concentration compared to the U-108 washed sludge solids. A comparison of the concentrations of the washed U-108 saltcake solids, following their acid dissolution and analysis by ICP-AES, and the U-108 washed sludge solids, following KOH fusion, acid dissolution and analysis by ICP-AES, is provided in Table 4.1.

Table 4.1. Composition of Major Bulk Components in Washed U-108 Saltcake (Rapko 1998) and Washed U-108 Sludge (this work)

Component	Washed U-108 Saltcake Solids (μg/g)	Washed U-108 Sludge Solids (μg/g)
Al	42600	126440
Cr	126000	200000
Fe	14300	15560
Na	48400	61720
Si	191000	32200
U	12500	26000

- SEM and XRD analysis of the washed U-108 sludge solids indicates the presence of two crystalline phases, gibbsite and hydroxycancrinite. Chromium is present as an amorphous material and is widely distributed throughout the solid particles. Aluminum is found both in crystalline solids and in amorphous solids. In the amorphous solids, Al is often found together with Cr.
- 24-h leaching contacts were performed. Chromate formation by permanganate was rapid and complete within 2 h. The rate of chromate formation was as follows: permanganate (low [OH^-], low T) ≈ permanganate (high [OH^-], high T) > peroxynitrite (high [OH^-], high T) > peroxynitrite (low [OH^-], low T) > high [OH^-], high T > low [OH^-], low T.
- The extent of Cr removal from the solids parallels the rate of chromate formation. The extent of Cr removal was permanganate (high [OH^-], high T), 99%, ≈ permanganate (low [OH^-], low T), 91%, > peroxynitrite (low [OH^-], low T), 60%, ≈ peroxynitrite (high [OH^-], high T), 58%, > high [OH^-], high

T, 13%, > low [OH^-], low T, 1%. There is reason to suspect that additional permanganate could have improved Cr removal under low-hydroxide/low-temperature conditions.

- Within the stated uncertainty for the Cr metal concentrations in solution as determined by ICP-AES, the chromate concentrations in solution were equivalent to the total Cr concentrations in solution.
- Oxidative alkaline leaching led to no apparent increase in the concentration of Am and Cm over that observed in the absence of added oxidants. Added oxidants led to no increase in the extent of ^{137}Cs removal, which was effective in all instances.
- Oxidative alkaline leaching led to an increase in the concentrations of Pu over those observed in the absence of added oxidant only for permanganate under conditions of high temperature and high hydroxide. The changes in ^{239,240}Pu concentrations as a result of changing leach conditions for the last seven sludge types examined by oxidative alkaline leaching are summarized in Table 4.2. Although the numbers are scattered, the general trend seems to be that the [Pu] concentrations follow as 0.1 M [OH^-] << 3 M [OH^-] ≈ 0.1 M [OH^-]/[MnO_4^-] << 3 M [OH^-]/[MnO_4^-].
- Using current glass-formulation models, oxidative alkaline leaching was found to substantially decrease the amount of glass required to immobilize washed U-108 tank sludge. Simple washing and caustic leaching had no beneficial impact. Only permanganate treatments removed sufficient Cr to remove the Cr concentration of the leached sludges as the limiting factor in waste oxide loading of the IHLW glass. By using permanganate as the leaching agent, a reduction in the final IHLW glass volume of 20 to 30 times appears possible.

In current and previous studies, large solution-to-solids ratios have been used so that sampling can be performed without significantly perturbing the solution-to-solids ratio. In any future studies of oxidative alkaline leaching, it is suggested that larger sludge samples be used and solution-to-solids ratios more likely to represent ratios used in actual waste processing be employed. In addition, work should continue to focus on high-impact tank sludge, i.e., tanks either with large concentrations of residual Cr, e.g., Tank 241-SY-102, or high Cr inventories, e.g., Tank 241-BY-112.

Table 4.2. ^{239,240}Pu Concentration Changes in Oxidative Alkaline Leaching Tests for Seven Sludge Sources

Washed Sludge Solid's Source	Leach Condition	^{239,240}[Pu], µCi/mL	Leach Solution to Solids Ratio (mL/g)	Reference
U-108 sludge	0.1 M $[OH^-]$, 30°C	3.75E-06	ca. 100	This work
U-108 sludge	3 M $[OH^-]$, 85°C	1.12E-05	ca. 100	This work
U-108 sludge	0.1 M $[OH^-]/[MnO_4^-]$, 30°C	1.16E-06	ca. 100	This work
U-108 sludge	3 M $[OH^-]/[MnO_4^-]$, 85°C	8.62E-04	ca. 100	This work
U-108 saltcake	0.1 M $[OH^-]/O_2$,80°C	< 2.08E-06	ca. 100	Rapko 1998
U-108 saltcake	3 M $[OH^-]/O_2$, 80°C	8.59E-05	ca. 100	Rapko 1998
U-108 saltcake	0.1 M $[OH^-]/[MnO_4^-]$, 80°C	2.42E-05	ca. 100	Rapko 1998
U-108 saltcake	3 M $[OH^-]/[MnO_4^-]$, 80°C	1.21E-03	ca. 100	Rapko 1998
U-109 saltcake	0.1 M $[OH^-]/O_2$,80°C	< 2.12E-07	ca. 100	Rapko 1998
U-109 saltcake	3 M $[OH^-]/O_2$, 80°C	7.28E-05	ca. 100	Rapko 1998
U-109 saltcake	0.1 M $[OH^-]/[MnO_4^-]$, 80°C	7.06E-05	ca. 100	Rapko 1998
U-109 saltcake	3 M $[OH^-]/[MnO_4^-]$, 80°C	2.18E-03	ca. 100	Rapko 1998
SX-108 sludge	0.1 M $[OH^-]/O_2$,80°C	6.30E-07	ca. 100	Rapko 1998
SX-108 sludge	3 M $[OH^-]/O_2$, 80°C	6.85E-05	ca. 100	Rapko 1998
SX-108 sludge	0.1 M $[OH^-]/[MnO_4^-]$, 80°C	6.29E-06	ca. 100	Rapko 1998
SX-108 sludge	3 M $[OH^-]/[MnO_4^-]$, 80°C	5.76E-05	ca. 100	Rapko 1998
S-110 sludge	0.1 M $[OH^-]$,30°C	4.71E-08	ca. 100	*
S-110 sludge	3 M $[OH^-]$, 85°C	6.88E-06	ca. 100	*
S-110 sludge	0.1 M $[OH^-]/[MnO_4^-]$, 30°C	6.83E-06	ca. 100	*
S-110 sludge	3 M $[OH^-]/[MnO_4^-]$, 85°C	1.40E-04	ca. 100	*
BY-110 sludge	0.1 M $[OH^-]/O_2$,80°C	2.00E-08	ca. 125	**
BY-110 sludge	3 M $[OH^-]/O_2$, 80°C	7.56E-06	ca. 125	**
BY-110 sludge	0.1 M $[OH^-]/[MnO_4^-]$, 80°C	4.16E-07	ca. 115	**
BY-110 sludge	3 M $[OH^-]/[MnO_4^-]$, 80°C	4.46E-04	ca. 135	**
S-107 sludge	0.1 M $[OH^-]/O_2$,80°C	4.00E-08	ca. 120	**
S-107 sludge	3 M $[OH^-]/O_2$, 80°C	1.62E-05	ca. 115	**
S-107 sludge	0.1 M $[OH^-]/[MnO_4^-]$, 80°C	1.82E-05	ca. 150	**
S-107 sludge	3 M $[OH^-]/[MnO_4^-]$, 80°C	5.91E-04	ca. 170	**

* Raw data from the testing reported in Rapko and Vienna (2002)

** Raw data from the testing reported in Rapko et al. (1997)

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