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Process Development for Permanganate Addition during Oxidative Leaching of Hanford Tank Sludge Simulants

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Abstract: In previous studies, we have examined using sodium permanganate for selectively oxidizing and removing chromium from washed Hanford tank sludges. The conclusion from the previous work was that contact with sodium permanganate in a minimally caustic solution, i.e., 0.1 to 0.25 M [OH^-] initially, provided maximum Cr dissolution while minimizing concomitant Pu dissolution. This report describes work focused on developing simulants to be used in pilot scale oxidative leaching tests; developing methods for monitoring chromium oxidation by permanganate; and identifying the Cr and Mn materials formed during the oxidative leaching process. The impact of such variables as the Cr compound used, agitation rate, temperature, hydroxide concentration, and initial MnO_4^-:Cr ratio on the rate and extent of chromate formation were examined.

Keywords: Chromiun; Chromium hydroxide; Chromium oxide; Oxidative Leaching; Oxyhydroxide; Permanganate

INTRODUCTION

Several studies over the past several years have explored the idea of selectively oxidizing poorly alkaline soluble Cr(III) to the more highly alkaline soluble Cr(VI) as a means to remove Cr from Hanford tank sludge solids (1–9). Removing Cr from the tank-waste solids is required in some cases so that the waste loading in the high-level waste form (borosilicate glass) is not constrained by the presence of Cr, which causes processing difficulties at relatively low concentrations. Although a variety of oxidants

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have been explored (1,4,9), most recent work in this area has focused solely on the use of alkaline permanganate solutions to accomplish selective Cr removal from Hanford high-level tank solids (6–8).

Oxidative leaching of Cr with sodium permanganate is part of the baseline high-level waste pretreatment process to be implemented in the Hanford Waste Treatment Plant (WTP). To support the design and construction of the WTP, a pilot plant will be constructed and operated to test critical processing steps. However, performing work on actual radioactive tank sludge is expensive and cumbersome, and for all practical purposes prohibitive at the pilot plant scale. Thus it is necessary to develop a simulant that mimics actual tank-waste leaching performance so that the effects of changing process variables on the oxidative alkaline leaching performance can be evaluated at the pilot plant scale.

We have undertaken a program to develop the required simulants for chromium leaching studies. The approach being taken is iterative in nature in that experiments will be performed with Cr(III) phases likely to be present in the tank wastes, and these will be compared to the results of bench-scale testing performed with actual radioactive tank waste material. The key parameter of interest is the relative rate of Cr(III) oxidation, with the intent that the simulant Cr(III) phase(s) will be chosen to approximate the rate of Cr(III) oxidation determined for the actual tank waste. We report here the evaluation of various Cr-containing materials for potential use in tank waste simulants. Based on the highly alkaline nature of the Hanford tank waste, chromium(III) oxides and hydroxides are considered to be good candidates for the simulated Cr(III) phases; so our initial investigations have focused on examining hydrous chromium hydroxide, chromium oxy/hydroxide, and chromium oxide. Results of these studies will be compared to the results of testing performed with actual tank waste (when available) so that recommendations can be made regarding the tank waste simulant composition.

EXPERIMENTAL SECTION

General Experimental Information

Hematite (Fe_2O_3) and Magnetite (Fe_3O_4) were obtained from Strem Chemicals, Inc. (Newburyport, MA). Goethite (FeOOH) and nickel hydroxide [$Ni(OH)_2$] were obtained from Alfa Aesar® (Ward Hill, MA). Zinc hydroxide [$Zn(OH)_2$] was obtained from Wintersun Chemical (Ontario, CA). Chromium(III) oxide was obtained from Baker and Adamson (Morristown, NJ). All of these commercially available products were used as received. The hydroxide concentrations in the stock sodium

hydroxide solutions were verified by titration with primary standard HCl solutions. The permanganate concentrations in stock sodium permanganate solutions were verified by titration against standard-grade sodium oxalate according to a literature procedure (10).

Ultraviolet-visible (UV-vis) spectrophotometric measurements were made on a 400-series charge-coupled device (CCD) array spectrophotometer (Spectral Instruments Inc.) with a 200- to 950-nm scanning range. The solutions were held in PLASTIBRAND® 1-cm cuvettes. UV-vis spectroscopic measurements were obtained as follows: sample aliquots were diluted as necessary with stock sodium hydroxide solutions (typically 0.1 M or 0.25 M), and the spectra from 250 to 900 nm were recorded. The chromate concentrations were determined by measuring the test solution's absorbance at 372 nm, which is the wavelength of maximum absorbance for chromate ion in the visible spectrum. The instrument was calibrated at this wavelength using standard-grade potassium dichromate in 1 M NaOH according to a published procedure (11).

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

The particle size distributions and particle surface area (calculated assuming spherical particles) were determined with a Mastersizer 2000 (Malvern Instruments, Inc., Southborough, MA 01772 USA) with a Hydro μP wet dispersion accessory. Samples were measured using a pump speed of 3000 rpm both before and after being subjected to sonication; surface area data after agitation are reported below.

Preparation of Hydrous Chromium(III) Hydroxide, $Cr(OH)_3 \cdot xH_2O$

Hydrous chromium(III) hydroxide was precipitated from ammonia solution in an adaptation of the approach used by Ratnasamy and Léonard (12). $CrCl_3 \cdot 6H_2O$ (35.636 g; 0.134 mole) was dissolved in 75 mL of deionized (DI) water. The resulting solution was filtered through a 0.45-μm nylon membrane and then slowly added (over a period of $\sim$10 min) to 150 mL of 4.9 M NH_4OH (prepared by mixing 50 mL of concentrated NH_4OH solution with 100 mL DI water) with stirring. After stirring for

$\sim$0.5 h, the chromium(III) hydroxide precipitate was filtered using a 0.45-μm polyether sulfone (PES) vacuum filter unit. The filtered solid was transferred to a beaker and washed with 200 mL of DI water and filtered again through the PES filter. The washing step was repeated, except that the final filtration was performed using a 0.45-μm Nylon membrane. The wet chromium(III) hydroxide filter cake was transferred to a watch glass and dried in vacuo over Drierite; the solid was occasionally broken up with a spatula to facilitate drying. The final dry weight was 18.3 g of $Cr(OH)_3 \cdot xH_2O$.

Preparation of Hydrated Chromium Oxyhydroxide, $Cr(O)(OH) \cdot xH_2O$

Chromium(III) oxyhydroxide hydrate was prepared as follows: 4 grams (about 0.01 mol) of $Cr(NO_3)_3 \cdot 9H_2O$ was placed in 84 mL of water in a Teflon beaker with a Teflon magnetic stirring bar with a graphite bottom suitable for heating on a hot plate. Sixteen mL of 19 M NaOH (304 mmol) was added to the well-stirred solution. The solution initially formed a precipitate, which then redissolved as more NaOH was added. The mixture was stirred and heated to about 90°C on a magnetic stirrer/hot plate. When the temperature reached about 80°C, a precipitate appeared. The system was heated at about 90°C for 2 hours. The system then was allowed to cool overnight and centrifuged. The supernatant was removed by decantation. The residual solids were well mixed with 100 to 200 mL of DI water, and the centrifuge/decant cycle was repeated for a total of four contacts with DI water. The residual solids then were dried under vacuum at approximately 80°C over the $\sim$3 days to yield about 1.04 grams of green solid (1.03 g expected for the monohydrate). Upon drying, the material appears as a glassy monolith. Grinding to a powder with a mortar and pestle, followed by grinding in a jitterbug apparatus for 1 to 10 minutes gave a material with a surface area of ca. $3\,m^2/g$, based on particle size analysis.

Preparation of Ferric Hydroxide

Ferric hydroxide was prepared from $FeCl_3 \cdot 6H_2O$ and NH_4OH in a manner similar to that described above for the hydrous chromium hydroxide. The ferric hydroxide was dried by spreading it out on a watch glass and drying in vacuo over Drierite until the mass was constant. To determine the water content of the ferric hydroxide product, two weighed aliquots were heated to 550°C to convert the material to Fe_2O_3. This gave an average Fe content for the product as 49.5 wt%, which suggests a formulation

of $Fe(OH)_3 \cdot 0.3H_2O$. Thus, the ferric hydroxide product was nearly anhydrous.

Preparation of the Cr(III)-Containing Simulant Solids

With Cr(III) Hydroxide as the Cr Source

The non-chromium components of the simulant were mixed in two batches (Table 1), each batch being ground in a jitterbug mill for 30 min. The two batches were then combined, yielding a net weight of 12.278 g of non-chromium powder recovered. This non-chromium component mixture was combined with $Cr(OH)_3 \cdot 2.2H_2O$ to yield a simulant with 19.8 wt% Cr. This material was mixed overnight using a rock-tumbler.

With Cr(III) Oxyhydroxide as the Cr Source

The non-chromium-containing components of the simulant were combined in the amounts listed in Table 2. This mixture of components was ground in a jitterbug ball mill for 30 min and then was sieved using a small USA Standard Sieve (Newark Wire Cloth Company) rated to 45 μm. The quantity of material that passed through the sieve (i.e., the fraction that was $\leq$45 μm) was 4.209 g. Subsequently, the portion that did not pass through the sieve was re-ground in the jitterbug ball mill and passed through the 45-μm sieve to give another 4.187-g fraction of material $\leq$45 μm. To prepare the Cr(O)(OH)-containing simulant, $Cr(O)(OH) \cdot H_2O$ was combined with the material described in Table 3 to achieve a Cr content of 23.2%. The combined materials then were mixed in a tumbler overnight.

Table 1. Preparation of non-chromium components for Cr hydroxide simulant

Component	Added to batch 1, g	Added to batch 2, g
$Fe(OH)_3$	1.502	1.500
Fe_2O_3	1.502	1.504
Fe_3O_4	1.502	1.502
FeO(OH)	1.502	1.502
$Ni(OH)_2$	0.152	0.152
$Zn(OH)_2$	0.151	0.151
Total Mass:	6.311	6.311

Table 2. Non-Cr components combined for Cr-oxide and Cr oxyhydroxide containing simulant

Component	Amount added, g
$Fe(OH)_3$	5.023
Fe_2O_3	5.017
Fe_3O_4	5.014
FeO(OH)	5.007
$Ni(OH)_2$	0.206
$Zn(OH)_2$	0.196
Total Mass:	20.463

With Cr(III) Oxide as the Cr Source

For a chromium-oxide-containing simulant, chromium(III) oxide was combined with the material described in Table 2 to achieve a Cr content of 26.4%. The combined materials then were mixed in a tumbler overnight.

Preparation of Manganese Solids by Reduction of Permanganate by Cr(III) Solids in Alkaline Solution

Three-quarters of a gram of $Cr(O)(OH)\cdot H_2O$ (7.3 mmol Cr) was placed in approximately 40 mL of 0.1 M NaOH at ambient temperature. A total of 8.5 mL of 0.94 M $NaMnO_4$ (8 mmol permanganate) in H_2O was added in 0.5-mL portions over the course of 2.5 hours. A purple solution resulted.

Table 3. FTIR data for hydrous chromium(III) hydroxide

Band position, cm^{-1}		
Experimental	Literature (11)	Band assignment (11)
513	495–530	Cr-O-Cr vibrations arising from groups of the type CrO_4^{x-} (x = 2, 3, or 4), which form from surface oxidation
844	845	
1279	Not Reported	(a)
1399	1385	Absorbed CO_2
1481	1488	
1626	1625	H_2O bend
3416	3420	ν(OH)

(a) The band at 1279 cm^{-1} is possibly due to absorbed NH_3.

The suspension was stirred at room temperature for a total of 6 hours after the first addition. The suspension was then filtered through a 0.45-micron nylon filter assembly and washed five times with 0.1 mL NaOH. Air was passed through the filter assembly until no visible liquid passed through, yielding 0.683 grams of dark-brown solids.

This procedure was repeated with suspension in 3 M NaOH. After 6 hours of contact time with permanganate, the solids were washed with 0.1 M NaOH and then air dried as described above, which isolated 0.588 grams of rust-brown solid.

The solids generated from both the 0.1 and 3 M hydroxide reactions were dissolved for analysis by potassium hydroxide fusion. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to determine the Mn and Cr content. XRD analysis indicated that both solids were amorphous.

RESULTS AND DISCUSSION

Preparation and Characterization of Chromium Compounds

Hydrous chromium(III) hydroxide was prepared by adding an aqueous solution of $CrCl_3$ into an ammonium hydroxide solution. The resulting amorphous blue-green solid was characterized by thermal gravimetric analysis and Fourier transform infrared (FTIR), and the particle-size distribution was determined. The number of waters of hydration was determined to be 2.4 by firing a measured amount of the product to Cr_2O_3 in a muffle furnace at 500°C. Based on the formulation as $Cr(OH)_3{\cdot}2.4H_2O$, the product yield was 93%. This material was ground in a jitterbug mill, leading to a slight decrease in the water content and yielding a material better formulated as $Cr(OH)_3{\cdot}2.2H_2O$, which was used in subsequent oxidative leaching experiments. The particle-size distribution measurement for $Cr(OH)_3{\cdot}2.2H_2O$ indicated a surface area of $1.4\,m^2/g$.

Table 3 presents the FTIR spectral data (as a KBr pellet) for this material and compares them to data taken from the literature. For the most part, the FTIR data for the hydrous chromium(III) hydroxide product prepared here agree with that reported in the literature. The exception is the band observed at $1279\,cm^{-1}$, which was not previously reported. This band might be due to absorbed ammonia.

Hydrated chromium(III) oxyhydroxide was prepared by heating a strongly alkaline solution of chromium(III) nitrate at 90°C for 2 hours. The product obtained in this manner was found to be amorphous. The FTIR spectrum indicated that this product was somewhat different than

the hydrous chromium(III) hydroxide, displaying spectral bands as follows (cm^{-1}): 3200 (s, vbr), 2004 (br), 1680, 1480, 1370. Thermal gravimetric analysis in air to 600°C (i.e., complete conversion to Cr_2O_3) indicated a single water of hydration, so the product is formulated as $Cr(O)(OH)\cdot H_2O$. Assuming this formulation, the product yield was 99%.

Chromium(III) oxide was obtained from commercial sources. XRD analysis of this material showed an excellent match for crystalline Eskolaite (Cr_2O_3). The particle-size distribution measurement for the commercially available Cr_2O_3 indicated a surface area of $3.55\,m^2/mL$. Thermal gravimetric analysis indicated this material to be anhydrous.

Characterization of the Manganese Solids Generated during Oxidative Alkaline Leaching of Cr(III)

A sample of chromium(III) oxyhydroxide was reacted with 1.05 equivalents of permanganate at an initial free hydroxide concentration of either 0.1 or 3 M. Table 4 presents the results of the ICP-OES analysis of the resulting solids. Clearly, only partial conversion of the available chromium occurred under the conditions used in this experiment, with the lower hydroxide reaction having an especially low conversion. The Mn solids generated were examined by XRD but were found to be amorphous.

The solids obtained were evaluated for their average oxidation state (expressed as an O:Mn ratio) using a procedure adapted from the reports of Murray (13,14). The method was validated by analyzing several known compounds: MnO, Mn_3O_4, Mn_2O_3, and MnO_2. The results are summarized in Table 5. This method indicates that the solids are predominantly Mn(IV) [as Mn(V) is unstable and Mn(VI) and Mn(VII) are soluble materials under the experimental conditions] along with some lower-oxidation-state Mn solids being present. Assuming the lower oxidation state solids to be Mn(III), this indicates that in 0.1 M hydroxide, 78% of the solids exist as Mn(IV) and 22% as Mn(III); in 3 M hydroxide, 94% of the solids exist as Mn(IV) and 6% as Mn(III).

Table 4. Elemental analysis for solids generated by permanganate contact with Cr(O)(OH) in either 0.1 M or 3 M NaOH

Element	0.1 M NaOH (μg/g)	3 M NaOH (μg/g)
Mn	75900	209000
Cr	359000	208000
% Cr converted	35%	68%

Table 5. Oxidation state determination of Mn solids according to the method of murray

O : Mn	MnO	Mn_3O_4	Mn_2O_3	MnO_2	Sample 0.1 M OH^-	Sample 3 M OH^-
1st try	1.00	1.38	1.53	1.98	1.88	2.03
2nd try	1.00	1.36	1.52	1.97	1.89	1.92
3rd try	–	1.37	1.48	2.05	1.89	1.95
Average	1.00	1.37	1.51	2.00	1.89	1.97
SD	0	0.01	0.03	0.04	0.01	0.06
Expected	1.00	1.33	1.50	2.00	NA	NA

NA = Not applicable.

Previous studies on the reduction of permanganate in basic media suggest that the generated Mn solids exist in the form of birnessite, [Na_4-$Mn_{14}O_{27}{\cdot}9H_2O$] (15). For this material, the average Mn oxidation state is 3.6. For the 0.1-M generated solids, the average oxidation state is 3.78; for the 3-M-hydroxide generated solids, the average oxidation state is 3.94. Consequently, if the primary material generated here is indeed birnessite, some additional higher Mn oxidation state material must also be present.

Oxidative Alkaline Leaching of Single Cr Compounds

Initial experiments were performed using the individual chromium compounds. The purpose of these tests was to optimize the experimental system. These tests used a large liquid-to-solid ratio (approximately 50 mL/0.1 grams solid) to prevent any significant change in the free hydroxide concentration as a result of the expected consumption of 1 equivalent of base during the oxidative alkaline leaching. Figure 1 presents the UV/vis spectra obtained during a room-temperature titration of hydrous chromium hydroxide with permanganate. This plot shows many features common to the reaction of permanganate with Cr(III) compounds. At a Mn:Cr ratio of 1.44, chromate (CrO_4^{2-}) permanganate (MnO_4^-) and manganate (MnO_4^{2-}) are all seen. Chromate has a characteristic band at 372 nm, permanganate has multiple characteristic bands centered around 525 nm (16), manganate has a characteristic broad band at 607 nm (16), and all are present when excess permanganate is added.

To eliminate the interferences from permanganate and manganate ion in the spectrophotometric determination of chromate ion, a series of reactions performed in which excess hydrogen peroxide was used to selectively remove all soluble Mn species from solution. In this case,

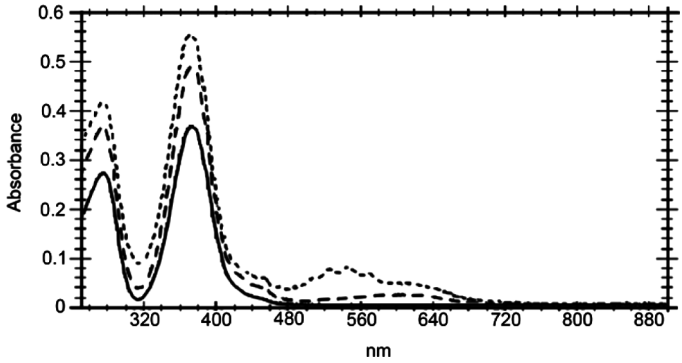

Figure 1. Plot of visible spectra for the reaction of 0.503 mmole of $Cr(OH)_3{\cdot}5.1H_2O$ with 0.9 M $NaMnO_4$ in 0.1 M NaOH at room temperature. Note that 0.56 mL of added permanganate would give a [Cr]:[Mn] of 1.0 mL. Legend: 0.9 M $NaMnO_4$ added = 0.4 (solid line), 0.6 (long dash), 0.8 (short dash); mole Mn/mole Cr = 0.72 (solid), 1.08 (long dash), 1.44 (short dash).

the chromium solids were reacted for 6 h with 1 equivalent of permanganate under differing conditions of starting Cr compound and temperature; excess soluble Mn was removed by contact with hydrogen peroxide; and the dissolved Cr as chromate was determined spectrophotometrically so that the fraction of dissolved Cr could be calculated. The results of these experiments are summarized in Table 6. The results indicate that the reaction of simple Cr compounds with permanganate in 0.1 M NaOH under comparable conditions appears to follow the order $Cr(OH)_3{\cdot}5.1\ H_2O$ (23°C) ~ Cr_2O_3 (80°C) > $Cr(O)(OH){\cdot}H_2O$ (80°C) > $Cr(O)(OH){\cdot}H_2O$ (23°C) >> Cr_2O_3 (23°C).

The final variable examined with pure Cr compounds was the type of agitation performed. The previous experiments were performed with

Table 6. Dissolution of Cr solids after 6 hours contact time with 1 equivalent of permanganate as determined by spectrophotometrically

Cr Compound	Temperature (°C)	% Cr dissolved as chromate
$Cr(OH)_3{\cdot}5.1H_2O$[a]	23	95
Cr_2O_3	23	9
Cr_2O_3	80	~100
$Cr(O)(OH){\cdot}H_2O$	23	35
$Cr(O)(OH){\cdot}H_2O$	80	61

[a]The $Cr(OH)_3{\cdot}5.1H_2O$ phase was prepared in the same manner as the $Cr(OH)_3{\cdot}2.2H_2O$ phase, except that it was not dried as rigorously.

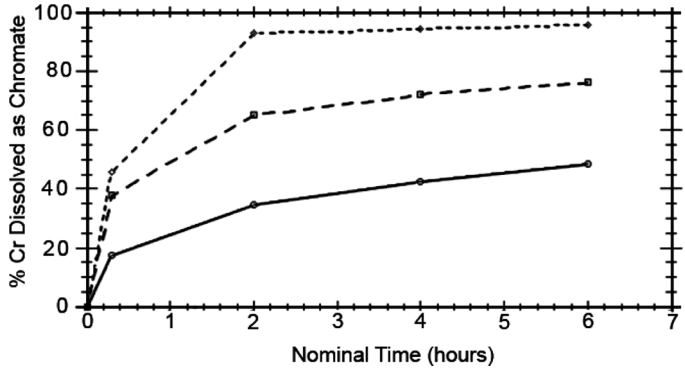

Figure 2. Influence of agitation type of % Cr dissolved as chromate for $Cr(OH)_3 \cdot 2.2\,H_2O$. Circles represent shaker table at 200 rpm, squares a 0.5-inch linear stir bar, and diamonds a 1-inch linear stir bar.

a mildly stirred solution using a linear, 0.5-inch Teflon-coated magnetic stirring bar. The stirring conditions were varied, and the rate of chromate formation was monitored with $Cr(OH)_3 \cdot 2.2\,H_2O$ as the Cr source at room temperature. The results are shown in Fig. 2, which shows clearly that the manner of agitation is important and needs to be controlled rigorously. It is of interest to note that many of the previous Hanford tank sludge studies were performed at 200 rpm on a shaker table, which yields only about half the formed chromate that more vigorous agitation can obtain.

Oxidative Alkaline Leaching of Cr Simulant

As noted in the experimental section, the chosen source of chromium was mixed with several other metals (Fe, Ni, Zn) to obtain a Hanford tank-waste simulant. The concentrations of these materials were not set to mimic any particular sludge composition, only to test the Cr compounds in the presence of other (presumed) inert material. The metals chosen were based on their relevance to criticality safety in the waste treatment plant currently under construction and were added in sufficient quantities so as to be readily detectable if significant amounts were dissolved in later, more extensive leaching studies.

Unless otherwise noted, the agitation for the simulant leaching tests was achieved using a 1-inch, finned magnetic stirring bar at a nominal speed of 500 rpm. This speed was chosen because it was the maximum speed that could be obtained without splashing the contents on the

beaker walls. Visual observation of the system indicated that the solids were well suspended under these conditions. To determine the reproducibility of the experimental results, an experiment was performed in which duplicate samples of the $Cr(O)(OH)\cdot H_2O$-based simulant were treated with permanganate (Mn:Cr = 1) in 0.25 M NaOH at 25°C. The rate of chromate formation as a function of time was found to agree very well between the duplicate runs, with the exception of the 8-hour point, where there was a 10% discrepancy.

Influence of Mixing Conditions

This set of experiments was designed to evaluate under more controlled conditions the impact of changing agitation rates on the removal of Cr from the $Cr(O)(OH)\cdot H_2O$-based simulant using materials with $Cr(O)(OH)\cdot H_2O$ with two different surface areas. The results are shown in Fig. 3. These results not only reinforce the earlier conclusion of the importance of sample agitation in chromate formation, but also note here the importance of surface area, where (compare the results shown in Fig. 3 at 8 hours) a 12% increase in surface area can lead to an approximately 25% increase in the extent of chromium dissolved by alkaline permanganate oxidation over relatively short times.

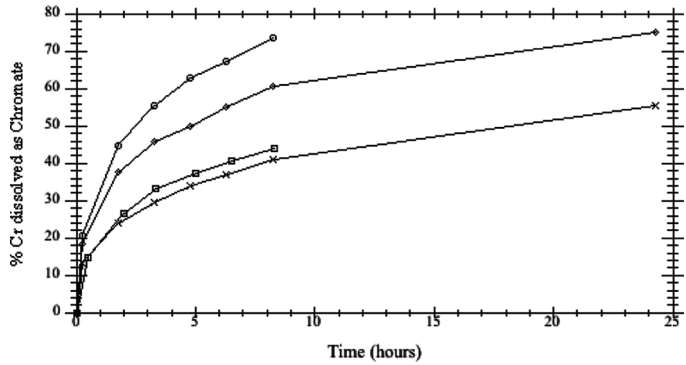

Figure 3. Impact of varying mixing conditions on chromate formation for a $Cr(O)(OH)\cdot H_2O$-based simulant at 0.25 M NaOH, 25°C, Initial [Mn]/[Cr] = 1. Circles represent 500-rpm stirring with surface area 3.34 m^2/g Cr(O)(OH) H_2O, squares represent 200-rpm shaking with surface area 3.34 m^2/g Cr(O)(OH) H_2O, diamonds represent 500-rpm stirring with surface area 2.92 m^2/g Cr(O)(OH) H_2O, and X represents 200-rpm shaking with surface area 2.92 m^2/g $Cr(O)(OH)\cdot H_2O$.

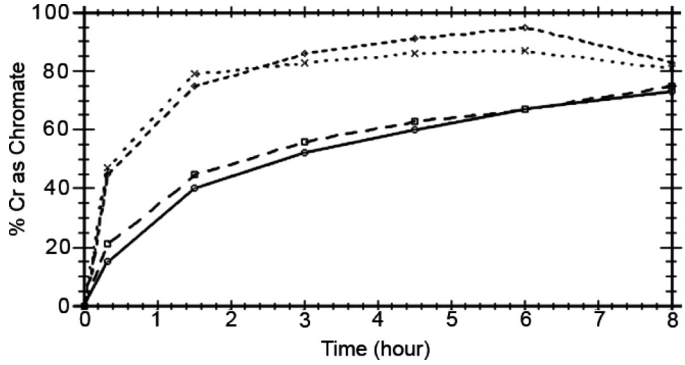

Figure 4. Impact of hydroxide on chromate formation for a $Cr(O)(OH)\cdot H_2O$-based simulant at 500-rpm stirring, 25°C, 1 equivalent permanganate, surface area 3.34 m^2/g $Cr(O)(OH)$ H_2O. Circles represent 0.1 M NaOH, squares represent 0.25 M NaOH, diamonds represent 1.25 M NaOH, and X represents 3 M NaOH.

Influence of Hydroxide Concentration

Testing was performed under identical conditions of temperature (25°C), molar equivalents of permanganate to Cr (1.0), and agitation conditions (500-rpm stirring), but with the hydroxide concentrations changed from 0.1 M to 3 M NaOH. The results (Fig. 4) indicate that while changes from 0.1 to 0.25 M NaOH and from 1.25 M to 3 M NaOH are minor, a marked increase in the extent of chromate formation is found upon changing the hydroxide concentrations from 0.25 M to 1.25 M NaOH. Mapping out the rate and extent of chromate formation between these hydroxide regimes would be worth further study. Extensive Cr oxidation at the higher hydroxide concentrations also is observed. The results show that 80% or more conversion of $Cr(O)(OH)\cdot H_2O$ to chromate is possible at room temperature, which is consistent with the extent of Cr dissolution in many Hanford tank sludges during oxidative alkaline leaching (3–8).

Influence of Varying Temperature from 25°C to 45°C

An experiment was conducted using the $Cr(O)(OH)\cdot H_2O$-based simulant to evaluate the effects of changing the temperature from 25°C to 45°C during treatment with permanganate (Fig. 5). This 20°C temperature change results in significant enhancement in the degree of chromate formation, although the changes are most dramatic early in the leaching

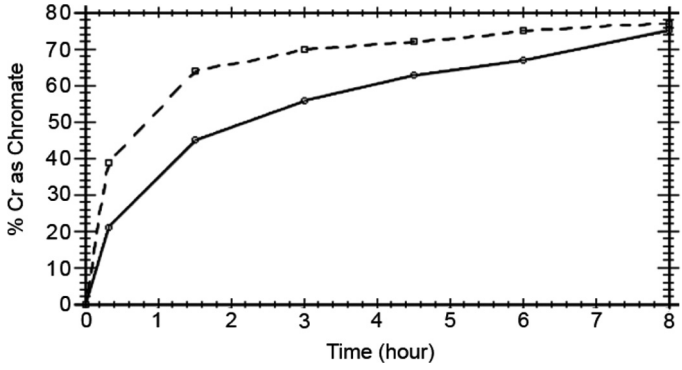

Figure 5. Impact of varying temperature on chromate formation for a $Cr(O)(OH)\cdot H_2O$-based simulant at 0.25 M NaOH, 500-rpm stirring, Initial [Mn]/[Cr] = 1. Circles represent 25°C contact with a surface area 3.34 m^2/g $Cr(OH)_3$-containing simulant, and squares represent 45°C contact with surface area 3.34 m^2/g $Cr(OH)_3$-containing simulant.

process and drift down to about a 10% enhancement after 6 hours of contact time.

Influence of Varying Initial [Mn:Cr]

To explore the effects of varying the Mn:Cr ratio at 25°C, a series of experiments was performed in which the reaction conditions were kept the same except for the initial permanganate:Cr ratio, which was varied between 0.75 and 1.25. The results are shown in Fig. 6. Although there appears to be some scatter in the data, especially with the latter parts of the [Mn:Cr] = 0.9 data, the results indicate that increasing the [Mn:Cr] = 0.75 to 0.9 results in a noticeable increase in the extent of chromate formation, with further increases in [Mn:Cr] having little observable impact.

A second set of experiments was performed at 45°C, again keeping all the reaction conditions the same except for the initial permanganate:Cr ratio, which was varied between 0.75 and 1.25. The results from these experiments are shown in Fig. 7 (on a slightly different y-scale than Fig. 6). In this case, the results are similar for [Mn:Cr] ratios of 0.75, 0.9, and 1.0, but a marked increase in Cr oxidation is seen at [Mn:Cr] = 1.25. The reason for marked increase in Cr(III) oxidation occurring at [Mn]/[Cr] > 1 at 45°C compared to at < 1 at 25°C is not obvious at this point.

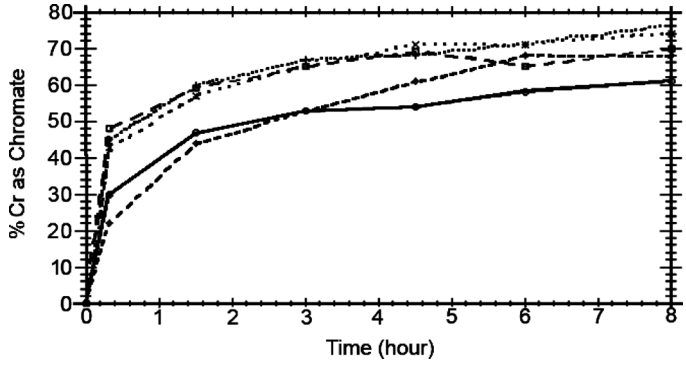

Figure 6. Impact of varying initial [Mn]:[Cr] on chromate formation for a $Cr(O)(OH)\cdot H_2O$-based simulant at 0.25 M NaOH, 500-rpm Stirring, 25°C, with a surface area 3.34 m^2/g $Cr(O)(OH)$ H_2O-containing simulant. Circles represent [Mn]:[Cr] = 0.75, squares represent [Mn]:[Cr] = 0.90, diamonds represent [Mn]:[Cr] = 1.0, X represents [Mn]:[Cr] = 1.1, and crosses represent [Mn]:[Cr] = 1.25.

Results for the Chromium(III) Oxide-Based Simulant

Experiments analogous to those described above were performed with the simulant that was prepared using Cr_2O_3 as the source of Cr. In general, the trends observed paralleled those observed for the $CrOOH\cdot H_2O$-based

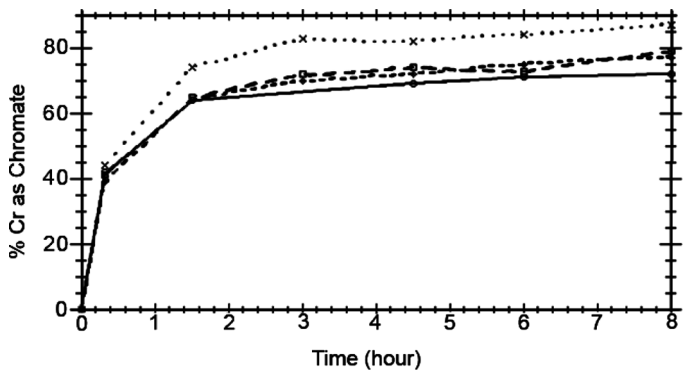

Figure 7. Impact of varying initial [Mn]:[Cr] on chromate formation for a $Cr(O)(OH)\cdot H_2O$-based simulant at 0.25 M NaOH, 500-rpm stirring, 45°C, with a surface area of 3.34 m^2/g $Cr(O)(OH)$ H_2O-containing simulant. Circles represent [Mn]:[Cr] = 0.75, squares represent [Mn]:[Cr] = 0.90, diamonds represent [Mn]:[Cr] = 1.0, and X represents [Mn]:[Cr] = 1.25.

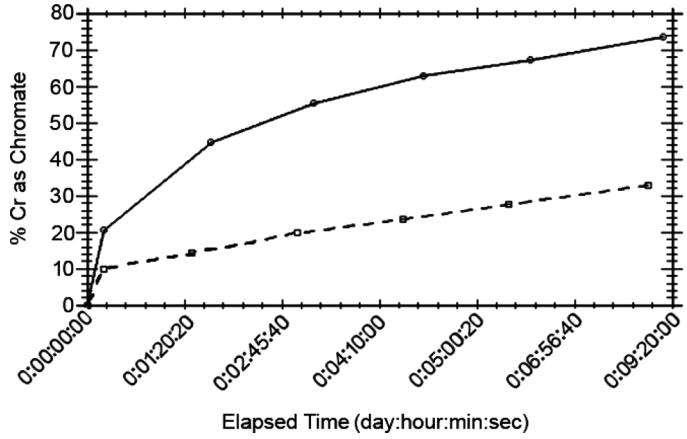

Figure 8. Impact of varying Cr in simulant phase on chromate formation for a $Cr(O)(OH)\cdot H_2O$-based simulant at 0.25 M NaOH, 500-rpm stirring, 25°C. Circles represent a 3.34 m^2/g surface area, $Cr(O)(OH)$ H_2O-containing simulant. Squares represent a 3.55 m^2/g surface area, Cr_2O_3-containing simulant.

simulant, except that the extent of Cr(III) oxidation was usually much less. Figure 8 provides a comparison of the results for the oxidation of the Cr_2O_3-based simulant with 1 equivalent of permanganate in 0.25 M NaOH at 25°C to that for the $CrOOH\cdot H_2O$-based simulant under identical conditions.

SUMMARY AND CONCLUSIONS

Key findings of this work include:

- The work with the non-radioactive simulants reveals several important design features to incorporate and/or verify the simulant. One striking feature was how, with both Cr(III) oxide at 80°C or $Cr(O)(OH)\cdot H_2O$ at 23°C, the manner of agitation affected the oxidation of Cr. Over an 8-hr contact time, an approximately 60% enhancement in the extent of $Cr(O)(OH)\cdot H_2O$ dissolution and an approximately 40% enhancement in the extent Cr(III) oxide dissolution were observed simply as a function of the type of sample agitation employed.
- The influence of temperature (45 vs. 25°C) depended strikingly on the material examined, with a 120% increase in chromate formation over an 8-hr time frame observed for chromium(III) oxide, but with almost no change for the $Cr(O)(OH)\cdot H_2O$. It should be noted that larger differences were observed for $Cr(O)(OH)\cdot H_2O$ over shorter reaction times.

- Hydroxide concentration also has an impact, with about a 20% enhancement being observed over 8 hours from 0.25 versus 3 M NaOH. $Cr(O)(OH)\cdot H_2O$ is rather interesting, with, like temperature, only a small, about 10% increase, being observed from 0.1 to 3 M NaOH over an 8-hr time frame. However, much greater changes were observed over shorter time frames. The changes with respect to hydroxide concentration appear non-linear, with little change being observed from 0.1 to 0.25 M or from 1.25 to 3 M NaOH, with a much larger change being observed from 0.25 to 1.25 M.
- As might be expected, the initial [Mn]:[Cr] ratio appears important up to near the stoichiometric ratio of 1:1. Above about a ratio of 0.9 and with either chromium(III) oxide or $Cr(O)(OH)\cdot H_2O$, little further increase in chromate oxidation is observed over the entire 8-hr time frame. The exception to this statement appears to be $Cr(O)(OH)\cdot H_2O$ contacted at 45°C, where excess permanganate does appear to somewhat enhance Cr oxidation.

In short, the features that might be expected to impact a solid-liquid reaction, the manner of agitation, temperature, and hydroxide concentration all participate, albeit to varying extents, in the degree of chromium oxidation by permanganate in alkaline solutions over a given time frame. The surface area of the Cr-containing phases would also be expected to significantly impact the rate of Cr oxidation with permanganate, but we have not yet systematically studied that parameter.

Information was collected in these tests concerning three phases of Cr, $Cr(OH)_3\cdot xH_2O$, $Cr(O)(OH)\cdot H_2O$, and Cr_2O_3, and will influence the choice of Cr source used for further simulant testing. The rate of chromium(III) oxide oxidation, especially at close to room temperature, was judged to be too slow compared to results from tests with actual tank waste to be a good Cr source for simulant preparation. Oxidation of $Cr(OH)_3\cdot xH_2O$, on the other hand, was judged to be too rapid as it essentially goes to completion at relatively short contact times. $Cr(O)(OH)\cdot H_2O$ reacts with permanganate at an intermediate rate and so seems to provide good intermediate performance, so its use in further simulant studies seems warranted.

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