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Characterization and oxidation of chromium(III) by sodium hypochlorite in alkaline solutions

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Abstract

Chromium exists in nuclear waste sludges and is a problematic element in the vitrification process of high-level nuclear wastes. It is therefore necessary to treat the waste sludges to remove chromium prior to vitrification, by caustic leaching or oxidation of Cr(III) to Cr(VI). The objective of this study is to investigate the effect of oligomerization of Cr(III) on its oxidation by hypochlorite in alkaline solutions.

Monomeric, dimeric and trimeric Cr(III) species in solution were separated by ion exchange. The kinetics of the oxidation of the separated species by hypochlorite in alkaline solutions was studied by UV/Vis absorption spectroscopy, and compared with the oxidation by hydrogen peroxide previously studied. Results indicate that hypochlorite can oxidize Cr(III) to Cr(VI) in alkaline solutions, but the rate of oxidation by hypochlorite is slower than that by hydrogen peroxide at the same alkalinity and concentrations of oxidants. The rate of oxidation of Cr(III) by both oxidants decreases as the concentration of sodium hydroxide is increased, but the oxidation by hypochlorite seems less affected by the degree of oligomerization of Cr(III) than that by peroxide. Compared with the oxidation by hydrogen peroxide where the major reaction pathway has an inverse order with respect to C_{NaOH} , the oxidation by hypochlorite has a significant reaction pathway independent of [OH⁻].

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1. Introduction

Chromium in nuclear waste sludges is a problematic constituent in the vitrification process of high-level nuclear wastes (HLW). At the operating temperature of the glass melter (1050–1150 °C), even relatively small amounts of chromium can result in the formation of a refractory spinel-type crystalline solid phase. The formation and settling of crystallites during the vitrification can adversely affect the process operation. Consequently, the allowable limits for chromium in the melter feed must be low. To decrease the volume of vitrified glass and significantly reduce the

cost of nuclear waste management, pretreatment techniques must be developed to remove chromium from HLW before vitrification.

The nuclear wastes stored in underground tanks at Hanford, Washington State of the United States are alkaline and consist of supernatant, salt cake and sludge. The sludge, containing most of the actinides as well as chromium (mostly Cr(III)), is the major source of the HLW. Different strategies are proposed to remove chromium from the sludge, including oxidative leaching under alkaline conditions. However, leaching results of actual tank sludge have indicated that the efficiency of removal is not as high as expected, due to a poor understanding of the chemical behavior of chromium in alkaline solutions. To develop efficient pretreatment strategies for the removal of chromium, systematic studies are needed to reveal the chemical speciation and its effect on the redox reactions of chromium in alkaline solutions.

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It is known that hydrolysis of Cr(III) leads to formation of various oligomers [1-8]. Recent studies have shown that the degree of oligomerization, while depending on alkalinity, temperature and aging time [9,10], affects the kinetics of oxidation of Cr(III) by hydrogen peroxide [9] and persulfate [11]. Hydrogen peroxide and persulfate could oxidize Cr(III) to Cr(VI) in alkaline solutions, but each has own shortcomings. Hydrogen peroxide has a strong tendency to decompose and generate gaseous products under alkaline conditions. Persulfate, on the other hand, may generate sulfate that causes problems in glass vitrification and increases the volume of nuclear wastes. Therefore, more oxidants need to be investigated. In this paper, we report the results of oxidation of Cr(III) by hypochlorite, another oxidant that has wide applications in water treatment.

The dissolved species of Cr(III) hydroxide of different degrees of oligomerization were separated by an ion exchange chromatography technique developed previously [3–10] and characterized by UV/Vis absorption spectroscopy. Kinetic experiments were conducted to determine the rate of oxidation of Cr(III) by hypochlorite in alkaline solutions. The rate of oxidation by hypochlorite is compared with that by hydrogen peroxide. The kinetic data, in conjunction with the information from characterization, help to reveal the effect of oligomerization on the rate of oxidation of Cr(III).

2. Experimental

2.1. Chemicals

All chemicals were reagent grade or higher and used without further purification. Solutions were prepared with deionized water from a Milli-Q system. Solutions of sodium hydroxide were prepared from an oversaturated sodium hydroxide solution and standardized by pH titration. Stock solutions of Cr(III) were prepared by dissolving $Cr(ClO_4)_3$. 6H₂O (Aldrich) in water. UV–Vis absorption spectra of the stock solutions were collected to confirm the absence of Cr(VI) in the solutions. The Cr(III) solutions of different acidity (to achieve different degrees of oligomerization) were prepared by adding appropriate amounts of NaOH solutions and stored in an inert-atmosphere (Ar) glove box. The Cr(III) solutions used in the characterization and the redox experiments were filtered prior to use, with the 0.2 µm nylon Acrodisc filter (Gelman). Solutions of sodium hypochlorite were prepared from a solution of 10% NaClO (Aldrich) and standardized by redox titrations with sodium thiosulfate standard solutions [12] prior to use.

2.2. Separation and characterization of chromium(III) oligomers

Chromium(III) oligomers were separated by an ion exchange method using Sephadex SP C-25 cation exchange resin (Aldrich) described in the literature [3–10]. The separation was improved in this work by using eluents of

increasingly higher ionic strength (from 1 to 4 mol dm⁻³ NaClO₄) and HClO₄ concentrations (from 0.01 to 0.04 mol dm⁻³). The solutions of the separated Cr(III) species were either immediately used for characterization and redox studies or stored in a refrigerator prior to use. UV–Vis absorption spectra of the solutions were obtained on a Cary-5G spectrometer.

2.3. Kinetic study of oxidation of Cr(III) by hypochlorite in alkaline solutions

The oxidation kinetics were studied by UV/Vis absorption spectroscopy on an Ocean Optics ST 2000 or a Cary-5G spectrometer, with most experiments carried out on the former instrument. Appropriate amounts of NaClO and NaOH were first mixed in a 1.0-cm cuvette to take the background reading. Immediately after an aliquot of Cr(III) solution was injected into the cuvette and rapidly mixed, the absorbance of Cr(VI) at 372 nm (A_t) was monitored as a function of time. When the reaction was completed, the absorbance at 372 nm was recorded as A_{∞} .

Redox experiments were conducted with large excess of sodium hypochlorite and hydroxide with respect to Cr concentrations. At time t, $[Cr_n(III)] (n = 1, 2 \text{ and } 3 \text{ for the monomer, dimer and trimer)}$ was equal to $([Cr(VI)]_{\infty} - [Cr(VI)]_t)/n$ and proportional to $(A_{\infty} - A_t)/n$, where $[Cr(VI)]_t$ and $[Cr(VI)]_{\infty}$ are the concentrations of Cr(VI) at time t and at the completion of the reaction, respectively. A statistical significance test [13] indicated that the kinetic traces of $\ln(A_{\infty} - A_t)$ were essentially linear functions of time, suggesting a first-order reaction with respect to $[Cr_n(III)]$. The reaction rate is expressed as Eq. (1) and the pseudo-first-order rate constant, k_{obs} , were calculated from the plots of $\ln(A_{\infty} - A_t)$ versus t.

$$-d[\operatorname{Cr}_{n}(\operatorname{III})]/dt = (1/n)d[\operatorname{Cr}(\operatorname{VI})]/dt = k_{\operatorname{obs}}[\operatorname{Cr}_{n}(\operatorname{III})] \quad (1)$$

The overall stoichiometry of the oxidation of Cr(III) by hypochlorite was determined by using excess amounts of sodium hypochlorite in the reaction mixture. After the oxidation of Cr(III) to Cr(VI) was completed, the concentration of Cr(VI) was determined by UV–Vis absorption at 372 nm while the remaining hypochlorite was determined by the titration method with sodium thiosulfate standard solutions [12].

3. Results and discussion

3.1. Characterization of the oligomers of Cr(III) in solution

The optical absorption spectra of the separated Cr(III) oligomer species in solution are shown in Fig. 1. As the degree of oligomerization of Cr(III) increases, the absorption peaks are slightly red-shifted and intensified. The positions and intensities of the spectra are identical to those observed in previous studies [9]. The structures of the Cr(III) oligomers in these solutions have already been determined by Extended X-Ray Absorption Spectroscopy



Fig. 1. Optical absorption spectra of Cr(III) species separated by ion chromatography: (top) monomer; (middle) dimer; (bottom) trimer.

(EXAFS) in the previous study [9]. Therefore, no EXAFS experiments were repeated in this work. The structures of the Cr(III) oligomers determined by EXAFS are also shown in Fig. 1. Detailed discussions on the EXAFS data and the structures are provided elsewhere [9].

The spectra of the Cr(III) stock solutions were checked before and after the redox experiments that lasted for a few months. No detectable changes were observed, confirming that the separated Cr(III) species were stable during the entire course of the redox experiments.

3.2. Oxidation of Cr(III) by sodium hypochlorite

3.2.1. Reaction orders

Kinetic experiments were conducted at different concentrations of NaOH and NaClO under the pseudo-first-order conditions with respect to Cr(III). The pseudo-first-order rate constant (Eq. (1)), k_{obs} , was calculated from the linear plot of $\ln (A_{\infty} - A_t)$ versus t. The results are summarized in Table 1.

At constant C_{NaOH} , k_{obs} increased proportionately with the increase of C_{NaCIO} as shown in Fig. 2, suggesting the reaction is first-order with respect to C_{NaCIO} . The slopes of the lines represent the values of k_{OH} (Table 1). At constant C_{NaCIO} , k_{OH} decreased as the concentration of NaOH was increased. Two models seem to interpret the results equally well: one model assumes there are two reaction pathways (dependent on or independent of [NaOH]); the other model excludes the pathway that is independent of [NaOH]. The reaction order with respect to [OH] was calculated to be -1 or -0.5 with the two models, respectively. At present, we do not have additional information to help select one of the two models. However, the first model that results in an integer reaction order (-1) appears more reasonable and it is similar to the model used to interpret the oxidation of Cr(III) by hydrogen peroxide [9]. Therefore, we elect to include both pathways that are dependent on and independent of [NaOH]. A general rate equation (Eq. (2)) can be suggested for the oxidation of Cr(III) to Cr(VI) by hypochlorite. The values of k_{OH} , k and k' are summarized in Table 1.

$$-d[Cr_n(III)]/dt = k_{obs}[Cr_n(III)]$$

= $k_{OH}[Cr_n(III)][NaClO]$
= $k[Cr_n(III)][NaClO](1/[OH^-] + k')$ (2)

3.2.2. Comparison of hypochlorite with hydrogen peroxide

Table 2 shows the comparison of the rate of oxidation of Cr(III) by hypochlorite in this study with that by hydrogen peroxide previously reported [9]. The results show the following similarities between the two oxidants: (1) both hypochlorite and peroxide can oxidize Cr(III) to Cr(VI) in alkaline solutions; (2) for both oxidants, the rate of oxidation decreases as the concentration of sodium hydroxide is increased. The results also show the following differences between the two oxidants: (1) in general, the oxidation of Cr(III) by hypochlorite is slower than that by peroxide at the same alkalinity and concentrations of oxidants (see the values of τ in Table 2); (2) the reaction pathway independent of [OH⁻] is more significant in the oxidation by hypochlorite than that by peroxide, suggested by the larger k' for hypochlorite; (3) the rate of oxidation by hypochlorite seems less affected by the degree of oligomerization of Cr(III) than that by peroxide.

3.2.3. Overall reactions and possible mechanisms

It was determined in this study that three moles of NaClO were consumed when two moles of Cr(III) were oxidized. The stoichiometric ratio suggests that chloride, instead of chlorine, is the end product of the reduction of hypochlorite by Cr(III). However, such information is not sufficient to reveal the actual reaction mechanism. At least two possible mechanisms can be suggested: (1) hypochlorite is reduced directly to chloride via a two-electron transfer reaction; (2) hypochlorite is reduced to chlorine via a oneelectron transfer. The chlorine rapidly disproportionates in alkaline solutions to chloride and hypochlorite and the latter reacts with another equivalent of Cr(III). Both mechanisms would result in a stoichiometric ratio of 2:3 (Cr(III)/ hypochlorite). At present, we do not have other experimental evidence to distinguish between the two possible mechanisms. Instead, we can only suggest the following overall reactions between the monomer, dimer or trimer of Cr(III) and hypochlorite in alkaline solutions. In the reactions, the dominant species of hypochlorite is assumed to be ClObecause the pK_a of HClO is about 7.4 [14].

Table 1	
Kinetic data for the oxidation of separated chromium(III) species by hypo	chlorite

Sample	$C_{\rm NaOH} \ ({\rm mol} \ {\rm dm}^{-3})$	$C_{\rm NaClO} \ ({\rm mol} \ {\rm dm}^{-3})$	$k_{\rm obs}~({\rm min}^{-1})$	$k_{\rm OH^-} \ ({\rm min^{-1}} \ {\rm mol^{-1}} \ {\rm dm^3})$	$k (\min^{-1})$	$k^{-1} (\mathrm{mol}^{-1}\mathrm{dm}^3)$
Cr(III) monomer	0.104	5.60E - 03 1.12E - 02 2.80E - 02 5.60E - 02	0.0046 0.0089 0.0213 0.0477	0.835 ± 0.021	0.068 ± 0.002	2.0 ± 0.2
	0.250	$\begin{array}{l} 1.12E - 02 \\ 2.80E - 02 \\ 5.60E - 02 \\ 1.12E - 01 \end{array}$	0.0041 0.0107 0.0209 0.0407	0.368 ± 0.003		
	0.500	$\begin{array}{l} 2.98E - 02 \\ 5.60E - 02 \\ 1.12E - 01 \\ 1.68E - 01 \end{array}$	0.0080 0.0149 0.0310 0.0476	0.282 ± 0.003		
	0.750	$\begin{array}{l} 2.98\mathrm{E} - 02 \\ 5.60\mathrm{E} - 02 \\ 1.12\mathrm{E} - 01 \\ 1.68\mathrm{E} - 01 \end{array}$	0.0064 0.0141 0.0284 0.0454	0.260 ± 0.006		
	1.00	$\begin{array}{l} 5.03\mathrm{E}-02\\ 1.12\mathrm{E}-01\\ 1.68\mathrm{E}-01\\ 2.23\mathrm{E}-01 \end{array}$	0.0105 0.0260 0.0359 0.0462	0.212 ± 0.004		
Cr(III) dimer	0.104	$\begin{array}{l} 1.12E - 02 \\ 2.79E - 02 \\ 5.58E - 02 \\ 1.12E - 01 \end{array}$	0.010 0.022 0.048 0.104	0.909 ± 0.019	0.070 ± 0.004	2.7 ± 0.2
	0.250	$\begin{array}{l} 1.12E - 02 \\ 2.79E - 02 \\ 5.58E - 02 \\ 1.12E - 01 \end{array}$	0.0049 0.0091 0.029 0.063	0.542 ± 0.026		
	0.500	$\begin{array}{l} 2.79\mathrm{E} - 02 \\ 5.58\mathrm{E} - 02 \\ 1.12\mathrm{E} - 01 \\ 1.68\mathrm{E} - 01 \end{array}$	0.010 0.019 0.042 0.060	0.361 ± 0.005		
	0.750	5.58E - 02 1.12E - 01 1.68E - 01 2.23E - 01	0.016 0.031 0.050 0.061	0.282 ± 0.005		
	1.00	$\begin{array}{l} 5.58E - 02 \\ 1.12E - 01 \\ 1.68E - 01 \\ 2.23E - 01 \end{array}$	0.013 0.028 0.041 0.055	0.246 ± 0.002		
Cr(III) trimer	0.104	1.12E - 02 2.79E - 02 5.58E - 02 1.12E - 01	0.010 0.020 0.040 0.055	0.704 ± 0.050	0.058 ± 0.006	2.9 ± 0.5
	0.250	1.12E - 02 2.79E - 02 5.58E - 02 1.12E - 01	0.006 0.012 0.025 0.049	0.440 ± 0.005		
	0.500	$\begin{array}{l} 2.79\mathrm{E} - 02 \\ 5.58\mathrm{E} - 02 \\ 1.12\mathrm{E} - 01 \\ 1.68\mathrm{E} - 01 \end{array}$	0.010 0.015 0.035 0.050	0.301 ± 0.007		
	0.750	5.58E - 02 1.12E - 01 1.68E - 01 2.23E - 01	0.012 0.023 0.036 0.046	0.209 ± 0.002		

Table 1 (continued)

Sample	$C_{\rm NaOH} \ ({\rm mol} \ {\rm dm}^{-3})$	$C_{ m NaClO} (m mol dm^{-3})$	$k_{\rm obs}~({\rm min}^{-1})$	$k_{\rm OH^-} \ ({\rm min}^{-1} \ {\rm mol}^{-1} \ {\rm dm}^3)$	$k (\min^{-1})$	$k^{-1} (\mathrm{mol}^{-1}\mathrm{dm}^3)$
	1.00	5.58E - 02	0.0113	0.206 ± 0.003		
		1.12E - 01	0.0218			
		1.68E - 01	0.0337			
		2.23E - 01	0.0472			
	4 2					

 $C_{\rm cr} = 1.42 \times 10^{-4}$ mol dm⁻³. The error limits for $k_{\rm OH^-}$, k, and k' represent the standard deviations at 95% confidence level. $-d[Cr_n(III)]/dt = k_{\rm obs}[Cr_n(III)] = k_{\rm OH}[Cr_n(III)][NaClO] = k[Cr_n(III)][NaClO](1/[OH^-] + k').$



Fig. 2. Pseudo first-order rate constant, k_{obs} , as a function of C_{NaCIO} at constant $C_{Cr}(1.42 \times 10^{-4} \text{ mol dm}^{-3})$ and different C_{NaOH} : (a) monomer; (b) dimer; (c) trimer. Symbols: C_{NaOH} (mol dm⁻³) = 0.104 (+), 0.250 (\bigstar), 0.500 (\blacklozenge), 0.750 (\blacktriangledown), 1.00 (\diamondsuit). Detailed conditions of the experiments are provided in Table 1.

Table 2				
Kinetic data for	the oxidation o	of Cr(III) by	hypochlorite and	hydrogen peroxide

Cr(III) species	Hypochlorite		Hydrogen peroxide [9]			
	$k (\min^{-1})$	$k' \pmod{-1}{\mathrm{dm}^3}$	τ^{a} (min)	$k (\min^{-1})$	$k' \pmod{-1}{\mathrm{dm}^3}$	τ^{a} (min)
Monomer	0.068 ± 0.002	2.0 ± 0.2	490	327 ± 6	0.07 ± 0.09	0.3
Dimer	0.070 ± 0.004	2.7 ± 0.2	390	11.3 ± 0.3	0.0 ± 0.1	9
Trimer	0.058 ± 0.006	2.9 ± 0.5	440	1.33 ± 0.04	1.34 ± 0.04	32
Unseparated and aged in 8 M NaOH	0.0048 ± 0.0026	2.6 ± 4.3	5800	0.032 ± 0.002	0.53 ± 0.01	2040

The error limits in brackets for k, and k' represent 3σ .

^a Reaction lifetime $\tau = 1/k_{obs}$. Values of τ were calculated for [oxidant] = 0.01 M and [OH⁻] = 1 M.

$$2Cr(OH)_{4}^{-} + 3ClO^{-} + 2OH^{-} \rightarrow 2CrO_{4}^{2-} + 3Cl^{-} + 5H_{2}O$$
(3)
$$Cr_{2}O_{2}(OH)_{4}^{2-} + 3ClO^{-} + 2OH^{-} \rightarrow 2CrO_{4}^{2-} + 3Cl^{-} + 3H_{2}O$$
(4)

$$2Cr_{3}O_{4}(OH)_{4}^{3-} + 9ClO^{-} + 6OH^{-} \rightarrow 6CrO_{4}^{2-} + 9Cl^{-} + 7H_{2}O$$
(5)

The formula of Cr(III) species in the above equations are postulated based on the structures in acidic solutions (Fig. 1), taking into consideration the likely conversion of hydroxo-bridges to oxo-bridges in alkaline solutions. As pointed out by Hall and Eyring [15], higher concentrations of hydroxide facilitate the conversion of hydroxo-bridges to oxo-bridges through deprotonation and/or dehydration. By conductometric titrations, they concluded that addition of sodium hydroxide could cause a large increase in the number of oxo-bridges formed [15].

Though the overall reactions (Eqs. (3)–(5)) all contain hydroxide on the reactant side, it does not mean that hydroxide would necessarily facilitate the oxidation of Cr(III) by hypochlorite in alkaline solutions. In fact, the rate of oxidation actually decreases as C_{NaOH} is increased (Table 1). This observation could suggest that, either the rate-determining step involves the weakening and release of one hydroxyl group from the Cr(III) moiety upon the attack by hypochlorite, or presumably the activated complex between Cr(III) and hypochlorite involves chromium species that are protonated at one of the hydroxyl groups. Alternatively, the observed decrease of reaction rate at higher C_{NaOH} could imply that the redox reaction occurs through intermediate states involving the protonated species of hypochlorite. Further mechanistic studies are needed to reveal the reaction mechanism.

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