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G. J. Lumetta[a]; B. M. Rapko[a]
[a] Pacific Northwest National Laboratory(a), Richland, Washington

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REMOVAL OF CHROMIUM FROM HANFORD TANK SLUDGES

G.J. Lumetta and B. M. Rapko
Pacific Northwest National Laboratory[a]
P.O. Box 999, MSIN P7-25
Richland, Washington 99352

ABSTRACT

Recent studies suggest that the chromium content in sludge wastes stored at the U.S. Department of Energy's Hanford Site will determine the amount of high-level borosilicate glass produced in immobilizing those wastes for disposal. Removing chromium from the sludge solids would reduce the mass of high-level borosilicate glass, which would likely result in a significant cost savings. We have been investigating oxidative leaching methods for removing chromium from Hanford wastes for a number of years. In these methods, chromium(III), which is insoluble under alkaline conditions, is converted to the soluble chromate ion. We have removed chromium on a laboratory scale from several different Hanford tank sludges. The most effective leaching agents investigated to date are permanganate and ozone, which readily oxidize chromium(III) to chromium(VI) under alkaline conditions.

INTRODUCTION

During the past few years, the primary mission at the U.S. Department of Energy's (DOE's) Hanford Site has changed from producing plutonium to restoring the environment. Large volumes of high-level radioactive wastes (HLW), generated during past plutonium production and other operations, are stored in underground tanks onsite. DOE plans to remediate the Hanford tank farms by retrieving, pretreating, immobilizing, and disposing of the wastes. The tank wastes will be partitioned into high-level and low-level fractions. The low-level waste (LLW) will be processed to remove ^{137}Cs (and possibly other radionuclides), immobilized in a glass matrix, and then disposed of by shallow burial onsite. The HLW will be immobilized in a borosilicate glass matrix; the resulting glass canisters will then be disposed of in a geologic repository (1). Because of the expected high cost of HLW immobilization and geologic disposal, pretreatment processes will be implemented to reduce the volume of immobilized high-level waste (IHLW).

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Caustic leaching is the baseline method for pretreating Hanford tank sludges. Caustic leaching is expected to remove a large fraction of the aluminum, which is present in large quantities in Hanford tank sludges. The aluminum will be removed by converting aluminum oxides/hydroxides to sodium aluminate. It is also expected that water-insoluble metal phosphates and sulfates will metathesize to insoluble hydroxides and soluble Na_3PO_4 and Na_2SO_4, thus removing significant portions of phosphorus and sulfur.

Chromium removal from certain Hanford tank sludges might be important due to the relatively low tolerance for chromium in the HLW immobilization process. Based on its known amphoteric behavior (2), chromium(III) is expected to be removed by caustic leaching according to the following equation:

$$Cr(OH)_3(s) + NaOH(aq) \rightarrow Na[Cr(OH)_4](aq) \qquad (1)$$

However, recent studies conducted at the Pacific Northwest National Laboratory (PNNL) have suggested that chromium's behavior in the caustic leaching process is more complex. Chromium(III) hydroxide does dissolve appreciably in high caustic solutions at room temperature, but heating such solutions causes guyanaite, syn-(CrOOH) to precipitate. This precipitate does not readily redissolve in aqueous caustic media. This observation is consistent with previous reports of low solubility of $Cr(OH)_3$ in acidic and near-neutral solutions at elevated temperature (2). The precipitation of CrOOH might explain the low removal efficiencies observed for chromium during caustic leaching tests with actual tank waste and the failure to observe any chromium(III) in the leachates (3-5). Because caustic leaching has not removed chromium very well from certain Hanford tank sludges, methods are being investigated to improve chromium removal from these sludges. These methods have primarily focused on oxidation to chromium(VI), which is soluble under alkaline conditions. We have reported previously on removing chromium from Hanford tank SY-102 sludge by treating it with permanganate (MnO_4^-) (6). This paper summarizes recent results of these studies conducted with a variety of different Hanford tank sludges.

EXPERIMENTAL

Sludges from Hanford tanks B-111, BY-110, S-107, SX-108, and SY-103 were tested in this study. These sludges were chosen because they were found to have significant concentrations of residual chromium after caustic leaching (4,7). In addition, most of these sludges represent major tank groups that are expected to contribute the largest amounts of residual chromium following the baseline pretreatment process (5,8). Before performing the chromium leaching tests, the sludges were subjected to the following pretreatment steps:

- washing with 0.01 *M* NaOH to remove soluble salts such as $NaNO_3$, $NaNO_2$, NaOH, Na_2CO_3, Na_3PO_4, etc.,

- twice leaching the sludge with 3 *M* NaOH at 100°C for 5 h to remove additional elements, such as Al^{3+} and such anions as PO_4^{3-},
- washing the leached sludge with 0.01 *M* NaOH to remove added NaOH and materials dissolved in the caustic leaching step.

The caustic leached and washed solids were then divided into several portions for the chromium leaching tests.

Table 1 summarizes these tests, which can be divided into two sets. The first set used sludges from tanks B-111 and SY-103. This set was designed to test the efficacy of MnO_4^- (at two stoichiometries), ozone (O_3), and a catalytic MnO_4^-/O_3 mixture. Control experiments were done in which the sludges were leached with 0.01 *M* NaOH; the control leach mixtures were exposed to the air through a condenser, but no air was actively bubbled through the mixture.

The starting OH^- concentration in these tests was 0.01 *M*. In the case of the MnO_4^- oxidations, OH^- is consumed according to the equation

$$Cr(OH)_3 + MnO_4^- + OH^- \rightarrow CrO_4^{2-} + MnO_2 + 2H_2O \quad (2)$$

Likewise, OH^- is consumed as ozone oxidizes chromium(III):

$$2Cr(OH)_3 + 3O_3 + 4OH^- \rightarrow 2CrO_4^{2-} + 3O_2 + 5H_2O \quad (3)$$

The consumption of OH^- would reduce the pH, which in turn might lead to the undesirable increases in the transuranic (TRU) concentrations in solution.[a] Hence, in the second set of tests (BY-110, S-107, and SX-108 sludges), higher initial OH^- concentrations were used. Indeed, two different OH^- concentrations (0.1 and 3 M) were evaluated in the second set of tests. Again, MnO_4^- and O_3 were evaluated, but O_2 was also tested as an oxidizing agent for chromium(III). Argon was used in the control experiments in the second set of tests so that atmospheric O_2 would not affect the results. The SX-108 sludge could not be tested with argon (control) and O_2 because of insufficient sample.

The flow rate of the gases was monitored with a flowmeter and set at 19 cc/min. Ozone was generated from O_2 by an Ozone Research & Equipment Corporation Model O3V5-0 ozonator and was bubbled directly into the leach slurries. Based on the calibration information contained in the instrument manual under the power and O_2 flow rate used in these tests, the gas that bubbled through the test slurries (~6 wt % O_3 in O_2) introduced an estimated 1.8 g of O_3/h. This kept these test solutions constantly in contact with fresh oxidant and introduced a significant amount of excess oxidant over the course of the experiment. Oxygen was introduced similarly. Argon was introduced directly through the flowmeter and into the test suspensions. The caustic leached and washed sludges were not analyzed before testing, so the exact chromium concentration was unknown. To determine the amount of MnO_4^- needed, the chromium concentrations previously reported for the caustic-leached sludges were used (4,7).

For the B-111 and SY-103 experiments (first set of tests), the leaching mixtures were stirred at room temperature for the first 16 h and then heated at 80°C for the remainder of the experiment. Test samples were taken immediately after the sludge solids were mixed with the oxidant and then after 5, 16, 23, 30, and 37 h of total reaction time. For the other tests (second set of tests), the chromium leaching mixtures were stirred at room temperature for the first 24 h and then heated at 80°C for the remainder of the

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[a] Plutonium solubility is known to increase with decreasing pH at pH less than 9 (9). In the tests where the initial NaOH concentration was 0.01 *M*, the pH values did fall below 9.

TABLE 1. CHROMIUM LEACHING TEST MATRIX

Tank							
B-111	BY-110	S-107	SX-108	SY-103	[NaOH] (*M*)	Oxidant	Oxidant:chromium stoichiometry
x				x	0.01	$KMnO_4$	1
x				x	0.01	$KMnO_4$	3
x				x	0.01	$KMnO_4/O_3$	0.1/Excess
x				x	0.01	O_3	Large Excess
x				x	0.01	None (Control)	Not Applicable
x				x	0.01	$KMnO_4$	3
	x	x	x		0.1	$KMnO_4$	2
	x	x	x		3	$KMnO_4$	2
	x	x	x		0.1	O_3	Large Excess
	x	x	x		3	O_3	Large Excess
	x	x			0.1	O_2	Large Excess
	x	x			3	O_2	Large Excess
	x	x			0.1	Argon (Control)	Not Applicable
	x	x			3	Argon (Control)	Not Applicable

experiment. Test samples were taken immediately after the sludge solids were mixed with the oxidant and then after 3, 7, 24, and 31 h of total reaction time. The aliquots were passed through a 0.2-μm nylon filter before analysis by ultraviolet-visible (UV-vis) spectroscopy to determine CrO_4^{2-}.

The leach mixtures from both sets of tests were centrifuged, and the supernatant liquids were decanted after the tests were completed. The free $[OH^-]$ of the supernatant after testing was measured through titration with a standard HCl solution using a Mettler DL21 automatic titrator equipped with a Ross combination pH electrode (Orion Research Inc., Boston, Massachusetts). The residual solids were twice washed with the appropriate concentration of NaOH to remove any components in the interstitial liquid. After each wash, the samples were centrifuged, and the supernatant was added to the final leachate. The washed residual solids were suspended in distilled water, transferred to a small glass vial, and dried to a constant weight at 105°C. These residual solids were dissolved for analysis through a sodium peroxide fusion (BY-110 and S-107), a KOH fusion (SX-108), or treatment with HNO_3/HF (B-111 and SY-103). The supernatant liquids and the dissolved residues were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to determine the major metallic elements. The activity due to TRU elements in both the supernatants and dissolved residues was determined by alpha spectroscopy.

RESULTS AND DISCUSSION

Figure 1 presents the CrO_4^{2-} concentration as a function of time for the SY-103 and B-111 sludges when subjected to the various leaching conditions. In both cases, some CrO_4^{2-} was observed in the control experiment. There are three potential explanations for this: (i) some component of the waste oxidized the chromium(III) to chromium(VI), (ii) O_2 from the atmosphere served as oxidant, or (iii) some chromium(VI) was already present in the sludge and was liberated as other sludge components dissolved. The latter explanation is unlikely because X-ray absorption spectroscopy for caustic-leached B-111 and SY-103 indicated little or no chromium(VI) (10). A definitive explanation could not be derived from these test data, but to eliminate the second possibility, the control sample was flushed with argon in subsequent tests (see below).

Adding one molar equivalent of MnO_4^- to both B-111 and SY-103 sludges caused CrO_4^{2-} to form rapidly. No additional CrO_4^{2-} formed after stirring B-111 sludge at room temperature for 16 h, but a slight increase occurred for SY-103 over this period. Heating at 80°C resulted in further slight increases in the CrO_4^{2-} concentrations for both of these sludges; however, the CrO_4^{2-} concentration had stabilized after 14 h at 80°C.

Ozone also oxidized the chromium in B-111 and SY-103 to CrO_4^{2-}. In this case, little additional CrO_4^{2-} formed upon heating the leaching mixtures. For SY-103, the catalytic MnO_4^-/O_3 system behaved in a very similar manner to O_3 itself; however, for B-111, the catalytic system led to improved chromium oxidation. Indeed, the data suggest that more chromium could have been removed if the reaction were carried out past 37 h.

To eliminate the potential complication caused by the presence of atmospheric O_2, the control experiments for tank BY-110 and S-107 sludges were purged with argon. Figure 2 presents the CrO_4^{2-} concentrations as a function of time for these control experiments. The CrO_4^{2-} concentrations were essentially constant over the 24-h period that the mixtures were stirred at room temperature. The CrO_4^{2-} concentrations increased appreciably after heating at 80°C for 7 h, especially at the higher OH^- concentration. These results suggest that either the wastes themselves contained a component capable of oxidizing chromium (III) or the chromium existed as chromium(VI) and was liberated as other waste components dissolved. As no X-ray absorption spectra were performed on the BY-110 and S-107 sludges, we could not distinguish between these two possibilities. Figure 2 also presents the results of leaching the

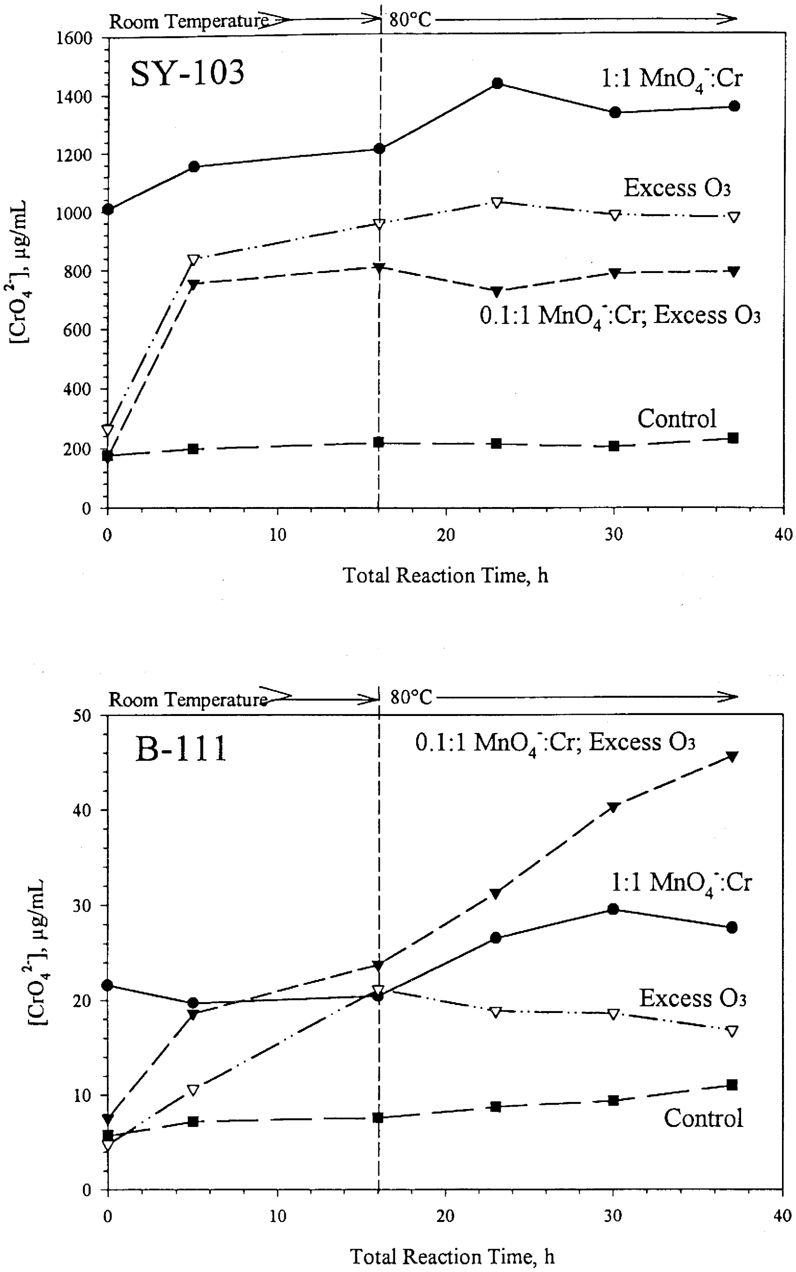
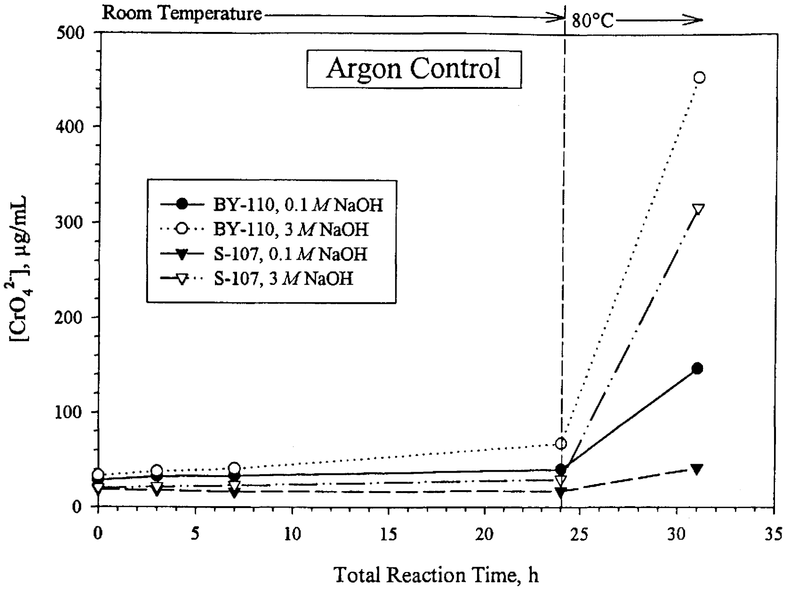


FIGURE 1. Chromate concentration as a function of time and temperature for treating SY-103 and B-111 sludges with permanganate and ozone.



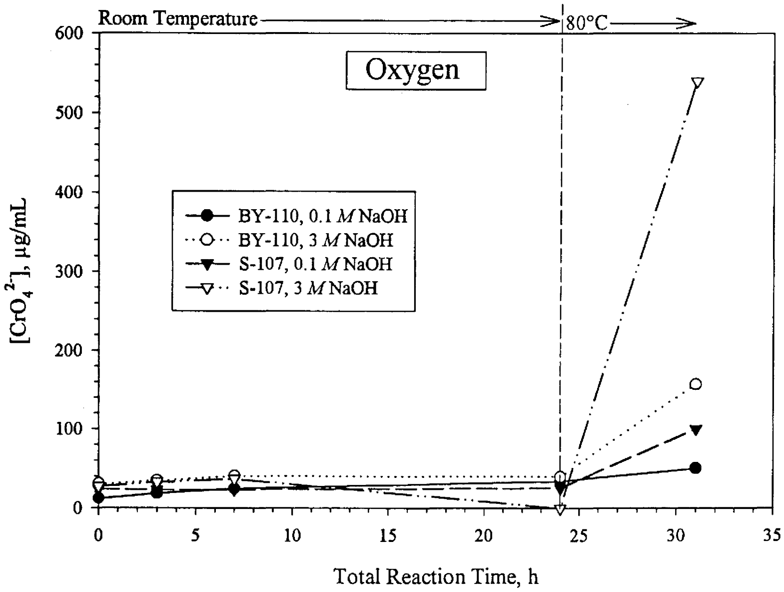


FIGURE 2. Chromate concentration as a function of time and temperature for treating BY-110 and S-107 sludges with argon (control) and oxygen.

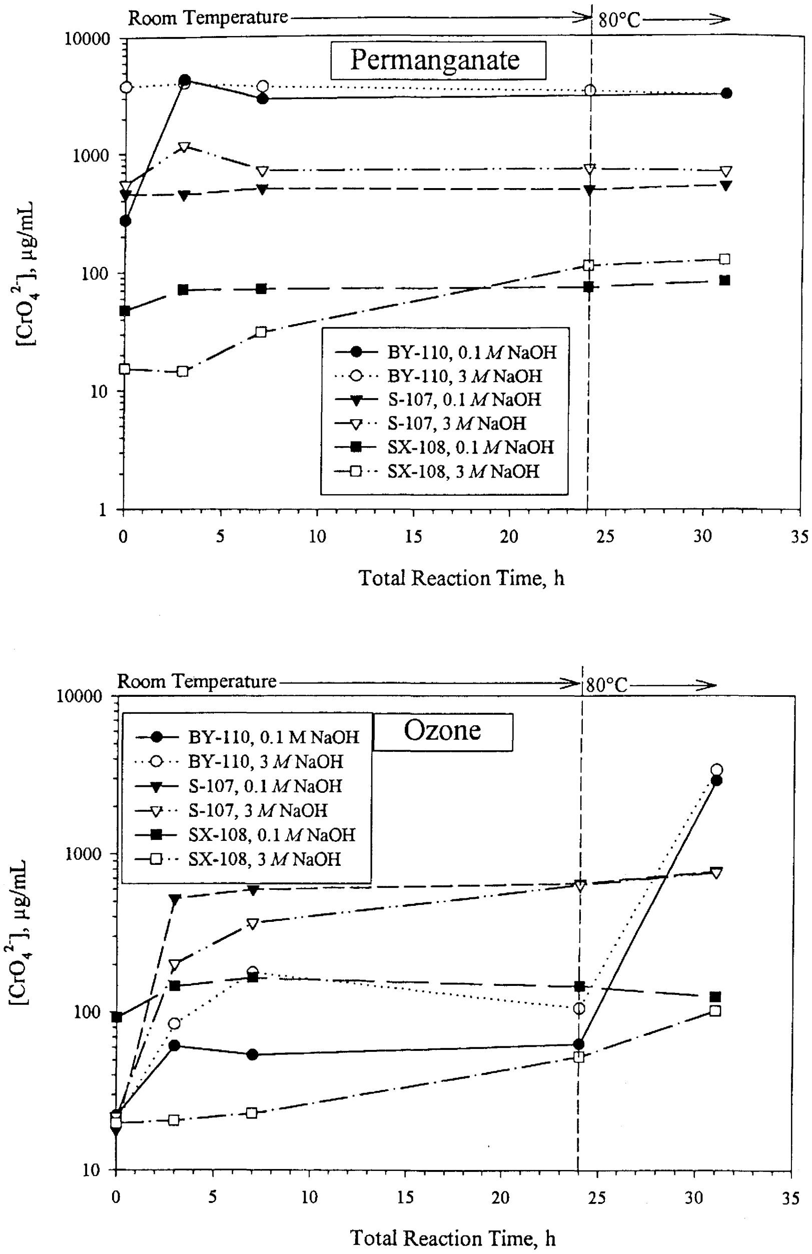


FIGURE 3. Chromate concentration as a function of time and temperature for treating BY-110, S-107, and SX-108 sludges with permanganate and ozone.

TABLE 2. CHROMIUM REMOVED BY OXIDATIVE LEACHING

Tank	Initial Chromium Concentration (wt %)	Test condition	Percent chromium removed
B-111	0.56	1:1 $KMnO_4$:Cr	18
		3:1 $KMnO_4$:Cr	18
		0.1:1 $KMnO_4$:Cr; Excess O_3	27
		Excess O_3	12
		Control; 0.01 *M* NaOH	5
SY-103	24	1:1 $KMnO_4$:Cr	90
		3:1 $KMnO_4$:Cr	60
		0.1:1 $KMnO_4$:Cr; Excess O_3	92
		Excess O_3	89
		Control; 0.01 *M* NaOH	34
BY-110	1.1	2:1 $KMnO_4$:Cr; 0.1 *M* NaOH	83
		2:1 $KMnO_4$:Cr; 3 *M* NaOH	94
		Excess O_3; 0.1 *M* NaOH	83
		Excess O_3; 3 *M* NaOH	90
		Excess O_2; 0.1 *M* NaOH	2
		Excess O_2; 3 *M* NaOH	11
		Argon; 0.1 *M* NaOH	8
		Argon; 3 *M* NaOH	28
S-107	1.3	2:1 $KMnO_4$:Cr; 0.1 *M* NaOH	58
		2:1 $KMnO_4$:Cr; 3 *M* NaOH	80
		Excess O_3; 0.1 *M* NaOH	84
		Excess O_3; 3 *M* NaOH	87
		Excess O_2; 0.1 *M* NaOH	8
		Excess O_2; 3 *M* NaOH	65
		Argon; 0.1 *M* NaOH	5
		Argon; 3 *M* NaOH	[a]
SX-108	0.58	2:1 $KMnO_4$:Cr; 0.1 *M* NaOH	22
		2:1 $KMnO_4$:Cr; 3 *M* NaOH	45
		Excess O_3; 0.1 *M* NaOH	42
		Excess O_3; 3 *M* NaOH	33

[a] Could not be calculated due to analytical difficulties.

BY-110 and S-107 sludges in the presence of O_2. The trends were the same as those for the argon control experiments, but the increase in CrO_4^{2-} concentration for S-107 at 3 M NaOH was much greater than that in the control experiment. Conversely, the increase in CrO_4^{2-} concentration for BY-110 at 3 M NaOH was much less than that in the control.

Figure 3 presents the CrO_4^{2-} concentrations during the MnO_4^- and O_3 treatments of BY-110, S-107, and SX-108 sludges. In all cases, MnO_4^- oxidized chromium(III) rapidly, with the reaction generally complete within the first 7 h. In general, O_3 also rapidly oxidized chromium(III) to chromium(VI). Heating

TABLE 3. TRANSURANIC CONCENTRATIONS IN THE LEACHATES

Tank	Test condition	Total alpha (µCi/mL)	[Pu] $(M)^a$	$[OH^-]$ $(M)^b$	Plutonium solubility $(M)^c$
B-111	1:1 $KMnO_4$:Cr	< 7.0E-6	< 4.7E-10	2.0E-04	> 1E-8
	3:1 $KMnO_4$:Cr	< 7.0E-6	< 4.7E-10	0.02	1.6E-9 to 2.5E-6
	0.1:1 $KMnO_4$:Cr; Excess O_3	< 6.0E-6	< 4.0E-10	3.0E-05	> 1E-8
	Excess O_3	< 2.0E-5	< 1.3E-9	1.0E-05	> 1E-8
	Control; 0.01 *M* NaOH	< 2.0E-5	< 1.3E-9	3.0E-04	> 1E-8
SY-103	1:1 $KMnO_4$:Cr	< 8.0E-6	< 5.4E-10	5.0E-07	> 1E-8
	3:1 $KMnO_4$:Cr	< 7.0E-6	< 4.7E-10	*d*	
	0.1:1 $KMnO_4$:Cr; Excess O_3	7.5E-05	5.1E-09	1.0E-07	> 1E-8
	Excess O_3	2.1E-04	1.4E-08	3.2E-08	> 1E-8
	Control; 0.01 *M* NaOH	6.7E-05	4.5E-09	0.003	3.2E-9 to 1.6E-5
BY-110	2:1 $KMnO_4$:Cr; 0.1 *M* NaOH	2.7E-05	1.8E-09	0.12	1.6E-9 to 3.2E-6
	2:1 $KMnO_4$:Cr; 3 *M* NaOH	4.1E-04	2.8E-08	2.59	3.2E-8 to 4.0E-5
	Excess O_3; 0.1 *M* NaOH	2.1E-05	1.4E-09	0.09	1.6E-9 to 2.0E-6
	Excess O_3; 3 *M* NaOH	1.6E-04	1.1E-08	2.77	3.2E-8 to 4.0E-5
	Excess O_2; 0.1 *M* NaOH	1.6E-05	1.1E-09	0.10	1.6E-9 to 3.2E-6
	Excess O_2; 3 *M* NaOH	< 3.0E-5	< 2.0E-9	2.90	5.0E-8 to 6.3E-5
	Argon; 0.1 *M* NaOH	2.3E-05	1.6E-09	0.16	1.6E-9 to 3.2E-6
	Argon; 3 *M* NaOH	< 3.0E-5	< 2.0E-9	2.81	5.0E-8 to 6.3E-5
S-107	2:1 $KMnO_4$:Cr; 0.1 *M* NaOH	2.2E-05	1.4E-09	0.11	1.6E-9 to 3.2E-6
	2:1 $KMnO_4$:Cr; 3 *M* NaOH	1.1E-03	7.2E-08	2.76	3.2E-8 to 4.0E-5
	Excess O_3; 0.1 *M* NaOH	< 6.0E-6	< 4.0E-10	0.45	> 1E-8
	Excess O_3; 3 *M* NaOH	7.6E-05	5.1E-09	2.88	5.0E-8 to 6.3E-5
	Excess O_2; 0.1 *M* NaOH	< 6.0E-6	< 4.0E-10	0.12	1.6E-9 to 3.2E-6
	Excess O_2; 3 *M* NaOH	< 5.0E-5	< 3.4E-9	2.82	5.0E-8 to 6.3E-5
	Argon; 0.1 *M* NaOH	< 4.0E-6	< 2.7E-10	0.10	1.6E-9 to 3.2E-6
	Argon; 3 *M* NaOH	< 5.0E-5	< 3.4E-9	2.92	5.0E-8 to 6.3E-5
SX-108	2:1 $KMnO_4$:Cr; 0.1 *M* NaOH	< 5.0E-6	< 3.4E-10	0.10	1.6E-9 to 3.2E-6
	2:1 $KMnO_4$:Cr; 3 *M* NaOH	4.8E-04	3.2E-08	2.62	3.2E-8 to 4.0E-5
	Excess O_3; 0.1 *M* NaOH	< 4.0E-6	< 2.7E-10	0.09	1.6E-9 to 3.2E-6
	Excess O_3; 3 *M* NaOH	< 2.0E-6	< 1.3E-10	2.70	3.2E-8 to 4.0E-5

[a] Assumes that all the alpha activity present is due to ^{239}Pu.

[b] Final free-hydroxide concentration of the leachate.

[c] Reference 11.

[d] Not measured.

at 80°C had no significant effect on the chromium(III) oxidation by MnO_4^- or O_3, except for the case of treating BY-110 sludge with O_3. In the latter case, a marked increase in the CrO_4^{2-} concentration occurred after heating.

Table 2 summarizes the amount of chromium removed from each of the sludges. Several anomalies are in the data, but some general trends can be gleaned. Permanganate was effective in removing chromium from the SY-103, BY-110, and S-107 sludges. Removing chromium from B-111 and SX-108 by treatment with MnO_4^- was much less effective. One possible explanation for poor chromium removal from B-111 is the existence of the mineral-phase $Bi_{38}CrO_{60}$ in that waste (4). We cannot yet definitively explain the poor removal from SX-108 sludge, but the oxidation might be slow due to inclusion of chromium within larger aluminum-containing particles. It has been hypothesized that more extensive caustic leaching of SX-108 sludge to better remove aluminum might also lead to better chromium leaching efficiency. Experiments are being planned to test this hypothesis.

Ozone was equally effective at removing chromium. The presence of a catalytic amount of MnO_4^- during the ozonolysis slightly improved chromium removal from B-111 sludge but provided no significant enhancement for the SY-103 sludge. Oxygen was generally ineffective at oxidizing chromium(III) under the conditions of these experiments. The exception to this was for S-107 sludge at 3 *M* NaOH; in that case, 65% of the chromium was removed by treating with O_2. For the oxidants investigated, chromium removal was better at 3 *M* NaOH than at 0.1 *M* NaOH, except for treating SX-108 with O_3.

The leachates containing the oxidized chromium must be handled as LLW. Thus, dissolution of transuranic elements (mainly plutonium and americium) during the leaching process is undesirable. Table 3 presents the total alpha-emitter concentrations found in each leachate solution. For the purposes of this discussion, we will assume that the alpha activity is primarily due to ^{239}Pu. Based on this assumption, the plutonium concentrations in the leachates have been determined and are presented in Table 3. Also presented in Table 3 is the solubility range expected for plutonium in each leachate solution based on plutonium solubility data compiled by Hobbs and Edwards (11). In all cases, the plutonium concentrations were either below the reported literature values or at the lower end of the solubility range. The literature values reflect the solubility of plutonium(IV) under alkaline conditions. Since plutonium(VI) would be expected to be much more soluble, it appears that little or no oxidation of plutonium to plutonium(VI) occurred in the chromium leaching tests.

CONCLUSIONS

Permanganate and O_3 are effective agents for oxidizing chromium(III) to chromium(VI) and thus provide a means to remove chromium from alkaline sludges. Studies with actual Hanford tank waste indicate that the reactions are rapid (usually complete within several hours). The chemistry of these tank sludges is complex, and chromium(VI) is sometimes formed even in the absence of an added oxidant. The mechanism(s) for this is not completely understood. Although plutonium was found in some of the leaching solutions, the amounts found suggested that this was simply an indication of the plutonium(IV) solubility rather than oxidation to plutonium(VI).

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