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Alkaline Leaching of Key, Non-Radioactive Component from Simulants and Hanford Tank Sludge 241-S-110: Results of FY01 Studies

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Summary

Pretreatment approaches are planned to improve the effectiveness of immobilizing Hanford tank waste by vitrification. 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. When present in the +3 oxidation state, chromium often dissolves poorly in the simple alkaline-wash and caustic-leach solutions proposed for Hanford sludge pretreatment. 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 persulfate, permanganate, and ferrate as selective chromium-leaching agents from washed Hanford Tank S-110 solids under varying conditions of hydroxide concentration, temperature, and time. Contacting the sludge with either 0.1 M or 3 M NaOH at either 30°C or 85°C generated relatively low amounts of chromate in solution and these did not appear to be complete by the end of the 48-h test.   Contacting the sludge with persulfate at a low-hydroxide concentration and low temperature also generated chromate very slowly and did not appear to be complete at the end of the 48-h test. However, raising the temperature resulted in enhanced formation of chromate and reached a steady chromate concentration within 48 h in either a low-hydroxide or a high-hydroxide solution.

Permanganate and ferrate solutions appear to generate chromate extremely rapidly, both at high and low temperature and high and low concentrations of hydroxide. The rates of chromate formation can be summarized as follows: permanganate (all conditions) ≈ ferrate (all conditions) ≈ persulfate (high hydroxide/high temperature) >> persulfate (high hydroxide/low temperature) ≈ persulfate (low hydroxide/high temperature) > high hydroxide/high temperature > persulfate (low hydroxide/low temperature) ≈ low hydroxide/high temperature >> low hydroxide/low temperature ≈ high hydroxide/low temperature.

The total chromium in the leach solutions was compared with the amount of chromate generated and, in all but one case, found to be identical within experimental error. The effectiveness of these various alkaline pretreatment solutions at removing chromium from washed Hanford Tank S-110 solids is summarized in Table S.1.

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. The results indicate that in no instance will either the leach solutions themselves or the leach solutions plus residual sludge washes generate a TRU waste.

Another aspect of the project was to examine whether an oxidant bound to an anion-exchange resin can be used to effectively oxidize chromium(III) in alkaline solutions. The experimental results remain

ambiguous to date; further work is required to reach any definitive conclusions as to the effectiveness of this approach.

The selective dissolution of solids containing mercury(II) oxide under alkaline conditions was examined. Various compounds were studied for their effectiveness in dissolving mercury under varying conditions of time, temperature, and hydroxide concentration in the leachate. Three compounds were studied: cysteine, iodide, and diethyldithiophosphoric acid (DEDTPA).

In low-hydroxide tests, a stoichiometric amount (2 equivalents) of DEDTPA has little impact on the amount of dissolved mercury after contact up to 1 week at room temperature. However, with stoichiometric (cysteine) or greater (iodide) amounts of ligand, both cysteine and iodide appear to react quickly and are effective at dissolving the bulk of the mercury present. However, with cysteine, the mercury concentration drops as the contact time is increased.

In high-hydroxide tests, stoichiometric or greater concentrations of cysteine and iodide, respectively, were effective at dissolving mercury(II) under alkaline conditions. On the other hand, after a day of stirring at room temperature in air, the mercury concentration in the cysteine solution began to decrease, with only about 60% of the initial mercury(II) solution concentration remaining in solution after 5 to 6 days.

Table S.1. Summary of Chromium Removal from Washed S-110 Sludge by Alkaline Leaching.

[OH]$_{initial}$, Oxidant		Temperature, °C	% Cr Removal	Residual [Cr], µg/g
0.1	None	30	5	23400
3	None	30	10	19700
0.1	MnO_4^-	30	87	3290
3	MnO_4^-	30	93	2130
0.1	$S_2O_8^{2-}$	30	48	13100
3	$S_2O_8^{2-}$	30	89	3000
1.1	FeO_4^{2-}	30	88	3190
3	FeO_4^{2-}	30	90	2650
0.1	None	85	25	22300
3	None	85	72	16900
0.1	MnO_4^-	80	90	2740
3	MnO_4^-	80	95	2310
0.1	$S_2O_8^{2-}$	80	89	3200
3	$S_2O_8^{2-}$	80	94	2610
1.1	FeO_4^{2-}	80	95	2310
3	FeO_4^{2-}	80	94	2520

Acronyms

AA	atomic absorption (spectroscopy)
ACL	Analytical Chemistry Laboratory
AEA	alpha-energy analysis
AES	atomic emissions spectroscopy
CCD	charged-coupled device
CMPO	octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide
DEDTPA	diethyldithiophosphoric acid
DOE	U.S. Department of Energy
EB	evaporator bottom
ESP	Efficient Separations and Processing Crosscutting Program
GEA	gamma energy analysis
HLW	high-level waste
ICDD	International Centre for Diffraction Data
ICP	inductively coupled plasma
IHLW	immobilized high-level waste
IUPAC	Internation Union of Pure and Applied Chemists
LAW	low-activity waste
MIX	mixture (of several miscellaneous wastes)
ORNL	Oak Ridge National Laboratory
PCT	product consistency test
PMP	polymethylpentene
PNNL	Pacific Northwest National Laboratory
R	reduction oxidation process
REDOX	reduction oxidation
RPL	Radiochemical Processing Laboratory
RSH	thiol group
SAL	Shielded Analytical Laboratory
SORWT	Sort on Radioactive Waste Type
TRU	transuranic
UV-vis	Ultraviolet-visible
WVDP	West Valley Demonstration Project
WTP	Waste Treatment Plant
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, nitrite, hydroxide, carbonate, phosphate and sulfate. The saltcake is a solid phase consisting primarily of the above-mentioned components as precipitated salts. The sludge portion is a solid phase that consists primarily of precipitated metal oxides/hydroxides. The tank waste contains both mixed-fission products, such as ^{137}Cs, ^{90}Sr, and ^{99}Tc, and actinides, primarily uranium, plutonium, and americium. The actinides and ^{90}Sr are mostly found in the sludge layer while the ^{137}Cs and ^{99}Tc are partitioned amongst all three phases.

The tank wastes will be separated into high-level waste (HLW) and low-activity waste (LAW) fractions. The LAW will be processed to remove most of the soluble radionuclides, with the remaining material 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 placed in a geologic repository. Because of the expected high costs associated with HLW immobilization and disposal, pretreatment processes will be performed to reduce the volume of the immobilized HLW (IHLW).

Caustic leaching is the baseline method for pretreating Hanford tank sludges (Orme et al. 1996). Caustic leaching is expected to remove a large fraction of the aluminum, which is present in large quantities in Hanford tank sludges, by converting poorly soluble aluminum oxides/hydroxides to the more soluble sodium aluminate. 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.

Chromium too can interfere with the HLW immobilization process, in particular by increasing the liquidus temperature 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 of chromium(III) (Rai et al. 1987), dissolution into alkaline solution as the tetrahydroxochromium(III) complex, [$Cr(OH)_4$], was anticipated. However, our prior studies indicated that the chromium behavior in the caustic leaching process is more complex. While substantial concentrations of chromium(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 the low solubility of $Cr(OH)_3$ in acidic and near-neutral solutions at elevated temperature (Lumetta et al. 1997).

While our previous studies indicate that chromium exists both in its +3 and +6 oxidation states in Hanford tank sludges, the dissolved chromium, regardless of its initial oxidation state in the sludge, is present in caustic leach solutions only in its +6 oxidation state (Rapko et al. 1996a). This implies that chromium initially in the +3 oxidation state undergoes oxidation upon dissolution. It follows that adding an oxidant might enhance the dissolution of water-insoluble chromium 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 chromium removal (Rapko et al. 1996a; Rapko et al. 1997; Rapko 1998; Delegard et al. 1993; Lumetta et al. 1995; Krot et al. 1999; Sylvester et al. 2001). Tested oxidants to date include ozone, O_3 (Rapko et al. 1996b; Rapko et al. 1997; Delegard et al. 1993), hydrogen peroxide, H_2O_2 (Rapko et al. 1997; Lumetta et al. 1995; Krot et al. 1999), permanganate, MnO_4^- (Rapko et al. 1996b; Rapko et al. 1997; Rapko 1998; 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). The results of these chromium-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 chromium can occur.

- Ozone has been shown to be both rapid and effective in several tests. There is some evidence for significantly enhanced and concomitant transuranic (TRU) dissolution.

- 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 chromium is complete. Little to no enhanced dissolution of radionuclides is observed.

- Persulfate is effective at oxidizing chromium(III) to chromate when found in the hydroxide form, the oxide form, and the oxyhydroxide form, and can also oxidize chromium(III) in nickel and iron spinel phases to chromate. However, persulfate is also capable of oxidizing TRU elements to alkaline-soluble forms, which is undesirable.

- Permanganate is both rapid and effective, with chromium dissolution effectively complete within hours. Only a modest enhanced dissolution of TRU elements is observed at low hydroxide concentrations.

- Ferrate is both rapid and effective, with chromium 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 type of oxidative leaching agent has its strengths and weakness. As noted above, 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 both quite soluble in alkaline solution. In addition, persulfate may be able to attack chromium 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 due to 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 could exacerbate the situation. Permanganate and ferrate, while rapid and generally effective at enhancing the dissolution of water-insoluble chromium, will add manganese and iron, 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 S-110 Hanford tank sludge with three oxidants: persulfate, $S_2O_8^{2-}$, permanganate, MnO_4^-, and ferrate, FeO_4^{2-}. Goals of this study are to evaluate each oxidant as a selective chromium leaching agent, including documenting the effectiveness and selectivity with respect to TRU dissolution of each oxidant under varying conditions of hydroxide concentration and temperature. Since, as noted above, each oxidant impacts the waste chemistry differently, we also evaluate the impact of oxidative alkaline leaching on loading of the resultant waste in glass.

Finally, as a variant on this approach, we have also begun a study directed at the question of whether an oxidant bound to an anion-exchange resin can be used to effectively dissolve chromium(III) from alkaline solutions. This report summarizes experiments performed by Lynntech, Inc., under subcontract to Pacific Northwest National Laboratory (PNNL), designed to address this point.

1.2   Mercury Dissolution Under Alkaline Conditions

In response to a call for the selective removal of mercury from solids under alkaline conditions, we initiated an investigation directed at the selective dissolution of mercury(II)-containing solids under alkaline conditions. This report describes a scoping study designed to evaluate compounds for effective mercury(II) dissolution under alkaline conditions. Variables studied include the dissolution agent, time, temperature, and hydroxide concentration.

The aqueous behavior of mercury(II) under alkaline conditions is straightforward. In the absence of complexants, mercury converts to its poorly soluble oxide, HgO (Greenwood and Earnshaw 1984). Indeed, the hydroxide form, $Hg(OH)_2$, is unknown. Mercury does bond strongly to sulfur-containing complexes; however, there appears to be little information on their stability under the highly alkaline conditions proposed for caustic leaching.

Recent work from this laboratory has shown that the presence of relatively low (10 mM or less) concentrations of low-molecular-weight compounds containing a thiol group, such as the amino acid cysteine, are extremely effective under acidic conditions at preventing the extraction of mercury by octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxides (CMPOs) or crown ether extractants over a broad range of acidic conditions (Rapko et al. 2000). However, it is well known that the thiol group, RSH, is readily oxidized in neutral to alkaline solutions to form disulfides (Smith and March 2001), RS-SR, so the stability of such complexes under alkaline processing conditions is problematic. However, complexes such as thiocarboxylates, R(S)(OH), and dithiocarboxylates, R(S)(SH), are also powerful and selective mercury(II) complexants and may be more stable than simple thiols under alkaline conditions.

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. Lynntech, Inc. prepared the ferrate stock solution as described previously (Sylvester et al. 2001). Hydroxide concentrations of the reagents were determined by titration with a standard HCl solution. Permangante and persulfate concentrations in the stock solutions were measured by titration with an oxalic acid solution (Jeffery et al. 1989). The as-received ferrate concentration in the initial stock solution was determined at PNNL by measuring the absorbance at 505 nm and using the known ferrate extinction coefficient of $\varepsilon_{505} = 1080$ M^{-1}cm^{-1}.

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 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 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) for the identification of crystalline phases. This measurement was performed according to the technical procedure PNL-ALO-268, Solids Analysis, X-ray Diffraction.

2.2 Description of the S-110 Sludge Sample

S-110 sludge belongs to Sort on Radioactive Waste Type (SORWT) Group I (Hill et al. 1995), which is the same classification as the previously studied S-107 tank sludge (Sylvester et al. 2001). The S-110 sludge derives primarily from waste streams associated with the reduction oxidation (REDOX) process (R), which is one of the major contributors to the Hanford single-shell tank waste, with one estimate (Colton 1997), suggesting that approximately 27% of the Hanford single-shell tank sludge is derived from this waste stream. A secondary stream for the S-110 sludge in the SORWT model comes from evaporator bottoms (EBs), and a tertiary stream has been assigned that is composed of a mixture (MIX) of several miscellaneous wastes.

An alternative description using cluster analysis (Hendrickson et al. 1998) assigned the sludge to Group 18. Contributing sources to the tanks of Group 18 involve the following waste types (Agnew 1997): A1SltCk, A2SltCk, BSltCk, S1SltCk, RSltCk, R, and S2SltCk, where

A1SsltCk = saltcake from the 242-A campaign,1976-1980
A2SltCk = saltcake from the 242-A campaign, 1981-1988
BSltCk = saltcake from 242-B operation, 1951-1953
S1SltCk = saltcake from the 242-S campaign, 1973-1976
RSltCk = saltcake from self condensation
R = REDOX waste
S2SltCk = saltcake from the 242-S campaign, 1977-1980.

The S-110 sludge sample used here was a composite of segments from two different core samples (Table 2.1). The composite sample was prepared at the Hanford 222-S Laboratory and shipped to the PNNL in March 2001.

Table 2.1. Description of S-110 Sludge Composite

Sample ID[a]	Core No.	Core Date	Tank Riser	Segment No.	Amount Added, g
S98T001898	240	May 1998	14	9	30.0
S98T001904	240	May 1998	14	10	30.7
S98T001978	241	June 1998	6	2	30.2
S98T001984	241	June 1998	6	3	30.0
S98T001994	241	June 1998	6	4	30.1
S98T002014	241	June 1998	6	7	30.0
S98T002026	241	June 1998	6	8	30.1
				Net Mass, g:	211.1
(a) Unique identifier used at the Hanford 222-S Laboratory.					

2.3 Initial Washing of the S-110 Solids

In the Radiochemical Processing Laboratory's (RPL) shielded analytical laboratory (SAL) hot cell facilities, the S-110 composite sample was transferred to a 500-mL high-density polyethylene bottle and contacted three times with fresh portions of 0.01 M NaOH, with the supernatant being removed after each contact. A slurry was prepared by adding a final portion of 0.01 M NaOH to the washed solids. Two weighed aliquots of the well-stirred suspension were removed and dried to a constant weight at 105°C. From this information, the slurry was determined to contain 7.72 wt% insoluble solids. The metal content of these dried solids was determined by inductively coupled plasma/atomic emissions spectroscopy (ICP/AES). The metals most prevalent in the washed S-110 sludge are reported in Table 2.2. Further experimental details on the preparation of the sludge composite, the washing of the S-110 tank sludge, and on the analysis of the washed S-110 sludge have been reported recently (Lumetta et al. 2001).

**Table 2.2. ICP-AES Determined Composition of Major
Components in Dilute Hydroxide-Washed S-110 Solids**

Component	Concentration, µg/g dried solids
Al	325000
Cr	23050
Fe	14150
Mn	5305
Na	30000
Si	5500
U	23500

2.4 Division of the Washed S-110 Solids and Chromium-Leach Experimental Details

In the SAL hot cells, 16 aliquots, each containing nominally 15 g of slurry and approximately 1 g of insoluble S-110 solids, were transferred to 125-mL polymethylpentene (PMP) bottles using a large (23-mL capacity) disposable polyethylene pipette. The PMP reaction bottles then were transferred from the SAL hot cells to a laboratory fume hood, and the reaction bottles were placed in an aluminum heating block in which five holes, sized to securely hold the sample bottles, were cut. This aluminum 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 100-mL total slurry volume.

Table 2.3 summarizes the experimental conditions targeted for the oxidative alkaline leaching tests. It should be noted that because of the strongly basic conditions under which the ferrate 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. Therefore, the low-hydroxide ferrate-containing solutions were prepared by adding just enough of the ferrate stock solution to introduce the desired equivalents of ferrate, followed with deionized water, to generate 100 mL of total slurry volume, i.e., no further hydroxide was added. Even so, the "low hydroxide," ferrate-containing solutions were about an order of magnitude (ca. 1.1 M) higher in hydroxide than the 0.1 M NaOH permanganate and persulfate solutions, whose stock solutions were prepared in deionized water.

Table 2.3. Experimental Conditions for Chromium Oxidative Alkaline Leach Testing

Oxidant	$[NaOH]_{initial}$, M	Temperature, °C	$[Cr]/[Oxidant]_{initial}$
None	0.1	30	NA
None	3	30	NA
None	0.1	85	NA
None	3	85	NA
$NaMnO_4$	0.1	30	1.5
$NaMnO_4$	3	30	1.5
$NaMnO_4$	0.1	80	1.5
$NaMnO_4$	3	80	1.5
$K_2S_2O_8$	0.1	30	3
$K_2S_2O_8$	3	30	3
$K_2S_2O_8$	0.1	80	3
$K_2S_2O_8$	3	80	3
$NaFeO_4$*	1.1	30	1.5
$NaFeO_4$	3	30	1.5
$NaFeO_4$*	1.1	80	1.5
$NaFeO_4$	3	80	1.5
NA = not applicable			

Initial aliquots generally were taken for analysis by UV-vis spectroscopy soon after the leach solution was introduced (typically about 0.5 h after mixing), and then intermittently for the remainder of the experiment. These aliquots were passed through a 0.2-μm Nylon® syringe filter and diluted as required with 0.1 M NaOH before analysis; excess undiluted leach solution was returned to the reaction vessel.

At the end of the 48-h leaching test, the test slurries were centrifuged (3000 rpm for a minimum of 5 min), and the supernatants were decanted from the residual solids. 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 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 of material before ICP-AES and radiochemical analysis.

Meanwhile, the 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. The radionuclide activities in both the acidified supernatants and dissolved residues were determined by alpha-energy analysis, gamma-energy analysis and total-beta analysis. Established procedures were used for all these analyses.[a]

2.4.1 IX Resin Testing - Experimental Details

Each anion-exchange resin was treated initially with excess NaOH to convert the resins to the hydroxide form. Ten milliliters of a 1 mM sodium or potassium solution containing the anion of interest was contacted with 1 g of resin. In an initial study, the contents of the vial as shaken and with the aliquots removed periodically passed through a 0.2-μm Nylon® syringe filter. The contents were then analyzed for metals content by atomic absorption (AA) spectroscopy and by UV-vis spectroscopy for chromate or permanganate as needed. These time-dependent experiments indicate that in all instances, a 1-h contact time was sufficient for the system to reach equilibrium.

Distribution measurements were calculated using the following equation:

$$K_d = [(C_i - C_0)/C_0] * (V/M) \tag{1}$$

where: C_0 = initial anion concentration
C_i = equilibrium anion concentration
V = solution volume in milliliters
M = resin mass in grams.

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

2.4.2 Mercury(II) Alkaline-Leach Testing – Experimental Details

2.4.2.1 Reagent Preparation

All chemicals were of reagent grade or higher unless indicated otherwise. A solution of $^{203}HgCl_2$ in 1 M HCl was obtained from Isotope Product Laboratories, Burbank, California. A suspension of ^{203}Hg-spiked mercuric oxide was prepared by dissolving 10.8 g (40 mmol) of $HgCl_2$ in 200 mL of water and adding 1 mL of the $^{203}HgCl_2$ stock solution. This amount of added ^{203}Hg was calculated to be sufficient to produce a specific activity of ca. 500,000 dpm/g of mercury. A 3 M NaOH solution then was slowly added to the well-stirred mercury solution until the pH reached 12.3. After digesting the precipitate for 2 h, the bulk of the supernatant was separated from the solids by centrifugation and supernatant decantation. The residual solid was suspended in 10 mL of pH 12 water and distributed as uniformly as possible into eight portions of the slurry, providing each portion with the total of 1 g (ca. 5 mmol) of mercury. Analysis of the supernatant indicated that essentially no ^{203}Hg activity remained in solution. The precipitate was stored as a wet slurry in closed vials for 3 days before the start of the low hydroxide leach tests and 8 days before starting the 3.0 M NaOH leach tests.

L-Cysteine hydrochloride hydrate (Aldrich Catalog number C12,180-0; 99% purity) and the ammonium salt of diethyl dithiophosphate (DEDTPA) (Aldrich 17,779-2, 95% purity) were used without further purification. Solutions of L-cysteine in NaOH were prepared immediately before contact with HgO to minimize any possible degradation of this ligand in this alkaline medium.

Calculated amounts of KI ("Baker Analyzed" Reagent) and I_2 were dissolved into 50-mL portions of 0.1 M and 3.0 M solutions of NaOH to generate solutions of 1 M in KI and 0.1 M in I_2.

Sodium hydroxide (0.1 M and 10 M) solutions were prepared and standardized by titration with standard HCl. A 3 M NaOH solution was generated by volumetric dilution from the 10 M NaOH stock solution.

2.4.2.2 Alkaline-Leach Experimental Conditions

During the initial part of the low hydroxide leach tests, 50 mM solutions of the complexing agents cysteine and DEDTPA and a solution of 1 M in KI were used at a solution-to-solids ratio (mL/g) of 50. This generates a ligand-to-Hg ratio of 0.5 for cysteine and DEDTPA and of 10 for KI. To generate at least a stochiometric (2:1) ratio of organic leaching agent, additional organic ligand sufficient to increase the solution concentration up to 200 mM was added between the second and the third kinetic points to the cysteine and DEDTPA test suspensions. Ligand ratios of 2:1 (cysteine and DEDTPA) and 10:1 (KI) were used for all of the high-hydroxide tests. Table 2.4 summarizes the experimental test conditions.

Samples were taken periodically for ^{203}Hg analysis at 1 h, 7 h, 1 day, 2 days, 3 days, and 4 days after contact of the suspension with the leaching solution at room temperature.

The ^{203}Hg activity was evaluated using the 279 KeV photo-peak of ^{203}Hg with a Ge detector. Each ^{203}Hg activity measurement was obtained by removing a ~1.5-mL solution aliquot from the test suspension followed by filtration through a 0.2-μm Nylon® syringe filter. After transferring a 1.00-mL portion of the filtered solution into an 8-mL (2-dram) vial for measurement, the remaining portion was returned to the reaction solution, and the stirring was resumed. By using a high-reaction volume-to-sample volume, sampling could occur while maintaining the liquid-to-solid ratio fairly constant throughout the entire test.

Table 2.4. Summary of Mercury(II) Alkaline Leaching Test Conditions

Test #	Bottle #	[OH], M	Complexant
1	I	0.1	None
2	V	3	None
3	II	0.1	200 mM L-cysteine[a]
4	VI	3	200 mM L-cysteine
5	III	0.1	200 mM DEDTPA[a]
6	VII	3	200 mM DEDTPA
7	IV	0.1	1M KI/0.1M I_2[b]
8	VIII	3	1M KI/0.1M I_2[c]

(a) see text for further discussion
(b) Solution remains dark brown throughout the experiment.
(c) Solution slowly changes from brown to yellow to colorless.

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 liquidu s temperature 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 = i^{th} component normalized mole fraction in glass
  N = number of components for which the model was fit
  r_α = normalized release of α (boron, sodium, and lithium) 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 ensure 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). The resulting glass compositions, estimated properties and waste loadings are tablulated in the Appendices.

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 Crystalline Phase Identification in Washed S-110 Tank Sludge

Figure 3.1 shows the results of the XRD analysis of the washed S-110 tank sludge. Both the actual measured diffraction pattern as well as the known 2-theta positions and intensities for the identified compounds are shown. As can be seen from Figure 3.1, only two crystalline phases are observed, boehmite, $Al(O)(OH)$, and gibbsite, $Al(OH)_3$. Using the peak areas and peak-intensity information from the 14.497° 2θ line and the 18.276° 2θ line line for boehmite and gibbsite, respectively, a ratio of 80 to 90% boehmite and 10 to 20% gibbsite can be estimated.

3.2 Chromate Formation During Oxidative Alkaline Leaching of Washed S-110 Sludge

The rates of chromate formation in the S-110 leach solutions as a function of time and reaction conditions are illustrated in Figure 3.2 for the low-temperature (ca. 30°C) tests and in Figure 3.3 for the high-temperature (ca. 80 to 85°C) tests. Both at high and low temperatures, the response of the leach solutions is similar. Contact with 0.1 M NaOH in the absence of added oxidant results in little chromate formation while contact with 3 M NaOH is more effective at generating chromate, presumably with atmospheric oxygen acting as the oxidant. Indeed, at elevated temperature, 3 M NaOH generates a substantial fraction of the maximum chromate concentrations observed during oxidant treatment.

Generation of chromate by contact with persulfate at low-hydroxide concentration and low temperature is slow and does not appear to have reached completion within the 48-h contact times employed. However, at elevated temperature in low hydroxide or in high hydroxide, the persulfate leach solutions do appear to reach a steady chromate concentration within 48 h.

Permanganate and ferrate solutions appear to act extremely rapidly, both at high and low temperature and high and low concentrations of hydroxide. Indeed, the first measured values, taken usually within 0.5 h of mixing, remain relatively unchanged during the two additional days of contact time. In conclusion, the rates of chromate formation appear as follows: permanganate (all conditions) ≈ ferrate (all conditions) ≈ persulfate (high hydroxide/high temperature >> persulfate (high hydroxide/low temperature) ≈ persulfate (low hydroxide/high temperature) > high hydroxide/high temperature > persulfate (low hydroxide/low temperature) ≈ low hydroxide/high temperature >> low hydroxide/low temperature ≈ high hydroxide/low temperature.
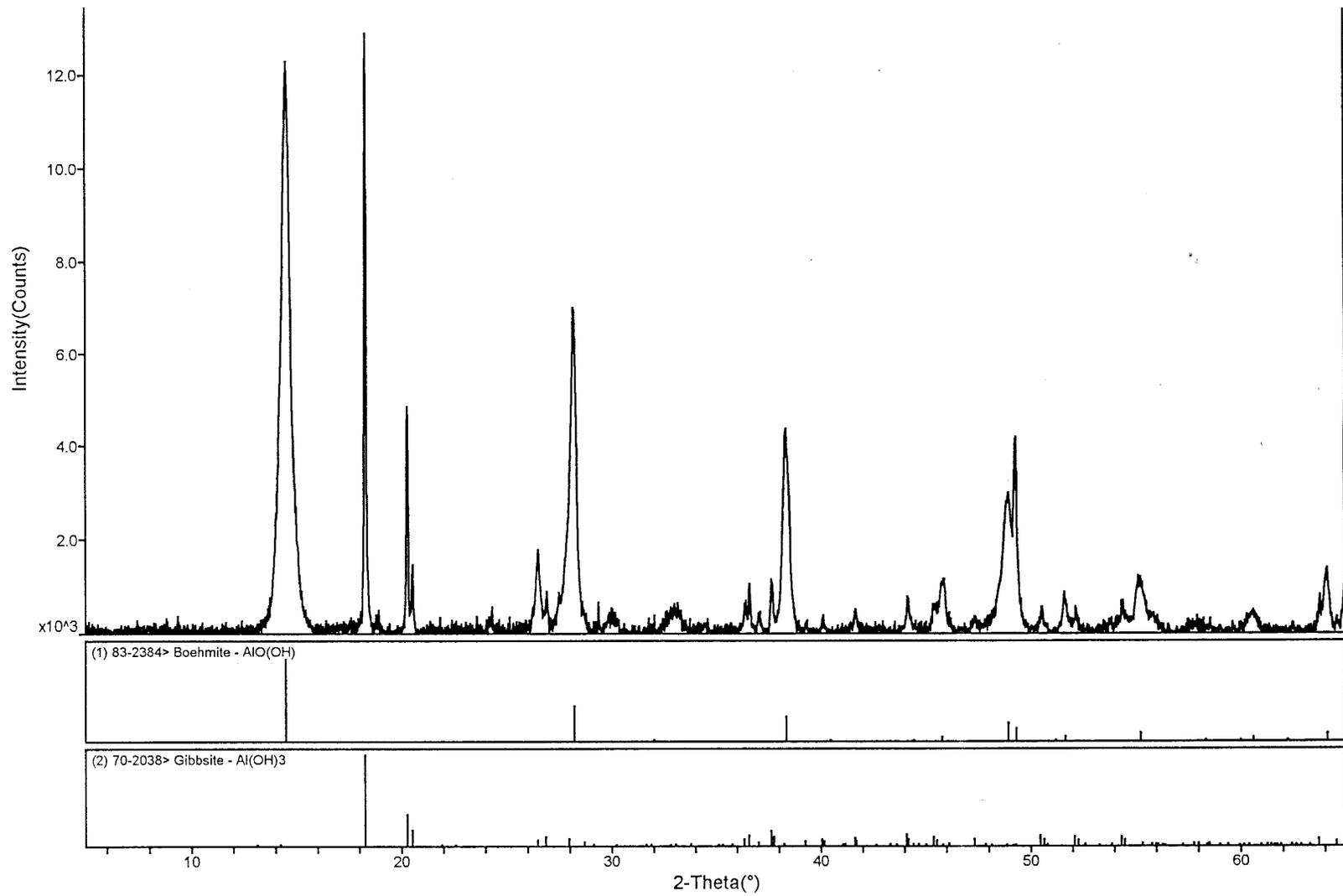
Figure 3.1. XRD of Washed S-110 Tank Sludge
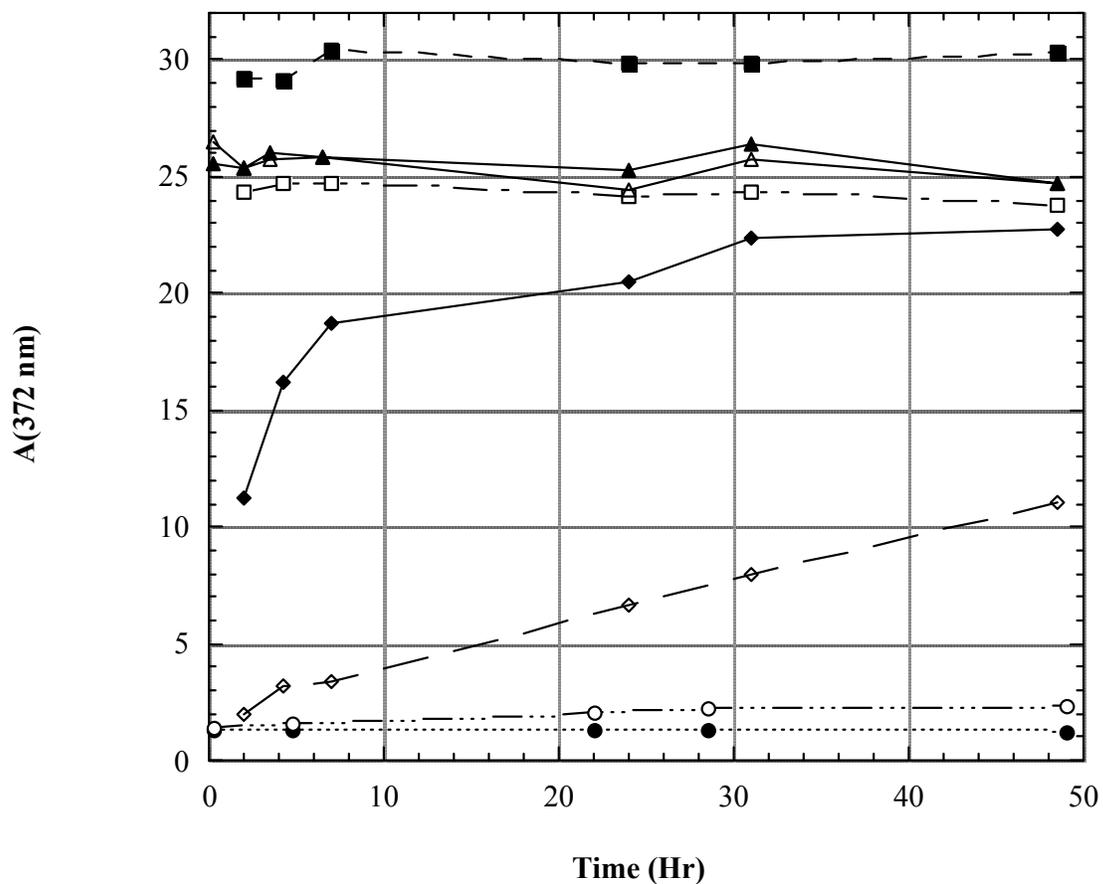
Figure 3.2. Chromate Formation Under Alkaline Conditions at Low Temperature (30°C)
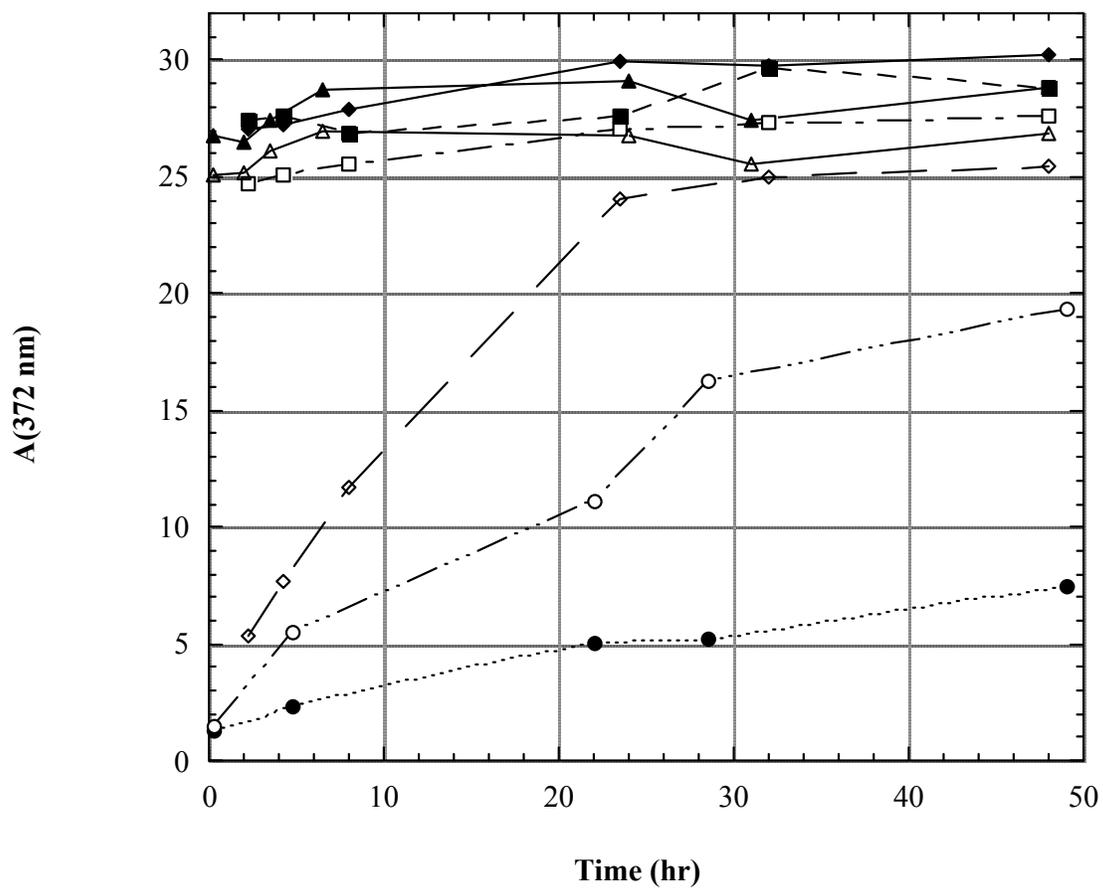
Legend		
	Filled Circles:	0.1 M NaOH
	Open Circles:	3 M NaOH
	Open Diamond:	0.1 M NaOH, persulfate
	Filled Diamond:	3 M NaOH, persulfate
	Open Square:	0.1 M NaOH, permanganate
	Filled Square:	3 M NaOH, permanganate
	Open Triangle:	1.1 M NaOH, ferrate
	Filled Triangle:	3 M NaOH, ferrate

Legend

Filled Circles:	0.1 M NaOH
Open Circles:	3 M NaOH
Open Diamond:	0.1 M NaOH, persulfate
Filled Diamond:	3 M NaOH, persulfate
Open Square:	0.1 M NaOH, permanganate
Filled Square:	3 M NaOH, permanganate
Open Triangle:	1.1 M NaOH, ferrate
Filled Triangle:	3 M NaOH, ferrate

Figure 3.3. Chromate Formation Under Alkaline Conditions at High Temperature (80 to 85°C)

3.3 Dissolution of Major, Bulk Sludge Components by Oxidative Alkaline Leaching of Washed S-110 Sludge.

Of the major bulk components found in washed S-110 tank sludge (Table 2.2), only aluminum, chromium, and silicon were found to any significant extent in the leach solutions. Occasionally, iron and manganese (especially in permanganate-containing leach solutions) were also found, generally at close to their detection limits. Table 3.1 summarizes the percent of each of the major bulk components removed in the low-hydroxide contacts, and Table 3.2 summarizes the component removal from high-hydroxide leach solutions.

Table 3.1. Major Component Removal from Oxidative, Alkaline Leach Solutions at 30°C, After 48 Hours

Initial [OH⁻], M	Oxidant	% Component Removed		
		Al	Cr	Si
0.1	None	1	5	76
3	None	7	10	78
0.1	MnO_4^-	3	87	77
3	MnO_4^-	15	93	81
0.1	$S_2O_8^{2-}$	2	48	76
3	$S_2O_8^{2-}$	8	89	89
1.1	FeO_4^{2-}	6	88	83
3	FeO_4^{2-}	9	90	84

Table 3.2. Major Component Removal from Oxidative, Alkaline Leach Solutions at 80 to 85°C After 48 Hours

Initial [OH⁻], M	Oxidant	% Component Removed		
		Al	Cr	Si
0.1	None	11	25	83
3	None	62	72	93
0.1	MnO_4^-	12	90	74
3	MnO_4^-	49	95	81
0.1	$S_2O_8^{2-}$	8	89	74
3	$S_2O_8^{2-}$	41	94	85
1.1	FeO_4^{2-}	51	95	85
3	FeO_4^{2-}	51	94	90

The amount of dissolved silicon appeared fairly consistent regardless of hydroxide concentration and temperature. The dissolution of aluminum, on the other hand, varied markedly with both hydroxide concentration and in a manner consistent with previously observed aluminum dissolution despite the relatively short contact times. Increases in hydroxide concentration from 0.1 to 3 M and temperature increases from 30 to 80–85°C both enhanced aluminum dissolution, with about 50% of the aluminum dissolving after a 48-h contact under the most favorable leaching conditions. Indeed, the 62% Al removal

achieved after leaching for 48 h with 3 M NaOH at 80 to 85°C (without oxidant) agrees well with that observed in separate parametric caustic leaching tests with this sludge (Lumetta et al. 2001). Because of the slow dissolution kinetics typically found for boehmite, more extended leaching times would be expected to increase aluminum dissolution, and indeed, recent studies of washed S-110 sludge verify this expectation (Lumetta et al. 2001).

Chromium dissolution was greatly enhanced by the presence of oxidant. At low temperatures and in the absence of added oxidant, little chromium was dissolved. Consistent with previous observations (Rapko 1998), increases in temperature and hydroxide concentration enhanced chromium dissolution even in the absence of added oxidant, presumably by the same mechanism but with atmospheric oxygen acting as the oxidant. Indeed, over 70% of the chromium remaining in washed S-110 sludge could be dissolved by simple stirring in 3 M NaOH at 80°C for 48 h. This result also agrees well with that observed in separate parametric caustic leaching tests with this sludge (Lumetta 2001). However, the rate and extent of chromium dissolution was always enhanced by the addition of oxidants. Generally, with the exception of persulfate at low hydroxide and low temperature, dissolutions of around 90 to 95% of the available chromium were observed. The final chromium concentrations in the oxidatively-leached S-110 sludge (Table 3.3 and Table 3.4) reflected this enhanced dissolution in their markedly lower chromium concentrations as compared to the simple washed S-110 sludge (Table 2.2). In the oxidatively leached sludge, residual chromium concentrations dropped from their initial > 20000 ppm to as low as 2000 to 3000 ppm.

Table 3.3. Final Major or Key Bulk Component Concentrations in Leached S-110 Sludge

$[OH^-]_{initial}$,	Oxidant	Temp, °C	Component Concentration in Leached Sludge (µg/g)							
			Al	Cr	Fe	Mn	Na	P	Si	U
0.1	None	30	350000	23400	14900	5550	12200	620	4900	24100
3	None	30	333000	19700	16100	5950	11800	420	4670	25000
0.1	MnO_4^-	30	332000	3290	13300	26900	15300	280	4930	21800
3	MnO_4^-	30	349000	2130	16700	27400	16200	310	4100	25800
0.1	$S_2O_8^{2-}$	30	338000	13100	14400	5390	12700	500	4900	23200
3	$S_2O_8^{2-}$	30	355000	3000	15900	5820	10200	490	2300	25800
1.1	FeO_4^{2-}	30	305000	3190	72700	5630	11100	310	2800	23200
3	FeO_4^{2-}	30	304000	2650	75300	4880	11700	310	2600	21600
0.1	None	85	310000	22300	15100	5510	19000	470	3800	23500
3	None	85	332000	16900	31600	12500	16200	390	3100	50900
0.1	MnO_4^-	80	330000	2740	14800	37500	16700	370	5450	25200
3	MnO_4^-	80	293000	2310	23000	48700	76100	250	2600	35600
0.1	$S_2O_8^{2-}$	80	358000	3200	16200	5850	13600	600	5180	25800
3	$S_2O_8^{2-}$	80	337000	2610	22700	8930	21600	510	3800	37000
1.1	FeO_4^{2-}	80	273000	2310	119000	8690	14000	310	3900	33400
3	FeO_4^{2-}	80	281000	2520	126000	9260	14500	250	2600	34900

3.4 Evaluating the Form of Chromium in Oxidatively Leached S-110 Tank Sludge

In line with our previous studies, the form of chromium in alkaline-leach solutions was evaluated by assuming two possibilities, chromium being present in the +6 oxidation state as chromate, CrO_4^{2-}, and chromium 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 chromium concentration in solution can be determined with good sensitivity by ICP-AES, so the ratio of chromate to total chromium can be effectively measured. Table 3.4 shows the molar ratio of the chromate concentration in the final leachate + washes solution as determined by visible spectroscopy with the total chromium concentration as determined by ICP-AES. Clearly, within the 15% uncertainty of the ICP-AES measurement, the chromate and total chromium concentrations were identical. The exception to this statement is the 3 M NaOH, 30°C results. However, in that test, the dilution of the tested solution was so large that the actual measured chromate absorbance was less than 0.1, which is close enough to the baseline so as to make this chromate measurement significantly more uncertain. In short, a comparison of the chromate to total chromium concentrations indicates that the bulk of the dissolved chromium in these alkaline leach solutions was present as chromate.

Table 3.4. The Measured Ratio of $[CrO_4^{2-}]/[Cr]$ in the Leachate + Final Wash Solutions

[OH]$_{initial}$, Oxidant		Temperature, °C	$[CrO_4^{2-}]/[Cr]$
0.1	None	30	1.11
3	None	30	0.75
0.1	MnO_4^-	30	1.06
3	MnO_4^-	30	1.16
0.1	$S_2O_8^{2-}$	30	0.93
3	$S_2O_8^{2-}$	30	0.97
1.1	FeO_4^{2-}	30	1.00
3	FeO_4^{2-}	30	1.10
0.1	None	85	0.86
3	None	85	0.93
0.1	MnO_4^-	80	1.00
3	MnO_4^-	80	1.09
0.1	$S_2O_8^{2-}$	80	0.95
3	$S_2O_8^{2-}$	80	1.01
1.1	FeO_4^{2-}	80	0.94
3	FeO_4^{2-}	80	1.01

3.5 Dissolution of Key Radionuclides From Washed S-110 Sludge by Oxidative Alkaline Leaching

The purpose of the oxidative alkaline leaching is to remove chromium 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 chromium dissolution; it also must be selective, especially with respect to radionuclides and in particular the TRU elements. Attention to enhanced TRU dissolution is important since oxidants could also act on these radionuclides and oxidize them, as well as chromium, to more soluble forms. In addition, the solution concentrations of TRU elements needed to transform a LAW stream to an HLW stream are stringent (> 100 nCi/g). Therefore, the concentration of radionuclides was examined by gamma-energy analysis (GEA) (focusing on [241]Am behavior) and alpha-energy analysis (AEA) (to evaluate both potential enhanced Pu dissolution as well as the total TRU concentration) and total beta analysis. The extent to which these components dissolve is shown in Table 3.5.

Clearly, adding oxidants enhanced the dissolution of the TRU elements. Although the high detection limits in the GEA analysis prevented distinguishing whether any Am dissolution actually occurred, alpha energy analysis indicated that the fraction of dissolved [239,240]Pu was consistently greater than the fraction of dissolved [238]Pu + [241]Am, suggesting that the bulk of the dissolved TRU was derived from Pu dissolution. Other radionuclide dissolution behavior was consistent with previous alkaline leaching studies. The bulk of the remaining ^{137}Cs in the washed S-110 sludge dissolves upon treatment with additional alkaline solution—the greater the hydroxide concentration in the leaching solution, the more effective the Cs removal. Little beta activity was found in the alkaline leaching solutions and appears independent of oxidant or hydroxide concentration. The identity of the dissolved beta-emitting radionuclide(s) was not determined.

The results presented in Table 3.5 do not address the question of whether the leachate solutions would be classified as an LAW or as HLW. This can be evaluated by considering the TRU concentration at 20 wt% Na_2O, which reflects the likely component concentrations in the immobilized LAW. Table 3.6 shows the TRU activity at 20 wt% Na_2O.

The results are presented in terms of two cases in Table 3.6. One case (Leachate & Washes) describes the TRU activity after concentration of the combined leachate plus three 0.1 M NaOH wash solutions to a sodium concentration equivalent to the 20 wt% Na_2O target for the immobilized glass, but does not take into account the density of the final combined solutions. Generally, these densities were around 1.01 g/mL for the low-hydroxide contacts and only 1.07 g/mL for the high-hydroxide contacts. Thus, the impact of a density correction on the reported TRU activities in Table 3.6 would be to drop those values by an additional 1 to 7%, which is insignificant for this analysis.

The second case considers only the original leach solution upon concentration to a sodium concentration equivalent to 20 wt% Na_2O and does include the density correction since these densities vary significantly from test to test. In this analysis, the total TRU activity in each leachate and washes solution was calculated and converted to a TRU concentration in nCi/mL using the initial leachate volume of 100 mL. The total amount of sodium in the initial leach solution was assumed to be due only to the amount of added NaOH from the stock solutions; i.e. the sodium contribution from the sludge was neglected. The component concentrations were then corrected from g/mL or nCi/mL to g/g or nCi/g by

dividing by the measured leach solution's density. The correction factor required to convert the Na concentration to that of 20 wt% Na_2O was calculated, and this concentration factor was applied to the TRU activity to give the initial leachate column in Table 3.6.

Table 3.5. Key Radionuclide Dissolution in Oxidative Alkaline Leachate Solutions

[OH]$_{initial}$, Oxidant		Temperature, °C	% Component Removed				
			^{137}Cs	Total α	$^{239,240}Pu$	^{241}Am	Total β
0.1	None	30	71	0.2	0.01	< 6	1
3	None	30	83	0.5	0.5	< 10	2
0.1	MnO_4^-	30	64	0.5	0.6	< 6	1
3	MnO_4^-	30	90	4.7	7	< 6	2
0.1	$S_2O_8^{2-}$	30	71	0.2	0.1	< 13	1
3	$S_2O_8^{2-}$	30	96	5.8	8	< 13	2
1.1	FeO_4^{2-}	30	89	5.7	9	< 14	2
3	FeO_4^{2-}	30	92	5.8	8	< 22	2
0.1	None	85	91	0.2	< 0.01	< 9	1
3	None	85	98	0.7	0.8	< 11	3
0.1	MnO_4^-	80	72	0.9	1.5	< 11	1
3	MnO_4^-	80	98	8.2	11	< 15	2
0.1	$S_2O_8^{2-}$	80	75	3.4	5.3	< 10	1
3	$S_2O_8^{2-}$	80	95	6.8	10	< 12	3
1.1	FeO_4^{2-}	80	95	0.8	1.1	< 19	2
3	FeO_4^{2-}	80	98	1.8	3	< 19	2

Table 3.6. TRU Leachate Concentration (nCi/g) at 20 wt% Na_2O

[OH]$_{initial}$, Oxidant		Temperature, °C	TRU Activity, nCi/g	
			Initial Leachate	Leachate & Washes
0.1	None	30	5.85E-02	3.07E-02
3	None	30	1.65E-01	1.96E-01
0.1	MnO_4^-	30	5.48E+00	2.54E+00
3	MnO_4^-	30	2.17E+00	2.53E+00
0.1	$S_2O_8^{2-}$	30	8.47E-01	3.92E-01
3	$S_2O_8^{2-}$	30	2.50E+00	2.97E+00
1.1	FeO_4^{2-}	30	9.74E+01	4.96E+00
3	FeO_4^{2-}	30	2.77E+00	3.09E+00
0.1	None	85	7.71E-02	1.93E-02
3	None	85	2.52E-01	3.15E-01
0.1	MnO_4^-	80	1.61E+01	7.64E+00
3	MnO_4^-	80	3.55E+00	4.30E+00
0.1	$S_2O_8^{2-}$	80	5.51E+01	2.70E+01
3	$S_2O_8^{2-}$	80	3.56E+00	4.27E+00
1.1	FeO_4^{2-}	80	1.09E+00	5.20E+01
3	FeO_4^{2-}	80	8.46E-01	9.51E-01

The conclusion derived from Table 3.6 is that in no instance will either the leach solutions themselves or the leach solutions plus washes generate a TRU waste. It should be noted, however, that in several instances with the initial leach solutions at low hydroxide, and in one instance with the low hydroxide leach and washes solution, the TRU levels (> 10 nCi/g but < 100 nCi/g) would generate a Class C LAW, and in one instance, the TRU concentration comes quite close to the LAW TRU limit. The larger concentration factors required to reach 20 wt% Na_2O, rather than significantly greater TRU concentrations in the liquids themselves, are the predominant reason for generating these potential Class C LAWs. In all other instances, the TRU content in the immobilized leach solutions would generate a Class A (< 10 nCi/g) LAW.

3.6 Impact of Oxidative Alkaline Leaching on HLW Glass Immobilization of S-110 Sludge

The ultimate goal of oxidative alkaline leaching is to eliminate chromium 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 chemical oxidants in achieving this task? In this section, we attempt to address this question.

One answer can be obtained from inspecting Table 3.3. Currently, if individual component concentration limits are used to examine what limits the amount of sludge loading in HLW glass, any chromium concentration in the leached sludge greater than 0.5 wt% chromium oxide in the sludge becomes problematic in that it may impact the percent of that sludge that can be loaded into the glass. Inspection of the chromium concentration in the initial washed S-110 sludge (Table 2.2) or in the leached S-110 sludges (Table 3.3) clearly indicates that simple washing or caustic leaching in the absence of added oxidants either at 0.1 or 3 M hydroxide at either 30°C or 80–85°C for 48 h may not provide adequate chromium removal. However, with the exception of persulfate at low hydroxide and low temperature, all added oxidants, after a 48-h contact at either 30°C or 80°C in either low or high hydroxide solution, provided sufficient chromium removal so that the sludge itself meets the 0.5 wt% chromium oxide specification.

On the other hand, the more sophisticated analysis described in the experimental section indicates that the loading of each waste in glass would be largely controlled by Al concentration in the waste, as shown in Figure 3.4. This result suggests that for S-110, the removal of Cr alone has little impact on glass volume, but that Al removal has a significant effect. Based on the strong relationship between Al concentration and waste loading, the mass of glass (M_G) per mass of initial, washed, waste (M_W) was estimated from the Al and total mass removal data. Figure 3.5 shows that significant differences in estimated glass production result from the different oxidative leaching techniques. Significantly, the most effective means of treating the waste was leaching with simple 3 M NaOH. This can be ascribed to having the highest Al removal with the concomitant largest mass reduction of any of the leach conditions. In summary, these results indicate that for the S-110 solids, the large initial aluminum concentration, the relatively short, 48-h, contact times employed, and the slow dissolution in caustic of the predominate aluminum phase, boehmite, all combined to make the effectiveness of pretreatment to be controlled by the amount of aluminum that remained in the residual solids together with the mass losses achieved from pretreatment.

Since the bulk of the aluminum should be removed with more extended leaching times, an alternative, hypothetical situation was explored where the aluminum concentration in the residual solids was decreased by 90%, but the final concentrations of the other metals were unaffected. This allowed a rough evaluation of the impact of enhanced chromium removal under more optimum leach conditions. Figure 3.8 shows the fraction of this low Al, oxidatively alkaline leached sludge that can be loaded into a HLW glass at the current 4 mass% MnO limit, and Figure 3.9 shows an analogous situation if the MnO limit was raised to a plausible 10-mass% limit.

The results illustrated in Figure 3.6 and Figure 3.7 show that in this hypothetical low Al S-110 washed sludge, only about 5 wt% sludge could be incorporated into the HLW glass. The most effective caustic leaching in the absence of oxidants will about double that to 10 wt% sludge in HLW glass. The use of oxidants allows for a further several-fold increase in the sludge loading in HLW. The best results are with persulfate and ferrate, which suggested that, at 4 wt% MnO, the added manganese adversely impacts sludge loading in glass. At 10 wt%, that restriction appears to relax as the permanganate-leached sludge now allows for the greatest sludge loading of all, with up to eight times the sludge loading than that possible for the low Al, washed solids. The tentative conclusion of these analyses is that the effective Al removal supplied by extended caustic leaching coupled with the enhanced chromium removal provided by added oxidants will positively impact S-110 sludge loadings in HLW glass.

One final set of calculations was made, and the results support the above-mentioned conclusion. In a recent study, an extensive 3 M caustic leaching of S-110 sludge was performed, which yielded the expected large reduction of Al (> 99%) from the waste (Lumetta et al. 2001). A glass composition was optimized for this sample, which showed a waste loading of 21 mass% (with a $M_G/M_{W,i}$ of 4.3), limited by the 1 mass% Cr_2O_3 limit in glass (Appendix A). If an additional 95% of the Cr were removed from this waste by oxidative leaching, the loading of waste would be increased to 39 mass% (with a $M_G/M_{W,i}$ of 2.2) with a 4 mass% MnO limit or to 51 mass% (with a $M_G/M_{W,i}$ of 1.7) with a 10 mass% MnO limit.

In summary, this study indicates that the amount of glass produced from the same amount of S-110 waste would be reduced by 20% by the almost quantitative Al removal available through an extended caustic leach. A further reduction of almost 50% in the amount of produced glass could then be obtained by oxidative leaching sufficient to remove 95% of the remaining Cr for a total of roughly 70% volume reduction in glass over that produced from untreated waste.
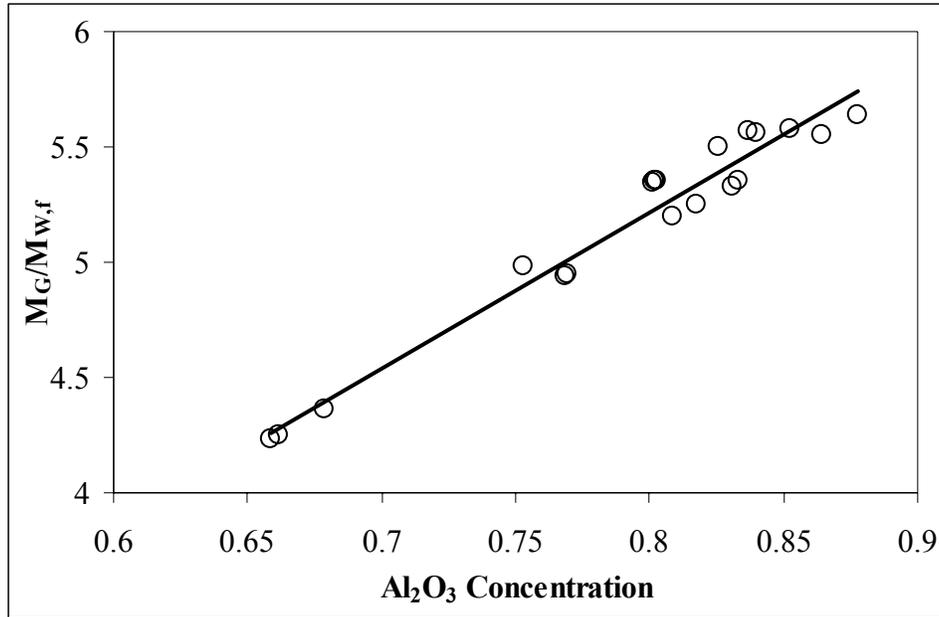
Figure 3.4. Estimated Glass Mass (M_G) per Final Waste Mass ($M_{W,f}$) as a Function of Al_2O_3 Concentration in Waste (mass%)
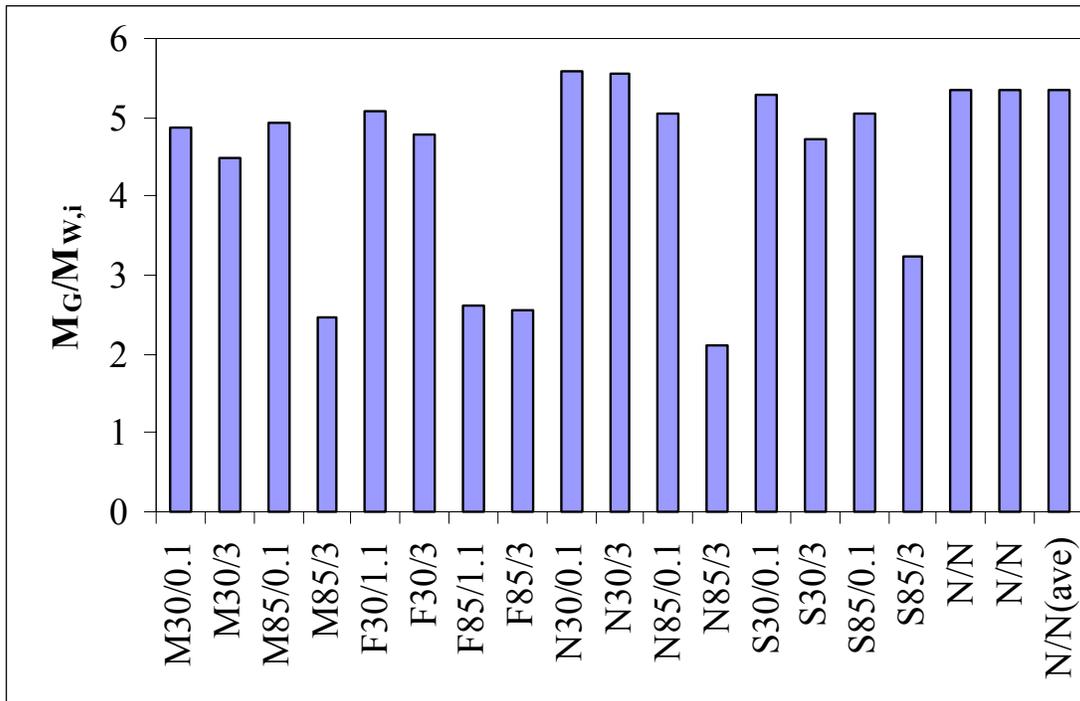
Figure 3.5. Estimated Glass Mass (M_G) per Initial Waste Mass ($M_{W,i}$) for Each Oxidative Leach Sample (M = permanganate; F = ferrate; S = persulfate; N = no added oxidant; N/N = washed S-110 sludge) (results from each duplicate measurements shown); Values Stand for Temperature and OH Concentration, Respectively
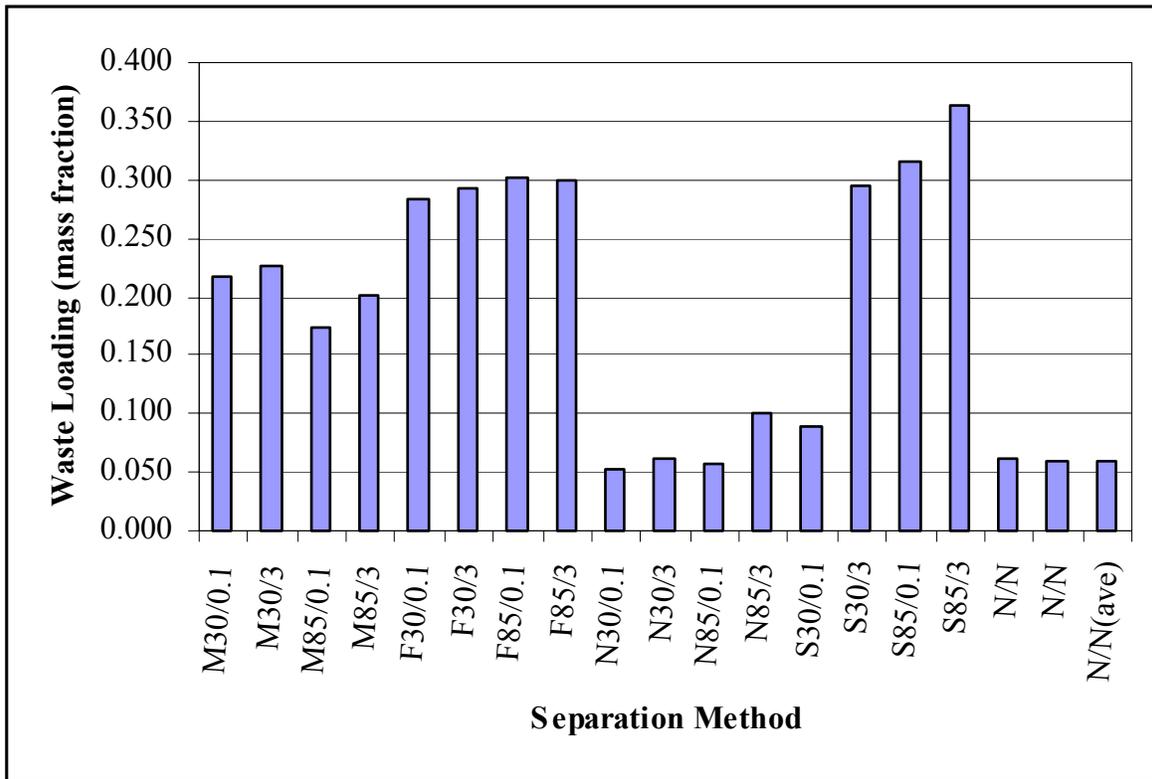
Figure Key: M = permanganate; F = ferrate; S = persulfate; N = no
added oxidant; N/N = washed S-110 sludge

Figure 3.6. Waste Loading of Low Al, Oxidatively Leached S-110 Sludge in HLW at 4 wt% MnO
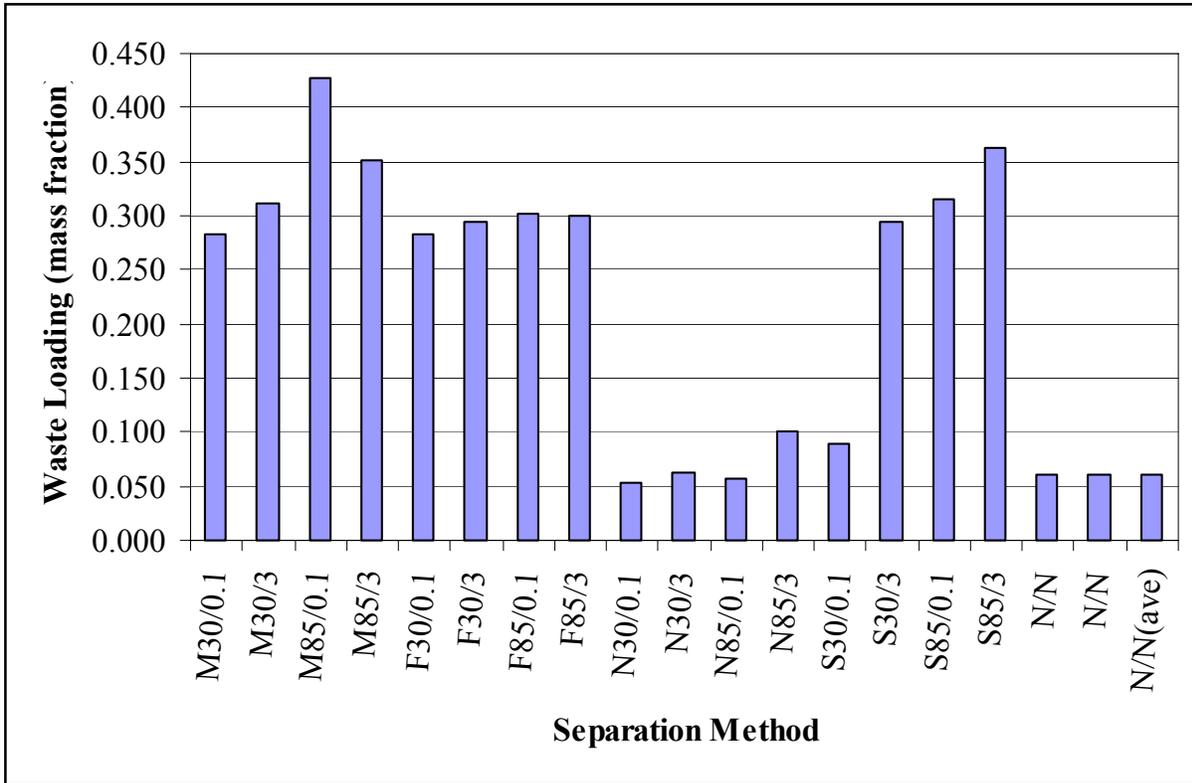
Figure Key: M = permanganate; F = ferrate; S = persulfate; N = no
added oxidant; N/N = washed S-110 sludge

Figure 3.7. Waste Loading of Low Al, Oxidatively Leached S-110 Sludge in HLW at 10 wt% MnO

4.0 Use of IX Resins as a Source of Oxidant in Oxidative Alkaline Leaching of Washed S-110 Sludge

Scoping studies were undertaken to evaluate the use of ion-exchange resins as a delivery source for oxidant. The questions addressed in this scoping study were:

- Can commercial anion-exchange resins be effectively loaded with an oxidant suitable for alkaline oxidative leaching of sludge?

- Is the introduced oxidant effective at oxidizing chromium(III) in alkaline solution?

- Does the generated chromate bind to the resin?

- Can the chromate-containing resin then be recycled and reused?

The resins examined in this study are all commercially available. Table 4.1 summarizes the resin tests, the type of functionality present in the resin, and the resin's commercial source.

Table 4.1. Tested Anion-Exchange Resins

Resin Name	Resin Manufacturer	Resin Type
A-300	Purolite	Type II gel
D-4152	Purolite	Type I gel
SBG-2OH	ResinTech Inc.	Type II gel
Dowex 22 Cl	Dow Chemical	Type II Macroporous
Dowex 2 X 8-100	Dow Chemical	Type II gel
Dowex MSA-1	Dow Chemical	Type I Macroporous
Dowex 1 X 4-50	Dow Chemical	Type I gel

All of these resins consist of derivatized polystyrene cross-linked with divinyl benzeneype. The Type I resins have quaternary ammonium sites and the Type II resins have dimethylethanol ammonium sites.

Before testing, all resins were converted to the hydroxide form, and their chromate and permanganate affinities were measured while in contact with a 1 M NaOH solution. The results are summarized in Table 4.2. In general, the resins' affinity for permanganate appears to be larger than their affinity for chromate, despite the greater negative charge possessed by chromate.

Each resin then was loaded with permanganate, and the permanganate-loaded resin was contacted with a solution containing a total of 10 μmol of chromium(III) in 1 M NaOH at room temperature. The mass of chromium(III) remaining in solution, of chromium(VI) now present in solution, and of chromium now present on the resin (calculated by mass balance) are shown in Table 4.3, and are illustrated in Figure 4.1.

Table 4.2. Chromate and Permanganate K_d Measurements for Anion-Exchange Resins From a 1 M NaOH Solution

Resin	Chromate Affinity		Permanganate Affinity	
	K_d	S.D. of K_d	K_d	S.D. of K_d
A-300	41.2	0.7	119	14
D-4152	ND[a]	ND	ND	ND
SBG-2OH	29.3	0.3	30.5	2.7
Dowex 22 Cl	56.7	0.01	474	14
Dowex 2 X 8-100	52.7	3.9	40	15
Dowex MSA-1	413	10	large[b]	
Dowex 1 X 4-50	261	55	9630	NO[c]
(a) Not Determined				
(b) No permanganate could be detected in the solution after resin contact				
(c) Insufficient testing to measure a standard deviation				

Table 4.3. Chromium Distribution in 1 M NaOH Following Contact of 10 μmol of Chromium(III) with Permanganate-Loaded Anion-Exchange Resins

Resin	Cr^{+6} (aq.)	Cr^{+3} (aq.)	On Resin
	μM	μM	μM
Dowex 2 X 8-100	2.88	4.81	2.31
A-300	2.39	5.65	1.96
SBG2-OH	1.58	5.04	3.38
Dowex 22 Cl	1.41	0.85	7.74
D-4152	1.18	—	8.90
Dowex 1X 4-50	0.95	2.63	6.42
Dowex MSA-1	0.54	0.31	9.14

The results presented in Table 4.3 and Figure 4.1 clearly indicate that the permanganate on the anion-exchange resins can oxidize dissolved chromium(III) in alkaline solution. The effectiveness of the resins in performing this oxidation depends on the form of the chromium attached to the anion-exchange resin at the conclusion of the experiment. If it was present as chromate, then resins such as D-4152 and MSA-1 were very effective at converting the chromium(III) to chromium(VI), with measured conversions of 95% or greater. If the chromium on the resins was present as chromium(III), then none of the resins were particularly effective at introducing permanganate for chromium(III) oxidation. Although the oxidation state of the chromium on the resin was not determined, it should be noted that the resins that sorbed the largest amount of chromium were also the resins with the highest K_d for chromate as reported in Table 4.2.

Finally, the capability to remove chromate and permanganate from the loaded resins was briefly explored. Contact of the loaded resins with 1 M HCl effectively removed all remaining manganese from the resin, but was only of modest effectiveness at removing any chromium present on the resins. Table 4.4 summarizes chromium removal following HCl contact.
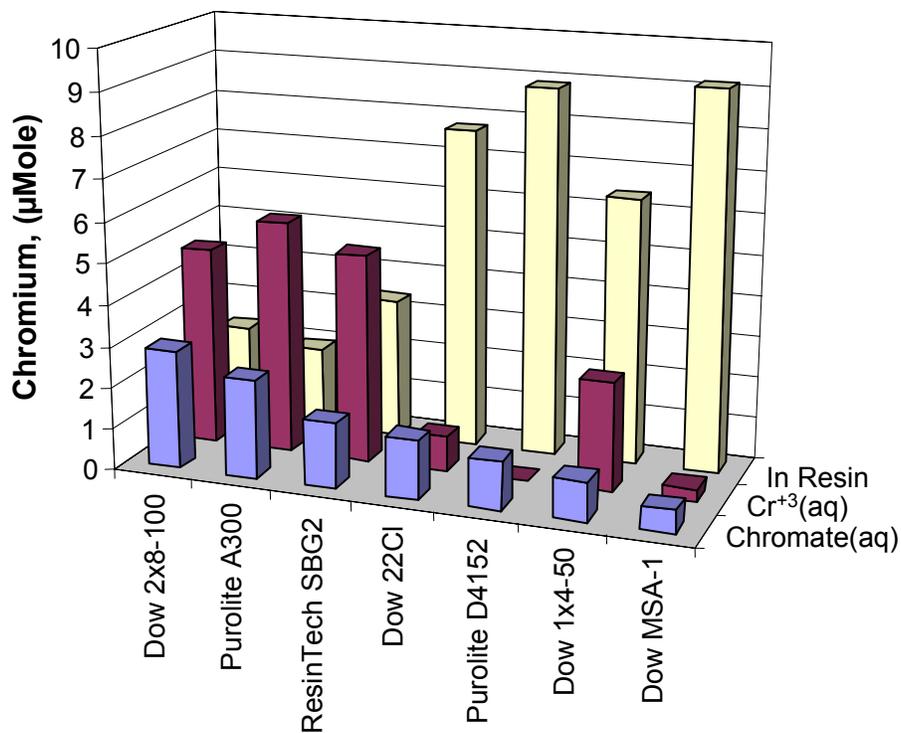
Figure 4.1. Distribution of 10 μmol Chromium(III) in 1 M NaOH Following Contact with Permanganate-Loaded Anion-Exchange Resin

Table 4.4. Removal of Chromium From Anion-Exchange Resin by Contact with 1M HCl

Resin	Uptake μM	Leached μM	Resin Remainder μM
2x8-100	2.31	0.64	1.66
A300	1.96	0.32	1.63
SBG2-OH	3.38	0.49	2.89
22 Cl	7.74	0.29	7.45
D4152	8.90	0.74	8.16
1x4-50	6.42	1.55	4.88
MSA-1	9.14	4.31	4.88

5.0 Dissolution of Mercury(II) Under Alkaline Conditions

5.1   Choice of Reagents

A search was performed of the International Union of Pure and Applied Chemists (IUPAC) database (Pettit and Powell 1993-1997) for molecules with a high affinity for mercury(II). As expected, most of the compounds with a high affinity for mercury(II) contain sulfur atoms. Although the majority of these compounds are based on the thiol functionality (RSH), the thiol functionality is known to be susceptible to oxidation, especially in alkaline solution, so examining compounds with alternative functional groups as well as thiols seemed prudent. In addition, to be an effective agent for mercury dissolution, the mercury complex would need to be soluble in alkaline solutions. Either formation of a salt complex or the absence of large organic (and so probably hydrophobic) content were also used as selection criteria; compound availability and a relative low reagent cost were also considered. Following the survey, three molecules were selected for examination; they are shown in Figure 5.1, and selected reported binding affinities to mercury(II) are summarized in Table 5.1.

Table 5.1. Binding Affinity of Selected Leaching Agent to Mercury(II)

Ligand	β_1	β_2	β_3	β_4
Cysteine[a]	37.8	44	—	—
Iodide[b]	12.87	23.82	27.60	29.83
DEDTPA[c]	Not Determined	29.1	—	—
(a) Measured at 25°C, aqueous solution (Basinger et. al. 1981)				
(b) Measured at 25°C, aqueous solution (Nagypol and Beck 1982)				
(c) Diethyldithiophosphoric acid, measured at 25°C, EtOH/H$_2$O solvent (Pettit and Powell 1993–1997).				

Each of the selected candidate leaching agents possesses a different type of functional group. Cysteine possesses a thiol functionality, DEDTPA possesses a dithiophosphate functionality, and iodide is a simple halide. DEDTPA was chosen because it has the shortest alkyl chain for this class of compounds that was readily available commercially; the shortness of the C$_2$ alkyl chains in DEDTPA maximizes the chances that a hydrophilic mercury-complex will be formed.

The use of iodide to selectively dissolve mercury(II) has been examined previously. General Electric developed the concept of using KI/I$_2$ to remove mercury from waste in 1992. More recently, staff at Oak Ridge National Laboratory (ORNL) examined KI/I$_2$ as a chemical leaching agent for mercury from solids consisting of mixed wastes and soils (Gates et. al. 1995). Significantly, it was shown that cerium did not dissolve from a synthetic soil treated with KI/I$_2$. However, these tests were performed under essentially neutral conditions, and it is prudent to test the process under the more alkaline conditions associated with sludge washing and caustic leaching.

Cysteine

Iodide

Diethyldithiophosphoric Acid (DEDTPA)
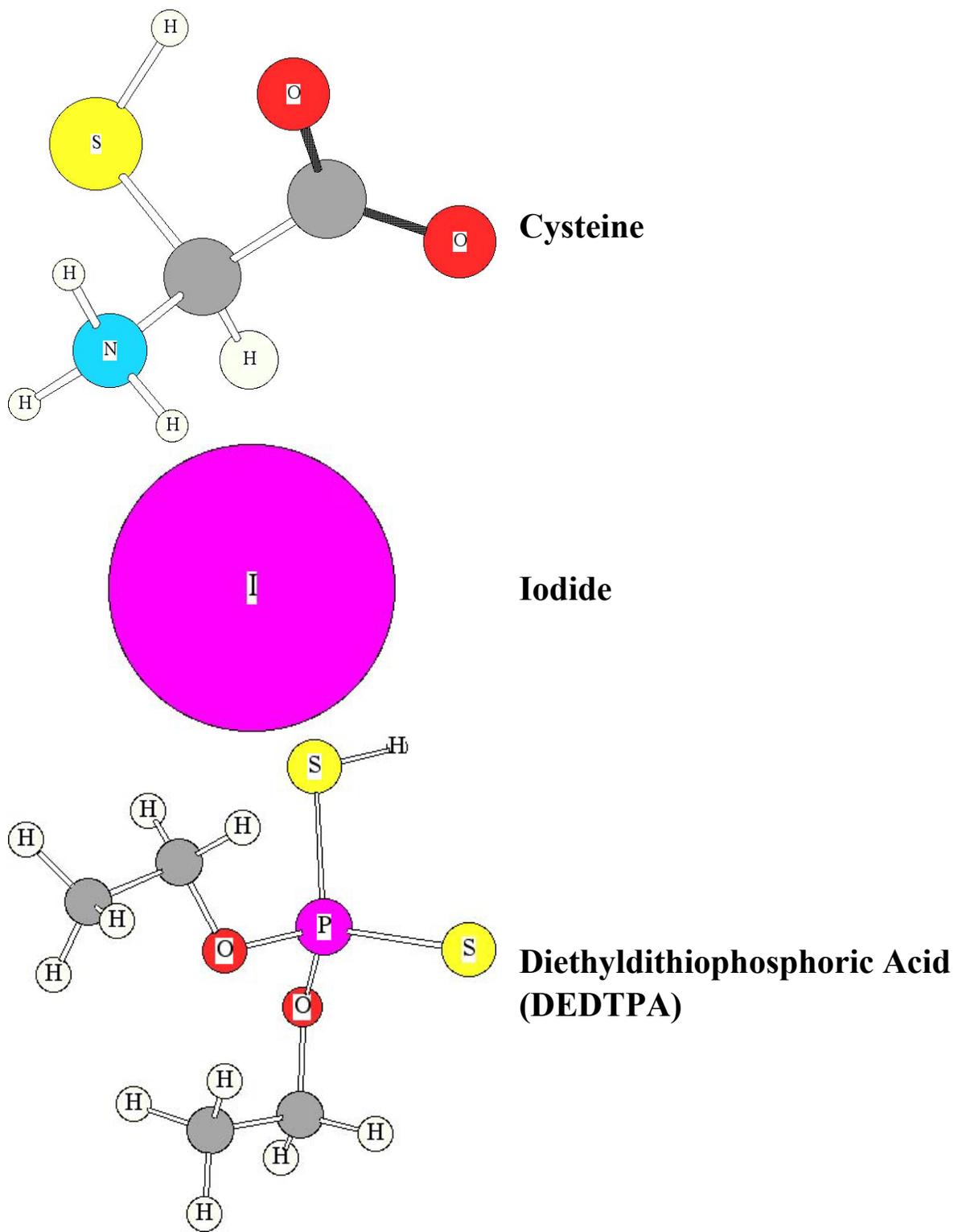
Figure 5.1. Compounds Tested as Alkaline Mercury(II) Leaching Agents

5.2 Results from Low Hydroxide Tests

The results from low-hydroxide leach solutions are shown in Table 5.2 and Figure 5.2. Immediately upon mixing, all visible solids in the KI/I_2 sample dissolved and remained dissolved throughout the experiment. This solution activity was assumed to be the activity for each solution under conditions of complete solids dissolution (generating a solution containing 5 mmol mercury in 50 mL or a solution 0.1 M in mercury) for the purposes of the % removed calculation in Table 5.2. Correction of the leachate solution's concentration for cysteine and DEDTPA from 50 mM to 200 mM resulted in an immediate decrease in pH for cysteine to ca. pH 2 and for DEDTPA to ca. pH 11. The solution's pH concentration was adjusted back to ca. 13 with NaOH. The results indicate, as expected, that little mercury is present in a simple 0.1 M hydroxide solution. The presence of a stoichiometric amount (2 equivalents) of DEDTPA had little impact on the amount of dissolved mercury after contact up to 1 week at room temperature. However, with stoichiometric (cysteine) or greater (iodide) amounts of ligand, both cysteine and iodide appeared to react quickly and were effective at dissolving the bulk of the mercury present. However, with cysteine, the mercury concentration dropped as the contact time at room temperature was increased. Concomitant with the decrease in dissolved mercury was the appearance of a black precipitate, suggestive of the formation of HgS.

Table 5.2. Concentration of Mercury(II) in 0.1 M NaOH Alkaline Leach Solutions

Time (contact hours)	Mercury(II) Concentration, mM			
	No Added Agent	0.2 M Cysteine	0.2 M DEDTPA	1 MKI/0.1 M I_2
1	0.34			96
5	0.26			90
45	0.29			96
52	0.42	90	0.25	96
70	0.33	93	1.63	109
140	0.37	83	2.70	101
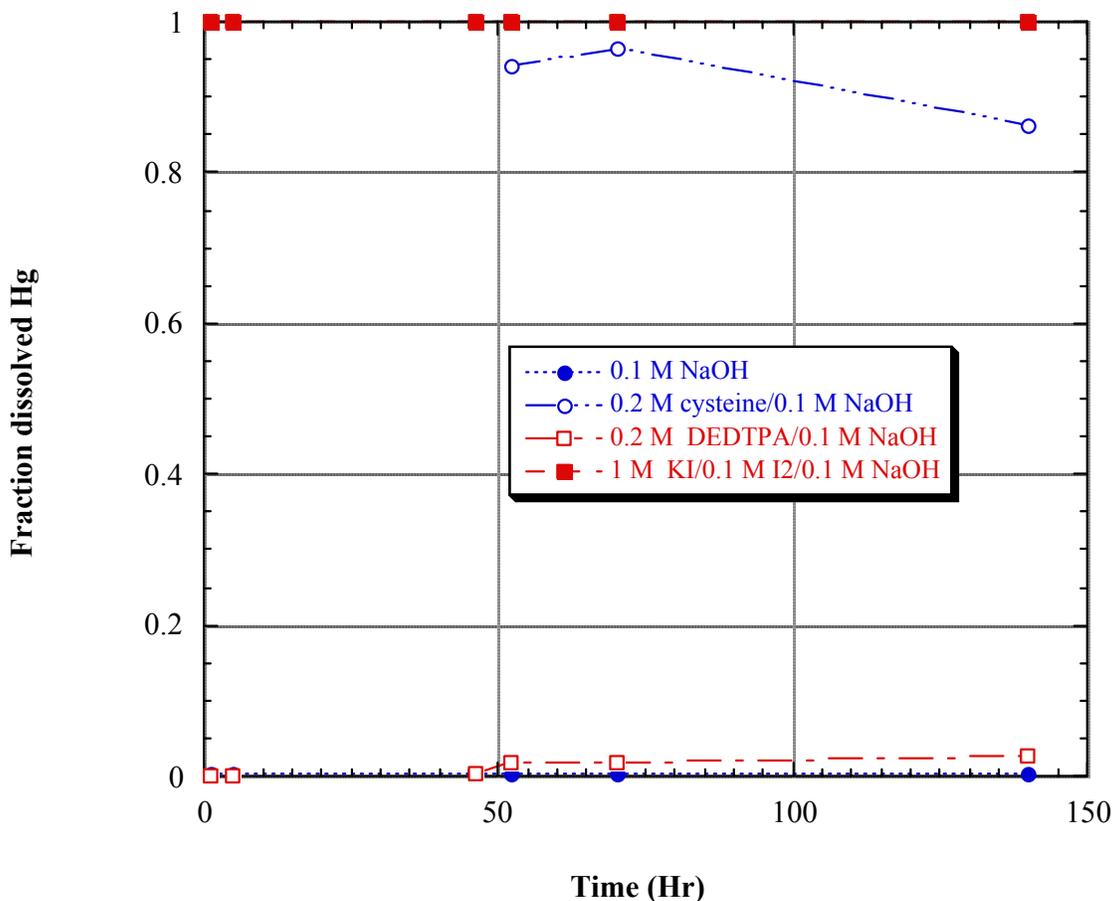
Figure 5.2. Mercury Dissolution into 0.1 M NaOH Leach Solutions

5.3 Results from High Hydroxide Leach Tests

The results from the 3 M NaOH leach tests are tabulated in Table 5.3 and shown graphically in Figure 5.3. The results are very similar to those found at 0.1 M hydroxide, but a few differences do exist. First, the color of the KI/I_2 solution quickly changed from brown to almost colorless, suggesting that the I_2 disappeared from the reaction mixture, probably because of its known tendency to disproportionate to iodide and an oxyacid in alkaline solutions (Greenwood and Earnshaw 1984). This had no impact on the dissolution of mercury(II); indeed it would be expected to enhance it as it would increase the iodide concentration in solution.

The cysteine suspension rapidly changed from yellow to black as the mercury dissolved, while the KI/I_2 suspension formed and remained as a yellow solution. Despite the rapid formation of a black suspension in the case of cysteine, Table 5.3 and Figure 5.3 again indicate that stoichiometric or greater concentrations of cysteine and iodide, respectively, were effective at mercury(II) dissolution under alkaline conditions. As was observed in the low-hydroxide tests, no loss of mercury from the aqueous phase was observed for iodine over the 5- to 6-day reaction time examined. On the other hand, after a day of stirring at room temperature in air, the mercury concentration in the cysteine solution began to

decrease, with only about 60% of the initial mercury(II) solution concentration remaining in solution after 5 to 6 days.

Table 5.3. Concentration of Mercury(II) in 3 M NaOH Alkaline Leach Solutions

Time (contact hours)	Mercury(II) Concentration, mM			
	No Added Agent	0.2 M Cysteine	0.2 M DEDTPA	1 MKI/0.1 M I$_2$
1	0.43	101	0.03	97
7	0.47	91	0.05	91
31	0.44	81	0.03	99
55	0.41	75	0.05	100
130	0.32	59	0.44	103
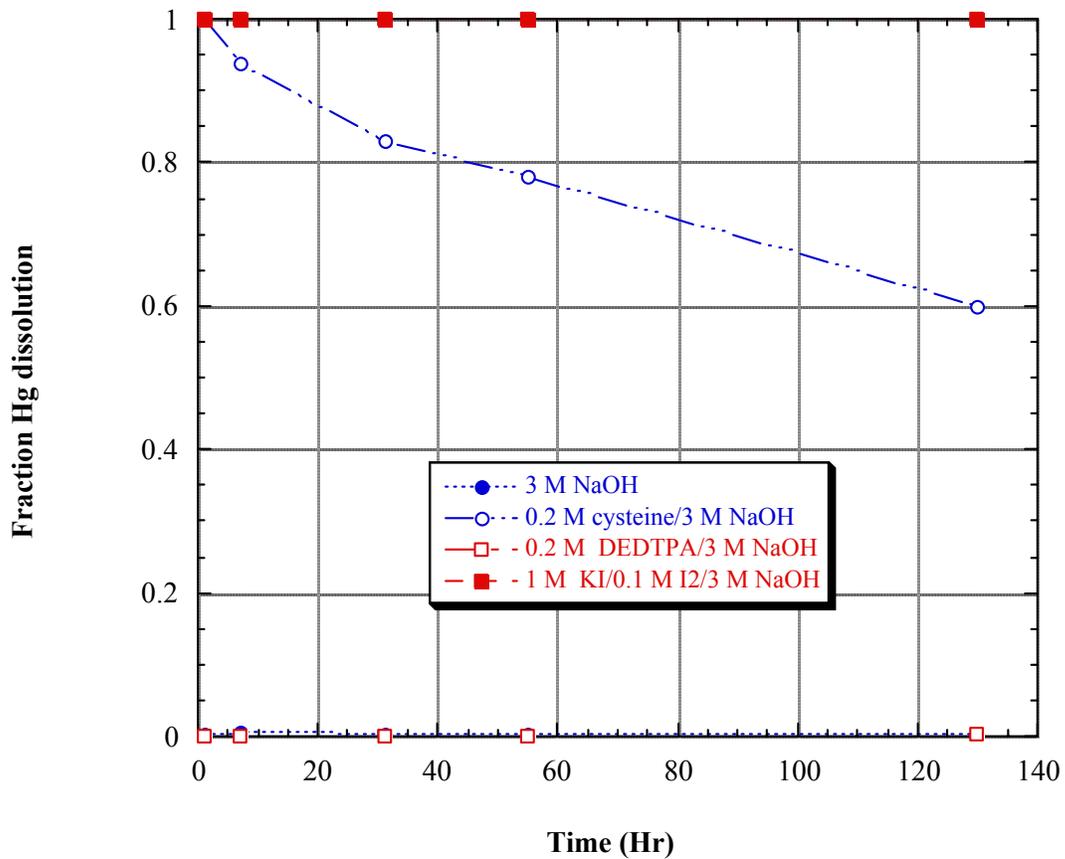
Figure 5.3. Mercury Dissolution into 3 M NaOH Leach Solutions

5.5

6.0 References

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Appendix A

**Glass Formulation Information for Long-Leached
(3 M NaOH, 100°C, 168 h) S-110 Sludge**

Appendix A: Glass Formulation Information for Long-Leached (3 M NaOH, 100°C, 168 h) S-110 Sludge

Oxide	Long Leach	LL-95%Cr	LL-95%Cr,10Mn
Starting Waste Mass	1.163	1.163	1.163
Final Waste Mass	1.061	1.013	1.013
Glass Composition			
Ag_2O	0.0000	0.0000	0.0000
Al_2O_3	0.0730	0.0396	0.0174
B_2O_3	0.0722	0.0500	0.0500
BaO	0.0005	0.0010	0.0013
BeO	0.0000	0.0000	0.0000
Bi_2O_3	0.0025	0.0050	0.0064
CaO	0.0046	0.0090	0.0117
CdO	0.0002	0.0003	0.0004
Ce_2O_3	0.0005	0.0009	0.0012
CoO	0.0000	0.0001	0.0001
Cr_2O_3	0.0100	0.0010	0.0013
CuO	0.0000	0.0000	0.0000
Fe_2O_3	0.0550	0.1079	0.1402
La_2O_3	0.0005	0.0011	0.0014
Li_2O	0.0500	0.0416	0.0110
MgO	0.0017	0.0033	0.0043
MnO	0.0204	0.0400	0.0520
MoO_3	0.0000	0.0000	0.0001
Na_2O	0.1395	0.1078	0.1312
Nd_2O_3	0.0008	0.0016	0.0020
P_2O_5	0.0005	0.0010	0.0012
PbO	0.0004	0.0009	0.0011
PdO	0.0004	0.0007	0.0010
SiO_2	0.4925	0.4408	0.3741
SrO	0.0024	0.0046	0.0060
ThO_2	0.0004	0.0008	0.0010
TiO_2	0.0002	0.0004	0.0005
U_3O_8	0.0707	0.1386	0.1802
V_2O_5	0.0000	0.0001	0.0001
Y_2O_3	0.0001	0.0003	0.0003
ZnO	0.0003	0.0005	0.0007
ZrO_2	0.0006	0.0013	0.0016
Total	1.0000	1.0000	1.0000

Loading Information

Mass of glass per mass of final waste	4.75	2.5372	1.9520
Loading	0.211	0.394	0.512
Density	2.63	2.84	2.99
Glass Mass/Initial Waste Mass	4.3	2.2	1.7

Estimated Properies and Restricted Component Levels

NM	0.0000	0.0000	0.0000
Na+Li+K	0.19	0.15	0.14
Normalized Si (np)	0.70	0.75	0.72
Normalized Alk (imm)	0.25	0.23	0.25
PCT B, new	1.00	0.40	0.42
PCT Li, new	0.88	0.42	0.38
PCT Na, new	0.86	0.44	0.67
PCT B, cvs	1.33	1.11	1.98
PCT Li, cvs	1.19	0.98	1.50
PCT Na, cvs	1.04	0.82	1.68
visc(T), new	6.00	6.00	6.00
visc(T), cvs	4.5	3.8	3.2
visc(1150), cvs	4.5	4.1	3.6
ec(T), cvs	54	44	34
ec(1150), cvs	53	44	34
spinel TL new	1000	959	1000
zircon TL new	536	617	548

Frit Composition

B_2O_3	0.0909	0.0810	0.1000
Fe_2O_3	0.0000	0.0000	0.0000
Li_2O	0.0632	0.0683	0.0220
Na_2O	0.1472	0.1023	0.1472
SiO_2	0.6150	0.7051	0.7308

Appendix B

Glass Formulation Information for Oxidatively-Leached S-110 Sludge at 4 mass% MnO

Appendix B: Glass Formulation Information for Oxidatively-Leached S-110 Sludge at 4 mass% MnO

Oxidant	NaMnO₄	NaMnO₄	NaMnO₄	NaMnO₄	NaFeO₄	NaFeO₄	NaFeO₄	NaFeO₄	None	None
Temp	30	30	85	85	30	30	85	85	30	30
[OH]	0.1	3	0.1	3	1.1	3	1.1	3	0.1	3
Glass Composition										
Al_2O_3	0.0722	0.0746	0.0515	0.0352	0.0706	0.0731	0.0492	0.0484	0.1489	0.1487
As_2O_5	0.0005	0.0005	0.0004	0.0003	0.0005	0.0006	0.0004	0.0004	0.0001	0.0000
B_2O_3	0.1500	0.1456	0.1500	0.1500	0.0500	0.0500	0.0500	0.0500	0.1500	0.1500
BaO	0.0001	0.0002	0.0001	0.0001	0.0002	0.0001	0.0002	0.0002	0.0000	0.0000
Bi_2O_3	0.0016	0.0018	0.0013	0.0015	0.0019	0.0018	0.0021	0.0022	0.0004	0.0005
CaO	0.0043	0.0043	0.0020	0.0021	0.0026	0.0027	0.0027	0.0027	0.0007	0.0007
CdO	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000
Cr_2O_3	0.0055	0.0035	0.0033	0.0021	0.0057	0.0049	0.0032	0.0034	0.0094	0.0095
Fe_2O_3	0.0415	0.0270	0.0568	0.0818	0.1274	0.1370	0.1624	0.1644	0.0275	0.0258
La_2O_3	0.0001	0.0002	0.0001	0.0002	0.0003	0.0002	0.0003	0.0003	0.0000	0.0001
Li_2O	0.0420	0.0494	0.0500	0.0500	0.0434	0.0447	0.0345	0.0500	0.0500	0.0500
MgO	0.0006	0.0007	0.0006	0.0007	0.0008	0.0008	0.0009	0.0009	0.0002	0.0002
MnO	0.0400	0.0400	0.0400	0.0400	0.0089	0.0080	0.0107	0.0109	0.0020	0.0025
Na_2O	0.1121	0.1079	0.0892	0.0774	0.1646	0.1651	0.1575	0.1424	0.1363	0.1360
Nb_2O_5	0.0002	0.0003	0.0003	0.0003	0.0004	0.0003	0.0004	0.0004	0.0001	0.0001
P_2O_5	0.0007	0.0008	0.0007	0.0004	0.0009	0.0009	0.0007	0.0005	0.0004	0.0003
PbO	0.0004	0.0003	0.0004	0.0002	0.0003	0.0003	0.0006	0.0007	0.0002	0.0002
SiO_2	0.4960	0.5059	0.5266	0.5287	0.4855	0.4744	0.4830	0.4813	0.4653	0.4646
SrO	0.0018	0.0021	0.0015	0.0017	0.0019	0.0019	0.0023	0.0024	0.0005	0.0006
TiO_2	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000
U_3O_8	0.0296	0.0344	0.0245	0.0267	0.0335	0.0324	0.0376	0.0376	0.0078	0.0097
ZnO	0.0003	0.0001	0.0003	0.0001	0.0002	0.0001	0.0003	0.0002	0.0001	0.0001
ZrO_2	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0003	0.0003	0.0001	0.0001
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Oxidant	NaMnO$_4$	NaMnO$_4$	NaMnO$_4$	NaMnO$_4$	NaFeO$_4$	NaFeO$_4$	NaFeO$_4$	NaFeO$_4$	None	None
Loading Information										
Glass Mass/Final Waste Mass	4.61	4.42	5.76	4.95	3.54	3.41	3.32	3.34	18.67	15.99
Loading	0.217	0.226	0.173	0.202	0.283	0.293	0.301	0.300	0.054	0.063
Density	2.53	2.53	2.53	2.55	2.63	2.65	2.67	2.68	2.43	2.44
Estimated Properies and Restricted Component Levels										
NM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na+Li+K	0.15	0.16	0.14	0.13	0.21	0.21	0.19	0.19	0.19	0.19
Normalized Si (np)	0.73	0.73	0.79	0.82	0.67	0.67	0.70	0.72	0.62	0.62
Normalized Alk (imm)	0.19	0.19	0.17	0.16	0.28	0.29	0.26	0.27	0.23	0.23
PCT B, new	1.00	1.00	1.00	1.00	1.00	1.00	0.94	1.00	1.00	1.00
PCT Li, new	0.93	0.97	0.99	1.00	0.75	0.74	0.69	0.78	0.77	0.77
PCT Na, new	0.70	0.68	0.64	0.64	1.00	1.00	1.00	0.97	0.57	0.57
PCT B, cvs	1.78	1.75	2.05	2.30	1.19	1.17	1.34	1.48	0.57	0.58
PCT Li, cvs	1.65	1.67	1.88	2.04	0.91	0.87	0.96	1.05	0.56	0.56
PCT Na, cvs	1.11	1.09	1.17	1.26	1.01	0.99	1.13	1.14	0.38	0.39
visc(T), new	6.00	5.71	6.00	5.64	5.43	4.73	6.00	3.94	6.00	6.00
visc(T), cvs	4.44	4.19	4.59	4.43	4.64	4.09	5.26	3.44	5.57	5.53
visc(1150), cvs	4.63	4.38	4.78	4.63	4.52	3.98	5.12	3.39	5.49	5.47
ec(T), cvs	34	37	32	29	57	60	46	56	43	43
ec(1150), cvs	33	36	31	29	57	60	46	57	43	43
spinel TL new	855	802	825	831	1000	1000	1000	1000	1000	1000
zircon TL new	631	628	683	716	510	510	542	558	614	613
Frit Composition										
B$_2$O$_3$	0.1909	0.1876	0.1811	0.1877	0.0692	0.0702	0.0710	0.0709	0.1585	0.1600
Fe$_2$O$_3$	0.0250	0.0000	0.0475	0.0763	0.0000	0.0000	0.0000	0.0000	0.0228	0.0194
Li$_2$O	0.0535	0.0638	0.0604	0.0626	0.0604	0.0631	0.0493	0.0713	0.0528	0.0533
Na$_2$O	0.1128	0.1076	0.0855	0.0152	0.2039	0.2053	0.1997	0.1778	0.1392	0.1395
SiO$_2$	0.6178	0.6410	0.6255	0.6582	0.6664	0.6614	0.6800	0.6800	0.4885	0.4921

Oxidant	None	None	K$_2$S$_2$O$_8$	K$_2$S$_2$O$_8$	K$_2$S$_2$O$_8$	K$_2$S$_2$O$_8$	None	None	None
Temp	85	85	30	30	85	85	0	0	0

Oxidant	None	None	K₂S₂O₈	K₂S₂O₈	K₂S₂O₈	K₂S₂O₈	None	None	None
[OH]	0.1	3	0.1	3	0.1	3	0	0	0
Glass Composition									
Al_2O_3	0.1489	0.1445	0.1483	0.1229	0.1222	0.1124	0.1487	0.1488	0.1487
As_2O_5	0.0001	0.0002	0.0002	0.0009	0.0008	0.0008	0.0000	0.0000	0.0000
B_2O_3	0.1500	0.1483	0.1500	0.1500	0.0759	0.0500	0.1500	0.1500	0.1500
BaO	0.0000	0.0001	0.0001	0.0003	0.0003	0.0004	0.0000	0.0000	0.0000
Bi_2O_3	0.0004	0.0010	0.0008	0.0026	0.0031	0.0031	0.0004	0.0004	0.0004
CaO	0.0006	0.0016	0.0009	0.0038	0.0038	0.0052	0.0005	0.0005	0.0005
CdO	0.0000	0.0001	0.0000	0.0001	0.0001	0.0001	0.0000	0.0000	0.0000
Cr_2O_3	0.0094	0.0100	0.0098	0.0080	0.0085	0.0067	0.0095	0.0095	0.0095
Fe_2O_3	0.0276	0.0183	0.0211	0.0416	0.0418	0.0573	0.0270	0.0272	0.0271
La_2O_3	0.0001	0.0002	0.0001	0.0004	0.0004	0.0005	0.0001	0.0001	0.0001
Li_2O	0.0500	0.0482	0.0500	0.0323	0.0500	0.0489	0.0500	0.0500	0.0500
MgO	0.0002	0.0006	0.0003	0.0016	0.0016	0.0021	0.0002	0.0002	0.0002
MnO	0.0020	0.0065	0.0036	0.0138	0.0136	0.0204	0.0019	0.0019	0.0019
Na_2O	0.1362	0.1354	0.1354	0.1357	0.1573	0.1599	0.1365	0.1365	0.1365
Nb_2O_5	0.0001	0.0003	0.0002	0.0008	0.0007	0.0010	0.0001	0.0001	0.0001
P_2O_5	0.0003	0.0004	0.0006	0.0021	0.0025	0.0021	0.0009	0.0009	0.0009
PbO	0.0002	0.0003	0.0003	0.0008	0.0012	0.0008	0.0002	0.0002	0.0002
SiO_2	0.4651	0.4575	0.4629	0.4219	0.4561	0.4444	0.4653	0.4654	0.4654
SrO	0.0005	0.0016	0.0008	0.0034	0.0034	0.0049	0.0004	0.0004	0.0004
TiO_2	0.0000	0.0001	0.0000	0.0002	0.0002	0.0002	0.0000	0.0000	0.0000
U_3O_8	0.0080	0.0243	0.0140	0.0557	0.0550	0.0770	0.0079	0.0077	0.0078
ZnO	0.0001	0.0002	0.0001	0.0002	0.0006	0.0002	0.0001	0.0001	0.0001
ZrO_2	0.0001	0.0002	0.0001	0.0004	0.0004	0.0006	0.0001	0.0000	0.0001
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Loading Information									
Glass Mass/Final Waste Mass	17.77	9.86	11.18	3.40	3.18	2.75	16.48	16.69	16.59
Loading	0.056	0.101	0.089	0.295	0.314	0.363	0.061	0.060	0.060
Density	2.43	2.47	2.44	2.57	2.60	2.67	2.43	2.43	2.43

Oxidant	None	None	$K_2S_2O_8$	$K_2S_2O_8$	$K_2S_2O_8$	$K_2S_2O_8$	None	None	None
Estimated Properies and Restricted Component Levels									
NM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na+Li+K	0.19	0.18	0.19	0.17	0.21	0.21	0.19	0.19	0.19
Normalized Si (np)	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
Normalized Alk (imm)	0.23	0.23	0.23	0.23	0.28	0.30	0.23	0.23	0.23
PCT B, new	1.00	1.00	1.00	1.00	0.71	0.53	1.00	1.00	1.00
PCT Li, new	0.77	0.79	0.78	0.76	0.59	0.47	0.77	0.77	0.77
PCT Na, new	0.57	0.59	0.57	0.66	0.60	0.53	0.57	0.57	0.57
PCT B, cvs	0.57	0.63	0.59	0.81	0.64	0.59	0.58	0.58	0.58
PCT Li, cvs	0.56	0.61	0.58	0.75	0.60	0.56	0.56	0.56	0.56
PCT Na, cvs	0.38	0.42	0.39	0.56	0.52	0.51	0.39	0.39	0.39
visc(T), new	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
visc(T), cvs	5.57	5.28	5.45	4.99	4.56	4.22	5.56	5.56	5.56
visc(1150), cvs	5.50	5.27	5.40	5.07	4.62	4.35	5.49	5.49	5.49
ec(T), cvs	43	44	44	36	62	68	44	44	44
ec(1150), cvs	43	43	43	36	61	67	43	43	43
spinel TL new	1000	1000	1000	993	1000	1000	1000	1000	1000
zircon TL new	614	605	611	607	519	499	613	613	613
Frit Composition									
B_2O_3	0.1589	0.1649	0.1646	0.2126	0.1102	0.0778	0.1595	0.1594	0.1595
Fe_2O_3	0.0227	0.0000	0.0119	0.0000	0.0000	0.0000	0.0226	0.0228	0.0227
Li_2O	0.0530	0.0536	0.0549	0.0456	0.0726	0.0765	0.0532	0.0532	0.0532
Na_2O	0.1365	0.1409	0.1391	0.1566	0.1811	0.1704	0.1329	0.1332	0.1331
SiO_2	0.4904	0.5062	0.5025	0.5852	0.6360	0.6753	0.4919	0.4915	0.4917

Appendix C

Glass Formulation Information for Oxidatively-Leached S-110 Sludge at 10 mass% MnO

Appendix C: Glass Formulation Information for Oxidatively-Leached S-110 Sludge at 10 mass% MnO

Oxidant	NaMnO$_4$	NaMnO$_4$	NaMnO$_4$	NaMnO$_4$	NaFeO$_4$	NaFeO$_4$	NaFeO$_4$	NaFeO$_4$	None	None
Temp	30	30	85	85	30	30	85	85	30	30
[OH]	0.1	3	0.1	3	1.1	3	1.1	3	0.1	3
Glass Composition										
Al$_2$O$_3$	0.0944	0.1024	0.1267	0.1384	0.0706	0.0731	0.0492	0.0484	0.1489	0.1487
As$_2$O5	0.0006	0.0006	0.0011	0.0005	0.0005	0.0006	0.0004	0.0004	0.0001	0.0000
B$_2$O$_3$	0.1231	0.1500	0.1500	0.1183	0.0500	0.0500	0.0500	0.0500	0.1500	0.1500
BaO	0.0002	0.0002	0.0003	0.0002	0.0002	0.0001	0.0002	0.0002	0.0000	0.0000
Bi$_2$O$_3$	0.0021	0.0025	0.0031	0.0026	0.0019	0.0018	0.0021	0.0022	0.0004	0.0005
CaO	0.0056	0.0059	0.0048	0.0036	0.0026	0.0027	0.0027	0.0027	0.0007	0.0007
CdO	0.0001	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000
Cr$_2$O$_3$	0.0072	0.0048	0.0081	0.0037	0.0057	0.0049	0.0032	0.0034	0.0094	0.0095
Fe$_2$O$_3$	0.0286	0.0371	0.0430	0.0363	0.1274	0.1370	0.1624	0.1644	0.0275	0.0258
La$_2$O$_3$	0.0002	0.0003	0.0004	0.0003	0.0003	0.0002	0.0003	0.0003	0.0000	0.0001
Li$_2$O	0.0222	0.0376	0.0500	0.0500	0.0434	0.0447	0.0345	0.0500	0.0500	0.0500
MgO	0.0008	0.0009	0.0014	0.0011	0.0008	0.0008	0.0009	0.0009	0.0002	0.0002
MnO	0.0523	0.0549	0.0984	0.0694	0.0089	0.0080	0.0107	0.0109	0.0020	0.0025
Na$_2$O	0.1767	0.1455	0.0901	0.1132	0.1646	0.1651	0.1575	0.1424	0.1363	0.1360
Nb$_2$O$_5$	0.0003	0.0005	0.0006	0.0005	0.0004	0.0003	0.0004	0.0004	0.0001	0.0001
P$_2$O$_5$	0.0010	0.0011	0.0017	0.0006	0.0009	0.0009	0.0007	0.0005	0.0004	0.0003
PbO	0.0006	0.0004	0.0009	0.0003	0.0003	0.0003	0.0006	0.0007	0.0002	0.0002
SiO$_2$	0.4423	0.4044	0.3536	0.4104	0.4855	0.4744	0.4830	0.4813	0.4653	0.4646
SrO	0.0023	0.0029	0.0036	0.0030	0.0019	0.0019	0.0023	0.0024	0.0005	0.0006
TiO$_2$	0.0001	0.0002	0.0003	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000
U$_3$O$_8$	0.0387	0.0472	0.0604	0.0463	0.0335	0.0324	0.0376	0.0376	0.0078	0.0097
ZnO	0.0004	0.0002	0.0006	0.0001	0.0002	0.0001	0.0003	0.0002	0.0001	0.0001
ZrO$_2$	0.0002	0.0003	0.0004	0.0004	0.0002	0.0002	0.0003	0.0003	0.0001	0.0001
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Loading Information										
Glass Mass/Final Waste Mass	3.53	3.22	2.34	2.85	3.54	3.41	3.32	3.34	18.67	15.99

C.1

Oxidant	NaMnO$_4$	NaMnO$_4$	NaMnO$_4$	NaMnO$_4$	NaFeO$_4$	NaFeO$_4$	NaFeO$_4$	NaFeO$_4$	None	None
Loading	0.283	0.311	0.427	0.351	0.283	0.293	0.301	0.300	0.054	0.063
Density	2.59	2.63	2.73	2.63	2.63	2.65	2.67	2.68	2.43	2.44

Estimated Properies and Restricted Component Levels

NM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na+Li+K	0.20	0.18	0.14	0.16	0.21	0.21	0.19	0.19	0.19	0.19
Normalized Si (np)	0.62	0.62	0.62	0.62	0.67	0.67	0.70	0.72	0.62	0.62
Normalized Alk (imm)	0.26	0.25	0.22	0.24	0.28	0.29	0.26	0.27	0.23	0.23
PCT B, new	1.00	1.00	0.13	0.16	1.00	1.00	0.94	1.00	1.00	1.00
PCT Li, new	0.82	0.87	0.18	0.19	0.75	0.74	0.69	0.78	0.77	0.77
PCT Na, new	1.00	0.81	0.11	0.14	1.00	1.00	1.00	0.97	0.57	0.57
PCT B, cvs	1.95	2.01	0.57	0.36	1.19	1.17	1.34	1.48	0.57	0.58
PCT Li, cvs	1.69	1.71	0.61	0.40	0.91	0.87	0.96	1.05	0.56	0.56
PCT Na, cvs	1.56	1.32	0.29	0.22	1.01	0.99	1.13	1.14	0.38	0.39
visc(T), new	6.00	3.00	3.12	6.00	5.43	4.73	6.00	3.94	6.00	6.00
visc(T), cvs	3.78	1.96	1.48	3.35	4.64	4.09	5.26	3.44	5.57	5.53
visc(1150), cvs	3.96	2.12	1.86	3.86	4.52	3.98	5.12	3.39	5.49	5.47
ec(T), cvs	44	49	46	47	57	60	46	56	43	43
ec(1150), cvs	43	48	45	46	57	60	46	57	43	43
spinel TL new	841	825	1000	936	1000	1000	1000	1000	1000	1000
zircon TL new	455	519	684	646	510	510	542	558	614	613

Frit Composition

B$_2$O$_3$	0.1708	0.2169	0.2603	0.1816	0.0692	0.0702	0.0710	0.0709	0.1585	0.1600
Fe$_2$O$_3$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0228	0.0194
Li$_2$O	0.0309	0.0544	0.0869	0.0768	0.0604	0.0631	0.0493	0.0713	0.0528	0.0533
Na$_2$O	0.2033	0.1619	0.0773	0.0000	0.2039	0.2053	0.1997	0.1778	0.1392	0.1395
SiO$_2$	0.5950	0.5668	0.5754	0.6226	0.6664	0.6614	0.6800	0.6800	0.4885	0.4921

Oxidant	None	None	K$_2$S$_2$O$_8$	K$_2$S$_2$O$_8$	K$_2$S$_2$O$_8$	K$_2$S$_2$O$_8$	None	None	None
Temp	85	85	30	30	85	85	0	0	0
[OH]	0.1	3	0.1	3	0.1	3	0	0	0

Glass Composition

Al$_2$O$_3$	0.1489	0.1445	0.1483	0.1229	0.1222	0.1124	0.1487	0.1488	0.1487

Oxidant	None	None	$K_2S_2O_8$	$K_2S_2O_8$	$K_2S_2O_8$	$K_2S_2O_8$	None	None	None
As_2O_5	0.0001	0.0002	0.0002	0.0009	0.0008	0.0008	0.0000	0.0000	0.0000
B_2O_3	0.1500	0.1483	0.1500	0.1500	0.0759	0.0500	0.1500	0.1500	0.1500
BaO	0.0000	0.0001	0.0001	0.0003	0.0003	0.0004	0.0000	0.0000	0.0000
Bi_2O_3	0.0004	0.0010	0.0008	0.0026	0.0031	0.0031	0.0004	0.0004	0.0004
CaO	0.0006	0.0016	0.0009	0.0038	0.0038	0.0052	0.0005	0.0005	0.0005
CdO	0.0000	0.0001	0.0000	0.0001	0.0001	0.0001	0.0000	0.0000	0.0000
Cr_2O_3	0.0094	0.0100	0.0098	0.0080	0.0085	0.0067	0.0095	0.0095	0.0095
Fe_2O_3	0.0276	0.0183	0.0211	0.0416	0.0418	0.0573	0.0270	0.0272	0.0271
La_2O_3	0.0001	0.0002	0.0001	0.0004	0.0004	0.0005	0.0001	0.0001	0.0001
Li_2O	0.0500	0.0482	0.0500	0.0323	0.0500	0.0489	0.0500	0.0500	0.0500
MgO	0.0002	0.0006	0.0003	0.0016	0.0016	0.0021	0.0002	0.0002	0.0002
MnO	0.0020	0.0065	0.0036	0.0138	0.0136	0.0204	0.0019	0.0019	0.0019
Na_2O	0.1362	0.1354	0.1354	0.1357	0.1573	0.1599	0.1365	0.1365	0.1365
Nb_2O_5	0.0001	0.0003	0.0002	0.0008	0.0007	0.0010	0.0001	0.0001	0.0001
P_2O_5	0.0003	0.0004	0.0006	0.0021	0.0025	0.0021	0.0009	0.0009	0.0009
PbO	0.0002	0.0003	0.0003	0.0008	0.0012	0.0008	0.0002	0.0002	0.0002
SiO_2	0.4651	0.4575	0.4629	0.4219	0.4561	0.4444	0.4653	0.4654	0.4654
SrO	0.0005	0.0016	0.0008	0.0034	0.0034	0.0049	0.0004	0.0004	0.0004
TiO_2	0.0000	0.0001	0.0000	0.0002	0.0002	0.0002	0.0000	0.0000	0.0000
U_3O_8	0.0080	0.0243	0.0140	0.0557	0.0550	0.0770	0.0079	0.0077	0.0078
ZnO	0.0001	0.0002	0.0001	0.0002	0.0006	0.0002	0.0001	0.0001	0.0001
ZrO_2	0.0001	0.0002	0.0001	0.0004	0.0004	0.0006	0.0001	0.0000	0.0001
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Loading Information									
Glass Mass/Final Waste Mass	17.77	9.86	11.18	3.40	3.18	2.75	16.48	16.69	16.59
Loading	0.056	0.101	0.089	0.295	0.314	0.363	0.061	0.060	0.060
Density	2.43	2.47	2.44	2.57	2.60	2.67	2.43	2.43	2.43
Estimated Properies and Restricted Component Levels									
NM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na+Li+K	0.19	0.18	0.19	0.17	0.21	0.21	0.19	0.19	0.19
Normalized Si (np)	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
Normalized Alk (imm)	0.23	0.23	0.23	0.23	0.28	0.30	0.23	0.23	0.23

Oxidant	None	None	K$_2$S$_2$O$_8$	K$_2$S$_2$O$_8$	K$_2$S$_2$O$_8$	K$_2$S$_2$O$_8$	None	None	None
PCT B, new	1.00	1.00	1.00	1.00	0.71	0.53	1.00	1.00	1.00
PCT Li, new	0.77	0.79	0.78	0.76	0.59	0.47	0.77	0.77	0.77
PCT Na, new	0.57	0.59	0.57	0.66	0.60	0.53	0.57	0.57	0.57
PCT B, cvs	0.57	0.63	0.59	0.81	0.64	0.59	0.58	0.58	0.58
PCT Li, cvs	0.56	0.61	0.58	0.75	0.60	0.56	0.56	0.56	0.56
PCT Na, cvs	0.38	0.42	0.39	0.56	0.52	0.51	0.39	0.39	0.39
visc(T), new	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
visc(T), cvs	5.57	5.28	5.45	4.99	4.56	4.22	5.56	5.56	5.56
visc(1150), cvs	5.50	5.27	5.40	5.07	4.62	4.35	5.49	5.49	5.49
ec(T), cvs	43	44	44	36	62	68	44	44	44
ec(1150), cvs	43	43	43	36	61	67	43	43	43
spinel TL new	1000	1000	1000	993	1000	1000	1000	1000	1000
zircon TL new	614	605	611	607	519	499	613	613	613
Frit Composition									
B$_2$O$_3$	0.1589	0.1649	0.1646	0.2126	0.1102	0.0778	0.1595	0.1594	0.1595
Fe$_2$O$_3$	0.0227	0.0000	0.0119	0.0000	0.0000	0.0000	0.0226	0.0228	0.0227
Li$_2$O	0.0530	0.0536	0.0549	0.0456	0.0726	0.0765	0.0532	0.0532	0.0532
Na$_2$O	0.1365	0.1409	0.1391	0.1566	0.1811	0.1704	0.1329	0.1332	0.1331
SiO$_2$	0.4904	0.5062	0.5025	0.5852	0.6360	0.6753	0.4919	0.4915	0.4917

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