

Development of Alkaline Oxidative Dissolution Methods for Chromium(III) Compounds Present in Hanford Site Tank Sludges

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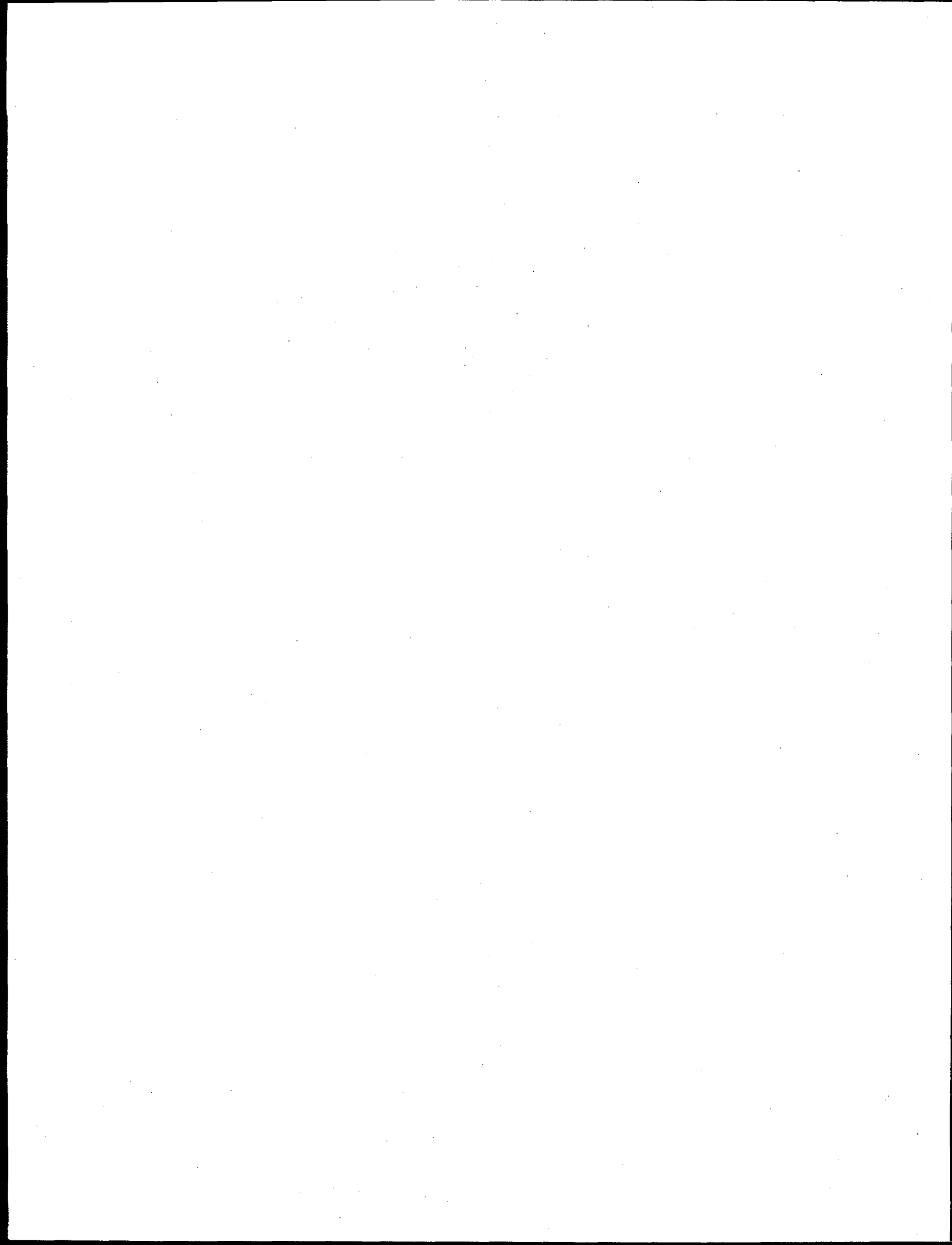
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Summary

The high-level radioactive waste sludge in the underground storage tanks at the Hanford Site contains various chromium(III) solid phases. Dissolution and removal of chromium from tank waste sludges is desirable prior to high-level waste vitrification because increased volume is required to incorporate the residual chromium. Unfortunately, dissolution of chromium from the sludge to form $\text{Cr}(\text{OH})_4^-$ through treatment with heated NaOH solution (also used to dissolve aluminum phases and metathesize phosphates to sodium salts) generally has been unsuccessful in tests with both simulated and genuine Hanford waste sludges. Oxidative dissolution of the Cr(III) compounds to form soluble chromate has been proposed as an alternative chromium solid phase dissolution method and results of limited prior testing have been reported.

The present systematic tests investigated oxygen gas, hydrogen peroxide, and sodium persulfate oxidants to dissolve Cr(III) under alkaline conditions to form soluble chromate. Permanganate and ozone also were considered for testing but were thought to be of secondary interest because of the insoluble residue (MnO_2 from permanganate) and complex equipment (necessary to generate ozone) implicit with use of these reagents. The oxygen and hydrogen peroxide reagents leave no condensable residue and sodium persulfate only leaves soluble sodium sulfate.

Crystalline $\text{Cr}(\text{OH})_3$, various hydrothermally aged amorphous Cr(III) oxide hydrates, mixed Fe(III)/Cr(III) oxide hydrates, and nickel and iron Cr(III) spinels, all of which have been identified or are likely constituents in Hanford tank wastes, were prepared and characterized for the dissolution tests. The effects of reagent and hydroxide concentrations, reaction temperature, and transition metal catalysts on reaction progress were investigated for each reagent as functions of reaction time. Reaction progress was measured by monitoring chromate concentration.

Oxidation of chromium compounds by dissolved oxygen was found to increase linearly with oxygen partial pressure and NaOH concentration. The rate also increased with temperature at low activation energy, 26–36 kJ/mol, reflecting the opposing influences of decreasing oxygen solubility and increasing underlying chemical reaction rate. The reaction apparently proceeds by way of dissolved Cr(III) species, is catalyzed by Ni(II), and is slower for the hydrothermally aged materials. Dissolution rates ranged from about 7×10^{-5} to 2.4×10^{-4} moles Cr(III)/liter-hour in 80°C, 3-M NaOH with one atmosphere pure oxygen for the various Cr(III) compounds tested. These low dissolution rates commend the use of oxygen reagent to waste tank processing where extended residence times may be practical.

Oxidative dissolution of Cr(III) compounds by hydrogen peroxide was hampered in the presence of greater than 0.5 g Fe(III)/liter and other catalysts for H_2O_2 decomposition and was less effective for materials that had undergone prolonged aging at high temperatures. Leaching was optimized at low excess NaOH and high temperatures (activation energy of ~82 kJ/mol). To prevent excessive loss of H_2O_2 to catalytic decomposition, the peroxide reagent must be added slowly and with intense stirring. Treatment of waste solids with H_2O_2 may only be attractive for freshly formed Cr(III) hydroxides [formed, for example, by alkaline metathesis of Cr(III)-bearing sludges] in the absence of decomposition catalysts such as Fe(III).

Oxidative dissolution of Cr(III) solid phases by persulfate was not strongly affected by the Cr(III) phase being tested. Even crystalline 800°C-fired Cr_2O_3 and NiCr_2O_4 spinel were oxidatively dissolved by persulfate though at slightly slower rates. The stoichiometry of one mole Cr(III) oxidized per 1.5 moles persulfate was observed. Optimum process conditions were ~70°C and 0.3 to 0.5 M excess NaOH. Higher temperatures and NaOH concentrations can lead to thermal decomposition of the oxidant in side reactions. The Cr(III) oxidation reaction was catalyzed by Co(II), Ni(II), Cu(II), and Fe(III). In 70°C,

2 M NaOH with four-fold excess persulfate, Cr(III) hydrated oxide initial dissolution rates on the order of $(2 \text{ to } 5) \times 10^{-3}$ moles/liter-minute were observed. The rapid reaction rates obtained with persulfate commend its use in process reactors. The persulfate reaction product is soluble sulfate; the sulfate partitions to the low-activity solution.

With strong oxidants, oxidative dissolution of plutonium oxide or sorbed Pu(IV) also can occur in alkaline solution. The oxygen and hydrogen peroxide reagents are not strong enough to promote Pu(IV) to the more soluble (V) or (VI) oxidation states and thus should not enhance plutonium solution concentrations. Persulfate, however, is strong enough to oxidatively dissolve plutonium. Fortunately, a simple method, thermal decomposition of excess persulfate followed by reduction of oxidized plutonium by H_2O_2 addition, should cause reprecipitation of the dissolved plutonium without causing unwanted reduction and precipitation of chromium.

These parametric tests have identified the range of optimum conditions for oxidative dissolution of Cr(III) from various simulant sludge phases using oxygen, hydrogen peroxide, and persulfate oxidants. However, it is necessary to test these reagents for their effects on genuine wastes to ensure their process efficacy.

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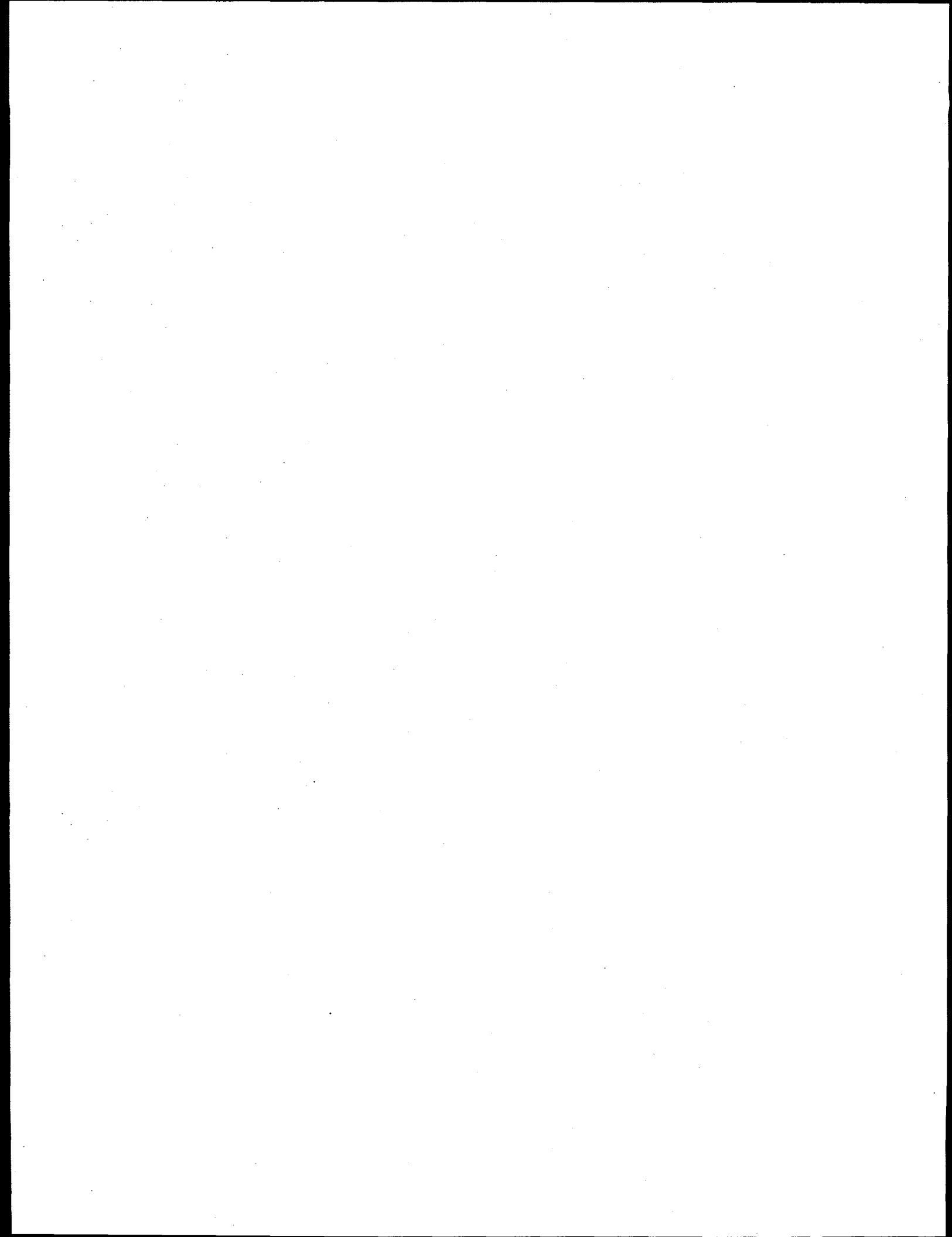
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1.0 Introduction

The high-level radioactive waste in underground storage tanks at the Hanford Site is alkaline and consists of solid crystalline salts (for example, sodium nitrate, nitrite, carbonate, phosphate), alkaline sludges of low solubility (transition metal hydroxides and phosphates, aluminum hydroxide, aluminosilicates), and the associated alkaline solutions. The wastes will be segregated into high-activity and low-activity streams before their separate vitrification and final disposal. The high-activity stream will contain most of the radionuclides and the bulk waste chemicals associated with the waste sludge. The low-activity stream will contain most of the alkali-soluble waste chemicals (primarily sodium salts) but relatively low concentrations of the radionuclides. Certain bulk components in the tank waste sludge (primarily aluminum, phosphate, and chromium) have relatively low solubilities in the waste glass compared with their inventories in the waste, and, if they remain in the waste sludge, will contribute significantly to the volume of the high-activity glass. Therefore, it is desirable to remove these dissolved nonradioactive components from the sludge by leaching and relegate them to the low-activity vitrified stream. Hot solutions of 3 M NaOH can be used to leach aluminum and phosphate phases [Lumetta et al. 1997]. However, chromium leaching by strong alkali is often insufficient [Lumetta et al. 1997] because of the very low solubility of aged Cr(III) hydroxide in hot NaOH solutions to form the $\text{Cr}(\text{OH})_4^-$ dissolved species [Felmy et al. 1994]. Instead, oxidation of Cr(III) compounds to form soluble chromate (CrO_4^{2-}) must be used as an alternative method to dissolve chromium from the alkaline tank sludge.

As shown in the technical literature [Berka et al. 1961; Gmelin 1963], oxygen gas, hydrogen peroxide, persulfate, permanganate, and ozone are effective Cr(III) oxidants in alkaline media. Of these reagents, oxygen, hydrogen peroxide, and persulfate are the most attractive for oxidative leaching of Cr(III) solids from Hanford tank sludges because they do not contribute to the sludge volume as permanganate does [Rapko 1998] and do not require specialized equipment as ozone does [Delegard et al. 1993]. The residual sodium sulfate produced from the persulfate oxidant is soluble in alkaline solution and should report to the low-activity stream while the oxygen gas and hydrogen peroxide leave no condensable residue.

The ability of oxygen to oxidize Cr(III) compounds in alkaline media has been known for a long time [Gmelin 1963]. However, this process was studied in detail only at rather high temperatures and pressures [Farrow and Burkin 1975]. Recently, several tests were performed to evaluate Cr(III) leaching by treating Hanford tank sludge with oxygen at atmospheric pressure [Rapko 1998]. The tests showed that nearly complete dissolution of Cr(III) compounds from genuine alkali-leached sludge residues from Tanks 241-U-108, 241-U-109, and 241-SX-108 could be achieved by bubbling pure O_2 through 80°C, 3-M NaOH suspensions of the respective sludges for four to six days. The reaction rate decreased significantly if 0.1 M NaOH were used.

Oxidative alkaline dissolution of Cr(III) solids by oxygen thus is a highly appealing method to remove chromium from Hanford tank sludge before its vitrification. However, the process must be studied more thoroughly and systematically to determine the optimum conditions of its performance. Parametric study of oxidation of Cr(III) solids by oxygen was one of the tasks of the present investigation.

Information on the interaction of Cr(III) solid phases with hydrogen peroxide (H_2O_2) is limited. According to early data, no reaction takes place in acidic or neutral media. In hot KOH solution, complete oxidation of Cr(III) was observed only by use of a five-fold stoichiometric excess of H_2O_2 [Gmelin 1963]. Application of hydrogen peroxide in 3 M NaOH to leach Cr(III) from sludge residues remaining after alkaline washing of simulated Tank 241-SY-101 waste and genuine wastes from Tanks 241-SY-101 and 241-SY-102 was tested recently at room temperature [Delegard 1995]. Though

effective Cr(III) oxidation was found for the simulant waste, little leaching was found for the genuine wastes. The low extent of leaching observed in the tests with genuine wastes may have been caused by the low oxidation reaction rate in comparison with the parasitic catalytic decomposition of H_2O_2 under the studied test conditions. To verify this assumption, the reaction of Cr_2O_3 with H_2O_2 was tested at room and elevated (80°C) temperatures [Rapko et al. 1997]. These tests also gave poor dissolution, probably because crystalline Cr_2O_3 is a very stable compound and acted mainly as a catalyst to decompose H_2O_2 [Voltz and Weller 1954]. In addition, crystalline Cr_2O_3 is not likely to be present in Hanford tank sludge because its crystallization in alkaline media only proceeds above 400°C [Ratnasamy and Leonard 1972; Mikhail and Selim 1974; Viktorov et al. 1994]. Based on the mixed results found for hydrogen peroxide, study of the oxidation of different Cr(III) compounds by hydrogen peroxide in alkali solutions over a wide range of conditions was undertaken as a separate goal of the present investigation.

The interaction of Cr(III) with persulfate primarily has been studied in acid solutions. Results on the reaction in alkaline media are old and limited [Gmelin 1963]. The early studies show that the process does not proceed at room temperature whereas Cr(III) is oxidized by persulfate easily and completely in boiling NaOH or KOH solutions. The promising but limited findings for persulfate motivated study of Cr(III) alkaline oxidation by persulfate for its use in processing Hanford tank sludge.

2.0 Experimental Materials and Methods

2.1 Reagents and Equipment

Reagent-grade $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cr}(\text{OOCCH}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used to prepare standard solutions of Cr(III), Fe(III), Fe(II), and Ni(II), respectively. Solution concentrations were determined by gravimetric analyses after evaporation of measured volumes (0.1 mL) of the solutions in platinum crucibles and calcination of the residues to their respective oxides. Standard 1-M $\text{S}_2\text{O}_8^{2-}$ solutions were prepared using chemical-grade $\text{Na}_2\text{S}_2\text{O}_8$. The solutions were analyzed by iodometric titration and stored in a refrigerator.

Working sodium hydroxide solutions were obtained by the dilution of 16.7-M chemical purity-grade NaOH; they were stored in polyethylene bottles. Standard solutions of other reagents were prepared by dissolving the salt (NaNO_3) in distilled water or by the dilution of respective solution reagents (NH_4OH , H_2O_2).

Powder x-ray diffraction patterns of solid samples were measured by an x-ray diffractometer ADP-10, using $\text{CuK}_{\alpha 1}$ -radiation (Philips PW 1140/90/96 generator, Holland). To take infrared (IR) spectra, 2–2.5 mg of compound were mixed with 200 mg of special purity-grade NaCl and ground into powder for 10 to 20 minutes in an agate mortar. The pulverized mixture was pressed into a transparent 2-cm-diameter disk in a die at 190 kP/cm² pressure. The disk was positioned in a special holder and placed in the compartment of an IR spectrophotometer (Specord-M80, Germany). The IR spectra were recorded in the range 350–4000 cm⁻¹.

The particle size distributions of some initial Cr(III) hydroxides were determined using the small-angle x-ray scattering (SAXS) technique [Plavnik 1986]. The SAXS intensity measurements were performed using a KRM-1 instrument (Russia) in the interval 0.05 to 10 degrees with variable step scanning. The samples studied by the SAXS technique were mixed with small volumes of $\text{C}_2\text{H}_5\text{OH}$ and uniform suspensions were placed as thin layers on a 0.02-mm Mylar film. After drying to a paste, additional layers of the suspension were placed on the same film. Layering was repeated three to five times to obtain a final deposit containing 350 to 500 mg over the 1x2-cm surface. Mylar film covered the samples to prevent further drying.

Thermostats (U-2 and U-10 models, Germany) were used to maintain constant ($\pm 0.2^\circ\text{C}$) solution temperature in the 30 to 90°C range. Precipitates were separated from supernatant liquids using medical centrifuges (model CLK-1, Russia) providing a field of 1,750-times the acceleration of gravity. Analytical sample masses were determined by a Sartorius microbalance with ± 1 µg sensitivity.

2.2 Preparation of the Chromium Solid Phases

Hanford tank waste sludges differ significantly in origin and composition and are extremely inhomogeneous. The inhomogeneity is reflected in the Cr(III) compounds found in the sludges: $\text{Al}_{1-x}\text{Cr}_x(\text{OH})_3$ (Cr-gibbsite), $\text{Fe}_{1-x}\text{Cr}_x(\text{OH})_3$ (Cr-ferrihydrite), CrOOH (grimaldite) [Whyatt et al. 1996], $\text{Fe}(\text{Cr,Fe})_2\text{O}_4$ (donathite), and unidentifiable non-crystalline or poorly crystalline phases [Lumetta 1997] all have been found in various wastes. Some Cr(III) compounds might be expected to decompose, with the associated formation of Cr(III) hydroxides, by washing and caustic leaching of the tank sludge. The spinel-type phases, however, are stable to attack by alkali [Markina and Freire 1984]. Because of the

diversity of phases observed in genuine Hanford tank wastes, Cr(III) hydroxide, mixed Fe(III)-Cr(III) hydroxide, and some representative spinel phases [NiCr_2O_4 and $\text{Fe}(\text{Cr,Fe})_2\text{O}_4$] were prepared for the present dissolution investigations.

Because Cr(III) compounds are prepared industrially for catalysts and other applications, the synthesis and properties of Cr(III) hydroxides have been described in many publications. Information from the technical literature of special interest in the preparation of Cr(III)-bearing phases for the present work is summarized.

Chromium(III) hydroxide, precipitated at room temperature from nitrate solutions by a small excess of NH_4OH , is a crystalline compound having an orthorhombic lattice of $\alpha\text{-Al}(\text{OH})_3$ (bayerite) structure [Milligan 1951; Ratnasamy and Leonard 1972]. The compound is unstable and with long-term storage or heating to greater than 60°C transforms into an amorphous product; the amorphous Cr(III) hydroxide is also formed by precipitating Cr(III) with alkalis from either cold or hot solutions.

The amorphous Cr(III) hydroxide, precipitated and coagulated at 80 to 85°C and dried at 30°C in air, is hygroscopic [Giovanoli and Stadelmann 1973] with a composition described by the formula $\text{Cr}(\text{OH})_3 \cdot 0.8\text{H}_2\text{O}$ (or $\text{Cr}_2\text{O}_3 \cdot 4.6\text{H}_2\text{O}$) [Giacomelli et al. 1995]. With increasing temperature, the amorphous Cr(III) hydroxide loses water in a stepwise manner with endotherms at 120 – 150°C and 250°C and then converts, with a sharp exothermic effect (glow phenomenon) at about 400°C , to form crystalline $\alpha\text{-Cr}_2\text{O}_3$ (corundum structure) [Ratnasamy and Leonard 1972; Giovanoli and Stadelmann 1973; Natarajan and Secco 1975].

The reported temperatures for $\alpha\text{-Cr}_2\text{O}_3$ formation from amorphous hydroxide differ significantly [Reznitskii et al. 1988; Shafer and Roy 1954]. However, these values are always higher than 380°C . The temperature of $\alpha\text{-Cr}_2\text{O}_3$ crystallization seemingly depends on the initial conditions of Cr(III) hydroxide precipitation [Viktorov et al. 1994] and on the atmosphere and the heating rate used to convert to the oxide [Burwell et al. 1960; Kittaka et al. 1985; Klissurski and Bluskov 1983].

Information on the chemical nature of amorphous Cr(III) hydroxide and the dehydration products formed before $\alpha\text{-Cr}_2\text{O}_3$ crystallization differ with respect to the intermediate appearance of CrOOH . The oxyhydroxide is known in three modifications: the rhombohedral ($R3m$) α -form [Thamer et al. 1957], the orthorhombic ($Pnnm$) β -phase isostructural with InOOH [Christensen 1966], and the orthorhombic ($Cmcm$) γ -form with a structure similar to böhmite ($\gamma\text{-AlOOH}$) or lepidocrocite ($\gamma\text{-FeOOH}$) [Hund 1959]. It was found that the amorphous products obtained by 60 – 240°C drying of crystalline Cr(III) hydroxide contain, in the arrangement of the oxygens nearest the Cr atom, elements of structure typical of $\gamma\text{-CrOOH}$ and $\alpha\text{-Cr}_2\text{O}_3$ [Ratnasamy and Leonard 1972]. Crystalline $\alpha\text{-CrOOH}$ forms upon prolonged hydrothermal 400°C treatment of Cr(III) hydroxide, especially in NaOH solutions [Laubengayer and McCune 1952]. However, studies by different physicochemical methods show the absence of any CrOOH phases as intermediates in the production of $\alpha\text{-Cr}_2\text{O}_3$ from Cr(III) hydroxide [Singh et al. 1983]. It may be that the CrOOH phases that form by high-temperature aging of Cr(III) hydroxide are very poorly crystalline.

Syntheses of different crystalline spinel-type chromites usually are conducted by calcining mixtures of the corresponding oxides at temperatures higher than 1000°C [Gmelin 1962; Ryabin et al. 1981]. The same compounds but in an amorphous state may be obtained by mutual precipitation of the respective hydroxides followed by precipitate coagulation at elevated temperatures [Yur'eva et al. 1968]. Similar methods can be used to prepare Fe(III)/Cr(III) hydroxide solid solutions [Sass and Rai 1987].

The Cr(III) compounds prepared for the present studies based on these literature findings are listed in Table 2.1. The compound compositions are for samples dried in a desiccator over KOH pellets. Methods used in the syntheses are described in the following paragraphs.

To prepare crystalline $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ (or $\text{Cr}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$; compound I), 10 mL of 0.1 M Cr(III) nitrate was added slowly, with intense stirring, to 25 mL of 0.2 M NH_4OH at room temperature. After about 1 hour of coagulation, the precipitate was separated from the mother solution by filtration, carefully washed with cold water, and dried in a desiccator over KOH pellets. The compound was identified by gravimetric analysis (calcination to Cr_2O_3 at $\sim 800^\circ\text{C}$) and by x-ray powder diffractometry.

To prepare amorphous Cr(III) hydroxide (compounds II through IX), 10–20 mmoles of the selected chromium(III) salt were added to a small excess of 0.5 M NH_4OH , and the precipitate formed was coagulated about one hour on a boiling water bath. The precipitate then was separated from the mother solution by centrifugation, washed two or three times with water, and transferred as a 3-M NaOH suspension into a Teflon test tube. The test tube was placed into a stainless steel autoclave and kept at the selected aging temperature for 15 or 20 hours. After heating, the solid phase was cooled, centrifuged from the mother liquor, washed by water until the solution phase had $\text{pH} < 9$, and dried in an N_2 or Ar flow (to avoid the partial oxidation of Cr(III) by atmospheric oxygen). The final product was analyzed gravimetrically (by calcination to Cr_2O_3 at $\sim 800^\circ\text{C}$ followed by weighing) and characterized by IR spectroscopy, x-ray powder diffractometry and, in some cases, particle size distribution by the SAXS technique. The hygroscopicities of the products were estimated by the measurement of the weight change of samples kept in desiccators over dry KOH and 25% H_2SO_4 (1.7 and 14.6 torr, respectively, water vapor pressure at 20°C compared with 17.4 torr over pure water).

Chromium(III) mixed hydroxides or spinel phases containing Fe(III), Fe(II), or Ni(II), were prepared by the slow addition of initial solutions containing mixed Cr(III) nitrate and the respective other metal salts, in the 2:1 mole ratio, to a small excess of boiling 0.25 M NaOH. The precipitates were coagulated for about 30 minutes and then treated in the same way as in the case of the Cr(III) hydroxides. The final products were analyzed gravimetrically following calcination at 800°C and, in the case of iron

Table 2.1. Cr(III) Compound Preparation for Dissolution Testing

Compound Number	Composition	Precursors ^(a)	Coagulation	
			Temperature, $^\circ\text{C}$	Time, hr
I	$\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$	A	20	1
II	$\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	B	100	15
III	$\text{Cr}_2\text{O}_3 \cdot 3.8\text{H}_2\text{O}$	A	100	20
IV	$\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	C	100	20
V	$\text{Cr}_2\text{O}_3 \cdot 2.9\text{H}_2\text{O}$	A	150	20
VI	$\text{Cr}_2\text{O}_3 \cdot 2.4\text{H}_2\text{O}$	A	200	20
VII	$\text{Cr}_2\text{O}_3 \cdot 2.35\text{H}_2\text{O}$	B	250	20
VIII	$\text{Cr}_2\text{O}_3 \cdot 2.3\text{H}_2\text{O}$	A	250	20
IX	$\text{Cr}_2\text{O}_3 \cdot 2.7\text{H}_2\text{O}$	A	250	20
X	$\text{NiCr}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$	D + 2A	100	25
XI	$\text{NiCr}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$	D + 2A	200	20
XII	$\text{Fe}_{0.67}\text{Cr}_{1.33}\text{O}_3 \cdot 2\text{H}_2\text{O}$	E + 2A	100	20
XIII	$\text{Fe}_{0.67}\text{Cr}_{1.33}\text{O}_3 \cdot 2\text{H}_2\text{O}$	E + 2A	200	20
XIV	$\text{FeCr}_2\text{O}_4 \cdot 2.5 \cdot 3\text{H}_2\text{O}$	F + 2A	100	20
(a) A - $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ C - $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ E - $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$				
B - $\text{Cr}(\text{CH}_3\text{COO})_3 \cdot 9\text{H}_2\text{O}$ D - $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ F - $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$				

compounds, by iodometric titration to determine Fe(II):Fe(III) concentrations after dissolving solid samples in 2 M HCl. The analytical results showed that iron(II) chromite suffered ~50% Fe(II) oxidation during its separation from the mother solution and subsequent drying. Therefore this product is considered to be a mixture of Fe(II) and Fe(III) compounds [that is, $\text{FeCr}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ and $1.5 \text{Fe}_{0.67}\text{Cr}_{1.33}\text{O}_3 \cdot y\text{H}_2\text{O}$ or $\text{FeCr}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ (compound XIV) and is listed in Table 2.1 with the other solid phases prepared for testing.

2.3 Characteristics of the Chromium Solid Phases

As expected, x-ray powder diffractometry showed that the Cr(III) hydroxide compound I, precipitated in dilute NH_4OH at room temperature, was crystalline with a bayerite structure (Figure 2.1). All other Cr(III) hydroxide compounds II–IX were practically amorphous (representative diffractograms given in Figure 2.2). Only very diffuse reflections, primarily for materials aged at elevated temperatures, were present in the diffractograms. It is difficult to attribute these reflections confidently to known crystalline Cr(III) compounds; however, compounds II–IX likely contain very fine crystallites of α - CrOOH and γ - CrOOH . This supposition is based on the observation of diffuse, but discernable, x-ray reflections at 13.5, 37.3, 47.4 and 61.2–62.2 degrees 2θ , corresponding, respectively, to d spacings of 6.5, 2.41, 1.92, and 1.51–1.48 Å. In comparison, the α - CrOOH diffraction pattern contains intense reflections at 2.41 and 1.49 Å; γ - CrOOH shows strong reflections at 6.5, 1.97, and 1.49 Å [Ryabin et al. 1981]. The very small crystallite sizes of the prepared Cr(III) hydroxides were confirmed by the SAXS technique. As seen in Figure 2.3, most of the material consists of particles with diameter (2R) less than 3 nm (30 Å).

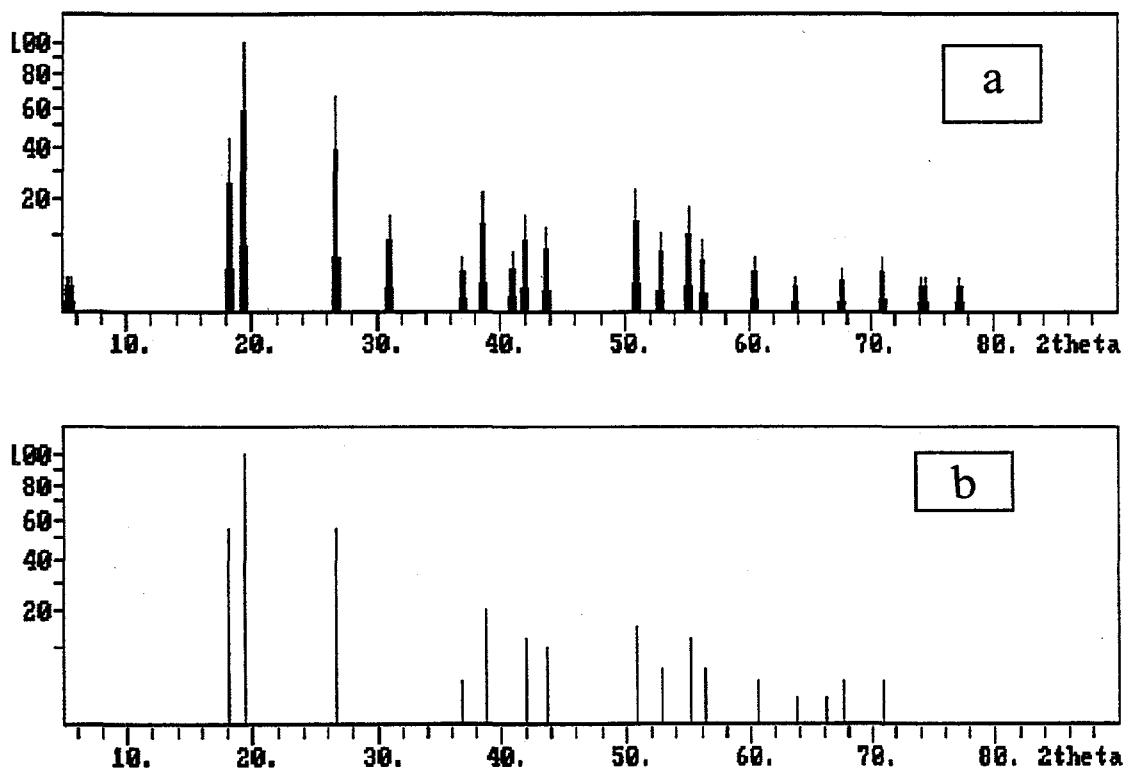


Figure 2.1. Diffractogram of $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$
a - compound I
b - Cr(III) hydroxide, bayerite structure [JCPDS file 16-817]
(Joint Committee on Powder Diffraction Standards)

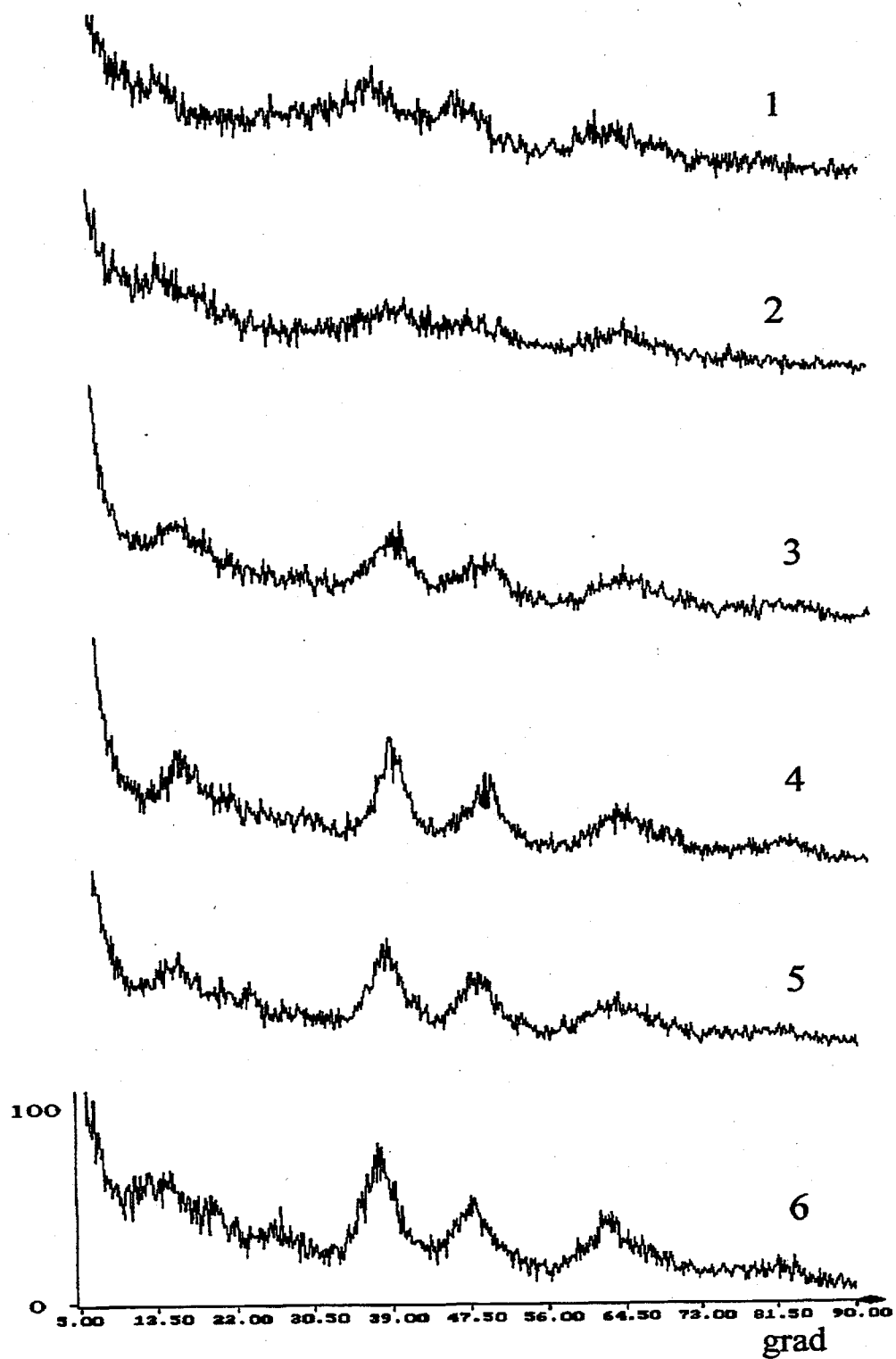


Figure 2.2. Diffractograms of Cr(III) hydroxide compounds:
1 - II; 2 - III; 3 - V; 4 - VI; 5 - IX; 6 - VII
(in order of increasing peak intensity)

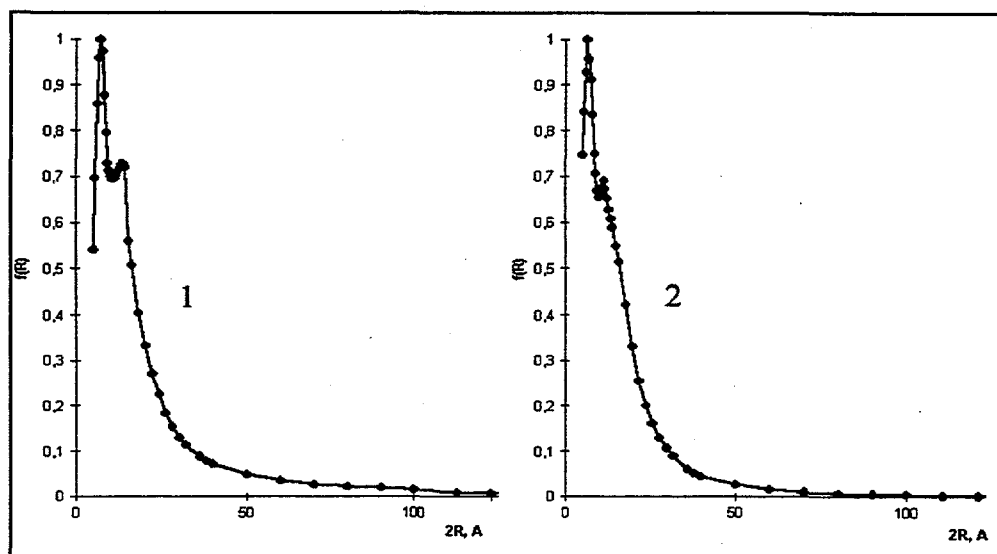


Figure 2.3. Volumetric Particle Size Distribution for Cr(III) Hydroxide Compounds:
1 - V; 2 - III

The IR spectra (Figure 2.4) of aged Cr(III) hydroxides (compounds II-IX) are similar to those described in the literature for Cr(III) hydroxide [Ratnasamy and Leonard 1972; Simonova 1973]. The spectra clearly display bands in the ranges 500–600, 1600–1650 and 3400–3600 cm^{-1} attributable to deformation vibrations of Cr-O bonds and the deformation and valent vibrations of water, respectively. Based on the spectra, it is difficult to confirm the presence or absence of CrOOH phases in II-IX. The CrOOH phases are characterized by a weak and broad band at $\sim 1600 \text{ cm}^{-1}$ [Snyder and Ibers 1962; Claydon et al. 1975] that would be obscured by the overlying bands from Cr(III) hydroxide.

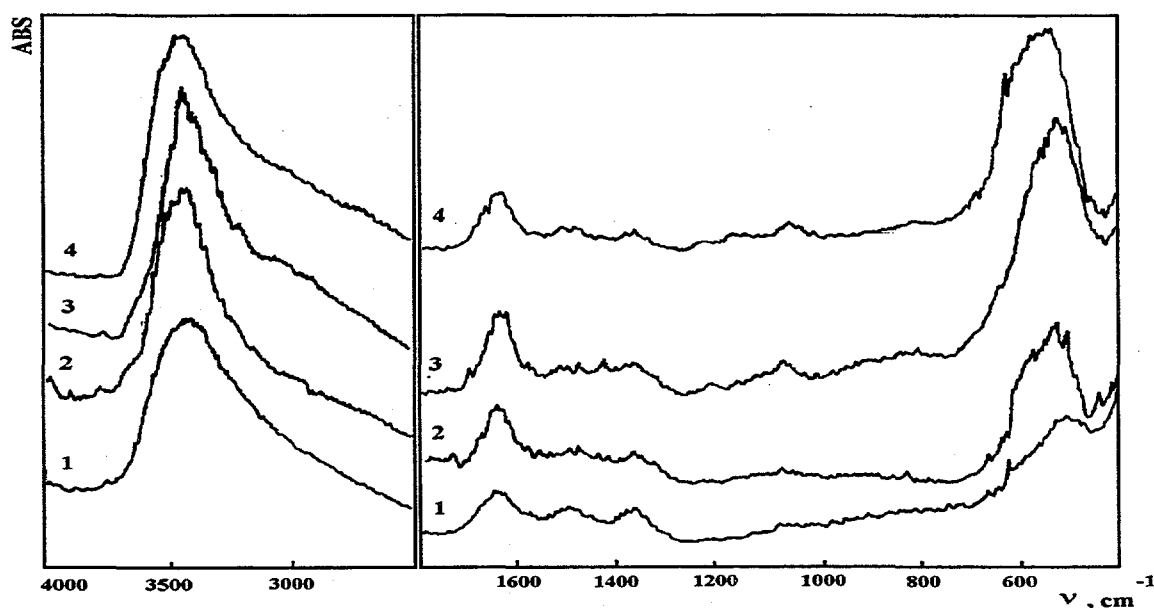


Figure 2.4. Infrared Spectra of Some Cr(III) Hydroxide Compounds:
1 - II; 2 - V; 3 - VI; 4 - VII

The Ni(II), Fe(II), and Fe(III) chromites (compounds X–XIV) also were largely amorphous (Figure 2.5). Their IR spectra, shown in Figures 2.6 and 2.7, seem to confirm the presence of spinel-type chromites [Yur'eva et al. 1968; Preudhomme and Tarte 1971] for compounds X, XI, and XIV.

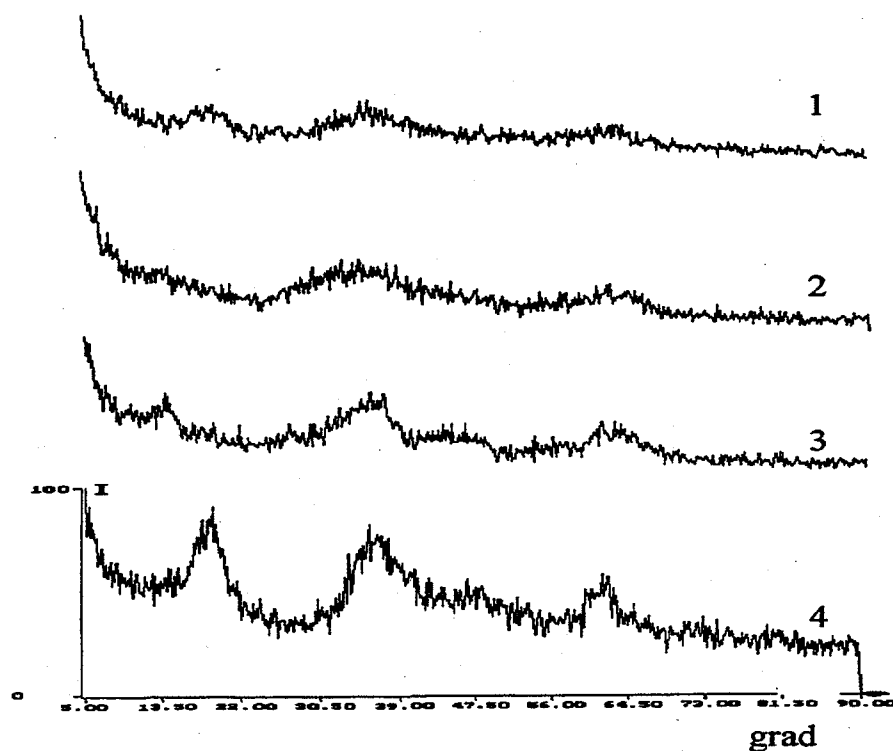


Figure 2.5. Diffractograms of Cr(III) Compounds:
1 - XIV; 2 - XII; 3 - XIII; 4 - X
(in order of increasing peak intensity)

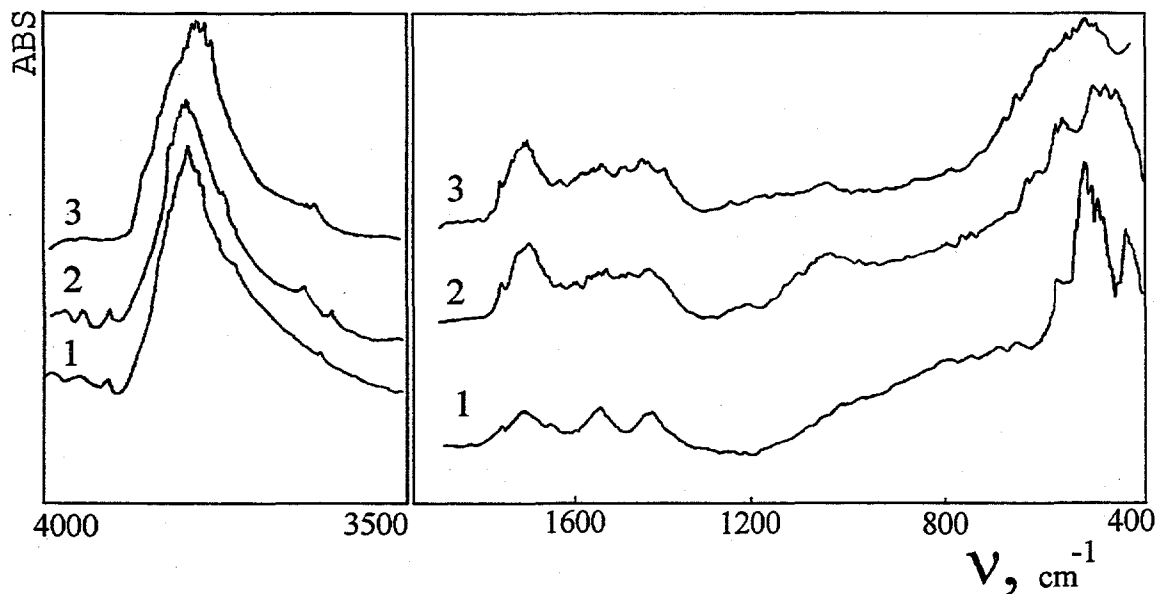


Figure 2.6. Infrared Spectra of Some Cr(III)/Fe(III) Hydroxide Compounds:
1 - XIV; 2 - XII; 3 - XIII

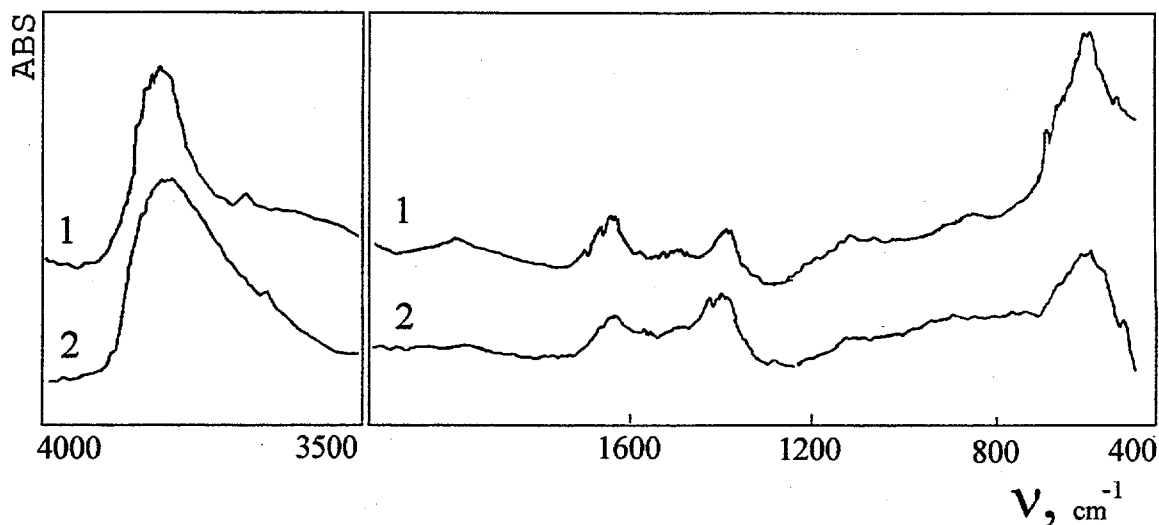


Figure 2.7. Infrared Spectra of $\text{NiCr}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ Compounds:
1 - X; 2 - XI

The Cr(III) hydroxide compounds have variable water content (Table 2.2). The water contents correlate qualitatively with the aging temperatures used in the compound preparation and with the apparent crystallinities indicated by the respective compounds' diffractograms (Figure 2.2). The water contents also depend on the drying conditions (Table 2.2). Separate tests showed that the water loss of the amorphous Cr(III) hydroxides is reversible. The hygroscopic properties of the compounds must be considered in interpreting the dissolution test characteristics.

Table 2.2. Hygroscopic Properties of Cr(III) Compounds

Compound Number	Compound Composition	Aging Temperature, °C	Hydrate number, x, after drying over		Δx
			KOH	25% H_2SO_4	
II	$\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	100	4.0	5.15	1.15
III	$\text{Cr}_2\text{O}_3 \cdot 3.8\text{H}_2\text{O}$	100	3.8	4.8	1.0
IV	$\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	100	4.0	5.1	1.1
V	$\text{Cr}_2\text{O}_3 \cdot 2.9\text{H}_2\text{O}$	150	2.9	4.4	1.5
VI	$\text{Cr}_2\text{O}_3 \cdot 2.4\text{H}_2\text{O}$	200	2.4	3.8	1.4
VII	$\text{Cr}_2\text{O}_3 \cdot 2.35\text{H}_2\text{O}$	250	2.35	3.8	1.45
VIII	$\text{Cr}_2\text{O}_3 \cdot 2.3\text{H}_2\text{O}$	250	2.3	3.35	1.05
IX	$\text{Cr}_2\text{O}_3 \cdot 2.7\text{H}_2\text{O}$	250	2.7	4.0	1.3
X	$\text{NiCr}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$	100	5.0	6.6	1.6
XI	$\text{NiCr}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$	200	4.0	5.7	1.7
XII	$\text{Fe}_{0.67}\text{Cr}_{1.33}\text{O}_3 \cdot 2\text{H}_2\text{O}$	100	2.0	2.9	0.9
XIII	$\text{Fe}_{0.67}\text{Cr}_{1.33}\text{O}_3 \cdot 2\text{H}_2\text{O}$	200	2.0	3.3	1.3
XIV	$\text{FeCr}_2\text{O}_4 \cdot 2.5 \cdot 3\text{H}_2\text{O}$	100	3.0	4.7	1.7

2.4 Experimental Procedure for Tests with Oxygen

The experimental investigation of the oxidative dissolution of Cr(III) compounds was performed using atmospheric air and pure oxygen at normal and elevated pressures. Tests to determine the initial reaction rate usually were performed by first bubbling oxygen or air at a slow rate through 5 or 10 mL of NaOH solution in a closed, thermostatted polyethylene reaction cell for 15–20 minutes at constant temperature. The cell contents then were agitated by a magnetic stirrer; the temperature was maintained at $\pm 2^\circ\text{C}$. Experiments with oxygen at elevated pressures were performed in a special plastic vessel fitted with a manometer to measure pressure with an accuracy of ± 0.1 atm. To avoid solution evaporation, the gas first was humidified by bubbling through a NaOH solution of the same concentration and temperature as used in the working cell. To remove the CO_2 contained in air, the gas was passed through a column filled with KOH pellets.

After achieving temperature equilibrium, a measured quantity (usually 0.1 mmole) of a Cr(III) compound was added to the cell and the suspension agitated by magnetic stirring for 6–12 hours. Periodically (e.g., 1–2 hour intervals), samples of the suspension were withdrawn, mixed with 3 mL of water to quench the reaction, and centrifuged to separate the solid phase. The Cr(VI) solution concentration was determined by measuring light absorbance at 373 nm. Using standard chromate solutions in 0.2–3 M NaOH, the molar extinction coefficient, ϵ , of CrO_4^{2-} at 373 nm was found to be $4850 \text{ M}^{-1}\text{cm}^{-1}$, in good agreement with related studies [$4836 \pm 20 \text{ M}^{-1}\text{cm}^{-1}$ at 372 nm (Rapko et al. 1997)]. It was confirmed that ϵ is practically independent of NaOH concentration over the studied range.

Experiments to study long-term interaction of Cr(III) compounds with oxygen were performed by the same method with suspension samples taken for analysis infrequently. Suspension volumes and NaOH concentrations were periodically adjusted during the experiments to maintain alkali and chromium concentrations constant within $\pm 5\%$.

2.5 Experimental Procedure for Tests with Hydrogen Peroxide

Tests on the kinetics of Cr(III) oxidation by hydrogen peroxide in alkaline solutions were usually conducted in this sequence: First, about 0.1 mmole of a Cr(III) compound was added to 5 mL of a standard NaOH solution in a thermostatted cell installed on a magnetic stirrer. In some cases, a known amount of catalyst was added to the Cr(III) compound suspension. After achieving thermal equilibrium (~ 15 minutes), a measured amount of H_2O_2 was added to the suspension. Samples of the reaction mixture were withdrawn periodically. The samples were quickly diluted by water to quench the reaction, the solid phase separated by centrifugation, and the solution analyzed for chromate concentration by measurement of optical absorbance at 373 nm.

To determine H_2O_2 consumption in the partial oxidation of Cr(III) compounds, a measured volume of NaOH solution was added to a known amount of the compound in a thermostatted cell. After achieving thermal equilibrium, 0.05-mL aliquots of a standard solution of H_2O_2 were introduced every two to three minutes. The extent of reaction was determined by the disappearance of solid phase, in the case of Cr(III) hydroxides, or by the spectrophotometric determination of Cr(VI) concentration in the solution phase after its separation from the test solid phases by centrifugation.

2.6 Experimental Procedure for Tests with Persulfate

Preliminary experiments showed that the rate of Cr(III) oxidation by $\text{S}_2\text{O}_8^{2-}$ strongly depends on alkali concentration and temperature. In 40–70°C, 0.3–3 M NaOH, the reactions proceed at rates convenient to measure by ordinary techniques. Such conditions were chosen for the primary tests. The tests usually were conducted by adding a known amount (usually 0.1–0.2 mmole) of a Cr(III) compound to 2–5 mL of a standard NaOH solution in a thermostatted cell installed on a magnetic stirrer. After the ~15 minutes taken to achieve thermal equilibrium, a measured amount of $\text{Na}_2\text{S}_2\text{O}_8$ solution was added to the suspension. After that, samples of reaction mixture were withdrawn periodically. The samples were quickly diluted by water, separated from the solid phase by centrifugation, and analyzed for chromate by measurement of the absorbance at 373 nm. Based on these results, the Cr(VI) concentrations were calculated as a function of time.

Special tests were performed to estimate the reaction stoichiometry under the tested conditions. In these tests, known amounts of Cr(III) hydroxide (compound II) were treated in NaOH solutions by different excess quantities of persulfate. The test durations were sufficient to permit completion of the reaction. Then the concentrations of Cr(VI) were determined in the final solutions or suspensions. The Cr(VI) yields were compared with the quantities of added $\text{S}_2\text{O}_8^{2-}$ to determine reaction stoichiometry.

3.0 Oxidative Alkaline Dissolution of Chromium(III) Compounds by Gaseous Oxygen

The primary objective of the tests to determine the initial Cr(III) oxidation rate by oxygen was to identify the optimum temperature and NaOH concentration to perform the process and to determine the effect of oxygen pressure on the reaction rate. Based on prior studies [Rapko 1998], these experiments were performed at 50–90°C using 0.2–5 M NaOH.

3.1 Tests with Atmospheric Oxygen

Preliminary tests showed that the Cr(III) hydroxide oxidation rate by atmospheric oxygen is slow and independent of the intensity of gas bubbling (used in combination with magnetic stirring to introduce the gas to solution). Thus it is most likely that Cr(III) reacts under these conditions only with dissolved oxygen and that the rates of oxygen supply to the solution phase in the present tests were higher than those of the ensuing Cr(III) oxidation.

Typical kinetic curves on the short-term reaction of Cr(III) hydroxides with atmospheric oxygen in alkaline suspensions are presented in Figure 3.1. The Cr(VI) concentration increases linearly with time. The kinetic curve slopes may be used to estimate the initial reaction rates, V_o , under the given conditions.

As seen in Table 3.1, the initial reaction rates, V_o , increase strongly with increasing NaOH concentration. To a first approximation, V_o is proportional to NaOH concentration, although this dependence actually is somewhat more complex.

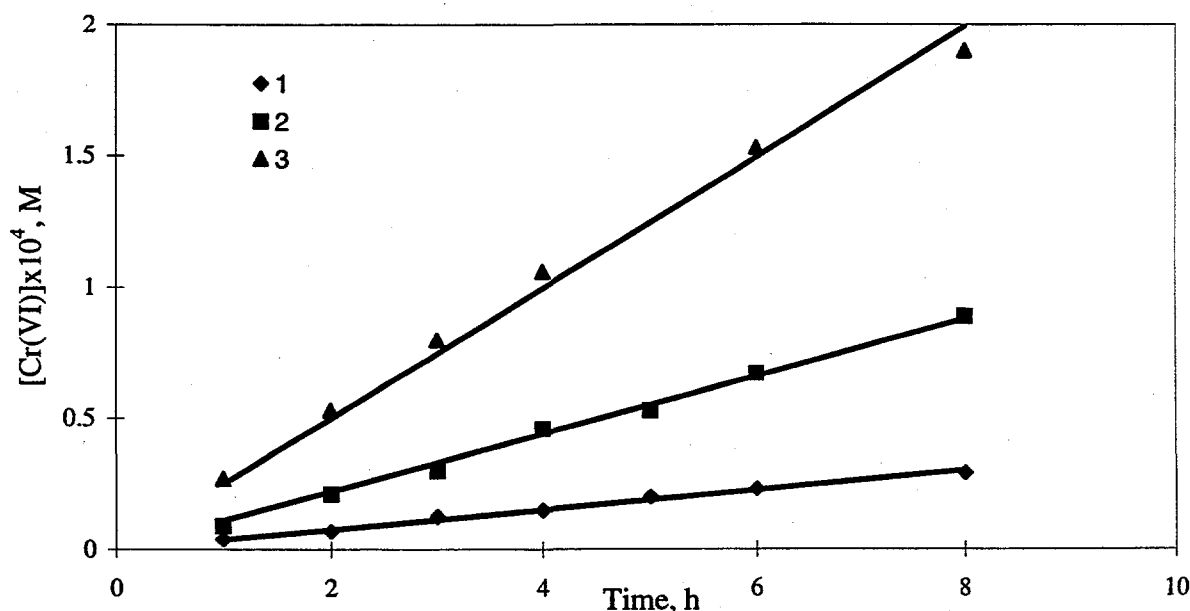


Figure 3.1. Kinetics of 0.02 M Cr(III) Hydroxide (compound VIII) Oxidation by Atmospheric Oxygen at 70°C: [NaOH], M: 1 - 1; 2 - 3; 3 - 5

Table 3.1. Effect of NaOH Concentration on the Oxidation Rate of 0.02 M Cr(III) Hydroxide Suspensions by Atmospheric Oxygen at 70°C

[NaOH], M	V _o , moles/liter-hour, for different Cr(III) compounds			
	II (100°C aging)	V (150°C aging)	VI (200°C aging)	VIII (250°C aging)
0.2	0.2x10 ⁻⁵	—	—	—
1.0	0.6x10 ⁻⁵	0.5x10 ⁻⁵	0.4x10 ⁻⁵	0.3x10 ⁻⁵
2.0	1.4x10 ⁻⁵	1.0x10 ⁻⁵	—	—
3.0	3.0x10 ⁻⁵	2.1x10 ⁻⁵	1.2x10 ⁻⁵	1.2x10 ⁻⁵
4.0	6.8x10 ⁻⁵	2.5x10 ⁻⁵	—	—
5.0	—	—	3.1x10 ⁻⁵	2.2x10 ⁻⁵

The initial rate of Cr(III) hydroxide oxidation depends also on temperature, but the rate is practically independent of Cr(III) solid compound concentration in the range 0.01 to 0.1 M (Table 3.2). The dependence of V_o on temperature is linear in Arrhenius coordinates (Figure 3.2), and the slope corresponds to a formal activation energy, E_a, of about 22 kJ/mole. This relatively low E_a is explained by the opposing effects of increasing temperature, which increased the reaction rate but decreased the solubility of oxygen in alkaline solution. Thus the increase in rate of Cr(III) reaction with oxygen caused by increasing temperature is offset to some extent by the concomitant decrease in rate caused by the decreased concentration of dissolved O₂.

The absence of an effect of Cr(III) hydroxide concentration in alkaline suspensions on V_o undoubtedly shows that the Cr(III) oxidation by oxygen proceeds through the preliminary dissolution of the solid phase. Because of the low reaction rate, a constant Cr(III) concentration is available in alkaline solution independent of the amount of solid phase in suspension. Thus, the following steps represent the mechanism of the reaction:

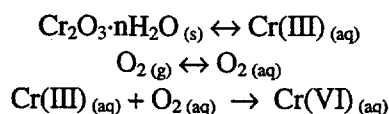


Table 3.2. Effect of Temperature and Cr(III) Compound Initial Concentration on Cr(III) Hydroxide Oxidation by Atmospheric Oxygen in 3 M NaOH

Compound Number	[Cr(III)] _o , M	T, °C	V _o , moles/liter-hour
II	0.01	70	2.7x10 ⁻⁵
	0.02		3.0x10 ⁻⁵
	0.10		2.9x10 ⁻⁵
II	0.02	45	1.6x10 ⁻⁵
		60	2.5x10 ⁻⁵
		80	3.6x10 ⁻⁵
V	0.02	60	1.4x10 ⁻⁵
		70	1.8x10 ⁻⁵
		75	1.8x10 ⁻⁵
		80	2.2x10 ⁻⁵
		90	2.7x10 ⁻⁵

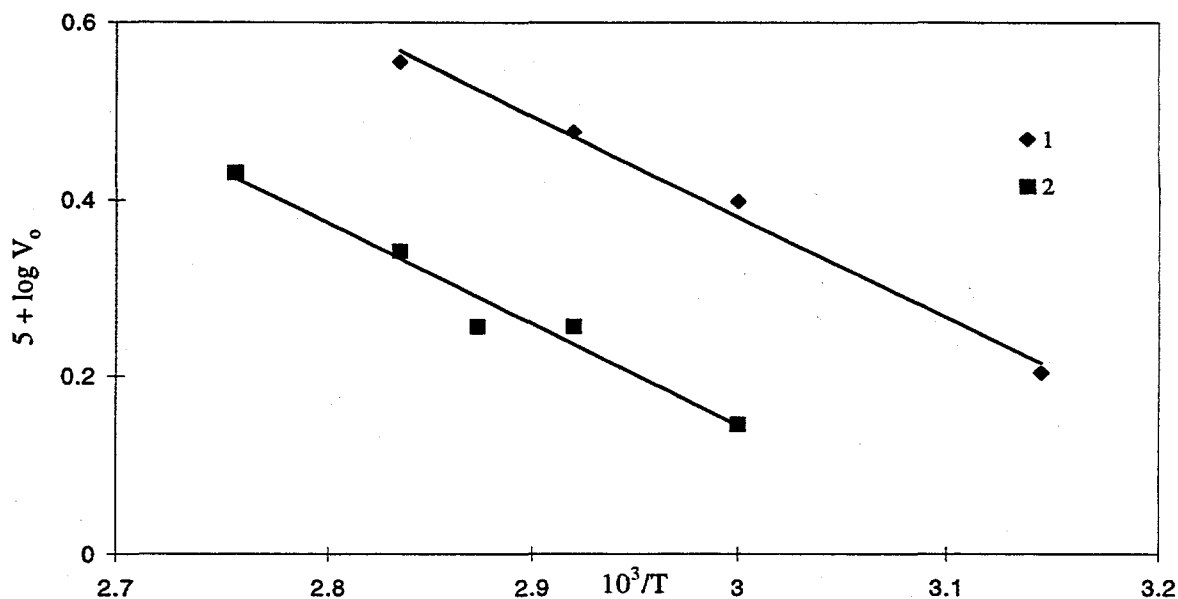


Figure 3.2. Effect of Temperature on Rate of Cr(III) Hydroxide Oxidation by Atmospheric Oxygen in 3 M NaOH: 1 - compound II; 2 - compound V

The temperature of Cr(III) hydroxide aging has little influence on the reaction rate. A small tendency towards decreasing V_o with increase in the temperature of the hydroxides' hydrothermal treatment is noted and V_o distinctly increases with increasing water content in the Cr(III) hydroxides (Table 3.3). The initial rate of atmospheric oxygen reaction with mixed compounds of Cr(III) and Ni(II) or Fe(III) is of the same order as observed for pure Cr(III) hydroxides. The slightly more rapid reaction of the Ni(II) compound may be attributed to the possible catalytic effect of Ni(II) on the reaction.

Table 3.3. Initial Reaction Rate, V_o , for the Oxidation of Cr(III) Compounds by Atmospheric Oxygen in 3 M NaOH

Compound Number	Compound	T, °C	V_o , moles/liter-hour
II	$\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	70	3.0×10^{-5}
III	$\text{Cr}_2\text{O}_3 \cdot 3.8\text{H}_2\text{O}$	70	2.2×10^{-5}
IV	$\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	70	2.6×10^{-5}
V	$\text{Cr}_2\text{O}_3 \cdot 2.9\text{H}_2\text{O}$	70	1.5×10^{-5}
VI	$\text{Cr}_2\text{O}_3 \cdot 2.4\text{H}_2\text{O}$	70	1.2×10^{-5}
VII	$\text{Cr}_2\text{O}_3 \cdot 2.35\text{H}_2\text{O}$	70	1.4×10^{-5}
VII	$\text{Cr}_2\text{O}_3 \cdot 2.35\text{H}_2\text{O}$	80	2.6×10^{-5}
VIII	$\text{Cr}_2\text{O}_3 \cdot 2.3\text{H}_2\text{O}$	70	1.6×10^{-5}
VIII	$\text{Cr}_2\text{O}_3 \cdot 2.3\text{H}_2\text{O}$	60	1.0×10^{-5}
IX	$\text{Cr}_2\text{O}_3 \cdot 2.7\text{H}_2\text{O}$	70	5.0×10^{-5}
IX	$\text{Cr}_2\text{O}_3 \cdot 2.7\text{H}_2\text{O}$	60	3.4×10^{-5}
X	$\text{NiCr}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$	80	4.9×10^{-5}
XII	$\text{Fe}_{0.67}\text{Cr}_{1.33}\text{O}_3 \cdot 2\text{H}_2\text{O}$	80	2.0×10^{-5}

The results of tests on longer-term oxidative dissolution of Cr(III) compounds by atmospheric oxygen showed that in all cases the reaction rates remained constant over the studied range of time (Figures 3.3 to 3.5). The rates are low at 80°C and 3 M NaOH. Though the reaction can be accelerated at higher temperatures and alkali concentrations, achieving the complete oxidative dissolution of Cr(III) hydroxides (or leaching of chromium from other compounds) by atmospheric oxygen at atmospheric pressure may be impractical in process reactors but feasible for in-tank processing at longer residence times.

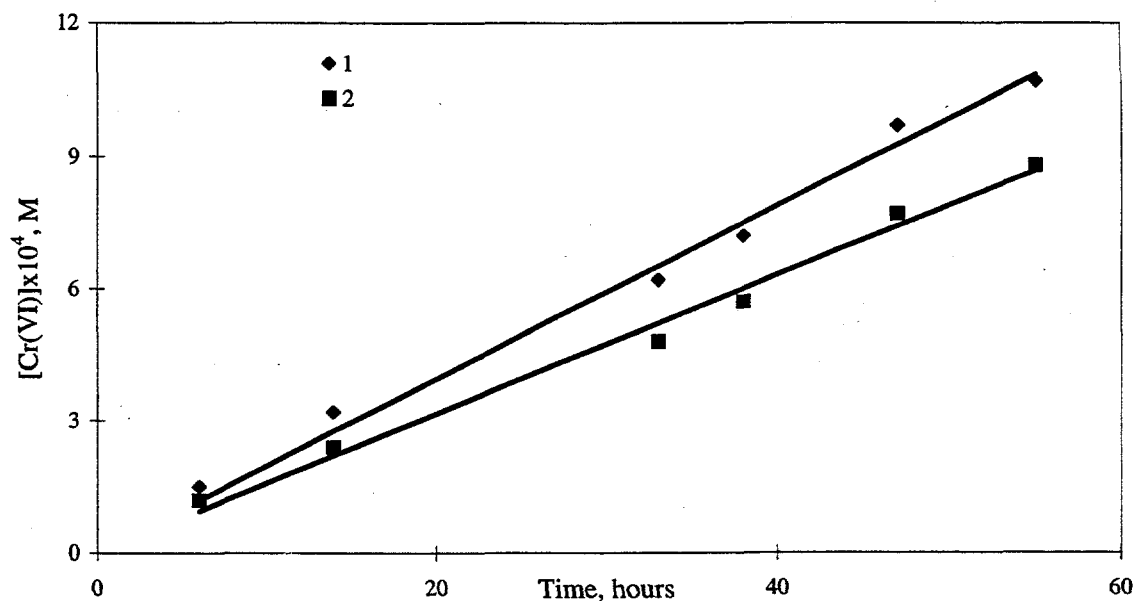


Figure 3.3. Long-Term Reaction of Cr(III) Compounds with Atmospheric Oxygen in 3 M NaOH at 80°C:
 1 - $\text{Cr}_2\text{O}_3 \cdot 3.8\text{H}_2\text{O}$ (compound III)
 2 - $\text{Cr}_2\text{O}_3 \cdot 2.4\text{H}_2\text{O}$ (compound VI)

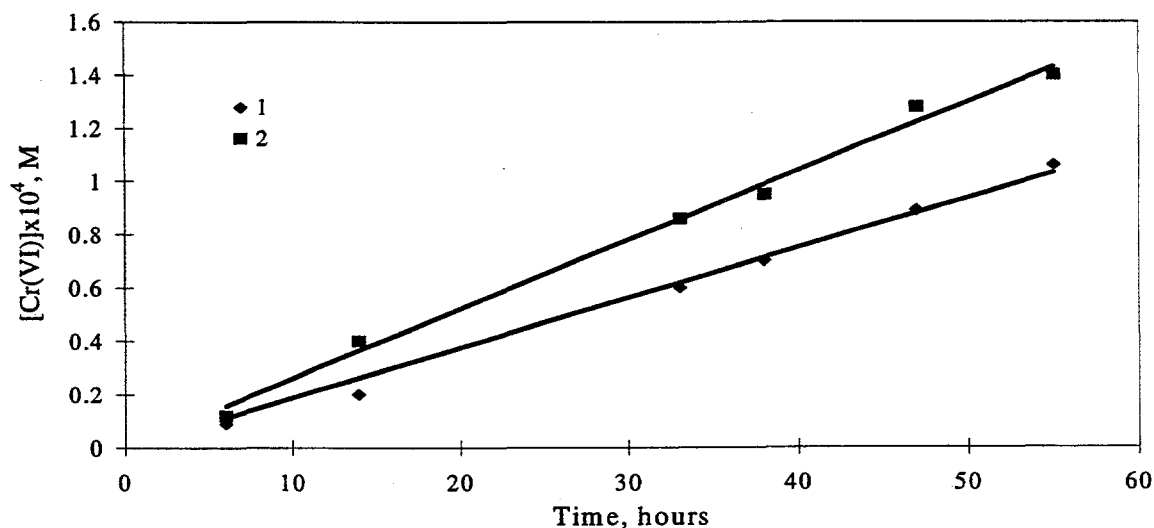


Figure 3.4. Long-Term Reaction of Cr(III) Compounds with Atmospheric Oxygen in 3 M NaOH at 80°C:
 1 - $\text{Cr}_2\text{O}_3 \cdot 2.9\text{H}_2\text{O}$ (compound V)
 2 - $\text{Cr}_2\text{O}_3 \cdot 2.3\text{H}_2\text{O}$ (compound VIII)

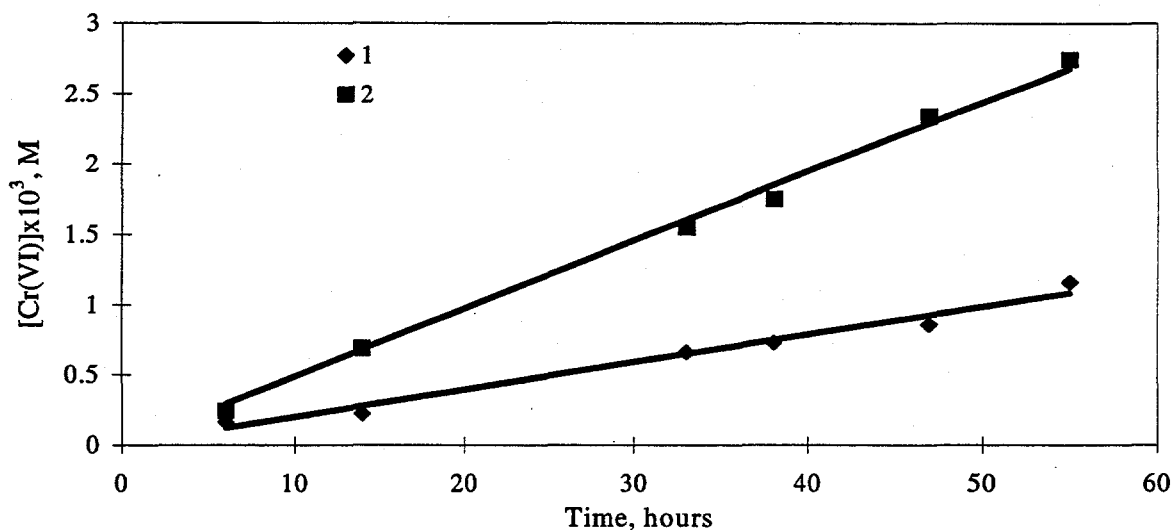


Figure 3.5. Long-Term Reaction of Cr(III) Compounds with Atmospheric Oxygen in 3 M NaOH at 80°C:
 1 - $\text{Fe}_{0.67}\text{Cr}_{1.33}\text{O}_3 \cdot 2\text{H}_2\text{O}$ (compound XII)
 2 - $\text{NiCr}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ (compound X)

3.2 Tests with Pure Oxygen

The kinetics of the reaction of Cr(III) hydroxides with pure oxygen in alkaline suspensions is similar to those obtained with air. In both cases, the reaction rates are practically linear but have different slopes (greater rate for pure oxygen) under similar conditions (compare Figures 3.1 and 3.6). This means that the mechanisms of Cr(III) oxidation by air and pure oxygen are the same; that is, the process proceeds through the dissolution of O_2 in alkaline solution.

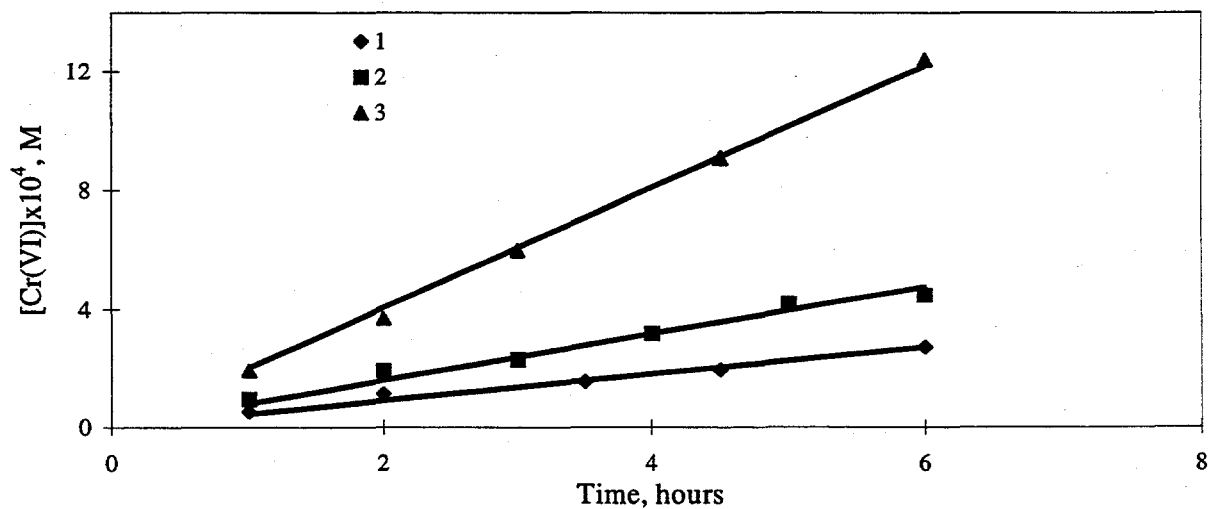


Figure 3.6. Kinetics of 0.02 M Cr(III) Hydroxide (compound II) Oxidation by Pure Oxygen at 70°C:
 [NaOH], M: 1 - 1; 2 - 2; 3 - 4

Data on the influence of reaction conditions on the initial oxidation rate of Cr(III) hydroxides are presented in Table 3.4. A number of conclusions can be drawn from these data:

1. The reaction rate depends strongly on alkali concentration. The initial rate, V_o , is approximately proportional to NaOH concentration, although the actual correlation between rate and NaOH concentration seems to be somewhat more complex.
2. The Cr(III) oxidation rate increases in changing from air to pure oxygen and finally pure oxygen under elevated pressure. The hypothesis that V_o is proportional to the oxygen partial pressure $[P(O_2)]$ under otherwise similar conditions was tested and confirmed by the straight-line dependence of V_o on $P(O_2)$ in logarithmic coordinates with slope near 1 (Figure 3.7).
3. The rate of reaction with oxygen does not change by increasing Cr(III) hydroxide suspension concentrations above 0.02 M in alkaline solution. But at Cr(III) concentration less than 0.02 M V_o decreases, and at the lower Cr(III) hydroxide concentrations the rate of Cr(III) hydroxide dissolution is likely near its oxidation rate. Thus, a decrease in hydroxide suspension concentration below 0.02 M decreases the steady-state Cr(III) solution concentration.

Table 3.4. Influence of Reaction Conditions on the Initial Rate of Cr(III) Hydroxide (compound II) Oxidation by Oxygen

[NaOH], M	[Cr(III)] _o , M	T, °C	P, atm.	V_o , moles/liter-hour
0.2	0.02	70.0	1	0.08×10^{-4}
1.0				0.40×10^{-4}
2.0				0.71×10^{-4}
3.0				1.32×10^{-4}
4.0				1.95×10^{-4}
5.0				2.34×10^{-4}
2.0	0.02	40.0	1	0.25×10^{-4}
		60.0		0.42×10^{-4}
		70.0		0.67×10^{-4}
		80.0		0.74×10^{-4}
		90.0		0.95×10^{-4}
4.0	0.02	45.0	1	0.55×10^{-4}
		60.0		1.12×10^{-4}
		70.0		1.80×10^{-4}
		80.0		2.27×10^{-4}
4.0	0.005	70.0	1	0.58×10^{-4}
	0.01			1.15×10^{-4}
	0.05			1.93×10^{-4}
1.0	0.02	70.0	2	0.75×10^{-4}
2.0			2	1.45×10^{-4}
3.0			2	2.6×10^{-4}
3.0			3	3.6×10^{-4}
4.0			2	3.5×10^{-4}
2.0	0.02	40.0	2	0.50×10^{-4}
		60.0		0.81×10^{-4}
		70.0		1.25×10^{-4}
		80.0		1.83×10^{-4}

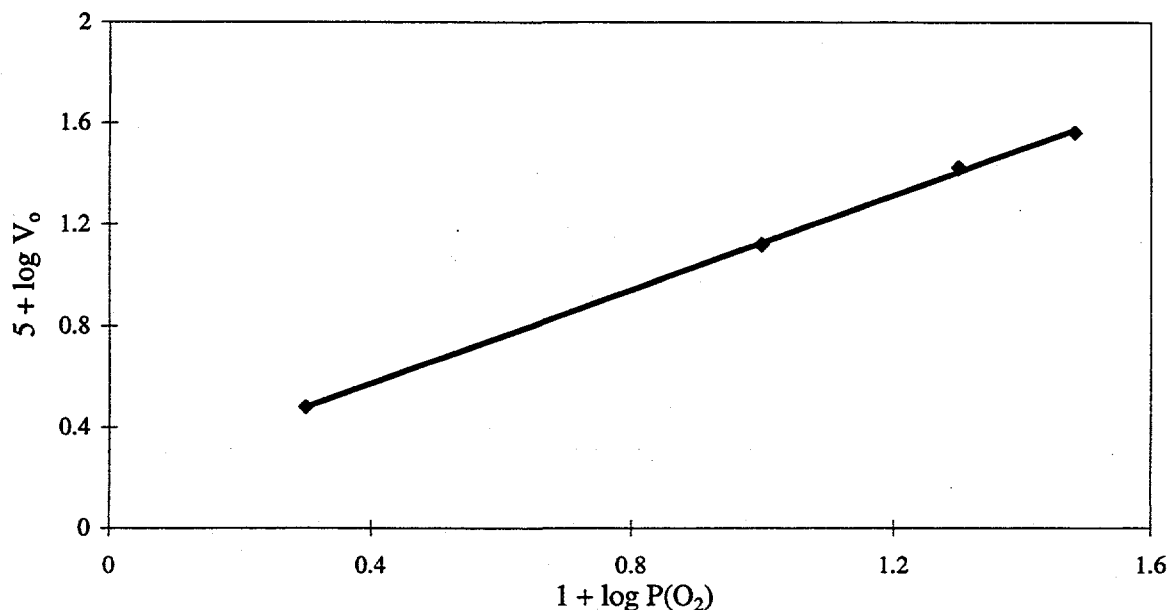


Figure 3.7. Influence of O_2 Pressure on the Oxidation Rate of 0.02 M Cr(III) Hydroxide (compound III) in 3 M NaOH at 70°C

As found in tests of oxidation by air, the initial rate of Cr(III) hydroxide oxidation in pure oxygen is not strongly dependent on temperature. The dependence of V_o on temperature is linear in Arrhenius coordinates (Figure 3.8), with slopes indicating a formal activation energy, E_a , in the range 26 to 36 kJ/mole. The decreasing oxygen solubility in alkaline solutions with increasing temperature undoubtedly contributes to the unusually low E_a .

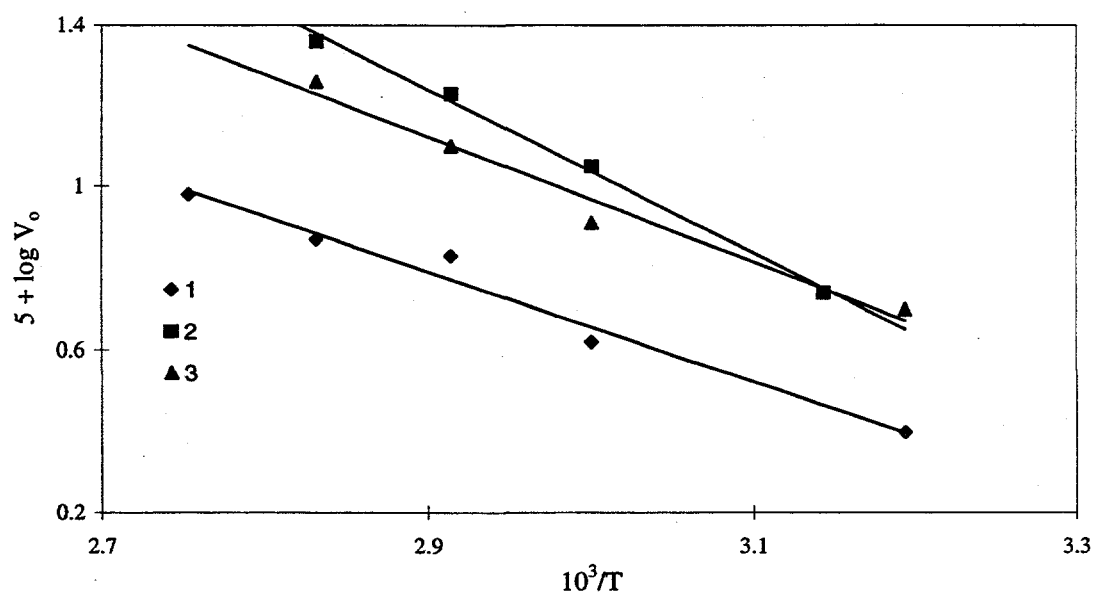


Figure 3.8. Effect of Temperature on the Rate of Cr(III) Hydroxide (compound II) Oxidation by Pure Oxygen; $[\text{Cr(III)}]_0 = 0.02 \text{ M}$:
 1 - 2 M NaOH, 1 atm O_2 ; 2 - 4 M NaOH, 1 atm O_2 ;
 3 - 2 M NaOH, 2 atm O_2

Data from Tables 3.5 and 3.6 illustrate the influence of the Cr(III) compound on the oxidative leaching rate. The tendency of V_o to decrease with increasing hydrothermal coagulation temperature is obvious but is not monotonic. Thus one of the Cr(III) hydroxide compounds (IX), hydrothermally treated at 250°C, showed an anomalously high oxidation rate by oxygen. A relatively high oxidative leaching rate of chromium also was observed in the case of the two $\text{NiCr}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ compounds (X and XI). It was postulated that Ni(II) is a catalyst for Cr(III) oxidation by O_2 in alkaline media. This supposition was verified by special tests in which the initial rate of O_2 reaction with Cr(III) hydroxide compounds IX and VI in 3 M NaOH at 70°C increased about two-fold after adding 2×10^{-3} M Ni(II).

The curves in Figures 3.9 to 3.11 describe the effects of more prolonged reaction of pure oxygen with different Cr(III) compounds in 3 M NaOH at 80°C. As expected, Cr(VI) accumulated in solution at approximately constant rates over the studied time intervals. Unfortunately, however, the dissolution process was slow under the test conditions, especially for the compounds aged at elevated temperatures.

Table 3.5. Comparison of the Oxidation Rates of Different Cr(III) Hydroxides by Oxygen

[NaOH], M	T, °C	V_o , moles/liter-hour, for various Cr(III) hydroxide compounds					
		II	III	V	VI	VII	IX
2	70	0.71×10^{-4}	0.55×10^{-4}	0.30×10^{-4}	0.45×10^{-4}	0.45×10^{-4}	0.90×10^{-4}
3	70	1.32×10^{-4}	1.22×10^{-4}	0.43×10^{-4}	0.50×10^{-4}	0.61×10^{-4}	1.20×10^{-4}
4	70	1.95×10^{-4}	--	0.80×10^{-4}	0.80×10^{-4}	1.10×10^{-4}	2.10×10^{-4}
3	60	1.10×10^{-4}	--	0.20×10^{-4}	0.40×10^{-4}	--	1.10×10^{-4}
3	80	1.85×10^{-4}	1.70×10^{-4}	0.70×10^{-4}	0.70×10^{-4}	0.9×10^{-4}	1.70×10^{-4}

Table 3.6. Comparison of the Oxidation Rates of Different Cr(III) Compounds by Oxygen

[NaOH], M	T, °C	V_o , moles/liter-hour, for various Cr(III) compounds				
		X	XI	XII	XIII	XIV
3.0	60	1.4×10^{-4}	1.0×10^{-4}	0.3×10^{-4}	0.2×10^{-4}	0.3×10^{-4}
3.0	70	1.8×10^{-4}	1.6×10^{-4}	0.6×10^{-4}	0.6×10^{-4}	0.5×10^{-4}
3.0	80	2.4×10^{-4}	1.9×10^{-4}	1.0×10^{-4}	0.9×10^{-4}	0.8×10^{-4}

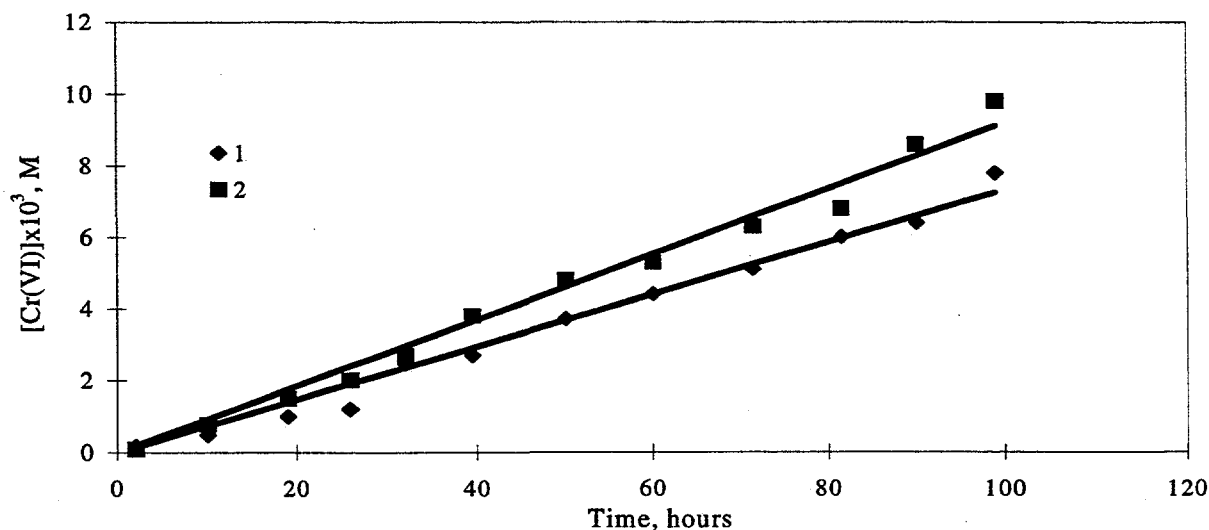


Figure 3.9. Long-Term Reaction of Cr(III) Hydroxides with 1 atm Pure Oxygen in 3 M NaOH at 80°C, $\text{Cr(III)}_0 = 0.02$ M: 1 - $\text{Cr}_2\text{O}_3 \cdot 3.8\text{H}_2\text{O}$ (compound III); 2 - $\text{Cr}_2\text{O}_3 \cdot 2.7\text{H}_2\text{O}$ (compound IX)

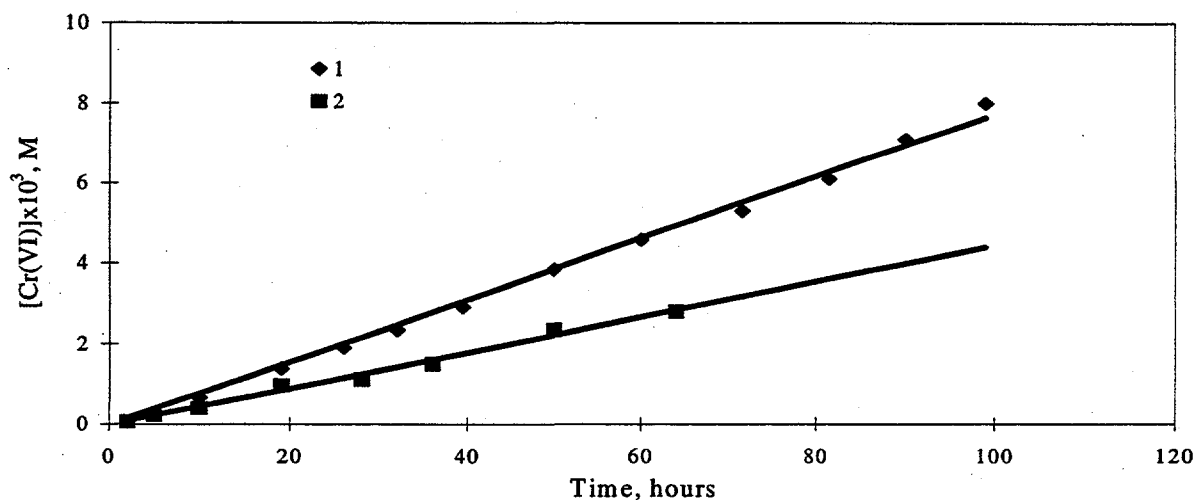


Figure 3.10. Long-Term Reaction of Cr(III) Compounds with 1 atm Pure Oxygen in 3 M NaOH at 80°C; $[\text{Cr(III)}]_0 = 0.02 \text{ M}$:
 1 - $\text{Cr}_2\text{O}_3 \cdot 2.9\text{H}_2\text{O}$ (compound V); 2 - $\text{Cr}_2\text{O}_3 \cdot 2.4\text{H}_2\text{O}$ (compound VI)

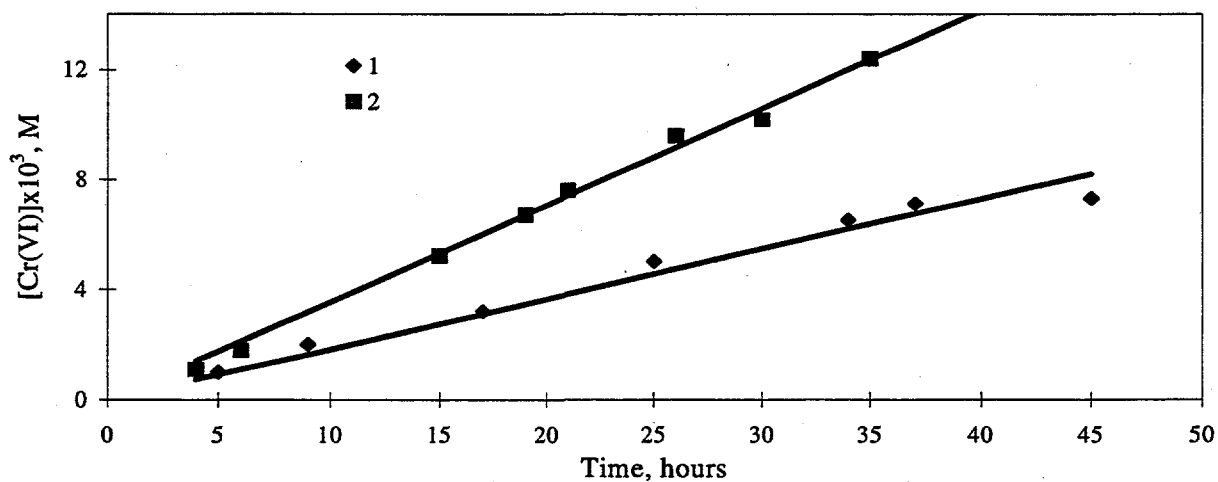


Figure 3.11. Long-Term Reaction of Cr(III) Hydroxides with Pure Oxygen with 2 atm Pressure in 3 M NaOH at 80°C; $[\text{Cr(III)}]_0 = 0.02 \text{ M}$:
 1 - $\text{Cr}_2\text{O}_3 \cdot 2.9\text{H}_2\text{O}$ (compound V)
 2 - $\text{Cr}_2\text{O}_3 \cdot 3.8\text{H}_2\text{O}$ (compound III)

4.0 Oxidative Alkaline Dissolution of Chromium(III) Compounds by Hydrogen Peroxide

4.1 Effect of Conditions on the Rate of Cr(III) Hydroxide Oxidation by H_2O_2

Preliminary tests showed that the oxidation of Cr(III) hydroxide compounds in 0.2 to 3 M NaOH proceeds at rates convenient for measurement at 40 to 80°C. These conditions were chosen for most testing. Typical kinetic curves of the reaction are seen in Figure 4.1. These curves cannot be described by a simple kinetic rate law because the Cr(III) oxidation is accompanied by pronounced catalytic decomposition of H_2O_2 . Therefore, the kinetic curves were used only to determine the initial reaction rate and, in some cases, the final yield of Cr(VI).

It is evident that the initial rate, V_o , of Cr(III) oxidation by H_2O_2 follows the expressions:

$$V_o = \lim (d[\text{Cr(VI)}]/d\tau) \text{ as } \tau \rightarrow 0$$

or

$$V_o \equiv k ([\text{Cr(III)}]_0)^m ([\text{H}_2\text{O}_2]_0)^n$$

where m and n are the reaction orders in terms of Cr(III) and H_2O_2 concentrations, k is the reaction rate constant, and τ is reaction time. The equation assumes that the rate of the heterogeneous reaction is controlled by solid-phase surface area and thus is proportional to uniform suspension concentration.

To estimate m and n , the dependence of V_o on $[\text{Cr(III)}]_0$ and $[\text{H}_2\text{O}_2]_0$ were determined for the Cr(III) hydroxide compound II. As seen from data in Table 4.1, V_o increases monotonically with increasing Cr(III) concentration under otherwise similar conditions. These data (Figure 4.2) show that $\log(V_o)$ increases linearly at slope ~ 1 with increase in $\log([\text{Cr(III)}]_0)$. Therefore, m is equal to 1.

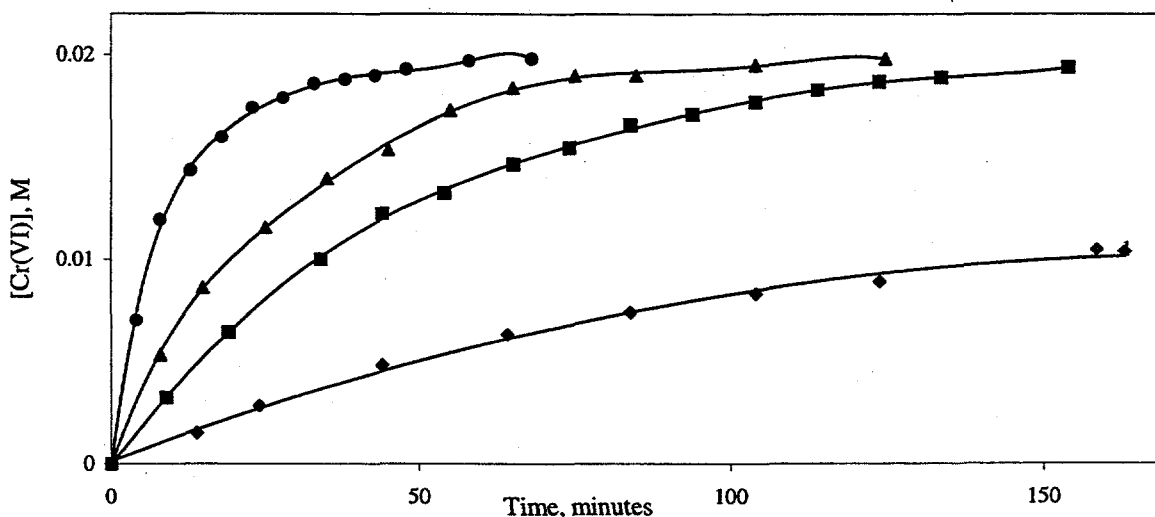


Figure 4.1. Kinetics of Oxidation of 0.02 M Cr(III) Hydroxide (compound II) by 0.1 M H_2O_2 :

1 - 3 M NaOH, 40°C; 2 - 0.5 M NaOH, 50°C
3 - 3 M NaOH, 60°C; 4 - 0.5 M NaOH, 70°C

Table 4.1. Initial Rate of $\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ (compound II) Oxidation by H_2O_2 in 3 M NaOH

$[\text{Cr(III)}]_0$, M	$[\text{H}_2\text{O}_2]_0$, M	T, °C	V_0 , moles/liter-minute
0.010	0.04	60.0	1.4×10^{-4}
0.016			1.9×10^{-4}
0.018			2.6×10^{-4}
0.020			3.0×10^{-4}
0.040			4.2×10^{-4}
0.068			8.7×10^{-4}
0.020	0.02	40.0	0.37×10^{-4}
	0.025		0.42×10^{-4}
	0.05		0.72×10^{-4}
	0.125		1.26×10^{-4}
	0.25		1.60×10^{-4}
0.020	0.02	60.0	1.78×10^{-4}
	0.02		2.00×10^{-4}
	0.04		3.02×10^{-4}
	0.10		5.25×10^{-4}
	0.10		6.10×10^{-4}
	0.20		8.60×10^{-4}
	0.20		8.70×10^{-4}

The dependence of V_0 on H_2O_2 concentration in logarithmic coordinates also is linear (Figure 4.3), but the slope (the exponent n) is ~ 0.62 . A fractional reaction order with respect to H_2O_2 concentration is difficult to explain. It may be that the actual reaction order is 1 but becomes less than 1 because H_2O_2 catalytic decomposition to form O_2 gas bubbles on the Cr(III) hydroxide particle surface decreases the surface exposed to the H_2O_2 solution for dissolution. The decreased surface area then would be reflected in the accompanying decrease in V_0 .

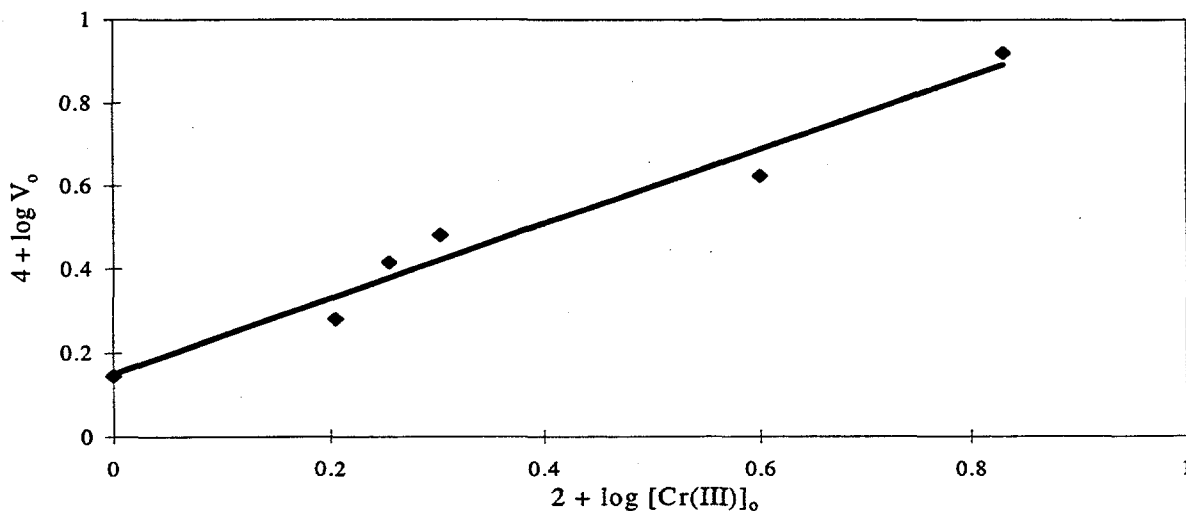


Figure 4.2. Effect of $[\text{Cr(III)}]_0$ on the Rate of $\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ (compound II) Oxidation by 0.04 M H_2O_2 at 60°C in 3 M NaOH

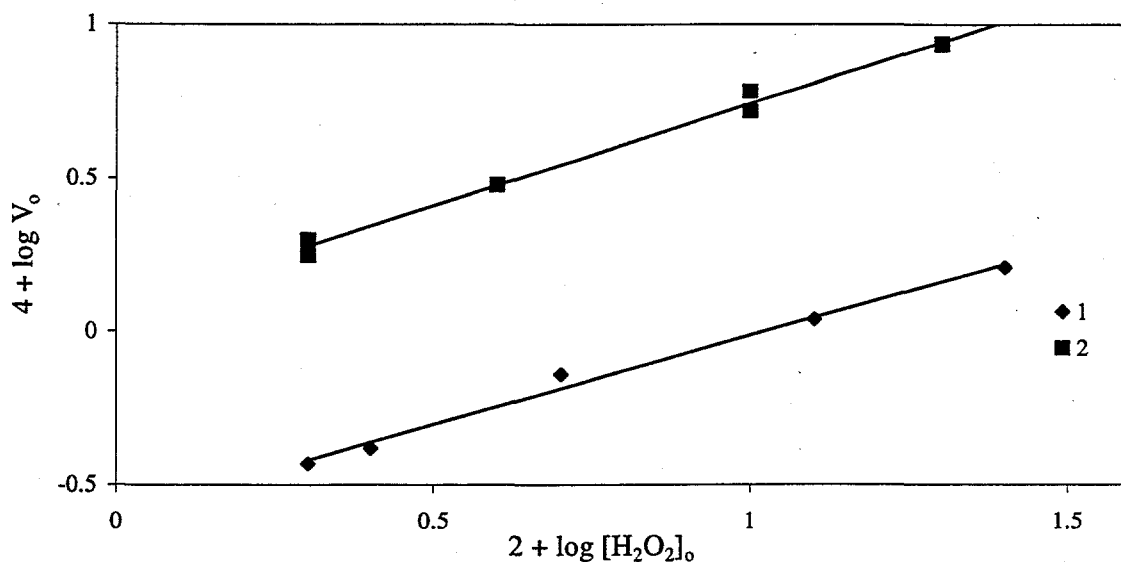


Figure 4.3. Effect of H₂O₂ Concentration on the Initial Rate of Oxidation of 0.02 M Cr(III) Hydroxide (compound II) in 3 M NaOH:
1 - 40°C; 2 - 60°C

The data presented in Table 4.2 show that the rate of Cr(III) oxidation at constant initial H₂O₂ concentration decreases steeply with increasing NaOH concentration and strongly increases with temperature. The dependence of V_o on temperature is linear in Arrhenius coordinates (Figure 4.4), with slope corresponding to an activation energy, E_a, of 82 kJ/mole at 0.5 M NaOH.

Table 4.2. Influence of Temperature and NaOH Concentration on Initial Rate of 0.02 M Cr₂O₃·4H₂O (compound II) Oxidation by H₂O₂

[H ₂ O ₂] _o , M	T, °C	[NaOH] _o , M	V _o , moles/liter-minute
0.04	30.0	0.5	0.31 x 10 ⁻⁴
	40.0		0.68 x 10 ⁻⁴
	50.0		1.87 x 10 ⁻⁴
	60.0		5.40 x 10 ⁻⁴
	70.0		9.46 x 10 ⁻⁴
	70.0		8.80 x 10 ⁻⁴
	80.0		25.0 x 10 ⁻⁴
	90.0		62.0 x 10 ⁻⁴
0.02	60.0	0.2	6.3 x 10 ⁻⁴
		0.2	8.3 x 10 ⁻⁴
		0.5	3.7 x 10 ⁻⁴
		1.0	2.8 x 10 ⁻⁴
		2.0	1.9 x 10 ⁻⁴
		3.0	1.6 x 10 ⁻⁴
		4.0	1.5 x 10 ⁻⁴

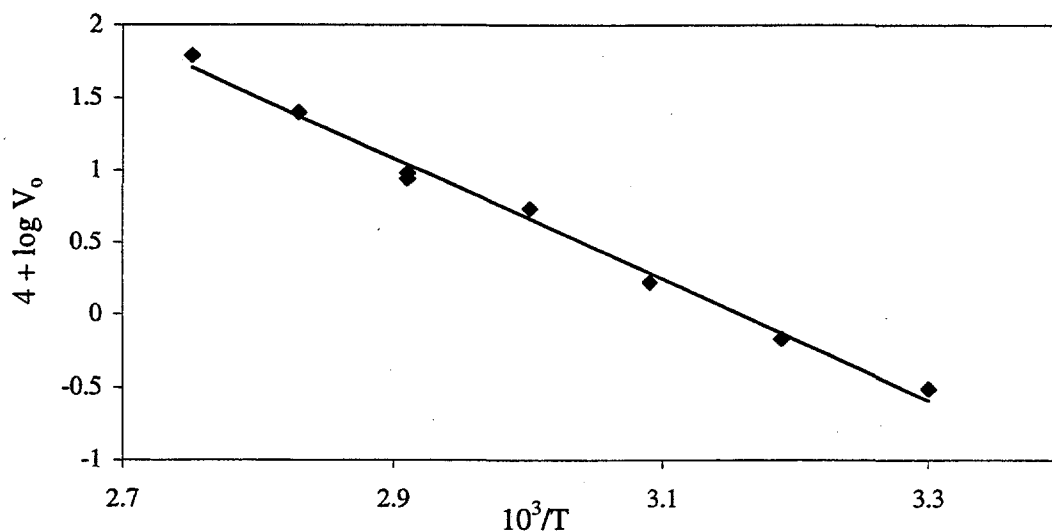


Figure 4.4. Effect of Temperature on the Initial Oxidation Rate of 0.02 M Cr(III) Hydroxide (compound II) by 0.04 M H_2O_2 in 0.5 M NaOH

Table 4.3 presents the initial oxidation rates of the Cr(III) hydroxides aged at various elevated temperatures. It is evident that aging Cr(III) hydroxide under hydrothermal conditions sharply decreases its oxidation rate by H_2O_2 . The lower oxidation rates may indicate that the more mineralized Cr(III) hydroxides are better catalysts for H_2O_2 decomposition.

Table 4.3. Initial Rate of Cr(III) Hydroxide Oxidation by 0.04 M H_2O_2

Compound Number	Coagulation Temperature, °C	[NaOH], M	T, °C	V_o , moles/liter-minute
II	100	0.2	60	10.4×10^{-4}
V	150			1.3×10^{-4}
VI	200			1.8×10^{-4}
VII	250			ND ^(a)
VIII	250			0.6×10^{-4}
II	100		75	31×10^{-4}
V	150			3.2×10^{-4}
VI	200			4.3×10^{-4}
VII	250			2.8×10^{-4}
VIII	250			1.3×10^{-4}
II	100	2.0	60	3.7×10^{-4}
V	150			0.4×10^{-4}
VI	200			0.5×10^{-4}
VII	250			ND ^(a)
VIII	250			0.3×10^{-4}
II	100		75	9.1×10^{-4}
V	150			0.8×10^{-4}
VI	200			1.4×10^{-4}
VII	250			1.1×10^{-4}
VIII	250			0.8×10^{-4}

(a) Not detectable compared with the rate of H_2O_2 catalytic decomposition.

4.2 Cr(III) Hydroxide Oxidation by H₂O₂ in the Presence of Some Catalysts

The Hanford tank waste residues will have complex compositions even after the salts have been dissolved by water and the sludge has been leached with strongly alkaline solution. The residual sludges will contain mixtures of low-solubility d-element compounds that, in some cases, can be effective H₂O₂ decomposition catalysts in alkaline media. On the other hand, the sludge compounds and trace solution concentrations of the d-elements also might catalytically enhance Cr(III) oxidation by H₂O₂. Therefore, a series of experiments was performed to determine the effects of Cu(II), Ni(II), Co(II), and Fe(III) additions on the rate of Cr(III) reaction with H₂O₂. The experiments were conducted under conditions in which the initial oxidation rates, V_o, in the absence of catalysts were 1.9x10⁻⁴ and 9.1x10⁻⁴ moles/liter-minute at 50 and 70°C, respectively.

As seen in Table 4.4, Cr(III) oxidation rates by H₂O₂ increase significantly in the presence of 10⁻⁵ M Cu(II) and Co(II). However, Ni(II) and Fe(III) at the same concentration have little effect on V_o. At higher (as much as 0.01 M) concentrations of all catalysts, the H₂O₂ decomposition becomes very fast,

Table 4.4. Oxidation of 0.02 M Cr₂O₃·4H₂O (compound II) in 0.5 M NaOH by 0.04 M H₂O₂ in the Presence of Catalysts^(a)

Catalyst	[Catalyst], M	T, °C	[Cr(VI)] ₁	[Cr(VI)] ₂	V _o , moles/liter-minute
None	--	50	--	--	1.9x10 ⁻⁴
None	--	70	--	--	9.1x10 ⁻⁴
Cu	1x10 ⁻⁵	50	1.6x10 ⁻³	1.9x10 ⁻³	5.3x10 ⁻⁴
	3x10 ⁻⁴		1.56x10 ⁻³	1.55x10 ⁻³	>5.2x10 ⁻⁴
	1x10 ⁻²		1.0x10 ⁻³	1.0x10 ⁻³	>3.3x10 ⁻⁴
	3x10 ⁻⁴	70	1.2x10 ⁻³	1.0x10 ⁻³	>4.0x10 ⁻⁴
	1x10 ⁻²		0.3x10 ⁻³	0.3x10 ⁻³	>1.0x10 ⁻⁴
	1x10 ⁻⁵	70	0.6x10 ⁻³	1.0x10 ⁻³	2.0x10 ⁻⁴
Ni	3x10 ⁻⁴		0.7x10 ⁻³	1.0x10 ⁻³	>2.3x10 ⁻⁴
	1x10 ⁻²		0.2x10 ⁻³	0.2x10 ⁻³	>0.7x10 ⁻⁴
	1x10 ⁻⁵	70	2.3x10 ⁻³	3.4x10 ⁻³	7.7x10 ⁻⁴
	3x10 ⁻⁴		1.86x10 ⁻³	3.64x10 ⁻³	>6.2x10 ⁻⁴
	1x10 ⁻²		0.9x10 ⁻³	1.0x10 ⁻³	>3.0x10 ⁻⁴
	1x10 ⁻⁵	70	1.24x10 ^{-3(b)}	2.3x10 ⁻³	6.2x10 ⁻⁴
Co	3x10 ⁻⁴		1.0x10 ⁻³	1.3x10 ⁻³	>3.4x10 ⁻⁴
	1x10 ⁻²		0.23x10 ⁻³	0.23x10 ⁻³	>0.8x10 ⁻⁴
	1x10 ⁻⁵	70	4.92x10 ⁻³	6.0x10 ⁻³	1.7x10 ⁻³
	3x10 ⁻⁴		3.23x10 ⁻³	3.4x10 ⁻³	>1.1x10 ⁻³
	1x10 ⁻²		0.58x10 ⁻³	0.58x10 ⁻³	>1.9x10 ⁻⁴
	1x10 ⁻⁵	70	0.56x10 ⁻³	0.89x10 ⁻³	1.9x10 ⁻⁴
Fe	3x10 ⁻⁴		0.46x10 ⁻³	0.6x10 ⁻³	>1.5x10 ⁻⁴
	1x10 ⁻²		0.44x10 ⁻³	0.5x10 ⁻³	>1.5x10 ⁻⁴
	1x10 ⁻⁵	70	2.50x10 ⁻³	4.4x10 ⁻³	8.3x10 ⁻⁴
	3x10 ⁻⁴		1.40x10 ⁻³	2.2x10 ⁻³	>4.7x10 ⁻⁴
	1x10 ⁻²		0.83x10 ⁻³	0.9x10 ⁻³	>2.8x10 ⁻⁴

(a) [Cr(VI)]₁ and [Cr(VI)]₂ are the concentrations of Cr(VI) after three and six minutes, respectively. Initial rate calculated based on the first three minutes.
(b) In this test, [Cr(VI)]₁ was at two minutes.

and Cr(III) oxidation practically ends after about three minutes' reaction with low yield of Cr(VI). This is shown by the low incremental concentrations of Cr(VI) dissolved after six minutes compared with the concentrations dissolved after three minutes (Table 4.4). Thus, with higher concentrations of candidate d-element catalysts, the initial oxidation rates of Cr(III), V_o , become less meaningful and are indicated by "greater than" values in Table 4.4.

Based on the observed parasitic loss of H_2O_2 in the presence of Fe(III) and other d-metals, the oxidative dissolution of Cr(III) hydroxides in the presence of significant concentrations of Fe(III) and other d-metals will be difficult to accomplish.

4.3 Rate of Oxidation of Other Cr(III) Compounds by H_2O_2 in Alkaline Media

Data in Table 4.5 show that the initial rates of Cr(VI) production are relatively high for the reaction of Ni(II) chromite and mixed Fe(III)/Cr(III) hydroxide compounds, aged at 100°C , with hydrogen peroxide. The same compounds aged at 200°C for 20 hours react very slowly with H_2O_2 . The catalytic decomposition of H_2O_2 also increases significantly for the aged compounds, especially at high NaOH concentration.

Table 4.5. Initial Oxidation Rate of Some Cr(III) Compounds by 0.04 M H_2O_2

Compound Number ^(a)	Temperature, °C		[NaOH], M	V _o , moles/liter-minute
	Aging	Dissolution		
X	100	60	0.2	3.1x10 ⁻⁴
XII				7.0x10 ⁻⁴
XI				0.5x10 ⁻⁴
XIII				1.2x10 ⁻⁴
X	100		2.0	1.3x10 ⁻⁴
XII				4.0x10 ⁻⁴
XI				0.2x10 ⁻⁴
XIII				0.6x10 ⁻⁴
X	100	75	0.2	6.1x10 ⁻⁴
XII				11.4x10 ⁻⁴
XI				1.3x10 ⁻⁴
XIII				2.0x10 ⁻⁴
X	100		2.0	2.5x10 ⁻⁴
XII				6.1x10 ⁻⁴
XI				0.6x10 ⁻⁴
XIII				1.2x10 ⁻⁴

(a) X - NiCr₂O₄·5H₂O (T_c=100°C)

XI - NiCr₂O₄·4H₂O (T_c=200°C)

XII - Fe_{0.67}Cr_{1.33}O₃·2H₂O (T_c=100°C)

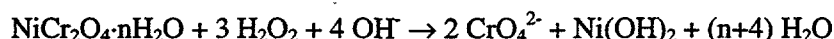
XIII - Fe_{0.67}Cr_{1.33}O₃·2H₂O (T_c=200°C)

4.4 H₂O₂ Consumption in the Complete Oxidation of Cr(III) Hydroxides

The theoretical consumption of hydrogen peroxide by oxidative dissolution of Cr(III) hydroxides, described by the following reaction:



is 1.5 moles per mole of Cr(III). The same H₂O₂ consumption may be expected for both Ni(II) chromite and Cr(III)/Fe(III) mixed hydroxide:



However, the actual H₂O₂ consumption for Cr(III) oxidation is significantly higher because of the catalytic decomposition of the oxidant. The relative contribution of the latter process depends on the Cr(III) oxidation conditions. As seen in Table 4.6, with stepwise addition of H₂O₂ solution (0.05 mL added every three minutes), the fraction of oxidant lost to catalytic decomposition decreases with increasing temperature. Increasing NaOH concentration increases the catalyst-mediated loss of H₂O₂. Therefore, the oxidative dissolution of Cr(III) hydroxide by H₂O₂ should be conducted at the lowest possible alkali concentration and at temperatures close to 100°C. In choosing the initial NaOH concentration, it also is necessary to account for the consumption of 2 moles OH⁻ per mole of Cr(III) to be oxidized.

The consumption of H₂O₂ in the oxidative dissolution of Cr(III) hydroxide increases sharply in the presence of Fe(III) (Table 4.7). The influence of Ni(II) on the consumption of H₂O₂ for Cr(III) hydroxide dissolution is much lower than that of Fe(III). The test results presented in Table 4.8 show that H₂O₂ is not effective for alkaline oxidative dissolution of Cr(III) hydroxides aged under hydrothermal conditions, even in the absence of additional catalysts. The completeness of Cr(III) oxidation generally decreases with increasing aging temperature.

Table 4.6. Consumption of H₂O₂ for Cr(III) Hydroxide (compound II) Oxidation in Alkaline Solutions^(a)

[Cr(III)], M	[NaOH], M	T, °C	[H ₂ O ₂], M	H ₂ O ₂ /Cr(III) mole ratio
0.02	0.3	50	1.0	6.5
		60		5.0
		75		3.1
		85		2.8
		90		2.6
0.02	1.0	70	1.0	4.0
0.05	2.0		2.0	4.0
0.10	2.0		2.0	3.2
0.20	2.0		4.0	3.1
(a) 10 mL of suspension.				

Table 4.7. Consumption of H_2O_2 for Complete Cr(III) Hydroxide (compound II) Oxidation in 70°C 2 M NaOH in the Presence of Catalysts^(a)

Catalyst	[Catalyst], M	[Cr(III)] ₀ , M	[H ₂ O ₂], M	H ₂ O ₂ /Cr(III) mole ratio
Fe(III)	1×10^{-4}	0.02	1.0	5.0
	1×10^{-2}	0.02	1.0	15
	2×10^{-2}	0.02	1.0	>20
	1×10^{-4}	0.05	2.0	4.0
	1×10^{-2}	0.05	2.0	8.0
Ni(II)	1×10^{-4}	0.02	1.0	3.7
	1×10^{-2}	0.015	1.0	5.1
	1×10^{-4}	0.05	2.0	4.0
	1×10^{-2}	0.05	2.0	6.1

(a) 10 mL of suspension.

Table 4.8. Oxidation of 0.022 M Aged Cr(III) Hydroxides in 0.3 M NaOH by H_2O_2 ^(a,b)

Compound Number	Temperature, $^\circ\text{C}$		[Cr(VI)], M	Cr(VI) Yield, %
	Aging	Dissolution		
V	150	70	7.9×10^{-3}	50
VI	200		10.8×10^{-3}	69
VIII	250		6.5×10^{-3}	41
V	150	85	12.5×10^{-3}	80
VI	200		10.4×10^{-3}	66
VIII	250		6.7×10^{-3}	42

(a) 5 mL suspension volume.
(b) Stepwise additions (0.05 mL every four minutes) to 2 mL total 1 M H_2O_2 : [~ 18 moles H_2O_2 /mole Cr(III)].

Significant catalytic loss of H_2O_2 was also observed in the oxidative reaction of H_2O_2 with $\text{NiCr}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ and mixed Cr(III) and Fe(III) hydroxides (Table 4.9). Especially low chromium leaching took place for the compounds aged hydrothermally at 200°C .

Table 4.9. Interaction of $\text{NiCr}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ (compounds X and XI) and $\text{Fe}_{0.67}\text{Cr}_{1.33}\text{O}_3 \cdot 2\text{H}_2\text{O}$ (compounds XII and XIII) with 1 M H_2O_2 in 0.3 M NaOH^(a,b)

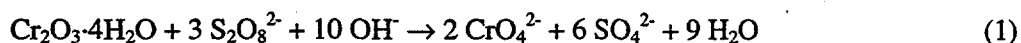
Compound Number	Temperature, $^\circ\text{C}$		[Cr(III)] ₀ , M	Cr(VI) Yield, %	
	Aging	Dissolution		1 mL 1 M H_2O_2	2 mL 1 M H_2O_2
X	100	70	1.4×10^{-2}	65	82
XI	200		2.9×10^{-2}	7	11
XII	100		3.0×10^{-2}	52	60
XIII	200		2.9×10^{-2}	9	13
X	100	85	2.8×10^{-2}	89	≥ 95
XI	200		3.0×10^{-2}	10	18
XII	100		2.9×10^{-2}	62	84
XIII	200		3.0×10^{-2}	11	16

(a) 5 mL suspension volumes.
(b) Stepwise additions (0.05 mL every four minutes) to 1 or 2 mL total 1 M H_2O_2 .

5.0 Oxidative Alkaline Dissolution of Chromium(III) Compounds by Persulfate

5.1 Data on the Kinetics and Mechanism of Cr(III) Hydroxide Oxidation

Studies were conducted to determine the stoichiometry of Cr(III) oxidation by persulfate. Results in Table 5.1 show that the complete oxidative dissolution of $\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ (compound II) is observed only at persulfate ($\text{S}_2\text{O}_8^{2-}$) to Cr(III) molar ratios greater than 1.5. At lower ratios, part of the solid phase remains in the suspension with the yield of Cr(VI) in solution corresponding to an $\text{S}_2\text{O}_8^{2-}$:Cr(VI) mole ratio close to 1.5. Thus, the stoichiometry of the oxidation of compound II by persulfate in NaOH solutions is expressed by the equation:



Typical kinetic curves of the reaction of Cr(III) hydroxide with persulfate in NaOH solutions are presented in Figure 5.1. Such curves were used to determine the initial reaction rates (that is, $V_o = d[\text{Cr(VI)}]/d\tau$ as $\tau \rightarrow 0$). Initial reaction rates may be used to establish reaction orders in terms of reactant concentrations and to reach conclusions on the reaction mechanism.

Initial reaction rates, V_o , for suspensions of different compositions are given in Table 5.2. The data show that the experimental rates of Cr(III) oxidation in alkaline solutions at less than 70°C are significantly higher than the reported rates of $\text{S}_2\text{O}_8^{2-}$ thermal decomposition [Kolthoff and Miller 1951]. On this basis, Cr(III) hydroxide appears to react directly with $\text{S}_2\text{O}_8^{2-}$. However, at greater than 80°C, the rate of $\text{S}_2\text{O}_8^{2-}$ thermal decomposition exceeds that of Cr(III) oxidation (Table 5.3). Under such conditions, the ion radical SO_4^- can participate in reactions to form Cr(VI).

The data of Table 5.2 also were used to estimate the reaction orders in terms of Cr(III) and $\text{S}_2\text{O}_8^{2-}$ concentrations. Both reaction orders are ~1 as shown by the linear dependencies of V_o on Cr(III) and $\text{S}_2\text{O}_8^{2-}$ concentrations (in logarithmic coordinates) with slopes of ~1 (Figures 5.2 and 5.3).

Table 5.1. Yield of Cr(VI) after Completion of the $\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ (compound II) Reaction with Persulfate

Initial composition, M			$[\text{S}_2\text{O}_8^{2-}]_0 / [\text{Cr(III)}]_0$	Conditions		$[\text{Cr(VI)}], \text{ M}$	$[\text{S}_2\text{O}_8^{2-}]_0 / [\text{Cr(VI)}]^{(a)}$
$[\text{NaOH}]_0$	$[\text{Cr(III)}]_0$	$[\text{S}_2\text{O}_8^{2-}]_0$		T, °C	Completion, min.		
3.0	0.056	0.2	3.57	71.0	25	0.055	3.64, complete
0.5	0.039	0.2	5.13	80.0	35	0.040	5.0, complete
2.5	0.123	0.1	0.81	71.0	81	0.067	1.49, incomplete
2.5	0.128	0.15	1.17	71.0	65	0.096	1.56, incomplete
2.5	0.136	0.15	1.10	71.0	75	0.098	1.53, incomplete

(a) Data in this column indicate whether complete or incomplete dissolution of the Cr(III) compound was observed.

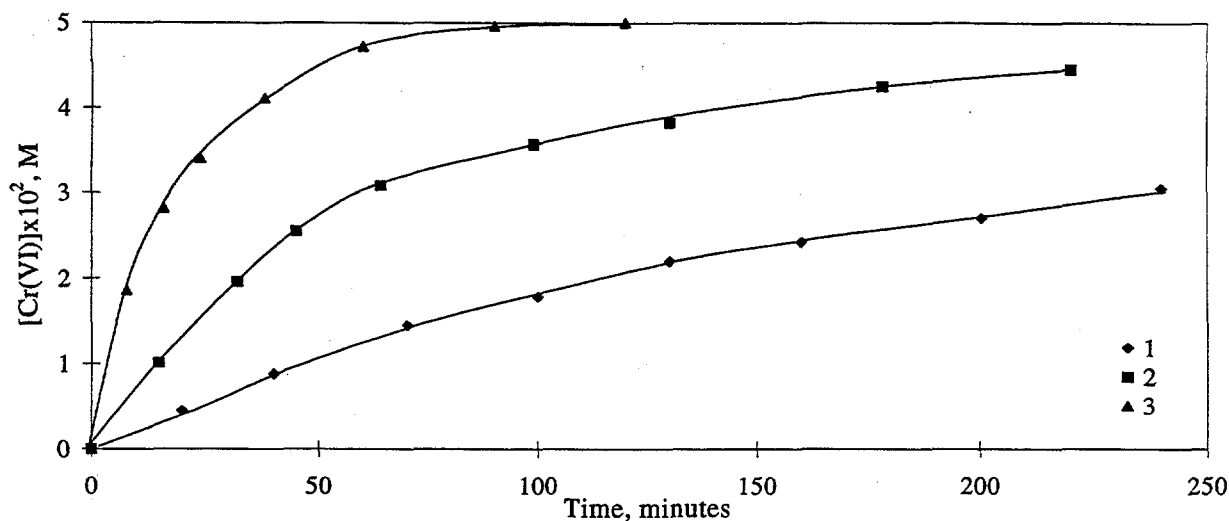


Figure 5.1. Kinetics of Oxidation of 0.05 M Cr(III) Hydroxide (compound II) by 0.2 M $\text{S}_2\text{O}_8^{2-}$ in 0.5 M NaOH: 1 - 41.5°C; 2 - 60.5°C; 3 - 80.0°C

Table 5.2. Effect of Composition on the Initial Rates of Cr(III) Hydroxide Oxidation by $\text{S}_2\text{O}_8^{2-}$

Compound Number	[NaOH] ₀ , M	T, °C	[Cr(III)] ₀ , M	[S ₂ O ₈ ²⁻] ₀ , M	V ₀ , moles/liter-minute
II	0.5	71.0	0.014	0.20	0.50 x 10 ⁻³
			0.024		0.94 x 10 ⁻³
			0.039		1.23 x 10 ⁻³
			0.050		1.75 x 10 ⁻³
			0.056		2.10 x 10 ⁻³
III	2.0	50.0	0.034	0.05	0.40 x 10 ⁻³
				0.10	0.74 x 10 ⁻³
				0.20	1.40 x 10 ⁻³
				0.40	3.30 x 10 ⁻³

Table 5.3. Effect of Temperature and NaOH Concentration on the Initial Rate of 0.05 M Cr(III) (compound II) Oxidation by 0.2 M $\text{S}_2\text{O}_8^{2-}$

T, °C	[NaOH] ₀ , M	V ₀ , moles/liter-minute
71.0	0.1	0.54 x 10 ⁻³
	0.2	0.98 x 10 ⁻³
	0.5	1.84 x 10 ⁻³
	1.0	3.5 x 10 ⁻³
	2.5	10.0 x 10 ⁻³
	3.0	15.0 x 10 ⁻³
41.5	0.5	0.27 x 10 ⁻³
41.5		0.34 x 10 ⁻³
60.5		0.79 x 10 ⁻³
71.0		1.75 x 10 ⁻³
80.0		2.44 x 10 ⁻³
95.0		4.80 x 10 ⁻³

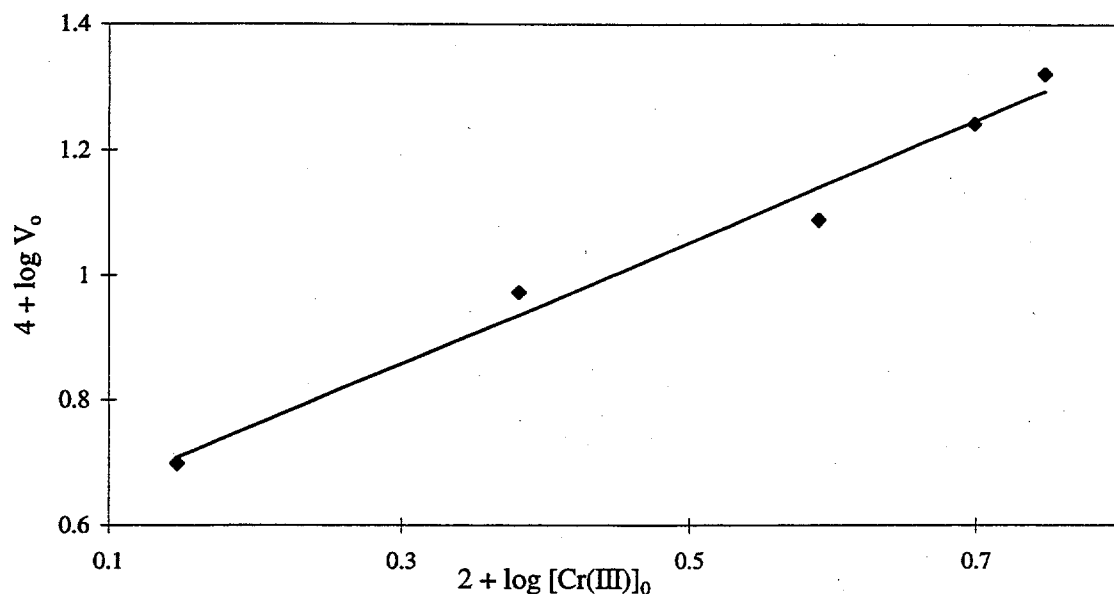


Figure 5.2. Effect of Initial Cr(III) Concentration on the Initial Oxidation Rate of Cr(III) Hydroxide (compound II) by 0.2 M $\text{S}_2\text{O}_8^{2-}$ at 71°C in 0.5 M NaOH

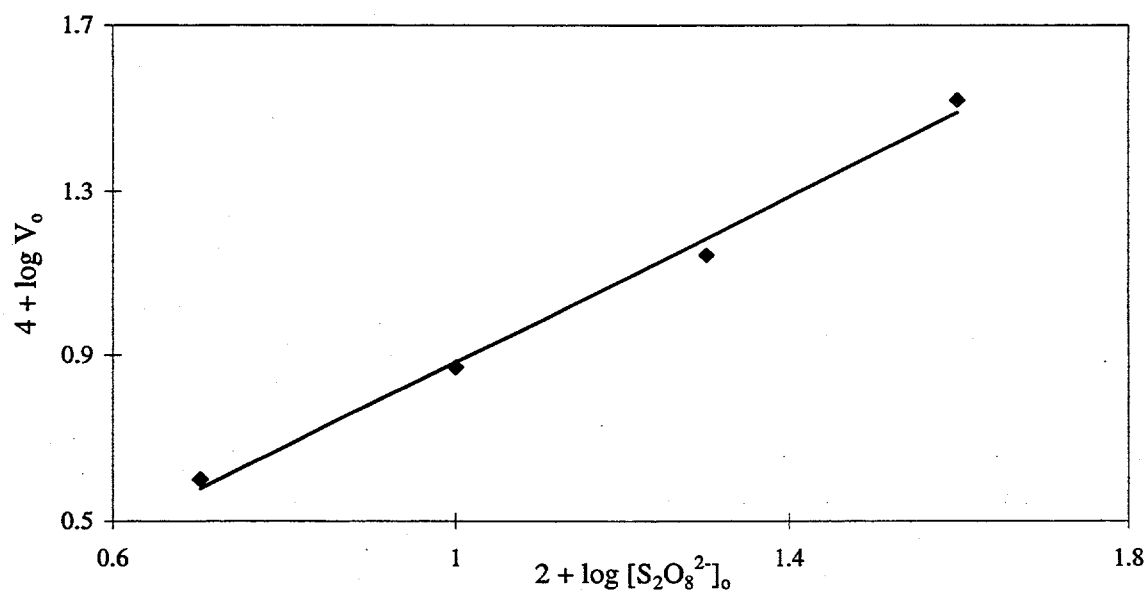


Figure 5.3. Effect of Initial $\text{S}_2\text{O}_8^{2-}$ Concentration on the Initial Oxidation Rate of 0.034 M Cr(III) Hydroxide (compound III) in 2 M NaOH at 50°C

The effects of temperature and NaOH concentration on the initial reaction rates, V_o , are presented in Table 5.3. These data, shown in Figure 5.4, indicate that the dependence of $\log(V_o)$ on inverse absolute temperature is linear with slope corresponding to a formal activation energy, E_a , of 53 kJ/mole. The dependence of V_o on NaOH concentration in the range 0.1-3 M in logarithmic coordinates (Figure 5.5) follows a straight line with the slope about 1. The deviation of experimental points from this dependence may be caused by the deviation of NaOH behavior from ideality with increasing alkali concentration.

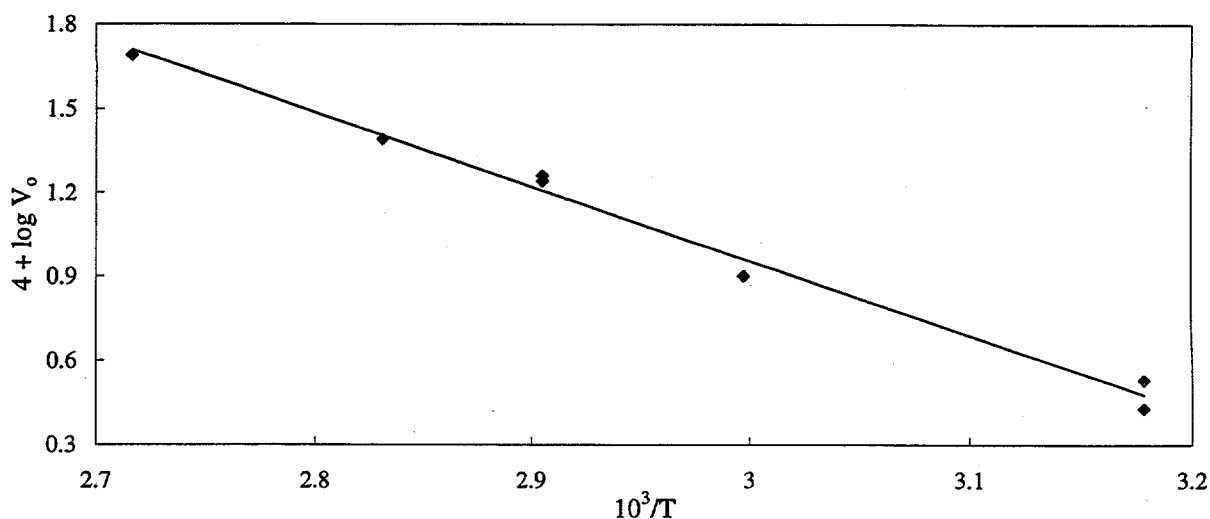


Figure 5.4. Effect of Temperature on the Initial Oxidation Rate of 0.05 M Cr(III) Hydroxide (compound II) by 0.2 M $S_2O_8^{2-}$ in 0.5 M NaOH

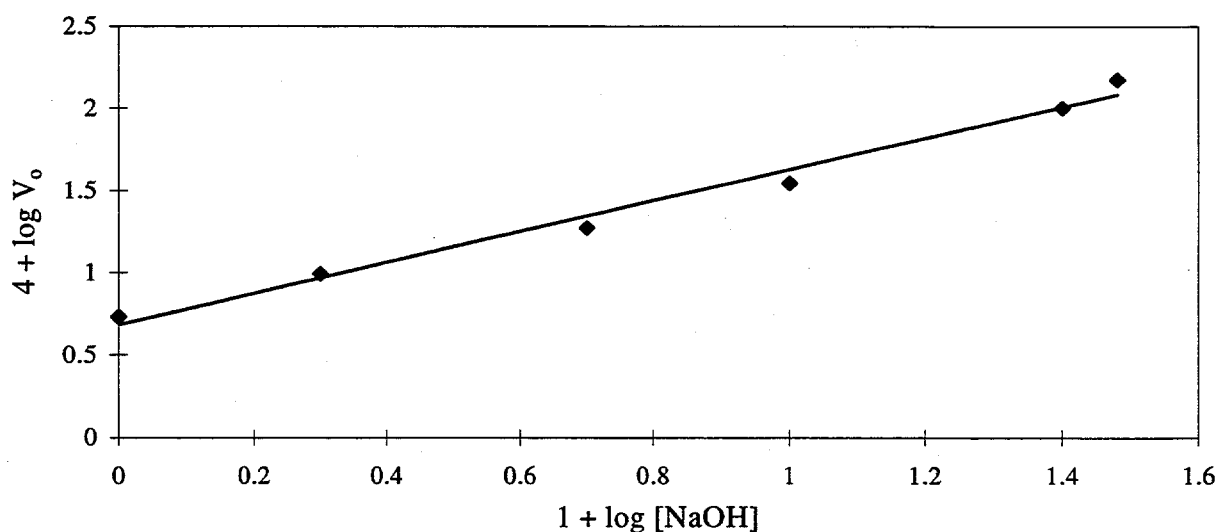


Figure 5.5. Effect of NaOH Concentration on the Initial Oxidation Rate of 0.05 M Cr(III) Hydroxide (compound II) by 0.2 M $S_2O_8^{2-}$ at 71°C

Based on these results, a kinetic equation for Cr(III) hydroxide oxidation by persulfate in NaOH (i.e., the decrease in Cr(III) concentration with time, τ) can be written as

$$d[Cr(III)]/d\tau = dC/d\tau = -kCC_1C_2 \quad (2)$$

where C , C_1 , and C_2 are the respective Cr(III), $S_2O_8^{2-}$, and NaOH concentrations. Average values of k were estimated to be 0.1, 0.18, and $0.35 \text{ M}^{-2}\text{min}^{-1}$ at 50, 60 and 70°C, respectively.

According to the stoichiometry expressed in equation (1), it is clear that

$$C_1 = C_{1i} - 1.5 (C_i - C) = a + 1.5 C, \text{ where } a = C_{1i} - 1.5 C_i$$

and

$$C_2 = C_{2i} - 5 (C_i - C) = b + 5 C, \text{ where } b = C_{2i} - 5 C_i$$

Here C_i , C_{1i} , and C_{2i} are initial values of C , C_1 , and C_2 respectively. Therefore,

$$dC/d\tau = -kC (a + 1.5 C) (b + 5 C) \quad (3)$$

The integral of equation (3) is complex:

$$k\tau = (1/ab) \ln[C_i/C] + [1.5/a(5a-1.5b)] \ln[(a+1.5C_{1i})/(a+1.5C)] + [5/b(1.5b-5a)] \ln[(b+5C_{2i})/(b+5C)] \quad (4)$$

but it satisfactorily describes the experimental kinetics and can be used to estimate the time required to oxidize Cr(III) hydroxide to a given extent by persulfate under selected reagent concentrations. In using equation (4), one must recognize that the value of k can change depending on the Cr(III) hydroxide compound and the reaction temperature being used. This stipulation is confirmed by the data presented in Table 5.4, which show the variation of k observed at given temperatures found for the seven Cr(III) hydroxide compounds. The k values do not vary regularly as a function of precipitate aging conditions. The lack of correlation may reflect the poor reproducibility of the initial Cr(III) hydroxide precipitation conditions.

Table 5.4. Effect of 0.03 M Cr(III) Hydroxide Compound on the Rate Constant k in 0.2 M Persulfate

Compound Number	Aging Temperature, °C, and Time, days	k, liter ² /moles ² -minute			
		2 M NaOH		0.5 M NaOH	
		70°C	50°C	70°C	50°C
I	20, 1	0.25	0.068	—	0.041
II	100, 15	0.33	0.071	0.30	0.083
III	100, 20	0.34	0.10	0.27	0.080
IV	100, 20	0.19	—	0.19	—
V	150, 20	0.18	0.046	0.12	0.033
VI	200, 20	0.22	0.081	0.24	0.060
VIII	250, 20	0.39	0.11	0.30	0.11

5.2 Data on Persulfate Reactions with Other Cr(III) Compounds

Preliminary data on the reaction of persulfate with other Cr(III) compounds in alkaline media are given in Table 5.5. The test results show that the oxidation of amorphous $\text{NiCr}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ and mixed Fe(III) and Cr(III) hydroxide compounds proceeds more rapidly than the oxidation of pure Cr(III) hydroxide under the same conditions. Even crystalline products obtained by 800°C calcination of Cr(III) hydroxide (compound III) and $\text{NiCr}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ (compound X) are oxidatively dissolved by persulfate in alkaline media. These respective calcined solids were found by x-ray diffractometry to be $\alpha\text{-Cr}_2\text{O}_3$ (Figure 5.6) and a mixture of $\alpha\text{-Cr}_2\text{O}_3$ and a spinel-type Ni(II) chromite, NiCr_2O_4 (Figure 5.7). More detailed study of these reactions, such as determining the effect of alkali concentration on the reactions' rates and stoichiometries, is required.

Table 5.5. Oxidation of Different Cr(III) Compounds by 0.2 M Persulfate in 2 M NaOH

Compound Number	Compound Composition	Aging or Calcination Temperature, °C	[Cr(III)] ₀ , M	Dissolution Temperature, °C	V _o , moles/liter-minute	Reaction Time, minutes
X	NiCr ₂ O ₄ ·5H ₂ O	100	0.038	50.0	~8x10 ⁻³	10
			0.027	39.5	2.4x10 ⁻³	25
XI	NiCr ₂ O ₄ ·4H ₂ O	200	0.028	39.5	~7x10 ⁻³	8
			0.018	50.0	>10x10 ⁻³	<5
--	NiCr ₂ O ₄	800	0.015	50.0	0.5x10 ⁻³	80
--	α-Cr ₂ O ₃	800	0.036	70.0	2.7x10 ⁻³	50
XII	FeCr ₂ O _{4.5} ·3H ₂ O ^(a)	100	0.023	39.5	1.6x10 ⁻³	90
			0.017	50	2.5x10 ⁻³	40
XIII	FeCr ₂ O _{4.5} ·3H ₂ O	200	0.030	39.5	2.5x10 ⁻³	60
			0.024	50	4.9x10 ⁻³	30

(a) FeCr₂O_{4.5}·3H₂O is Fe_{0.67}Cr_{1.33}O₃·2H₂O.

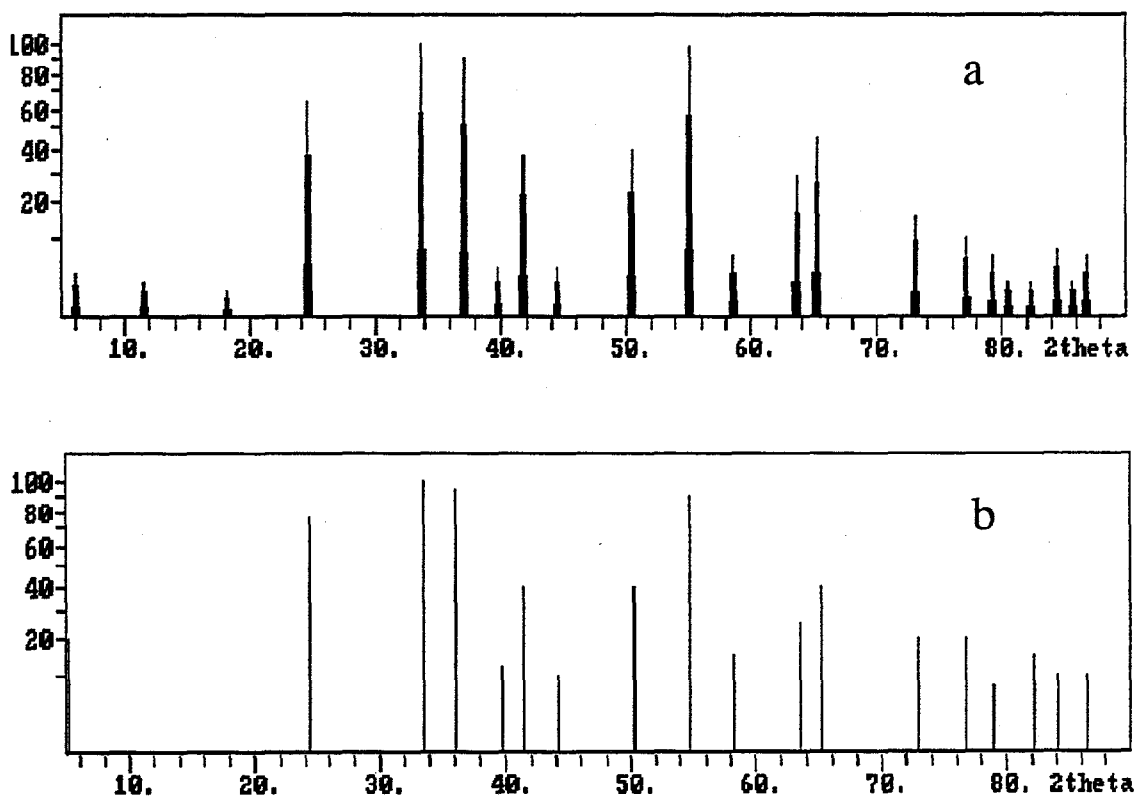


Figure 5.6. Diffractogram of Cr(III) Oxides

a - Cr₂O₃·3.8H₂O (compound III) Calcined at 800°C

b - Literature Data for α-Cr₂O₃ [Newnham and de Haan 1962]

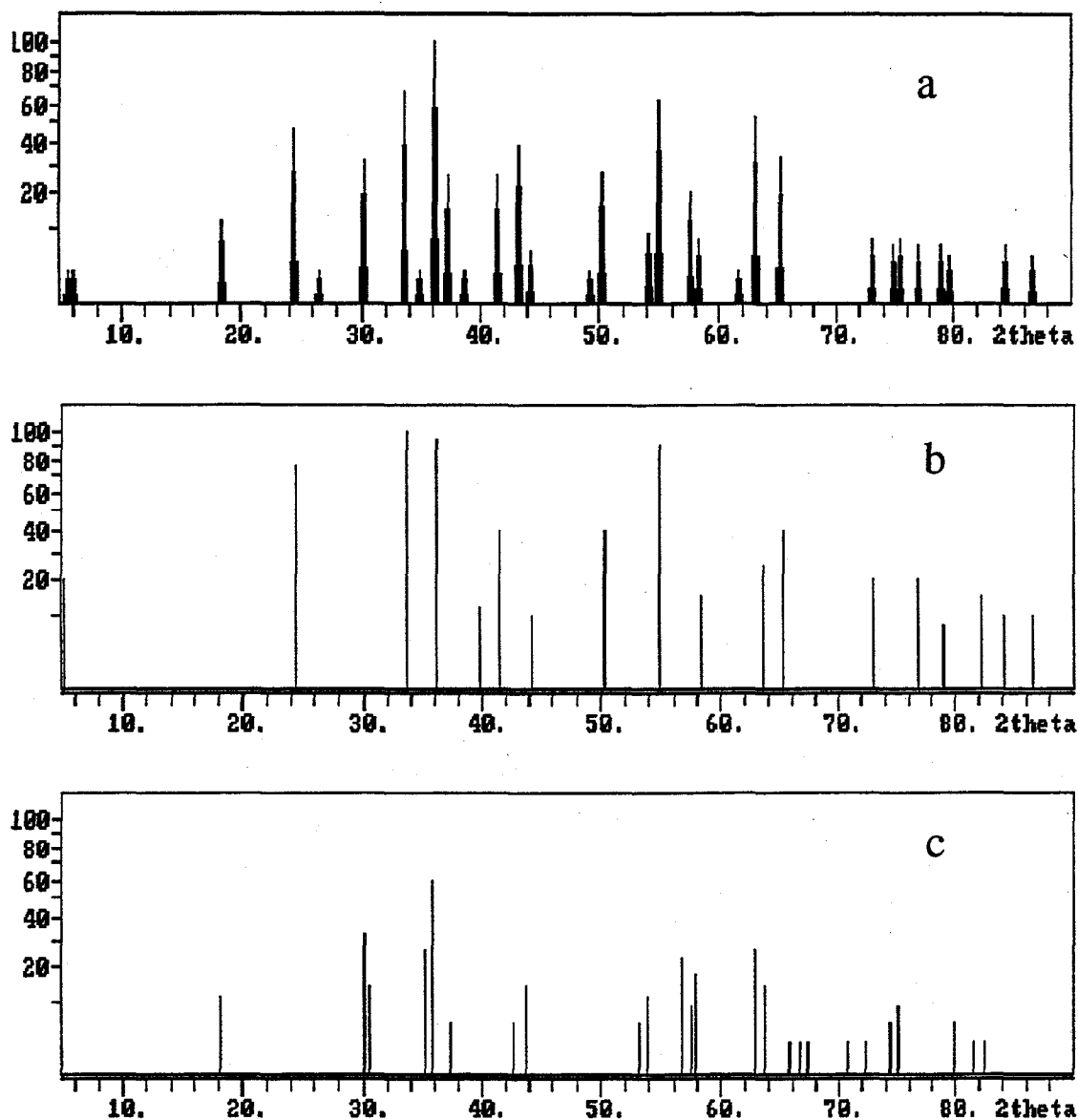


Figure 5.7. Diffractogram of NiCr_2O_4 -Materials
 a - $\text{NiCr}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ (compound X) calcined at 800°C
 b - $\alpha\text{-Cr}_2\text{O}_3$ [Newnham and de Haan 1962]
 c - NiCr_2O_4 spinel [JCPDS file 23-1272]

The high reactivity of mixed Cr(III) compounds toward persulfate can be explained by the catalytic effect of the associated Ni(II) or Fe(III). This hypothesis was confirmed by a number of additional tests. As seen in Table 5.6, the initial rate of Cr(III) hydroxide oxidation by persulfate in the presence of Fe(III), Ni(II), Co(II), and Cu(II) is significantly higher than that observed without the added d-elements under otherwise comparable alkaline conditions. Co(II) showed especially high catalytic activity. The catalysis likely is caused by the formation of intermediate reaction products of d-elements with persulfate in NaOH solution.

Table 5.6. Initial Oxidation Rate of 0.03 M Cr(III) Hydroxide by 0.2 M Persulfate in 50°C 2 M NaOH in the Presence of Some Catalysts

Catalyst	[Catalyst], M	V _o , moles/liter-minute, for compound number	
		III	VI
None	0	1.3x10 ⁻³	1.1x10 ⁻³
Fe(III)	3x10 ⁻⁴	1.3x10 ⁻³	2.8x10 ⁻³
	1x10 ⁻²	1.5x10 ⁻³	3.2x10 ⁻³
Co(II)	3x10 ⁻⁴	3.2x10 ⁻³	~6x10 ⁻³
	1x10 ⁻²	4.5x10 ⁻³	11x10 ⁻³
Ni(II)	3x10 ⁻⁴	2.2x10 ⁻³	3.8x10 ⁻³
	1x10 ⁻²	4.5x10 ⁻³	5.2x10 ⁻³
Cu(II)	3x10 ⁻⁴	2.3x10 ⁻³	3.1x10 ⁻³
	1x10 ⁻²	2.0x10 ⁻³	3.4x10 ⁻³

The test data show persulfate to be a very effective reagent for the oxidative dissolution of Cr(III) solid phases in alkaline solution. Successful application of this oxidant to dissolution of Cr(III) from Hanford tank waste sludges of different origin and composition is expected because S₂O₈²⁻ reacts even with well-crystallized and stable Cr(III) compounds. The presence of iron and other d-elements in some sludges likely promotes Cr(III) oxidative dissolution through catalytic pathways. However, suppositions on the role of catalysis should be verified as part of a greater parametric study of persulfate interaction with different Cr(III) compounds and subsequent confirmatory tests with genuine Hanford tank waste sludges.

6.0 Summary and Conclusions

Results obtained in the course of this investigation led to the following key conclusions concerning the oxidative dissolution of Cr(III) solid phases under alkaline conditions by oxygen gas, hydrogen peroxide, and persulfate. Studies were most extensive for Cr(III) hydroxide phases because they seem to be the most likely form of Cr(III) in Hanford tank sludge, especially after caustic treatment.

Oxygen

The rates of O₂ reaction with aged amorphous Cr(III) hydroxides, as well as with other Cr(III) solid phase compounds, depend very strongly on NaOH concentration and, to a lesser extent, on temperature. Increase of either NaOH concentration or temperature significantly accelerates oxidative dissolution by oxygen to form soluble Cr(VI). Therefore, the choice of optimum reaction conditions also should account for the associated economic and technical reasons in addition to the impact of the reaction products and conditions on subsequent processing of the alkaline Cr(VI) leachates.

The oxidation of Cr(III) solid phases in alkaline solution by oxygen first requires dissolution of O₂ gas into the solution phase. The concentration of dissolved oxygen and, in turn, the rates of oxidation were found to be proportional to the O₂ partial pressure in the gas. As a result, using air instead of pure oxygen for oxidative leaching of chromium from the tank sludge decreases the rate of Cr(VI) formation four- to five-fold under otherwise similar conditions. Practical technical difficulties in attaining effective oxygen saturation of great volumes of alkaline sludge suspensions may be anticipated.

All experiments described in this report were performed using pure Cr(III) compounds. However, genuine tank sludges are complex and have variable composition with many elements. Genuine sludges, therefore, may catalyze the reaction of Cr(III) with oxygen. The catalytic action of Ni(II) on Cr(III) hydroxide oxidation by O₂ was detected in this investigation. It is reasonable to suppose that oxidative chromium leaching from genuine tank sludges will proceed in some cases with higher rates than those found for the present tests with model sludge compounds.

Oxidative leaching of chromium from the Hanford tank sludge by oxygen has some advantages. One advantage concerns the expected behavior of plutonium, likely present as Pu(IV) hydrous oxide or sorbed as a Pu(IV) species on sludge solids in tank waste. Plutonium(IV) hydrous oxide has been shown not to react with oxygen and chromate in alkaline media [Shilov et al. 1996a]. Thus, it is reasonable to expect that Cr(VI) leachates, obtained by oxidation of Cr(III) solid compounds with oxygen, will not have enhanced plutonium concentrations, and thus facilitate their further processing.

Hydrogen Peroxide

Oxidative leaching of chromium(III)-bearing compounds by hydrogen peroxide was not always successful; it was particularly ineffective in the presence of greater than 0.5 g Fe(III)/liter and other catalysts for H₂O₂ decomposition. Hydrogen peroxide can oxidize and dissolve Cr(III) hydroxides that have not undergone prolonged aging at high temperatures. Such hydroxides may be formed by the metathesis of Cr(III)-bearing compounds (e.g. phosphates, silicates, mixed hydroxides with aluminum) in the course of alkaline leaching of Hanford tank sludge to dissolve aluminum- and phosphate-rich phases. Therefore, leaching using hydrogen peroxide should be tested on residues remaining after water and caustic washing of actual tank sludges.

Optimum oxidative leaching of Cr(III) solid compounds from tank sludge by H_2O_2 is attained at low excess NaOH (0.02 - 0.1 M) and at temperatures higher than 80°C. In determining the amount of excess NaOH, it is necessary to account for the stoichiometric requirement of 1.5 moles of OH^- per mole of Cr(III) in the reaction with H_2O_2 . The H_2O_2 should be added slowly (over a period of one to two hours) in the form of a diluted (1-2 M) solution with intense stirring of the alkaline sludge suspension. By employing such conditions, the catalytic decomposition of the oxidant may be decreased. The H_2O_2 concentration has a greater influence on the H_2O_2 self-decomposition rate than on the Cr(III) oxidation rate. Therefore, maintenance of low H_2O_2 concentrations decreases the parasitic loss of H_2O_2 to self-decomposition.

Treatment of Hanford tank sludge by oxidative dissolution of Cr(III) compounds in alkaline H_2O_2 may only be attractive with freshly formed Cr(III) hydroxides and not with aged Cr(III) solids or solids with significant concentrations of H_2O_2 decomposition catalysts. However, oxidation by H_2O_2 has a number of obvious advantages. First, it proceeds at low NaOH concentrations and leaves no residues in the waste. This allows the final leachates to have simpler compositions more amenable to subsequent processing. In addition, Pu(IV) is not oxidized or complexed by dilute H_2O_2 at low NaOH concentrations [Shilov et al. 1996b]. Therefore, H_2O_2 will not increase plutonium concentrations in the product leachates.

Persulfate

Oxidative dissolution of Cr(III) solid phases from Hanford tank sludge by persulfate is expected to be very effective and not strongly dependent on the sludge composition, provided that the Cr(III) is present at the solid surface and not entrapped in an otherwise low-solubility phase [e.g., Cr(III) substituted in Al_2O_3]. This expectation is based on observation of the rapid oxidation of Cr(III) from stable crystalline compounds, including $\alpha\text{-Cr}_2\text{O}_3$, by persulfate in alkaline solution.

The molar reaction stoichiometry of Cr(III) with $\text{S}_2\text{O}_8^{2-}$ at temperatures lower than 70°C is 1:1.5 and is not complicated by thermal decomposition of the oxidant. The optimum process conditions require reaction at ~70°C in 0.3-0.5 M excess NaOH. Under these conditions, complete Cr(III) oxidation is achieved in 1-2 hours.

The reaction of Cr(III) with persulfate in alkaline media is significantly accelerated in the presence of Co(II), Ni(II), and other d-element ions. Because of this, as in the case of oxygen, oxidative leaching of chromium from the genuine tank sludge by persulfate may proceed more rapidly or under milder conditions than described in the previous paragraph in the absence of catalysts.

It must be noted that persulfate is a very strong oxidant in alkaline media and can oxidize Pu(IV) to higher, more soluble, oxidation states [Shilov et al. 1996a]. Extensive plutonium dissolution therefore is expected in oxidative leaching of Cr(III) compounds from tank sludge by persulfate. Fortunately, a simple method exists to decrease the plutonium concentration in the leachate produced by the persulfate treatment. This method, heating the leachate to 80-90°C to decompose excess persulfate and then adding small amounts of H_2O_2 to reduce plutonium to Pu(IV) [Shilov et al. 1996b], is easily performed and should remove most plutonium from solution without causing unwanted reduction of Cr(VI) to reprecipitate Cr(III) solid phases.

The test data show that persulfate is a promising reagent for oxidative leaching chromium from Hanford tank waste sludges. However, the reaction of Cr(III) compounds in various simulated and genuine sludges with persulfate in alkaline solution requires additional detailed parametric study.

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