



Project Summary

The Fate of Chromium (III) in Chlorinated Water

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Although hexavalent chromium, Cr(VI), is not normally found in surface water, the oxidation of trivalent chromium, Cr(III), to the more toxic Cr(VI) in chlorinated water is thermodynamically feasible and was the subject of this study. It was found that free available chlorine (FAC) readily converts Cr(III) to Cr(VI) at a rate that is highly dependent upon pH, total organic carbon (TOC), and chloride concentrations while combined chlorine (CAC) does not oxidize Cr(III).

In deionized water and in a background of 0.010 M NaCl (355 mg/L chloride), the highest oxidation rate occurs in the 5.5-6.0 pH range. Results with natural waters indicate that a similarly fast oxidation rate can occur in this same pH range. The aquatic humus in natural water, however, inhibits while chloride concentration catalyzes the rate of Cr(VI) formation. As expected, the initial Cr(III) oxidation rate increases with increasing FAC concentration and Cr(III) level. Monochloramine, a form of CAC, did not oxidize Cr(III) at any tested pH between 6 and 8.5.

Finally, the results of this study suggest that the oxidation of Cr(III) to Cr(VI) would rarely occur to a significant extent during drinking water chlorination because of the presence of naturally occurring organics (TOC) present, the low concentrations of Cr(III) in natural waters, the probable removal of insoluble $\text{Cr}(\text{OH})_3$ during coagulation, and the increasing trend to use combined chlorine for disinfection. However, in Cr(III)-contaminated waters that are relatively free of organic contamination and have pH's in the 5-7

range, FAC readily converts Cr(III) to the more toxic hexavalent variety.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Chromium typically occurs in surface waters in the trivalent (Cr(III)) oxidation state. The trivalent chromium cation is always complexed with H_2O , hydroxide ion, or other common ligands including chloride and fulvate anions. The industrial sources of chromium are chrome plating, leather tanning, and corrosion inhibition. Additionally, many industries use chromates as a cooling-water corrosion inhibitor. Due to wastewater discharges into receiving waters used for drinking water supply, both Cr(VI) and Cr(III) can enter drinking water treatment systems through raw water intakes. However, due to the insolubility of Cr(III) and the reactivity of Cr(VI), serious industrial contamination of drinking water by chromium is quite rare.

Previous studies on the transformation between these oxidation states have been conducted. In one such study it was found the Cr(III) was very slowly oxidized to Cr(VI) by dissolved oxygen in Lake Mendota (Wisconsin) water—2 $\mu\text{g/L}$ Cr(VI) was produced per week in filtered lake water spiked with 125 $\mu\text{g/L}$ Cr(III). Oxidation by chlorination, the most popular disinfection alternative, however, had been ignored as of the initiation of this study (June 1983). The overall

objective of the present study was to determine to what extent Cr(III) is converted to Cr(VI) in chlorinated water at the practical dosages of chlorine used for disinfection, and in the presence of aquatic humus, which is known to complex Cr(III) and react with chlorine. The potential for Cr(III) oxidation by monochloramine was also studied because of a trend to use chloramines for drinking water disinfection to avoid formation of trihalomethanes.

Initial experiments dealing with the solubility of 200 $\mu\text{g/L}$ total Cr(III) in the pH range of 5-10 indicated that, as expected, the solubility was highly pH-dependent. Furthermore, the longer the Cr(III)-spiked solutions aged, the lower the Cr(III) solubility. These observations, added to the fact that water quality criteria and effluent standards are generally based on total (soluble and particulate) chromium, led us to work with total as opposed to soluble Cr(III) concentrations. In the usual test, the background waters were spiked with 200 $\mu\text{g/L}$ Cr(III), pH adjusted, and then allowed to age for 1 or 4 days before chlorine was added to oxidize Cr(III) to Cr(VI). Depending on pH and aging time, approximately 5%-90% of the total Cr(III) present was insoluble as defined by retention on a 0.45 μm membrane filter. The results of this study must be interpreted in light of these solubility observations.

After acquiring data on the Cr(III) oxidation reaction at various pH levels and in the presence of various concentrations of chloride, ammonia, and TOC, the oxidation reaction was modeled. This was done to facilitate the prediction of the Cr(III) oxidation rate in typical drinking water sources contaminated with Cr(III).

Analytical Methods

Chromium Analyses

Total Cr was analyzed using graphite furnace atomic absorption (GFAA) spectroscopy as specified in U.S. EPA's *Methods for Chemical Analysis of Water and Wastes* (method 218.2). Prior to analysis all samples were acidified with 4 mL HNO_3/L of sample (pH = 1.2). The minimum detectable concentration was approximately 1.0 $\mu\text{g/L}$ and the precision was $\pm 3\%$ relative standard deviation (rsd) at 100 $\mu\text{g/L}$ Cr. For purposes of this study, soluble chromium is the Cr in the filtrate of a previously-boiled and rinsed 0.45 μm membrane filter.

Cr(VI) was determined by measuring the absorbance of the red complex that developed between diphenylcarbazide and chromate (Cr(VI)) at pH 1.2. Absorbance was measured at 540 nm with a Hitachi Perkin-Elmer spectrophotometer* using a very long (10.0-cm) absorption cell. Using the method of standard additions to avoid absorbance errors in the presence of chlorine, the detection limit was found to be 0.001 mg/L and the precision was 3% rsd at 100 $\mu\text{g/L}$ Cr(VI).

Chlorine Analyses

Free and combined chlorine were analyzed using the DPD (N, N-diethyl-p-phenylene-diamine) colorimetric method and the 100-mL-sample-size DPD-FAS (ferrous ammonium sulfate) titration method, both of which are described in *Standard Methods* (15th edition, sections 408E and 408D, respectively). The methods were used concurrently to verify one another.

TOC Analyses

Trace levels of TOC in the deionized water produced by two Continental Water Systems mixed-bed deionizers in series were measured using a Dohrman Model DC-54 Ultra-low Level TOC Analyzer utilizing persulfate-catalyzed, UV oxidation. The high levels of TOC (> 1.0 mg/L) found in Houston tap and raw waters were determined using a Beckman Model 915 B high-temperature (950°C) TOC analyzer. The results indicated 0.2 mg/L TOC in the deionized water, 3.8 mg/L in the tap water, and 15.0 mg/L in the raw water before treatment.

Batch Experiments for Cr(III) Oxidation

A 20-L, stirred batch reactor was employed for the Cr(III) solubility and oxidation experiments. In a typical experiment, an appropriate volume of CrCl_3 solution (200 mg/L Cr(III)) was pipetted into 20 L of continuously mixed background water in a rectangular polyethylene carboy (see Figure 1). Within 1-2 min, the pH was adjusted to the predetermined experimental value using 1.0 N H_2SO_4 or 1.0 N NaOH solution. Control reactors with no Cr(III) or no chlorine were used as appropriate.

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use

Prior to the addition of chlorine, the Cr(III) added was allowed to hydrolyze to produce the species expected to be present in aged natural waters. To check the extent of hydrolysis and $\text{Cr}(\text{OH})_3$ precipitation, solubility tests in deionized water and 0.01 M NaCl solution were performed using the same 20-L reactor by frequent analysis for both total (unfiltered) and soluble (filtered) Cr.

Hexavalent chromium, chlorine, and pH were frequently monitored during the course of each chlorine oxidation batch experiment. For all batch experiments the aging time was defined as the time between Cr(III) addition and chlorine addition to the background water. After aging, an oxidation batch test was initiated by pipetting an appropriate volume of chlorine solution (3,000 mg/L Cl_2) into both the control and the test batches. Then the pH of both batches was quickly readjusted to the predetermined initial pH by dropwise addition of 1.0 H_2SO_4 or 1.0 N NaOH solution.

Effect of pH on Cr(III) Solubility

The effect of pH on Cr(III) solubility in deionized water and 0.01 M NaCl was investigated. Figure 2 shows that, at 100-200 $\mu\text{g/L}$ Cr(III), the solubility of Cr(III) in 0.01 M NaCl rapidly decreases with time at pH's between 6.5 and 9.0. The maximum precipitation rate occurred in the 7-8 pH range. The main Cr(III) species in that pH range is believed to be insoluble $\text{Cr}(\text{OH})_3(\text{s})$. When pH becomes greater than 10, $\text{Cr}(\text{OH})_3(\text{s})$ redissolves further complexation with OH^- to yield the anionic species $\text{Cr}(\text{OH})_4^-$. At acidic pH's, the cation complexes Cr^{3+} , $\text{Cr}(\text{OH})_2^+$, and $\text{Cr}(\text{OH})_2^+$ are predominant. For all hydroxylated species, the octahedral coordination sites not occupied

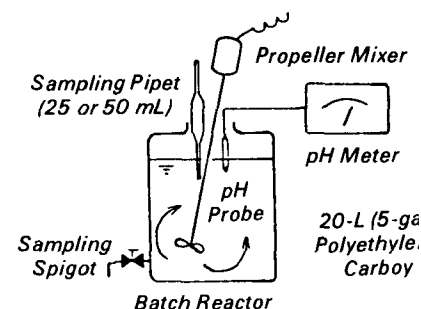


Figure 1. Batch reactor for Cr(III) chlorination experiments.

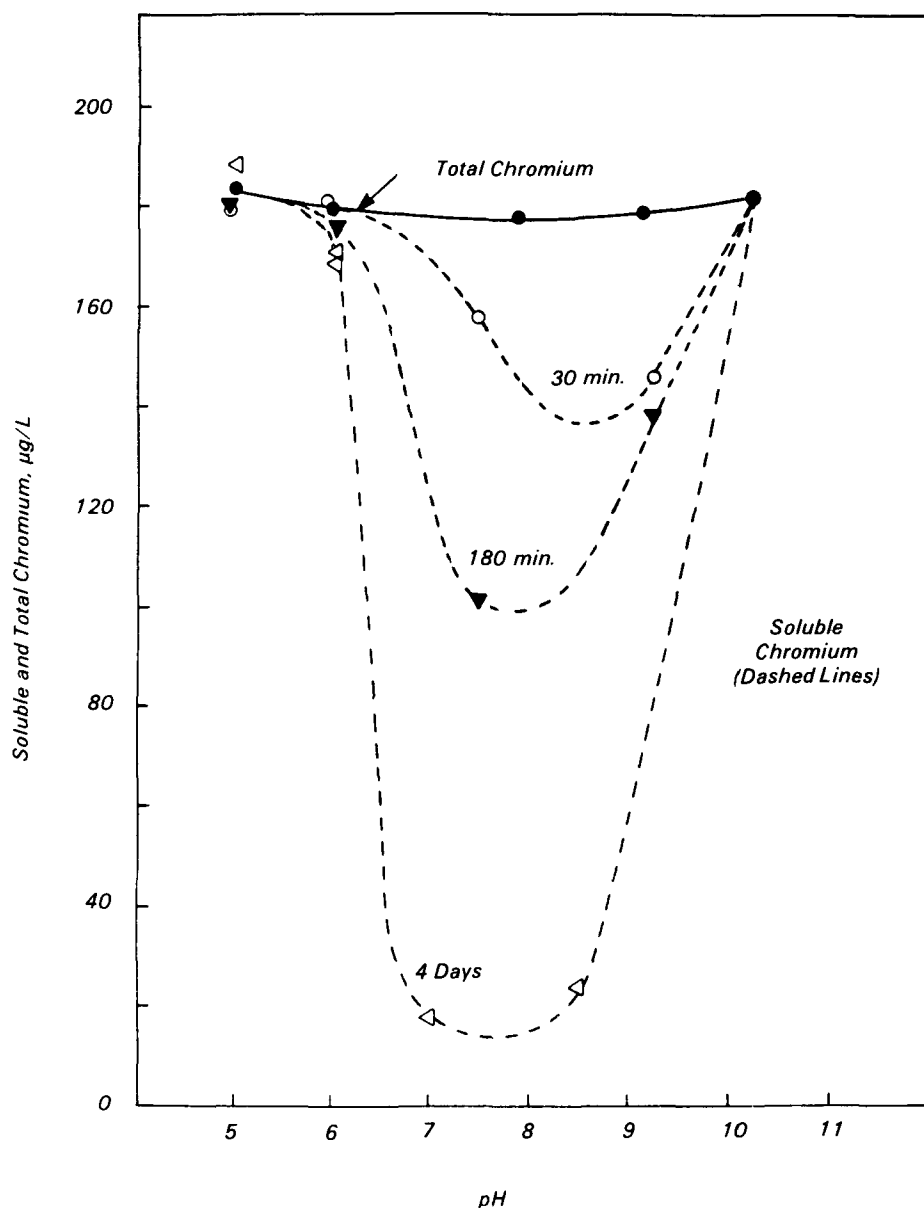


Figure 2. Solubility of Cr(III) in the control reactor containing 0.01M NaCl as a function of pH and time, no Cr(IV) present

OH^- are presumed to be occupied by H_2O or Cl^- depending on the Cl^- concentration.

A comparison of the solubility data in deionized water (Figure 3) and 0.01 M NaCl (Figure 2) suggests that the chloride anion has no significant effect on the $\text{Cr}(\text{OH})_3$ precipitation rate in the 7-10 pH range. The presence of chloride does, however, appear to reduce the $\text{Cr}(\text{OH})_3$ precipitation rate in the 5-6 pH range compared to deionized water. No appreciable precipitation of Cr(III) in 0.01 M NaCl was observed between pH 5 and

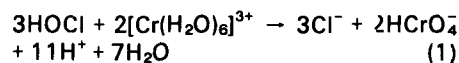
6. This improved Cr(III) solubility in the presence of Cl^- at reduced (5-6) pH may be explained by the fact that chloride ion can substitute for the hydroxide ligand to form a soluble complex chlorochromium(III) molecule. This is also the pH range in which the maximum oxidation rate occurred using free chlorine.

Cr(III) Oxidation in 0.01 M NaCl and Deionized Water

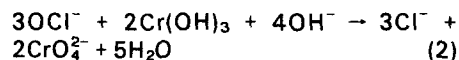
It can be seen in the batch test data for 0.01 M NaCl shown in Figure 4 that

50 µg/L Cr(VI) was exceeded in approximately 60 min contact time at pH 6. Also, the percent Cr(III) conversion for 1 day was slightly increased in 0.01 M NaCl (Figure 4) compared to deionized water (not shown). Less oxidation of Cr(III) occurred in deionized water under similar conditions. Compared to the oxidation kinetics in deionized water, the presence of chloride enhances the Cr(VI) formation rate for the same 3.0 mg/L chlorination starting with 180-200 µg/L total Cr(III).

The experimental results lead us to suggest the following reactions to explain the observed effects of pH and the chloride ion on the reaction rate. In acidic solution, e.g., $\text{pH} < 5.0$, the presence of OH^- can be ignored and the oxidation of hydrated Cr(III) by HOCl is relatively fast; it can be written as Reaction 1.



It is evident from the proposed reaction that Cl^- and H^+ ions should inhibit the rate since they are products. But the observed effects of both these ions in the 5-8 pH range is just the opposite, i.e., increasing concentrations of Cl^- and H^+ speed up the rate. Presumably, both these ions hinder the formation of $\text{Cr}(\text{OH})_3(\text{s})$ and Cr(III)-hydroxide complexes, which are quite stable with respect to chlorine oxidation. The experimental results indicate that Reaction 2, occurring in the 8-10 pH range, is very slow.



If Reactions 1 and 2 are considered alone, chloride ion should theoretically inhibit the Cr(VI) formation rate, and yet it does not do so even at very high (0.6 M) chloride concentrations. At low pH, the expected pH effect on Reaction 1 did occur in all the tests, i.e., lowering the pH to below 5.0 in deionized water and in 0.01 M NaCl did eliminate or substantially reduce the Cr(III) oxidation rate.

Cr(III) Oxidation in Houston Tap Water (3.8 mg/L TOC)

The lack of Cr(III) oxidation in previously filtered Houston tap water aged 1 day after Cr(III) spiking is represented in Figure 5 as a function of pH. Compared to the rates in deionized water and 0.01

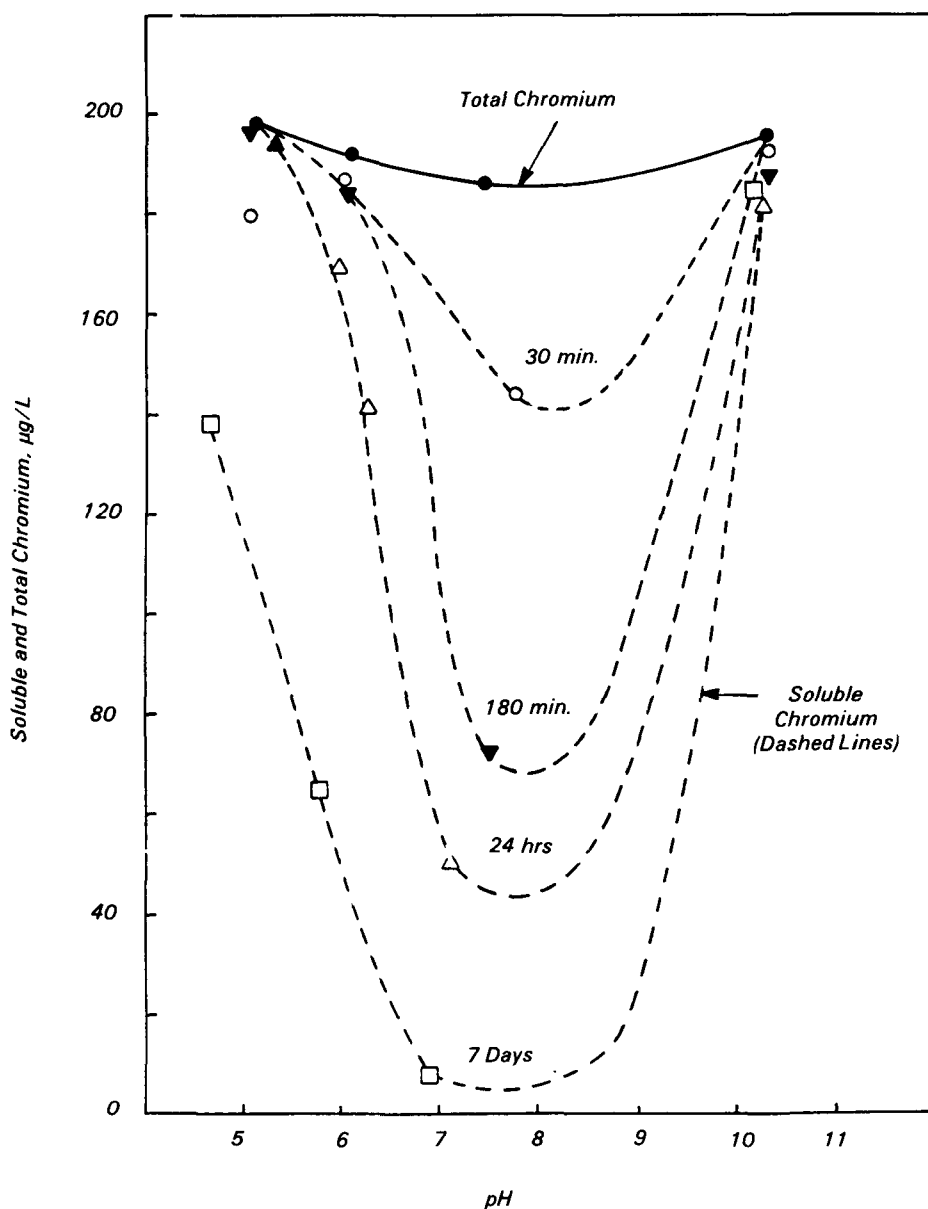


Figure 3. Solubility of Cr(III) in the deionized water control reactor as a function of time and pH, no Cr(VI) present.

M NaCl, also shown in Figure 5, the Cr(VI) formation rate in tap water at 3.0 mg/L chlorination was insignificant throughout the 5-8 pH range. Undoubtedly, the elimination of the oxidation of Cr(III) by free chlorine resulted, in part, from the lowering of the FAC concentration by rapid substitution and addition reactions between chlorine and humic material (3.8 mg/L TOC). These reactions between chlorine and humic material occurred because an analysis of aged Houston tap water showed insignificant

concentrations of other chlorine-reactive species such as ammonia.

An additional factor, Cr(III) complexation, is responsible for the much slower oxidation of Cr(III) in TOC-contaminated tap water. For example, in the pH 6 experiments with 12 vs. 3 mg/L chlorination, the average FAC concentration in the tap water during the first 2 hr following 12 mg/L chlorination was roughly 6 mg/L, i.e., double the 3 mg/L FAC in the deionized water tests. Yet the Cr(III) oxidation rates were essentially

identical. Here the decrease in the expected oxidation rate of Cr(III) exposed to 6 mg/L FAC (avg) is attributed to formation of stable Cr(III) complexes with the humic material in the tap water. The existence of these chromium-organic complexes in fresh and salt water is well documented and is the subject of continuing investigations by other researchers.

When examining the results in Figure 5, keep in mind the fact that in deionized water and in 0.01 M NaCl there was a variable amount of soluble Cr(III) present due to formation of $\text{Cr}(\text{OH})_3(\text{s})$ as a function of pH and aging time (see Figures 2 and 3). With Houston tap water an additional factor, Cr(III) complexation by organic matter is responsible for a further decrease in the amount of Cr(III) available for oxidation by chlorine.

Cr(III) Oxidation in Filtered Raw Water (10 mg/L TOC)

The results of Cr(III) oxidation in Houston raw water prior to treatment by coagulation, flocculation, and filtration at the Houston Water Treatment Plant are shown in Figure 6, which includes the results of three batch tests at pH 6 following 3, 6, or 12 mg/L chlorination. The original filtered raw water samples were diluted with deionized water to prepare the 10 mg/L TOC raw water. It is clear from Figure 6 that the presence of a high concentration of humic material influenced the Cr(III) oxidation by chlorine in the raw water containing 10 mg/L TOC. No Cr(VI) was found at the end of 1 day following initial dosages of 3.0 or 6.0 mg/L chlorine. Substantial Cr(VI) production did, however, occur with 12 mg/L chlorination. Unlike tap water containing only 3.8 mg/L TOC, the FAC concentration resulting from 12 mg/L chlorination decayed to an undetectable concentration after 1 day. The concentration of Cr(VI) in this high TOC, raw water was substantially lower even though there were nearly equal residual free chlorine concentrations (5 mg/L maintained during the first 4 hr of contact). This again suggests that Cr(III) is strongly complexed by the organic matter in the raw water. This is not to suggest that Cr(VI) production is always inhibited at 3-6 mg/L chlorination in natural waters containing TOC. Cr(VI) production is possible at lower TOC levels, e.g., 1-2 mg/L, and in fresh Cr(III) solutions in which the Cr(III) has not had time to hydrolyze and form $\text{Cr}(\text{OH})_3(\text{s})$.

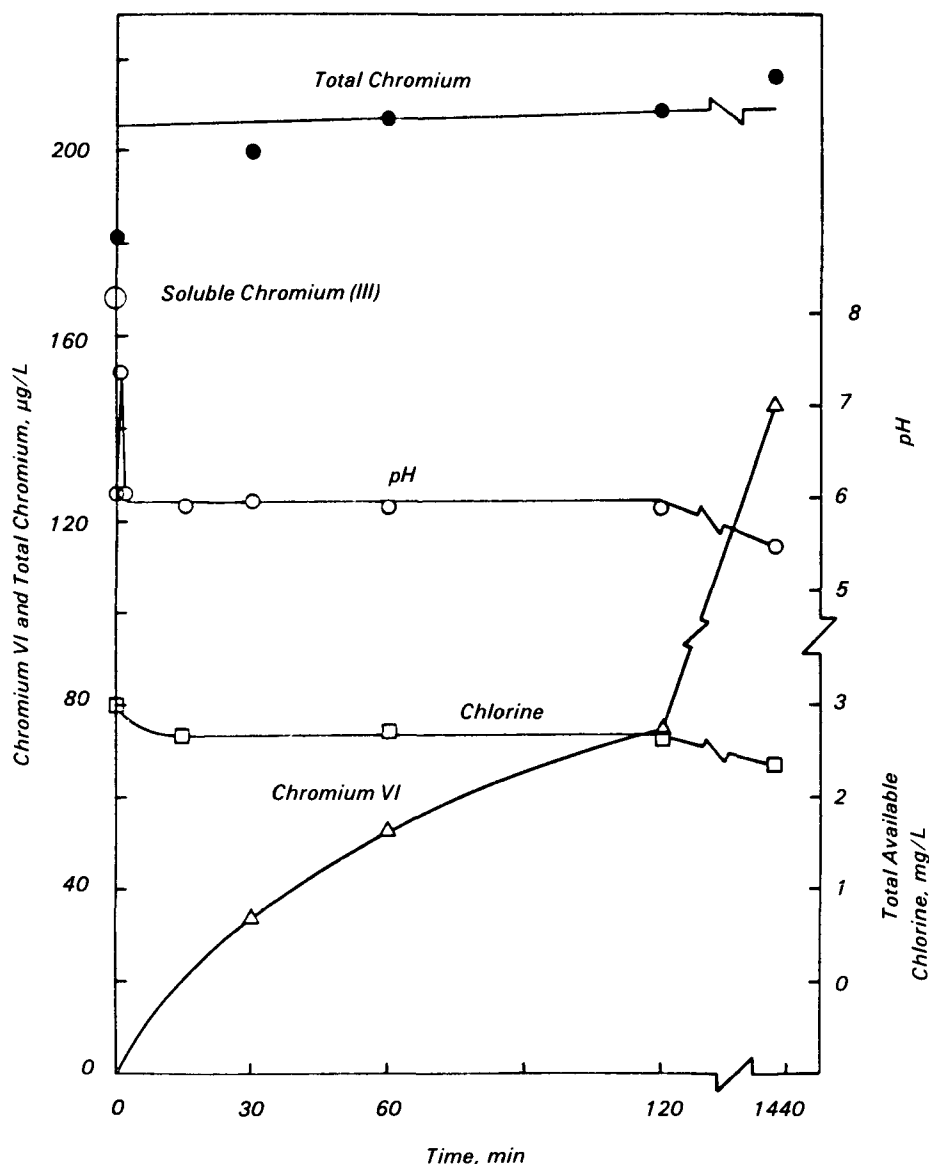


Figure 4. Cr(III) oxidation in 0.01 M NaCl at pH 6, 4 day Cr(III) aging before 3 mg/L chlorination.

Oxidation of Cr(III) under such conditions was observed in a separate EPA study by Ulmer.

Attempted Monochloramine Oxidation of Cr(III) in 0.01 M NaCl

Ammonia-N ($\text{NH}_3\text{-N}$) was added, using NH_4Cl , to give twice the $\text{NH}_3\text{-N}$ concentration needed to produce monochloramine. The experimental data showed that monochloramine, a combined form of chlorine which is produced almost instantaneously from the reaction of

ammonia with chlorine, cannot oxidize Cr(III) under the experimental conditions. No Cr(VI) was found even after 24 hr of oxidation at pH levels 6, 7, and 8.5 in 0.01 M NaCl spiked with 200 µg/L total Cr(III).

The Effect of Chloride Ion on the Cr(III) Oxidation Rate

It is evident from Figure 7 that the previously mentioned enhancement of the Cr(III) oxidation rate due to chloride continues far beyond 0.01 M (3550 mg/L chloride). It is still evident at a chloride

concentration of 0.6 M (21,200 mg/L chloride), typical of sea water. Furthermore, the enhancement is seen in very dilute chloride solutions, e.g., 0.001 M (35.5 mg/L Cl^-). Ligands other than chloride, e.g., sulfate, may produce similar rate-enhancing results.

Reaction Rate Modeling

As expected from the simplest and most complicated models of Cr(III) chlorination, the rate increases with increasing Cr(III) and free chlorine concentrations. Using a simple rate model with no back reaction, the Cr(III) oxidation rate was third order in Cr(III) concentration at pH 6.0 in 0.01 M NaCl, but only 0.8 order in Cr(III) at pH 4.5. Using the same model, the Cr(III) oxidation rate was found to be 0.56 order in HOCl concentration at pH 5.5 in 0.01 M NaCl. Such simple models quantify the relative sensitivity of the rate to Cr(III) and HOCl concentration but should not be taken as truly representative of the true chlorination reaction involving various complexes of Cr(III) with Cl^- , OH^- , and H_2O .

Conclusions

The fundamentals of the Cr(III)-chlorine oxidation reaction in deionized water, dilute NaCl, and natural water have been elucidated by this experimental study utilizing aged Cr(III) solution containing soluble, insoluble and complexed Cr(III). Cr(III) can be oxidized to Cr(VI) by free chlorine at a rate that is highly dependent on pH, chlorine dosage, chloride concentration, and TOC concentration. Combined chlorine in the form of monochloramine cannot oxidize Cr(III) to Cr(VI), even under the most favorable conditions of pH and chloride concentration.

The optimum pH range for Cr(III) oxidation by free chlorine is 5.5-6.0. It is theorized that above this pH range, the increasing presence of OH^- ligands causes the formation of insoluble $\text{Cr}(\text{OH})_3(\text{s})$ and the soluble but stable and hard-to-oxidize complexes such as CrOH^{2+} , $\text{Cr}(\text{OH})_2^+$, $[\text{Cr}(\text{OH})_4]^-$, and polynuclear complexes like $\text{Cr}_3(\text{OH})_4^{5+}$ and $\text{Cr}_2(\text{OH})_2^{4+}$. Below the optimum pH, the increasing presence of H^+ ion, a product of the oxidation reaction, inhibits the formation of Cr(VI).

Starting with 200 µg/L total Cr(III) and 3 mg/L free chlorine, approximately 12 µg/L Cr(VI) were produced during the first hour in the optimum pH range in deionized water while 65 µg/L Cr(VI) were produced in 0.01 M NaCl (355 mg/L

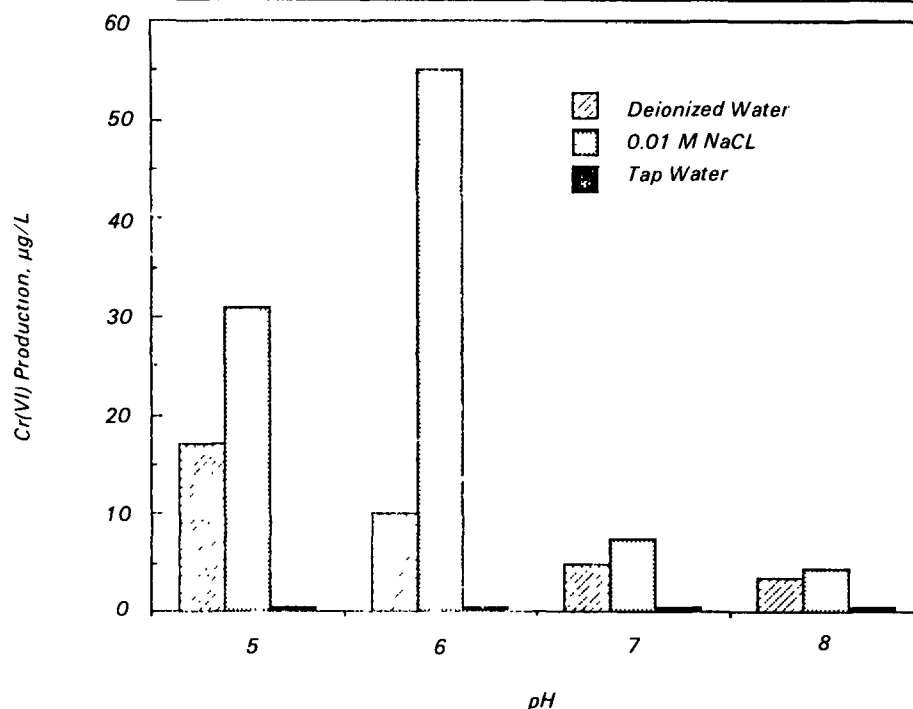


Figure 5. *Cr(VI) production during 1 hr following 3 mg/L chlorination as a function of pH in deionized water, 0.01 M NaCl and Houston tap water containing approximately 200 µg/L total Cr(III). All Cr(III)-spiked solutions were aged 1-3 days prior to chlorination. No measurable oxidation occurred in tap water containing 2.8 mg/L TOC.*

L chloride) under optimum conditions. The rate-enhancing influence of the chloride ion on the chlorine oxidation of Cr(III) continued throughout the 0.001-0.6 M NaCl range. At 3 mg/L chlorine and a pH near the optimum, the oxidation rate was found to be 0.35 order in chloride concentration. Apparently the chloro-Cr(III) complexes that form in the presence of excess chloride ions are more susceptible to oxidation by free chlorine than are the aquo- and hydroxyl-complexes.

The rapid Cr(III) oxidation rate observed in deionized water was not reproduced in raw or treated natural waters containing TOC due to the presence of aquatic humus. The fulvate and humate anions appear to complex the Cr(III) strongly and protect it from chlorine oxidation. Additionally, the TOC is oxidized by free chlorine, thereby reducing the free available chlorine concentration. No observable Cr(VI) was produced from 200 µg/L total Cr(III) at pH 7.5 and a 3 mg/L chlorine dose. If enough chlorine is added, however, Cr(III) can be oxidized

to Cr(VI) in spite of the TOC present. Furthermore, if the Cr(III) solutions are chlorinated immediately after Cr(III) addition, higher levels of Cr(VI) are expected due to the higher concentrations of non-hydrolyzed Cr(III).

Starting with a relatively high (200 µg/L) concentration of total Cr(III), in a solution aged for 1 or more days, it is unlikely that a significant concentration, e.g., 50 µg/L, of Cr(VI) would be produced as a result of typical (e.g., 1-3 mg/L) free chlorine dosages to natural surface waters containing 2-10 mg/L TOC. Experimentally, no Cr(VI) was produced even after 24 hr following application of 3 mg/L free chlorine to Houston tap water aged 1 day following Cr(III) spiking.

The full report was submitted in fulfillment of Cooperative Agreement No. 807939 by the University of Houston under the sponsorship of the U.S. Environmental Protection Agency.

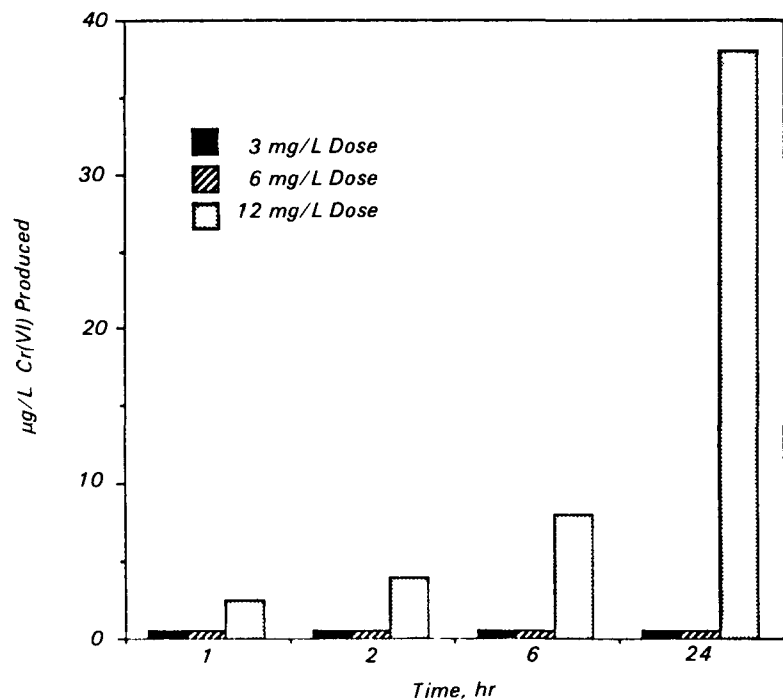


Figure 6. Cr(III) oxidation in raw water containing 10 mg/L TOC as a function of time following 3.6 and 12 mg/L chlorination, pH = 6 and Cr(III) initial = 200 µg/L. No measurable Cr(III) oxidation occurred at 3 or 6 mg/L chlorination. All Cr(III)-spiked solutions were aged 1 day prior to chlorination.

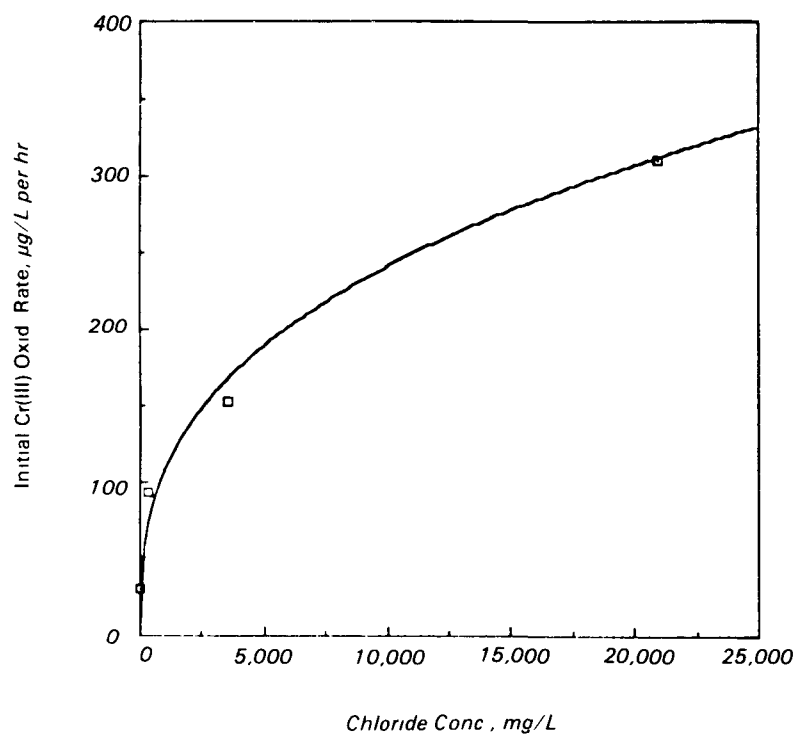


Figure 7. Initial Cr(III) oxidation rate as a function of chloride concentration at pH 6.0 and 3.0 mg/L chlorination.

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*The complete report, entitled "The Fate of Chromium(III) in Chlorinated Water,"
(Order No. PB 88-130 992/AS; Cost: \$14.95) will be available only from:*

National Technical Information Service

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The EPA Project Officer can be contacted at:

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