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Occurrence and Transformation of Chromium in Drinking Water Distribution Systems

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Occurrence and Transformation of Chromium in Drinking Water Distribution Systems

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by

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Dedication

This dissertation is dedicated to my amazing parents. You came to this country nearly forty years ago and the countless sacrifices you've made on your journey have allowed me to prosper on my journey. Thank you for your unwavering support and unconditional love in all the things I have done and aspire to do. You finally have a doctor in the family!

ABSTRACT OF THE DISSERTATION

Occurrence and Transformation of Chromium in Drinking Water Distribution Systems

by

Michelle Chebeir

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, September 2017
Dr. Haizhou Liu, Chairperson

Current reductive water treatment processes typically transform soluble Cr(VI), a toxic carcinogen to particulate Cr(III), a micronutrient. These processes do not completely and effectively remove residual Cr(III) particles. Furthermore, it is assumed that Cr(III) entering a drinking water distribution remains chemically inert. However, this is not the case. Nationwide surveys have observed an increase of Cr(VI) levels from the entry point to the point of distribution. Cr can accumulate in corrosion scales and act as an unrecognized *in situ* source for the inadvertent generation of Cr(VI), especially in the presence of a residual disinfectant.

The goal of this dissertation is to elucidate the transformation of Cr(III) solids to Cr(VI) in drinking water conditions. First, extensive data mining was done on the data reported as part of the U.S. EPA's Unregulated Contaminants Monitoring Rule. It was observed that Cr(VI) levels in drinking water averaged from non-detectable to 97 µg/L at the entry point to drinking water distribution systems with the majority of sample detections ranging between 0.03 to 5 µg/L. Additionally, it was calculated that 20% of Cr(III) solids can be potentially oxidized to Cr(VI), especially in the presence of a residual disinfectant. Second, the kinetics of Cr(III) solids oxidation and subsequent formation of Cr(VI) by chlorine were investigated. Batch experiments were carried out with chromium hydroxide, chromium oxide, copper chromite, and iron chromium hydroxide as model Cr(III) sources. It was found that Cr(VI) was produced with the consumption of chlorine, suggesting that Cr(III) was oxidized to toxic Cr(VI) at environmentally relevant time scales. Third, the impact of pH (6-8.5), bromide concentration (0.1-5 mg/L), alkalinity (1-5 mM) and iron content (0.84-8.4 mM). The results highlighted that the presence of low level of bromide catalyzed the formation rates of Cr(VI) by one order of magnitude whereas increasing iron decreases Cr(VI) formation rates. Fourth, a lack of stoichiometric conversion between the molar amount of chlorine consumed and Cr(VI) generated was observed, suggesting the formation of Cr intermediates. The outcome of this study aimed to inform Cr(III) control strategies to minimize Cr(VI) formation in drinking water distribution systems.

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Chapter 1

Introduction

Water distribution systems and public health

Water distribution systems in the U.S. are beginning to show their age as alarming reports of crumbling pipes and water contamination continue to arise.[1-6] Beyond the simple means of transporting water to consumers, water distribution systems represent a complex geochemical reactor with many interacting components such as pipe materials, organic matter, accumulated trace chemicals and residual disinfectants. The recent water and public health crisis of Flint, Michigan brought to light the importance of water quality and chemistry in distribution systems.[7] Corrosion of piping can lead to elevated levels of iron and lead in drinking water and costly damage control.[8-10] Furthermore, trace metals can accumulate within corrosion scales at higher levels observed in natural environments and flowing water. [11, 12] It is assumed that these accumulated are chemically inert and therefore, pose no threat to the public health. The stability of these accumulated trace metals can be impacted with changing water chemistry in a distribution system and result in a detrimental impact to public health due to their inadvertent release. [13] For example, as observed in the Flint crisis, the switch to a different, more corrosive water source caused lead to leach into the drinking water. [14, 15] Chromium (Cr) has been identified as a trace metal contaminant of concern that can accumulate in the corrosion scales of distribution systems [11,13] and is the focus of this dissertation.

Chromium toxicity and regulation

The oxidation state of Cr greatly affects its mobility, toxicity and presence in the environment.[16,17] While chromium exists in six oxidation states (0-VI), trivalent (Cr(III)) and hexavalent (Cr(VI)) chromium are most relevant to environmental systems. [16,17]

Trivalent chromium is considered to be a nutrient in mammalian diets in trace amounts; it aids in the metabolism of glucose and lipids.[18-20] In contrast, hexavalent chromium is a toxic carcinogen. Exposure to Cr(VI) through respiratory, oral, and dermal pathways is associated with lung and gastrointestinal cancers as well as skin ulcerations. [21-24]

There is no federal regulation solely for Cr(VI). The U.S. Environmental Protection Agency regulates chromium at 100 μg/L as total Cr (Cr(III) + Cr(VI)).[25] California was the only state to have a regulation for Cr(VI); however, the 10 μg/L regulation for Cr(VI) was invalidated by the Sacramento County Superior Court in May 2017 and required the California State Water Board to adopt a new maximum contaminant level (MCL) for Cr(VI) that is proven to be economically feasible for utilities. [26] Total Cr and Cr(VI) were both monitored as part of the third round of the Unregulated Contaminants Monitoring Rule (UCMR) in order to determine the need or adjustment to the federal regulation. [27] Regardless, Cr(VI) is present in drinking water distribution systems and poses a great risk to the public health. Knowledge of chromium in each oxidation state rather than total chromium is vital in order to minimize potential public health risks.

Chromium sources and occurrence in distribution systems

Chromium is applied in a multitude of metallurgical and chemical industries.[19] Chromium containing compounds are applied in the making of paints, pigments, paper, electroplating, and leather tanning. [28-30] Hexavalent chromium is the form of chromium most often produced from anthropogenic processes and has been classified as a strong carcinogen.[31-33] In addition, *in-situ* generation of $Cr(III)_{(s)}$ can occur from the corrosion of stainless steels which contain moderate levels of Cr in their alloys.[34,35] Stainless steels are mainly applied in the piping materials of distribution lines for potable water as well as for water storage tanks. The chromium content of the two most commonly applied steels, 304L and 316L varies from 12-20%.[36] Cr(III) solids (e.g. $Cr_rO_{3(s)}$) are formed in corrosion scales and come into contact with treated drinking water.[37,38]

Sources are not solely anthropogenic; chromium exists as the 21st most abundant element in the earth's crust, thus highlighting importance of naturally occurring chromium in soils and aqueous environments. [39, 40] Chromium exists in natural waters in a variety of different forms.[16,39,41] It can exist as a free ion (Cr(III)) or it can form complexes with inorganic ligands such as chlorides, hydroxides and sulfates as well as organic ligands such as NOM and EDTA.[16,39,41,42] Chromium can exists as a mineral ore in the environment as an oxide with iron and other transition metals (i.e. iron chromite $FeCr_2O_4$ or copper chromite $Cu_2Cr_2O_5$).41[39-43] Chromium containing minerals can be oxidized by manganese (VI) oxides to generate naturally occurring Cr(VI).[44,45] Conversely, it can be reduced to Cr(III) in the presence of Fe(II), Mn(II) and humic substances in groundwater.[17,46,47]

The transport and fate of Cr is highly dependent on its speciation. At neutral pH, amorphous or solid $Cr(OH)_3$ exists as the predominant species of Cr(III) and is mostly immobile in aqueous environments.[16] Cr(VI) may be present in aqueous solutions mainly as chromate, dichromate, chromic acid and hydrogen dichromate; however, the latter two species have been detected only in strongly acidic solutions.[19] In typical surface waters around pH 7, chromate (CrO_4^{2-}) is the predominant form of Cr(VI). [16,19] As industrial Cr(VI) discharges have become more controlled, geological weathering has become a major source of Cr(VI) in drinking water sources.

Cr(VI) treatment technologies

Because Cr(III) species exist as a solid at circumneutral pH that limits their solubility,[48] adaptive water treatment typically reductively transforms soluble Cr(VI) to particulate Cr(III) before removing them by filtration. Reduction methods can be grouped into three categories: chemical, biological and electrochemical. [49-53] The most traditional industrial reducing agents used in chemical reduction methods are sulfur compounds and iron salts (e.g. $FeSO_4$, Na_2SO_3) and subsequently precipitate out $Cr(OH)_3$ in basic conditions. [54 - 57] While the resulting effluent contains little to no residual Cr(VI), precipitation results in the formation of a Cr(III)-containing solid waste or sludge. The use of excessive reagents and waste management can drive up the costs of chemical treatment. Electrochemical reduction methods have a unique versatility in their potential capability to treat liquids, gases and solids. [58 - 61] Similar to chemical methods, electrocoagulation electrodes (made either iron, aluminum, or an alloy) reduce Cr(VI), followed by $Cr(OH)_3$ precipitation. Electrochemical treatment limitations stem from high operating costs even at optimum conditions. Biological reduction can occur aerobically, anaerobically or through a combination of both. [62-64] Reduction efficiencies and kinetics are dependent on factors such as initial Cr(VI) concentration, microorganism resistance, carbon (electron donor) sources and pH among other variables. Few large-scale applications have been applied due to slow reaction kinetics. Recently, alternative reduction treatment technologies using TiO_2 photocatalysts [65-67] or organic polymers [68-70] have been proposed.

Misconceptions of current Cr(VI) control strategies

Reductive treatments treat Cr(VI) to Cr(III), but may not actually remove the resulting particles; they may be inefficient in achieving a low level of total chromium. [71, 72] It is believed that the risk of Cr(VI) is removed and its fate is controlled by its conversion to Cr(III). The impact of the formed Cr(III) solids are assumed to have a negligible impact on downstream processes as they have a low solubility. However, it should not be presumed that Cr(III) is chemically inert as it enters a distribution system. More interestingly, the carry-over of residual Cr(III) can undergo an inadvertent re-oxidation to Cr(VI) by disinfectants may occur in water disinfection and distribution systems. [73-76] The accumulation of non-toxic Cr(III) in distribution systems could become an *in situ* source for chromium that could be oxidized to Cr(VI) in favorable redox conditions. This unintentional transformation could essentially result in a widespread occurrence of Cr(VI) at the consumer tap. Thus, pathways leading to the re-oxidation of Cr(III) to Cr(VI) in drinking water distribution systems need to be further studied and identified.

Aim and Scope

The aim of this research was to understand the behavior of various Cr(III) solids in the presence of residual disinfectants, primarily chorine, and the impacts of water chemical parameters on the oxidation of Cr(III) to Cr(VI). Literature research on Cr(III) oxidation is focused on Cr(III) dissolved phases in conditions somewhat irrelevant to drinking water[73,74,76] conditions as well as oxidation by MnO_2 in natural environments.[77,78] Thus, the reactivity of Cr(III) solid phases is relatively unknown. Specifically, this work identified and characterized four Cr(III)-containing solids relevant to drinking water systems. Reductive treatment technologies for Cr(VI) result in the generation of amorphous $Cr(OH)_{3(s)}$.[79] Dehydration leads to the formation of crystalline $Cr_2O_{3(s)}$ which can also form in the corrosion scales of stainless steel piping.[80, 81] In addition, the formation of $Cu_2Cr_2O_{5(s)}$ [82] and $Fe_xCr_{(1-x)}(OH)_{3(s)}$ [83, 84] have been in observed in copper and iron containing systems, respectively.

The reactivity of these solids with chlorine was investigated. Furthermore, the impact of varying water chemical parameters on the kinetics of Cr(III) solid phase oxidation was quantified. Finally, the mechanism of electron transfer during the oxidation of Cr(III) to Cr(VI) was proposed from the evaluation of reaction stoichiometry. Overall, this dissertation aimed to further the understanding of Cr(VI) occurrence due to redox-driven transformations that may occur at the water-pipe interface in a distribution system. The aim and scope of this dissertation was addressed in three core chapters: the occurrence and speciation of chromium in drinking water distribution systems (Chapter 2) and the kinetics and mechanisms of Cr(VI) generation via the oxidation of Cr(III) solid phases by chlorine (Chapters 3 and 4).

Research objectives

This overall objective of this PhD research was to identify pathways of which non-toxic Cr(III) solids may be oxidized to toxic Cr(VI) from the entrance of the water treatment plant to the consumer tap. The overlying hypothesis was that the presence of disinfectants and other water chemical parameters impact the redox conditions that influence the transformation of Cr(III) and thus, occurrence of Cr(VI) in drinking water. This research focused on transformation of Cr(III) solids to Cr(VI) in drinking water treatment conditions by studying the (1) reactivity and oxidation of typical Cr(III) solids by chlorine (2) the effects of different water chemical parameters on the conversion of Cr(III) to Cr(VI), and (3) the mechanism of electron transfer and surface redox processes involved in Cr(III) oxidation. Specifically, the research objectives are:

(1) ***Explore the occurrence of Cr solids in drinking water distribution systems:*** The occurrence of Cr(VI) and total Cr in distribution systems is not well documented. In Chapter 2, the pathways of chromium occurrence were further investigated and clarified. In order to achieve this objective, an analysis of the U.S. EPA's Third Round of the Unregulated Contaminants Monitoring Rule reported occurrence data on Cr(VI) and total Cr in drinking water systems was conducted. The statistical analysis was conducted on the compiled data based upon geographic region, water source, utility size, residual disinfectant type and sampling location within the distribution system.

(2) ***Investigate the oxidation of Cr(III) solids by residual disinfectants:*** The reactivity of typical Cr(III) solids with disinfectants has not been thoroughly assessed. The oxidation of four common Cr(III) solids: chromium hydroxide ($Cr(OH)_{3(s)}$), chromium oxide ($Cr_2O_{3(s)}$), copper chromite ($Cu_2Cr_2O_{5(s)}$), and iron chromite ($Fe_xCr_{(1-x)}(OH)_{3(s)}$) by free chlorine (HOCl) was studied. It is hypothesized that these Cr(III) solids will exhibit different reactivities that affect the oxidation of Cr(III) to Cr(VI).

To test this hypothesis, batch experiments in the presences of chlorine with $Cr(OH)_{3(s)}$, $Cr_2O_{3(s)}$, and $Cu_2Cr_2O_{5(s)}$ were conducted in Chapter 3 and with iron chromite of varying iron content in Chapter 4.

(3) ***Examine the effects of varying water chemical parameters on Cr(III) oxidation:*** The effects of water chemical parameters such as pH, presence of halides, alkalinity and iron content were evaluated in environmentally relevant conditions. The existence of these varying parameters was studied at typical drinking water conditions in order to determine any catalytic or inhibitory effects on the oxidation of Cr(III) and subsequent formation of Cr(VI) in the presence of disinfectants.

In Chapter 3, the impact of pH and bromide on Cr(III) solid oxidation was evaluated. Similarly, the impact of pH, bromide, alkalinity and iron on the oxidation of iron chromite by chlorine was examined in Chapter 4.

(4) ***Identify the mechanism of the electron transfer process during the oxidation of Cr(III) to Cr(VI):*** The mechanism of Cr(III) oxidation is not well-defined by literature. The oxidation of Cr(III) to Cr(VI) was hypothesized to involve multiple electron transfer steps that can include the formation of Cr(VI) and Cr(V) intermediates. The identification of these intermediates may address the importance of fundamental steps of redox reactions to aid in the mitigation of Cr(VI) formation. In order to elucidate this mechanism, the stoichiometry of the oxidation reactions in Chapters 3 and 4 was evaluated which allowed for a proposed mechanism of intermediate formation.

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Chapter 2

Occurrence and Speciation of Chromium in Drinking Water Distribution Systems

Previously published in *Environmental Science: Water Research and Technology*

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Abstract

Chromium can exist as both trivalent Cr(III) and hexavalent Cr(VI) in typical drinking water conditions, with Cr(VI) of particular concern due to its high toxicity and new regulatory perspectives. This study critically reviewed the occurrence and speciation of chromium in drinking water distribution systems in the U.S., based on a detailed analysis of the up-to-date EPA Unregulated Contaminant Monitoring Rule (UCMR) database. Data show that the nationwide Cr(VI) levels in drinking water ranged from non-detectable to 97 µg/L at the entry point to drinking water distribution systems, and between non-detectable and 67 µg/L at the maximal residence time of distribution systems with maximal residence time. Geographic distributions show that higher drinking water Cr(VI) concentrations were observed in Southwest U.S. and were closely associated with the dependence of groundwater as a drinking water source. While Cr(VI) and total chromium concentrations showed either an increase or a decrease between the entry point and the maximal residence time of drinking water distribution systems, they suggested complex physicochemical processes that can act as both sources and sinks of chromium in distribution systems, including the oxidation of Cr(III)-containing solids by residual disinfectants and the adsorption of Cr(VI) by corrosion scales. Time-dependent data analysis revealed that a considerable fraction of Cr(III) at the entry point to distribution systems was inadvertently converted to Cr(VI) by the time the drinking water reached the maximal residence time of distribution systems, and this conversion was positively correlated to the presence of residual disinfectants. Data analyses suggest that the reactivity of downstream water distribution should be managed to control chromium in tap water.

Introduction

Hexavalent chromium Cr(VI) is an emerging contaminant due to its toxicity and new drinking water regulatory standards.[1-3] While chromium can exist in six oxidation states (from 0 to VI), trivalent Cr(III) and hexavalent Cr(VI) are the stable forms in aquatic environments.[4,5] Exposures to Cr(VI) through respiratory, oral, and dermal pathways are associated with lung and gastrointestinal cancers as well as skin ulcerations,[2,6-9] while Cr(III) is considered a micro-nutrient and aids in the metabolism of glucose and lipids.[10,11] Anthropogenic release of Cr(VI) comes from chemical industries and products, including paints, pigments, paper, electroplating and leather tanning.[12,13] In addition, Cr(VI) is naturally occurring in aquifer minerals and exists as the 21st most abundant element in the earth's crust.[14,15] Weathering of Cr(III)-containing aquifers leads to natural-occurring Cr(VI) in groundwater.[16-18]

In drinking water conditions, Cr(VI) exists as the oxyanion CrO_4^{2-}, whereas Cr(III) has a very low solubility and can exist as various Cr(III) solids.[19-21] California recently set a new drinking water Cr(VI) standard of 10 µg /L.[3] The U.S. EPA has not yet decided whether or not to regulate Cr(VI).[22] In addition, California also has a stricter regulation for total chromium than the U.S. EPA, *i.e.*, 50 µg/L *vs*. 100 µg/L.[22] A better understanding of the nationwide chromium occurrence and speciation in drinking water will help water utilities to prepare and develop effective control strategies in the future.

The existing regulatory framework mainly addresses chromium occurrence at point of treatment prior to entering water distribution systems. However, drinking water resides in distribution systems much longer than that in treatment facilities (*i.e.*, days *vs.* hours), and there are many reactive components in distribution systems, including pipeline materials and residual disinfectants. For example, chromium has been widely used in pipe materials (*e.g.*, cast iron and stainless steel) and may leach into drinking water due to corrosion processes.[23-32] In addition, as pipes corrode, iron oxide corrosion products adsorb Cr(VI) that is even present at trace levels in treated drinking water.[30- 36] Thermodynamic considerations suggest that adsorbed Cr(VI) can be reduced to Cr(III) by green rusts and other reducing agents in corrosion products and consequently exists as different Cr(III) minerals in drinking water distribution systems.[26,27, 37 - 44] Cr(VI) can accumulate to extremely high levels in the corroded solids over decades. Recent nationwide surveys show that chromium accumulates extensively, reaching concentrations as high as 0.5% in the corrosion scales.[33,45-47] These levels far exceed its natural abundance in aquifer sediments, turning corrosion scales in water distribution systems into potential *in situ* sources of chromium.

There are several reaction pathways from source water to the tap that can impact the occurrence and speciation of Cr species in drinking water (Figure 1).

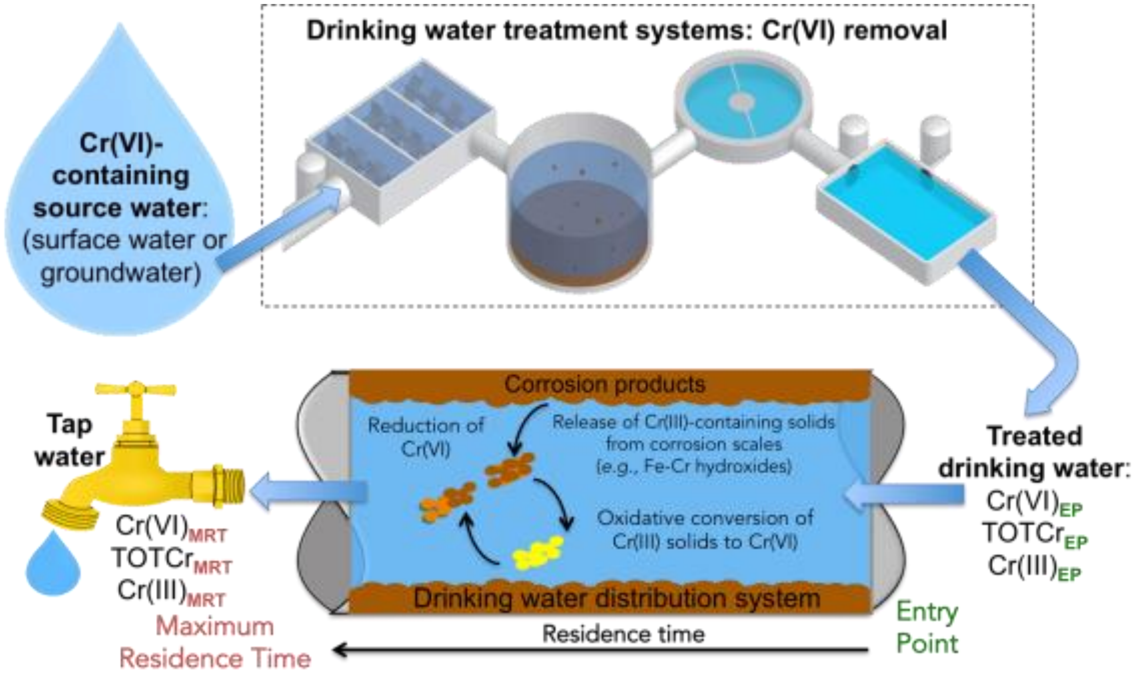


Figure 2.1 A schematic illustration of pathways that can impact the occurrence and speciation of chromium in drinking water.

Cr(VI) concentrations in tap water can vary depending on the type of residual disinfectants and the residence time in the water distribution systems – from the entry point (EP) to the distribution system (*i.e.*, effluent from drinking water treatment plant) to the maximum residence time (MRT) in the distribution system (*i.e.*, exit point at the tap). Recent studies show that Cr(III) can be oxidized by residual disinfectants.[48-53] Currently, there is little knowledge on the chemical stability of accumulated chromium in water distribution systems.

Considering the emerging concerns with Cr(VI) on its toxicity and regulatory perspective, the objective of this frontier review was to critically analyze the state of Cr(VI) in U.S.

drinking water and distribution systems, based on the up-to-date US EPA monitoring database, with special focuses on the geographic distributions of Cr(VI) in drinking water and changes of Cr speciation in water distribution systems.

Methods and Database

To analyze the state of chromium in drinking water of public water systems, field sampling data from the up-to-date US EPA's third round of Unregulated Contaminants Monitoring Rule (UCMR3) monitoring program were individually compiled and analyzed. A total of 38,000 samples from 3,613 public water systems nationwide were reported based on nationwide UCMR3 monitoring activities from 2013 to 2014.[22] Detailed data mining was conducted on the basis of sample geographic region, drinking water source, size of the water utilities, types of residual disinfectant and sampling location within the distribution system. For each sample in the database, total Cr (TOTCr) was measured with EPA method 200.8 with a minimal reporting level of 0.2 µg/L, Cr(VI) was measured with EPA method 218.7 with a minimal reporting level of 0.03 µg/L, and Cr(III) was calculated as the difference between TOTCr and Cr(VI).

Statistical analysis conducted in this review study was based on the total number of samples and the number of water utilities, respectively. This eliminated potential bias from geographic regions with more samples or more participating water utilities. In particular, the sample-number-based analysis counted each sample in the database as one independent event, regardless of the sample location and time. In comparison, the water-utility-based analysis only counted the fact that Cr levels fell into a particular range. For example, if a water utility reports 20 samples with Cr ranging between 1 and 5 µg/L and 10 samples between 5 and 10 µg/L, all 30 samples will be counted for sample-number-based analysis; however, this utility would only be counted once each for the category of a Cr level at 1-5 and 5-10 µg/L, respectively. With respect to the analysis of sampling locations within distribution systems, reported data from the same systems (matched by sample and utility codes in the database) were compared to examine the changes of Cr concentration and speciation between the EP and MRT of distribution systems. In the conducted statistical analysis, values below the detection limit of 0.03 µg/L, non-detectable samples, were assumed to have a concentration of 0 µg/L. In addition, the impact of residual disinfectants on the fate of Cr in distribution systems was investigated by correlating the type of disinfectants with changes of Cr speciation.

Results and Discussion

Cr(VI) occurrence in drinking water

Analysis show that Cr(VI) is detected in treated drinking water prior to entering drinking water distribution systems nationwide. Of a total of 22,724 samples reported in this category, 2% of them had Cr(VI) concentrations higher than 10 µg/L,14% of the samples were between 1 and 10 µg/L, 56% were between 0.03 and 1 µg/L and 28% were below 0.03 µg/L, *i.e.*, the minimal reporting limit (Figure 2.2A). These results are consistent with a prior observation on the basis of a smaller number of samples nationwide that a large fraction of samples had Cr(VI) concentrations less than 1 µg/L.[54] The monitoring data examined in this study came from 3,613 public water systems, of which 3,113 are large systems that serve more than 10,000 people. On the basis of the numbers of water utilities, 1% of participating utilities reported Cr(VI) levels greater than 10 µg/L, 12% of utilities were between 1 and 10 µg/L, 55% were between 0.03 and 1 µg/L and 32% were below 0.03 µg/L (Figure 2.2B).

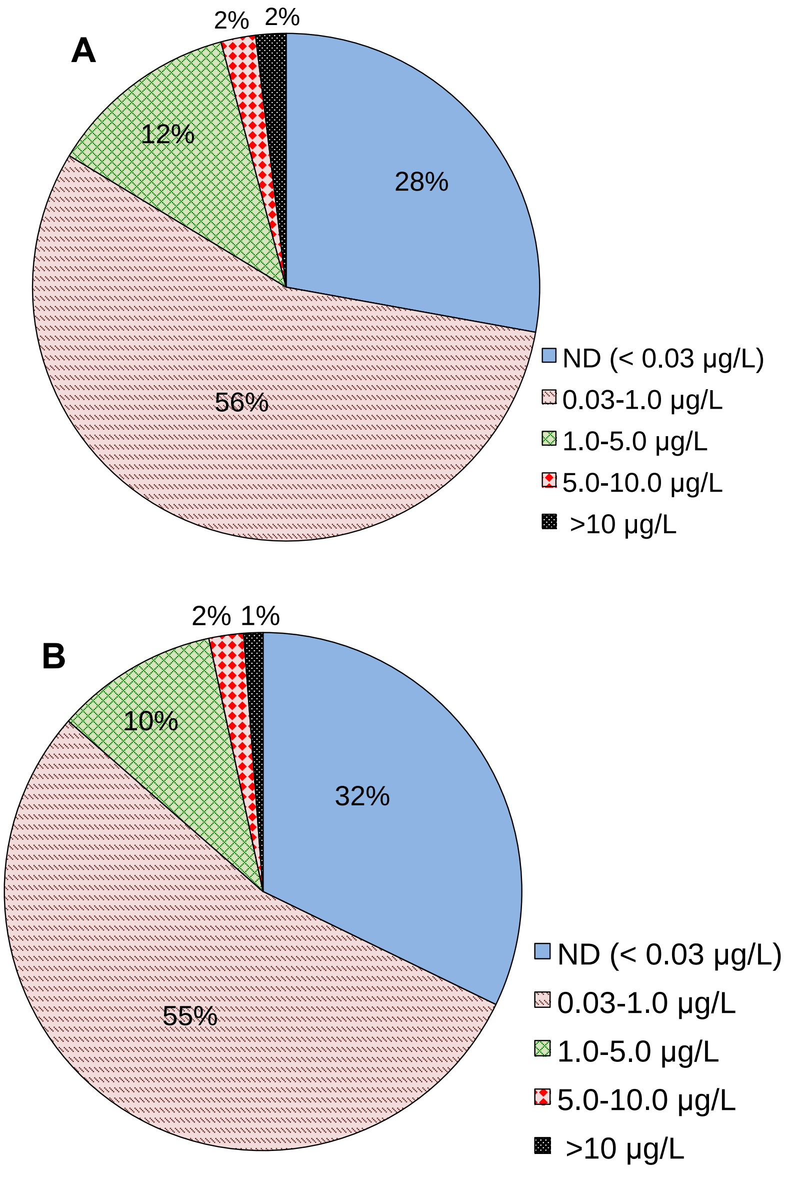


Figure 2.2 Distributions of Cr(VI) concentrations in drinking water. This analysis is based on data from 3,613 water utilities in the USPEA UCMR3 database. (A) Sample-based Cr(VI) distribution at the entry point to the water distribution systems based on 22,724 detections. (B) Water system-based Cr(VI) distribution at the entry point to the water distribution systems based on 3,613 utilities.

The statistical distribution of Cr(VI) levels in treated drinking water before entering distribution systems was further analyzed based on the reporting water utilities in each US EPA region (Figure 3).

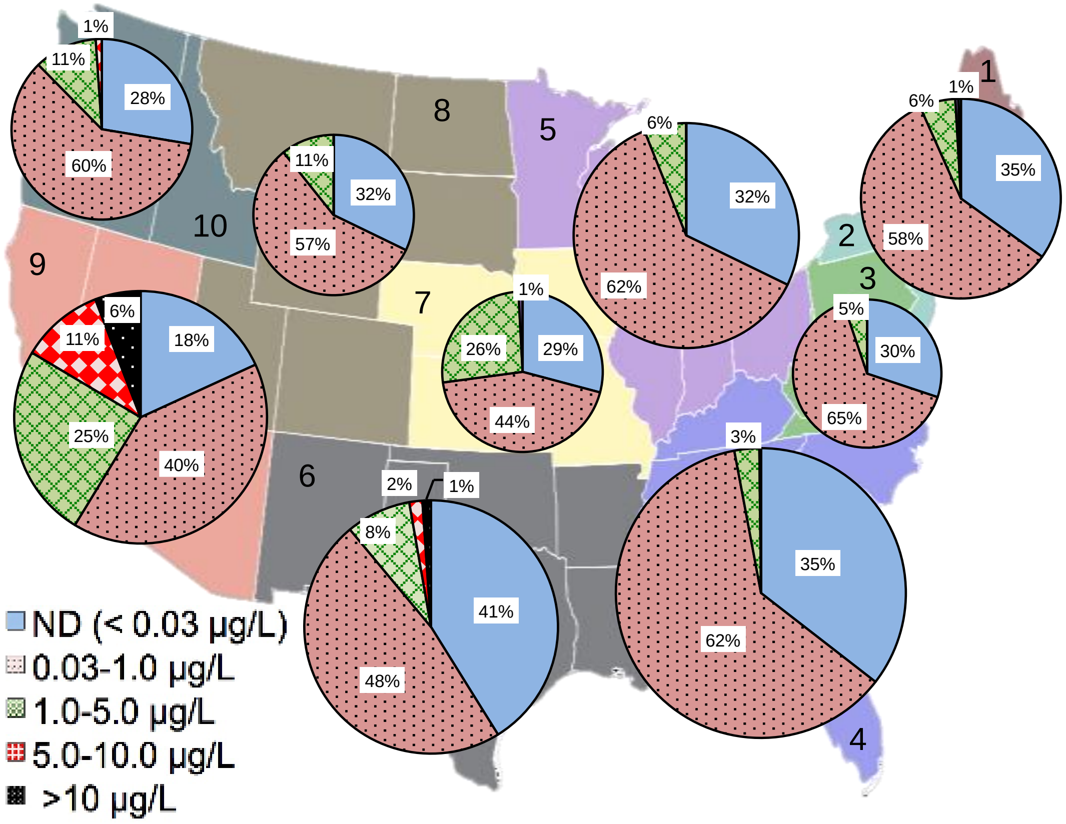


Figure 2.3 Geographic distributions of Cr(VI) concentrations in treated drinking water at the entry point to distribution systems. The analysis was based on the total number of public water systems in ten US EPA Regions.

EPA Regions 4, 5, 6 and 9 had the largest number of monitoring water systems in the database due to large populations in these regions. Among all regions, EPA Regions 6 and 9 have the highest percentage of water utilities with Cr(VI) levels greater than 10 µg/L (1.6% and 6.1%, respectively) and Cr(VI) levels between 1 and 10 µg/L, i.e., 10% and 19%, respectively (Figure 2.3). Region 9 was also previously observed as a region with the greatest levels of Cr(VI).[54] Region 6 covers the states of Texas, Oklahoma, New Mexico, Louisiana, and Arkansas. Region 9 includes the western states of California, Nevada and Arizona.

Data analysis shows that the occurrence of Cr(VI) in drinking water prior to distribution system entrances was highly associated with the dependence of groundwater as the drinking water source (Figure 2.4A). For example, of all water systems with Cr(VI) levels higher than 10 µg/L, nearly 90% of them depended on groundwater as the primary drinking water source, whereas for water systems with low Cr(VI) levels between 0.03 and 1 µg/L, only 48% of them primarily used groundwater. In EPA Regions 6 and 9, groundwater is the major water source for systems with Cr(VI) concentrations greater than 10 µg/L (Figure 2.4A). Previous observations also found that that higher concentrations of Cr(VI) were more likely found in groundwater than in surface water.[54]

This positive correlation between the occurrence of Cr(VI) in drinking water and its dependence on groundwater source is consistent with available geochemistry literature on the contribution from natural-occurring Cr(VI) in aquatic environments. Cr(III)-containing aquifers are widely present in the arid alluvial basins in the Southwestern U.S. that is largely covered by these two EPA regions.[18,55-58] For example, elevated Cr(VI) levels up to 300 mg/L are observed in California, resulting from the oxidation of Cr(III)-containing minerals by MnO_2 in serpentine soils on geological time scales.[15-17, 59-56] With the exception of EPA Region 3, more than 50% of participating public water systems in all EPA regions depend on groundwater as the source water, and Region 9 has the highest percentage at 75% (Figure 2.4B).

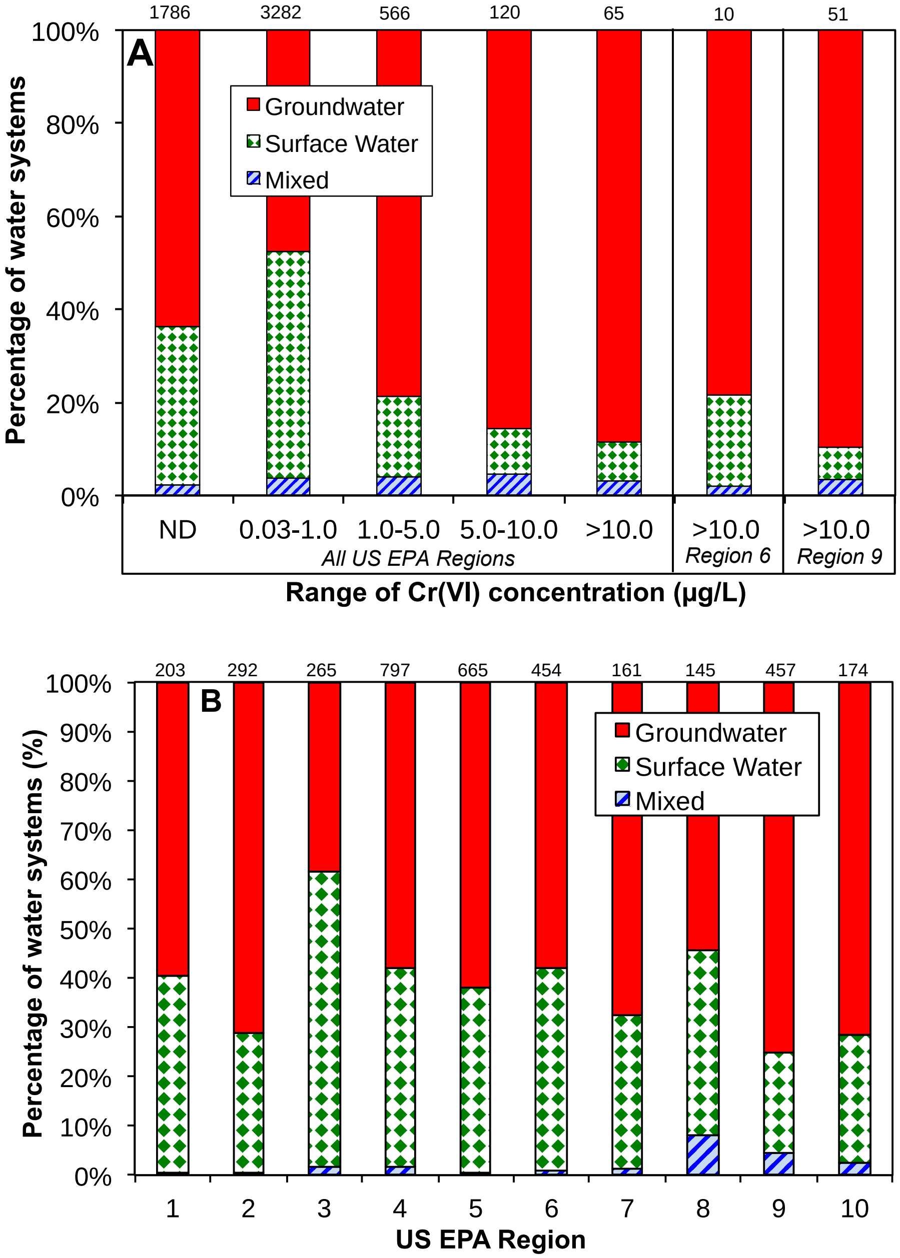


Figure 2.4 Sources of drinking water and its correlation with the Cr(VI) occurrence in drinking water and geographic location. The analysis was based on the total number of public water systems in ten US EPA Regions. (A) Distribution of water systems on the basis of Cr(VI) occurrence; (B) Distribution of water systems on the basis of Geographic EPA regions. “Mixed” means a combination of groundwater and surface water. Numbers on the top of the bars in Figure 2.4A mean the total frequencies of detections reported by water systems in each category. Cr(VI) occurrence data from a total of 3,613 water systems were reported in the UCMR3 database.

Meanwhile, conventional water treatment processes (*e.g.*, coagulation and sand filtration) are not effective in reducing high Cr(VI) in source water to a non-detectable level. Although new treatment technologies are proposed (*e.g.*, ion exchange and other reductive approaches), implementation will take years to come. Therefore, contribution of Cr(VI) from geological weathering of aquifer minerals has a major contribution to its occurrence in treated drinking water, *i.e.*, at the entry point to water distribution system.

Cr(VI) occurrence at the maximal residence time of water distribution systems

At the maximal residence time of water distribution systems (15,886 samples from the database), 1% of samples had Cr(VI) concentrations higher than 10 µg/L, 11% of the samples were between 1 and 10 µg/L, 68% of samples had Cr(VI) concentrations between 0.03 and 1 µg/L, and 20% were below 0.03 µg/L (Figure 2.5A). Compared to Cr(VI) distribution at the entry point of distribution systems (Figure 2.2A), the major change was a 12% increase of samples with Cr(VI) concentration ranging between 0.03 and 1 µg/L at the maximal residence time which was accompanied by a 1%, 3% and 8 % decrease in the > 10 µg/L, 1-5 µg/L, and ND ranges respectively. Geographic distributions on the basis of the number of water systems show that EPA regions 6 and 9 had the highest percentage of water systems with Cr(VI) concentrations higher than 10 µg/L at the maximal residence time of distribution systems (Figure 2.5B). Compared to Cr(VI) concentrations at the entry point to the distribution systems, Region 9 showed an 8% increase of Cr(VI) in the range of 0.03 to 1 µg/L at the maximal residence time of distribution system and a 2% decrease in the 5-10 µg/L range. Northeast (combined Regions 1 and 2) and Northwest (Region 10) showed a 15% and 13% increase of Cr(VI) in the range of 0.03 to 1 μg/L at the maximal residence time of distribution system, respectively.

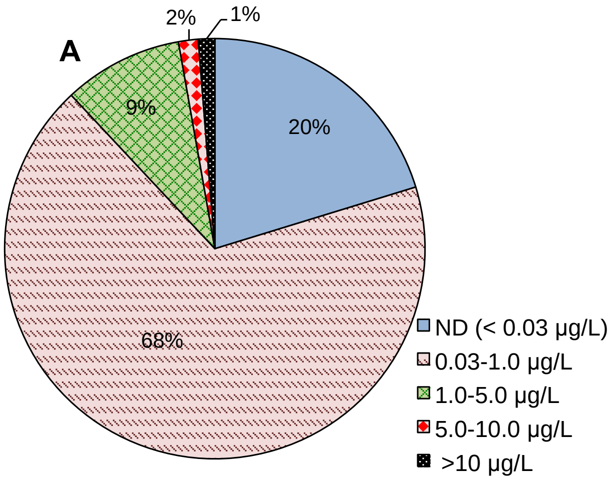
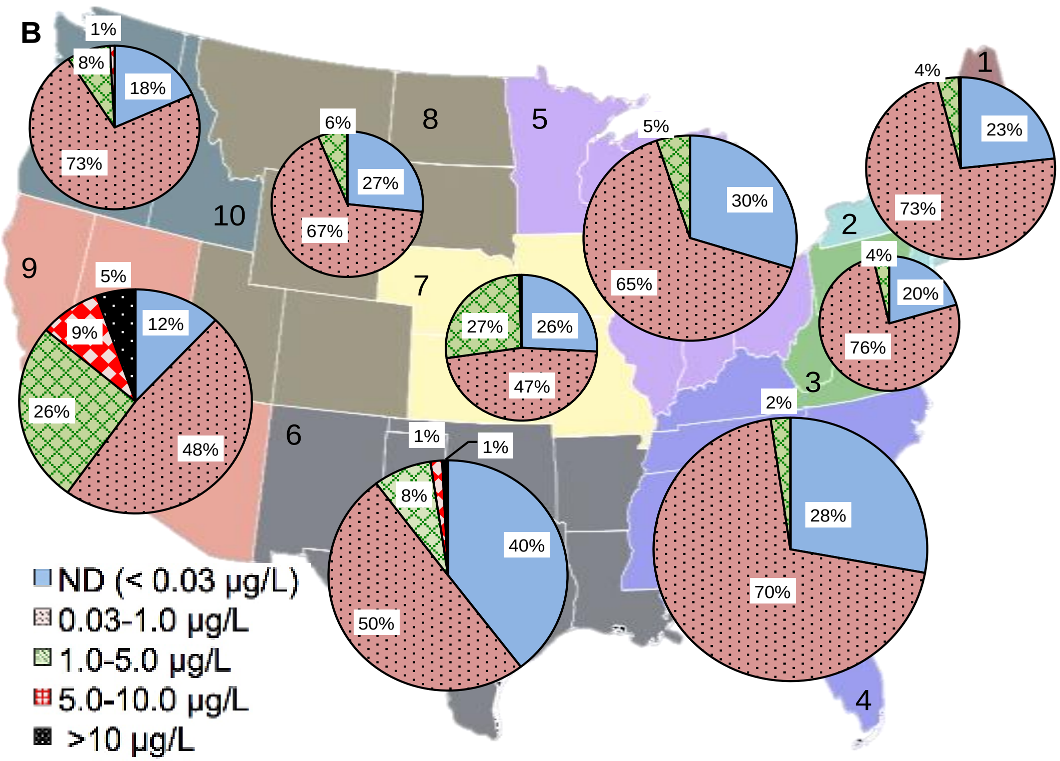


Figure 2.5 The Cr(VI) distribution at the maximal residence time of water distribution systems with a maximal residence time.

(A) Cr(VI) distribution at the maximal residence time of the water distribution systems. The analysis was based on a total of 15,886 samples from the EPA UCMR3 database.

(B) Geographic distributions of Cr(VI) concentrations at the maximal residence time of drinking water distribution systems on the basis of 3,613 water systems.



The database was further grouped to pair Cr(VI) measurements at the entry and maximal residence time of the same water distribution systems. These pairs of samples provided snapshots of the changes of Cr speciation and concentration in distribution systems. A total of 4,517 pairs of measurements were obtained from 2,174 distribution systems. The 25th, 50th and 90th percentile distributions of Cr(VI) concentrations at the entry point of distribution systems were 0.09, 0.76 and 2.40 µg/L, respectively. The 25th, 50th and 90th percentile distributions of Cr(VI) concentrations at the maximal residence time were 0.11, 0.24 and 2.30 µg/L respectively (Figure 2.6A). There were also trace levels of Cr(III) at the entry point of the distribution system. The 25th, 50th and 90th percentile distributions of Cr(III) concentrations at the entry point of distribution systems were 0.25, 0.38 and 2.50 µg/L, respectively (Figure 2.6A). Of all distribution systems, 41% showed an increase of Cr(VI) concentration from the entry to the maximal residence time. Based on the 75th and 90th percentile sample distributions, Cr(VI) concentration increased by 0.04 and 0.21 µg/L in distribution systems, respectively (Figure 2.6B). Our analysis also showed that 1% of the samples that had increases in Cr(VI) concentration resulted in a Cr(VI) concentration exceeding 10 µg/L at the tap water with the maximal residence time in a distribution system.

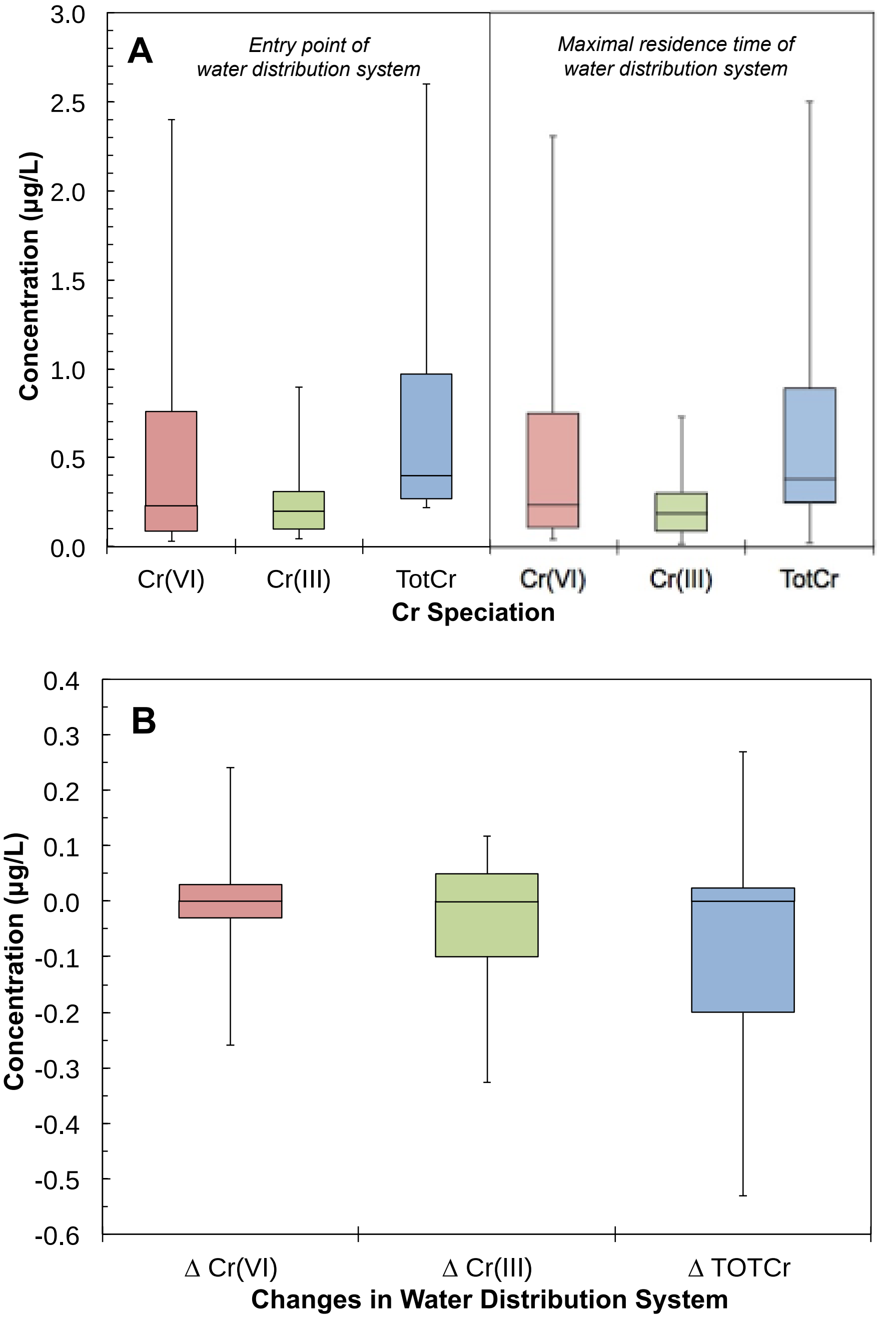


Figure 2.6 Box plot of Cr speciation and concentration in water distribution systems. (A) Distributions of Cr species concentrations at the entry point and maximum residence time of water distribution systems. (B) Changes of Cr(VI), TOTCr, and Cr(III) concentrations in water distribution systems. The whiskers of the boxplot represent the 10th and 90th percentiles of concentration. The lower quartile, middle and upper quartile represent the 25th, 50th and 75th percentile values.

Changes of total chromium in water distribution systems

Total chromium (TOTCr) represents both Cr(III) and Cr(VI) species. There are a total of 6,577 pairs of samples in the UCMR database that were taken concurrently at the entry and maximal residence time of the same water distribution systems. The 25th, 50th and 90th percentile distributions of TOTCr concentrations at the entry point were 0.27, 0.40 and 2.60 µg/L. The corresponding concentrations at the maximal residence time were 0.25, 0.38 and 2.50 µg/L, respectively (Figure 6A). Overall, TOTCr concentrations between the entry point and maximal residence time can either increase or decrease (Figure 6B). Increases in TOTCr are likely derived from accumulated Cr leaching from the corrosion scales in distribution systems.[27-29] Drinking water chemical conditions affect these release processes. Previous studies have shown that changes in pH and chloride levels can promote corrosion and the release of Cr-Fe complexes from scales.[62-65] Decreases of TOTCr can result from the adsorption of Cr(VI) onto iron oxides in corrosion scales such as magnetite, goethite and hematite. Sorption may then be followed by the potential reduction of Cr(VI) to Cr(III) and sequestration of Cr(III) in the distribution system.[66,67]

Changes of Cr speciation in water distribution systems

The database had samples with both TOTCr and Cr(VI) concentrations measured concurrently at the entry and maximal residence time of 4,517 water distribution systems. The difference between TOTCr and Cr(VI) concentration represents Cr(III) concentration. The 25th, 50th and 90th percentile distributions of Cr(III) at the entry point were 0.10, 0.20 and 0.90 µg/L, respectively (Figure 2.6A). The presence of Cr(III) at the entry point can come from different sources. For example, highly soluble Cr(VI) can be reductively transformed to particulate Cr(III) before removal in a water treatment plant.[68-72] Albeit that, trace levels of Cr(III) residual can exist.[68] Additional Cr(III) can also be introduced with impurities of iron-based coagulants during treatment.[72] These can result in a carry-over of residual Cr(III) to subsequent water distribution system.

Once in the distribution system, Cr(III) levels showed either a decrease or an increase from entry point to the maximum residence time. For example, the 10th and 90th percentile of samples show a decrease of 0.33 and an increase of 0.12 µg/L, respectively (Figure 2.6B). A decrease in Cr(III) can result from the oxidation of Cr(III) to Cr(VI). Cr(III) can also adsorb onto iron oxides such as hematite in corrosion scales.[73] An increase in Cr(III) can be attributed to the release of Cr-containing particles from corrosion scales in the distribution system.

To further assess the contribution of Cr(III) oxidation to the increase of Cr(VI) concentrations in water distribution systems, the percentage of Cr(III) at entry point that can be transformed to Cr(VI) in the distribution system is calculated based on the monitoring data. By comparing the change of Cr(VI) concentration in a distribution system with respect to Cr(III) at the entry point, the fraction of Cr(III) that is oxidized to Cr(VI) in a distribution system is calculated using Equation 1:

$$f_{Cr(III)oxidized} = \frac{[Cr(VI)]_{MRT}-[Cr(VI)]_{EP}}{[Total\ Cr]_{EP}-[Cr(VI)]_{EP}} \qquad (1)$$

$[Cr(VI)]_{EP}$ and $[Cr(VI)]_{MRT}$ are Cr(VI) concentrations at the entry point and the maximal residence time of a distribution system, respectively. $[TOTCr]_{EP}$ is the concentration of total Cr at the entry point. The denominator of Equation 1 represents Cr(III) concentration at the entry point. In some distribution systems the concentration of TOTCr was less than that of Cr(VI) at the entry point, which was likely caused by differences in sensitivities of analytical methods between TOTCr and Cr(VI). These samples were not included in the calculation.

This calculation shows that a considerable fraction of Cr(III) can be oxidized in a distribution system and contributes to changes in Cr speciation and an inadvertent transformation to Cr(VI) (Figure 2.7A). Interestingly, the fraction of oxidizable Cr(III) varies with the type of residual disinfectant. Of the disinfectants monitored in the UCMR3 data, the two most commonly used residual disinfectants are free chlorine and chloramine. There is a high likelihood of an increase in Cr(VI) concentration in water distribution system when free chlorine is used as a residual disinfectant (Figure 2.7A). The 50th and 90th percentile oxidizable Cr(III) fractions were approximately 20% and 67%, respectively. A lower likelihood of Cr(VI) increase exists if chloramine is used as the residual disinfectant. With chloramine as a residual disinfectant, 58% of Cr(VI) samples showed an increase in Cr(VI) concentration. The 50th and 90th percentile oxidizable Cr(III) fractions were approximately 12% and 54%, respectively. There was a 15% increase in the maximal oxidizable Cr(III) fraction between chlorine and chloramine (Figure 2.7A). This is consistent with the fact that chlorine is a stronger oxidant than chloramine.[74] It is important to note that this data analysis was limited by a small number of samples and distribution systems with an identified disinfectant in the UCMR3 database. However, previous observations also showed a positive correlation between the increase of Cr(VI) and TOTCr concentration with the presence of chlorine as the residual disinfectant.[48,54] In samples with no disinfectant specified (most likely predominated by chlorine system), fraction of oxidizable Cr(III) is very similar to that in the chlorinated system.

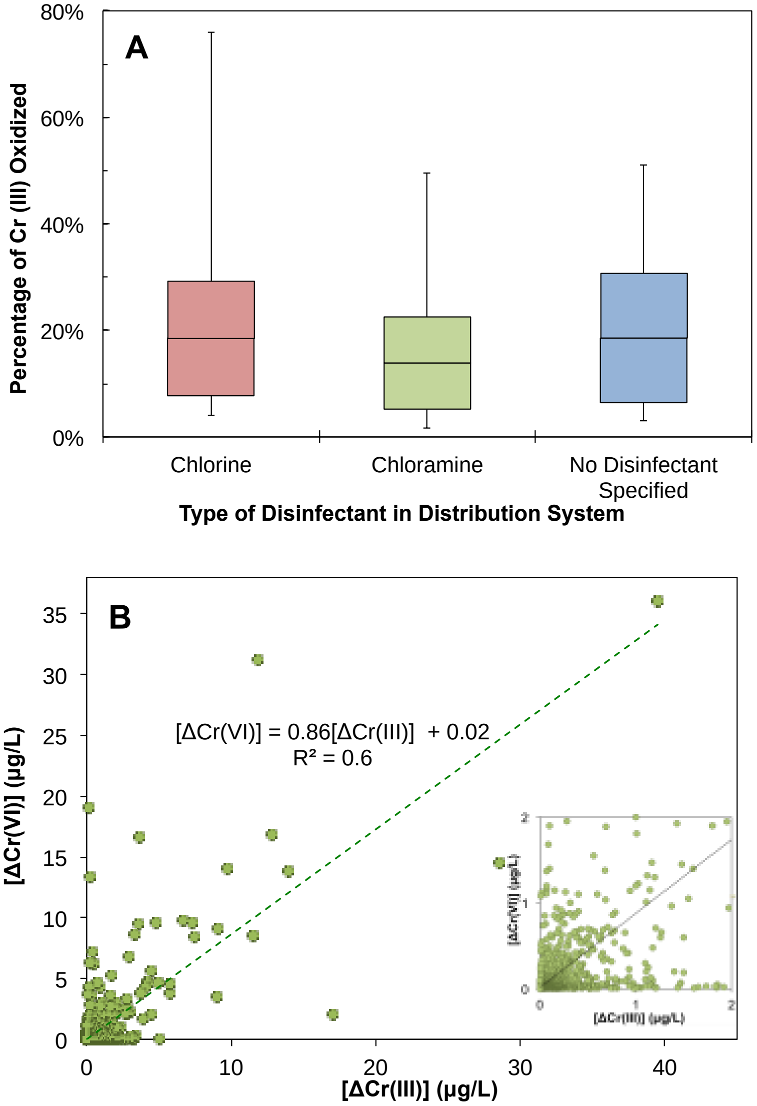


Figure 2.7 Evaluation of the fate of Cr(III) in water distribution systems. (A) The percentage of Cr(III) that can be oxidized, calculated based on 4,517 paired measurements of samples at the entry point and maximal residence time of water distribution systems in UCMR3 database. The whiskers of the boxplot represent the 10th and 90th percentiles of concentration. The lower quartile, middle and upper quartile represent the 25th, 50th and 75th percentile values. (B) The correlation between the decrease of Cr(III) and the increase of Cr(VI) in water distribution systems. 68 sample pairs were identified with free chlorine as the residual disinfectant, 85 sample pairs with chloramine as the residual disinfectant, and the rest of samples (11,507) did not specify which disinfectant was used.

The increase in Cr(VI) and decrease in Cr(III) were further analyzed to identify the mechanism of Cr(III) changes in a distribution system (Figure 2.7B). There is a positive correlation between the decrease of Cr(III) (*i.e.*, $\Delta Cr(III)_{EP\text{-}MRT}$) and the increase of Cr(VI) (*i.e.*, $\Delta Cr(VI)_{MRT\text{-}EP}$) with a R^2 value of 0.6. The slope of the correlation is less than 1, suggesting that decreases in Cr(III) were not fully accounted for by increases in Cr(VI). This indicates that while the oxidation of Cr(III) to Cr(VI) can cause decreases in Cr(III), it is not the only mechanism that contributes to Cr(III) decreases in this complex system. Additional decreases in Cr(III) can potentially result from its deposition and sequestration to corrosion scales. In these scenarios, this would result in an overall decrease in TOTCr. As the water enters the distribution system, the complex physiochemical reactions result in a conversion of Cr(III) to Cr(VI), which eventually leads to an elevated level of Cr(VI) when the drinking water leaves the distribution system with the maximum residence time, *i.e.*, at the tap. This data analysis suggests that water distribution systems can be dynamic reactors that act as potential sources for Cr(VI) release and reoccurrence, most likely via the oxidation of Cr(III) to Cr(VI) by chlorine.

Conclusions

The analysis of the USEPA's UCMR3 database showed that the Cr(VI) was detected in treated drinking water across U.S. at varying levels. EPA regions 6 and 9 have the highest percentage of water systems that exhibit Cr(VI) levels greater than 10 µg/L (1.6% and 6.1%, respectively), which is strongly associated with groundwater as the drinking water source and indicates the importance of naturally-occurring Cr(VI) from geological weathering. Based on the sampling data in water distribution systems, there is 41% chance that Cr(VI) concentration increased from the entry to the maximum residence time. This increase of Cr(VI) can be contributed considerably by the oxidation of Cr(III) residuals in water distribution system, and the fraction of oxidizable Cr(III) increased in the presence of chlorine in comparison to chloramine. Total chromium levels also exhibited changes in water distribution systems, most likely contributed by the release of Cr(III)-containing particles due to corrosion and adsorption of Cr(VI) by corrosion scales.

Acknowledgements

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Chapter 3

Kinetics and Mechanisms of Cr(VI) Formation via the Oxidation of Cr(III) Solid Phases by Chlorine in Drinking Water

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Abstract

Hexavalent chromium Cr(VI), typically existing as the oxyanion form of CrO_4^{2-}, is being considered for more stringent drinking water standards by regulatory agencies. Cr(VI) can be inadvertently produced via the oxidation of trivalent chromium Cr(III) solids. This study investigated the kinetics and mechanisms of Cr(III) solids oxidation by chlorine in drinking water and associated Cr(VI) formation. Batch experiments were carried out with three Cr(III) solids of environmental relevance, *i.e.*, chromium hydroxide $Cr(OH)_{3(s)}$, chromium oxide $Cr_2O_{3(s)}$ and copper chromite $Cu_2Cr_2O_{5(s)}$. Impacts of water chemical parameters including pH (6.0-8.5) and bromide concentration (0-5 mg/L) were examined. Results showed that the rapid oxidation of Cr(III) solid phases by chlorine was accompanied by Cr(VI) formation and an unexpected production of dissolved oxygen. Analysis of reaction stoichiometry indicated the existence of Cr intermediate species that promote the auto-catalytic decay of chlorine. An increase in pH modestly enhanced Cr(VI) formation due to changes of reactive Cr(III) surface hydroxo species. Bromide, a trace chemical constituent in source waters, exhibited a catalytic effect on Cr(VI) formation due to an electron shuttle mechanism between Cr(III) and chlorine and the bypass of Cr intermediate formation. The kinetics data obtained from this study suggest the oxidation of Cr(III) solids by chlorine in water distribution system can contribute to Cr(VI) occurrence in tap water, especially in the presence of a trace level of bromide.

Introduction

The presence of hexavalent chromium Cr(VI) in drinking water is an increasing concern in recent years, as it can cause adverse human health effects, including lung cancer, stomach cancer and dermatitis.[1-6] Cr(VI) typically exists as an oxyanion (*i.e.*, chromate CrO_4^{2-}) in drinking water and is released from both anthropogenic and natural sources. Anthropogenic sources include industrial waste discharges from tanneries and electroplating, metallurgical smelting of chromite ore and corrosion of metal alloys.[7-9] Naturally occurring Cr(VI) typically originates from geological weathering of Cr-containing aquifer minerals.[10-16] As an emerging contaminant, a new drinking water standard of Cr(VI) was set at 10 µg/L in California in 2014,[17] and a new U.S. EPA regulation may also be proposed in the future.[18] Based on the most recent sampling data from U.S. EPA's third round Unregulated Contaminant Monitoring Rule (UCMR3), 63% of the participating public water systems nationwide detected Cr(VI) at the endpoint of the drinking treatment plant.[18]

Knowledge of chromium in each oxidation state rather than total chromium is vital to control its occurrence. Trivalent chromium Cr(III), which is much less toxic than Cr(VI) and even a micro-nutrient, most exists as solids with limited solubility at circumneutral pH.[19-20] Typical Cr(III) solids relevant to drinking water systems include chromium hydroxide $Cr(OH)_{3(s)}$, chromium oxide $Cr_2O_{3(s)}$ and copper chromite $Cu_2Cr_2O_{5(s)}$. Chromium hydroxide $Cr(OH)_{3(s)}$ can form via reductive transformation of Cr(VI) during the coagulation step of water treatment and contribute to Cr(III) residual in drinking water.[21-27] In cases where Fe(II) is used as the reductant during coagulation, $Cr(OH)_{3(s)}$ can co-exist with Fe(III) hydroxide.[21,25,28] In addition, chromium has been widely used in plumbing materials (*e.g.*, stainless steel) in water distribution systems.[29-31] As a result, Cr(III) solids are formed in corrosion scales and in contact with treated drinking water.[32,33] $Cr_2O_{3(s)}$ is detected in corrosion products from water distribution systems.[34,35] $Cu_2Cr_2O_{5(s)}$ can be potentially found in aquatic environment from anthropogenic sources given its wide industrial use.[19,33,36] Studies show that chromium is one of the most abundant inorganic contaminants accumulated in drinking water distribution systems.[37,38]

The ultimate occurrence of Cr(VI) in tap water is controlled by the complex chromium redox chemistry from the source water to the water distribution system; however, current Cr(VI) control strategies mainly target upstream treatment processes. To develop effective strategies to minimize Cr(VI) in tap water, it is important to understand chromium redox chemistry in the presence of disinfectants,[39] especially in water distribution systems. Field monitoring data point to the importance of oxidative conversion of Cr(III) to Cr(VI) in drinking water distribution systems. 35% of the monitored water distribution systems in EPA UCMR3 database showed an increase of Cr(VI) concentration from the point of entry to the maximum residence time.[18] This trend was positively correlated to the presence of free chlorine as a residual disinfectant. There are reports that show increases of Cr(VI) and total Cr concentrations in water distribution systems,[40,41] and indicate an inadvertent re-oxidation of Cr(III) residual to Cr(VI) by chlorine can potentially occur.

Prior studies have shown that Cr(III) species, especially in soluble forms, can be oxidized by chlorine to generate Cr(VI).[20,42-46] For example, chlorine can oxidize dissolved Cr(III) solutes.[39,42] Residual chlorine can also oxidize Cr from corroded stainless steel pipes.[23] In addition, chlorine at an extremely high concentration (1,400 mg Cl_2/L) can oxidize $Cr(OH)_{3(s)}$ via a dissolution-induced pathway at extremely acidic or alkaline pHs.[46] These studies point to the importance of Cr(III) oxidation by chlorine as a source of Cr(VI). There is, however, a very limited understanding of the reactivities of different environmentally relevant Cr(III) solids with chlorine, especially in drinking water chemical conditions.

Furthermore, the impacts of water chemical parameters on the reactivities of Cr(III) solids remain largely unexplored. Solution pH can significantly impact the speciation of surface complexes of Cr(III) solids.[39,46] A systematic understanding of pH effects on all relevant Cr(III) solid phases is needed. In addition, bromide is an important drinking water chemical constituent. Its concentration in natural environment ranges from a few µg/L to several mg/L worldwide,[47-49] and varies between 24 µg/L and 4.0 mg/L in U.S. source waters.[50,51] Wastewater discharges from energy and oil sectors in U.S. can increase bromide concentration by as much as 20 times in the future.[52] Although the occurrence of bromide raises concerns on metal release and disinfection by-products formation,[53,54] its impact on Cr release has not been explored.

The objectives of this study were to investigate the kinetics and mechanisms of Cr(VI) formation via the oxidation of three model Cr(III) solids by chlorine in drinking water, with emphases on the effects of pH and bromide, and to examine the formation of Cr intermediate species during the oxidative process. By measuring the rates of chlorine consumption, Cr(VI) formation and oxygen production in different chemical conditions, it became possible to gain insight into the mechanism of Cr(III) oxidation and the complex nature of elemental reactions involving Cr redox cycles in drinking water systems.

Materials and Methods

All chemicals used in this study were reagent grade or higher. All solutions were prepared using deionized water (resistivity>18.2 MΩ, Millipore System). Three Cr(III) solids were prepared: $Cr(OH)_{3(s)}$, $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$. Amorphous $Cr(OH)_{3(s)}$ was synthesized via a precipitation method provided as Text A.A.1 in Appendix A. Crystalline $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$ were obtained from Fisher Scientific. All three solids were sequentially sieved through NO. 50, 170 and 325 mesh sieves. The fractions retained between NO. 170 and NO. 325 sieves (with nominal particle sizes between 45 and 90 µm) were collected and used in this study.

Oxidation experiments were conducted in a 200-mL glass batch reactor that was continuously stirred at 23 °C. A 300 mg/L stock solution of chlorine (Cl_2) diluted from a NaOCl solution (Sigma Aldrich) was freshly prepared and kept at a concentration varying between 2 mg Cl_2/L (this chlorine concentration is typical for drinking water) and 20 mg Cl_2/L in different experiments (*i.e.*, between 28 and 280 µM). In some experiments, 20 mg/L of bromine solutions were prepared by adding an excess of bromide (10%) to a chlorine solution at pH 6. The concentration of chlorine was verified by titration with potassium permanganate.[55] The choice of a chlorine concentration higher than 2 mg Cl_2/L in those experiments did not change the redox potential of chlorine compared to that in drinking water conditions (*i.e.*, E^0_{HOCl/Cl^-} =1.41 V *vs.* standard hydrogen electrode) and provided useful insight into the oxidation kinetics.

To start an experiment, 200 mL of chlorine solution was quickly mixed with a pre-determined amount of a Cr(III) solid. The molar ratio of Cr(III) to chlorine varied between 1:10 and 10:1. The solution pH was maintained at a constant value between 6.0 and 8.5 (±0.1 pH units from the target) with a Eutech Instrument Alpha pH200 controller. Droplets of 50 mM $HClO_4$ or 50 mM NaOH were automatically titrated to the reactor that was sealed with Parafilm with minimum headspace. In some experiments, bromide ranging between 0.1 and 5 mg/L was added to the reactor. The solution ionic strength was kept at 10 mM by adding a requisite amount of $NaClO_4$.

At pre-determined time intervals, samples were taken from the system and filtered through 0.22-µm Millipore filters. For experiments conducted at pH 6.0 and 6.5, the solution pH was raised to 8.0 before sampling to recover any Cr(VI) that could be adsorbed on Cr(III) solids. Less than 20% of Cr(VI) was adsorbed on Cr(III) solids and fully recovered (Figure A.A.1 in Appendix A). Chlorine concentration in the filtrate was measured using a modified (DPD) method,[55] in which thioacetamide was added to eliminate the potential interference caused by Cr(VI) (Figure A.A.2). The concentration of Cr(VI) was monitored using a modified diphenylcarbazide (DPC) method,[55] with excess $(NH_4)_2SO_4$ added to covert chlorine to chloramine and prevent it from interfering with DPC reagent (Figure A.A.3). Other solution constituents did not cause any interference on DPC method.

Concentrations of chloride, bromide and bromate were measured by a Dionex DX-120 ion chromatography connected with an IonPac AS22 column and AG22 guard column. Eluent composed of 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ was run at a flow rate of 0.6 mL/min using a 250-µL sample loop. The BET surface area of Cr(III) solids was measured using a Micromeritics ASAP 2020 Surface Area and Porosity analyzer. Zeta potential of Cr(III) solids was measured from a 0.2 g/L suspension using a Zeta Potential Analyzer (Brookhaven Instruments).

Results and Discussion

Kinetics of Cr(VI) formation via Cr(III) solids oxidation by chlorine and pH impact

Based on thermodynamics calculation (Text A.A.2 in Appendix A), the oxidation of Cr(III) solids by chlorine is favorable in typical drinking water conditions (Table 3.1). This thermodynamics relationship is consistent with prior reports.[20,23,39] The oxidation of Cr(III) solid phases by chlorine proceeds via the following reactions:

$$2Cr(OH)_{3(s)} + 3HOCl \rightarrow 2CrO_4^{2-} + 3Cl^- + 7H^+ + H_2O \qquad (1)$$

$$Cr_2O_{3(s)} + 3HOCl + 2H_2O \rightarrow 2CrO_4^{2-} + 3Cl^- + 7H^+ \qquad (2)$$

$$Cu_2Cr_2O_{5(s)} + 3HOCl \rightarrow 2CrO_4^{2-} + 3Cl^- + 3H^+ + 2Cu^{2+} \qquad (3)$$

Table 3.1 Summary of redox potential of different redox couples at pH 7.

Chemical Species	**Redox Potential (V) in Typical Drinking Water Chemical Condition***	**Redox Potential (V) in Initial Experimental Condition****	**Redox Potential (V) in Final Experimental Condition*****
$HOCl/Cl^-$	1.41	1.42	1.40
$CrO_4^{2-}/Cr(OH)_{3(s)}$	0.16	0.13	0.16
$CrO_4^{2-}/Cr_2O_{3(s)}$	0.16	0.13	0.17
$CrO_4^{2-}/Cu_2Cr_2O_{5(s)}$	0.20	0.17	0.21

* Typical drinking water chemical conditions: $[Cl_2]$=2 mg/L, $[Cl^-]$=7 mg/L and [Cr(VI)] =10 µg/L.
** Initial experimental condition: $[Cl_2]$=20 mg/L, and $[Cl^-$ =20 mg/L and [Cr(VI)] = 1×10^{-5} µg/L.
*** Final Experimental Condition: $[Cl_2]$=0.2 mg/L,$[Cl^-]$=20 mg/L and [Cr(VI)]=10 mg/L.

Three Cr(III) solids exhibited different reaction kinetics with chlorine based on experimental observations (Figure 3.1A). Chlorine was stable in the control without any Cr(III) solid. Approximately 10% of chlorine was consumed in the presence of $Cr_2O_{3(s)}$ within 300 minutes. More than 90% of chlorine was consumed in the presence of either $Cr(OH)_{3(s)}$ or $Cu_2Cr_2O_{5(s)}$ within the same reaction time. Accompanied with chlorine consumption, Cr(VI) was formed (Figure 3.1B). The difference in reactivity among the three Cr(III) solids was caused by distinct surface areas and reactive sites among the Cr(III) solids. BET surface areas of three Cr(III) solids varied by two orders of magnitude (Table 3.2). The consumption of chlorine and formation of Cr(VI) were consistently observed at varying Cr(III)-to-chlorine molar ratios (Figure 3.2).

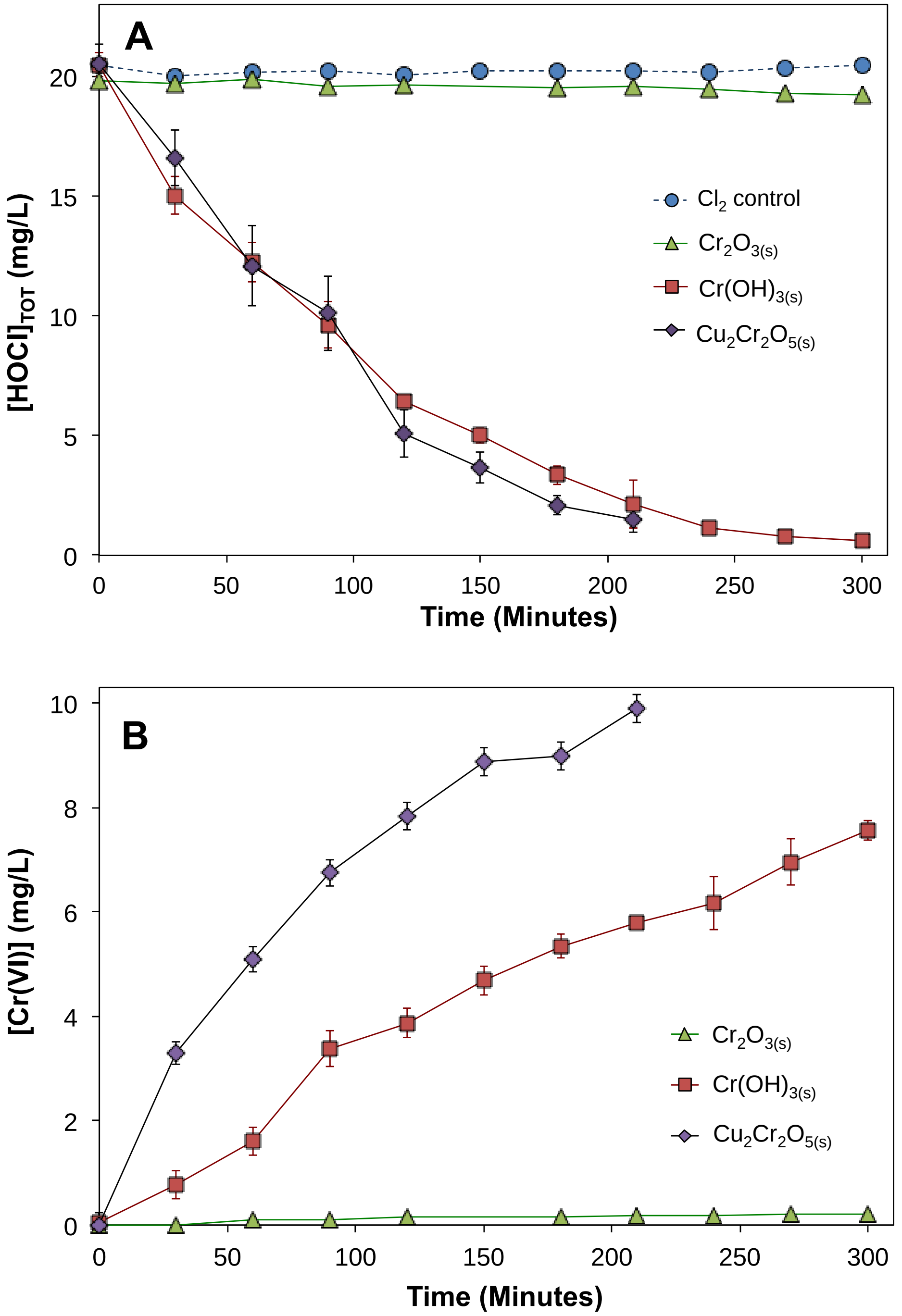


Figure 3.1 The oxidation of three Cr(III) solids by chlorine. (A) Chlorine consumption profile; (B) hexavalent chromium formation profile. pH=7.0, initial [HOCl]$_{TOT}$= 20 mg Cl_2/L, molar ratio of Cr(III)/Cl_2=10:1, ionic strength=10 mM.

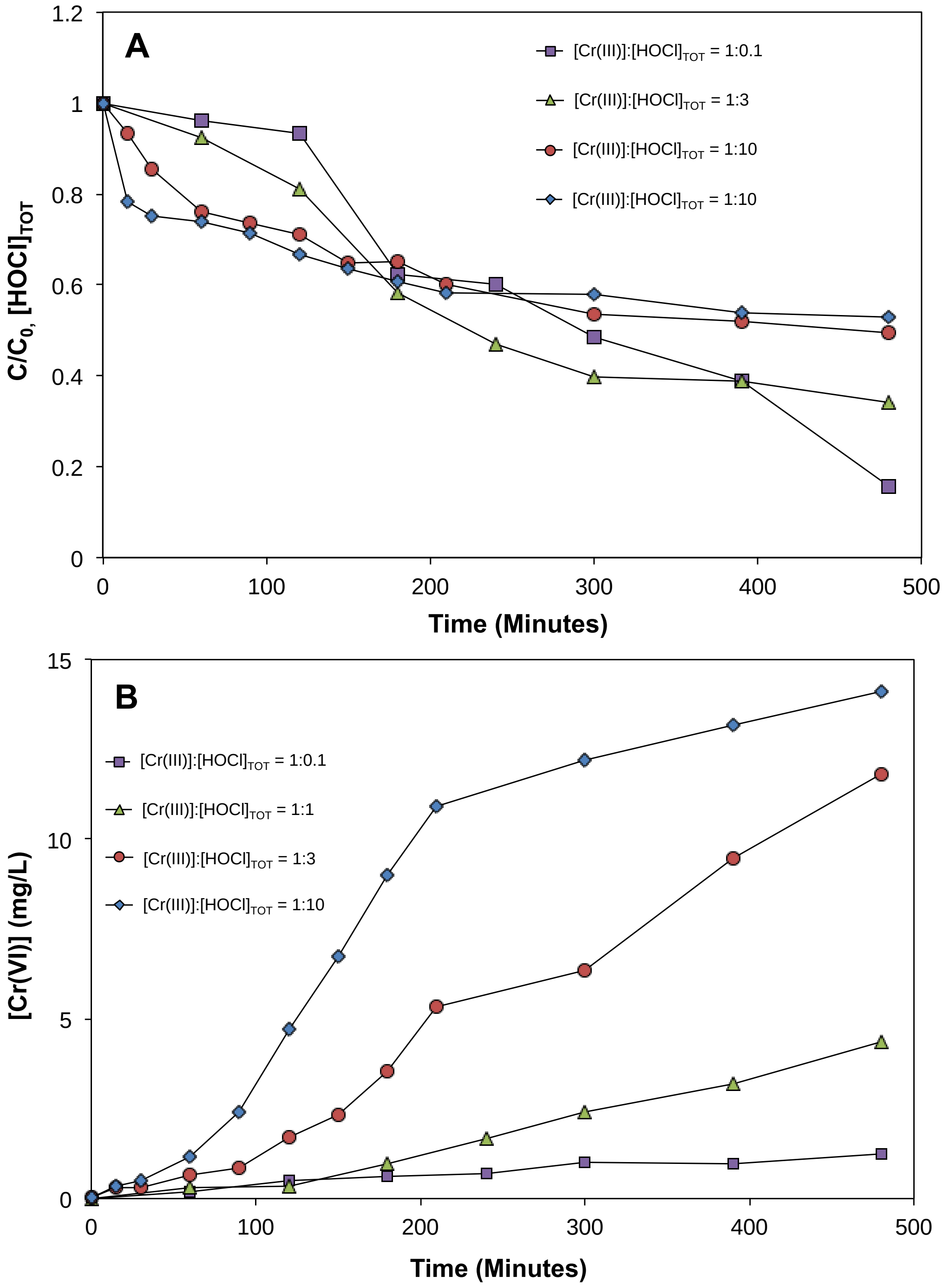


Figure 3.2 Effect of initial Cr(III)-to-chlorine molar ratio on the Cr(III) oxidation by chlorine. (A) Chlorine consumption; (B) Cr(VI) formation with time on $Cr(OH)_{3(s)}$ oxidation. Cr(III):Cl_2 ratio was varied. Initial [Cr(III)]=0.28 mM. Ionic strength=10 mM. pH=7.

Table 3.2 Summary of the chemical properties and environmental relevance of three Cr(III) solids investigated in this study.

Cr(III) Solids	**pH_{pzc}**	**BET Surface Area (m^2/g)**	**Relevance to Drinking Water**	**References**
Chromium hydroxide $Cr(OH)_{3(s)}$	7.9	159.3	Precipitate during Fe(II)-assisted coagulation step in drinking water treatment.	21-27,33-34
Chromium oxide $Cr_2O_{3(s)}$	3.5	1.9	Corrosion product in water distribution systems.	33-35,37
Copper chromite $Cu_2Cr_2O_{5(s)}$	7.4	39.9	Potential wastewater contaminant and corrosion product in copper piping.	36

To quantify the reaction kinetics of Cr(III) oxidation by chlorine, a second-order kinetics model was developed to describe the rate of chlorine consumption and Cr(VI) formation:

$$\frac{d[HOCl]_{TOT}}{dt} = -k_{Cl_2}[Cr(III)_{(s)}][HOCl]_{TOT}(S_{Cr(III)_{(s)}}) \tag{4}$$

$$\frac{d[(Cr(VI)]_{TOT}}{dt} = k_{Cr(VI)}[Cr(III)_{(s)}][HOCl]_{TOT}(S_{Cr(III)_{(s)}}) \tag{5}$$

k_{Cl_2} in Equation 4 and $k_{Cr(VI)}$ in Equation 5 are the surface area normalized rate constants for chlorine consumption and Cr(VI) formation, respectively ($L \bullet m^{-2} \bullet s^{-1}$). [$Cr(III)_{(s)}$] is the concentration of Cr (III) solids (g/L). $[HOCl]_{TOT}$ is the total concentration of free chlorine including both hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), *i.e.*,

$[HOCl]_{TOT}=[HOCl]+[OCl^-]$ (mol/L). $S_{Cr(III)(s)}$ is the BET surface area of a particular Cr(III) solid (m^2/g) (Table 3.2).

Solution pH had a modest impact on the reaction kinetics (Figures 3.3-3.5). Based on data fitting with the kinetics model, the chlorine consumption rate constant k_{Cl_2} shows a dependence on pH (Figure 3.6A). For $Cr_2O_{3(s)}$, k_{Cl_2} increased by 200% when the solution pH increased from 6.0 to 8.5. For $Cu_2Cr_2O_{5(s)}$, the rate constant increased by approximately 450% within the same range of pH increase. For $Cr(OH)_{3(s)}$, the rate constant increased with pH and reached the maximum at pH 7.0. The model-fitted rate constant $k_{Cr(VI)}$ was also impacted by pH (Figure 3.6B). For $Cr_2O_{3(s)}$, the rate of Cr(VI) formation increased by 35% with an increase of pH from 6.0 to 8.5. For $Cu_2Cr_2O_{5(s)}$, the rate increased by 100% with the same change of pH. For $Cr(OH)_{3(s)}$, the rate of Cr(VI) formation increased by approximately 425% when pH changed from 6.0 to 7.0. Comparing all three Cr(III) solids, the rates of Cr(VI) formation at typical drinking water pHs (7.0-8.0) followed the order of $Cu_2Cr_2O_{5(s)} > Cr(OH)_{3(s)} > Cr_2O_{3(s)}$ (Figure 3.6B). The rate at which $Cu_2Cr_2O_{5(s)}$ was converted to Cr(VI) by chlorine was approximately one order of magnitude higher than $Cr_2O_{3(s)}$.

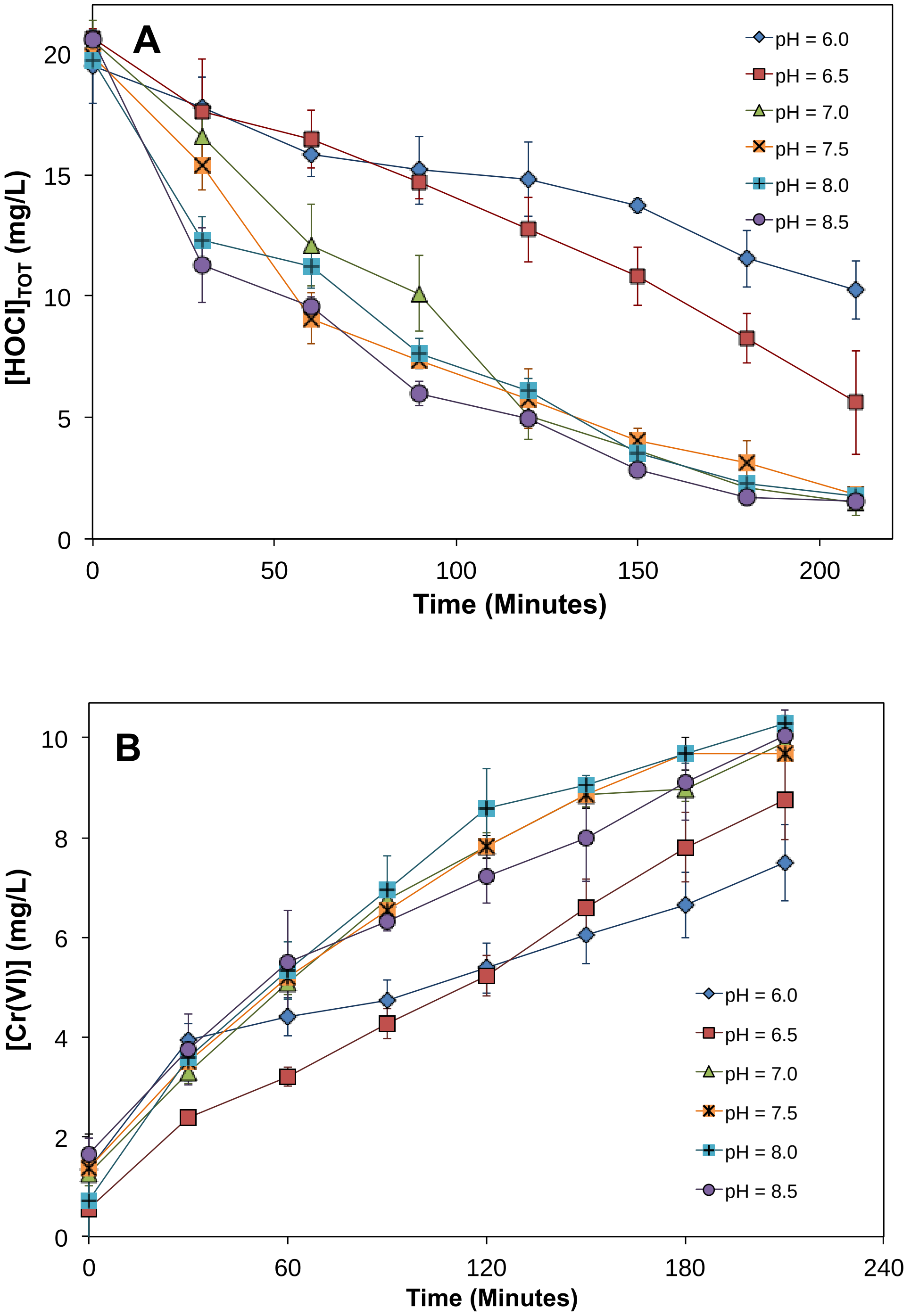


Figure 3.3 Impact of pH on the oxidation of $Cu_2Cr_2O_{5(s)}$ by chlorine. (A) Chlorine consumption profile; (B) Cr(VI) formation profile. Initial [HOCl]=20 mg/L as Cl_2, $[Cu_2Cr_2O_{5(s)}]$=2.8 mM, molar ratio of Cr(III)/Cl_2=10:1, ionic strength=10 mM.

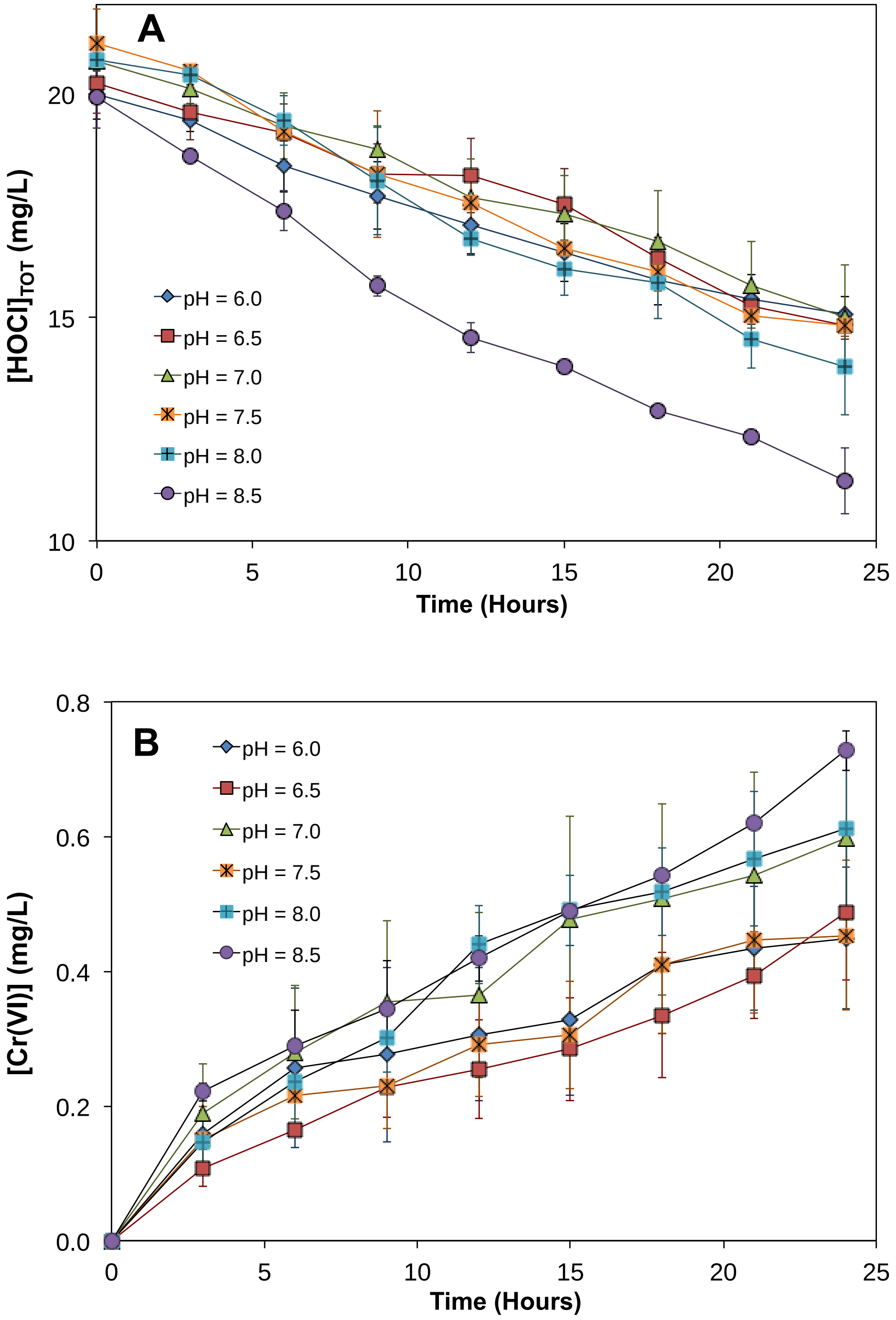


Figure 3.4 Impact of pH on the oxidation of Cr_2O_3(s) by chlorine. (A) Chlorine consumption profile; (B) Cr(VI) formation profile. Initial [Cl_2]=20 mg/L as Cl_2, [$Cr_2O_{3(s)}$]=2.8 mM, molar ratio of Cr(III):Cl_2=10:1, ionic strength=10 mM.

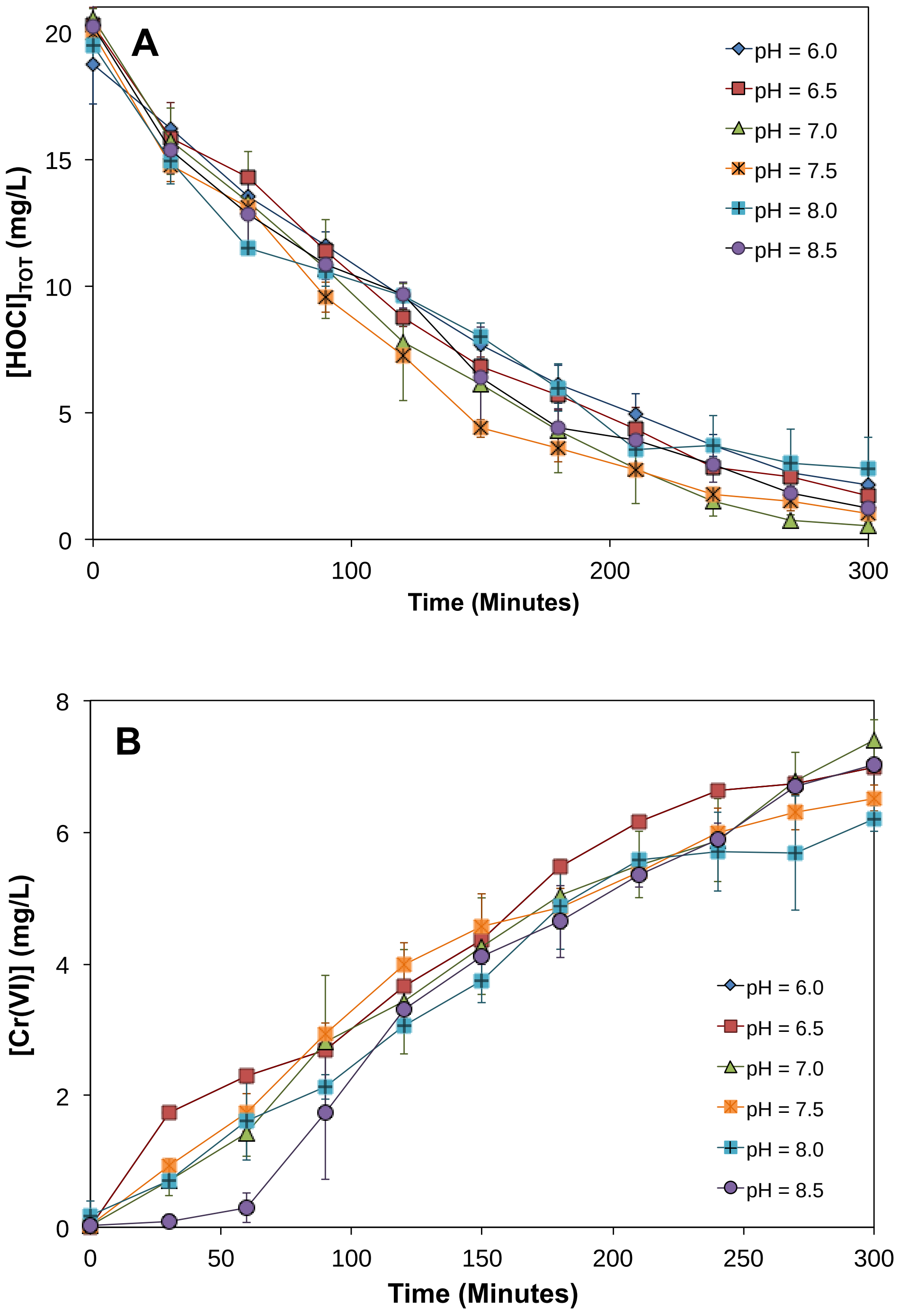


Figure 3.5 Impact of pH on the oxidation of $Cr(OH)_{3(s)}$ by chlorine. (A) Chlorine consumption profile; (B) Cr(VI) formation profile. Initial $[Cl_2]$=20 mg/L as Cl_2, $[Cr(OH)_{3(s)}]$=2.8 mM, molar ratio of Cr(III):Cl_2=10:1, ionic strength=10 mM.

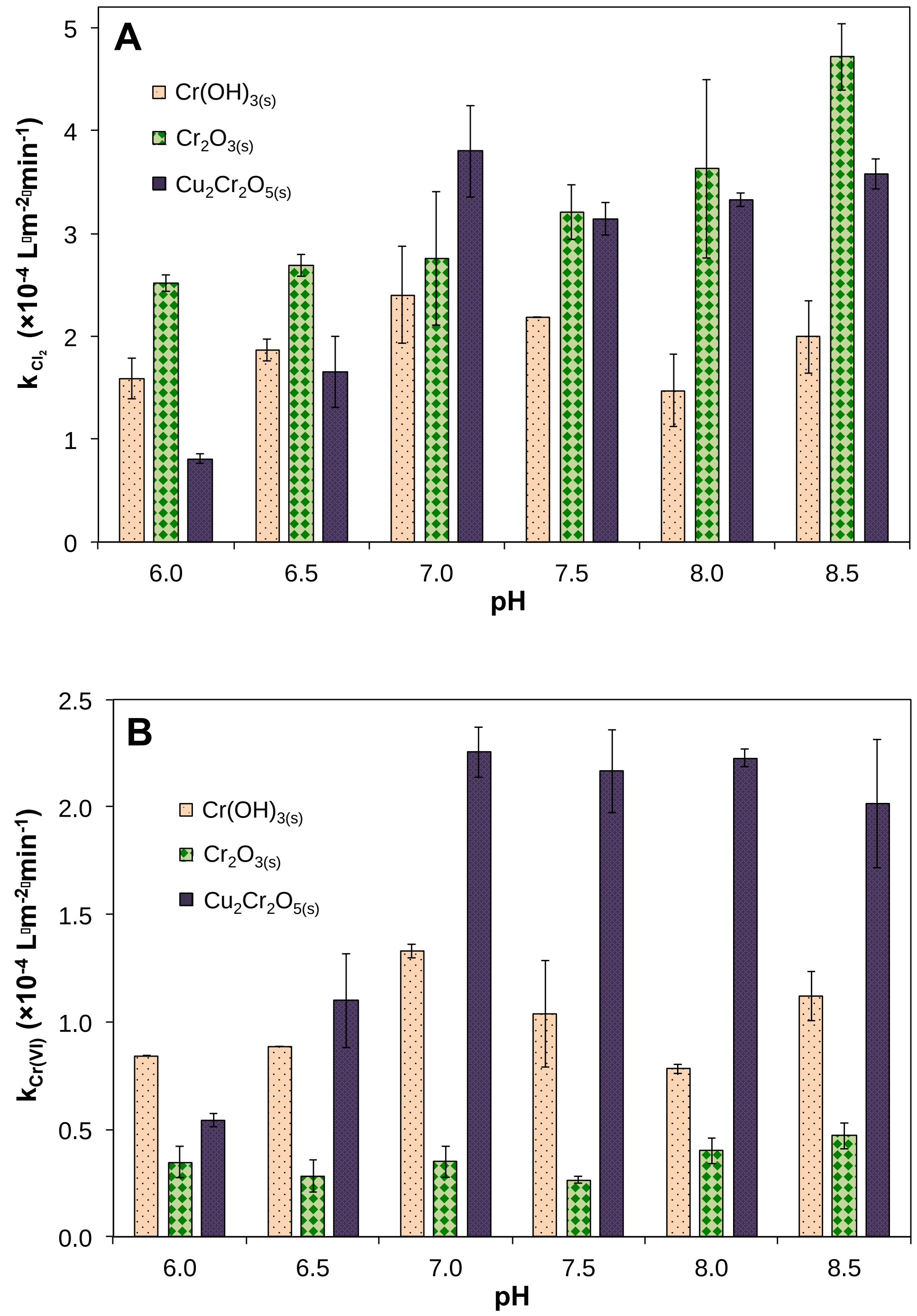


Figure 3.6 Effect of pH on the surface area normalized second-order rae constants of Cr(III) oxidation by chlorine. (A) Chlorine consumption rate; (B) Cr(VI) formation rate. Initial [Cr(III)]=2.8 mM, [Cl_2]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, ionic strength=10 mM.

The unique effects of pH on the oxidation rate of Cr(III) solids can be attributed to three factors. First, pH affects chlorine speciation. Chlorine exists as HOCl or OCl^- with a pK_a of 7.6. HOCl is more oxidative and more electrophilic than OCl^-.[56,57] Second, pH affects speciation of Cr(III) surface hydroxo species. Similar to other transition metals,[58-61] the predominance of Cr(III) surface hydroxo complexes with different coordination numbers of -OH groups varies with pH.[7,62,63] Because each surface hydroxo species possesses distinct reactivity with chlorine, the resultant reactivities of Cr(III) solids changes with pH.

Third, each Cr(III) solid has distinct Cr(III) surface species, as shown by the changes of zeta potential with pH (Figure 3.7). At neutral pH, the surface of $Cr_2O_{3(s)}$ was negatively charged, whereas the other two Cr(III) solids were positively charged. Change of zeta potential that exceeded 40 mV between pH 6.0 and 8.5 suggests that protonation-active Cr(III) hydroxo species exist on the surface of all three Cr(III) solids. The negative shift of zeta potential with pH suggests the formation of negatively charged Cr(III) hydroxo surface species whose existence has been postulated.[64] These negatively charged Cr(III) hydroxo species are stronger nucleophiles and more likely to be oxidized by HOCl. The differences among the three Cr(III) solids are evidently due to a higher prominence of protonation-active surface sites on the surface of $Cr(OH)_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$, and a very different structural organization among these Cr(III) solids.

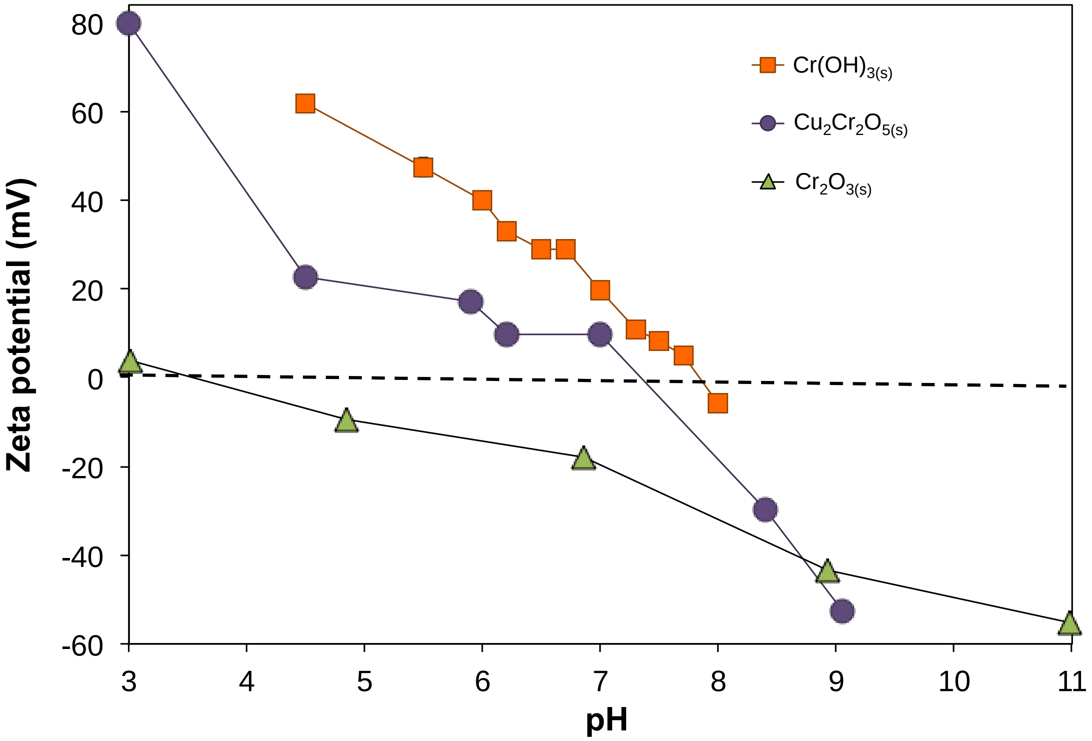


Figure 3.7 Change in zeta potential with pH for all three Cr(III) solids. pH was varied by adding varying amounts of $HClO_4$ and NaOH. Ionic strength=10 mM. Suspension of Cr(III) solids=0.2 g/L.

Reaction stoichiometry and chlorine auto-catalytic decay by Cr(III)

Based on the theoretical stoichiometry of chlorine oxidation (Reactions 1-3), the ratio of cumulative Cr(VI) formation to cumulative chlorine consumption at any reaction time (denoted as $\Delta[Cr(VI)]/\Delta[HOCl]_{TOT}$) is expected to be 0.67. However, experimental data showed that this ratio was much less than the theoretical value (Figure 3.8 -3.10). Therefore, the yield of Cr(VI) did not account for all the chlorine consumed during chlorine oxidation of Cr(III) solids.

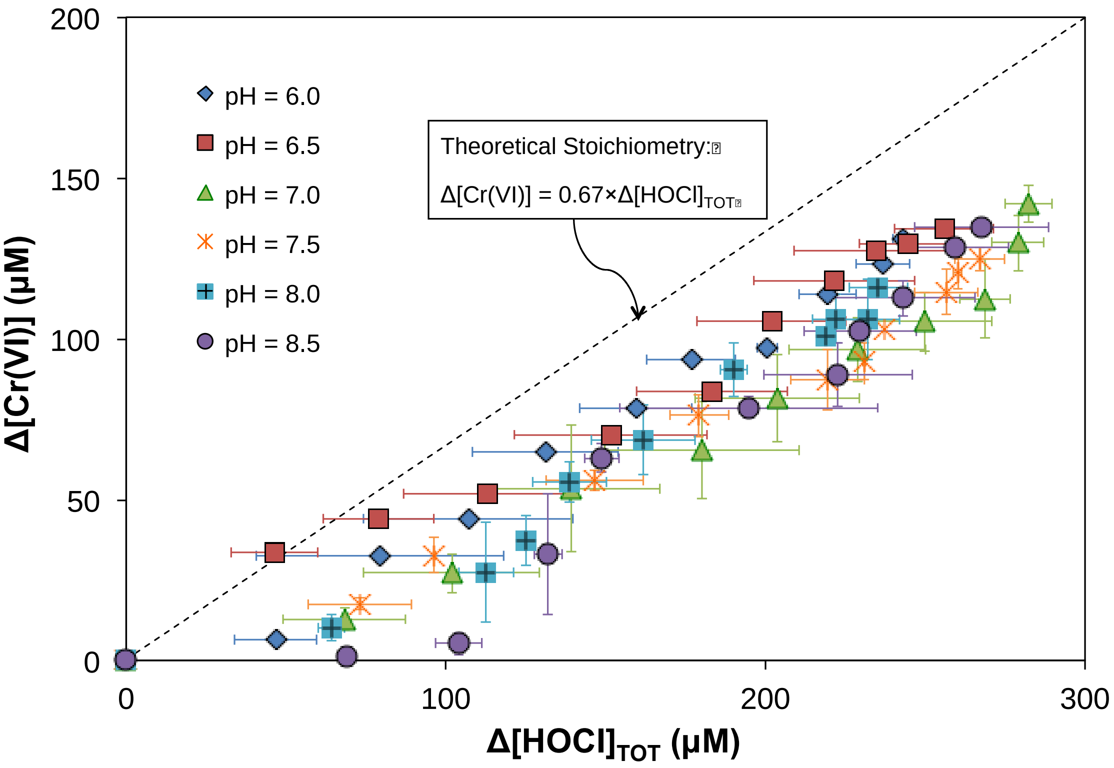


Figure 3.8 The experimentally observed stoichiometry of cumulative Cr(VI) formation with respect to cumulative chlorine consumption. The theoretical stoichiometry is 0.67, but the experimentally observed values were below 0.67. Initial $[Cl_2]$=20 mg/L as Cl_2, $[Cr(OH)_{3(s)}]$=2.8 mM, Cr(III):HOCl=10:1. Bromide was not present.

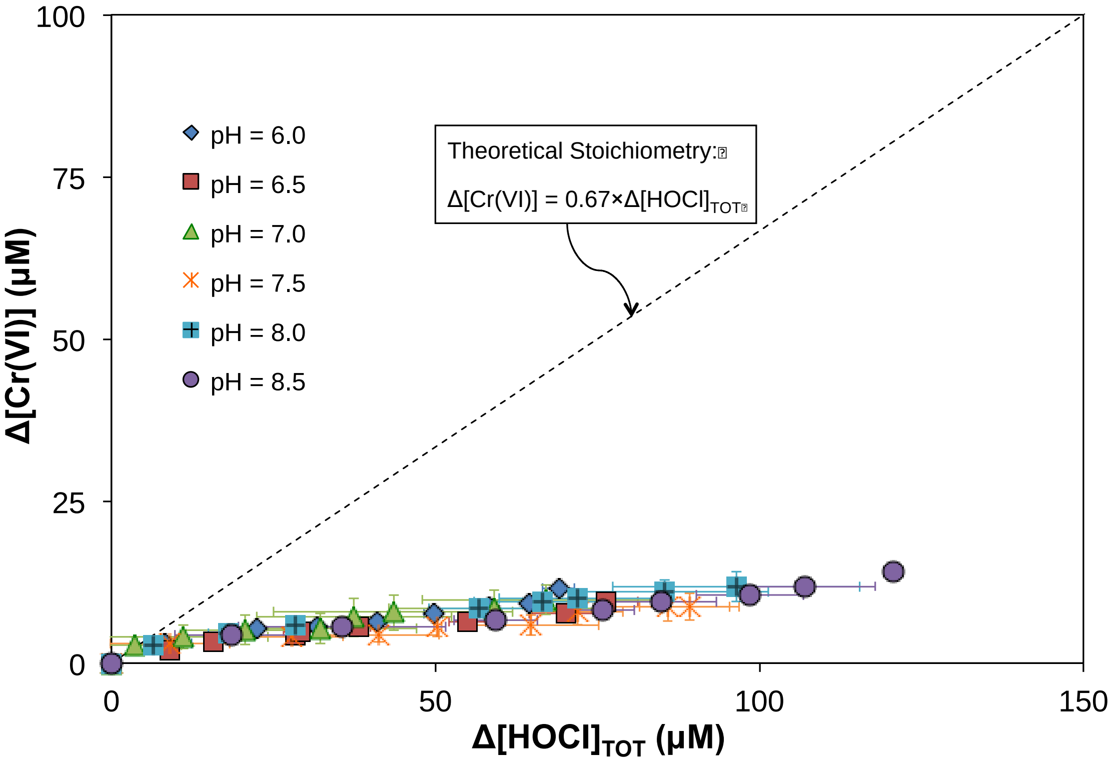


Figure 3.9 Cumulative Cr(VI) formation vs. Cl_2 consumption at varying pHs for $Cr_2O_{3(s)}$ oxidation by chlorine. Molar ratio of Cr(III):Cl_2 was 10:1 with the initial concentration of Cr(III) at 2.8 mM. Ionic strength of solution was 10 mM $NaClO_4$. pH was regulated with 0.05 mM $HClO_4$ and NaOH. The theoretical stoichiometric molar ratio of ΔCr(VI):ΔCl_2 is 0.67.

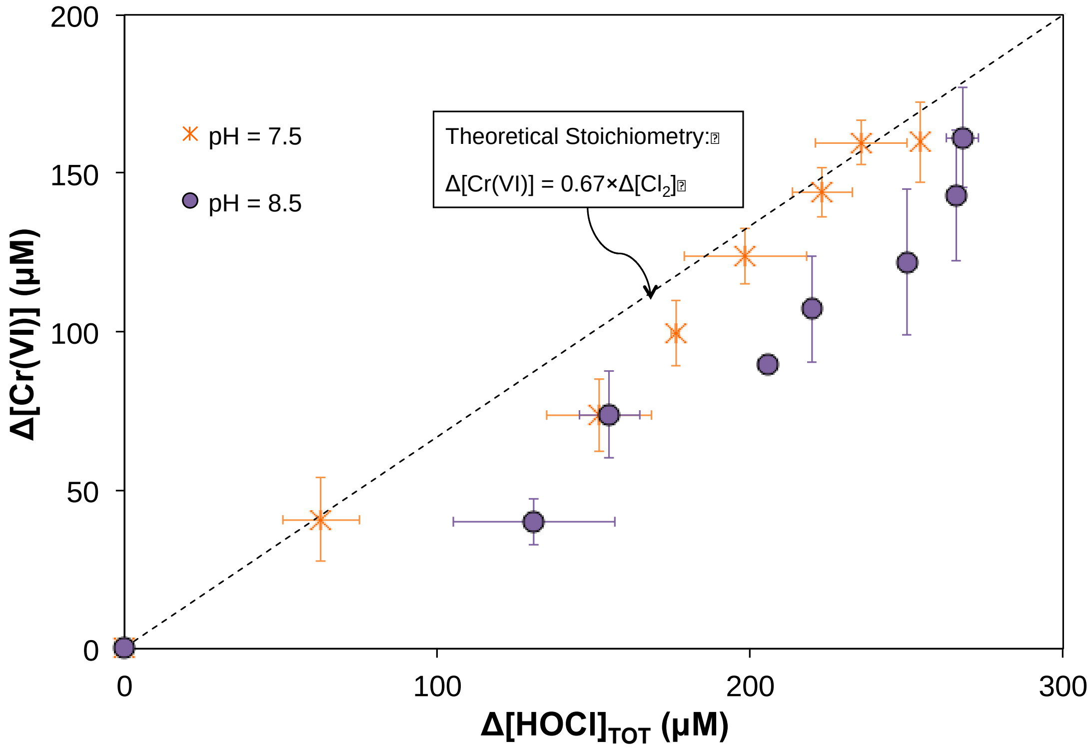


Figure 3.10 Cumulative Cr(VI) formation vs. Cl_2 consumption at varying pHs for $Cu_2Cr_2O_{5(S)}$. Molar ratio of Cr(III):Cl_2 was 10:1 with the initial concentration of Cr(III) at 2.8 mM. Ionic strength of solution was 10 mM $NaClO_4$. pH was regulated with 0.05 mM $HClO_4$ and NaOH. The theoretical stoichiometric molar ratio of ΔCr(VI):ΔCl_2 is 0.67.

The observed stoichiometry suggests that the oxidation of Cr(III) by chlorine is simultaneously accompanied by an auto-catalytic decay of chlorine, and it proceeds with the formation of chromium intermediates as part of a multi-step oxidation process. The oxidation of Cr(III) solids by chlorine can generate Cr(V) intermediate species in the form of Cr(V) oxide (denoted as *Cr(V)O**) as the first step (Reaction 6):

$$Cr(III)_{(s)} + HOCl \rightarrow Cr(V)O^{*} + Cl^{-} + H^{+} \qquad (6)$$

Unstable *Cr(V)O** intermediates can quickly decompose to Cr(III) and generate dissolved oxygen (Reaction 7):

$$Cr(V)O^{*} \rightarrow Cr(III)_{(S)} + \frac{1}{2}O_2 \qquad (7)$$

The overall reaction becomes:

$$HOCl \xrightarrow[Cr(V)O^{*}]{Cr(III)} \frac{1}{2}O_2 + H^{+} + Cl^{-} \qquad (8)$$

Reaction 8 predicts an auto-catalytic decay of chlorine in the presence of Cr(III) solids. This process involves unstable Cr intermediates that facilitate the decomposition of chlorine to Cl^- and dissolved O_2. Based on the experimental data, the fraction of chlorine that underwent auto-catalytic pathway accounted for 5%, 30% and 70% of total chlorine consumption during the oxidation of $Cu_2Cr_2O_{5(s)}$, $Cr(OH)_{3(s)}$ and $Cr_2O_{3(s)}$, respectively. This follows exactly the descending order of Cr(VI) formation rates among the three solids (Figure 3.6B). As more chlorine undergoes auto-catalytic pathway (Reaction 8), less chlorine is readily available to converts Cr(III) to Cr(VI) (Reactions 1-3), which results in the overall stoichiometry of $\Delta[Cr(VI)]/\Delta[HOCl]_{TOT}$ to be less than the theoretical value of 0.67. Previous studies reported Cr intermediates including pentavalent Cr(V) and tetravalent Cr(IV) during the redox cycling between Cr(III) and Cr(VI).[65 - 68] These intermediates are also formed when Cr(VI) is reduced by cytoplasmic fluids in human cells.[69-72] Auto-catalytic decay of chlorine by other transition metals such as Cu(II) in drinking water was also reported.[73,74]

To further assess the auto-catalytic decay of chlorine by Cr(III) solids, additional oxidation experiments were conducted in the absence of oxygen with a suspension of $Cr(OH)_{3(s)}$, $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$, respectively, and dissolved O_2 concentrations were measured. Results showed that dissolved O_2 was produced when $Cr(OH)_{3(s)}$ was mixed together with chlorine in 300 minutes (Figure 3.11A). This was accompanied by the consumption of chlorine and formation of Cr(VI) (Inserted graph in Figure 3.11A). In the control experiments with only $Cr(OH)_{3(s)}$ or chlorine, no O_2 was produced (Figure 3.11A). By subtracting the amount of chlorine consumed by auto-catalytic decay based on O_2 production (*i.e.*, $2\times\Delta[O_2]$, based on Reaction 8) from total chlorine consumption, the amount of chlorine that directly oxidized $Cr(OH)_{3(s)}$ (*i.e.*, $\Delta[HOCl]_{TOT} - 2\times\Delta[O_2]$) showed the expected stoichiometry of 0.67 with respect to Cr(VI) formation (Figure 3.11B). Similar trend of dissolved O_2 production and stoichiometry were observed for $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$, respectively (Figures 3.12 and 3.13). This correlation strongly supports the existence of auto-catalytic decay of chlorine and the involvement of Cr intermediate species, *e.g.*, Cr(V).

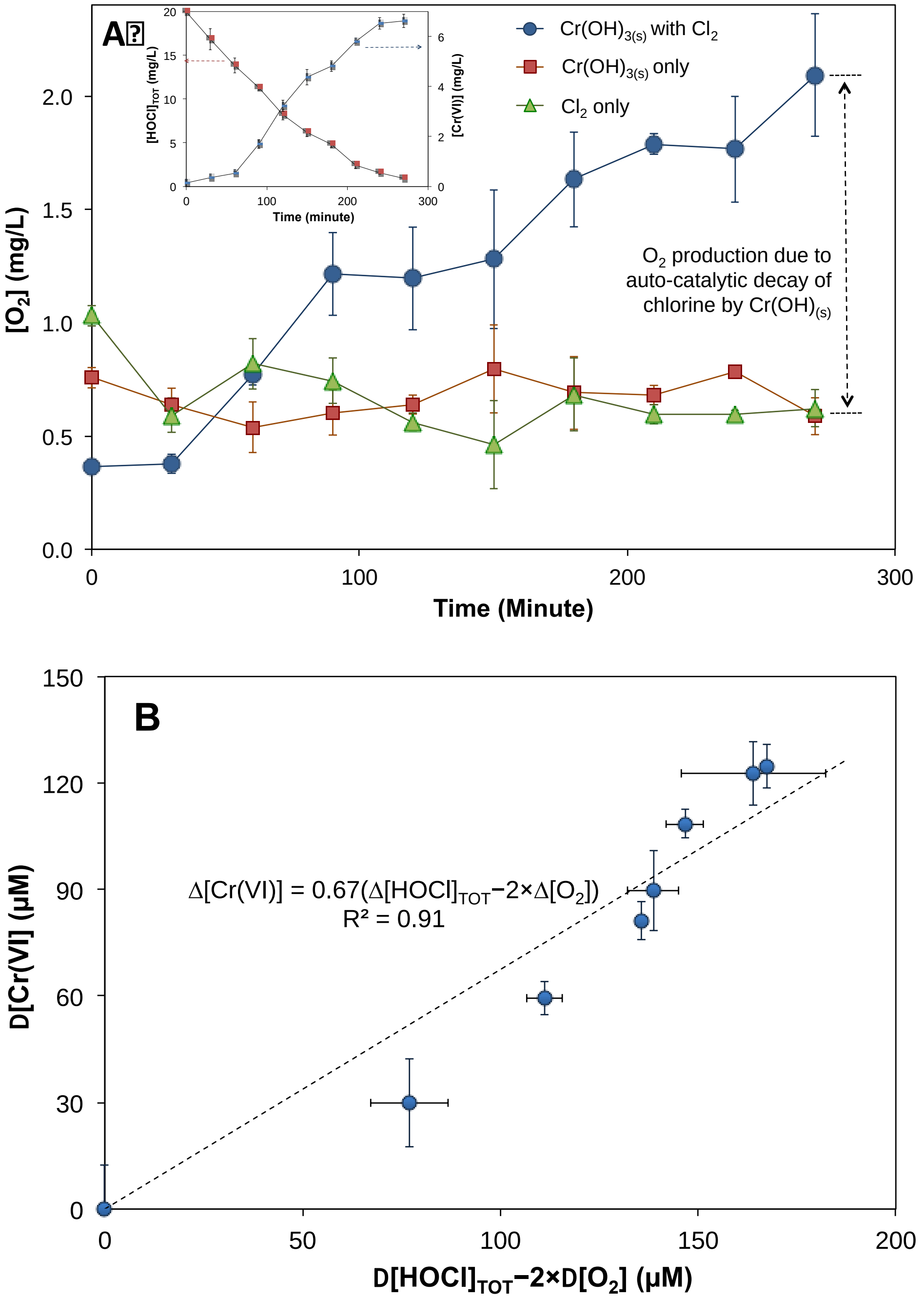


Figure 3.11 Oxidation of Cr(OH)$_{3(s)}$ by chlorine. (A) Production of dissolved O_2; (B) Revised stoichiometry of Cr(VI) formation considering the auto-catalytic decay of chlorine. Initial [Cl_2]=20 mg Cl_2/L, molar ratio of Cr(III)/Cl_2=10:1, pH=7.0, ionic strength=10 mM.

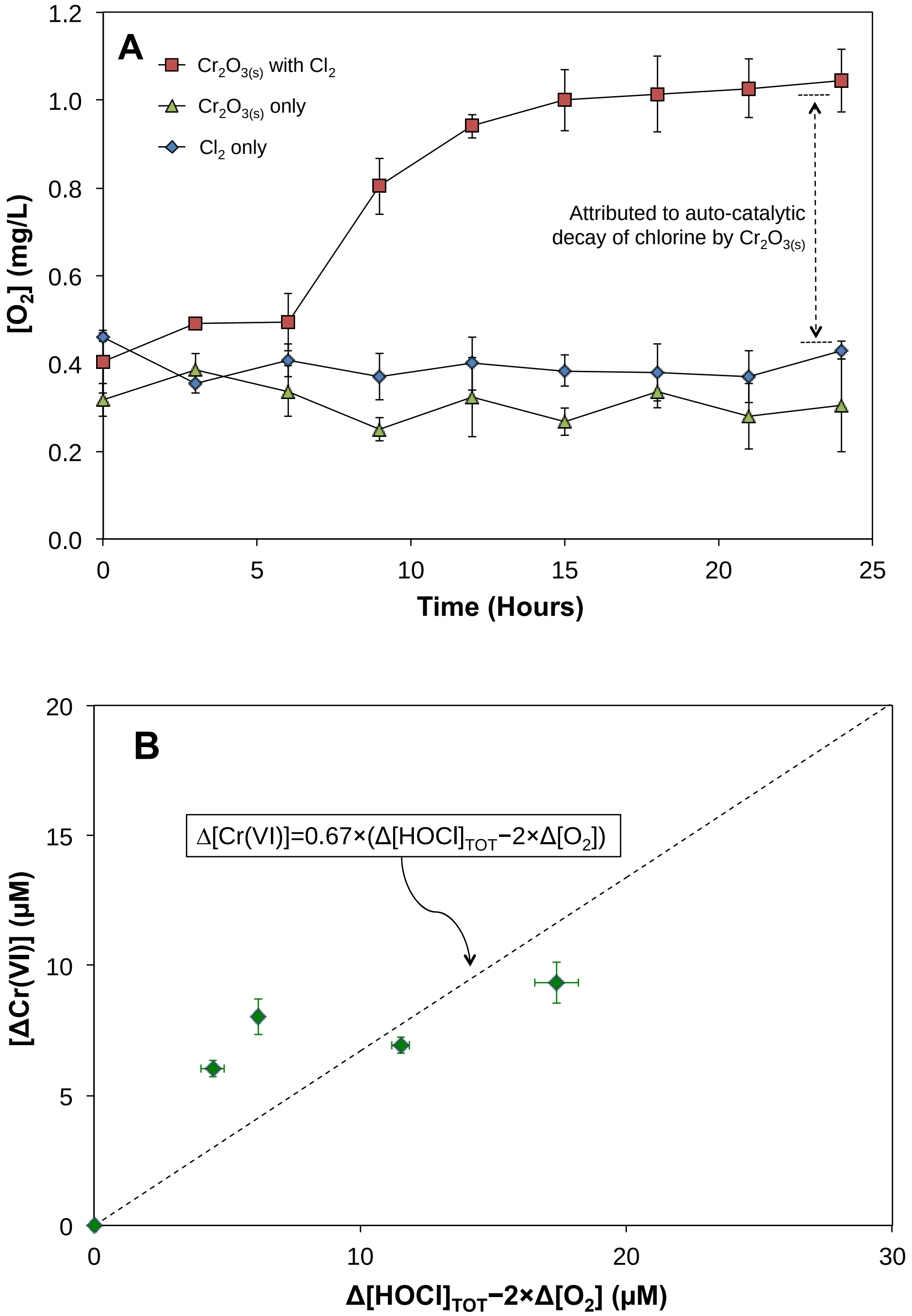


Figure 3.12 Oxidation of $Cr_2O_{3(s)}$ by chlorine. (A) Dissolved O_2 profile; (B) Revised stoichiometry of Cr(VI) formation considering catalytic decay of chlorine. Initial $[Cl_2]$=20 mg Cl_2/L, molar ratio of Cr(III)/Cl_2=10:1, pH=7.0, ionic strength=10 mM.

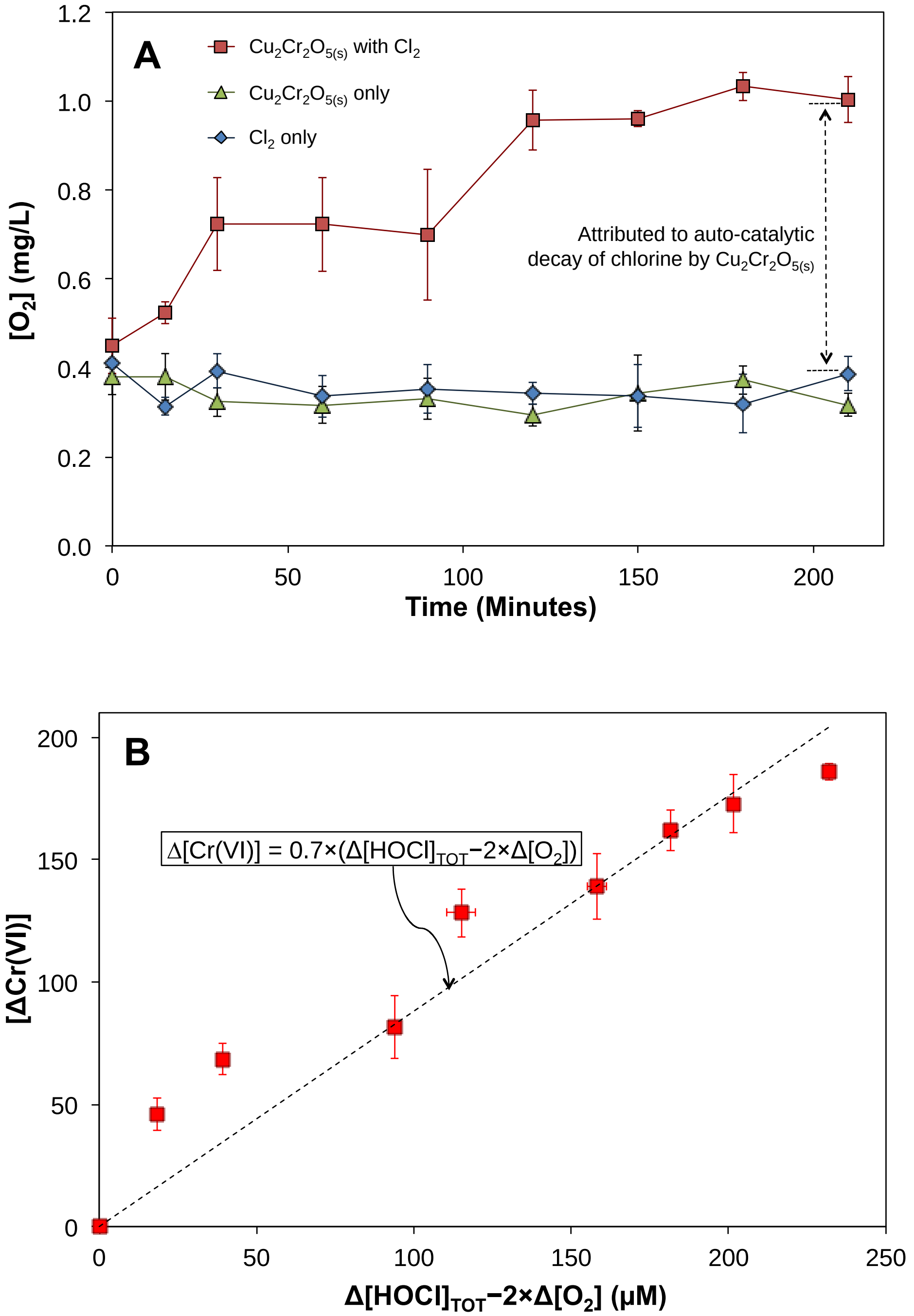


Figure 3.13 Oxidation of $Cu_2Cr_2O_{5(s)}$ by chlorine. (A) Dissolved O_2 profile; (B) Revised stoichiometry of Cr(VI) formation considering catalytic decay of chlorine. Initial $[Cl_2]$=20 mg Cl_2/L, molar ratio of Cr(III)/Cl_2=10:1, pH=7.0, ionic strength=10 mM.

Impact of bromide on Cr(III) solids oxidation by chlorine

The presence of bromide significantly accelerated the oxidation of Cr(III) solids by chlorine (Figure 3.14). For example, after 24 hours of oxidation of $Cr_2O_{3(s)}$, chlorine consumption increased by 50% when bromide concentration increased from 0 to 0.1 mg/L, and further increased by 50% when 5 mg/L of bromide was present after reaction (Figure 3.14A). Meanwhile, Cr(VI) formation increased by one order of magnitude when bromide concentration increased from 0 to 0.1 mg/L, and further increased by 100% when 5 mg/L of bromide was present (Figure 3.14B). The enhancement in reaction rate was particularly significant at bromide levels less than 1 mg/L. In systems with $Cr(OH)_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$, similar catalytic effects in the presence of bromide were observed (Figures 3.15 and 3.16).

The effects of bromide on chlorine consumption and Cr(VI) formation result from a catalytic reaction mechanism. Bromide readily reacts with HOCl to generate bromine, specifically, hypobromous acid (HOBr) in the pHs examined in this study:[75]

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad k_5 = 1.55\times10^{3}\ M^{-1}s^{-1} \qquad (9)$$

Under the conditions studied here (*i.e.*, $[Br^-]$=0.1-5.0 mg/L; $[Cr(III)_{(s)}]$=2.8 mM), Reaction 9 is much faster than any of Reactions 1-3 and essentially accounts for all the chlorine consumption. As Reaction 9 proceeds, HOBr can oxidize $Cr(III)_{(s)}$ to generate Cr(VI) and reproduce bromide. In the case of $Cr(OH)_{3(s)}$:

$$2Cr(OH)_{3(s)} + 3HOBr \rightarrow 2CrO_4^{2-} + 3Br^- + 7H^+ + H_2O \qquad (10)$$

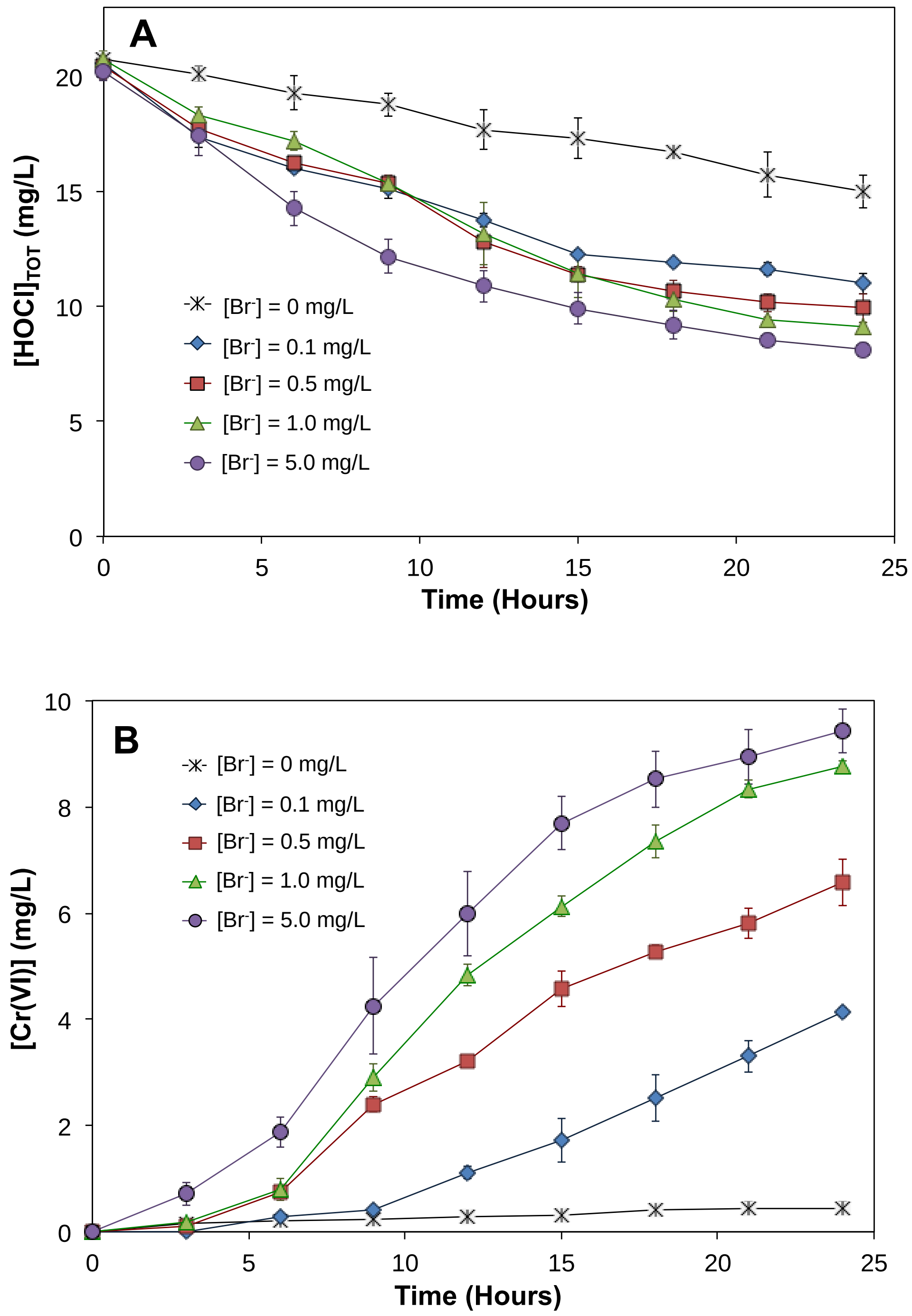


Figure 3.14 Impact of bromide concentration on the oxidation of $Cr_2O_{3(s)}$ by chlorine. (A) Chlorine consumption profile; (B) Cr(VI) formation profile. Initial [Cl_2]=20 mg/L as Cl_2, [$Cr_2O_{3(s)}$]=2.8 mM, Cr(III): Cl_2=10:1, pH=7.5, ionic strength = 10 mM.

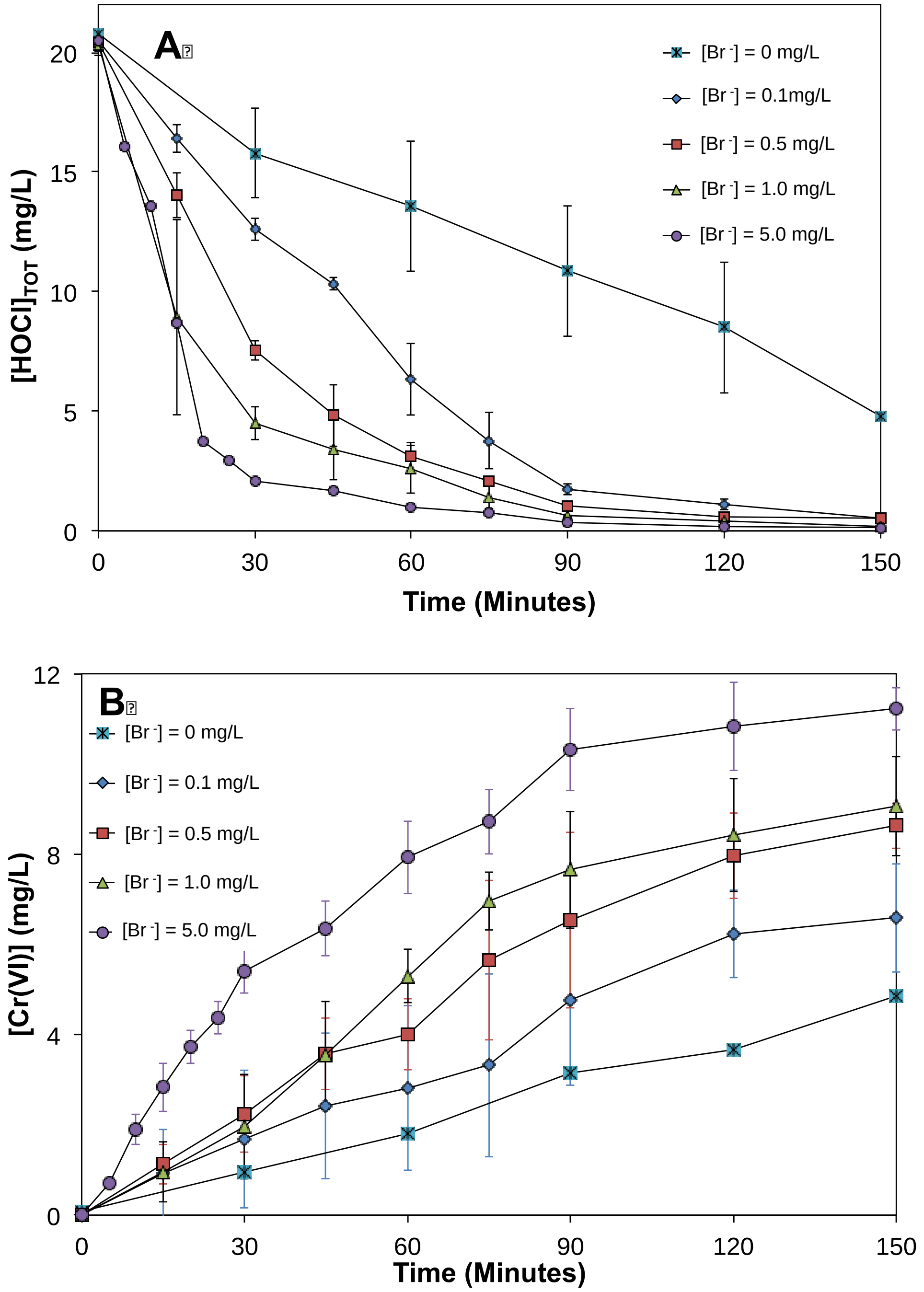
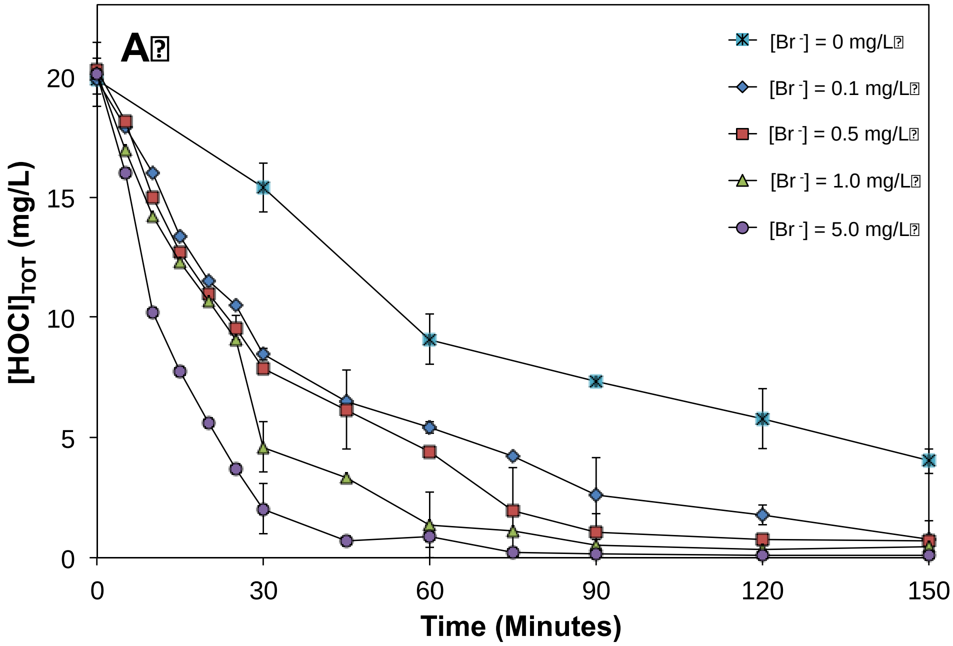


Figure 3.15 Impact of bromide concentration on the oxidation of $Cr(OH)_{3(s)}$ by chlorine. (A) Chlorine consumption profile; (B) Cr(VI) formation profile. $[Cl_2]$=20 mg/L as Cl_2, $[Cr(OH)_{3(s)}]$=2.8 mM, Cr(III):Cl_2=10:1, pH=7.5



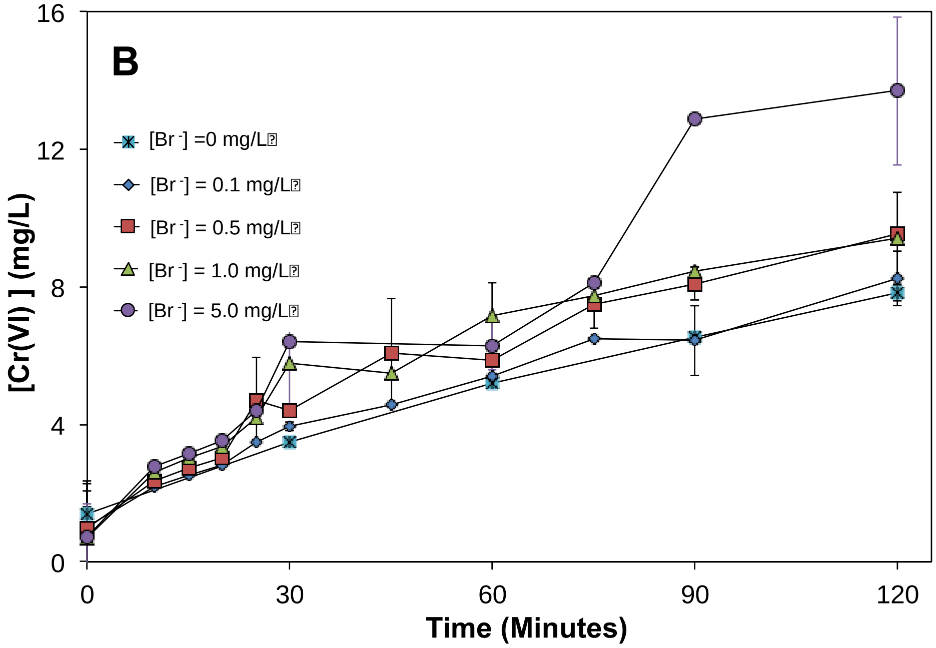


Figure 3.16 Impact of bromide concentration on the oxidation of $Cu_2Cr_2O_{5(s)}$ by chlorine. (A) Chlorine consumption profile; (B) Cr(VI) formation profile. $[Cl_2]$=20 mg/L as Cl_2, $[Cu_2Cr_2O_{5(s)}]$=2.8 mM, Cr(III):Cl_2=10:1, pH=7.5

The surface area normalized rate constants of Reaction 10 at pH 7.0 and 7.5 are 1.2×10^{-3} and 1.5×10^{-3} $L\cdot m^{-2}\cdot min^{-1}$, respectively, calculated from the oxidation of $Cr(OH)_{3(s)}$ by HOBr (Figure 3.17). Meanwhile, the rates of $Cr(OH)_{3(s)}$ oxidation by HOCl (Reaction 1) are 2×10^{-4} and 2.2×10^{-4} $L\cdot m^{-2}\cdot min^{-1}$ at these two pHs (Figure 3.6A). Bromine oxidation rates are approximately 6 times of the chlorine oxidation rates with respect to $Cr(OH)_{3(s)}$ (Reaction 10 *vs*. Reaction 1). Prior studies demonstrated that HOBr is more electrophilic than HOCl and therefore more reactive toward electron-rich compounds including Mn(II),[53] ammonia,[76] phenols,[77, 78] steroid estrogens,[79] and dissolved organic matter with amines and phenolic moieties.[80,81] In the redox system of this study, the reactive surface sites of Cr(III) solids serve as electron-rich centers to react with HOBr. Combining Reactions 9-10, the overall bromide-catalyzed oxidation of $Cr(OH)_{3(s)}$ by chlorine becomes (Reaction 11):

$$2Cr(OH)_{3(s)} + 3HOCl \xrightarrow[HOBr]{Br^-} 2CrO_4^{2-} + 3Cl^- + 7H^+ + H_2O \qquad (11)$$

Similarly, bromide-catalyzed oxidation of $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$ by chlorine can proceed, respectively (Reactions 12-13):

$$Cr_2O_{3(s)} + 3HOCl + 2H_2O \xrightarrow[HOBr]{Br^-} 2CrO_4^{2-} + 3Cl^- + 7H^+ \qquad (12)$$

$$Cu_2Cr_2O_{5(s)} + 3HOCl \xrightarrow[HOBr]{Br^-} 2CrO_4^{2-} + 3Cl^- + 3H^+ + 2Cu^{2+} \qquad (13)$$

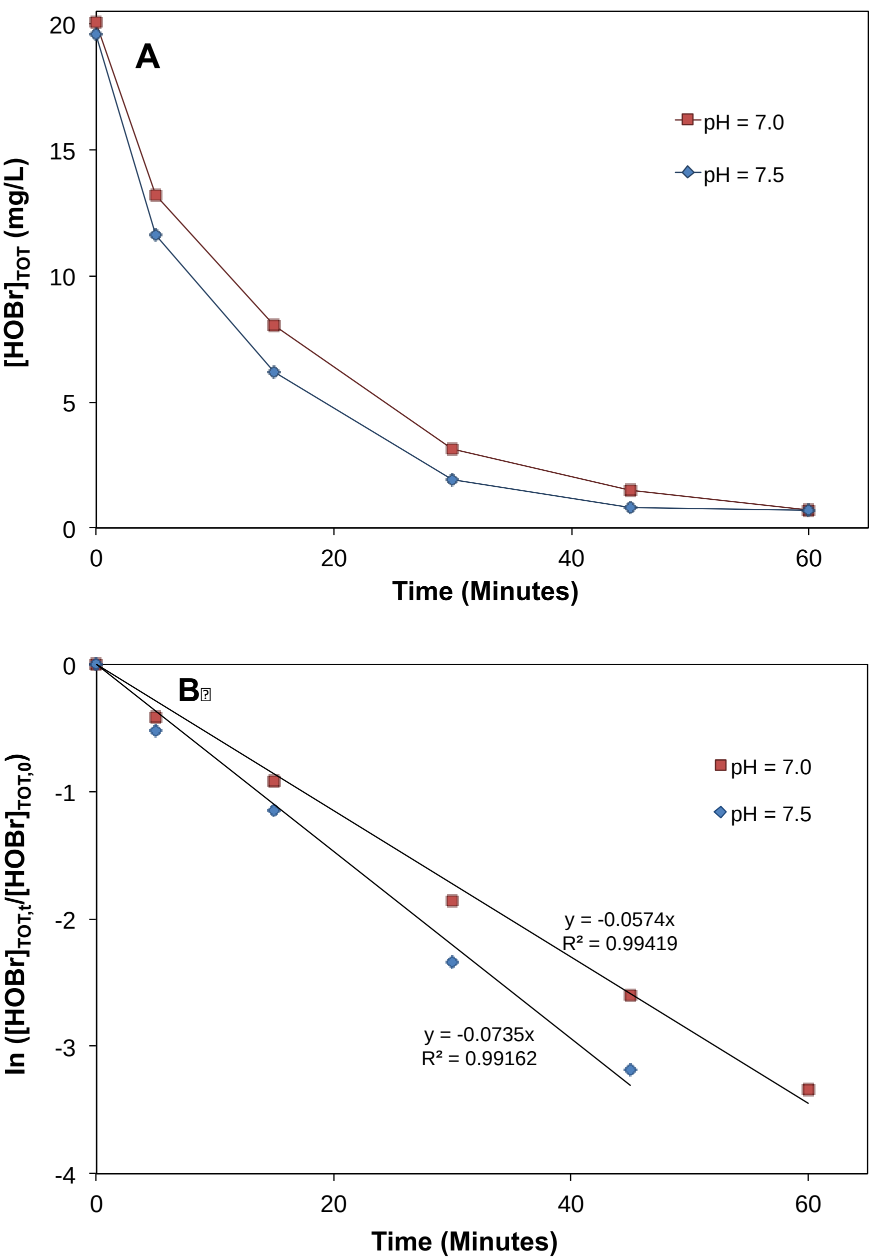


Figure 3.17 The reaction kinetics of oxidation of $Cr(OH)_{3(s)}$ by HOBr at pH 7 and 7.5. (A) Consumption of HOBr with time; (B) Correlation of HOBr consumption rate with a first-order reaction kinetics. Initial [HOBr]=0.28 mM, molar ratio of Cr(III):HOBr = 10:1. Ionic strength=10 mM. The pseudo first-order rate constants from Figure S14B was divided by the molar concentration and BET surface area of $Cr(OH)_{3(s)}$ to obtain the second-order rate constants of 1.2 and 1.5×10^{-3} $L\cdot m^{-2}\cdot min^{-1}$ at pH 7.0 and 7.5, respectively. This value is referred to as $k_{formation}$ in Text A.A.3 in the Appendix.

Bromide essentially acts as an electron shuttle that catalytically promotes the oxidation of $Cr(III)_{(s)}$ by chlorine. Based on the kinetics model (Equations 4-5), surface area normalized rate constants of Reactions 11-13 were obtained with different bromide concentrations (Figure 3.18). In general, the presence of bromide ranging between 0.1 and 1.0 mg/L increased both k_{Cl_2} and $k_{Cr(VI)}$ by 3 to 20 times. The catalytic effect was less prominent when bromide concentration was higher than 1 mg/L, indicating that the oxidation rate was limited by the availability of reactive Cr(III) surface sites at higher bromide concentrations.

In addition, calculation based on steady-state assumption of HOBr and Br^- shows that HOBr concentration was approximately 8 times higher than that of Br^- at a given reaction time (Text A.A.3 in Appendix A). The formation of bromate (BrO_3^-) was negligible from the reaction, although other studies reported the formation of BrO_3^- via HOBr decay during the chlorination of transition metals such as Cu(II).[54]

Furthermore, the observed stoichiometry of $\Delta[Cr(VI)]/\Delta[HOCl]_{TOT}$ during chlorine oxidation of $Cr(III)_{(s)}$ increased significantly and approached 0.67 in the presence of bromide (Figure 3.19), which was consistent with the expected stoichiometry (Reactions 11-13). Because HOBr is the actual oxidant that drives the oxidation of Cr(III) in bromide-catalyzed oxidation, the data suggest that HOBr oxidizes Cr(III) solid phases with a stoichiometric conversion to Cr(VI), possibly without the auto-catalytic decay of HOBr or formation of Cr intermediate species.

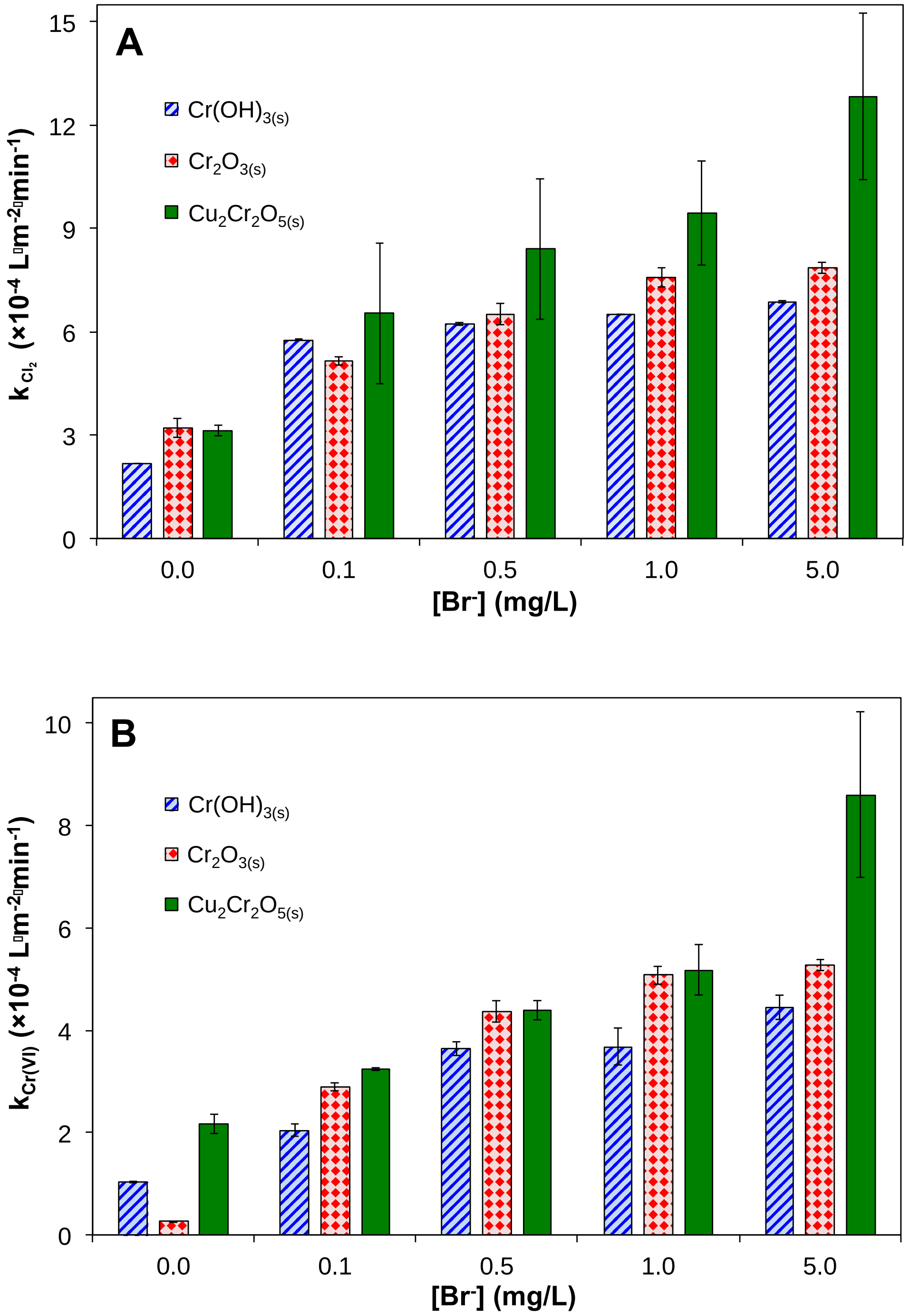


Figure 3.18 Effect of bromide on the surface area normalized second-order rate constants of Cr(III) oxidation by chlorine. (A) Chlorine consumption rate; (B) Cr(VI) formation rate. Initial [Cr(III)]=2.8 mM, [Cl_2]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, ionic strength=10 mM. pH=7.5.

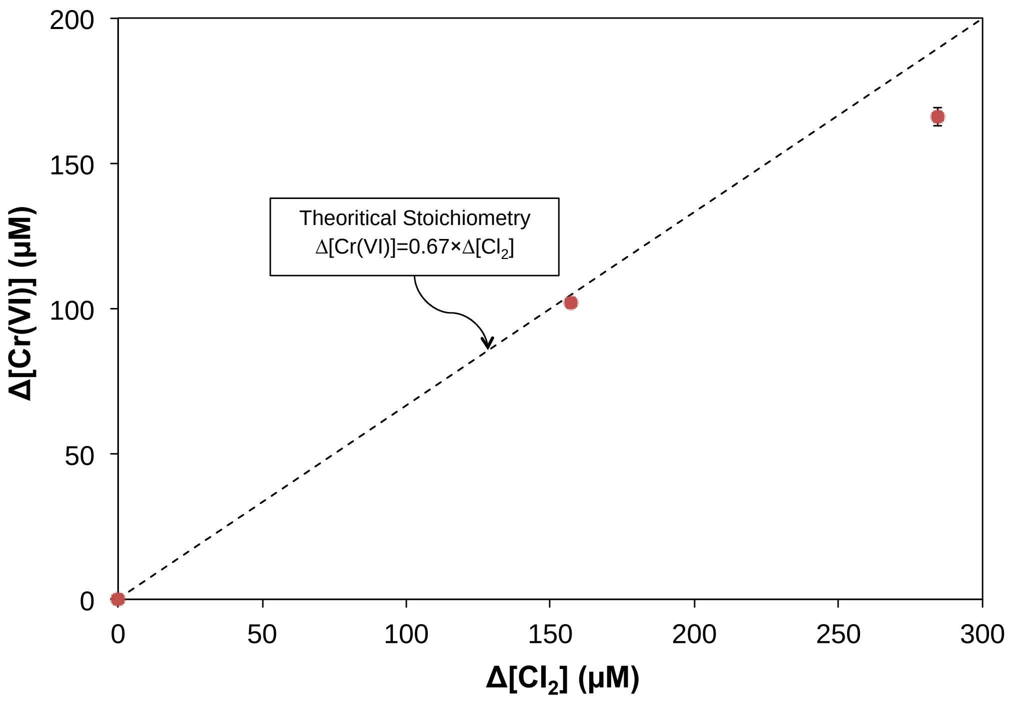


Figure 3.19 Correlation between cumulative Cr(VI) formation and cumulative chlorine consumption Δ[Cl_2] in the presence of bromide during the oxidation of $Cr(OH)_{3(s)}$ by chlorine. Initial [$Cr(OH)_{3(s)}$]=2.8 mM, molar ratio of Cr(III):Cl_2=10:1, [Br^-]=5 mg/L, ionic strength=10 mM,. pH=7.0.

To further examine the unique pathway of $Cr(III)_{(s)}$ oxidation involving bromide, additional oxidation experiments were conducted between each Cr(III) solid and HOBr. Results show that the pathway of $Cr(III)_{(s)}$ oxidation by HOBr is very different from oxidation by HOCl. Oxidation of $Cr_2O_{3(s)}$ by HOBr at pH 7.0 exhibited a negligible production of dissolved O_2 (Figure 3.20A), although rapid HOBr consumption and Cr(VI) formation occurred (inserted plot in Figure 3.20A). In contrast to chlorine system, the stoichiometry of [Cr(VI)]/Δ$[HOBr]_{TOT}$ followed the expected value of 0.67 (Figure 3.20B). The other two Cr(III) solids also exhibited stoichiometry similar to 0.67 during HOBr oxidation (Figure 3.21).

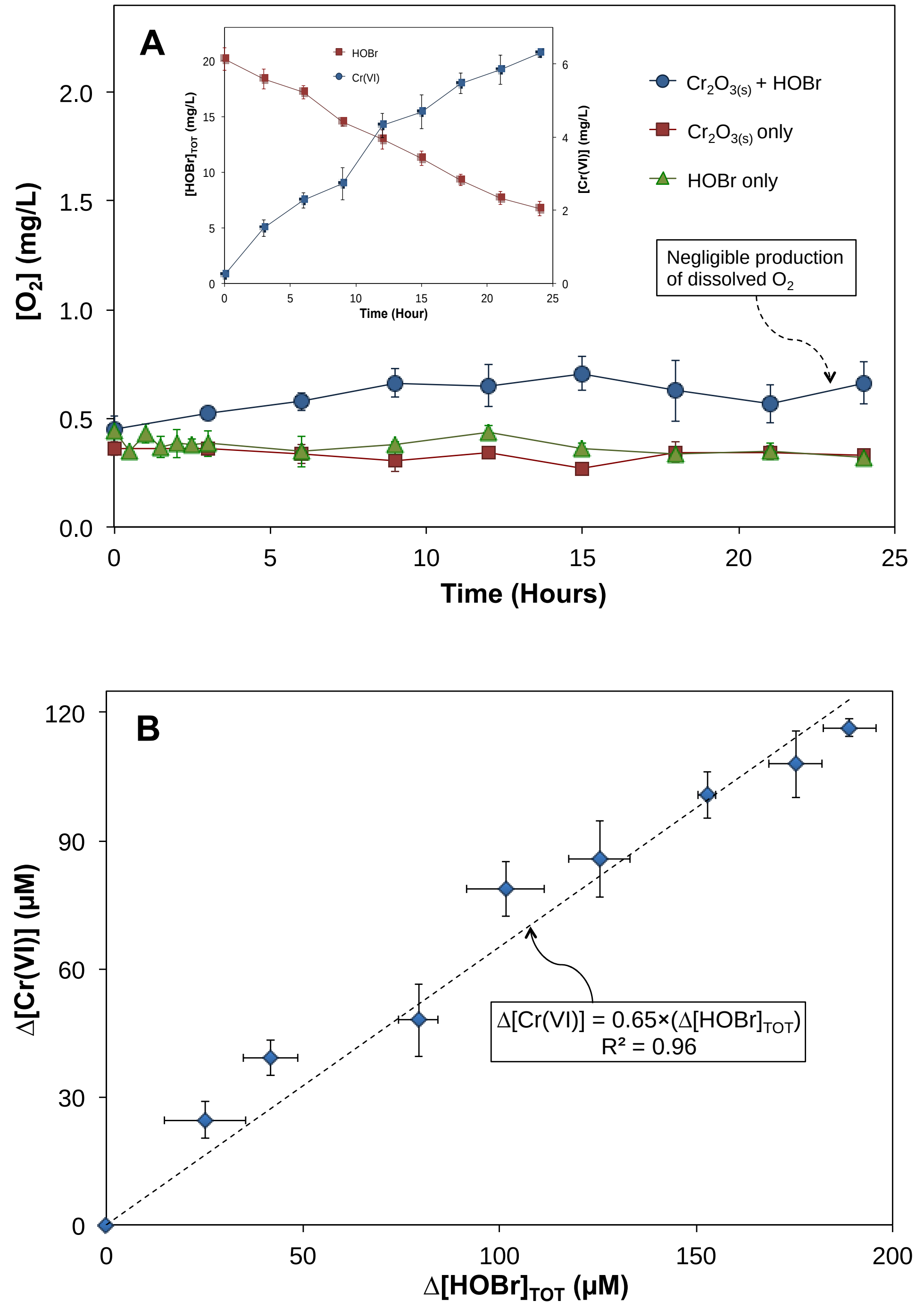


Figure 3.20 Oxidation of $Cr_2O_{3(s)}$ by HOBr. (A) Measurements of dissolved O_2; (B) Stoichiometry of Cr(VI) formation with HOBr consumption. Initial [HOBr]=280 μM, molar ratio of Cr(III)/Cl_2=10:1, pH=7.0, ionic strength=10 mM.

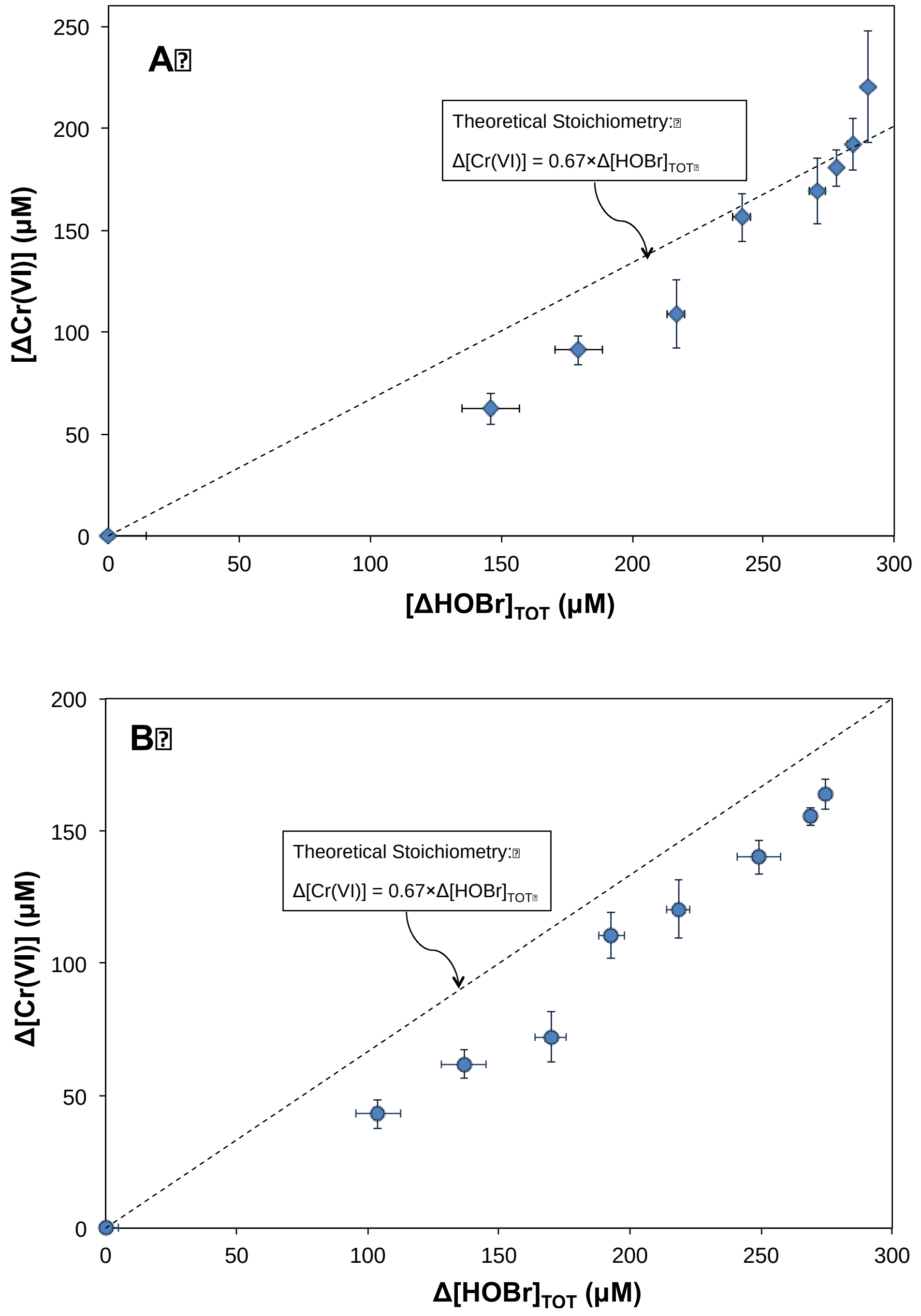


Figure 3.21 Stoichiometry of Cr(VI) formation with HOBr consumption during the oxidation of Cr(III)$_{(s)}$ by HOBr. (A) $Cu_2Cr_2O_{5(s)}$; (B) $Cr(OH)_{3(s)}$. Initial [HOBr]=280 μM, molar ratio of Cr(III):Cl_2=10:1, pH=7.0, ionic strength=10 mM.

The stoichiometry analysis indicates that bromine oxidation of Cr(III) solids does not generate significant Cr intermediates that can subsequently dissociate to produce O_2. Bromine does not undergo auto-catalytic decay in the presence of Cr(III) solids. This mechanism explains the observed higher rate constants of Cr(VI) formation during bromine oxidation. Because the oxidation of Cr(III) solids by chlorine in the presence of bromide is essentially driven by bromine (Reaction 9), a reaction pathway that bypasses the formation of Cr intermediates can significantly increase the yield of Cr(VI), which is consistent with the observed catalytic effect of bromide on Cr(VI) formation.

Environmental implications

Findings from this study demonstrated possible Cr(VI) reoccurrence in drinking water distribution systems due to the oxidation of Cr(III) solids by chlorine, especially in the presence of trace levels of bromide. Based on the rate constants obtained from this study and the statistical distribution of bromide concentrations in U.S. source waters, the kinetics model predicts Cr(VI) can be generated in drinking water distribution systems from cumulated Cr(III) solids (Text A.A.4 in Appendix A). For example, considering a typical residence time of two days in a drinking water distribution system that contains 100 µg/L of $Cr(OH)_{3(s)}$ and a chlorine residual of 0.3 mg/L, Cr(VI) concentration in tap water can increase by 2.5, 3.0 and 4.6 µg/L by the catalytic effect of bromide, based on 5th, 50th and 95th percentile distribution of bromide concentrations, respectively (Figure 3.22). The existence of $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{3(s)}$ as Cr(III) solids in water distribution system can increase Cr(VI) level by 0.3 to 5 µg/L. In addition, Cr(VI) formation in the tap can be further enhanced with an increase of residence time in water distribution systems (Figure 3.22).

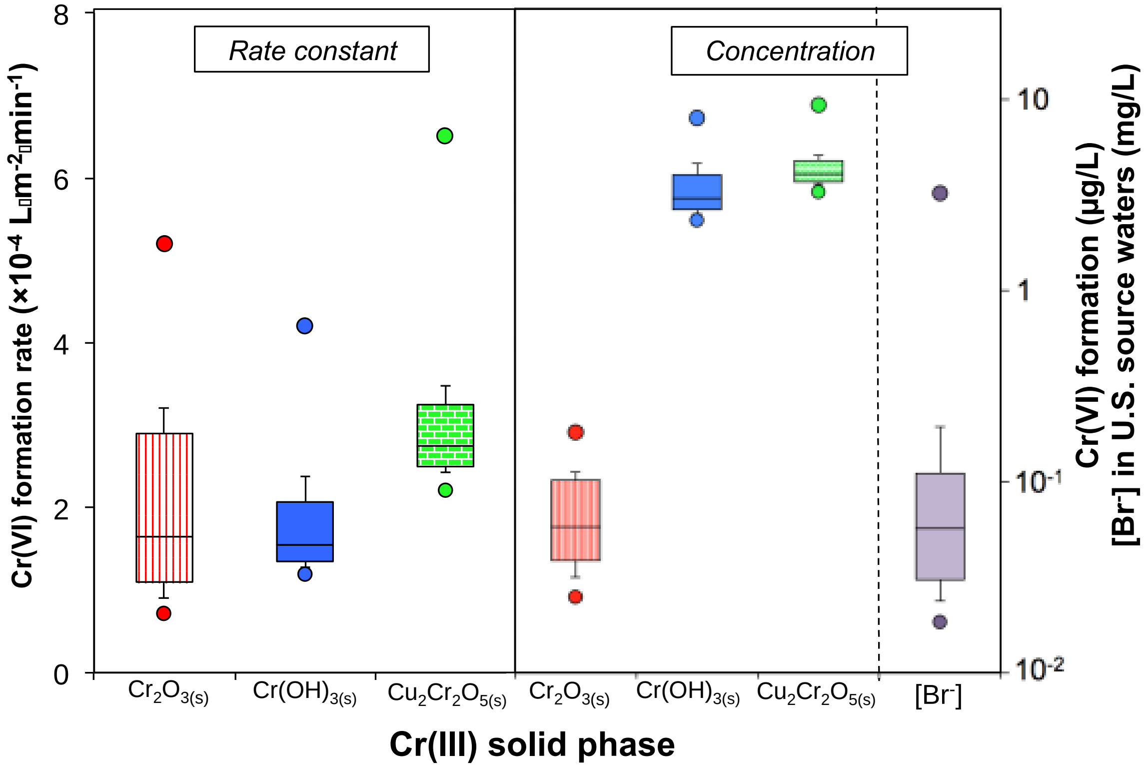


Figure 3.22 Box plot of predicted Cr(VI) formation rate constants and the enhanced Cr(VI) formation in drinking water distribution system. Solid line in each box is median value. lower and upper box edges are 25th and 75th percentiles, respectively. Whisker bars represents 5th and 95th percentiles. Solid dots are the minimum and maximum values. The percentile distributions are predicted based on statistical distributions of bromide concentration in U.S. source waters (*refs. 49-51*). The kinetics model simulation on enhanced Cr(VI) formation is based on a water distribution system with 0.3 mg/L chlorine residual, 100 µg/L residual Cr(III) solids and a residence time of 2 days.

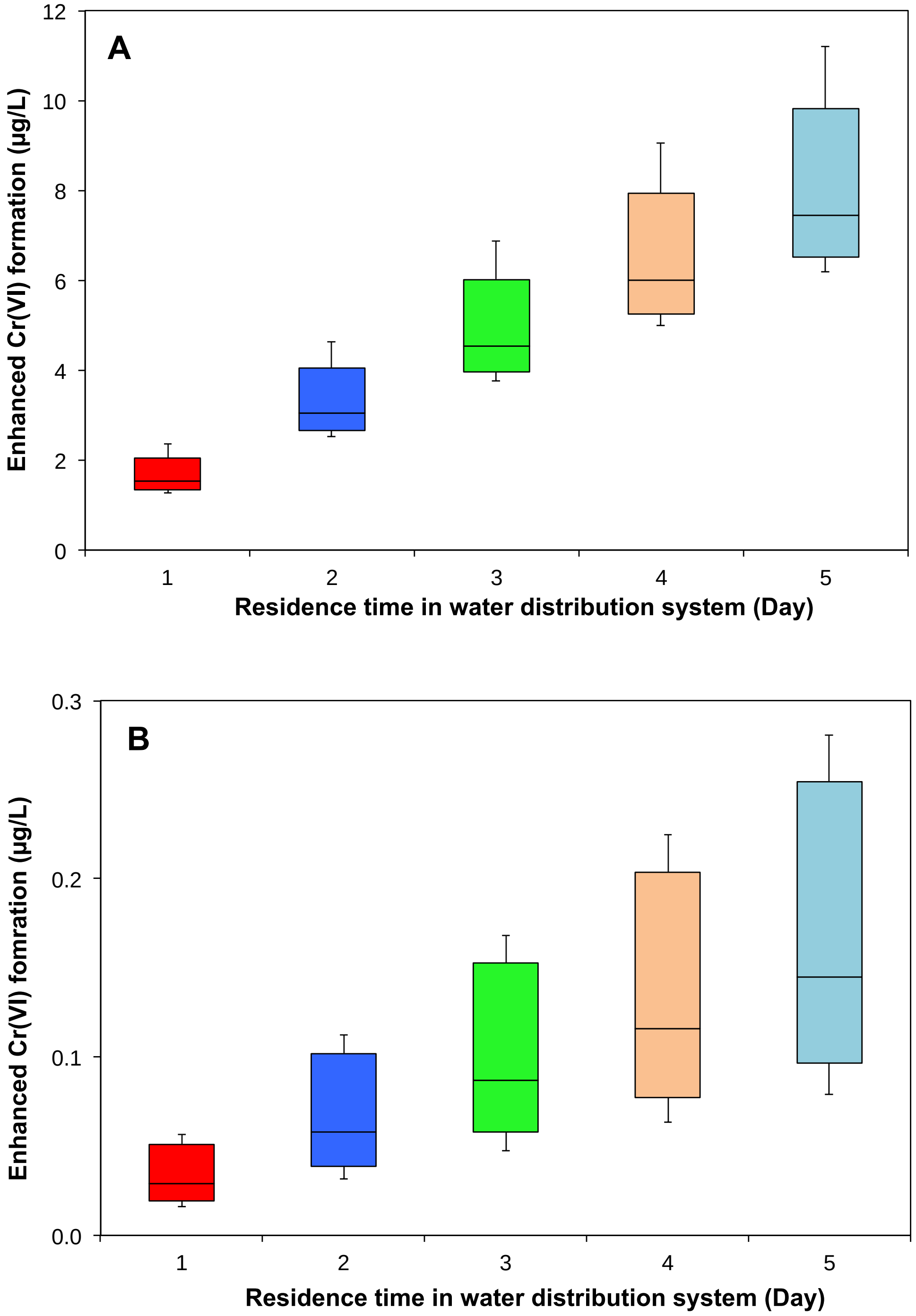


Figure 3.23 Kinetics model prediction of enhanced Cr(VI) formation via Cr(III) solid phases oxidation by chlorine due to the catalytic effect of bromide in U.S. source waters. (A) Cr(VI) formation via $Cr(OH)_{3(s)}$ oxidation; (A) Cr(VI) formation via $Cr_2O_{3(s)}$ oxidation.

As adaptive strategies including water reuse are widely employed to augment water supplies, an accumulation of salts including bromide over time can take place. In addition, an increase of salinity can come from sources including effluent from gas drilling operations, agricultural runoff and seawater intrusion. Strategies to reduce bromide levels in source waters can be effective for water utilities to minimize the occurrence of Cr(VI) in chlorinated water distribution systems. Additionally, the mitigation of Cr(VI) occurrence in drinking water could be achieved by the use of a residual disinfectant less oxidative than chlorine. Examination on the reaction stoichiometry suggests the importance of Cr intermediates including Cr(V) to the yield of Cr(VI) during Cr(III) oxidation. Formation of Cr intermediates can promote the catalytic decay of chlorine without producing Cr(VI). Beyond the three Cr(III) solids investigated in this study, Cr(III) can exist as a co-precipitate with Fe(III) oxyhydroxides in water distribution systems. The reactivities of Fe(III)-Cr(III) oxides also need to be further ascertained.

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Chapter 4

Formation of Hexavalent Chromium via Iron Chromite Oxidation by Chlorine in Drinking Water: Role of Iron, Bromide, pH and Carbonate

In preparation for *Environmental Science and Technology*

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Abstract

The occurrence of chromium (Cr) as an inorganic contaminant in drinking water is widely reported. One source of Cr is the accumulation in iron-containing corrosion scales of drinking water distribution systems as iron chromite, *i.e.*, $Fe_xCr_{(1-x)}(OH)_{3(s)}$, where x represents the Fe(III) molar content and typically varies between 0.25 and 0.75. This study investigated the kinetics of inadvertent Cr(VI) formation via the oxidation of iron chromite by chlorine as a residual disinfectant in drinking water, and examined the impacts of Fe(III) content, and drinking water chemical parameters including pH, bromide and alkalinity on the rate of Cr(VI) formation. Data showed that an increase of Fe(III) molar content in $Fe_xCr_{(1-x)}(OH)_{3(s)}$ resulted in a significant decrease in the stoichiometric Cr(VI) yield and the rate of Cr(VI) formation, mainly due to the scavenging of chlorine by Fe(III). An increase in alkalinity enhanced the rate of Cr(VI) formation, likely due to the formation of Fe(III)-carbonato surface complexes that slowed down the scavenging reaction with chlorine. The presence of bromide significantly accelerated the oxidation of iron chromite by chlorine, resulting from the catalytic effects of bromide acting as an electron shuttle. The impact of solution pH on the oxidation of iron chromite by chlorine was negligible. These findings suggested that the oxidative conversion of chromium-containing iron corrosion products in drinking water distribution systems can lead to the occurrence of Cr(VI) at the tap, and the abundance of iron, alkalinity and bromide levels affect the extent of Cr(VI) formation.

Introduction

Chromium (Cr) can exist as hexavalent Cr(VI) and trivalent Cr(III) in drinking water conditions. Cr(VI) is highly mobile and toxic, whereas Cr(III) forms minerals with low solubility at circumneutral pH and is also considered a micro-nutrient. [1,2] California set a new drinking water regulation specifically for Cr(VI) at 10 μg/L in 2014.[3] The U.S. EPA regulates total chromium in drinking water at 100 μg/L, and a federal regulation solely for Cr(VI) is likely to be established in the future.[4] Geogenic Cr(VI) sources originate from the natural weathering of Cr(III)-containing aquifer minerals. [5-7] Traditional anthropogenic sources typically come from industrial waste discharge.[8-10]

In recent years, *in situ* generation of Cr(VI) in drinking water distribution systems from Cr-containing corrosion scales has drawn increasing attention.[11-13] For example, corrosion products in stainless steel pipes contains up to 26% of Cr by weight.[14] Aging water distribution infrastructure also accumulate extremely high levels of Cr – it is typically present at trace levels below regulatory standards in flowing water, but over decades it can accumulate to very high levels in the corroded solids.[15-18] The accumulated Cr exists as different Cr(III) minerals, including chromium hydroxide $Cr(OH)_{3(s)}$, chromium oxide $Cr_2O_{3(s)}$, copper chromite $Cu_2Cr_2O_{5(s)}$ and iron chromite.[17,19-22]

In particular, chromium can accumulate extensively in iron corrosion scales over time,[23-26] considering that nearly 70% of pipes in water distribution systems in the U.S. are composed of iron materials.[27] When co-existing with iron, Cr(III) forms mixed phases of iron chromite, *i.e.*, $Fe_xCr_{(1-x)}(OH)_{3(s)}$, where x represents the Fe(III) molar content and typically varies between 0.25 and 0.75.[28-33] In addition, iron chromite has been widely observed in aquifer materials. Natural occurrence of Cr(VI) in groundwater largely results from geological weathering of iron chromite, in which process Cr(III) is oxidized by Mn(IV) oxides to Cr(VI).[34-36]

The stability of iron chromite in drinking water distribution systems depends on a cascade of redox processes.[37-39] In particular, the oxidation of iron chromite by the residual disinfectant chlorine can take place in distribution systems, and results in an inadvertent generation of Cr(VI) at the tap. Nationwide surveys have indicated that the reaction pathways depended on Cr(III) speciation and its redox reactivity in distribution systems.[13,40,41] Field sampling data from the third round of US EPA's Unregulated Contaminant Monitoring Rule (UCMR3) indicated that Cr(VI) levels increased from the entry to exit point of many distribution systems nationwide, and this trend correlated with the presence of chlorine as the residual disinfectant.[13] Recent studies also showed that the oxidation of Cr(III) solid phases by chlorine increased Cr(VI) levels in drinking water.[42-45] In addition, mixed phases of Cr(III) oxides with other metals, *e.g.,* Cu(II) as $Cu_2Cr_2O_{5(s)}$, exhibit a higher redox reactivity than pure phases of Cr(III). Similarly, Fe(III)-containing iron chromite could also exhibit unique reactivity with chlorine to generate Cr(VI), albeit that the reaction kinetics have not been well investigated.

Furthermore, the impacts of important water chemical parameters including pH, bromide and alkalinity on the reactivity of iron chromite remain unknown. Alkalinity and pH are important corrosion control strategies for distribution systems.[46-48] They impact complexation of metal surface carbonato and hydroxo species, and consequently surface redox reactivity of metal oxides.[49] pH can also impact the speciation of chlorine and its oxidative capacity. Bromide exhibits a catalytic effect on the chlorine-driven oxidation of transition metals.[50,51] Recent studies show that bromide level in drinking water can increase by as much as 20 times in the future due to seawater intrusion, desalination, water reuse and brine discharge from alternative energy production (*e.g.*, shale gas).[47,52]

Considering the importance of understanding the reactivity of iron chromite and consequently the development of effective Cr(VI) control strategies to maintain aging water distribution infrastructure, the objectives of this study were to investigate the reactivity of iron chromite with chlorine and the mechanisms of Cr(VI) generation, and to quantify the impacts of Fe(III) molar content, alkalinity, pH and bromide on the reaction kinetics and stoichiometry.

Materials and Methods

All chemicals used in this study were reagent grade or higher. All solutions were prepared using Milli-Q (MQ) water (resistivity>18.2 MΩ, Millipore System). Iron chromite solids with different Fe(III) molar contents were synthesized using a standard protocol.[53] In brief, solutions of $Fe(NO_3)_3$ and $CrCl_3$ were mixed at a molar ratio of either 0.3:1, 1:1 or 3:1 at pH 7 for 3 days. Ferrihydrite $Fe(OH)_{3(s)}$ was synthesized via the hydrolysis of $Fe(NO_3)_3$ at pH 7.[54] All solids were washed with MQ water three times before they were centrifuged, frozen overnight and lyophilized for at least 24 hours. The freeze-dried solids were sequentially sieved through NO. 50, 170 and 325 mesh sieves. Sieved particles with nominal sizes between 45 and 90 μm were collected and used in this study. To confirm the molecular formula of the synthesized iron chromite, particles were acid digested, and Cr and Fe percentages were analyzed with an Agilent 7700 Series Inductively Coupled Plasma Mass Spectrometer. The BET surface area of solids was measured using a Micromeritics ASAP 2020 surface area analyzer. Zeta potential of the solids was measured using a 0.2 g/L suspension using a Zeta Potential Analyzer (Brookhaven Instruments).

A 28-mM free chlorine stock solution of diluted from a NaOCl solution (Sigma Aldrich) was freshly prepared every week. The concentration of chlorine was verified by titration with potassium permanganate.[55] Before the start of an experiment, all solutions were purged with N_2 gas to remove the dissolved O_2. 0.28 mM of chlorine (*i.e.*, 20 mg Cl_2/L) was quickly added into the reactor tube and mixed with iron chromite. This chlorine concentration was higher than typical residual disinfectant concentration drinking water, but provided useful insight into reaction kinetics. The dosages of different iron chromite solids were controlled so that the initial Cr(III) molar concentration was constant at 2.8 mM, corresponding to a Cr(III)-to-chlorine ratio of 10:1.

The solution pH was maintained at a targeted value (±0.2 pH units) between 6.0 and 8.5 with 10 mM phosphate buffer. The presence of phosphate buffer had a negligible impact on the reaction kinetics (Figure A.B.1 in Appendix B). Bromide ranging between 0.1 and 1 mg/L was added. Alkalinity was varied between 1 and 5 mM with the addition of bicarbonate. In carbonate-containing experiments, 10 mM MOPS (3-morpholinopropane-1-sulfonic acid) was used as the buffer to control pH at 7 and to remove any potential effects between phosphate and carbonate; the coexistence of carbonate and phosphate was found to impact the speciation of iron reaction products.[56,57] The solution ionic strength was kept at 10 mM by adding a requisite amount of $NaClO_4$. In some experiments, ferrihydrite instead of iron chromite was used to examine the effect of Fe(III) on chlorine decay. In some experiments containing iron chromite or ferrihydrite, an excess of 1 mM of benzoic acid (BA) was added as a radical probe in order to determine if any hydroxyl or chlorine-based radicals were generated during chlorine oxidation.

All chlorine oxidation experiments were conducted in sealed glass reactor tubes with no headspace. Reactor tubes were covered in foil to protect from light and placed on a rotator to ensure continuous mixing. Sacrificial tubes were removed from the rotator at pre-determined time intervals for chemical analyses. Dissolved O_2 concentration of the suspension was measured immediately using a Mettler Toledo probe. After that, concentrated NaOH was added to the suspension to release potentially adsorbed Cr(VI) from iron chromite, followed by filtration through 0.22-μm Millipore filters. The concentration of Cr(VI) in the filtrate was measured using the diphenylcarbazide (DPC) method.[55] Chlorine concentration was measured using a modified (DPD) method, in which thioacetamide was added to eliminate any potential interference from Cr(VI).[45,55] Data modeling using the Goal Seek function with Microsoft Excel was applied to correlate the relationship between the chlorine consumption and Cr(VI) generation rates.

Results and Discussion

Oxidation of iron chromite by chlorine and Cr(VI) formation

The redox potential of iron chromite was lower than that that of HOCl/Cl$^-$ redox couple under the experimental conditions in this study as shown in Table 4.1, signifying that the oxidation of iron chromite by chlorine is thermodynamically favourable (calculations shown in Text A.B.1 in the Appendix B). To examine the reaction kinetics, a second-order reaction kinetics model was introduced to quantify the rates of chlorine consumption and Cr(VI) formation:

$$\frac{d[Cl_2]}{dt} = -k_{Cl_2}[Cr(III)_s][Cl_2](S_{Cr(III)_{(s)}}) \qquad (1)$$

$$\frac{d[Cr(VI)]}{dt} = k_{Cr(VI)}[Cr(III)_s][Cl_2](S_{Cr(III)_{(s)}}) \qquad (2)$$

k_{Cl_2} and $k_{Cr(VI)}$ are the surface-area normalized rate constants for chlorine consumption and Cr(VI) formation, respectively (L·m^{-2}·min^{-1}). [Cl_2] is the free chlorine concentration (mol/L), [$Cr(III)_{(s)}$] is the concentration of Cr(III) in iron chromite (g/L), and $S_{Cr(III)(s)}$ is the BET surface area of iron chromite (m^2/g).

Different iron chromite solids with varying Fe(III) molar contents exhibited similar surface-area normalized rates of chlorine consumption at pH 7, averaging at 6.2 ×10^{-4} L·m^{-2}·min^{-1} (Figure 4.1A). These k_{Cl_2} values were 2 to 3 times higher than the rates observed with pure phases of Cr(III) oxides, *e.g.*, $Cr(OH)_{3(s)}$ and $Cr_2O_{3(s)}$.[45] Meanwhile, the rate of Cr(VI) formation decreased significantly with increasing Fe(III) content. The value of $k_{Cr(VI)}$ decreased from 1.5 ×10^{-4} to 1.9 ×10^{-5} L·m^{-2}·min^{-1} when the Fe(III) content (*i.e.*, x value in $Fe_xCr_{(1-x)}(OH)_{3(s)}$) increased from 0.25 to 0.75 (Figure 4.1B). These rates of Cr(VI) formation were similar to those of $Cr(OH)_{3(s)}$ and $Cr_2O_{3(s)}$.[45] This trend suggested that the presence of Fe(III) in Cr(III)-containing solids promoted chlorine consumption but not promoting Cr(VI) formation.

Table 4.1 Characteristics of synthesized iron chromite FexCr(1-x)(OH)3

Fe:Cr Molar Ratio	**Molecular Formula**	**BET Surface Area (m^2/g)**	**log K_{sp}**	**E $(V)_{t=0}$**
0.3:1	$Fe_{0.25}Cr_{0.75}(OH)_3 \cdot 1.4H_2O$	279	-33.8	0.29
1:1	$Fe_{0.5}Cr_{0.5}(OH)_3 \cdot H_2O$	355	-34.5	0.59
3:1	$Fe_{0.75}Cr_{0.25}(OH)_3 \cdot 1.3H_2O$	198	-34.7	1.06

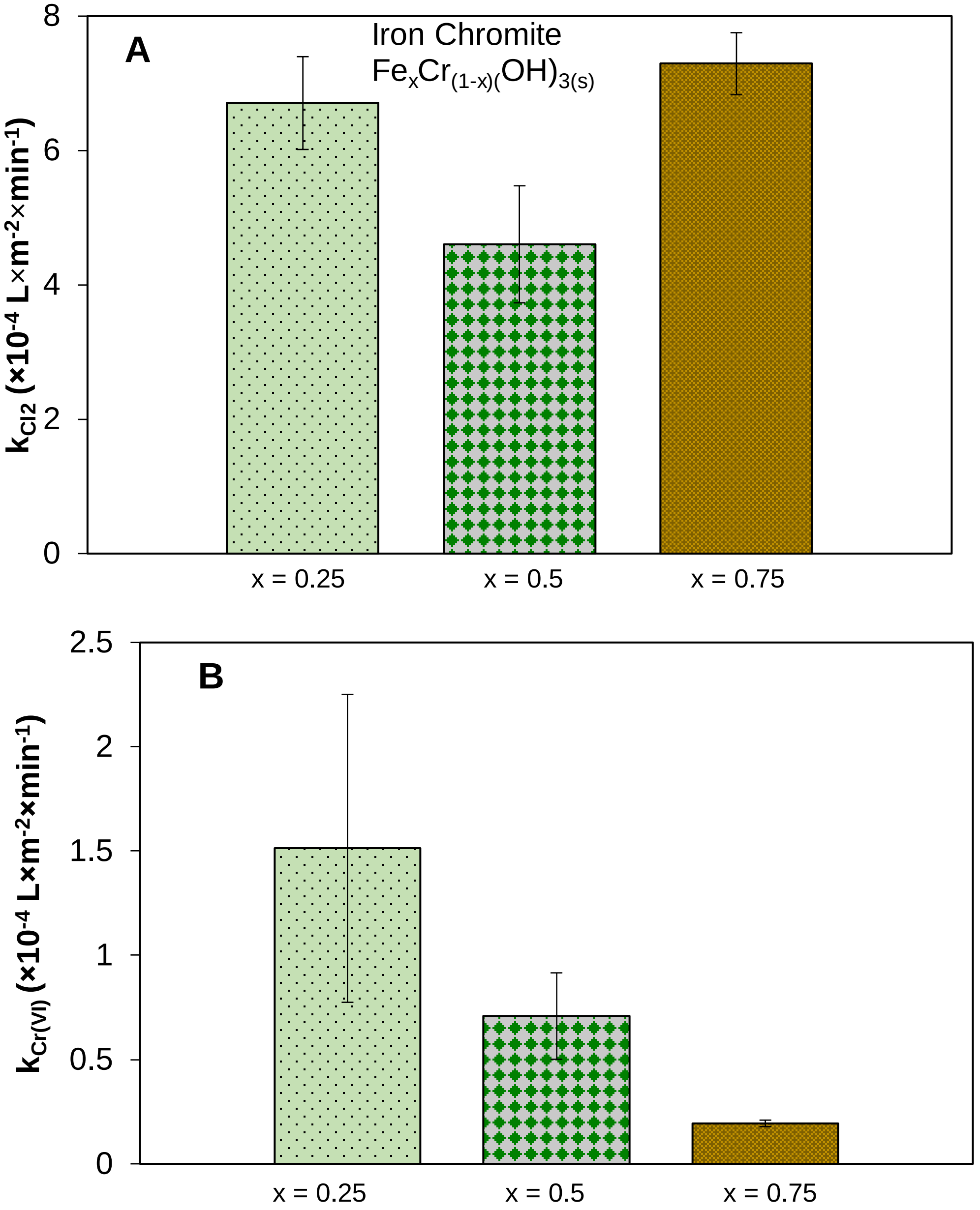


Figure 4.1 (A) Chlorine consumption and (B) Cr(VI) formation rates during the oxidation of iron chromite by chlorine. Initial conditions: [Cr(III)]=2.8 mM, [HOCl]=20 mg/L, [$NaClO_4$ (IS)]=10 mM. System buffered with 10 mM phosphate buffer at pH 7.

Impact of water chemical parameters on iron chromite oxidation kinetics

Bromide. The presence of bromide enhanced the reaction kinetics. As the bromide concentration increased from 0 to 1 mg/L, chlorine consumption accelerated (Figure 4.2A) and the value of k_{Cl_2} approximately doubled (Figure 4.2B). Meanwhile, an enhanced Cr(VI) formation was observed (Figure 4.3A), and the rate of $k_{Cr(VI)}$ increased by approximately 3 times (Figure 4.3B). The promotive effects of bromide on the oxidation reaction resulted from an electron shuttle mechanism. Bromide readily reacted with HOCl to generate hypobromous acid (HOBr).[58] Prior studies demonstrated that HOBr is more electrophilic than HOCl and consequently exhibited a faster kinetics in oxidizing electron-rich compounds including transition metals and organics.[50,59,60]Control experiments with HOBr also showed that HOBr oxidized iron chromite much faster than HOCl did (Figure 4.4). Therefore, in a bromide-containing system, HOBr becomes the primary oxidant as bromide essentially acts as an electron shuttle that drives the oxidation of iron chromite solids to Cr(VI) by chlorine:

$$Fe_xCr_{(1-x)}(OH)_{3(s)} + HOCl \overset{Br^-}{\underset{HOBr}{\overset{\curvearrowleft}{\underset{\hookrightarrow}{\longrightarrow}}}} CrO_4^{2-} + Fe^{3+} + H^+ + Cl^- \tag{3}$$

In addition, the Cr(VI) formation rate was sensitive to the effect of low level bromide (0.1 mg/L) regardless of Fe(III) content. There was an average 66% increase in Cr(VI) formation rate with the introduction of 0.1 mg/L bromide. There was only an average 30% increase in Cr(VI) formation rate as bromide concentration doubled from 0.1 to 0.2 mg/L. (Figure 4.3B). This is likely due to the limitation of reactive Cr(III) sites on the iron chromite surface.

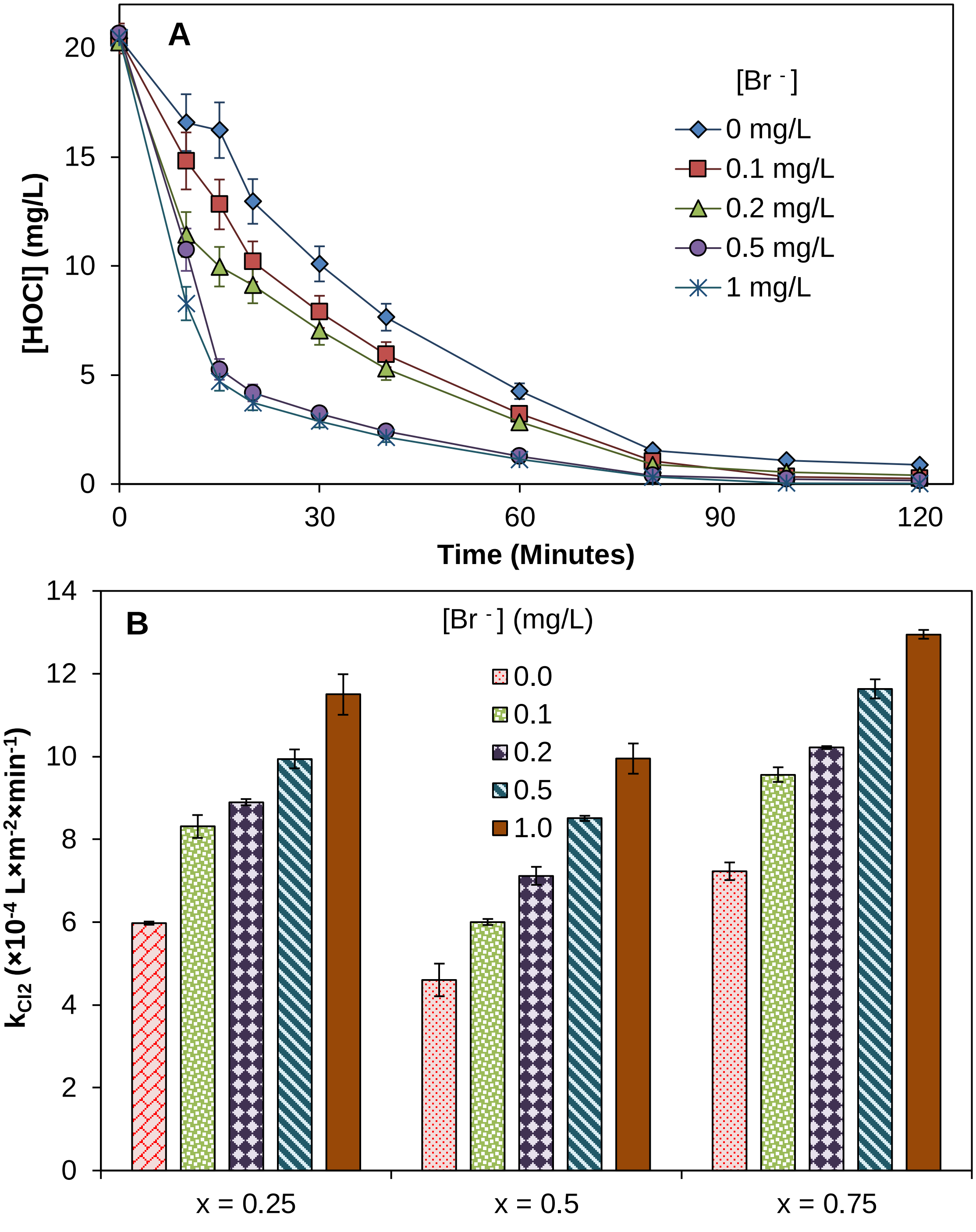


Figure 4.2 (A) Time profile for chlorine consumption for 0.5 Fe(III) molar content (B) Effect of bromide on the surface area normalized second-order chlorine consumption rate constants of iron chromite oxidation by chlorine. Initial [Cr(III)]=2.8 mM, [HOCl]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, ionic strength=10 mM. pH =7

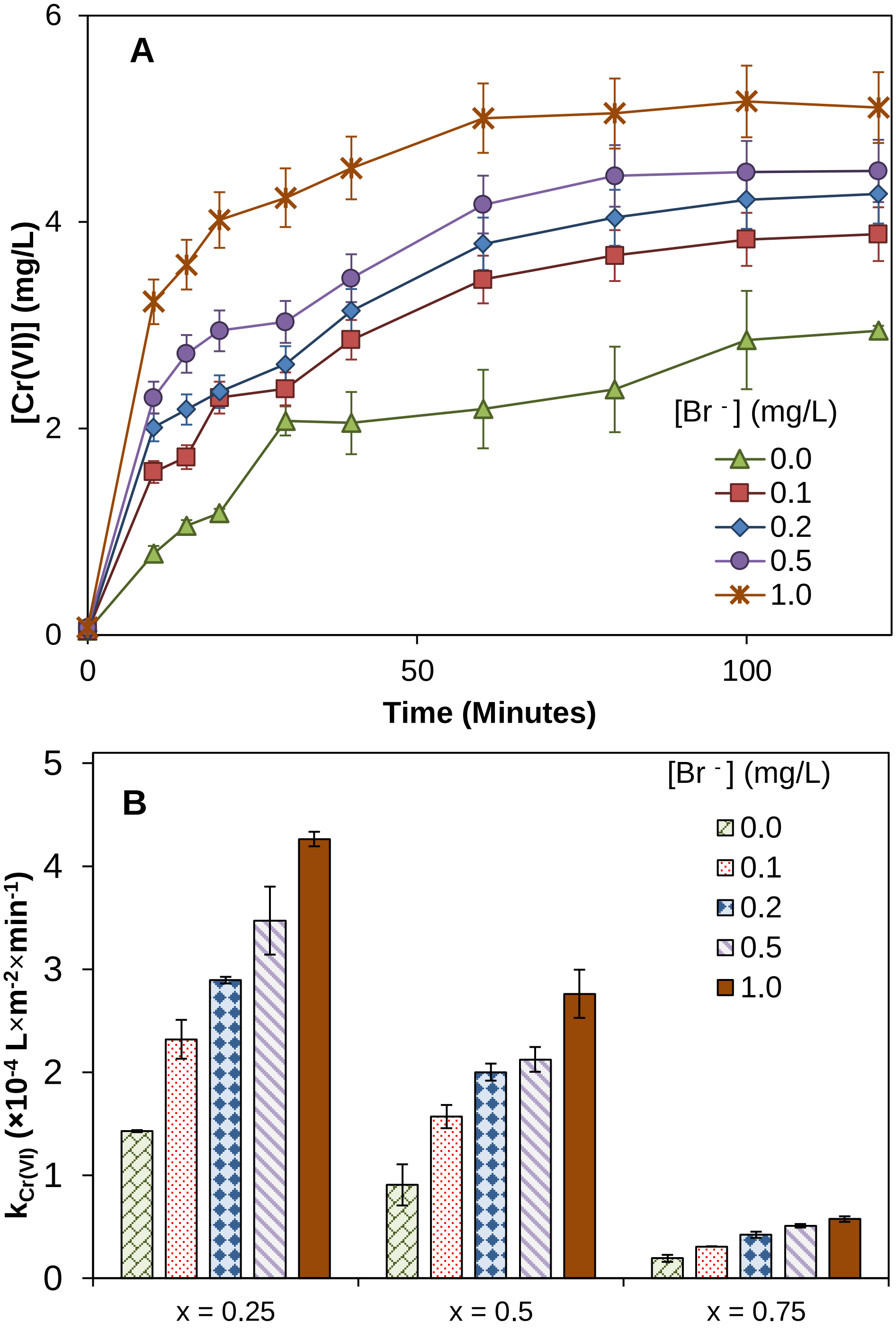


Figure 4.3 A) Time profile for Cr(VI) generation for iron chromite with 0.5 Fe(III) molar content. (B) Effect of bromide on the surface area normalized second-order Cr(VI) formation rate constants of iron chromite oxidation by chlorine. Initial [Cr(III)]=2.8 mM, [HOCl]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, ionic strength=10 mM. pH =7

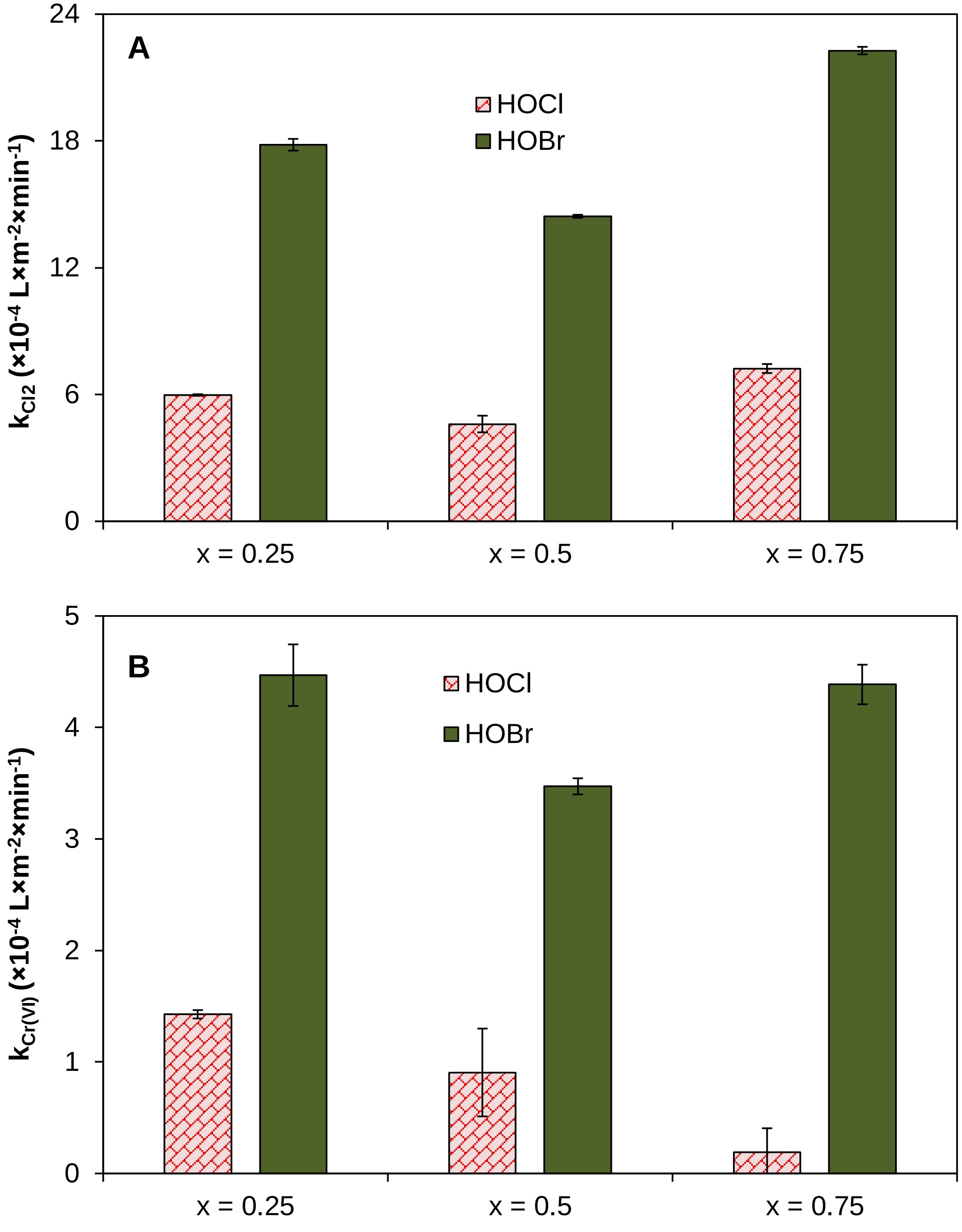


Figure 4.4 Impact of chlorine vs. bromine on the surface area normalized second-order (A) chlorine consumption and (B) Cr(VI) formation rate constants of iron chromite oxidation. Initial [Cr(III)]=2.8 mM, [HOX]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, ionic strength=10 mM. pH = 7

Carbonate. Carbonate exhibited a moderate impact on the reaction kinetics. With increasing total carbonate concentration ($TOTCO_3$) from 0 to 5 mM at pH 7.0, the rate of chlorine consumption increased by an average of 75% (Figure 4.5). Similarly, the amount of Cr(VI) generated with 5 mM $TOTCO_3$ was three times of that without carbonate (Figure 4.6A). The rate of Cr(VI) formation increased by 130%, 135%, and 250% with increasing Fe(III) content (Figure 4.6B).

The impact of carbonate on the reaction kinetics is likely due to the formation of Fe(III)-carbonato complexes, which has been known to decrease the redox reactivity of Fe(III) surface sites. [49, 52] Consequently, the presence of carbonate suppressed the reactivity of Fe(III)-containing surface sites on iron chromite with respect to chlorine, and increased the availability of Cr(III)-containing surface site on iron chromite to chlorine oxidation. Furthermore, carbonate had a negligible effect on the redox reactivity of non-Fe(III) containing Cr(III) solids, *e.g.*, $Cr(OH)_{3(s)}$ (Figure 4.7). This implied that Cr(III)-carbonato surface complexation reaction was negligible. This trend was consistent with the observation that carbonate mainly impacted the reactivity of Fe(III) surface site rather than Cr(III) sites.

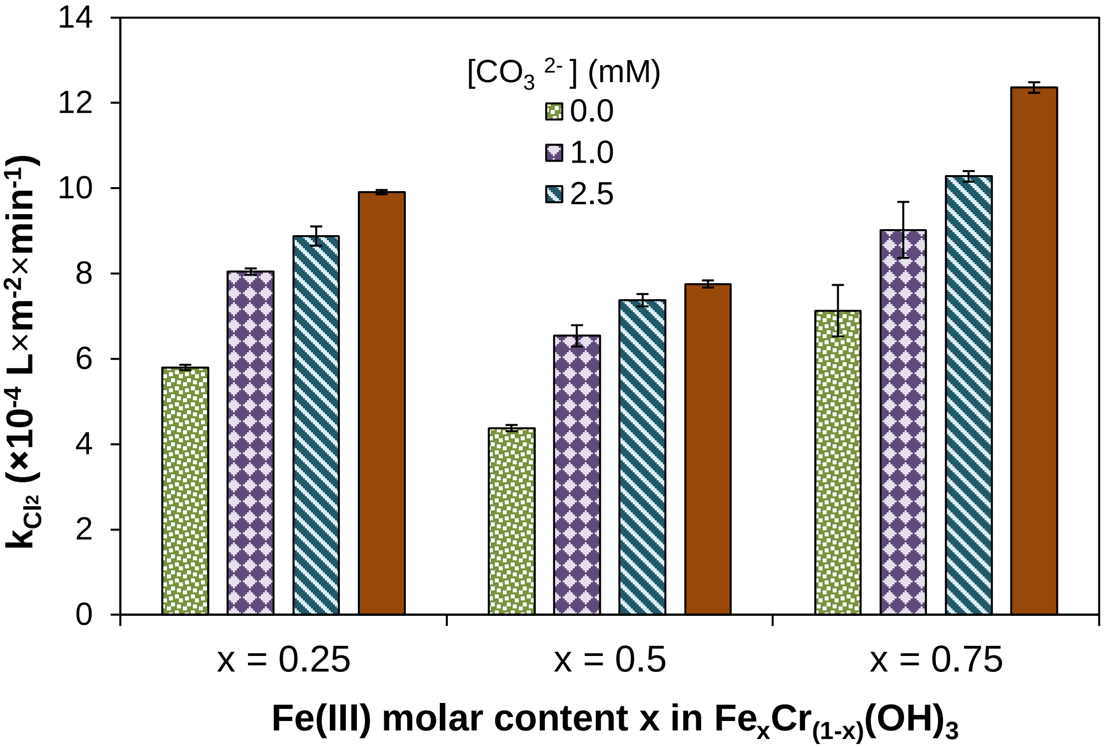


Figure 4.5 Impact of carbonate concentration on chlorine consumption rates due to the oxidation of iron chromite by chlorine.. [Cl_2]=20 mg/L as Cl_2, [Cr(III)]=2.8 mM, Cr(III): Cl_2=10:1, pH=7 MOPS Buffer, ionic strength = 10 mM.

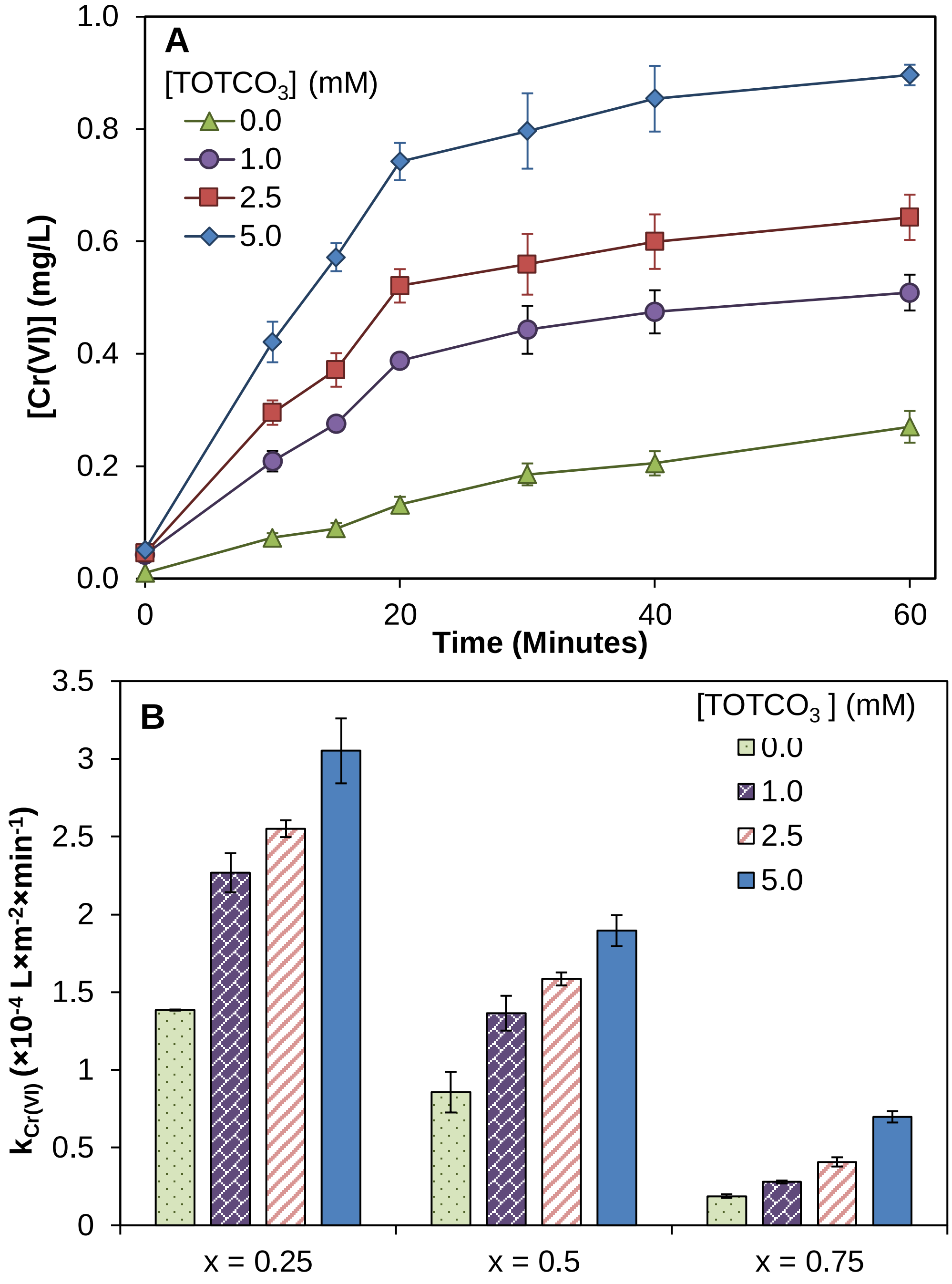


Figure 4.6 (A) Impact of carbonate concentration on chlorine consumption the oxidation of iron chromite with 0.75 Fe(III) molar content by chlorine. (B) Effect of carbonate on the surface area normalized second-order Cr(VI) formation rate constants of iron chromite oxidation by chlorine. Initial [Cr(III)]=2.8 mM, [HOCl]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, ionic strength=10 mM. pH =7 MOPS Buffer

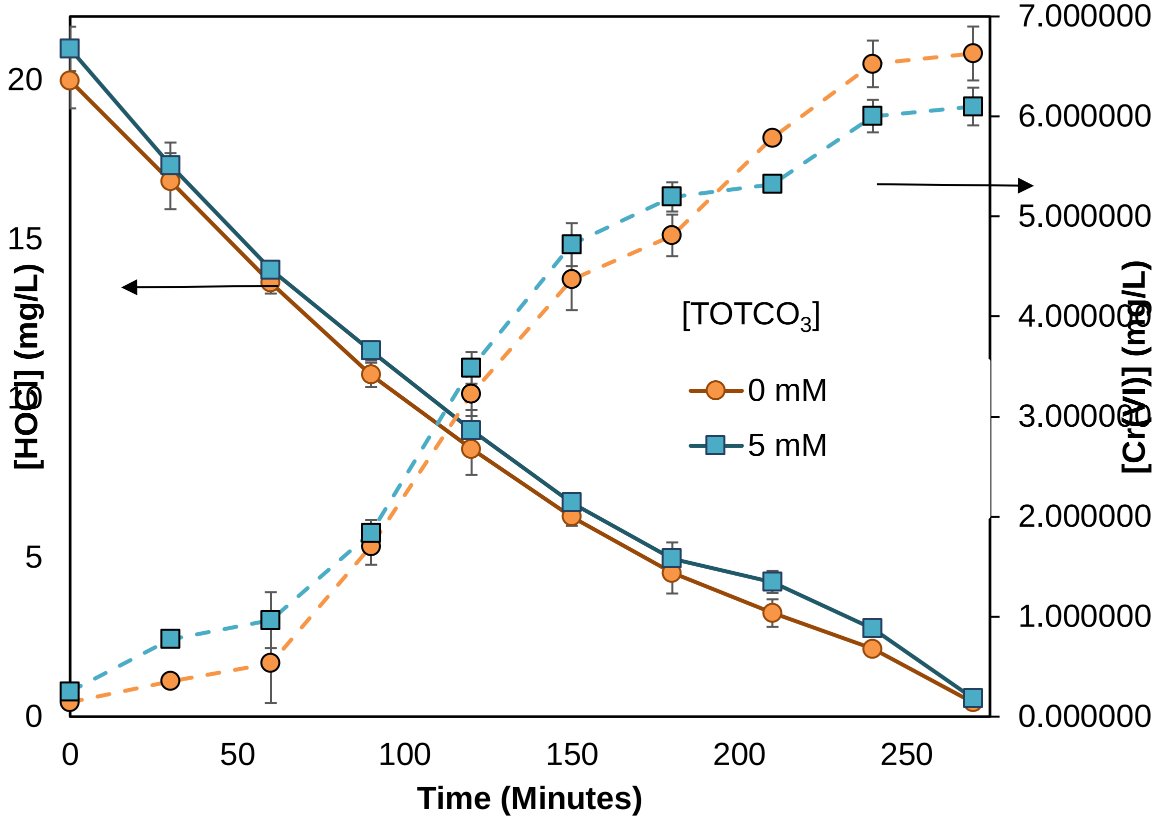


Figure 4.7 Impact of alkalinity on $Cr(OH)_3$. Initial [Cr(III)]=2.8 mM, [HOCl]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, ionic strength=10 mM, pH =7 MOPS Buffer

pH. The reaction kinetics was observed to decrease with increasing pH (Figure 4.8). The rate of chlorine consumption decreased by an average of 40% with varying Fe(III) molar content with increasing pH. The chlorine consumption rate of iron chromite with 0.75 Fe(III) molar content declined from 9.2×10^{-4} to 5.3×10^{-4} $L \cdot m^{-2} \cdot min^{-1}$ when pH increased from 6.0 to 8.5. The Cr(VI) formation rate from iron chromite with 0.25 Fe(III) content decreased by 67% from 2.4×10^{-5} to 0.8×10^{-5} $L \cdot m^{-2} \cdot min^{-1}$ when pH increased from 6.0 to 8.5. This trend was likely associated with the surface hydroxo complexation on iron chromite. The solution pH affects Cr(III)-hydroxo surface complexation.[38, 61] Measurement of zeta potential showed that the surface charge of iron chromite became more negative with increasing pH, suggesting that a higher extend of surface hydroxo complexation (Figure 4.9). The data also indicated that Cr(III) surface complexes with more hydroxo groups that are predominated at higher pHs had a lower reactivity with chlorine.

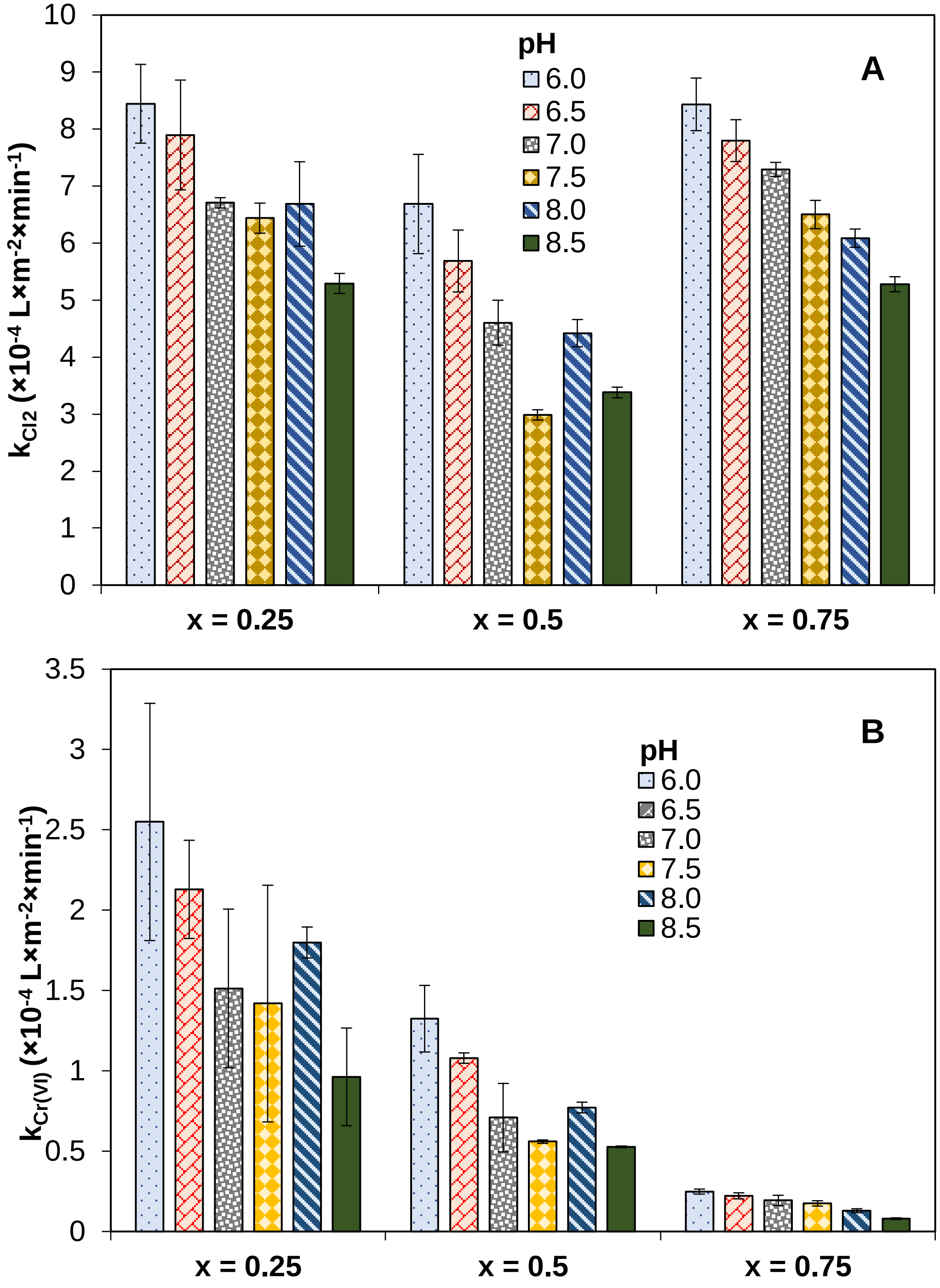


Figure 4.8 Effect of pH on the surface area normalized second-order (A) HOCl consumption and (B) Cr(VI) formation rate constants of iron chromite oxidation by chlorine. Initial [Cr(III)]=2.8 mM, [HOCl]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, ionic strength=10 mM.

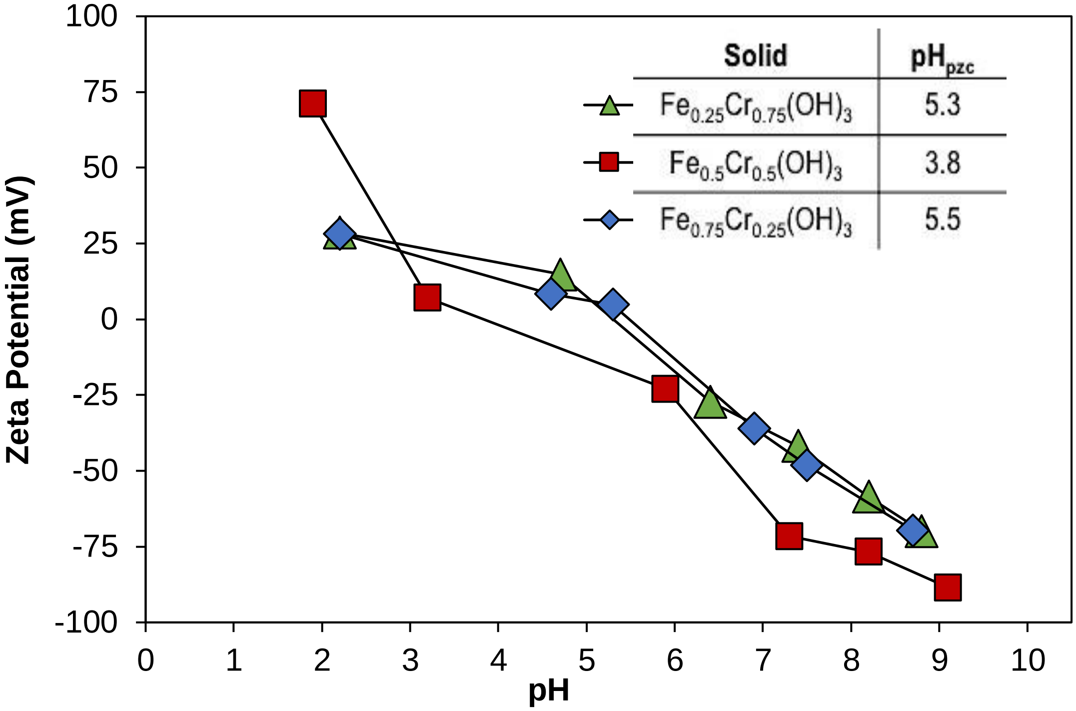
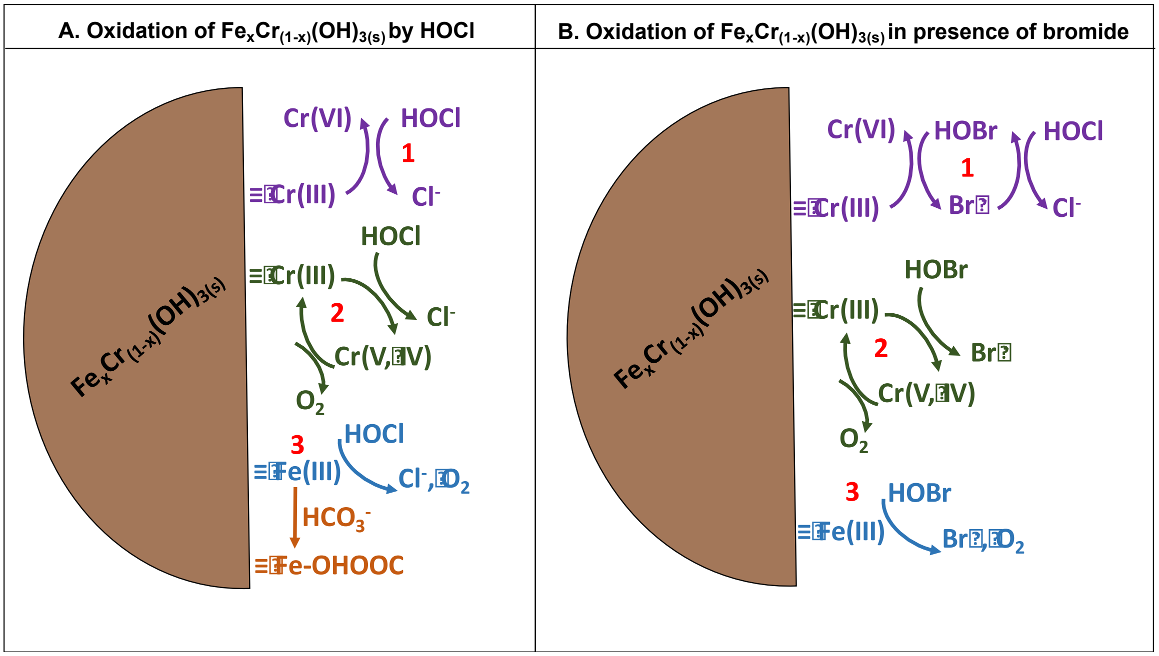


Figure 4.9 Zeta potential for all three synthesized solids. pH was varied by adding varying amounts of $HClO_4$ and NaOH. Ionic strength=10 mM. Suspension of Cr(III) solids=0.2 g/L.

Impact of iron content of iron chromite on reaction stoichiometry

The theoretical stoichiometry of the reaction, defined as the moles of Cr(VI) generated to the moles of chlorine consumed, *i.e.*, Δ[Cr(VI)]/Δ[HOCl], is 0.67. Experimental data with iron chromite showed that the 50th percentile observed stoichiometric ratio of ΔCr(VI)/ ΔHOCl was between 0.02 and 0.24 at varying pH, much lower than the theoretical value of 0.67 (Figure 4.10). This implied that the amount of chlorine consumed was not fully accounted for by the amount of Cr(VI) generated (reaction mechanism 1 in Scheme 4.1A). Furthermore, iron chromite with an increasing Fe(III) content from x = 0.25 to 0.75 exhibited a significantly lower stoichiometric ratio. (Figure 4.10). The under-stoichiometric formation of Cr(VI) was likely associated with the formation of Cr(IV) or Cr(V) intermediates.[45] Auto-decomposition of these intermediates and reproduce Cr(III) and dissolved O_2. This is represented as reaction mechanism 2 in Scheme 4.1A. The presence of intermediate formation was confirmed with an average 215% increase in oxygen generation during the oxidation of iron chromite (Figure 4.11). However, when the pathway of Cr intermediate formation was taken into account, the reaction stoichiometry was still below the theoretical value (Figure 4.10). This suggested that another unique reaction mechanism that contributed to chlorine consumption without Cr(VI) generation.

Scheme 4.1 Mechanisms of chlorine decay and disproportionation.



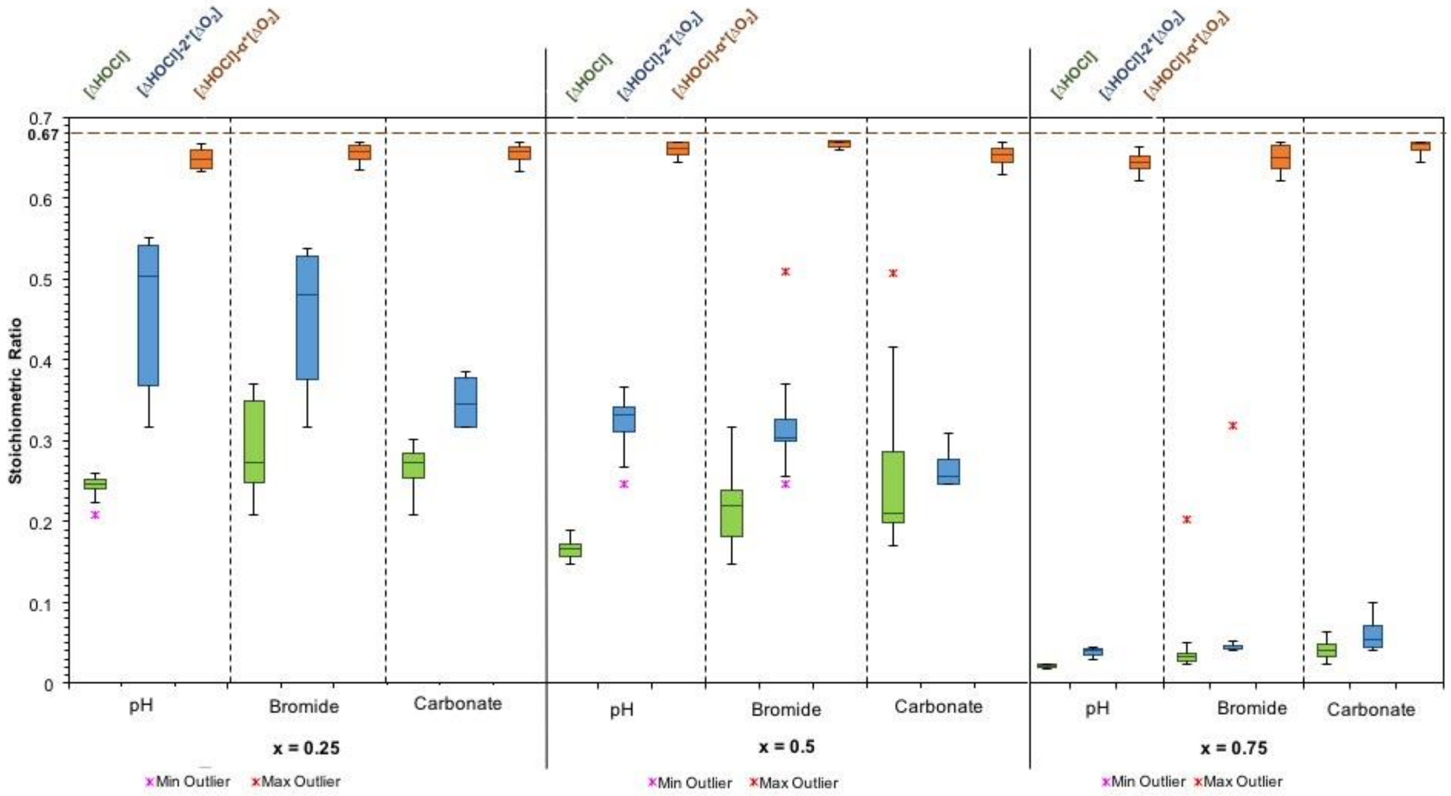


Figure 4. 10 Average stoichiometric ratio for varying water quality parameters and Fe(III) molar content x. The green box plots represent the stoichiometric ratio based on ΔCr(VI) vs, ΔHOCl. The blue box plots represent the stoichiometric ratio based on ΔCr(VI) vs, ΔHOCl - $2\Delta O_2$. The orange box plots represent the stoichiometric ratio based on ΔCr(VI) vs, ΔHOCl - $\alpha\Delta O_2$. The whiskers of the boxplot represent the 10th and 90th percentiles of concentration. The lower quartile, middle and upper quartile represent the 25th, 50th and 75th percentile values.

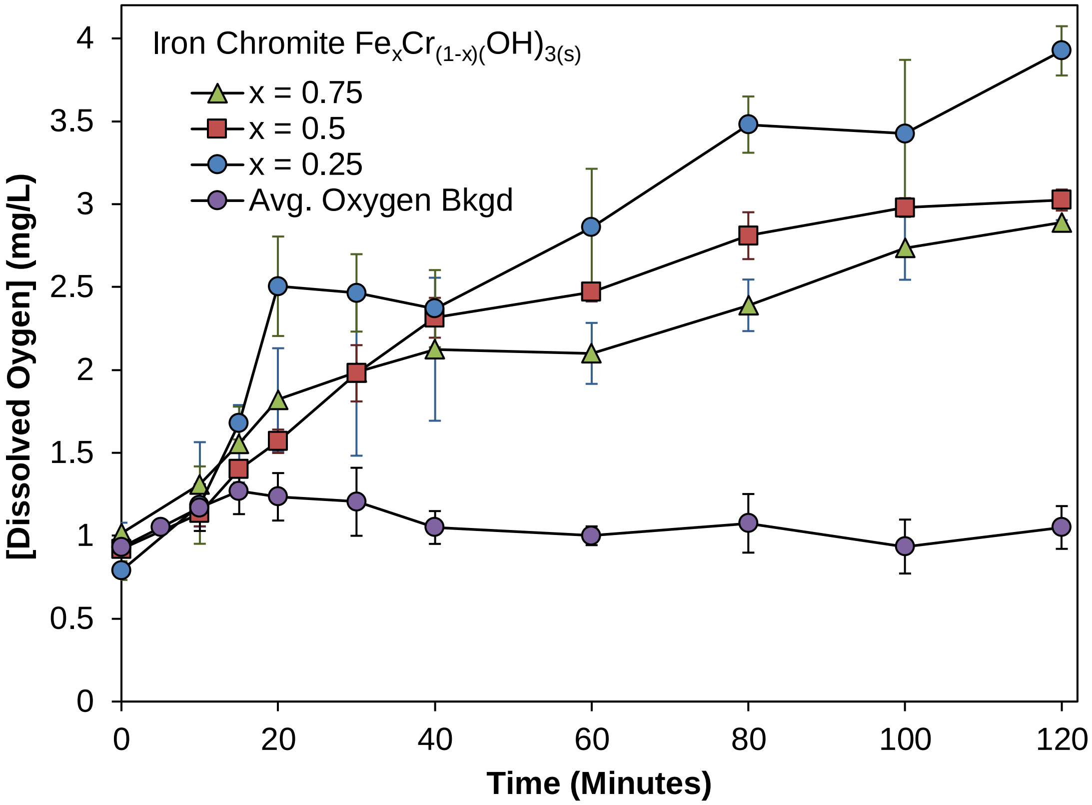


Figure 4.11 Oxygen generation over the course of the reaction. Initial conditions: [Cr(III)]=2.8 mM, [HOCl]=20 mg/L, Ionic strength = 10 mM. System buffered with 10 mM phosphate buffer at pH 7. The average oxygen background represents an average of the background oxygen levels for four control experiments: chlorine only and the three solids.

To investigate the unique reaction mechanism specific to iron chromite, additional control experiments were conducted in the presence of a pure phase of Fe(III) solid, *i.e.*, ferrihydrite $Fe(OH)_{3(s)}$. Data showed that chlorine decay took place and was accelerated with increasing Fe(III) dosage (Figure 4.12A). Furthermore, decay was accompanied by the generation of dissolved O_2 (Figure 4.12B). For example, the presence of 0.84 mM ferrihydrite resulted in a 45% increase of oxygen accumulation in comparison to background levels. As the Fe(III) molar content in iron chromite increased from 0.25 to 0.75, there was nearly a 20% increase in oxygen generation (Figure 4.12B).

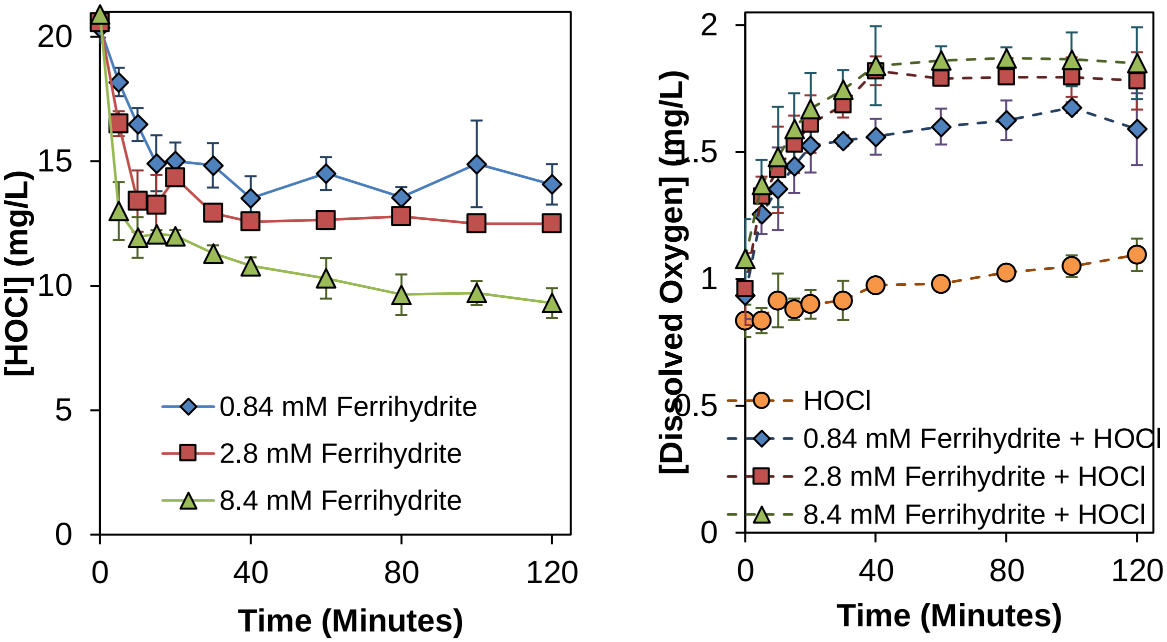


Figure 4.12 (A) Chlorine decrease in the presence of ferrihydrite. (B) Oxygen generation in the presence of ferrihydrite. Average background oxygen is 1 mg/L. Initial conditions: [HOCl]=20 mg/L, [NaClO4 (IS)]=10 mMm, pH = 7.

A correlation between oxygen generation and chlorine decay in the presence of ferrihydrite exhibited a stoichiometric ratio of 0.1 (Figure 4.13). Oxygen generation in the presence of ferrihydrite suggested the disproportionation of chlorine enhanced by Fe(III) surface sites (reaction mechanism 3 in Scheme 4.1A). This phenomenon of enhanced oxidant decay (*e.g.*, HOCl, HOBr, ClO_2) has been previously observed with copper, iron and nickel oxides. [51,62] This strongly supports that oxygen generation resulted from Fe(III)-induced chlorine decay and is consistent with the observed under-stoichiometry with iron chromite.

The disproportionation of chlorine in the presence of a metal oxide can also involve the generation of short-lived intermediate radicals such as hydroxyl radical ($HO^\bullet$), chlorine atom ($Cl^\bullet$) and chlorine dimer $Cl_2^{\bullet-}$ before the formation of chloride and oxygen.[63, 64] These reactions were discussed in Text A.B.2 in Appendix B. To further evaluate the chlorine disproportionation pathway with iron chromite, experiments were conducted with the addition of benzoic acid (BA) as a scavenger for all reactive radicals, because BA reacts quickly with $HO^\bullet$, $Cl^\bullet$ and $Cl_2^{\bullet-}$, but does not interfere with chlorine (Figure 4.14A). There was also no observed effect of BA on chlorine decay in the presence of iron chromite (Figure 4.14B). Results showed that in the presence of 1 mM BA, oxygen generation from ferrihydrite/chlorine system was suppressed by 30% in comparison to the system without BA (Figure 4.16A). Similarly, a 22% decrease in O_2 generation was observed during the chlorine oxidation of iron chromite when 1 mM of BA was present (Figure 4.16B). Results from BA scavenging experiments strongly suggested that the Fe(III)-driven chlorine disproportionation and associated radical generation acted as another pathway for chlorine consumption with iron chromite.

Accordingly, reaction stoichiometry was further adjusted to consider the pathway of Fe(III)-induced chlorine decay and O_2 generation. A fitting coefficient α was introduced to quantify the extent of side reactions that consumed chlorine to generate O_2 in the presence of iron chromite. While optimizing the stoichiometric ratio to the ideal value of 0.67, the best fit for the defined parameter α was determined. The value of α represented the amount of oxygen generation in the iron chromite/chlorine system due to the different mechanisms for chlorine decay without converting Cr(III) to Cr(VI). When all three mechanisms were considered and subtracted from the observed chlorine consumption (ΔHOCl - $\alpha*\Delta O_2$), the stoichiometry approached the expected value of 0.67 (Figure 4.10). The 50th percentile value for ΔHOCl - $\alpha*\Delta O_2$ at varying pH was 0.65, 0.64, and 0.63 with increasing Fe(III) molar content.

Furthermore, α values were determined under each chemical condition with varying levels of pH, carbonate, and bromide. Overall, regardless of the varying water quality parameter, α increased as the molar content of Fe(III) in iron chromite increased from 0.25 to 0.75; however, different water chemical parameters exhibited distinct impacts on the sensitivity of α values to Fe(III) molar contents in iron chromite (Figure 4.16). For example, α increased by approximately 70% when Fe(III) molar content increased from 0.25 to 0.75 in the presence of bromide and carbonate, respectively. This was observed in Figure 4 as the stoichiometric ratios in systems containing bromide (0.1 – 5 mg/L) and carbonate (1 – 5 mM) are generally higher than systems solely considering the impact of pH (6-8.5). Bromide allowed for the formation of HOBr, which increased chlorine consumption. Our previous work reported that the oxidation of non-Fe(III) containing Cr(III) solids by HOBr exhibited the ideal stoichiometry of 0.67.[45] Increased α values were observed due to the disproportionation of HOCl, HOBr and the potential formation of bromide-containing radicals or bromochlorides.[65] These bromide species are likely to have higher reacitvities than solely chlorine species. And in the presence of metals such as Fe(III), the rate of disproportionation is potentially increased in comparison to a system without bromide. Thus, the reaction mechanism 3 in Scheme 4.1B results in increased α values due to increased rates of disproportionation and generation of oxygen. Carbonate-containing systems have the highest α values. This may be due to proposed formation of iron carbonato complexes with increasing iron content in the iron chromite solids and subsequent enhanced formation of Cr(VI). Despite the reduced redox activity of iron in the presence of carbonate, it is likely that chlorine disproportionation still occurs (reaction mechanism 3 in Scheme 4.11A). Carbonate can also react with $OH^{\cdot}$ and $Cl^{\cdot}$ radicals to form carbonate radicals that can further react with $HOCl/OCl^-$ to further contribute to their decay and the eventual generation of O_2. Thus, the increases of oxygen generation and α values are due to the formation of Cr intermediates and decay of chlorine due to disproportionation and radical formation.

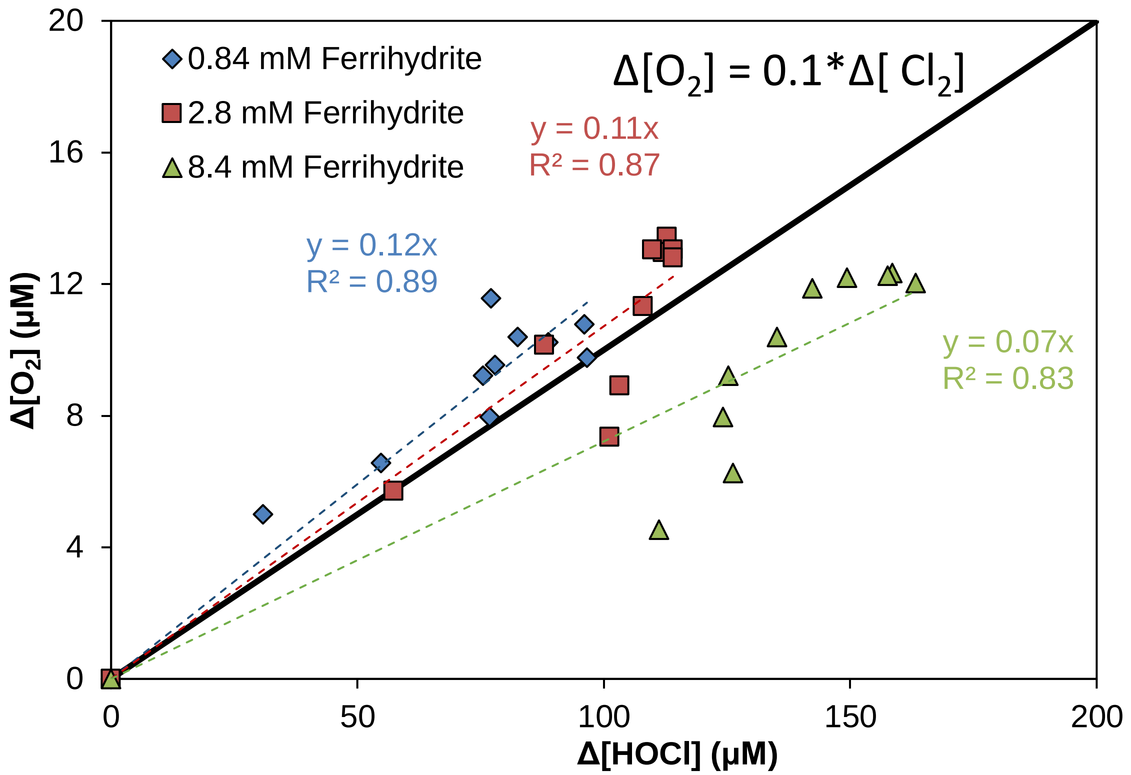


Figure 4.13 Stoichiometry between oxygen formation and chlorine consumption in the presence of ferrihydrite. Initial [CrIII)]=2.8 mM, [HOCl]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, [Benzoic Acid (BA)]=1 mM, ionic strength=10 mM, pH =7

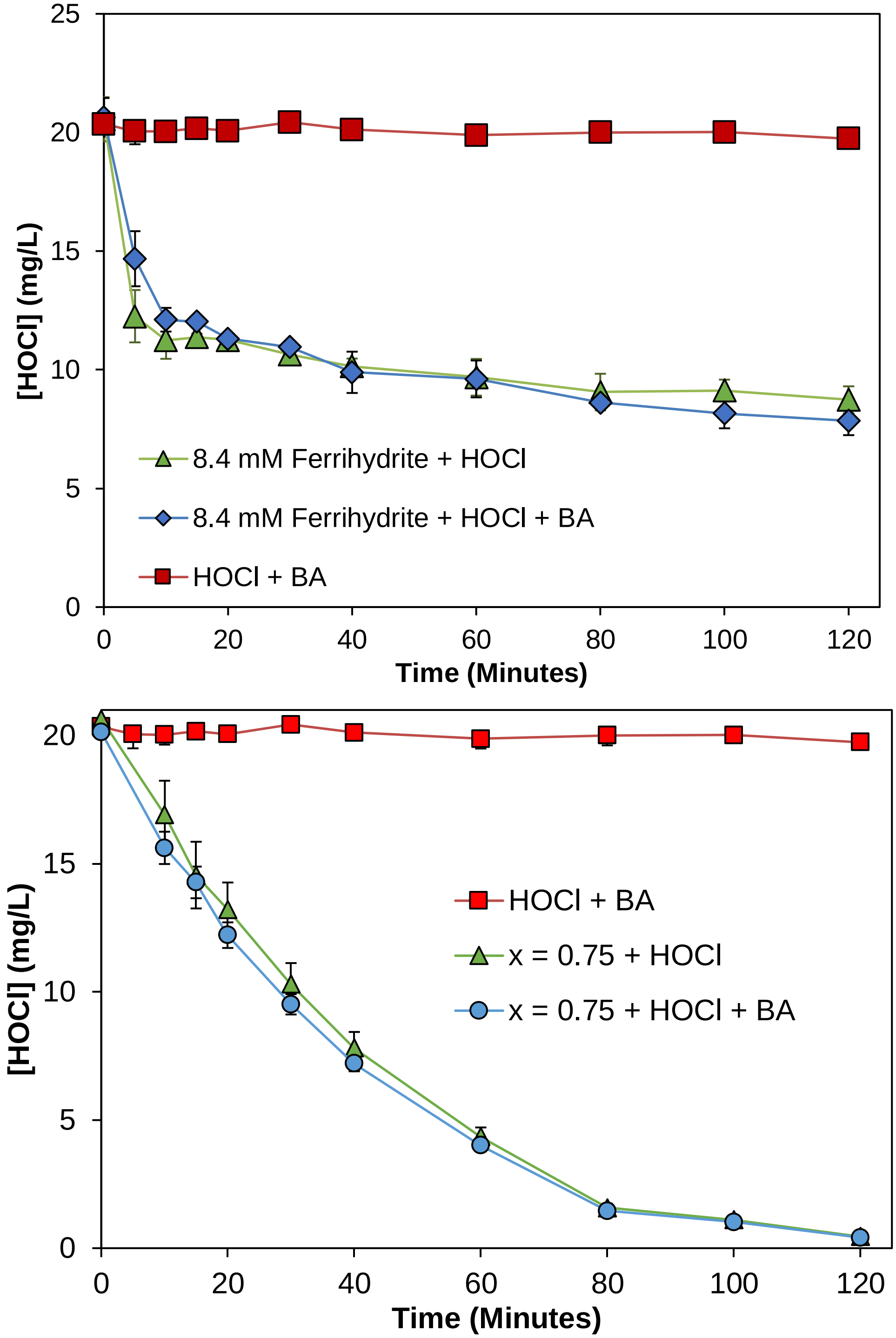


Figure 4.14 Chlorine consumption with time (A) in the presence of ferrihydrite and benzoic acid. (B) in the presence of 0.75 Fe(III) molar content and benzoic acid. Initial [Fe(III)]=2.8 mM, [HOCl]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, [Benzoic Acid (BA)]=1 mM, ionic strength=10 mM, pH =7

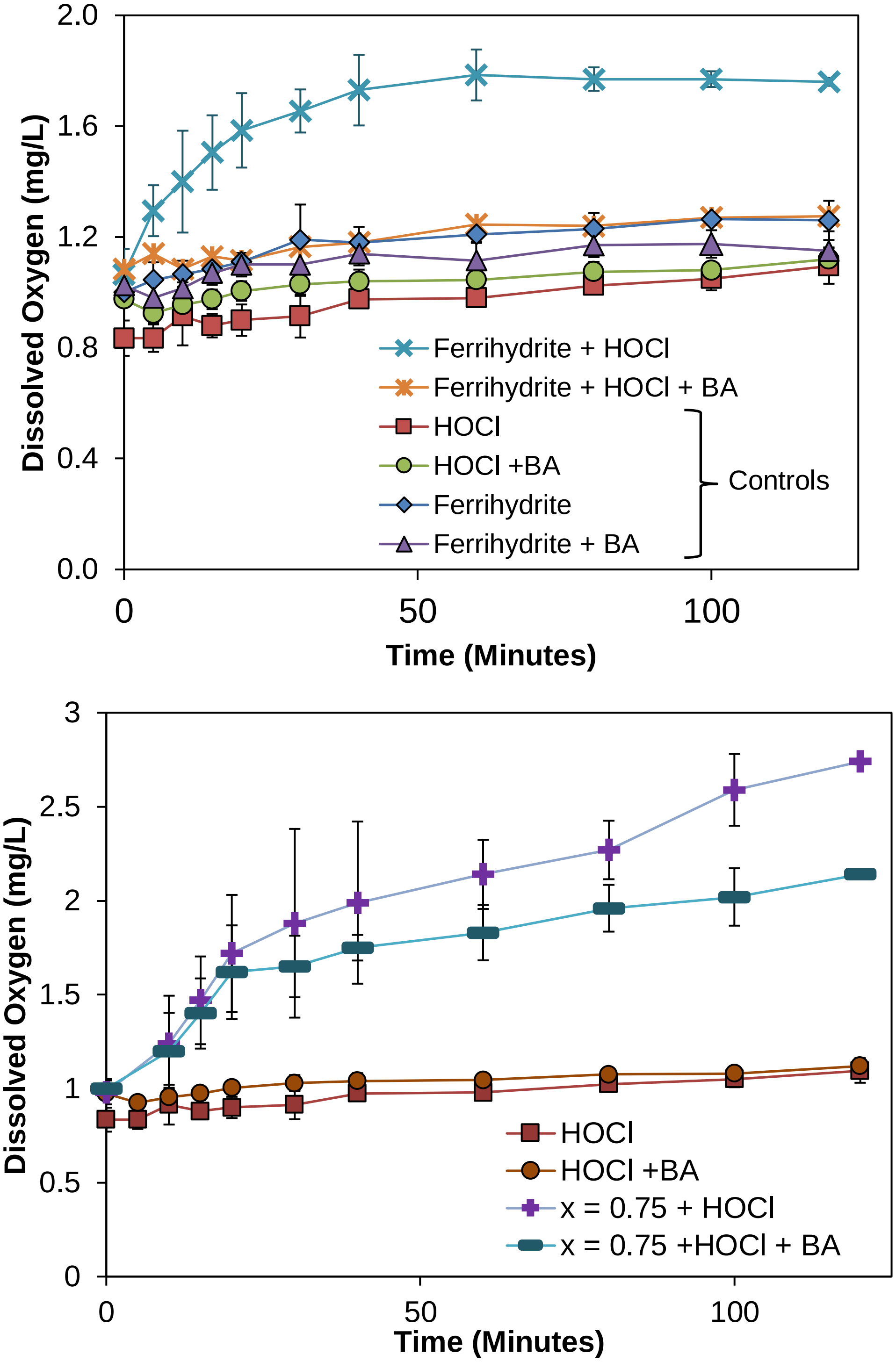


Figure 4.15 Oxygen generation with time (A) in the presence of ferrihydrite and benzoic acid. (B) in the presence of 0.75 Fe(III) molar content and benzoic acid. Initial [Fe(III)]=2.8 mM, [HOCl]=20 mg Cl_2/L, Cr(III):Cl_2=10:1, [Benzoic Acid (BA)]=1 mM, ionic strength=10 mM, pH =7

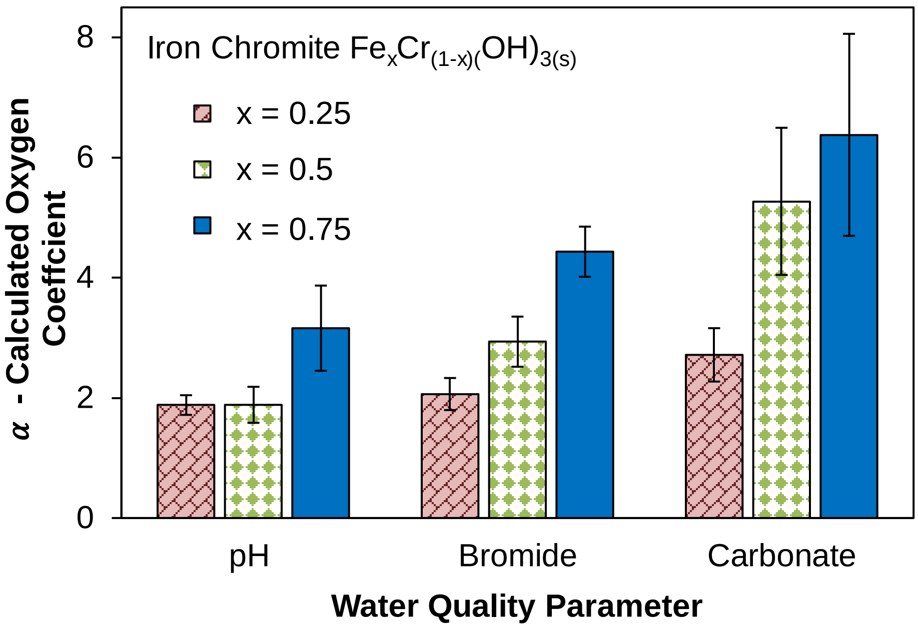


Figure 4.16 Calculated oxygen coefficient α for varying water quality parameters.

Environmental Implications

Drinking water distribution systems represent complex geochemical reactors lined with corrosion scales that are a source for a variety of trace metal contaminants including chromium. This study studied the underlying mechanisms between iron and chromium with varying water quality parameters. Most importantly, it was found that the presence of iron greatly impacts Cr(VI) formation. As water infrastructure ages in more and more cities, water quality becomes increasingly important. For example, changes in alkalinity can impact surface complexation of iron corrosion scales. The consequent release of accumulated Cr(III) can be oxidized by chlorine to Cr(VI) and potentially accelerated by the presence of trace concentrations of bromide. Systems with lower levels of corrosion (newer distribution systems) may potentially experience greater changes and increases in Cr(VI) whereas systems which are be more heavily corroded may cause Cr(III) and other trace metals to sorb and accumulate.

Acknowledgements

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Chapter 5

Summary and Conclusions

The overall goal of this research was to identify pathways of which non-toxic Cr(III) solids may be oxidized to toxic Cr(VI) from the entrance of the water treatment plant to the consumer tap. In order to achieve this goal, the occurrence of chromium in drinking water distribution systems was explored using the U.S. EPA's UCRM3 database (Chapter 2) as well as the kinetics of Cr(III) solid phase oxidation by chlorine and how the varying chemical parameters impact the formation of Cr(VI) (Chapters 3 and 4).

5.1. Occurrence and Speciation of Chromium in Drinking Water Distribution Systems

In Chapter 2, a review of Cr(VI) and total Cr occurrence was conducted based upon a detailed analysis of the UCMR3 database. This confirmed the nationwide detection of Cr(VI) in treated drinking water. Four key findings can be drawn from the work presented in Chapter 2. First, there was a strong correlation between geographical location and Cr(VI) concentration. EPA Regions 6 and 9 (American Southwest) had the highest percentage of water utilities reporting Cr(VI) levels greater than 10 μg/L. Overall, Region 9 (California, Nevada and Arizona) had the greatest levels overall. This was associated with the natural occurrence of Cr(VI) in the arid alluvial basins in these southwestern states. Second, the presence of Cr(VI) was highly dependent on the type of drinking water source. Increased concentrations of Cr(VI) were observed in water systems using groundwater as a drinking water source. This highlighted the contribution of Cr(VI) from geological weathering of aquifer minerals contribution to its occurrence in treated drinking water. Third, there are changes in Cr speciation from the entry point to the exit point of the distribution system. Cr(VI) entry points and exit points were paired and it was observed that 41% of systems showed an increase in Cr(VI). Changes in total Cr were also observed. This was likely derived sorption and desorption of Cr from corrosion scales. Fourth, the contribution of Cr(III) oxidation to the increase of Cr(VI) concentrations in water distribution systems was assessed. On average, 20% of Cr(III) entering a distribution system can be oxidized in a distribution system and contribute to changes in Cr speciation and an inadvertent transformation to Cr(VI). In addition, the likelihood of an increase in Cr(VI) concentration in water distribution system was increased in the presence of a residual disinfectant. There was a good correlation with Cr(III) decreases and Cr(VI) increases in a distribution system.

Overall, Chapter 2 shed light upon the complex physiochemical reactions that can result in a conversion of Cr(III) to Cr(VI), leading to increased levels of Cr(VI) in tap water. Distribution systems can act as complex reactors with sources and sinks for Cr and more importantly, as a source for Cr(VI) reoccurrence due to the oxidation of Cr(III) by residual disinfectants.

5.2. Kinetics and Mechanisms of Cr(VI) Formation via the Oxidation of Cr(III) Solid Phases by Chlorine in Drinking Water

The results presented in Chapter 3 contain several key findings. In comparison to similar studies of Cr(III) oxidation, this work investigated the oxidation of Cr(III) solid phases at relevant drinking water conditions rather than dissolved phases. Batch experiments of three Cr(III) solids were exposed to chlorine: $Cr(OH)_{3(s)}$, $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$. The first major finding of this work was that the oxidation of the three

Cr(III) solid phases by chlorine was thermodynamically favorable in typical drinking water conditions. Furthermore, each solid exhibited different reaction kinetics with chlorine based on experimental observations due to the distinct surface areas and reactive sites among the Cr(III) solids. Comparing all three Cr(III) solids, the rates of Cr(VI) formation and chlorine consumption followed the order of $Cu_2Cr_2O_{5(s)}$ > $Cr(OH)_{3(s)}$ > $Cr_2O_{3(s)}$. The modest impact of pH on the reaction kinetics further supported the distinct reactivity of each solid with chlorine due to different Cr(III) surface hydroxo species.

The second major finding of this work was the proposed formation of Cr intermediates during the oxidation of Cr(III) to Cr(VI). Upon evaluation of reaction stoichiometry, the ideal stoichiometry of 0.67 was not achieved. This indicated that the yield of Cr(VI) did not account for all the chlorine consumed during chlorine oxidation of Cr(III) solids. The under-stoichiometric yield suggested that the Cr(III) oxidation by chlorine is concurrently accompanied by an auto-catalytic decay of chlorine and proceeds with the formation of chromium intermediates as part of a multi-step oxidation process. This was confirmed by the generation of dissolved oxygen due to chlorine decay. When the contributions of chlorine decay due to both Cr(VI) and oxygen generation, ideal stoichiometry was achieved, implying the existence of Cr intermediate species.

Finally, the third major finding of this work was the enhanced formation of Cr(VI) in the presence of bromide, especially at a low level of bromide (0.1 mg/L). The presence of bromide essentially acts as an electron shuttle that catalytically promotes the oxidation of Cr(III) solids by chlorine. This is driven by the formation of bromine which does not undergo autocatalytic decay in the presence of Cr(III) solids (unlike chlorine) as observed by increased Cr(VI) formation and an ideal reaction stoichiometry of 0.67. Overall, Chapter 3 emphasized the need for strategies to mitigate and minimize Cr(VI) occurrence through the use of alternative disinfectants to chlorine and the reduction of bromide levels in source waters.

5.3. Inadvertent Generation of Cr(VI) via Iron Chromite Oxidation by Chlorine in Drinking Water: Role of Iron, Bromide, pH, and Alkalinity

The analysis in Chapter 4 further explored the reactivity of Cr(III) solids, but more specifically Cr complexed with Fe in the form of iron chromite ($Fe_xCr_{(1-x)}(OH)_{3(s)}$). Three solid different molar Fe content (x) were synthesized: x = 0.25, 0.5, and 0.75. This work investigated the impact of four major parameters: pH, bromide concentration, alkalinity and iron content (x).

First, the impact of pH on oxidation kinetics was modest. Overall, as pH increased from 6 to 8.5, chlorine consumption and Cr(VI) formation rates decreased. This correlated with decreasing zeta potential. This indicated that as the surface charges of the iron chromites became more negative, there was a decreasing reactivity with chlorine. Second, as observed in Chapter 3, there was the same trend of increasing Cr(VI) formation with increasing bromide concentration. However, the promotive effects of bromide did not result in the expected reaction stoichiometry of 0.67. This suggested that the presence of iron contributed to the disproportionation of chlorine and bromine that was not observed solely in the presence of Cr(III). Third, the impact of carbonate had a comparable promotive effects of Cr(VI) formation to bromide. While carbonate typically reduces the redox activity of metals, this was not observed with pure Cr(III) solids (e.g. $Cr(OH)_{3(s)}$). This meant that carbonate does not complex with Cr. It was then hypothesized that the formation of Fe(III)-carbonato complexes in the presence of carbonate allowed for the availability of Cr(III) to be oxidized by chlorine, resulting in increased Cr(VI) formation.

Finally, the major key finding of Chapter 4 was how the presence of Fe(III) in iron chromite accelerated chlorine consumption without promoting Cr(VI) formation. It was observed that Cr(VI) formation decreased significantly as iron content increased. Furthermore, iron chromite with an increasing Fe(III) content exhibited a lower stoichiometry. Under-stoichiometric formation was observed at all parameters varied. This suggested that beyond the previously identified mechanisms of chlorine consumption (Cr(VI) formation and auto-catalytic decay in Chapter 3), the increasing presence of iron caused increasing consumption of chlorine. It was identified that chlorine decay was due to two potential pathways with the major pathway being chlorine disproportionation in the presence of iron and a minor pathway of radical generation similar to a Fenton-like reaction. When all three mechanisms of Cr(VI) formation, O_2 generation due to intermediate formation and iron induced chlorine decay, the ideal reaction stoichiometry was achieved. Overall, these findings suggested that the presence of iron in corrosion scales can play a significant role on Cr(VI) formation and shed light on the impact of changing water quality may have on metal release in more corroded, older distribution systems.

5.4. Broader impact and future studies

Findings from this PhD work had significant implications for understanding the occurrence of hexavalent chromium in drinking water in the presence of varying water treatment and chemical parameters. It demonstrated the importance of Cr(III) oxidation and Cr(VI) re-occurrence in the distribution system. It was that the existence of Cr(III) solids present in drinking water distribution systems should be considered as a potential source of Cr(VI). If toxic Cr(VI) can be formed from oxidation of commonly observed Cr(III) solid phases in the water treatment and distribution system, the prediction of the rate at which Cr(VI) is formed in chlorinated water can be estimated. Even if total Cr levels complies with the current U.S. EPA drinking water regulation, it is necessary to differentiate between Cr(III) and Cr(VI) due to the likelihood that Cr(III) can be completely converted to Cr(VI) at environmentally relevant time scales. While the intermediates could further convert to Cr(VI) by disinfectants, they may promote the catalytic decay of chlorine without producing Cr(VI). Therefore, the reactivity and favorability of intermediate formation can affect the yield of Cr(VI) in chlorinated water.

The results of this proposed work demonstrated that it cannot be assumed that transformations of Cr(III) in downstream treatment processes are irrelevant to the occurrence of Cr(VI). The identification of the oxidative interactions between chlorine and Cr(III) solid phases serves an important pathway that offers strategies for public utilities to minimize the formation of Cr(VI) occurrence in tap water. The presence of residual disinfectants such as chlorine is positively correlated with Cr(VI) re-occurrence in drinking water distribution systems. Future studies into Cr(III) solid reactivity with other typical residual disinfectants such as chloramine and chlorine dioxide warrants further exploration.

Additionally, this work highlighted the significance of the impact of water chemical parameters on observing the fate and transformation of Cr(III) solids. It was observed that bromide played a surprising role as a catalyst for Cr(VI) formation. The increased presence of halides in drinking water sources is of great concern due to water reuse applications and seawater intrusion. The presence of halides contributes to the formation of regulated disinfection byproducts such as trihalomethanes (THM). Because halide levels are not monitored, correlations between halide concentration and THM formation could potentially be studied to assess any potential relationships to increased occurrence of Cr(VI) in drinking water. In addition, similar future studies in the presence of iodide can further shed light on this novel catalytic mechanism.

As aforementioned, corrosion continues to be an issue of aging water distribution infrastructure. Given that Cr can accumulate in corrosion scales, the correlation between corrosion rate and metal release needs further investigation. This would help to quantify to quantify the relative and more realistic contribution of pre-existing Cr(III) scales to the formation of Cr(VI) in distribution systems. The application of a broad range of water quality parameters such as flow conditions and presence of residual disinfectants can help to assess the conditions that lead to increases in corrosion, consequent metal release and the deterioration of water quality.

Appendix A:

Supporting Information for Chapter 3

Text A.A.1: Synthesis of chromium hydroxide $Cr(OH)_{3(s)}$

Chromium nitrate nonahydrate $Cr(NO_3)_3{\cdot}9H_2O$ (Acros Organics) was brought to a pH of 10 using 1 M sodium hydroxide NaOH at which $Cr(OH)_{3(s)}$ precipitated. The suspension was then magnetically stirred for 24 hours to fully precipitate out Cr(III) hydroxide. Following that, the suspension was transferred to 50 mL tubes and centrifuged (Beckman Coulter Avant JE) at 3000 G for 5 minutes. The supernatant was decanted and a new batch of DI water was added for centrifugation. This cleaning procedure was repeated for 8 times until the supernatant reached a pH 7, indicating all impurities had been removed. The purified $Cr(OH)_3$ particles were then dried with a freeze dryer (VirTis Benchtop SLC). Acid digestion and ICP-MS were conducted in order to determine the presence of hydrates. The resulting formula of the synthesized Cr(III) solid was $Cr(OH)_3{\bullet}2H_2O$. XRD was performed in order to determine the crystallinity of each of the solids.

Text A.A.2: Standard redox potential calculation for Cr(III) solids

The standard redox potential (E^o) for each of the three Cr(III) solids was calculated as:

$$E^o = (0.059)pe^o$$

pe^o represents pe^o represents the equilibrium constant of a redox reaction in which the oxidant gains one electron. K is the equilibrium constant of a redox reaction in which the oxidant gains n_e of electrons.

$$pe^o = \frac{1}{n_e}\log K$$

pe^o represents the standard redox potential in which the reduced species releases one electron and K is the equilibrium rate constant.

The standard redox potential of amorphous $Cr(OH)_{3(s)}$ is calculated as follows:

Redox half reaction $K_1=10^{76.97}$ (1)[1]
$CrO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O$
Precipitation $K_2=10^{+0.49}$ (2)[2]
$Cr(OH)_2^+ + H_2O \leftrightarrow Cr(OH)_{3\,(s)} + H^+$
Complexation $K_3=10^{+18.38}$ (3)[1]
$Cr^{3+} + 2OH^- \leftrightarrow Cr(OH)_2^+$
Dissociation of water $K_4=10^{-28}$ (4)[1]
$2H_2O \leftrightarrow 2OH^- + 2H^+$

Combine Reactions 1 to 4:
$CrO_4^{2-} + 5H^+ + 3e^- \leftrightarrow Cr(OH)_{3\,(s)} + H_2O$ $K_5=10^{+67.84}$ (5)
$pe^o=\frac{1}{3}(\log K) = \frac{1}{3}(67.84) = 22.61$
$E^o = 1.33$ V

The standard redox potential of chromium oxide $Cr_2O_{3(s)}$ is calculated as follows:

$2CrO_4^{2-} + 16H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 8H_2O$ $K_1=10^{153.94}$ (6)[1]

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[1] Benjamin, M.M. *Water Chemistry 2nd Edition*; Waveland Press Inc. Long Grove, IL, 2015.

[2] Visual Minteq Software Database. http://vminteq.lwr.kth.se (accessed on 7/10/2015).

$2Cr(OH)_2^+ \leftrightarrow Cr_2O_{3\,(s)} + 2H^+ + H_2O$ $K_2=10^{+1.32}$ (7)[2]
$2Cr^{3+} + 4OH^- \leftrightarrow 2Cr(OH)_2^+$ $K_3=10^{+36.76}$ (8)[1]
$4H_2O \leftrightarrow 4OH^- + 4H^+$ $K_4=10^{-56}$ (9)[1]

Combine Reactions 6 to 9:
$2CrO_4^{2-} + 10H^+ + 6e^- \leftrightarrow Cr_2O_{3\,(s)} + 5H_2O$ $K_5=10^{+136.05}$ (10)
$pe^o=\frac{1}{6}(\log K) = \frac{1}{6}(136.05) = 22.67$

The standard redox potential of copper chromite $Cu_2Cr_2O_{5(s)}$ is calculated as follows:

First, the equilibrium constant K must be calculated:

$2CuO_{(am)} + Cr_2O_{3\,(s)} \leftrightarrow Cu_2Cr_2O_{5(s)}$ $\Delta G^o_{formation}=-1056\ \frac{J}{mol}$ (11)[3]

$\Delta G^o=-RT\ln K=(-8.314\ \frac{J}{mol*K})(298K)(\ln K)$

$\ln K = 0.4262$

Oxidation potential calculation using calculated K:
$2CrO_4^{2-} + 16H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 8H_2O$ $K_1=10^{153.94}$ (12)[1]
$2Cr(OH)_2^+ \leftrightarrow Cr_2O_{3\,(s)} + 2H^+ + H_2O$ $K_2=10^{+1.32}$ (13)[2]
$2Cr^{3+} + 4OH^- \leftrightarrow 2Cr(OH)_2^+$ $K_3=10^{+36.76}$ (14)[1]
$4H_2O \leftrightarrow 4OH^- + 4H^+$ $K_4=10^{-56}$ (15)[1]
$Cu^+ \leftrightarrow Cu^{2+} + e^-$ $K_5=10^{-2.69}$ (16)[1]
$Cu^{2+} + H_2O \leftrightarrow CuO_{(am)} + 2H^+$ $K_6=10^{-8.45}$ (17)[1]
$CuO_{(am)} + Cr_2O_{3\,(s)} \leftrightarrow Cu_2Cr_2O_{5(s)}$ $K_7=10^{+0.4262}$ (18)

Combine Reactions 12 to 18
$CrO_4^{2-} + 8H^+ + 5e^- + Cu^{2+} \leftrightarrow Cu_2Cr_2O_{5(s)} + 5H_2O$ $K_8=10^{+125.30}$ (19)
$pe^o=\frac{1}{6}(\log K) = \frac{1}{6}(136.05) = 22.67$
$E^o = 1.337\ V$

To calculate the redox potential (E) for $CrO_4^{2-}/Cr(OH)_{3(s)}$ in typical drinking water conditions (Table S1), Nernst equation was applied:

$$pe = \frac{1}{n_e}\log\frac{\{Red\}}{\{Ox\}} + \frac{n_H}{n_e}pH - pe^o$$

$$pe = \frac{1}{3}\log\frac{\{Cr(III)\} = 1}{[\{Cr(VI)\} = 1x10^{-10}\,mM\,]} + \frac{5}{3}(7) - 22.16 = 7.70$$

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[3] Jacobs, K.T. Gibbs energy of formation of $CuCrO_4$ and phase relations in the system Cu-Cr-O below 735 K. *Thermochimica Acta*. **1992**, *208*, 341-348.

$$E = \frac{7.70}{0.059} = 0.13\ V$$

The rest of the redox potentials were calculated and listed in Table 3.1. Throughout the course of the reaction, the oxidation potential of the HOCl/Cl- redox couple is always greater than that of each of the three Cr(III) solids. This relationship holds in typical drinking water chemical conditions. Therefore, the experimental conditions did not change the thermodynamics boundary of the redox system compared to drinking water conditions. For example, in typical drinking water conditions – 2 mg/L of chlorine, 7 mg/L of chloride and pH at 7 – the redox potential of $HOCl/Cl^-$ redox couple is 1.41 V. This is much higher than the redox potentials of $CrO_4^{2-}/Cr(III)_{(s)}$ for all three Cr(III) solids, with 0.16 V, 0.16 V and 0.20 V for $Cr(OH)_{3(s)}$, $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$, respectively.

Text A.A.3: Calculation on bromide catalytic effects

The first-order rate constant of HOBr decay (0.0553 min^{-1} calculated from the slope of data in Figure 3.17 was divided by the concentration of Cr(III) in the system (2.8 mM) to get a second order rate of 19.8 M^{-1} s^{-1} (referred to as k$_{formation}$).

Mass balance on bromide:

$$\frac{d[Br^-]}{dt} = k_{formation}[HOBr]\left[Cr(III)_{(s)}\right] - k_{consumption}[HOCl][Br^-]$$

At steady-state condition, $\frac{d[Br^-]}{dt} = 0$. Therefore:

$$\frac{[HOBr]_{ss}}{[Br^-]_{ss}} = \frac{k_{consumption}[HOCl]_t}{k_{formation}[Cr(III)_{(s)}]_t}$$

At initial experimental conditions, [HOCl]$_i$ = 0.28 mM and [Cr(III)]$_i$ = 2.8 mM. From literature and experimental calculations, k$_{consumption}$=1550 M^{-1} s^{-1} and k$_{formation}$=19.8 M^{-1} s^{-1}, respectively. Therefore:

$$\frac{[HOBr]_{ss}}{[Br^-]_{ss}} = \frac{(1550)(1)}{(19.75)(10)} = 7.85$$

A value of 7.85 indicates that the steady state concentration of HOBr is significantly greater than the steady state concentration of Br$^-$ in the system.

Text A.A.4: Kinetics Model Prediction on Cr(VI) formation in drinking water

Considering a drinking water distribution system with a residual chlorine of 0.3 mg/L. and a Cr(III) solid of 100 µg/L, this level of chlorine residual is within the typical concentration range of disinfectant residual in distribution system, and the level of Cr(III) still meets the EPA regulation on total Cr level (Maximum Contamination Level = 100 µg/L). Based on the second-order reaction kinetics model established in this study, Cr(VI) formation in drinking water from Cr(III) solid oxidation by chlorine can be predicted as a function of residence time in the distribution system:

$$Cr(VI) = Cr(III)_{(S),initial}\{1 - \exp(-k_{Cr(VI)}\left(S_{Cr(III)_{(s)}}\right)\left[MW_{Cr(III)_{(s)}}\right][HOCl]_{TOT}t)\}$$

$Cr(III)_{(s),initial}$ is the initial concentration of a particular type of residual Cr(III) solid in drinking water distribution system (100 µg/L). $k_{Cr(VI)}$ is the surface area normalized rate constant of Cr(VI) formation ($L{\cdot}m^{-2}{\cdot}s^{-1}$). $S_{Cr(III)(s)}$ is the BET surface area of a particular Cr(III) solid (m^2/g). $MW_{Cr(III)(s)}$ is the molecular weight of the corresponding Cr(III) solid (g/mol). $[HOCl]_{TOT}$ is the total concentration of free chlorine including both hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), *i.e.*, $[HOCl]_{TOT}=[HOCl]+[OCl^-]$ (mol/L). *t* is the residence time of distributions system.

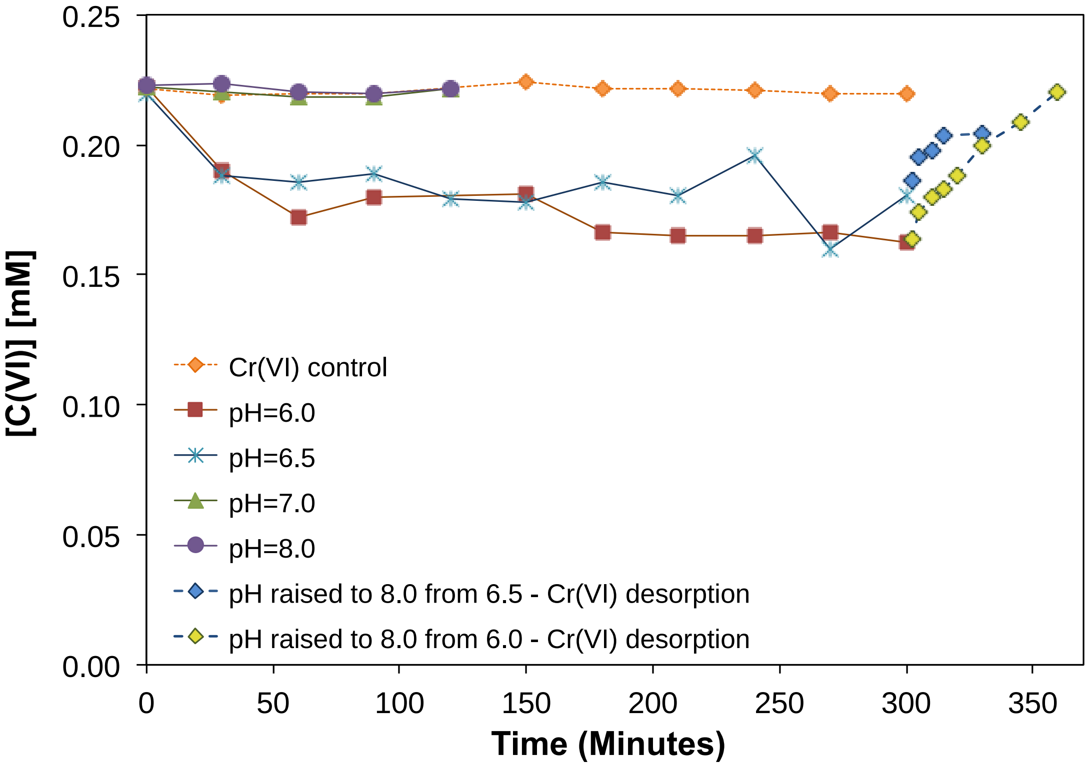


Figure A.A.1 Experiments on the adsorption and desorption of Cr(VI) on $Cr(OH)_{3(s)}$. Initial $[Cr(OH)_{3(s)}]$= 2.8 mM, initial [Cr(VI)]=0.22 mM. Ionic strength=10 mM.

The adsorption of Cr(VI) on $Cr(OH)_{3(s)}$ was negligible when the solution pH was equal or above 7.0, as shown by the Cr(VI) measurements at pHs 7.0 and 8.0. Approximately 20% of Cr(VI) was absorbed on $Cr(OH)_{3(s)}$ when he solution pH was below 7.0, as shown in the Cr(VI) measurements at pHs 6.5 and 6.0. The adsorbed Cr(VI) was recovered by increasing the solution pH to 8.0. For example, when the solution pH was raised from 6.5 to 8.0, 100% of the Cr(VI) was recovered in 45 minutes.

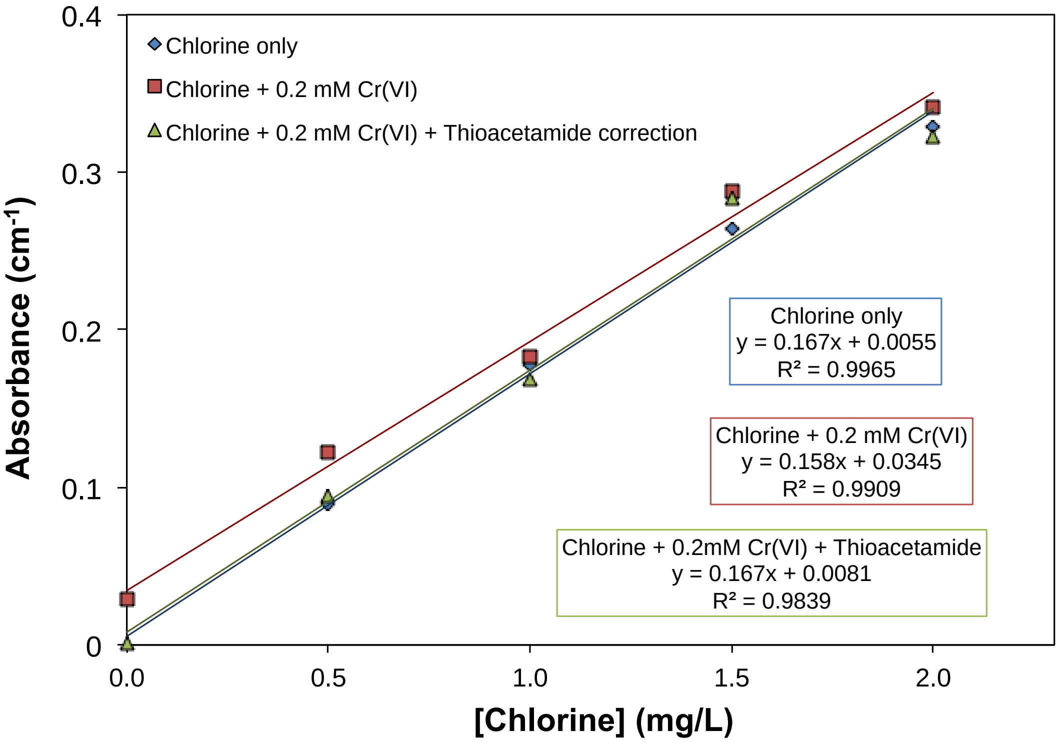


Figure A.A.2 Measurements of free chlorine by DPD method. The interference caused by the presence of Cr(VI) was eliminated when the DPD method was modified with the addition of thioacetamide.

The standard DPD colorimetric method for chlorine measurement can be subject to interference caused by Cr(VI). This interference comes from the oxidation of DPD by Cr(VI). To account for any Cr(VI) interference in DPD, thioacetmide was added to quench chlorine and quantify any absorbance induced by Cr(VI). For example, when 0.2 mM Cr(VI) coexisted with chlorine, the difference of absorbance in the samples without thioactamide addition (red square dots) and the ones with thioactamide addition (green triangle dots) was contributed by Cr(VI). This is seen by the upward shift in the y-axis values (red squares *vs*. green triangles). When thioacetamide was added (green triangles), this interference was effectively removed as the y-axis values were the same as the ones in samples without Cr(VI) (green triangles *vs*. blue diamonds). In all samples taken from actually oxidation experiments, the amount of Cr(VI) was much lower than 0.2 mM Cr(VI). Therefore, chlorine concentration was accurately measured without Cr(VI) interference in all experimental samples.

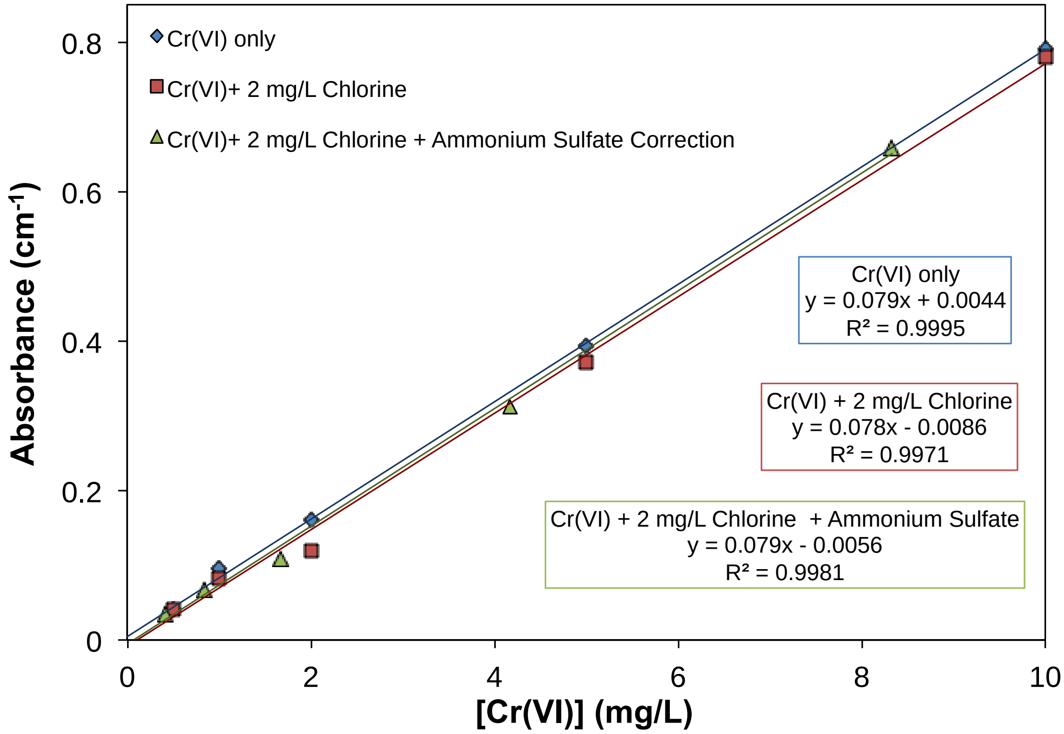


Figure A.A.3 Measurements of Cr(VI) by DPC method. The possible interference caused by the presence of chlorine was eliminated when the DPD method was modified with the addition of ammonium sulfate.

The standard DPC colorimetric method for Cr(VI) measurement could be subject to interference caused by chlorine. This interference may come from the oxidation of DPC by chlorine. Results showed that chlorine did not cause a significant interference on Cr(VI) measurement, as indicated by the difference of absorbance between the samples with chlorine (red square dots) and the one without chlorine (blue diamond dots). The addition of ammonium sulfate quenched any possible interference from chlorine, allowing for an accurate reading of the Cr(VI) absorbance, as indicated by the green triangle dots. The addition of ammonium sulfate converted chlorine to chloramine. Chloramine did not oxidize DPC within the time scale of measurements and possible chlorine interference was eliminated.

Appendix B:

Supporting Information for Chapter 4

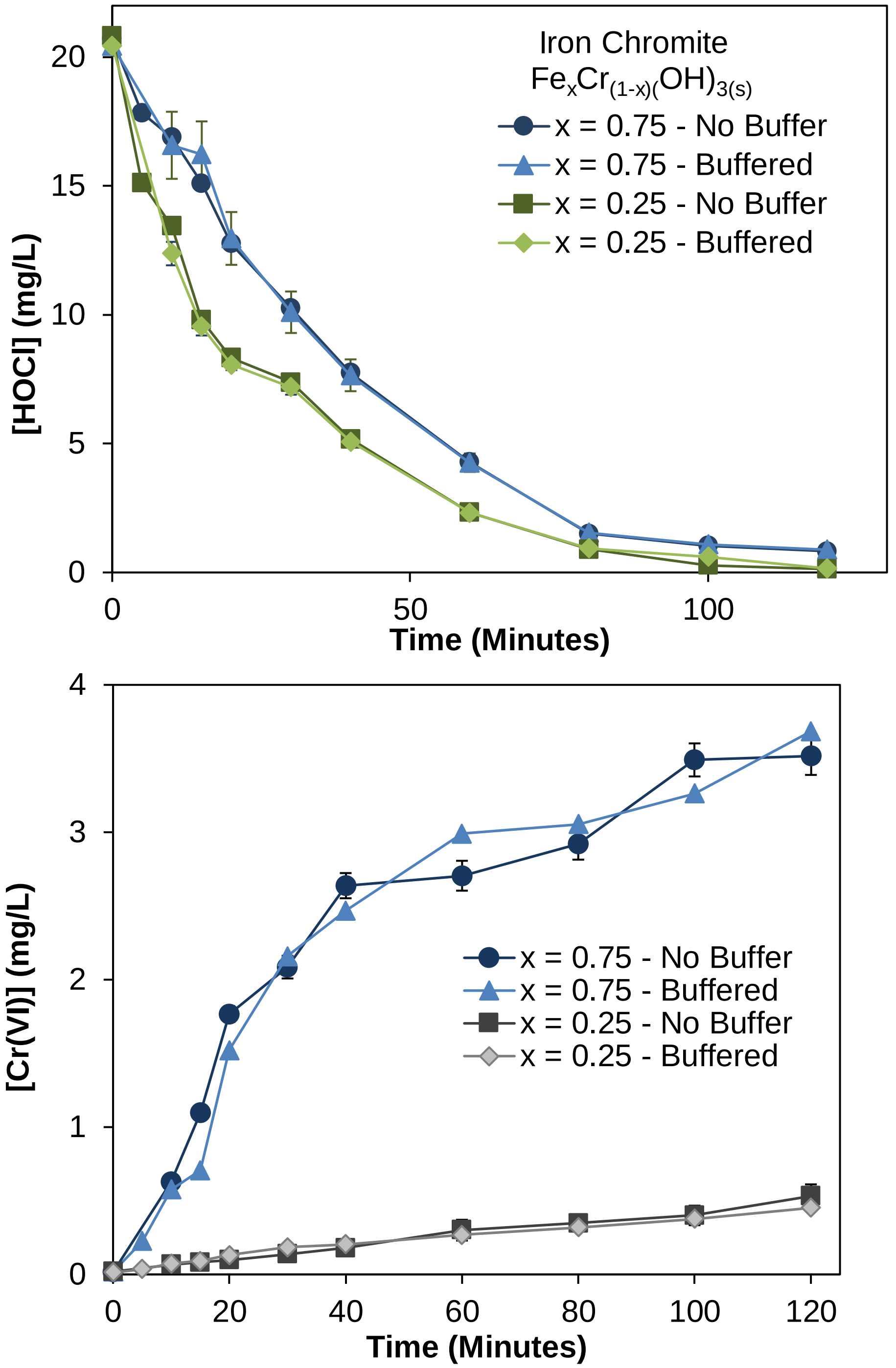


Figure A.B.1 (A) Chlorine consumption and (B) Cr(VI) formation during the oxidation of iron chromite by chlorine. Initial conditions: [Cr(III)]=2.8 mM, [HOCl]=20 mg/L, [$NaClO_4$ (IS)]=10 mM. This graph shows that phosphate buffer has no effect on the surface redox chemistry of the solid. The batch reactor system with no buffer was kept at pH 7 using a pH titration system that added small drops of 0.05 M of NaOH and $HClO_4$.

Text A.B.1 Determination of K_{sp} and E^o from log K

K_{sp} (the solubility product constant) is the equilibrium constant for a solid substance dissolving in an aqueous solution. In order to determine the K_{sp} for the synthesized $Fe_xCr_{(1-x)}OH_{3(s)}$, a 1.25 g/L solution of solid was kept under continuous mixing until the pH was stabilized. This indicated that equilibrium had been reached. The ionic strength of the solution was kept 10 mM with sodium perchlorate ($NaClO_4$). The following equation was used to calculate K_{sp}:

$$\mathrm{Fe_xCr_{(1-x)}(OH)_3} \rightleftharpoons \mathrm{xFe^{3+}} + \mathrm{(1-x)Cr^{3+}} + \mathrm{3OH^-}$$

$$K_{sp} = (\gamma_{Fe} * [Fe])^x * (\gamma_{Cr} * [Cr])^{(1-x)} * [OH^-]^3$$

The activity coefficient (γ) was assumed to be 1 due to the low ionic strength of the solution. The units of concentration were in M and a, b, c are the stoichiometric coefficients of the solids. The pH of each $Fe_xCr_{(1-x)}OH_{3(s)}$ at equilibrium is reported below. After equilibrium was reached, a sample was taken and filtered using a 0.22 μM filter. The dissolved fraction was then measured using ICP-MS. The dissolved concentration for each solid was reported and the K_{sp} calculated in the table below.

Iron chromium hydroxide	pH_{eq}	$[Fe^{3+}]$ (mM)	$[Cr^{3+}]$ (mM)	**K_{sp}**	log K_{sp}
$Fe_{0.25}Cr_{0.75}(OH)_3$	4.36	0.0038	0.0212	$1.66\text{x}10^{-31}$	-33.77
$Fe_{0.5}Cr_{0.5}(OH)_3$	4.27	0.0008	0.0321	$3.33\text{x}10^{-32}$	-34.48
$Fe_{0.75}Cr_{0.25}(OH)_3$	4.19	0.0037	0.0196	$2.09\text{x}10^{-32}$	-34.68

log K can be converted into pe^o dividing by the number of electrons transferred in the oxidation process. To determine the standard reduction potential E_H^o, the following equation was used:

$$E_H^o = (0.059\,V)pe^o$$

Fe(III) molar content	w/Fe(OH)$_{3(s)}$		w/out Fe(OH)$_{3(s)}$	
	$\mathbf{E_H^o}$ (V)	**E (V)**	**$\mathbf{E_H^o}$ (V)**	**E (V)**
0.25	**1.79**	**0.29**	**2.79**	**0.58**
0.5	**2.87**	**0.59**	**3.31**	**0.72**
0.75	**6.08**	**1.06**	**9.06**	**1.16**

The calculation for E_H^o is shown for each solid is shown in the tables below.

E was calculated using the experimental conditions at t = 0 minutes at pH 7 with the Nerst equation:

$$pe = pe^o - \frac{1}{N_{e^-}} \log\left(\frac{Red}{Ox}\right) - \left(\frac{N_{H^+}}{N_{e^-}}\right) pH$$

where N_{e^-} is the number of electrons consumed, N_{H^+} is the number of H^+ generated, [Red] is the concentration of Cr(III) ($[Cr(III)]_{t=0}$ =2.8 mM), [Ox] is the concentration of Cr(VI) at t = 0.

Calculation of $\mathbf{Fe_{0.5}Cr_{0.5}(OH)_{3(s)}}$ reduction potential assuming precipitation of $\mathbf{Fe(OH)_{3(s)}}$

Chemical Reaction	log K
$Fe_{0.5}Cr_{0.5}(OH)_3 + 3H^+ \rightleftharpoons 0.5Fe^{3+} + 0.5Cr^{3+} + 3H_2O$	-34.47 (log K_{sp})
$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_{3(s)}$	38.80 (log K_{s0})
$Cr^{3+} + 3OH^- \rightleftharpoons Cr(OH)_{3(s)}$	32.65 (log K_{s0})
$Cr(OH)_3 \rightleftharpoons Cr(OH)_2{}^+ + OH^-$	-6.35 (log K_3)
$Cr(OH)_2{}^+ + H_2O \rightleftharpoons CrO_4{}^{2-} + 6H^+ + 3e^-$	-67.376 (log K_{eq})
$H_2O \rightleftharpoons H^+ + OH^-$	-14 (K_w)
Σ log K = -34.47 + (38.8 + log 0.5) + (32.65 + log 0.5) + (-6.35 + log 0.5) + (-67.376 + log 0.5) + (2.5 x -14) = -72.96	
$Fe_{0.5}Cr_{0.5}(OH)_3 \rightleftharpoons 0.5CrO_4{}^{2-} + 0.5Fe(OH)_3 + 1.5e^- + 2.5H^+$	**log K = -72.96** **pe° = -48.64** *Oxidation*
$0.5CrO_4{}^{2-} + 0.5Fe(OH)_3 + 1.5e^- + 2.5H^+ \rightleftharpoons Fe_{0.5}Cr_{0.5}(OH)_3$	**log K = 72.96** **pe° = 48.64** *Reduction*
$\mathbf{E_H^o} = (0.059\ V)pe^o = \mathbf{2.87\ V}$	
Using experimental conditions t=0, $\mathbf{E = 0.59\ V}$	

Calculation of $\mathbf{Fe_{0.25}Cr_{0.75}(OH)_{3(s)}}$ reduction potential assuming precipitation of $\mathbf{Fe(OH)_{3(s)}}$

Chemical Reaction	log K
$Fe_{0.25}Cr_{0.75}(OH)_3 + 3H^+ \rightleftharpoons 0.25Fe^{3+} + 0.75Cr^{3+} + 3H_2O$	-33.77 (log K_{sp})
$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_{3(s)}$	38.80 (log K_{s0})
$Cr^{3+} + 3OH^- \rightleftharpoons Cr(OH)_{3(s)}$	32.65 (log K_{s0})
$Cr(OH)_3 \rightleftharpoons Cr(OH)_2{}^+ + OH^-$	-6.35 (log K_3)
$Cr(OH)_2{}^+ + H_2O \rightleftharpoons CrO_4{}^{2-} + 6H^+ + 3e^-$	-67.376 (log K_{eq})
$H_2O \rightleftharpoons H^+ + OH^-$	-14 (K_w)
Σ log K = -33.77 + (38.8 + log 0.25) + (32.65 + log 0.75) + (-6.35 + log 0.75) + (-67.376 + log 0.75) + (2.25 x -14) = -69.23	
$Fe_{0.25}Cr_{0.75}(OH)_3 \rightleftharpoons 0.75CrO_4{}^{2-} + 0.25Fe(OH)_3 + 2.25e^- + 3.75H^+$	**log K = -68.53** **pe° = -30.45** *Oxidation*
$0.75CrO_4{}^{2-} + 0.25Fe(OH)_3 + 2.25e^- + 3.75H^+ \rightleftharpoons Fe_{0.25}Cr_{0.75}(OH)_3$	**log K = 68.53** **pe° = 30.45** *Reduction*
$\mathbf{E_H^o} = (0.059\ V)pe^o = \mathbf{1.79\ V}$	
Using experimental conditions t=0, $\mathbf{E = 0.29\ V}$	

Calculation of $\mathbf{Fe_{0.25}Cr_{0.75}(OH)_{3(s)}}$ reduction potential assuming no precipitation of $\mathbf{Fe(OH)_{3(s)}}$

Chemical Reaction	log K
$Fe_{0.25}Cr_{0.75}(OH)_3 + 3H^+ \rightleftharpoons 0.25Fe^{3+} + 0.75Cr^{3+} + 3H_2O$	-33.77 (log K_{sp})
$Cr^{3+} + 3OH^- \rightleftharpoons Cr(OH)_{3(s)}$	32.65 (log K_{s0})
$Cr(OH)_3 \rightleftharpoons Cr(OH)_2{}^+ + OH^-$	-6.35 (log K_3)
$Cr(OH)_2{}^+ + H_2O \rightleftharpoons CrO_4{}^{2-} + 6H^+ + 3e^-$	-67.376 (log K_{eq})
$H_2O \rightleftharpoons H^+ + OH^-$	-14 (K_w)
Σ log K = -33.77 + (32.65 + log 0.75) + (-6.35 + log 0.75) + (-67.376 + log 0.75) + (2.25 x -14) = -106.73	
$Fe_{0.25}Cr_{0.75}(OH)_3 \rightleftharpoons 0.75CrO_4{}^{2-} + 0.25Fe^{3+} + 2.25e^- + 3.75H^+$	**log K = -106.73** **pe^o = -47.44** *Oxidation*
$0.75CrO_4{}^{2-} + 0.25Fe^{3+} + 2.25e^- + 3H^+ \rightleftharpoons Fe_{0.25}Cr_{0.75}(OH)_3$	**log K = 106.73** **pe^o = 47.44** *Reduction*
$\mathbf{E_H^o} = (0.059\ V)pe^o = \mathbf{2.79\ V}$	
Using experimental conditions at t=0, $\mathbf{E = 0.58\ V}$	

Calculation of $\mathbf{Fe_{0.75}Cr_{0.25}(OH)_{3(s)}}$ reduction potential assuming precipitation of $\mathbf{Fe(OH)_{3(s)}}$

Chemical Reaction	log K
$Fe_{0.75}Cr_{0.25}(OH)_3 + 3H^+ \rightleftharpoons 0.75Fe^{3+} + 0.25Cr^{3+} + 3H_2O$	-34.68 (log K_{sp})
$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_{3(s)}$	38.80 (log K_{s0})
$Cr^{3+} + 3OH^- \rightleftharpoons Cr(OH)_{3(s)}$	32.65 (log K_{s0})
$Cr(OH)_3 \rightleftharpoons Cr(OH)_2{}^+ + OH^-$	-6.35 (log K_3)
$Cr(OH)_2{}^+ + H_2O \rightleftharpoons CrO_4{}^{2-} + 6H^+ + 3e^-$	-67.376 (log K_{eq})
$H_2O \rightleftharpoons H^+ + OH^-$	-14 (K_w)
Σ log K = -34.68 + (38.85 + log 0.75) + (32.65 + log 0.25) + (-6.35 + log 0.25) + (-67.376 + log 0.25) + (2.75 x -14) = -77.39	
$Fe_{0.75}Cr_{0.25}(OH)_3 \rightleftharpoons 0.25CrO_4{}^{2-} + 0.75Fe(OH)_3 + 0.75e^- + 1.25H^+$	**log K = -77.39** **pe^o = -103.18** *Oxidation*
$0.25CrO_4{}^{2-} + 0.75Fe(OH)_3 + 0.75e^- + 1.25H^+ \rightleftharpoons Fe_{0.75}Cr_{0.25}(OH)_3$	**log K = 77.39** **pe^o = 103.18** *Reduction*
$\mathbf{E_H^o} = (0.059\ V)pe^o = \mathbf{6.08\ V}$	
Using experimental conditions at t=0, $\mathbf{E = 1.06\ V}$	

=

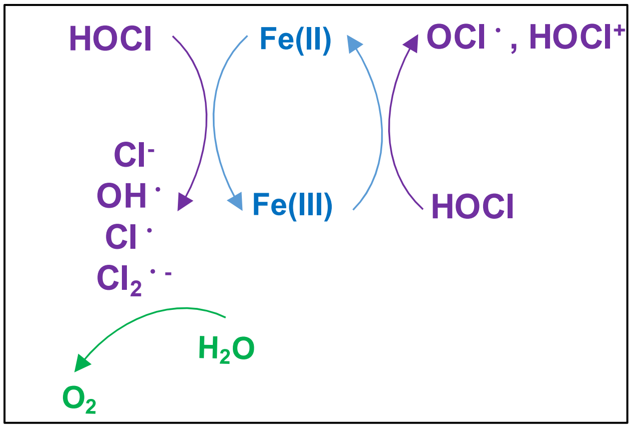
Calculation of $\mathbf{Fe_{0.75}Cr_{0.25}(OH)_{3(s)}}$ reduction potential assuming precipitation of $\mathbf{Fe(OH)_{3(s)}}$

Chemical Reaction	log K
$Fe_{0.75}Cr_{0.25}(OH)_3 + 3H^+ \rightleftharpoons 0.75Fe^{3+} + 0.25Cr^{3+} + 3H_2O$	-34.68 (log K_{sp})
$Cr^{3+} + 3OH^- \rightleftharpoons Cr(OH)_{3(s)}$	32.65 (log K_{s0})
$Cr(OH)_3 \rightleftharpoons Cr(OH)_2{}^+ + OH^-$	-6.35 (log K_3)
$Cr(OH)_2{}^+ + H_2O \rightleftharpoons CrO_4{}^{2-} + 6H^+ + 3e^-$	-67.376 (log K_{eq})
$H_2O \rightleftharpoons H^+ + OH^-$	-14 (K_w)
Σ log K =-34.68 + (32.65 + log 0.25) + (-6.35 + log 0.25) + (-67.376 + log 0.25) + (2.75 x -14) = -77.39	
$Fe_{0.75}Cr_{0.25}(OH)_3 \rightleftharpoons 0.25CrO_4{}^{2-} + 0.75Fe(OH)_3 + 0.75e^- + 1.25H^+$	**log K = -115.16** **pe^o = -153.48** *Oxidation*
$0.25CrO_4{}^{2-} + 0.75Fe(OH)_3 + 0.75e^- + 1.25H^+ \rightleftharpoons Fe_{0.75}Cr_{0.25}(OH)_3$	**log K = 115.16** **pe^o = 153.48** *Reduction*
$\mathbf{E_H^o} = (0.059\ V)pe^o = \mathbf{9.06\ V}$	
Using experimental conditions at t=0, $\mathbf{E = 1.16\ V}$	

Text A.B.2 Radical reactions and mechanism

Similar to the mechanism in a Fenton-like reaction, the oxidation of iron could potentially HOCl to form HOCl$^{\cdot-}$. This radical then can react with various species present to form other powerful radicals that eventually degrade to O_2. Given the presence of chlorine, the question arises whether which radical species are likely to form and dominate (e.g. OH$^{\cdot}$, Cl$^{\cdot}$, Cl$_2^{\cdot-}$). It is proposed that the following reactions occur.

Scheme 1 Proposed reaction scheme for to the impact of iron on HOCl decay



1. Because of the inherent presence of Cl$^-$, HOCl$^{\cdot-}$ can form Cl$_2^{\cdot-}$:

$$HOCl^{\cdot-} + Cl^- \rightarrow Cl_2^{\cdot-} + OH^-$$

2. Also, HOCl$^{\cdot-}$ can auto-decompose to form OH$^{\cdot}$:

$$HOCl^{\cdot-} \rightarrow OH^{\cdot} + Cl^-$$

3. After its formation, Cl$_2^{\cdot-}$ can react with water to regenerate HOCl$^{\cdot-}$:

$$Cl_2^{\cdot-} + Cl^- \rightarrow HOCl^{\cdot-} + Cl^- + H^+$$

4. Cl$_2^{\cdot-}$ autodecays into Cl$^{\cdot}$:

$$Cl_2^{\cdot -} \rightarrow Cl^{\cdot} + Cl^{-}$$

5. $HOCl^{\cdot -}$ can also be regenerated from $OH^{\cdot}$ reaction with Cl^{-} :

$$OH^{\cdot} + Cl^{-} \rightarrow HOCl^{\cdot -}$$

Based on the proposed reaction mechanism, it is likely that $OH^{\cdot}$ is the primary radical formed, followed by $HOCl^{\cdot -}$ and $Cl_2^{\cdot -}$. $Cl^{\cdot}$ may be present, but is less likely than other radicals to be formed. It is also proposed that the reduction of iron is accompanied with the formation of HOCl or OCl^{-} (depending on reaction pH) to $OCl^{\cdot}$ or $HOCl^{+}$. This postively charged hypochlorite radical has been reported during the aqueous decmoposition of HOCl and in the presence of catalysts.