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Ferrate Treatment for Removing Chromium from High-Level Radioactive Tank Waste

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A method has been developed for removing chromium from alkaline high-level radioactive tank waste. Removing chromium from these wastes is critical in reducing the volume of waste requiring expensive immobilization and deep geologic disposition. The method developed is based on the oxidation of insoluble chromium(III) compounds to soluble chromate using ferrate. This method could be generally applicable to removing chromium from chromium-contaminated solids, when coupled with a subsequent reduction of the separated chromate back to chromium(III). The tests conducted with a simulated Hanford tank sludge indicate that the chromium removal with ferrate is more efficient at 5 M NaOH than at 3 M NaOH. Chromium removal increases with increasing Fe(VI)/Cr(III) molar ratio, but the chromium removal tends to level out for Fe(VI)/Cr(III) greater than 10. Increasing temperature leads to better chromium removal, but higher temperatures also led to more rapid ferrate decomposition. Tests with radioactive Hanford tank waste generally confirmed the simulant results. In all cases examined, ferrate enhanced the chromium removal, with a typical removal of around 60–70% of the total chromium present in the washed sludge solids. The ferrate leachate solutions did not contain significant concentrations of transuranic elements, so these solutions could be disposed as low-activity waste.

Introduction

Restoration of the U.S. Department of Energy's (DOE's) Hanford Site in Washington State constitutes one of the largest environmental remediation projects ever undertaken (1). Disposal of the ~200,000 m³ of radioactive tank waste is the most daunting challenge facing Hanford (2). Sixty-seven of the 177 underground storage tanks at Hanford have leaked, and there is mounting concern about the mobility of the radionuclides released to the environment during these leaks and potential future leaks. For nearly 50 years, plutonium production was the primary mission at the Hanford Site. The Hanford tank wastes are chemically complex having been generated during implementation of three major plutonium separation processes and other operations at the site.

These tank wastes consist of three general phases: supernate, salt cake, and sludge. The liquid supernate is highly

alkaline with high salt content (mainly sodium nitrate, nitrite, hydroxide, carbonate, phosphate, and sulfate). The salt cake is a solid phase formed by concentrating the liquids past the point of saturation, so it consists mainly of the sodium salts listed above. The sludge phase consists mainly of insoluble metal oxides/hydroxides. Typical metals present in the sludge include Al, Bi, Cr, Fe, Mn, Si, and U. The wastes contain mixed fission products (e.g., ¹³⁷Cs, ⁹⁰Sr, ⁹⁹Tc), uranium, and transuranic (TRU) elements (e.g., plutonium and americium). The TRU elements and ⁹⁰Sr are mostly located in the sludge layer, while the ¹³⁷Cs and ⁹⁹Tc are partitioned between the supernate, saltcake, and sludge.

The 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 waste (HLW) and low-activity waste (LAW) fractions. The LAW will be processed to remove ¹³⁷Cs and ⁹⁹Tc, immobilized in a glass matrix, and then disposed of by shallow burial onsite. The HLW will be immobilized in a borosilicate glass matrix and cast into stainless steel canisters, which will then be disposed of in a geologic repository (3). 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). Removing aluminum, phosphorus, sulfur, and chromium from the HLW solids is essential to reducing the IHLW volume.

Caustic leaching is the baseline method for pretreating Hanford tank sludges. Caustic leaching is expected to remove a large fraction of the aluminum, present in large quantities in Hanford tank sludges, by converting poorly soluble aluminum oxides/hydroxides to more soluble sodium aluminate. It is also expected that water-insoluble transition metal phosphates and sulfates will metathesize to insoluble transition metal hydroxides and soluble Na₃PO₄ and Na₂SO₄, thus removing significant portions of phosphorus and sulfur.

Chromium can interfere with the HLW immobilization process by forming spinel phases in the melter. These spinels adversely effect the melter performance by accumulating as solid phases separate from the molten glass, leading to pouring difficulties, cold cap freezing, and foam stabilization (4). Relatively low concentrations of chromium in the HLW can cause spinel formation. For these reasons, removing chromium from Hanford tank sludges is an important pretreatment objective.

Based on its known amphoteric behavior (5), chromium(III) should dissolve in alkaline solution as the tetrahydroxochromium(III) complex, [Cr(OH)₄]⁻. However, recent work in our laboratory indicates chromium 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 (6). This observation is consistent with previous reports of low solubility of Cr(OH)₃ in acidic and near-neutral solutions at elevated temperature (5). The precipitation of CrOOH also 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 (6).

We have been investigating oxidative leaching methods for removing Cr from Hanford tank sludge solids by converting insoluble Cr(III) species into soluble chromate (7, 8). Our previous work has focused on using permanganate,

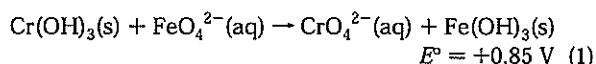
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ozone, or O₂ as oxidant. Russian researchers have investigated using O₂, hydrogen peroxide, and persulfate for oxidizing Cr(III) in Hanford sludges (9). Although O₂ is an attractive oxidant because it is readily available and leaves no additional solid residue, it reacts slowly with the Cr(III) in the sludge solids (8). Ozone oxidizes Cr(III) more quickly than O₂, but its corrosivity and need for generating equipment is a major concern for nuclear applications (7, 8). The Russian workers reported that Cr(III) oxidation with H₂O₂ was hampered by catalytic decomposition of the H₂O₂ in the presence of Fe(III) (9), which is consistent with observations previously made by us (10). Permanganate rapidly oxidizes Cr(III) to Cr(VI) in alkaline solution and is thus an effective chromium leaching agent (7, 8, 10). However, using permanganate adds MnO₂ to the sludge solids. The limits for manganese in the HLW glass formulation are not well established above 3 wt % Mn in the glass, so there is some uncertainty in using permanganate. We report here the use of ferrate, FeO₄²⁻, for leaching Cr from radioactive Hanford tank sludge solids. Although using ferrate results in the addition of Fe(OH)₃ to the HLW solids, the additional Fe is insignificant with respect to the Fe inventory already present in the waste.

By using FeO₄²⁻ to oxidatively leach Cr from the tank sludge solids, the Cr is transferred to the LAW stream in the chromate form. There it will be immobilized in a glass waste form. Due to the toxicity and mobility of Cr(VI), it would likely be desirable to reduce the Cr(VI) to Cr(III) before immobilizing the LAW. A number of reducing agents are available to do this. For example, we have shown that hydroxylamine will reduce Cr(VI) to Cr(III) in tank waste solutions (10). Iron(II) is another potential candidate for reducing Cr(VI) to Cr(III) (11, 12). Although the work described here is specific to treatment of Hanford tank sludges, there may be other potential applications where removal of Cr from a solid waste is necessary. It should be kept in mind, of course, that in most cases reduction of the separated Cr(VI) to the less problematic Cr(III) will be required before final disposition.

The ferrate anion contains iron in the +6 oxidation state and thus is a strong oxidizer; it is known to oxidize Cr(III) to Cr(VI) in strongly alkaline solution (13). Aqueous solutions of FeO₄²⁻ are deep purple in color with a broad asymmetrical absorption peak at 505 nm with an extinction coefficient of 1070 M⁻¹cm⁻¹ (14, 15). This serves as a convenient method of determining FeO₄²⁻ concentrations in aqueous media. Ferrate has already been evaluated for numerous applications related to water treatment including the destruction of organic compounds (16), the destruction of cyanide (17), the removal of heavy metal ions by coprecipitation (18), and removal of americium and plutonium from wastewaters (19).

In alkaline media, ferrate reacts with chromium(III) hydroxide according to eq 1 (the E° value was derived from the standard reduction potentials listed in ref 20). This reaction can be exploited to remove chromium from the sludge solids.



The iron hydroxide byproduct is compatible with proposed HLW glass formulations and is also likely to cause the coprecipitation of TRU elements that may have been solubilized during the oxidative treatment (21, 22). A series of studies was conducted to test this method using a nonradioactive Hanford sludge simulant. Based on the initial favorable results, tests were then conducted using actual Hanford tank waste. The results of these studies are presented here.

TABLE 1. Preparation and Composition of Hanford Sludge Simulant

component	salt used	mass salt added, g	component concn in wet sludge, mg/g
Al	Al(NO ₃) ₃ ·9H ₂ O	695.27	71.2
Ca	Ca(NO ₃) ₂ ·4H ₂ O	2.56	1.43
Cr	Cr(NO ₃) ₃ ·9H ₂ O	14.37	4.84
Fe	Fe(NO ₃) ₃ ·9H ₂ O	7.23	2.45
Mn	Mn(NO ₃) ₂	1.90	1.67
P	Na ₃ PO ₄ ·12H ₂ O	7.56	1.15
Si	H ₂ SiO ₃	3.86	27
Sr	Sr(NO ₃) ₂	0.33	0.21
Zn	Zn(NO ₃) ₂ ·6H ₂ O	0.51	0.41
Zr	ZrO(NO ₃) ₂	3.50	3.79

Experimental Section

Materials and Methods. All reagents used were of analytical grade or higher. Ferrate was produced in-house using a proprietary Lynntech method involving electrochemical oxidation of a high purity (99.9+%) iron wire. The solution consists of Na₂FeO₄ (nominally 50 to 70 mM) in aqueous NaOH (5 to 10 M). This method is superior to other methods of producing ferrate, such as oxidation of Fe(III) salts with chlorine, which leads to the presence of chloride in the ferrate solution. Potential metallic impurities (e.g., Ni) are insoluble in the highly alkaline solution. Atomic absorption spectrometry was performed using a Varian AA-875 atomic absorption spectrophotometer. For the tests with nonradioactive material, UV-vis measurements were performed on a Shimadzu model 2101 PC double beam UV-vis spectrophotometer and inductively coupled atomic emission spectrometry (ICP) analyses were performed by the Geochemical and Environmental Research Group at Texas A&M University, College Station, Texas. For the tests with radioactive Hanford tank sludge, UV-vis spectra were recorded with a Spectral Instruments 400 series CCD array ultraviolet visible (UV-vis) spectrophotometer equipped with a fiber optic probe. ICP analyses were performed on a Thermo Jarrell Ash Model 61 inductively coupled atomic emission spectrometer. The TRU concentrations of the leachate solutions were determined by measuring the total alpha activity using a Ludlum model 43-10 alpha scintillation detector after evaporating a 0.01-mL aliquot on a stainless steel planchet.

Preparation of Hanford Tank Sludge Simulant. The initial studies of Cr leaching with FeO₄²⁻ were conducted with a simulated Hanford tank sludge. Table 1 lists the constituents of the simulated sludge. The indicated salts were added to approximately 500 mL of deionized water with vigorous stirring. The pH was adjusted to 12 with 10 M NaOH, and the mixture was boiled for 6 h. During this digestion process, deionized water was added as needed to maintain the initial volume. The mixture was allowed to cool and settle overnight, and then the clear liquid was decanted. The settled solids were centrifuged, and the liquid was discarded. The centrifuged solids were washed with approximately 300 mL of 0.1 M NaOH, and the wet sludge was stored in a sealed bottle until used.

The composition of the tank sludge simulant (Table 1) was determined by dissolving a known mass of sludge in HNO₃/HF. It was necessary to heat the mixture to ensure complete dissolution. The resulting solution was analyzed for Zr, P, and Si by ICP and Sr, Ca, Fe, Al, Mn, Zn, and Cr by AAS. The moisture content was determined to be 67.5 wt % by drying to a constant weight at 105 °C.

General Procedure for Testing with the Hanford Tank Sludge Simulant. To test the ability of FeO₄²⁻ to remove Cr from the simulated Hanford tank sludge, the following general procedure was followed. A weighed aliquot (nominally 0.5

g) of the wet sludge was shaken with FeO_4^{2-} solution at ambient temperature for 24 h. The specific conditions were varied for kinetic and temperature-dependence tests. Appropriate blank tests were run under identical conditions in the absence of FeO_4^{2-} . Ferrate concentrations were determined by light absorption at 505 nm. Upon completion of the contact, the mixture was filtered through a 0.2- μm syringe filter, and the clarified liquid was analyzed for Cr using AAS. The percentage of the total Cr removed was then calculated from the amount of Cr found in solution, and the amount originally present in the sludge aliquot that was treated.

Chromium(III)/Ferrate Reaction Kinetics. Chromium oxide (0.05 g; 0.66 mmol; 99.995%, Aldrich Chemical Co., Milwaukee, Wisconsin) was shaken at ambient temperature with 50 mL of 18 mM (0.9 mmol) FeO_4^{2-} solution (3 or 5 M in NaOH) for varying time intervals. After reacting for the desired time interval, the mixture was filtered through a 0.2- μm syringe filter, and the clarified liquid was analyzed for Cr using AAS. Control experiments were performed under identical conditions without FeO_4^{2-} . In all cases, less than 0.3% of the Cr was oxidized in the control experiments.

Ferrate Leaching of Hanford Tank S-107 Sludge. *Preparation of Sludge.* Several 20-mL portions of 0.01 M NaOH were used to suspend and transfer a sample of sludge from Hanford waste tank 241-S-107 (S-107) into a 125-mL plastic bottle. The bottle was then filled with additional 0.01 M NaOH and stirred for approximately 15 min at room temperature. The sample was centrifuged for 5 min at 1200G, and the centrifuged liquid was removed. The bottle was filled with additional 0.01 M NaOH, stirred for 15 min, and centrifuged for 5 min at 1200G, and the centrifuged liquid was again removed. This process was repeated for a total of three contacts of the S-107 sludge with 0.01 M NaOH. No color was observed in the final 0.01 M NaOH wash solution, indicating that effectively all of the Cr initially present as CrO_4^{2-} had been removed. This treatment was undertaken to wash soluble salts (e.g., NaNO_3 and Na_2CrO_4) from the S-107 waste. The remaining centrifuged sludge solids were stirred in 90 mL of deionized water, and approximately equal aliquots were transferred into eight 100-mL polypropylene bottles and one 20-mL borosilicate glass vial, with the mass of each transferred portion being recorded. The sample in the borosilicate glass vial was dried to a constant weight at 105 °C, and the moisture content of the slurry was determined to be 92.4 wt %.

Testing Procedure. Specific amounts of the stock FeO_4^{2-} , 10 M NaOH (to achieve a nominal $[\text{OH}^-]$ of 3 M), and deionized water (to yield a total suspension volume of 100 mL) were added to each aliquot of washed sludge. The samples were placed in groups of 4 in an aluminum heating block on top of a five-place heater-stirrer, with the fifth place occupied by a plastic bottle filled with water. The temperature during the experiment was controlled to $\pm 2^\circ\text{C}$ and monitored by a thermocouple immersed in the water-filled bottle. Stirring was stopped at approximate intervals of 0, 1, 5, and 20+ h, the solids were allowed to settle for a few minutes, and aliquots of the clear supernatant were removed. Each aliquot was filtered through a 0.2-micron syringe filter, and the UV-vis spectrum of the filtered aliquots (280 to 800 nm) was recorded. The chromate concentrations were determined by measuring the test solution's absorbance at 372 nm, which is the wavelength of maximum absorbance for an alkaline solution of chromate in the visible spectrum. The instrument was calibrated using standards-grade potassium dichromate in 0.05 M KOH according to standard procedures (23).

After the UV-vis measurement, the aliquot was returned to the appropriate test vessel. Upon completion of the leaching, the samples were centrifuged, the leachate solutions were decanted, and the residual solids were stirred with approximately 30 mL of 0.01 M NaOH. These wash solutions

were stirred for at least 30 min at room temperature, the samples were centrifuged, and the wash solution was combined with the leachate solution. This process was repeated until the wash solutions appeared colorless. No more than two washes were required for any test sample to meet this condition. The combined leachate and wash solutions were weighed, their densities were determined, and the UV-vis spectrum of the solutions was taken. Aliquots were then taken, filtered through a 0.2- μm syringe filter, and analyzed for metals by ICP. The alpha activity from TRU elements (Pu, Am, Cm) was determined by performing a total alpha assay. The residual solids were extracted with approximately 10 mL of hot 6 M HCl, followed by three additional contacts with approximately 3 mL of hot 6 M HCl to dissolve any residual chromium that might have remained in the solids. The densities of the combined HCl leach solutions were determined. Aliquots were then filtered through a 0.2- μm syringe filter and analyzed for metals and TRU. In the case of the untreated S-107 sample, both the HCl leach solution and the solids that remained after the acid leach were submitted for analysis. The acid-insoluble solids were solubilized for analysis by KOH fusion.

Results and Discussion

Effect of Sodium Hydroxide Concentration. The effect of NaOH concentration on Cr removal was explored by contacting 0.5-g aliquots of the wet Hanford waste simulant with 50 mL of ~ 13 mM ferrate solutions (14-fold molar excess of FeO_4^{2-}) of variable NaOH concentration at ambient temperature for 24 h. Control experiments were conducted by contacting the wet sludge simulant with NaOH solutions under identical conditions in the absence of FeO_4^{2-} . Figure 1a presents the results. The slight Cr dissolution (1.5 to 7.1% corresponding to 0.014 to 0.066 mM Cr) that occurred in the absence of FeO_4^{2-} is consistent with the solubility of Cr(III) at high pH (5). Under these specific conditions, the ferrate treatment resulted in 6- to 31-fold increases in the amount of Cr removed. The fact that complete oxidation of the available Cr was not achieved suggests that the Cr in the sludge simulant was not all in a readily oxidizable form and/or other species in the sludge consumed FeO_4^{2-} . However, in many cases the solutions still had the purple color indicative of FeO_4^{2-} at the end of the experiment. The presence of unreacted FeO_4^{2-} coupled with less than 100% Cr(III) oxidation supports the hypothesis that some of the Cr in the sludge is present in a form that is not readily available to the oxidizing agent. It is possible that some fraction of the Cr is present in poorly soluble mixed Fe/Cr or Mn/Cr oxides or other mixed oxides. Such species have been identified in actual Hanford tank sludges (6).

Effect of $\text{FeO}_4^{2-}/\text{Cr}^{3+}$ Ratio. The effect of the FeO_4^{2-} concentration on Cr removal was explored by contacting 0.5-g aliquots of the wet Hanford waste simulant with 50 mL of 3 M NaOH containing 1, 2, 3, 5, 7, or 10 mM FeO_4^{2-} solution at ambient temperature for 24 h. Figure 1b presents the results. The Cr removal increased with increasing FeO_4^{2-} concentration, but the shape of the curve suggests a leveling of the amount of Cr removed at higher $\text{FeO}_4^{2-}/\text{Cr}^{3+}$ ratios.

Higher $\text{FeO}_4^{2-}/\text{Cr}^{3+}$ ratios were investigated by contacting 0.5-g aliquots of the wet Hanford waste simulant with variable volumes of 3 M NaOH containing 12 mM FeO_4^{2-} solution at ambient temperature for 24 h. Figure 1c presents the results. Although the data are somewhat scattered, it is clear that there is a limit of $\sim 60\%$ Cr removal under these conditions (3 M NaOH, ambient temperature, 24-h contact).

The volume of FeO_4^{2-} solution required per unit mass of sludge was investigated by keeping the solution volume constant (50 mL) and varying the mass of simulated Hanford sludge used. Aliquots (0.1- to 5-g) were mixed with 50 mL of 13 mM FeO_4^{2-} solution in 3 M NaOH at ambient temperature

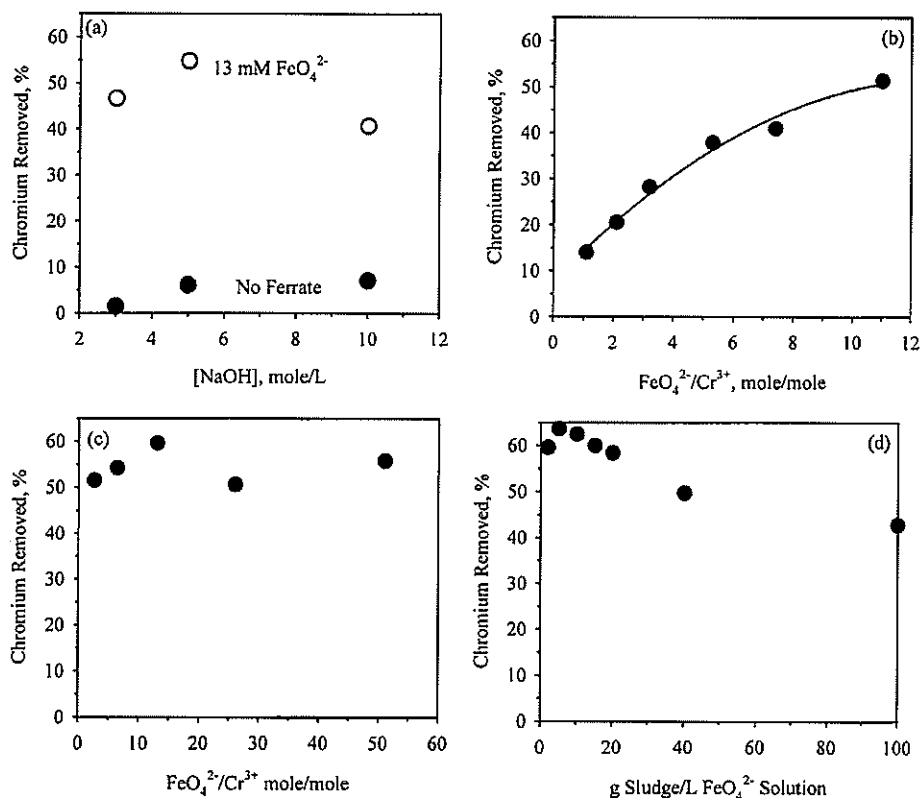


FIGURE 1. Ferrate leaching tests with simulated Hanford tank sludge. (a) Dependence on NaOH concentration. (b) Effect of increasing the $\text{FeO}_4^{2-}/\text{Cr}^{3+}$ molar ratio at constant solution-to-sludge ratio [100 mL solution/g sludge; 3 M NaOH]; the line represents a second-order polynomial fit of the data, $y = -0.26x^2 + 6.74x + 7.77$. (c) Effect of increasing the $\text{FeO}_4^{2-}/\text{Cr}^{3+}$ molar ratio at constant FeO_4^{2-} concentration [12 mM in 3 M NaOH]. (d) The effect of increasing the sludge-to-ferrate ratio (50 mL, 13 mM FeO_4^{2-} , 3 M NaOH).

for 24 h. Figure 1d presents the results. Again, the maximum amount of Cr removed was ~60% despite the excess of FeO_4^{2-} , suggesting only a little over half of the Cr can be readily oxidized at room temperature. Slightly better Cr removal is achieved with higher solution-to-solids ratios. This could be simply attributed to the higher relative $\text{Fe(VI)}/\text{Cr(III)}$ molar ratio. But poorer mixing at low solution-to-solids ratios might have also contributed to this effect.

Comparison of the data in Figure 1b and 1d suggests that the absolute FeO_4^{2-} concentration plays a significant role in the Cr removal. For example, in one test 50 mL of 1 mM Fe(VI) in 3 M NaOH was mixed with 0.5 g of sludge [$\text{Fe(VI)}/\text{Cr(III)} = 1.1$] resulting in 14% Cr removed (Figure 1b). Yet in another test, 50 mL of 13 mM Fe(VI) in 3 M NaOH was mixed with 5 g of sludge [$\text{Fe(VI)}/\text{Cr(III)} = 1.4$] resulting in 43% Cr removed (Figure 1d). Thus, despite the similar $\text{Fe(VI)}/\text{Cr(III)}$ ratios, significantly different results were obtained. It appears that very low FeO_4^{2-} concentrations are not very effective even with a sufficient molar excess of FeO_4^{2-} over Cr(III) .

Effect of Temperature on Chromium Removal. The effect of temperature on Cr removal was investigated by treating 0.5-g aliquots of the simulated Hanford tank sludge with NaOH/ FeO_4^{2-} solutions at 50, 70, and 105 °C (Table 2). The results indicate that increasing temperature leads to increased Cr removal both for NaOH alone and with FeO_4^{2-} . No attempt was made to discern whether the increased Cr removal in the absence of FeO_4^{2-} was due to improved Cr(III) dissolution or oxidation to Cr(VI) by adventitious oxygen. But based on our previous observations, it was likely due to the latter (6). The best result (90% Cr removal) was obtained by treating the sludge with 12 mM $\text{FeO}_4^{2-}/3$ M NaOH for 24 h at 70 °C. A similar result was obtained by treating the sludge with 12 mM $\text{FeO}_4^{2-}/3$ M NaOH for 6 h at 105 °C. However, FeO_4^{2-}

TABLE 2. Effect of Temperature on Chromium Removal from Simulated Hanford Tank Sludge

[NaOH], M	[FeO_4^{2-}], mM	T, °C	contact time, h	Cr removed, %
3	0	~20	24	1.5 ± 0.1
3	0	50	24	34.5 ± 2.4
3	0	70	5.5	21.4 ± 3.2
3	0	105	6	59.5 ± 9.8
5	0	~20	24	6.1 ± 0.2
5	0	50	24	36.3 ± 1.1
5	0	70	5.5	27.8 ± 0.7
5	0	70	24	31.4 ± 0.1
5	0	105	6	59.0 ± 1.8
3	13	~20	24	46.7 ± 5.3
3	12	50	24	67.9 ± 2.2
3	12	70	5.25	54.5 ± 1.8
3	12	70	24	90.0 ± 1.5
3	12	105	6	87.0 ± 0.6
5	13	~20	24	54.8 ± 2.2
5	12	50	24	86.0 ± 1.7
5	12	70	6.5	76.9 ± 2.8
5	12	70	24	87.8 ± 2.0
5	12	105	6	85.2 ± 0.3

rapidly decomposes at 105 °C. So FeO_4^{2-} utilization at 105 °C is not recommended as it might lead to the production of large volumes of secondary waste.

Kinetics of Chromium(III) Oxidation by Ferrate. The kinetics of Cr(III) oxidation by ferrate was investigated using Cr_2O_3 . This eliminated potential complications due to other sludge components and allowed the reaction between FeO_4^{2-} and Cr(III) to be more closely evaluated. The results presented in Figure 2 indicate the $\text{Fe(VI)}/\text{Cr(III)}$ reaction is relatively slow. In 3 M NaOH, maximum Cr oxidation was obtained after 5.5 h; even longer was required to reach maximum Cr

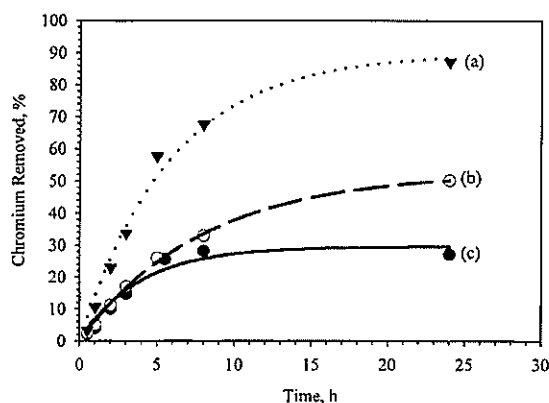


FIGURE 2. Chromium oxide dissolution as a function of time: (a) 5 M NaOH, 31 mM FeO_4^{2-} , $y = 89.9(1 - e^{-0.17x})$; (b) 5 M NaOH, 18 mM FeO_4^{2-} , $y = 52.7(1 - e^{-0.13x})$; (c) 3 M NaOH, 18 mM FeO_4^{2-} , $y = 29.6(1 - e^{-0.26x})$.

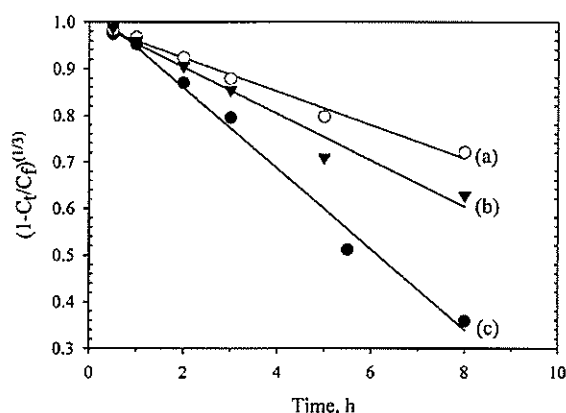


FIGURE 3. Inverse-cubic function plots for Cr_2O_3 oxidation: (a) 5 M NaOH, 18 mM FeO_4^{2-} , $k_{\text{obs}} = 0.036 \pm 0.002 \text{ h}^{-1}$, $r^2 = 0.987$; (b) 5 M NaOH, 31 mM FeO_4^{2-} , $k_{\text{obs}} = 0.050 \pm 0.004 \text{ h}^{-1}$, $r^2 = 0.974$; (c) 3 M NaOH, 18 mM FeO_4^{2-} , $k_{\text{obs}} = 0.087 \pm 0.004 \text{ h}^{-1}$, $r^2 = 0.990$.

oxidation in 5 M NaOH. This slow oxidation process is a reflection of the more refractory nature of Cr_2O_3 relative to the Cr in the simulated sludge. As was seen with the simulated tank sludge, Cr oxidation was greater in 5 M NaOH than in 3 M NaOH. Figure 2 indicates that Cr oxidation was significantly improved when the initial FeO_4^{2-} concentration was increased to 31 mM.

The experiment described by Figure 2 was performed mainly to obtain kinetics information needed to implement a ferrate oxidation process; however, some mechanistic information can be gleaned from the data. To a first approximation, the $\text{FeO}_4^{2-}/\text{Cr}_2\text{O}_3$ reaction is consistent with the reaction occurring at the surface of the particles at a rate proportional to the surface area. Under such conditions, the following equation applies (24)

$$\left(1 - \frac{C_t}{C_f}\right)^{1/3} = 1 - k_{\text{obs}}t \quad (2)$$

where C_t is the Cr concentration at time t , C_f is the final Cr concentration, and $k_{\text{obs}} = k/r_0\rho$ (k is the rate constant, r_0 is the initial particle radius, and ρ is the particle density). Plots of $(1 - C_t/C_f)^{1/3}$ versus time yield straight lines with slope $-k_{\text{obs}}$ (Figure 3), supporting the reaction model indicated by eq 2. Thus, the $\text{FeO}_4^{2-}/\text{Cr}_2\text{O}_3$ reaction rate is dictated by the particle surface area indicating a direct reaction of FeO_4^{2-} with Cr(III) at the Cr_2O_3 surface. The k_{obs} values indicate the reaction to be slower at higher hydroxide concentration. This is con-

TABLE 3. Results of Ferrate Leaching With Hanford Tank S-107 Sludge

[OH ⁻], M	Fe(VI)/Cr(III), mol/mol	T, °C	amount removed, %				
			Al	Ca	Cr	Si	TRU ^a
3.0	0	50	46	0	18	77	<0.3
2.4	12	50	50	0	63	69	<0.3
2.1	18	50	51	23	64	64	<0.3
1.8	24	50	37	0	45	61	<0.3
3.0	0	70	54	0	28	79	<0.2
2.4	12	70	54	38	64	69	<0.3
2.1	18	70	49	21	64	71	<0.3
1.9	24	70	48	0	63	65	<0.3

^a TRU = transuranic elements, measured as the total alpha activity. For the Hanford tank S-107 sludge, this includes plutonium, americium, and curium isotopes (20).

sistent with the oxidation of other substrates with ferrate, in which the reaction rates were found to decrease with increasing pH (17, 25, 26, 27). More detailed kinetic studies are required to fully elucidate the reaction mechanism.

Chromium Removal from Actual Hanford Tank Waste. Table 3 summarizes the results of treating Hanford tank S-107 sludge with FeO_4^{2-} . The components reported are Al, Ca, Cr, Si, and the TRU elements. Sodium and Fe are not reported because additional quantities of these elements were introduced in the form of NaOH and FeO_4^{2-} , respectively. Two major S-107 sludge components, U and Zr, are not reported in Table 3 as they were never detected in the leaching solutions.

Treatment of the S-107 sludge with FeO_4^{2-} more than doubled the fraction of Cr removed compared to that obtained in the absence of FeO_4^{2-} . The level of Cr removal achieved (~60%) is such that the volume of immobilized HLW would no longer be dictated by the Cr content (assuming a limit of 0.5 wt % Cr_2O_3 in the HLW glass). The amount of Fe added into the HLW solids from the reduction of FeO_4^{2-} would have no impact on the immobilized HLW volume.

Comparing the amount of chromate ion (determined by UV-vis spectrophotometry) to the amount of total chromium (determined by ICP) indicated that, within experimental error, all of the dissolved chromium was present as chromate ion. Most of the Cr oxidation occurred in the first hour and was generally complete after 5 h. Under the conditions examined the Cr removal was independent of the Fe(VI)/Cr(III) ratio. This is consistent with the trend shown in Figure 1b as the minimum Fe(VI)/Cr(III) ratio examined with the S-107 sludge was 12. No significant differences in Cr removal were observed between 50 and 70 °C. Consistent with previous observations (28) and results obtained with the sludge simulant, in the absence of FeO_4^{2-} increasing temperature slightly increased chromium dissolution.

Except in a few instances, little Ca was removed from the S-107 sludge. Aluminum and Si were removed to a significant extent, and there is some evidence that the silicon removal correlates positively with the free-hydroxide concentrations. On the other hand, Al removal remained fairly independent of the hydroxide concentration. Aluminum and Si removal showed little dependence on temperature.

The behavior of the TRU elements in the leaching process is very important. The TRU elements must remain in the solids so that the leaching solution can be handled as LAW. Little dissolution of the TRU elements occurred in the experiments conducted here. The amount of added FeO_4^{2-} , the change from 3 to 2 M NaOH, and the change in leaching temperature from 50 °C to 70 °C all had little observable effect on the TRU behavior. The most important question is whether the ferrate-leachate solutions can be classified as HLW or LAW. To address this question, a calculation was performed to determine the TRU concentration that would

result if the solution were concentrated to the point of 20 wt % Na₂O, such as might be present in the final immobilized LAW form. The result of this calculation indicated that the projected TRU content of the immobilized LAW waste form would be < 0.25 nCi/g in all cases. This is more than an order of magnitude below the Class A low-level waste TRU specification of 10 nCi/g.

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