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Selective Leaching of Chromium from Washed 241-S-110 Hanford Tank Sludge

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ABSTRACT

This report describes our continuing studies directed at enhancing the dissolution of Cr(III) from Hanford tank sludges by treatment with oxidants under alkaline conditions. This study evaluates the use of ferrate, $FeO_4{}^{2-}$, permanganate, $MnO_4{}^{-}$, and persulfate, $S_2O_8{}^{2-}$, for selectively removing chromium from washed Hanford Tank 241-S-110 sludge. Variables examined include the initial hydroxide concentration, time, and temperature. It was found that all oxidants enhanced both the rate and extent of chromium dissolution, with more than 90% of the total chromium being dissolved under optimum conditions after 48-h contact times. The dissolved chromium was determined to be present as chromate, $CrO_4{}^{2-}$. Elevated transuranic (TRU) element concentrations in the leach solutions were observed, attributed to enhanced Pu dissolution, but in all cases, an immobilized form of the leach solutions would not be a TRU waste. Evaluation of the immobilized high-level waste (IHLW) that would be generated following oxidative alkaline leaching indicates that

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both extensive Al and Cr removal are needed to maximize the benefit of pretreatment. The amount of IHLW waste would be reduced by 20% by the almost quantitative Al removal documented to be possible through an extended caustic leach. Oxidative leaching of chromium sufficient to remove 95% of the remaining Cr provides for a further reduction of almost 50% in the amount of glass produced, for a total of roughly 70% volume reduction in glass over that produced from the washed, but otherwise untreated, 241-S-110 sludge.

Key Words: Ferrate; Permanganate; Persulfate; Oxidative leaching; Hanford tank sludge.

INTRODUCTION

Currently, there are approximately 200,000 m^3 of radioactive waste in the 177 underground storage tanks located at the U.S. Department of Energy's (DOE's) 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 previously 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 among all three phases.

These 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 into 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.[1] 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.[2] 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.[3,4] 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),[5] dissolution into alkaline solution as the tetrahydroxochromium(III) complex, $[Cr(OH)_4{}^-]$, was anticipated. However, prior studies indicate 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, and this precipitate does not readily redissolve in aqueous caustic media.[6] This observation also is consistent with previous reports of the low solubility of $Cr(OH)_3$ in acidic and near-neutral solutions at elevated temperature.[7]

While previous studies have indicated 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.[8] 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, $CrO_4{}^{2-}$.[9]

Studies over the last several years with Hanford tank sludge simulants and with actual Hanford tank sludges, have revealed that treating water-washed and caustic-leached solids with oxidants can significantly increase the effectiveness of chromium removal.[10–16] Tested oxidants to date include ozone, O_3,[10,11,13] hydrogen peroxide, H_2O_2,[11,14,15] permanganate, $MnO_4{}^-$,[10–12,14] oxygen, O_2,[12,15] persulfate, $S_2O_8{}^{2-}$,[15] and ferrate, $FeO_4{}^{2-}$.[16] 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(III) 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 rate of chromium(III) oxidation is relatively slow and suggests 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(III) dissolution complete within hours. Little enhanced dissolution of TRU elements is observed.
- Ferrate is both rapid and effective, with chromium(III) dissolution 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 weaknesses. As noted, 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 capable of attacking 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 TRU waste 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; 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.

In this report, we describe our most recent examination of oxidative alkaline leaching for the removal of water-insoluble chromium from Hanford tank sludge. The tested sludge in this study is from Hanford Tank 241-S-110, and the effectiveness and selectivity of three oxidants, persulfate, permanganate, and ferrate, on chromium dissolution are examined. Other key variables we evaluate include time, hydroxide concentration, and temperature. Since, as noted, each oxidant impacts the waste chemistry differently, we also evaluated the impact of oxidative alkaline leaching on loading of the resultant waste in glass.

EXPERIMENTAL DESCRIPTION

General

All reagents used in this work were of reagent-grade purity or higher. Lynntech, Inc. (College Station, TX) prepared the ferrate stock solution, as described previously.[16] Hydroxide concentrations of the reagents were determined by titration with a standard HCl solution. Permanganate and persulfate concentrations in the stock solutions were measured by titration with an oxalic acid solution.[17] The as-received ferrate concentration in the initial stock solution was determined at Pacific Northwest National Laboratory (PNNL) by measuring the absorbance at 505 nm and using the known ferrate extinction coefficient of $\varepsilon_{505} = 1080\,\mathrm{M^{-1}\,cm^{-1}}$.

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.[18]

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 K-α radiation and a solid-state detector. Measurement parameters include operation at 2-KW power and 0.02 degrees and 20 sec/step over a 2θ range of 5 to 65 degrees. The diffraction patterns were compared with known 2θ/intensity data from the International Centre for Diffraction Data (ICDD) database 49 (through 1999) to identify crystalline phases.

Description of the S-110 Sludge Sample

S-110 sludge belongs to Sort on Radioactive Waste Type (SORWT) Group I,[19] which is the same classification as the previously studied S-107 tank sludge.[16] 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[20] suggesting that approximately 27% of the Hanford single-shell tank sludge is derived from this waste stream. A secondary stream for S110 sludge comes from evaporator bottoms (EBs), and a tertiary stream composed of a mixture (MIX) of several miscellaneous wastes has been identified. The S-110 sludge sample was a composite of segments from two different core samples (Table 1). The composite sample was prepared at the Hanford 222-S Laboratory and shipped to PNNL in March 2001.

Initial Washing of the S-110 Solids

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 mass% 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. Further experimental details on the preparation of

Table 1. Description of S-110 sludge composite.

Sample ID[a]	Core number	Core date	Tank riser	Segment number	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.

the sludge composite, the washing of the S-110 tank sludge, and on the analysis of the washed S-110 sludge have been documented recently.[21]

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

Sixteen 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 were transferred into an

Table 2. ICP-AES determined composition of major components in dilute hydroxide-washed S-110 solids.

Component	Concentration, μg/g dried solids
Al	325,000
Cr	23,050
Fe	14,150
Mn	5,305
Na	30,000
Si	5,500
U	23,500

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 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 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

Table 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.

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.

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 (1700 *g* for at least 5 minutes) 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 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 analyses.[22]

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[23] recently compiled an expansive database of key properties of HLW glasses. First-order expansions of product consistency test (PCT) response, viscosity–temperature data, and liquidus 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 is the i^{th} component normalized mole fraction in glass, N is the number of components for which the model was fit, r_α is the normalized release of α (boron, sodium, and lithium) from a PCT, $T_{L,\beta}$ is the liquidus temperature in the β primary phase field (spinel and zircon), T is absolute temperature, and $r_{\alpha i}$, a_i, b_i, and $T_{\beta i}$ are the fitted model coefficients for the i^{th} component. Model coefficients from Hrma et al[23] 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[2] were used, and for electrical conductivity (ε) and density, (ρ) coefficients from Hrma et al[4] 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 may be 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 4. 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

Table 4. Glass property and composition constraints.

Constraint	Value	Unit	Purpose
Melter operating temperature (T_M)	1150	°C	Processability
T_L (sp)	≤ 1000	°C	Processability
T_L (zr)	≤ 1000	°C	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

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.[3]

RESULTS AND DISCUSSION

Crystalline Phase Identification in Washed S-110 Tank Sludge

Figure 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 2θ

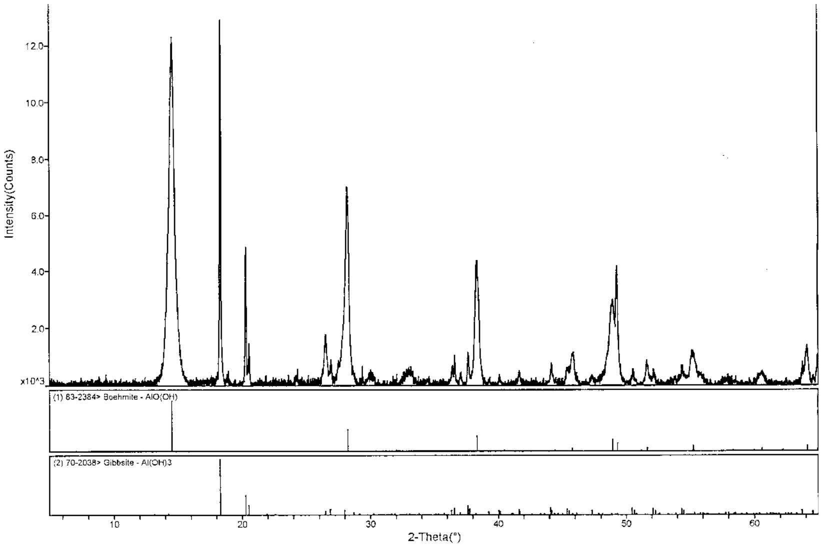

Figure 1. XRD of washed S-110 tank sludge.

positions and intensities for the identified compounds are shown. As can be seen from Fig. 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 for boehmite and gibbsite, respectively, a ratio of 80 to 90% boehmite and 10 to 20% gibbsite can be estimated.

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 Fig. 2 for the low-temperature (ca. 30°C) tests and in Fig. 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. Indeed, at elevated temperature, 3-M NaOH generates a substantial fraction of the maximum chromate concentrations observed during oxidant treatment.

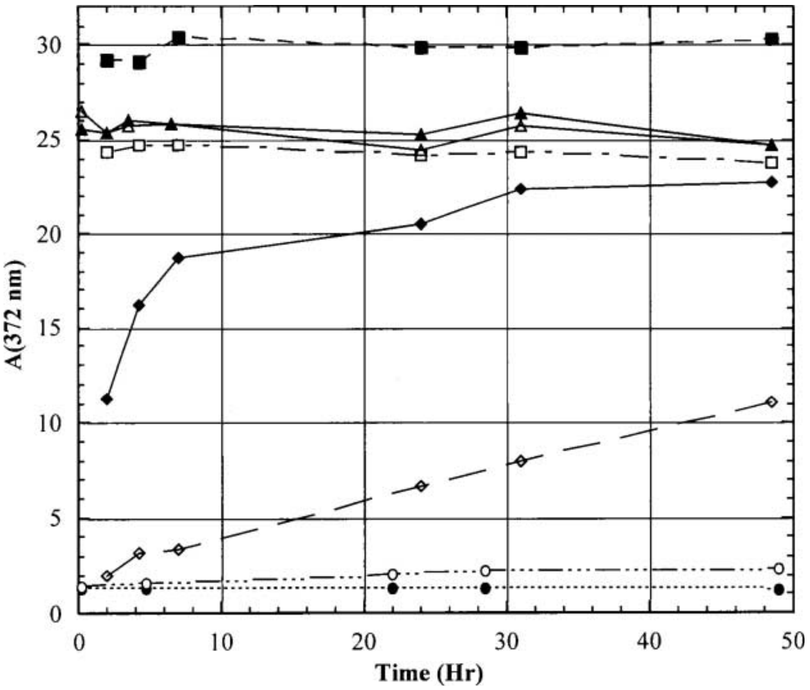

Figure 2. Chromate formation under alkaline conditions at low temperature (30°C). Filled circle: 0.1-M NaOH; open circle: 3-M NaOH; open diamond: 0.1-M NaOH, persulfate; filled diamond: 3-M NaOH, persulfate; open square: 0.1-M NaOH, permanganate; filled square: 3-M NaOH, permanganate; open triangle: 1.1-M NaOH, ferrate; and filled triangle: 3-M NaOH, ferrate.

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 2 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

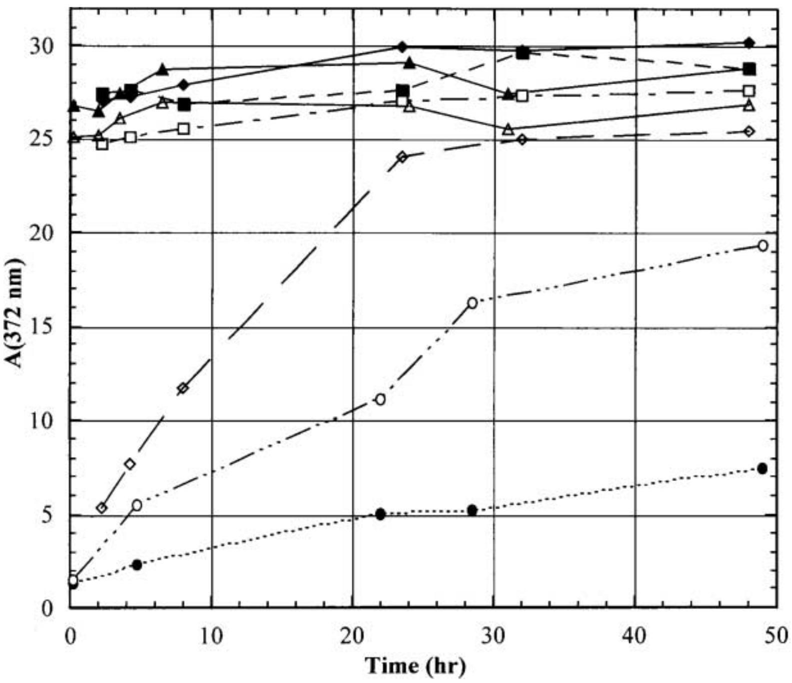

Figure 3. Chromate formation under alkaline conditions at high temperature (80 to 85°C). Filled circle: 0.1-M NaOH; open circle: 3-M NaOH; open diamond: 0.1-M NaOH, persulfate; filled diamond: 3-M NaOH, persulfate; open square: 0.1-M NaOH, permanganate; filled square: 3-M NaOH, permanganate; open triangle: 1.1-M NaOH, ferrate; and filled triangle: 3-M NaOH, ferrate.

(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.

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 (see Table 2), only aluminum, chromium, and silicon were found to any significant extent in the leach solutions. Occasionally, iron and manganese (in permanganate-containing leach solutions) were also found, generally at

Table 5. Major component removal from oxidative, alkaline leach solutions at 30°C, after 48 hours. (The last four columns indicate the % component removed.)

Initial $[OH^-]$, M	Oxidant	Total mass	Al	Cr	Si
0.1	None	0	1	5	76
3	None	0	7	10	78
0.1	MnO_4^-	8	3	87	77
3	MnO_4^-	16	15	93	81
0.1	$S_2O_8^{2-}$	5	2	48	76
3	$S_2O_8^{2-}$	16	8	89	89
1.1	FeO_4^{2-}	−3	6	88	83
3	FeO_4^{2-}	3	9	90	84

close to their detection limits. Table 5 summarizes the percentage of each of the major bulk components removed in the low-hydroxide contacts, and Table 6 summarizes the component removal from high-hydroxide leach solutions.

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 dissolutions despite the relatively short contact times. Increases in hydroxide concentration from

Table 6. Major component removal from oxidative, alkaline leach solutions at 80 to 85°C after 48 hours. (The last four columns indicate the % component removed.)

Initial $[OH^-]$, M	Oxidant	Total mass	Al	Cr	Si
0.1	None	8	11	25	83
3	None	58	62	72	93
0.1	MnO_4^-	5	12	90	74
3	MnO_4^-	44	49	95	81
0.1	$S_2O_8^{2-}$	9	8	89	74
3	$S_2O_8^{2-}$	39	41	94	85
1.1	FeO_4^{2-}	38	51	95	85
3	FeO_4^{2-}	40	51	94	90

0.1 to 3 M and temperature increases from 30 to 80 to 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. Because of the slow dissolution kinetics typically found for boehmite, more extended leaching times would be expected to increase aluminum dissolution, and recent studies of washed S-110 sludge verify this expectation.[21]

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,[12] 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.[21] 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, chromium dissolutions of around 90 to 95% were observed. The final chromium concentrations in the oxidatively-leached S-110 sludge (Table 7) reflected this enhanced dissolution in their markedly lower chromium concentrations as compared to the simple washed S-110 sludge (see Table 2). In the oxidatively leached sludge, residual chromium concentrations generally dropped from their initial $>20{,}000$ ppm to as low as 2000 to 3000 ppm.

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

In our previous studies on chromium dissolution into alkaline-leach solutions, the form of chromium in alkaline-leach solutions was evaluated by considering chromium to be present either in the $+6$ oxidation state as chromate, CrO_4^{2-}, or 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

Table 7. Final major or key bulk component concentrations in leached S-110 sludge. (The last eight columns indicate the component concentration in leached sludge, μg/g.)

$[OH^-]_{initial}$	Oxidant	Temperature (°C)	Al	Cr	Fe	Mn	Na	P	Si	U
0.1	None	30	350,000	23,400	14,900	5,550	12,200	620	4,900	24,100
3	None	30	333,000	19,700	16,100	5,950	11,800	420	4,670	25,000
0.1	MnO_4^-	30	332,000	3,290	13,300	26,900	15,300	280	4,930	21,800
3	MnO_4^-	30	349,000	2,130	16,700	27,400	16,200	310	4,100	25,800
0.1	$S_2O_8^{2-}$	30	338,000	13,100	14,400	5,390	12,700	500	4,900	23,200
3	$S_2O_8^{2-}$	30	355,000	3,000	15,900	5,820	10,200	490	2,300	25,800
1.1	FeO_4^{2-}	30	305,000	3,190	72,700	5,630	11,100	310	2,800	23,200
3	FeO_4^{2-}	30	304,000	2,650	75,300	4,880	11,700	310	2,600	21,600
0.1	None	85	310,000	22,300	15,100	5,510	19,000	470	3,800	23,500
3	None	85	332,000	16,900	31,600	12,500	16,200	390	3,100	50,900
0.1	MnO_4^-	80	330,000	2,740	14,800	37,500	16,700	370	5,450	25,200
3	MnO_4^-	80	293,000	2,310	23,000	48,700	76,100	250	2,600	35,600
0.1	$S_2O_8^{2-}$	80	358,000	3,200	16,200	5,850	13,600	600	5,180	25,800
3	$S_2O_8^{2-}$	80	337,000	2,610	22,700	8,930	21,600	510	3,800	37,000
1.1	FeO_4^{2-}	80	273,000	2,310	119,000	8,690	14,000	310	3,900	33,400
3	FeO_4^{2-}	80	281,000	2,520	126,000	9,260	14,500	250	2,600	34,900

more than two orders of magnitude lower.[6] 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, with the presence of chromium(III) assumed to be responsible for observed differences. Table 8 shows the molar ratios of the chromate concentrations in the final leach + washes solutions, as determined by visible spectroscopy to the total chromium concentrations as determined by ICP/AES. Clearly, within the 15% uncertainty assigned to the ICP-AES measurement, the chromate and total chromium concentrations were identical. The exception to this statement is from the 3-M NaOH, 30°C test. However, in that test, the dilution of the tested solution was so large that the measured chromate absorbance was significantly 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, if not all, of the dissolved chromium in these alkaline leach solutions was present as chromate.

Table 8. Measured ratio of $[CrO_4^{2-}]/[Cr]$ in the leach + 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

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 but 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. The solution concentrations of TRU elements needed to transform a LAW stream to a TRU stream (>100 nCi/g) are stringent. 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 9.

Clearly, adding oxidants enhanced the dissolution of the TRU elements. Although the high detection limits in the GEA analysis prevented distinguishing directly whether any Am dissolution actually occurred,

Table 9. Key radionuclide dissolution in oxidative alkaline leachate solutions. (The last five columns indicate the percentage component removed.)

$[OH]_{initial}$	Oxidant	Temperature (°C)	^{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

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, and 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 9 do not address the question of whether the leachate solutions would generate a low-level immobilized waste or a TRU immobilized waste. This can be evaluated by considering the TRU concentration at 20 mass% Na_2O, which reflects the likely component concentrations in the immobilized LAW. Table 10 shows the TRU activity at 20 mass% Na_2O.

Two cases are presented in Table 10. One case (leachate and 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

Table 10. TRU leachate concentration (nCi/g) at 20 mass% Na_2O. (The last two columns indicate TRU activity, nCi/g.)

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

the 20 mass% 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 10 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 mass% Na_2O and does include the density correction since these densities vary markedly from test to test. In this analysis, the total TRU activity in each leachate and wash 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 density. The correction factor required to convert the Na concentration to that of 20 mass% Na_2O was calculated. This concentration factor was applied to the TRU activity to give the initial leachate column in Table 10.

The conclusion derived from the calculations summarized in Table 10 is that in no instance will either the leach solutions themselves or the leach solutions plus washes generate a TRU immobilized 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 low-level waste (LLW). In one instance, the TRU concentration comes quite close to the LLW TRU limit. The larger concentration factors required to reach 20 mass% Na_2O in these low sodium leachates, rather than significantly greater TRU concentrations in the liquids themselves, are the predominant reason for generating these potential Class C LLWs. In all other instances, the TRU content in the immobilized leach solutions would generate a Class A ($<$ 10 nCi/g) LLW.

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 minimize the amount of sludge produced from a given amount of HLW sludge. 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 7. Currently, if individual component concentration limits solely 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 mass% chromium oxide in the sludge becomes problematic in that it may impact the percentage of that sludge that can be loaded into the glass. Inspection of the chromium concentration in the initial washed S-110 sludge (see Table 2) or in the leached S-110 sludges (see Table 7) 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 to 85°C for 48 h, may not provide adequate chromium removal. However, with the exception of persulfate at low hydroxide and low temperature, all leaching with 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 mass% 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 Fig. 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

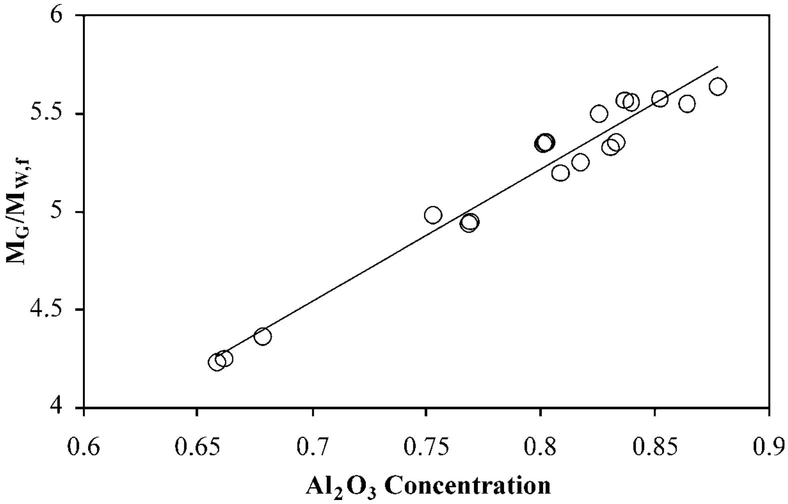

Figure 4. Estimated glass mass (M_G) per final waste mass ($M_{W,f}$) as a function of Al_2O_3 concentration in waste (mass%).

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 reported in Tables 5 and 6. Figure 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. 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 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

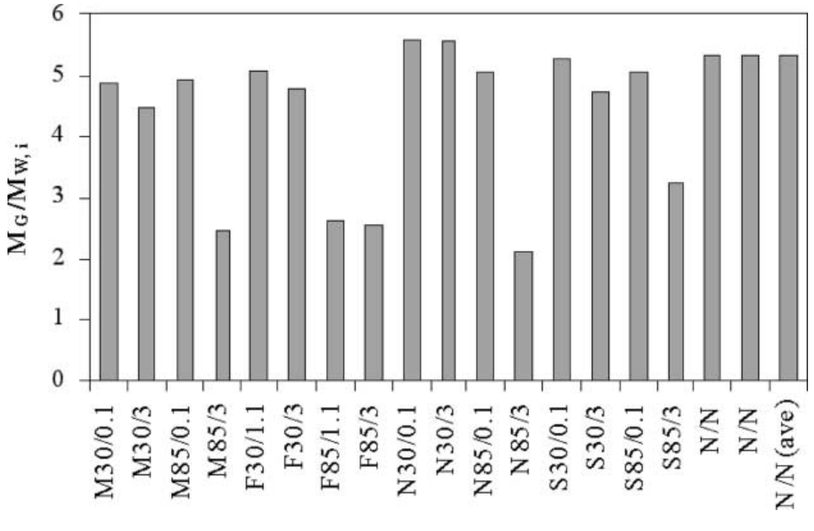

Figure 5. Estimated glass mass (M_G) per initial waste mass ($M_{W,i}$) for each oxidative leach sample. M = Permanganate; F = ferrate; S = persulfate; N = no added oxidant; and N/N = washed S-110 sludge. Results from each duplicate measurements shown. Values stand for temperature and OH concentration, respectively.

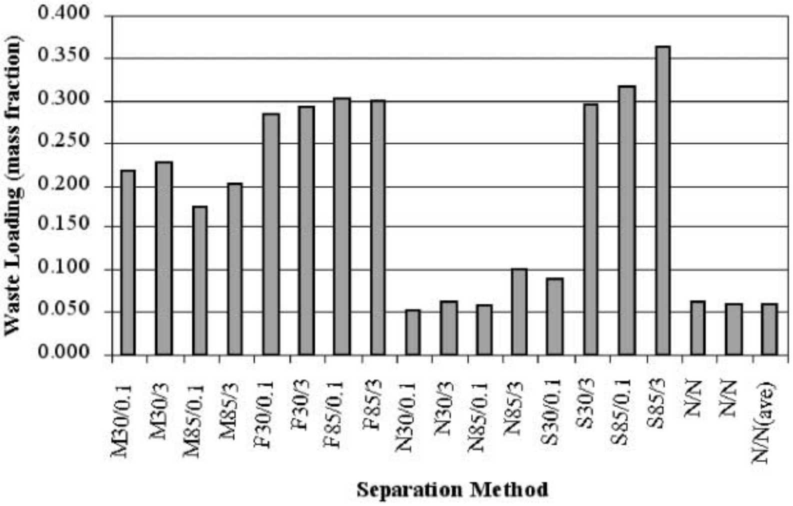

Figure 6. Waste loading of low Al, oxidatively leached S-110 sludge in HLW at 4 mass% MnO. M = Permanganate; F = ferrate; S = persulfate; N = no added oxidant; and N/N = washed S-110 sludge.

chromium removal under more optimum leach conditions. Figure 6 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 Fig. 7 shows an analogous situation if the MnO limit were raised to a plausible 10-mass% limit.

The results illustrated in Figs. 6 and 7 show that in this hypothetical low Al S-110 washed sludge, only about 5-mass% sludge could be incorporated into the HLW glass. The most effective caustic leaching in the absence of oxidants could about double to this incorporation to 10-mass% 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-mass% MnO, the added manganese adversely impacts sludge loading in glass. At 10 mass%, 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.

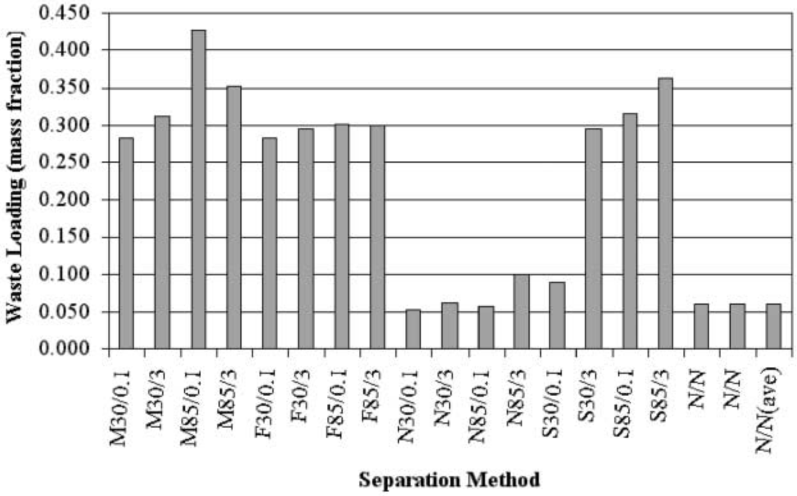

Figure 7. Waste loading of low Al, oxidatively leached S-110 sludge in HLW at 10 mass% MnO. M = Permanganate; F = ferrate; S = persulfate; N = no added oxidant; and N/N = washed S-110 sludge.

One final set of calculations was made, and the results support the previously-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.[21] 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.

CONCLUSION

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.

ACRONYMS

AEA	alpha-energy analysis
CCD	charged-coupled device
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EB	evaporator bottom
GEA	gamma-energy analysis
HLW	high-level waste
ICDD	International Centre for Diffraction Data
ICP/AES	inductively coupled plasma/atomic emissions spectroscopy
IHLW	immobilized high-level waste
LAW	low-activity waste
LLW	low-level waste
MIX	mixture
PCT	product consistency test
PMP	polymethylpentene
PNNL	Pacific Northwest National Laboratory
REDOX	reduction oxidation
SORWT	Sort on Radioactive Waste Type
TRU	transuranic (waste)
UV–vis	ultraviolet visible
WTP	Waste Treatment Plant
WVDP	West Valley Demonstration Project
XRD	X-ray diffraction

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