EVALUATION OF THE USE OF FERROUS IRON

FOR CHLORITE REMOVAL UNDER ALKALINE
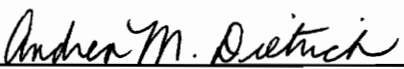
pH CONDITIONS

by

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(ABSTRACT)

Chlorine dioxide has gained much attention for use as a possible alternative disinfectant in water treatment plants due to concerns regarding trihalomethane formation in drinking waters which utilize chlorine as the primary disinfectant and the strict regulations regarding THM's and THMFP (MCL of 0.080 mg/L for TTHMs) (Pontius, 1993). Although the use of ClO_2 as a disinfectant prevents the formation of THM's, concern exists regarding the potential health risks due to the disinfection-by-products of chlorite and chlorate.

The main objective of this project was to study the removal of chlorite by reaction with ferrous iron under elevated pH conditions. The stoichiometry of the reaction was evaluated under the following conditions: solution pH of 6.0 to 10.0, O_2(aq) concentration of 0.5 to 10 mg/L, and solution DOC concentrations of 0 to 15 mg/L. Mass balances were conducted to define the speciation of the oxychlorine residuals associated with the reduction of ClO_2^- by Fe(II).

Ferrous iron dosing from 10 to 20 percent in excess of the theoretical amount required (3.3 mg Fe(II) per mg ClO_2^-) provided for sufficient ClO_2^- removal over the targeted pH range. No significant ClO_3^- residuals were detected as a result of the studied reaction, although trace amounts of O_2(aq) presented a competing reaction over the pH range of 7.0 to 10.0. The impact of DOC content on the removal of ClO_2^- by Fe(II) was negligible over the pH range of 8.0 to 9.0, though testing at solution pH values of 10.0 indicated inefficient ClO_2^- removal. Results from the mass balance studies indicated that approximately 95 percent of the residual was attributed to Cl^-.

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The author extends his sincere appreciation to his parents, Gene and Martha, for their constant support and encouragement. This thesis is dedicated to his wife, Diane, who provided him the motivation and support necessary for project completion.

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CHAPTER I

INTRODUCTION

Chlorine dioxide (ClO_2) has gained much attention for use as a possible alternative disinfectant in water treatment plants due to concerns regarding trihalomethane (THM) formation in drinking waters which utilize chlorine as the primary disinfectant and the strict regulations regarding THM's and THMFP (MCL of 0.080 mg/L for TTHMs) (Pontius, 1993). Although the use of ClO_2 as a disinfectant prevents the formation of THM's, concern exists regarding the potential health risks due to the disinfection-by-products (DBPs) of chlorite (ClO_2^-) and chlorate (ClO_3^-). In order for ClO_2 to become an acceptable (ie. both economically and technically) alternative disinfectant, it is necessary to reduce or eliminate the DBP's associated with its use.

Research conducted by Iatrou and Knocke (1992) concentrated on the removal of ClO_2^- by reaction with ferrous iron (Fe(II)). Reaction rates and stoichiometric amounts were determined for the Fe(II)/ ClO_2^- reaction at pH values ranging from 5.0 - 7.0. The possible formation of ClO_3^- as a by-product of the Fe(II)/ClO_2^- reaction was also monitored throughout the study.

Results from the study indicated that ClO_2^- removal by reaction with Fe(II) was a feasible alternative for drinking

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water treatment. Interferences due to dissolved oxygen (O_2(aq)) concentrations were found to be minimal. Further, no evidence of a ClO_3^- by-product due to the removal of ClO_2^- by Fe(II) was discovered.

The overall goal of this research was to study the Fe(II)/ClO_2^- reaction under elevated pH conditions which would be applicable to the utilization of this technology in water treatment plants that practice lime-soda ash softening (ie. under elevated pH conditions). Specific research objectives were to:

(1) evaluate the stoichiometry of the Fe(II)/ClO_2^- reaction under alkaline pH conditions, including possible interferences due to the presence of O_2(aq);

(2) determine whether ClO_3^- is formed when Fe(II) and ClO_2^- react under alkaline pH conditions; and

(3) evaluate the impact of dissolved organic carbon (DOC) on the stoichiometry of Fe(II)/ClO_2^- reaction.

CHAPTER II

LITERATURE REVIEW

Introduction

This section details information relative to the study of the oxidation of Fe(II) by ClO_2^-. Topics to be addressed include ClO_2 uses and chemistry, health concerns related to ClO_2 and its disinfection-by-products, removal of ClO_2 inorganic by-products from solution, oxidation of Fe(II) by $O_2(aq)$, and reactions between Fe(II) and aquatic DOC.

ClO_2 Uses and Chemistry

ClO_2 has many possible uses in the treatment of drinking water, including iron and manganese removal, color removal, and taste and odor reduction. The use of ClO_2 in water treatment facilities would prevent the formation of THM's and lower the THM formation potential (THMFP) within the water being treated (AWWA, 1990), and also effectively inactivates bacteria and viruses over a relatively broad pH range (Aieta, et al, 1984). As a result of the problems concerning THM production with the use of chlorine as a disinfectant, the U.S. Environmental Protection Agency (USEPA) recommended the use of ClO_2 as both a primary and supplemental disinfectant in 1983 (Weredehoff, et al, 1987). USEPA also declared that the combined residuals of ClO_2 and its DBP's (ie. chlorite and chlorate) should not exceed 1.0

mg/L (USEPA, 1983). Recent updates reported in the <u>American</u> <u>Water Works Association Journal</u> indicate a potential future MCL of 1.0 mg/L for ClO_2^- and a maximum residual disinfectant level of 0.8 mg/L for ClO_2 (Pontius, 1993).

ClO_2 maintains several advantages with respect to chlorine; not only does it prevent the formation of THM's, ClO_2 has a higher solubility in water, is less sensitive to pH changes, and maintains approximately 2.5 times the oxidizing power of chlorine (Handbook of Chlorination, 1972). ClO_2 is prepared on-site due to its high reactivity. Methods utilized in the generation of ClO_2 include the chlorine-chlorite process, the chlorine-chlorite process coupled with hypochlorite feeding systems, acid generation which involves the mixing of hydrochloric acid with chlorine prior to reaction with sodium chlorite, and the use of Anthium Dioxide (a stabilized aqueous solution of ClO_2). The basis for the most frequently utilized generation method (ie. chlorine-chlorite process) is illustrated by Equation #1, which normally occurs under low pH conditions (ie. pH 2-4) (Handbook of Chlorination, 1972 and Aieta, <u>et al</u>, 1986).

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \qquad [1]$$
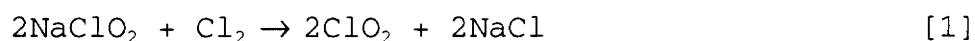
Application of ClO_2 within a treatment scheme normally occurs before settling or filtration and/or after filtration with dosages ranging from 0.1 - 5.0 mg/L (Aieta, <u>et al</u>, 1986).

The disproportionation of ClO_2 in alkaline solutions (illustrated in Equation #2) results in the formation of ClO_2^- and ClO_3^- (AWWA, 1990):

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \qquad [2]$$
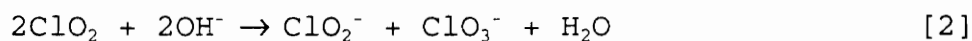
Studies by Weredehoff, et al, (1987) indicated that seventy percent (70%) of the ClO_2 consumed during water treatment resulted in the formation of ClO_2^-. Gordon et al, (1990), Miller et al, (1978) and White, (1972) concur that the predominant by-product of ClO_2 reactions in water treatment is ClO_2^-. As illustrated by the half-reaction presented in Equation #3, the reduction of ClO_2 to ClO_2^- involves a one electron transfer (Handbook of Chlorination, 1972).

$$ClO_2 + e^- \rightleftharpoons ClO_2^- \qquad [3]$$

In the presence of free chlorine species, the oxidation of ClO_2^- will result in the production of chloride (Cl^-), ClO_2, or ClO_3^-.

$$HOCl + ClO_2^- + OH^- \rightarrow ClO_3^- + Cl^- + H_2O \qquad [4]$$

$$HOCl + 2ClO_2^- \rightarrow 2ClO_2 + Cl^- + OH^- \qquad [5]$$
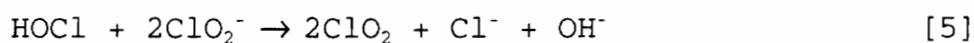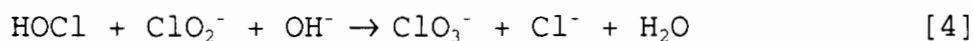
The reaction shown as Equation #5 predominates at pH 5. Studies conducted by Weredehoff et al, (1987) indicate that the reaction shown as Equation #4 with its associated production of ClO_3^- was the pathway of ClO_2^- oxidation most commonly occurring under typical water treatment conditions. Reported stoichiometries were 0.89 moles of ClO_2^- per 1.0 mole of Cl_2 (Weredehoff, et al, 1987).

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Bolyard _et al_ (1993) conducted a survey which investigated the occurrence of ClO_3^- in drinking waters. This study found both ClO_2^- and ClO_3^- residuals in water being treated with ClO_2. Initial ClO_2 doses ranged from 0.07 - 2 mg/L and resulted in 15 - 740 ug/L and 21 - 330 ug/L of ClO_2^- and ClO_3^-, respectively. All of the waters studied by Bolyard _et al_ maintained a free chlorine residual during distribution.

Werdehoff _et al_ (1987) suggested that ClO_2 dosing during water treatment should not exceed 1.2 - 1.4 mg/L due to the previously cited mechanisms which result in the production of ClO_2^- and ClO_3^- residuals and the USEPA declaration that ClO_2 and its DBP's shall not exceed 1.0 mg/L. Therefore, one can realize the importance of studying methods for the removal of ClO_2 disinfection-by-products in order to make it possible to utilize ClO_2 doses that would be more beneficial within the water treatment industry.

Health Concerns Related to ClO_2 and its Disinfection-By-Products

With USEPA's recommendation of ClO_2 use in water treatment utilities, it was necessary to conduct toxicological studies focusing on ClO_2, ClO_2^-, and ClO_3^-. USEPA's Health Effects Research Laboratory (HERL) funded several such studies which generated health related data corresponding to ClO_2 and its DBP's.

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Studies conducted by Bull (1980) involved exposure to 100 mg/L dose equivalents of ClO_2, ClO_2^-, and ClO_3^-. The following health concerns were discerned from the results:

- o increased mortality rates in rats
- o production of methemoglobinemia
- o production of methemoglobinemia in the blood of humans, rats and guinea pigs via ClO_2^- ingestion

Studies conducted by Condie (1986) resulted in further evidence that ClO_2, ClO_2^-, and ClO_3^- could be associated with effects on the hemopoietic system, with the most emphasis correlated with the presence of ClO_2^-. Other findings of this study were the possibility that ClO_2 may increase cardiovascular disease risk in pigeons and that ClO_3^- (3400 mg/kg) poisoning in humans could result in the following conditions:

- o cyanosis
- o methemoglobinemia
- o renal failure
- o congested kidneys
- o hypothemic
- o convulsions
- o coma

Couri et al (1982) also reported that hemolytic anemia in rats and mice could be associated with ClO_2, ClO_2^-, and ClO_3^- ingested via drinking water, with ClO_2^- being the most significant species of concern.

For those more interested in the toxicological effects of ClO_2 and its disinfection-by-products, reference should be made to the previously cited studies and the USEPA HERL.

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Removal of ClO_2 Inorganic By-Products from Solution

Interactions with Ferrous Iron

Studies conducted by Ondrus and Gordon (1972) reported the reduction of ClO_2^- by reaction with Fe(II) under low pH conditions (ie. pH < 2.0). The investigation led to the development of the following mechanism which was proposed to detail the Fe(II)/ClO_2^- reaction:

$$HClO_2 \leftrightarrow H^+ + ClO_2^- \tag{6}$$

$$HClO_2 + Fe(II) \rightarrow Fe(III) + [Cl(II)] \text{ (slow)} \tag{7}$$

$$ClO_2^- + Fe(II) \rightarrow Fe(III) + [Cl(II)] \text{ (slow)} \tag{8}$$

$$[Cl(II)] + Fe(II) \rightarrow Fe(III) + HOCl \text{ (fast)} \tag{9}$$
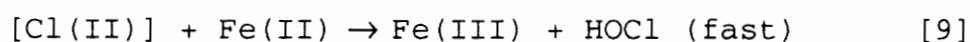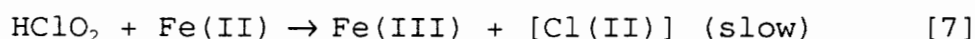
This mechanism can be summarized by the overall reaction depicted in Equation # 10.

$$ClO_2^- + 2Fe(II) + 3H^+ \rightarrow 2Fe(III) + HOCl + H_2O \tag{10}$$
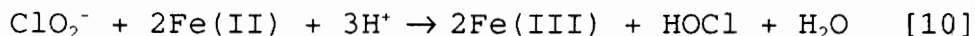
Investigations conducted by Griese et al (1991) at the Evansville, IN., water treatment plant reported that the ClO_2^- ion was efficiently removed from solution with the application of reduced iron chloride ($FeCl_2$). These studies were conducted over a pH range of 6.0 - 7.0 and resulted in complete removal of ClO_2^- in less than 15 minutes when reacted with a 10 to 1 excess of Fe(II). The presence of O_2(aq) resulted in minimal interferences on the ClO_2^-/Fe(II) reaction. Insignificant increases in ClO_3^- residuals were also reported with no evidence that ClO_3^- removal was produced by Fe(II) addition.

In a more recent study Griese et al (1992) reported that the application of ClO_2 (produced electrochemically) coupled with $FeCl_2$ (at 20-50 mg/L) addition effectively reduced residual ClO_2^- (produced from ClO_2 doses ranging from 2-5 mg/L) and lowered the presence of ClO_3^-. Minimization of the ClO_3^- residual was related to the more efficient ClO_2 generation method, and it was also reported that the reduction of ClO_3^- by $FeCl_2$ was ineffective. Chlorate formation associated with prefiltration chlorination established the importance of ClO_2 and ClO_2^- removal prior to post chlorination (Griese, et al, 1992).

Based on the redox reaction between Fe(II) and ClO_2^-, the theoretical stoichiometry indicates that 3.3 mg Fe(II) are required to completely reduce 1.0 mg of ClO_2^- to chloride (Cl^-).

$$4Fe(II) + ClO_2^- + 10H_2O \rightleftharpoons 4Fe(OH)_3(s) + Cl^- + 8H^+ \qquad [11]$$
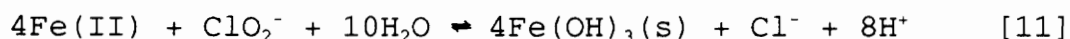
Studies conducted by Iatrou and Knocke (1992) concerning the removal of ClO_2^- by Fe(II) described an experimental stoichiometric ratio of 3.1 mg Fe(II)/ mg ClO_2^- (pH range of 5.0 - 7.0). The authors also reported that ClO_2^- would be effectively removed by Fe(II) within 1-2 minutes under typical water treatment conditions. The possible occurrence of ClO_3^- as a by-product of the Fe(II)/ClO_2^- reaction was also investigated by Iatrou and Knocke. The authors did not detect significant (>0.03 mg/L) ClO_3^- formation when solutions containing initial ClO_2^- concentrations of 4 mg/L

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were treated with Fe(II) for solution pH values from 5.5 -
8.0. Interferences due to O_2(aq) concentrations were found
to be minimal under the pH conditions prevalent to the
study. The authors indicated that residual Fe(II) was
effectively removed by O_2(aq) at pH 7.0; however, results
suggested minimal removal of excess Fe(II) by O_2(aq) at
solution pH values less than 6.3.

Sulfur dioxide - sulfite ion and Sodium Thiosulfate

Gordon et al (1990) reported that ClO_2^- removal by
sulfur dioxide - sulfite ion (SO_2-SO_3^{2-}) was represented by
the following reaction at pH values ranging from 4.0 - 7.5.

$$2SO_3^{2-} + ClO_2^- \rightleftharpoons 2SO_4^{2-} + Cl^- \qquad [12]$$
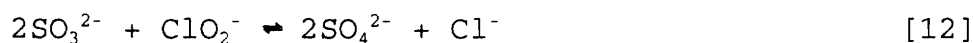
Utilizing Equation #12, the theoretical stoichiometry for
Reaction [12] was reported as 2 moles SO_3^{2-} per mole of ClO_2^-
reduced to Cl^-. The authors also reported fast rates of
reaction utilizing a 10 to 1 SO_2-SO_3^{2-}/ClO_2^- dose with initial
ClO_2^- concentrations of 0.5 to 7.0 mg/L. Chlorite reduction
was accomplished within 1 minute at pH values less than 5.0
and within 15 minutes at pH 6.5. No ClO_3^- removal was
reported.

Griese et al (1991) reported effective ClO_2^- reduction
by SO_2-SO_3^{2-} at solution pH values ranging from 4.0-8.5.
However, significant ClO_3^- formation was observed when the
reaction was conducted in the presence of O_2(aq). These
results were consistent with those reported by Dixon et al
(1991) who indicated the occurrence of significant ClO_3^-

formation when SO_2-SO_3^{2-} was utilized for ClO_2^- removal in the presence of O_2(aq).

Sodium thiosulfate (40 mg/L) has been reported to efficiently reduce ClO_2^- at concentrations up to 4.0 mg/L (Griese, et al, 1991). However, reaction performance was very dependent upon pH and contact time. For example, as solution pH was lowered from 6.8 to 6.4 sodium chlorite removal efficiencies increased from 10 to 90 percent (contact time = 30 minutes). For the test conducted at pH 6.4 an additional 90 minutes of contact time resulted in ClO_2^- residuals below the detection limit established for the study. Insignificant amounts of ClO_3^- formation were reported when utilizing sodium thiosulfate to reduce ClO_2^-.

Granular Activated Carbon

Studies conducted by Voudries et al (1983) reported that ClO_2^- was reduced to Cl^- by surface reactions on granular activated carbon (GAC). These findings were noticed during column and batch tests. The study noted significant decreases in the reaction rate between ClO_2^- and GAC when the ratio of 80-90 mg ClO_2^- per gram GAC was exceeded. Cl^- was the only oxychlorine residual detected after the ClO_2^-/GAC reaction.

Dixon et al (1991) reported that ClO_2^- removal by GAC was greatly influenced by the empty-bed contact time (EBCT) within the column. Greater ClO_2^- removal efficiencies were realized by increasing the EBCT within the GAC column. The

authors also reported that the GAC provides a medium for the reaction of ClO_2^- and free chlorine which resulted in the production of significant amounts of ClO_3^-. Vel Leitner et al (1992) published results which likewise showed both Cl^- and ClO_3^- by-product formation following the interaction of ClO_2^- with GAC. These tests were conducted at a solution pH of 7 and an initial ClO_2^- concentration of 50 mg/L. Formation of ClO_3^- as a by-product may greatly limit the use of GAC as a ClO_2^- removal process since ClO_3^- is very stable in water and not easily removed.

Oxidation of Fe(II) by Oxygen

Stumm and Lee (1961) investigated the Fe(II) oxidation by $O_2(aq)$, describing a two-step iron removal process:

$$Fe(II) + 1/4O_2 + H^+ \rightarrow Fe(III) + 1/2H_2O \qquad [13]$$

$$Fe(III) + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \qquad [14]$$
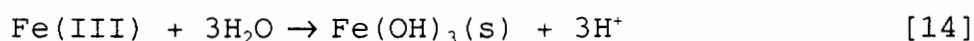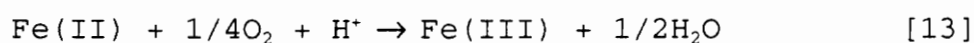
The two equations combine to yield an overall reaction stoichiometry of:

$$2Fe(II) + 1/2O_2 + 5H_2O \rightleftharpoons 2Fe(OH)_3(s) + 4H^+ \qquad [15]$$
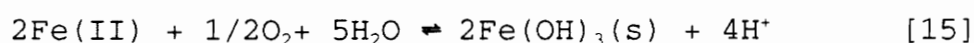
The theoretical stoichiometry of the $O_2(aq)$/Fe(II) reaction is 0.14 mg O_2 per mg of Fe(II) oxidized. Stumm and Lee also reported that the oxidation rate of Fe(II) significantly increased as solution pH, alkalinity, and/or temperature increased.

Iatrou and Knocke (1992) reported that minimal Fe(II) oxidation by $O_2(aq)$ was noticed at pH values equal to or

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less than 6.3. When excess amounts of Fe(II) were present at solution pH values equal to or greater than 7.0, the oxidation of Fe(II) by O_2(aq) was reported to be rapid (reaction time of less than five minutes). Effective Fe(II) oxidation by O_2(aq) was observed between pH 6.3 and 7.0 provided sufficient reaction time (ie. one hour or greater) is provided. Due to the objectives of the present research (ie. study of the Fe(II)/ClO_2^- reaction at elevated pH), it was necessary to determine if the presence of O_2(aq) would interfere with the desired reduction of the ClO_2^- ion by Fe(II).

Reactions Between Fe(II) and Aquatic Organics

Thurman (1985) described DOC as those aquatic organic species that penetrate through a 0.45 um membrane filter. The author reported that iron complexed by this DOC can be very resistant to oxidation. Alberta et al (1983) reported that iron complexation by DOC was dependent upon the type of DOC present as well as the specific dissolved iron species (Fe(II) vs. Fe(III)) in solution. Effects of solution pH on iron complexation were evaluated by Oldham and Gloyna (1969) for test solutions involving a DOC concentration of 50 mg/L and 2.1 mg/L soluble iron. Their results indicated essentially no iron complexation at pH 5, but significant complexation at pH 8. Knocke et al (1990) reported that DOC species with molecular weight values greater than 30

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kilodaltons (kD) exhibited a greater potential to complex soluble iron. These studies also indicated that the ability of this DOC to complex iron was enhanced at higher pH values.

Jobin and Ghosh (1972) proposed that organic materials such as humic and tannic acids retard the oxidation of Fe(II) by O_2(aq). They hypothesized that the decreased rate of Fe(II) oxidation was due to DOC species containing hydroxyl and carboxylic functional groups. Theis and Singer (1974) likewise reported reduced Fe(II) oxidation rates in the presence of a variety of dissolved organic compounds.

Research studies have also investigated the ability of other oxidants to remove Fe(II) from solution when DOC is present. For example, Knocke et al (1991) reported that $KMnO_4$ and ClO_2 both oxidized uncomplexed Fe(II) extremely fast (< 5 seconds) for pH values of 5.5 and above. However, the presence of DOC in solution greatly reduced the ability of either oxidant to promote effective iron removal. Similar results were observed by Knocke et al (1992) who studied Fe(II) complexed by humic and fulvic materials. The authors observed that better iron removal was observed when lower molecular weight DOC was present in solution.

More recent work by Knocke et al (1994) showed that strong oxidants such as HOCl, ClO_2, and $KMnO_4$ can effectively oxidize Fe(II) in the presence of DOC. The authors used ferrozine to differentiate the presence of

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Fe(II) from Fe(III). Knocke et al also showed that significant amounts of DOC can adsorb onto oxidized iron particles, producing stable iron colloids that readily pass through 0.45 um membrane filters. Thus, these results help to explain the earlier findings reported by Knocke et al (1991) and Knocke et al (1992). What these authors interpreted as poor oxidation may in fact have been a problem with the inability of their 0.45 um filters to capture colloidal iron particles.

Knocke et al (1994) also observed that ClO_2 and HOCl dosages for complexed Fe(II) oxidation were typically well above the stoichiometric requirement, suggesting that DOC exerts a competitive demand for both oxidants.

Given its ability to both complex Fe(II) and exert an oxidant demand, the presence of DOC in solution will most likely have a significant impact on the interaction between Fe(II) and ClO_2^-.

Summary

From the literature, it is evident that a thorough investigation of the Fe(II):ClO_2^- reaction at solution pH values ranging from 8.0 to 10.0 is necessary. ClO_2^- removal by reaction with Fe(II) was indicated to be applicable to water treatment processes that operate within the pH range of 5.0 to 7.0. As observed from the studies cited in the literature review the occurrence of ClO_3^- as a by-product of

the $Fe(II):ClO_2^-$ reaction in this pH range was found to be insignificant. Studies of the reaction under elevated pH conditions would also need to focus on the possibility of a reaction by-product (ie. ClO_3^-).

The oxidation of $Fe(II)$ by $O_2(aq)$ was reported to increase with associated increases in solution pH, thereby making it necessary to determine whether the presence of $O_2(aq)$ would inhibit the $Fe(II):ClO_2^-$ reaction at pH values ranging from 8.0 to 10.0.

Iron complexed by DOC was reported to be resistant to oxygenation; and increases in solution pH from 5.0 to 8.0 indicated increased iron complexation. Studies also showed that chemical doses of ClO_2 and $HOCl$ were required to be in excess of stoichiometric requirements in order to achieve complexed $Fe(II)$ oxidation. These findings necessitate the importance of studying the effects of solution DOC on the $Fe(II):ClO_2^-$ reaction at elevated solution pH values.

CHAPTER III

EXPERIMENTAL MATERIALS AND METHODS

Introduction

Research conducted by Iatrou and Knocke (1991) concentrated on the removal of ClO_2^- by reaction with Fe(II) within the pH range of 5.0 - 7.0. This project was a continuation of that research with the major deviation being the emphasis on reaction evaluation under alkaline pH conditions. Most of the methods utilized throughout the project were developed during the original study and were adhered to as closely as possible during the progression of this study.

The stoichiometry of the reaction between Fe(II) and ClO_2^- was observed under several different variables. These included a solution pH of 6.0 - 10.0, O_2(aq) concentrations of <0.5 - 10 mg/L, and dissolved organic matter concentrations ranging from 0 - 15 mg/L (DOC). Experiments were also conducted to determine the speciation of the oxychlorine residuals (ie. ClO_2, Cl_2, and ClO_3^-) formed during the removal of ClO_2^- by Fe(II).

Preparation of Test Solutions

All test and stock solutions were prepared by utilizing distilled-deionized water which was processed through a Milli-Q reagent water system by Millipore Corporation

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(Milford, MA). Background ions were added to the test water in order to provide for hardness and alkalinity. These included calcium chloride (4 meq/L), calcium sulfate (4 meq/L), sodium sulfate (0.5 meq/L), and sodium bicarbonate (4 meq/L).

Whenever test conditions required the use of low O_2(aq) concentrations, the stock water was initially processed through the Millipore system and then deaerated by bubbling with nitrogen gas for 15 minutes. This routinely produced solution O_2(aq) concentrations below 0.5 mg/L. After deaeration, the required background ions were added to the stock solution. Although the intent of the study was to obtain a deaerated test solution, slight amounts of O_2(aq) were inadvertently added to solution during transfer to the reaction vessels. Experiments that involved the presence of significant O_2(aq) required that the stock water be aerated for approximately 15 minutes prior to the addition of the background ions.

Chlorite stock solutions were prepared using anhydrous sodium chlorite ($NaClO_2$) flakes (Eastman Kodak Company, Rochester, NY) which were dissolved in Milli-Q water. Solution pH was maintained at 7 or higher by the addition of sodium bicarbonate prior to the addition of the sodium chlorite. Once prepared, the ClO_2^- stock solution was contained in an amber bottle which was wrapped with aluminum foil and sealed with parafilm. These precautions were

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necessary in order to minimize the photolytic decomposition of the ClO_2^- solution (Gordon, et al, 1990). The ClO_2^- stock solution was stored at 4°C when not in use. Analytical tests were conducted daily to quantify the stock solution concentration, and a fresh batch was prepared every 48 hours (Iatrou & Knocke, 1992).

Ferrous iron solutions were prepared using ferrous sulfate ($FeSO_4 \cdot 7H_2O$) crystals (Fisher Scientific). Milli-Q water was deaerated with nitrogen gas for approximately 15 minutes and the solution pH was adjusted to less than 2 using 10% nitric acid prior to the addition of the ferrous sulfate crystals. The Fe(II) stock solution was contained in a glass bottle that was sealed with parafilm. The stock solution was stored at 4°C when not in use. Daily tests were conducted in order to check the titre of the Fe(II) stock solution. Fresh solutions were prepared every 48 hours or when evidence of Fe(II) oxidation to Fe(III) was visually detected.

Stock DOC solutions were prepared by utilizing a humic source obtained from the Great Dismal Swamp, Sulfolk, Virginia. The source material had been previously extracted by Shorney (1992) using the isolation procedures outlined by Thurman and Malcolm (1981). The stock concentration was obtained by filtering the humics source through a 30K (30000 Dalton apparent molecular weight cut-off) Amicon (Danvers, MA) ultrafiltration cell. Prior to filtration, the 30K

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filter was soaked in Milli-Q water for 1 hour. The water was changed three times during the 1 hour soaking period (Shorney, 1992). The filter was then placed in the ultrafiltration cell, and three aloquits (120 mL) of Milli-Q water were passed through the filter. These precautions were utilized in order to prevent organics initially present on the filter from contaminating the stock DOC concentration. Once the titre (1170 mg/L) of the DOC stock solution was determined, it was placed in an amber glass container and stored at 4°C until needed.

Solution pH was measured using a Fisher Accumet pH Meter (Model 610A). Solution pH was adjusted by utilizing sodium bicarbonate, sodium hydroxide, or nitric acid addition.

Chlorite Analysis Methods

Research conducted by Iatrou and Knocke (1992) compared ClO_2^- analysis by the use of a computer aided titrimeter (CAT) utilizing the amperometric methods outlined by Aieta et al (1984) and ion chromatography (utilizing an AS9 anion column). This comparison showed a very close correlation between the two methods for the analysis of ClO_2^- at the concentrations studied throughout the course of the research. The current research study relied on the CAT utilizing the methods proposed by Aieta et al (1984) as the primary method used for ClO_2^- analysis. Initial testing

also confirmed close correlation between ClO_2^- concentrations obtained by the ion chromatograph and the CAT.

The Aieta et al (1984) method for ClO_2^- analysis is based on the pH dependent reaction of chlorine species with iodide. At pH values equal to or less than 2, all ClO_2^- present in a solution containing iodide will be reduced to Cl^- via a four electron transfer as depicted in Equation #18.

$$ClO_2^- + 4I^- + 4H^+ \rightleftharpoons 2I_2 + Cl^- + 2H_2O \qquad [18]$$
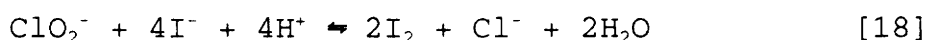
Based on this reaction, sample preparation consisted of the addition of 2 mL of 2.5M HCl and 1 gram of potassium iodide (KI) granules. After mixing, the 200 mL sample reacted in the dark for five minutes prior to amperometric titration. The titrant used during the analysis was 0.00564N phenylarsine oxide (PAO).

In order to determine the actual ClO_2^- concentration of the sample, the amount of titrant used (in mL) was recorded and utilized in the following equation,

$$ClO_2^-, mg/L = \frac{mL\ titrant}{sample\ vol.} *0.00564*16863 \qquad [19]$$

where,

   0.00564 = the normality (eq/L) of PAO titrant

   16863 = equivalent weight of ClO_2^- (mg ClO_2^-/eq)

The detection limit for ClO_2^- concentrations determined by the use of the CAT analysis method was evaluated by analysis of a sample containing only Milli-Q water. The amount of titrant used to reach the endpoint with this sample was 0.14 mLs. According to Equation #19, this corresponds to a detection limit of approximately 0.07 mg/L ClO_2^- for analysis conducted by the utilization of the CAT.

All samples collected for ClO_2^- analysis were either placed in amber glassware or glassware wrapped in aluminum foil. These precautions were taken to help minimize the effects of photolytic decomposition (Gordon, et al, 1990). Samples were also filtered through a 0.45 micron filter prior to collection and analysis. The filtration step removed any oxidized Fe(III) particles that were present. These particles can also react with KI under these conditions, producing an overestimation of the actual ClO_2^- concentration. Samples were stored at 4°C prior to analysis. All samples were analyzed for ClO_2^- on the same day as collection.

Chlorate Analysis Methods

Analysis for ClO_3^- was conducted by the use of ion chromatography. The ion chromatograph utilized was a Dionex Series 2010i equipped with an IonPac AS9 Separator Column and IonPac AG9 Guard Column. The general operational conditions for the ion chromatograph analysis were based on

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research conducted by Ledder (1991) which involved the
analysis of ClO_2^- and ClO_3^- ions in drinking water. The
operational parameters include:

Eluent - 2.8 mM $NaHCO_3$/ 0.4 mM Na_2CO_3
Eluent Flow Rate - 2.0 mL/min
Regenerant - 0.050 N H_2SO_4
Sample Loop Volume - 100 uL

Every ClO_3^- sample was also analyzed for both ClO_2^- and
Cl^- residuals. This made it necessary to use two different
output ranges for the data, dependent on both the expected
concentrations and desired detection limits. For the higher
concentrations associated with ClO_2^- and Cl^-, an output range
of 100 was used; while for the lower concentrations
associated with the ClO_3^- residual, an output range of 10
was utilized. This operational technique was easily
accomplished due to the separation times of the anions of
concern. The separation times associated with ClO_2^-, Cl^-,
and ClO_3^- were approximately 1.7, 2.4, and 5.2 minutes,
respectively, therefore allowing the operator to switch the
output range from 100 to 10 after the elution of the Cl^-
peak but not before the conductivity returned to stable
baseline conditions. Under the conditions outlined above,
the detection limit for the ClO_3^- analysis was considered to
be 0.03 mg/L.

The ion chromatograph results illustrated the
occurrence of a significant water dip (ie. an output below
the baseline reading) which could have interfered with the

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ClO_2^- peaks. In order to prevent this disturbance, all samples were spiked with fluoride which elutes prior to ClO_2^- and alleviates the masking of the ClO_2^- peak (Ledder, 1991).

Samples for ClO_3^- analysis were collected in amber glassware and stored at 4°C between collection and analysis. ClO_3^- analysis was performed on the same day the sample was collected.

Residual Iron Analysis Method

Residual iron analysis was conducted by the use of Perkin-Elmer (Norwalk, CT) Model 703 Atomic Absorption Spectrophotometer. The following operational characteristics were used:

        wavelength - 248.8 nm
        slit width - 0.2 nm
        linear range - 10.0 mg/L

Under these conditions, a detection limit of 0.03 mg/L was established for iron (Iatrou & Knocke, 1992).

Sample preparation involved filtration through a 0.45 micron filter and acidification to less than pH 2 with a 10% nitric acid solution. The amount (3-4 drops) of nitric acid necessary to produce the acidic conditions cited above was placed in the sample containers prior to sample collection. All samples were collected and analyzed in glass bottles.

DOC Analysis Method

DOC analysis was conducted by the use of a Dorhmann Total Organic Carbon Analyzer (Santa Clara, CA). All samples were filtered through a 30K ultrafiltration cell prior to analysis. Filter preparation consisted of the same procedures outlined in the previous section concerning stock solution preparation. Further sample preparation included decreasing sample pH to less than 2 by the addition of 85% phosphoric acid followed by purging with oxygen for approximately five minutes prior to sample injection. All samples were collected and analyzed in glass bottles.

Stoichiometry of Ferrous Iron - Chlorite Reaction

Equation #11 previously described the stoichiometry of the reaction between Fe(II) and ClO_2^-. Theoretically, 3.3 mg of Fe(II) are required to completely reduce 1 mg of ClO_2^- to Cl^-. The stoichiometry of the reaction was evaluated within the pH range of 6.0 to 10.0 at a solution temperature of 25°C. Tests were also conducted under both deaerated and aerated conditions in order to describe the possible effects that the presence of $O_2(aq)$ might have upon the observed Fe(II):ClO_2^- reaction stoichiometry.

After deaeration or aeration, the following background ions were added to the experimental test solution: 4 meq/L calcium chloride or calcium sulfate, 4 meq/L sodium bicarbonate, and 0.5 meq/L sodium sulfate. The solution was

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then dosed with ClO_2^- to produce an initial concentration of approximately 4 mg/L. The test solution was then equally divided between the reaction vessels to be used during the test. All reaction vessels were covered with aluminum foil in order to minimize light interference (Gordon, et al, 1990).

Each test solution was dosed with the appropriate amount of Fe(II) followed by immediate pH adjustment with sodium hydroxide or nitric acid. Fe(II) dosing ranged from 25 - 300% of the stoichiometric amount defined by equation #11. After Fe(II) dosing and pH adjustment, the reaction was allowed to proceed for five minutes which allowed ample time for the ClO_2^- reduction to occur. Iatrou and Knocke (1992) reported that essentially complete ClO_2^- reduction occurred within 20 seconds. Samples were collected for analysis following the completion of the five minute reaction period. All samples were filtered through a 0.45 micron filter prior to subsequent species analyses.

Stoichiometric testing conducted under low (< 0.5 mg/L) O_2(aq) concentrations were performed in 300 mL BOD bottles in order to minimize oxygen transfer during the time allotted for the Fe(II) to react with the ClO_2^-. Mixing during the specified reaction time was accomplished by utilization of a multi-plate magnetic stirring apparatus. Solution O_2(aq) concentrations were monitored prior to Fe(II) dosing and sample collection with the use of a Yellow

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Stone Instrument (Yellow Springs, OH) Model 57 Oxygen Meter. Experiments involving aerated solutions were conducted in square plastic jars (1 L capacity) using a Phipps & Bird (Richmond, VA) jar test apparatus for mixing.

Determination of Oxychlorine Residual Speciation

Tests were conducted to determine if the ClO_2^- present in solution was completely reduced to Cl^- during the $Fe(II)/ClO_2^-$ reaction as predicted by Equation #11. Ondrus et al, (1972) and Fabian et al, (1992) identified various side-reactions which may occur during the reduction of ClO_2^- causing the formation of various volatile chlorine species. For example, the following reactions could occur during the $Fe(II)/ClO_2^-$ reaction, thus preventing the complete reduction of the ClO_2^- ion to Cl^- (Fabian & Gordon, 1992):

$$Fe(II) + ClO_2^- \leftrightharpoons Fe(III) + \{Cl(II)\} \qquad [20]$$

$$Fe(II) + HClO_2 \leftrightharpoons Fe(III) + \{Cl(II)\} \qquad [21]$$

$$\{Cl(II)\} + ClO_2^- \leftrightharpoons ClO^- + ClO_2 \qquad [22]$$
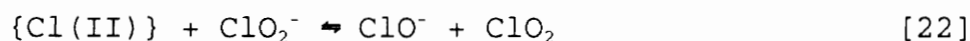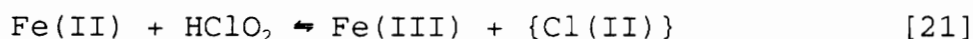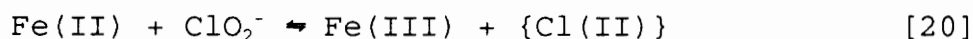
These side-reactions suggest the following reaction that was proposed by Fabian et al (1992):

$$Fe(II) + 2ClO_2^- + 3H^+ \leftrightharpoons Fe(III) + HOCl + ClO_2 + H_2O \qquad [23]$$

It was necessary to use the analytical techniques outlined by Aieta et al (1984) in order to quantify species such as ClO_2 and chlorine (Cl_2). Utilizing the computer aided titrimeter (CAT), $0.00564N$ PAO as the titrant, and by adjusting the pH of the test samples and reacting with KI,

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it was possible to quantify the volatile chlorine species mentioned above. The following equations represent the reactions upon which the analytical procedure developed by Aieta *et al* (1984) was based:

$$Cl_2 + 2I^- \rightleftharpoons I_2 + 2Cl^- \tag{24}$$

$$2ClO_2 + 2I^- \rightleftharpoons I_2 + 2ClO_2^- \tag{25}$$

$$2ClO_2 + 10I^- + 8H^+ \rightleftharpoons 5I_2 + 2Cl^- + 4H_2O \tag{26}$$

$$ClO_2^- + 4I^- + 4H^+ \rightleftharpoons 2I_2 + Cl^- + 2H_2O \tag{27}$$

$$ClO_3^- + 6I^- + 6H^+ \rightleftharpoons 3I_2 + Cl^- + 3H_2O \tag{28}$$
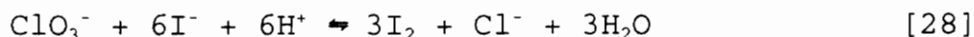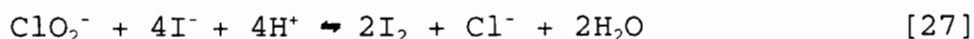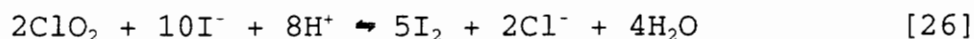
The reader is referred to Aieta *et al* (1984), for the specific steps and calculations that were used to determine residual ClO_2, ClO_2^-, and Cl_2 concentrations.

Due to the volatile nature of certain oxychlorine species that were tested for, it was necessary to develop an experimental test method that would help to minimize the loss of ClO_2 and Cl_2 during the reaction period. This required the use of a reaction vessel that prevented atmospheric interactions and one that would also remain headspace free throughout the time allotted for the $Fe(II)/ClO_2^-$ reaction to proceed.

Reactions for this set of experiments were conducted within a reaction vessel which could be sealed to the atmosphere by the use of a rubber stopper. The reaction vessel also contained a sampling port which was located just below the stopper opening; this allowed for sample collection by the insertion of plastic tubing which extended

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to the bottom of the vessel. During testing, the plastic tubing was closed by the use of a clamp. The tubing used created an airtight fit when inserted into the sampling port.

The reaction vessel was completely filled with the test solution (dosed with both background ions and ClO_2^-, and deaerated), and the appropriate pH adjustments were made prior to Fe(II) dosing. Immediately upon dosing the test solution with Fe(II), the rubber stopper was inserted which minimized atmospheric (O_2(aq)) interferences and provided for no headspace within the reaction vessel. The Fe(II):ClO_2^- reaction was allowed to proceed for approximately five minutes while being stirred by the use of a magnetic stirring plate.

At the end of the five minute reaction period, the solution was dosed with both a pH 7 phosphate buffer and potassium iodide solution in accordance with the methods outlined by Aieta et al (1984). This step fixed the volatile oxychlorine residuals in solution for subsequent analysis. Samples were collected by opening the clamp on the plastic tube. Samples were filtered as previously outlined and analyzed for ClO_2, free chlorine, ClO_2^-, ClO_3^-, and soluble iron using methods described in this chapter. These tests were conducted for pH values ranging from approximately 8.0 to 10.0, an initial ClO_2^- concentration of

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approximately 8.0 mg/L, and Fe(II) stoichiometric dosing of 50 and 100%.

Effects of Aquatic Organics on the Fe(II)/ClO_2^- Reaction

Tests were conducted to analyze the possible effects that DOC may have upon the Fe(II)/ClO_2^- reaction. These tests used a standard jar test apparatus for mixing. The reaction vessels were wrapped in aluminum foil in order to minimize photolytic effects on ClO_2^-. The tests were conducted at pH values ranging from approximately 8.0 - 10.0; initial ClO_2^- concentrations of approximately 8 mg/L; and Fe(II) doses of 120 and 160% of the stoichiometric requirement for ClO_2^- reduction. The stock solution was aerated prior to species addition by bubbling with oxygen for approximately 15 minutes. Six solutions were dosed with DOC (0 - 15 mg/L) prior to Fe(II) addition, and samples were collected so that initial DOC concentrations could be verified.

After dosing with Fe(II), the Fe(II):ClO_2^- reaction was allowed to proceed for approximately five minutes, at which time samples were collected for the analysis of residual DOC, Fe(II), ClO_2^-, and ClO_3^-. All DOC samples were filtered through a 30K ultrafiltration cell prior to analysis on the TOC apparatus; Fe(II) samples were filtered through both a 30K ultrafiltration cell and a 0.45um filter prior to

analysis, and all other samples were treated as previously discussed.

Similar tests were also conducted under closed system conditions (ie. minimization of O_2(aq) interferences) in order to determine if the presence of O_2(aq) was important when considering DOC effects on the Fe(II):ClO_2^- reaction. This was accomplished by utilizing reaction vessels which could be closed to the atmosphere while allowing for the insertion of a O_2(aq) probe for constant O_2(aq) measurements throughout the five minute reaction period. Solution preparation methods, sampling techniques, and analysis procedures were the same as previously stated.

General Glassware and Plasticware Washing

All glassware and plasticware were soaked in a 10% nitric acid solution for approximately eight hours every two weeks or sooner if any evidence of Fe(III) oxide build-up was present. Daily washing and rinsing of glassware was performed by using deionized-distilled water.

CHAPTER IV

RESULTS

Introduction

This chapter presents the data obtained while pursuing the previously stated objectives of the study. The results will be divided into sections pertaining to the stoichiometry of the ferrous iron/chlorite reaction at elevated solution pH, chlorate analysis, mass balance of the oxychlorine residuals associated with the reaction, and impacts of DOC on the reaction.

Stoichiometry of the Fe(II)/ClO$_2^-$ Reaction at Elevated pH

Stoichiometric testing conducted with low O$_2$(aq) concentrations (< 0.5 mg/L) were performed at solution pH values of 6, 7, 8, 9, and 10. These tests were performed so that the stoichiometry of the Fe(II)/ClO$_2^-$ reaction could be described with minimal interferences from O$_2$(aq). Tables 1 through 5 present the data collected for the stoichiometric experiments with respect to the pH values previously mentioned. Dosing with Fe(II) was based on the stoichiometry presented by equation #11, which indicates that 3.3 mg Fe(II) are required to completely reduce 1 mg of ClO$_2^-$ to Cl$^-$.

Tables 1 and 2 present data corresponding to tests conducted at solution pH values of 6 and 7, respectively.

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Table 1: Evaluation of the Stoichiometry for the Fe(II)/ Chlorite Reaction In Low Dissolved Oxygen Solutions with pH of 6.0.

pH	Chlorite, mg/L			Fe(II), mg/L			Actual % Stoich. Dosing	Observed Fe(II):Chlorite Rxn. Ratio [1]
	Initial	Final	Difference	Initial	Final	Difference		
6.0	4.2	1.6	2.5	6.2	0.3	5.9	45	2.4
5.9	4.0	1.8	2.2	6.2	0.1	6.1	47	2.8
6.0	3.9	1.4	2.5	7.0	0.3	6.7	55	2.7
5.8	4.1	0.1	4.0	12.7	2.7	10.1	94	2.5
6.0	4.0	0.1	3.9	12.4	2.2	10.2	94	2.6
5.9	4.1	0.2	3.9	13.3	0.2	13.1	99	3.4
6.1	4.0	0.2	3.9	13.3	1.4	11.8	100	3.1
6.1	3.8	0.1	3.7	13.9	3.6	10.4	111	2.8
6.1	4.0	0.5	3.5	26.5	12.9	13.7	199	3.9
6.0	4.0	0.3	3.8	26.5	13.1	13.4	200	3.6
6.1	3.9	0.3	3.6	27.1	16.8	10.3	210	2.9

Note : Actual % stoich. dosing based on 3.3 mg Fe(II)/ mg Chlorite
[1] mg Fe(II)/ mg Chlorite

Table 2: Evaluation of the Stoichiometry for the Fe(II)/ Chlorite Reaction in Low Dissolved Oxygen Solutions with pH of 7.0.

pH	Chlorite, mg/L			Fe(II), mg/L			Actual % Stoich. Dosing	Observed Fe(II):Chlorite Rxn. Ratio [*]
	Initial	Final	Difference	Initial	Final	Difference		
6.9	4.0	1.1	2.9	6.4	0.05	6.4	49	2.2
7.0	4.0	1.4	2.6	6.4	0.04	6.4	49	2.5
6.8	4.5	0.3	4.1	10.1	0.25	9.9	69	2.4
7.0	4.5	0.3	4.2	10.1	0.02	10.1	69	2.4
7.0	4.3	0.5	3.8	15.3	2.10	13.2	108	3.5
7.1	4.3	0.4	3.9	15.3	1.42	13.9	108	3.6
7.0	3.9	0.4	3.6	14.4	1.69	12.7	111	3.5
7.0	3.9	0.3	3.6	14.4	1.22	13.2	111	3.6
7.1	4.3	0.6	3.7	41.6	8.90	32.7	292	8.9
6.9	4.3	0.5	3.9	41.6	8.42	33.2	292	8.6
6.9	4.3	0.6	3.8	48.6	10.8	37.8	339	10.0
7.3	4.3	1.6	2.8	48.6	5.44	43.2	339	15.6

Note : Actual % stoich. dosing based on 3.3 mg Fe(II)/ mg Chlorite
[*] mg Fe(II)/ mg Chlorite

These data indicate an Fe(II):ClO_2^- reaction ratio of
approximately 2.5 mg Fe(II) per mg ClO_2^- at Fe(II) doses
ranging from 45 to 70 percent of the theoretical amount
required. When the Fe(II) dosing approached 100 percent, an
Fe(II):ClO_2^- ratio of approximately 3.3 was observed.
Further investigation of the data in Tables 1 and 2 shows
significant increases in the observed Fe(II):ClO_2^- reaction
ratio at Fe(II) doses in excess of 100 percent (ie. 3.3 mg
Fe(II)). At solution pH values of 6 and 7, Fe(II) dosing at
70 percent or greater than the theoretical amount required
effectively reduced ClO_2^- concentrations ranging from 4.5 to
3.8 mg/L to residual levels equal to or less than 0.6 mg/L.

Table 3 contains the stoichiometric test data
corresponding to solution pH values ranging from 7.8 to 8.0.
It is evident that at Fe(II) doses ranging from 81 to 84
percent the observed Fe(II):ClO_2^- reaction ratio is
approximately 3.1 mg Fe(II) per mg ClO_2^-. Fe(II) dosing at
97 to 113 percent produces an observed reaction ratio of
4.5, while dosing at 135 to 140 percent produced reaction
ratios of approximately 4.7. At Fe(II) doses in excess of
200 percent of the theoretical amount, significant increases
in the Fe(II):ClO_2^- reaction ratio were noticed. At Fe(II)
doses in excess of 100 percent of the theoretical amount
required, ClO_2^- concentrations of 3.66 to 7.06 mg/L were
essentially eliminated (ie. 0.07 mg/L).

Table 3: Evaluation of the Stoichiometry for the Fe(II)/ Chlorite Reaction In Low Dissolved Oxygen Solutions with pH of 8.0.

pH	Chlorite, mg/L			Fe(II), mg/L			Actual % Stoich. Dosing	Observed Fe(II):Chlorite Rxn. Ratio [1]
	Initial	Final	Difference	Initial	Final	Difference		
8.0	7.5	2.0	5.5	13.2	0.03	13.2	53	2.4
7.9	3.9	0.7	3.2	10.4	0.30	10.1	81	3.2
8.0	3.9	0.8	3.1	10.4	0.10	10.3	81	3.3
8.0	3.7	0.1	3.7	10.3	0.13	10.2	84	2.8
7.8	4.2	0.8	3.5	13.6	0.12	13.5	97	3.9
8.0	4.1	0.8	3.3	13.6	0.17	13.4	101	4.1
8.0	7.1	0.1	7.0	26.4	0.13	26.3	113	3.8
8.0	3.7	0.1	3.6	16.8	0.17	16.6	139	4.6
7.9	3.7	0.1	3.6	16.8	0.1	16.7	139	4.6
7.9	3.7	0.1	3.7	17.3	0.13	17.2	140	4.7
8.0	3.7	0.1	3.7	17.3	0.12	17.2	140	4.7
7.9	3.9	0.1	3.8	48.3	0.26	48.0	377	12.6
7.8	3.9	0.1	3.8	48.3	0.31	48.0	377	12.6
7.8	3.9	0.1	3.8	54.4	1.28	53.1	423	13.9
7.8	3.9	0.1	3.8	54.4	3.28	51.1	423	13.3

Note : Actual % stoich. dosing based on 3.3 mg Fe(II)/ mg Chlorite
[1] mg Fe(II)/ mg Chlorite

Figure 1 illustrates the stoichiometric data presented in Tables 1, 2, and 3. From this illustration one can discern the increases in the observed stoichiometry at dosing stoichiometries equal to or greater than 100 percent for solutions with pH values of 7 and 8.

Table 4 contains the stoichiometric test data corresponding to solution pH values ranging from 8.9 to 9.1. At Fe(II) doses ranging from 51 to 80 percent of the theoretical requirement, the observed Fe(II):ClO_2^- reaction ratio ranged from 2.3 to 4.0 mg Fe(II) per mg ClO_2^-. Fe(II) doses ranging from 103 to 112 percent produced an observed Fe(II):ClO_2^- reaction ratio of approximately 3.8, while dosing in excess of 200 percent produced even more significant increases in the observed reaction ratio. ClO_2^- concentrations ranging from 4.5 to 7.8 mg/L were reduced to less than 0.3 mg/L by the Fe(II) doses utilized for the targeted solution pH of 9.0.

Table 5 contains the stoichiometric test data corresponding to solution pH values ranging from 9.9 to 10.0. Fe(II) dosing at approximately 50 to 105 percent the theoretical amount indicated an Fe(II):ClO_2^- reaction ratio of 3.5 mg Fe(II) per mg ClO_2^-.

Figure 2 illustrates the stoichiometric data presented in Tables 3, 4, and 5. From this representation the trend

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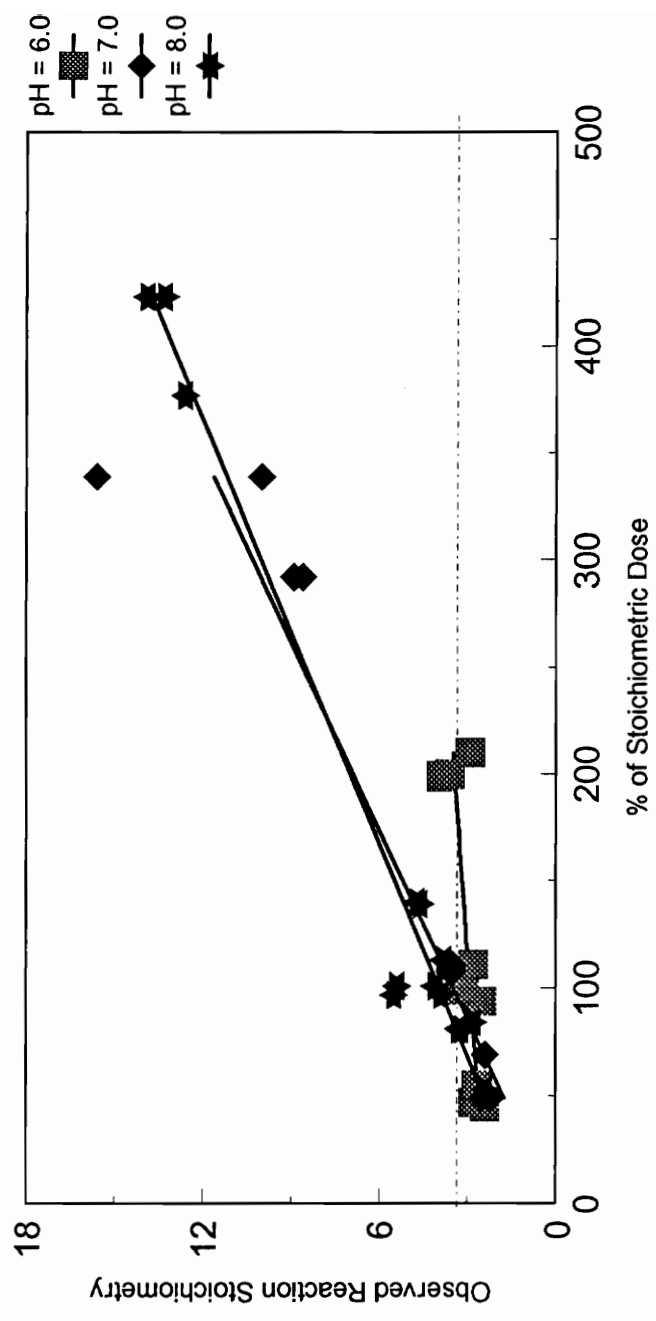
Figure 1: Observed Fe(II)/Chlorite Reaction Stoichiometry in Low Dissolved Oxygen Solutions with pH Values of 6, 7, and 8.

Table 4: Evaluation of the Stoichiometry for the Fe(II)/ Chlorite Reaction in Low Dissolved Oxygen Solutions with pH of 9.0.

pH	Chlorite, mg/L			Fe(II), mg/L			Actual % Stoich. Dosing	Observed Fe(II):Chlorite Rxn. Ratio '
	Initial	Final	Difference	Initial	Final	Difference		
8.9	7.9	2.2	5.7	13.2	0.03	13.2	51	2.3
8.9	6.7	3.6	3.1	13.3	0.03	13.3	60	4.3
8.9	6.7	3.3	3.3	13.3	0.03	13.3	61	4.0
8.9	4.5	0.7	3.8	11.8	0.03	11.8	80	3.1
9.0	4.5	0.3	4.2	11.8	0.03	11.8	80	2.8
8.9	7.8	0.1	7.7	26.4	0.03	26.4	103	3.4
9.1	7.5	0.1	7.5	26.4	0.03	26.4	106	3.5
8.9	4.9	0.1	4.9	18.2	0.10	18.1	112	3.7
9.0	4.9	0.8	4.1	18.2	0.06	18.1	112	4.4
8.9	4.7	0.2	4.5	33.6	0.05	33.6	219	7.5
9.0	4.7	0.1	4.6	33.6	0.06	33.5	219	7.3

Note : Actual % stoich. dosing based on 3.3 mg Fe(II)/ mg Chlorite

' mg Fe(II)/ mg Chlorite

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Table 5: Evaluation of the Stoichiometry for the Fe(II)/ Chlorite Reaction In Low Dissolved Oxygen Solutions with pH of 10.0.

pH	Chlorite, mg/L			Fe(II), mg/L			Actual % Stoich. Dosing	Observed Fe(II):Chlorite Rxn. Ratio [a]
	Initial	Final	Difference	Initial	Final	Difference		
9.9	7.7	3.7	4.1	13.3	0.03	13.3	52	3.3
10.0	7.1	3.2	3.9	13.2	0.03	13.2	56	3.4
10.0	7.6	0.1	7.5	26.4	0.03	26.4	105	3.5

Note : Actual % stoich. dosing based on 3.3 mg Fe(II)/ mg Chlorite

[a] mg Fe(II)/ mg Chlorite
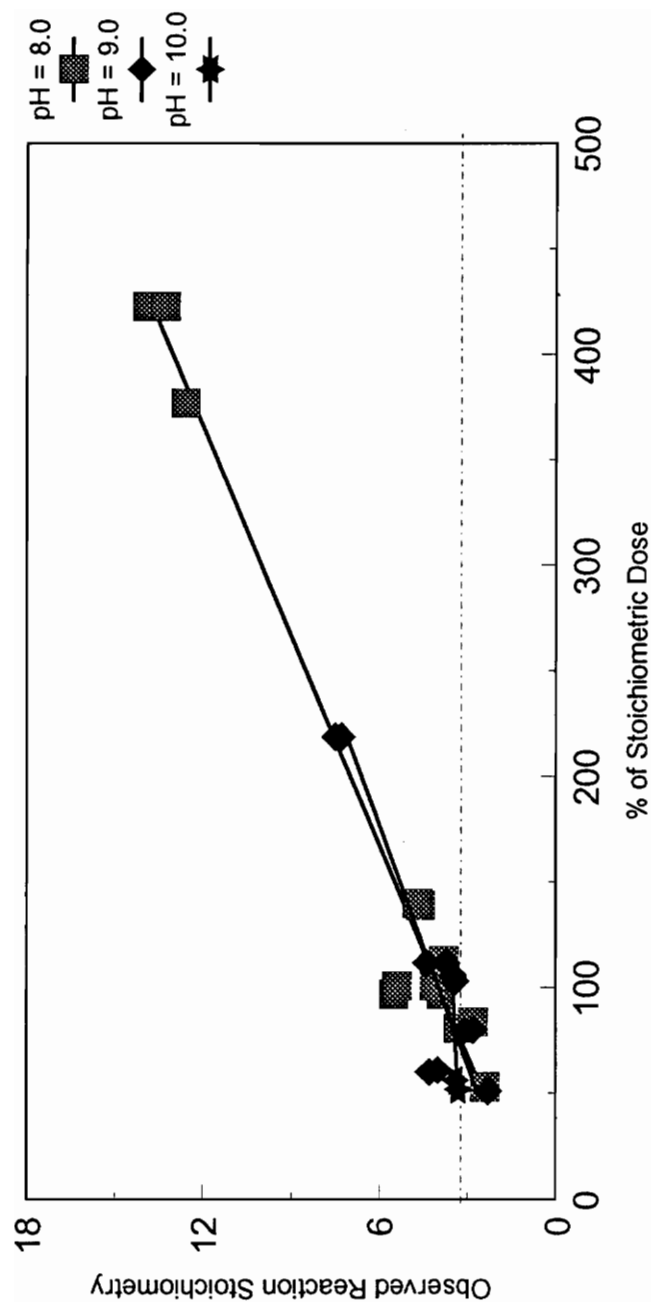
Figure 2: Observed Fe(II)/Chlorite Reaction Stoichiometry in Low Dissolved Oxygen Solutions with pH Values of 8, 9, and 10.

of increasing observed stoichiometry associated with stoichiometric dosing in excess of 100 percent (ie. 3.3 mg Fe(II)/ mg ClO_2^-), for solution pH values ranging from 8 to 10, can clearly be noted.

Stoichiometric testing conducted with high $O_2(aq)$ solutions (ie. dissolved oxygen concentration of approximately 10 mg/L) was performed at pH values of 8, 9, and 10. These tests were conducted to determine if the presence of dissolved oxygen in solution would interfere with the oxidation of Fe(II) by ClO_2^-, and to describe the stoichiometry of the Fe(II)/ClO_2^- reaction in solutions containing significant amounts of dissolved oxygen. Tables 6 through 8 present the data collected for these stoichiometric experiments.

Table 6 presents the data collected for the stoichiometric testing at solution pH values ranging from 7.9 to 8.0. At Fe(II) dosing below 100 percent the theoretical requirement (ie. 30 percent), the observed Fe(II):ClO_2^- reaction ratio was 2.8 mg Fe(II) per mg ClO_2^-. Fe(II) doses of 113 percent indicated a significant increase in the observed Fe(II):ClO_2^- reaction ratio, which was 3.9. Tests involving Fe(II) doses in the range of 120 to 136 percent of the theoretical amount indicated an Fe(II):ClO_2^- ratio of 4.4. The presence of dissolved oxygen in the test solution did not seem to effect the reduction of ClO_2^- by

Table 6: Evaluation of the Stoichiometry for the Fe(II)/ Chlorite Reaction In Oxygenated Solutions with pH of 8.0.

pH	Chlorite, mg/L			Fe(II), mg/L			Actual % Stoich. Dosing	Observed Fe(II):Chlorite Rxn. Ratio [+]
	Initial	Final	Difference	Initial	Final	Difference		
8.0	4.6	2.7	1.9	4.5	0.07	4.4	30	2.4
7.9	4.6	3.2	1.4	4.5	0.06	4.4	30	3.1
8.0	3.5	0.2	3.4	13.2	0.03	13.2	113	3.9
8.0	3.5	0.2	3.4	13.2	0.04	13.2	113	3.9
7.9	4.2	0.1	4.1	16.5	0.04	16.5	120	4.0
8.0	4.2	0.1	4.1	16.5	0.04	16.5	120	4.0
7.9	4.4	0.2	4.2	19.7	0.06	19.6	136	4.7
8.0	4.4	0.2	4.2	19.7	0.06	19.6	136	4.7

Note: Actual % stoich. dosing based on 3.3 mg Fe(II)/ mg Chlorite
    [+] mg Fe(II)/ mg Chlorite

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Fe(II). Chlorite concentrations ranging from 3.5 to 4.6 mg/L were consistently reduced to less than 0.2 mg/L with Fe(II) doses greater than 100 percent of the theoretical amount required.

Table 7 contains the data related to the stoichiometric tests conducted at a solution pH value of 9.0. Fe(II) dosing at 61 percent of the theoretical amount required, yielded an observed stoichiometry of 3.6 mg Fe(II) per mg ClO_2^-. Fe(II):ClO_2^- reaction ratios of 4.3 and 5.7 were observed for Fe(II) doses of 125 and 163 percent of the theoretical requirement, respectively. As indicated in Table 7, residual ClO_2^- concentrations were equal to or less than 0.2 mg/L when the Fe(II) dosing exceeded 100 percent of the theoretical value of 3.3 mg Fe(II) per mg ClO_2^-.

Table 8 presents the data obtained during the stoichiometric tests conducted over the pH range of 10.0 to 10.1. Fe(II) dosing at 58 percent of the theoretical amount resulted in Fe(II):ClO_2^- reaction ratios of approximately 3.8 mg Fe(II) per mg ClO_2^-. Fe(II):ClO_2^- reaction ratios of 4.2 and 6.3 were observed at Fe(II) doses of 112 to 127 percent and 184 percent, respectively. ClO_2^- concentrations were effectively reduced to levels less than 0.4 mg/L at Fe(II) dosing in excess of 100 percent of the theoretical requirement.

Figure 3 provides an overlay of the information contained in Tables 6, 7, and 8, so that the trend of

Table 7: Evaluation of the Stoichiometry for the Fe(II)/ Chlorite Reaction in Oxygenated Solutions with pH of 9.0.

pH	Chlorite, mg/L			Fe(II), mg/L			Actual % Stoich. Dosing	Observed Fe(II):Chlorite Rxn. Ratio [1]
	Initial	Final	Difference	Initial	Final	Difference		
9.0	4.1	2.2	1.9	8.3	0.11	8.2	61	4.2
9.0	4.1	1.4	2.7	8.3	0.13	8.2	61	3.0
9.0	4.3	0.2	4.1	17.6	0.17	17.4	125	4.3
9.0	4.3	0.1	4.2	17.6	0.22	17.4	125	4.2
9.0	4.0	0.2	3.8	21.3	0.02	21.3	163	5.6
9.0	4.0	0.2	3.7	21.3	0.04	21.3	163	5.7
9.0	3.7	0.2	3.5	27.7	0.06	27.6	229	7.9
9.0	3.7	0.1	3.6	27.7	0.06	27.6	229	7.8

Note : Actual % stoich. dosing based on 3.3 mg Fe(II)/ mg Chlorite

[1] mg Fe(II)/ mg Chlorite

Table 8: Evaluation of the Stoichiometry for the Fe(II)/ Chlorite Reaction In Oxygenated Solutions with pH of 10.0.

pH	Chlorite, mg/L			Fe(II), mg/L			Actual % Stoich. Dosing	Observed Fe(II):Chlorite Rxn. Ratio [a]
	Initial	Final	Difference	Initial	Final	Difference		
10.0	4.3	2.2	2.1	8.3	0.15	8.2	58	3.8
10.1	4.3	2.2	2.2	8.3	0.07	8.2	58	3.8
10.0	4.3	0.2	4.1	17.9	0.18	17.7	127	4.3
10.0	4.3	0.2	4.1	17.9	0.19	17.7	127	4.3
10.0	5.7	0.4	5.4	21.2	0.10	21.1	112	3.9
10.0	5.7	0.6	5.1	21.2	0.07	21.1	112	4.1
10.0	4.6	0.2	4.4	27.8	0.06	27.7	184	6.3
10.0	4.6	0.2	4.4	27.8	0.13	27.7	184	6.2

Note : Actual % stoich. dosing based on 3.3 mg Fe(II)/ mg Chlorite
[a] mg Fe(II)/ mg Chlorite
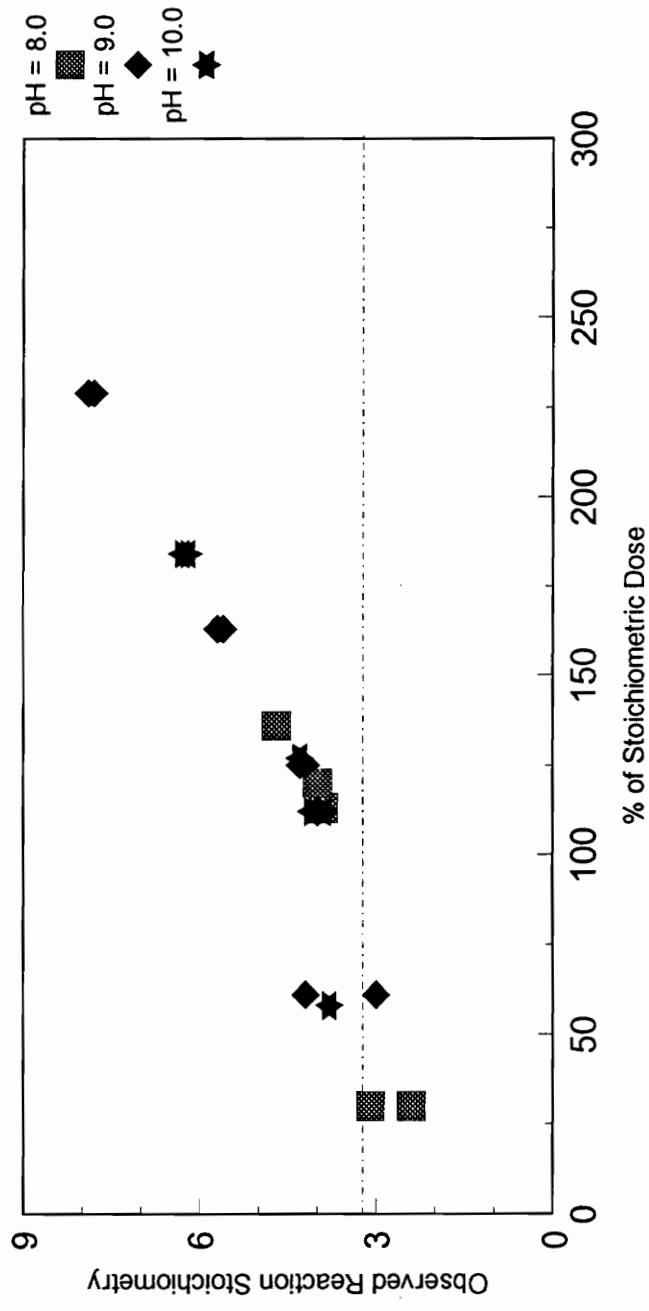
Figure 3: Observed Fe(II)/Chlorite Reaction Stoichiometry in Oxygenated Solutions with pH Values of 8, 9, and 10.

increasing $Fe(II):ClO_2^-$ reaction ratios with associated increases in dosing stoichiometry can be shown to exist at all of the pH values studied.

Figure 4 illustrates percent ClO_2^- removal as a function of dosing stoichiometry for tests conducted in deaerated waters with solution pH values ranging from 6 to 8. This plot indicates that 85 to 100 percent ClO_2^- removal occurs when the $Fe(II)$ dosing stoichiometry is in excess of 100 percent over the pH range of 6 to 8. Figure 5 illustrates percent ClO_2^- removal as a function of dosing stoichiometry for tests conducted in waters with low $O_2(aq)$ concentrations and solution pH values ranging from 8 to 10. From this plot one can see that 100 percent ClO_2^- removal was attained at $Fe(II)$ dosing stoichiometries in excess of the theoretical requirement. Comparisons between Figures 4 and 5 illustrate that a higher percentage of ClO_2^- removal was attained at solution pH values of 8, 9, and 10.

Figures 6, 7, and 8 illustrate overlays of ClO_2^- removal as a function of actual dosing stoichiometry for tests conducted in solutions with both high and low concentrations of $O_2(aq)$ and pH values of 8, 9, and 10, respectively. These graphical representations suggest that $O_2(aq)$ concentrations pose minimal effects on the $Fe(II):ClO_2^-$ reaction.

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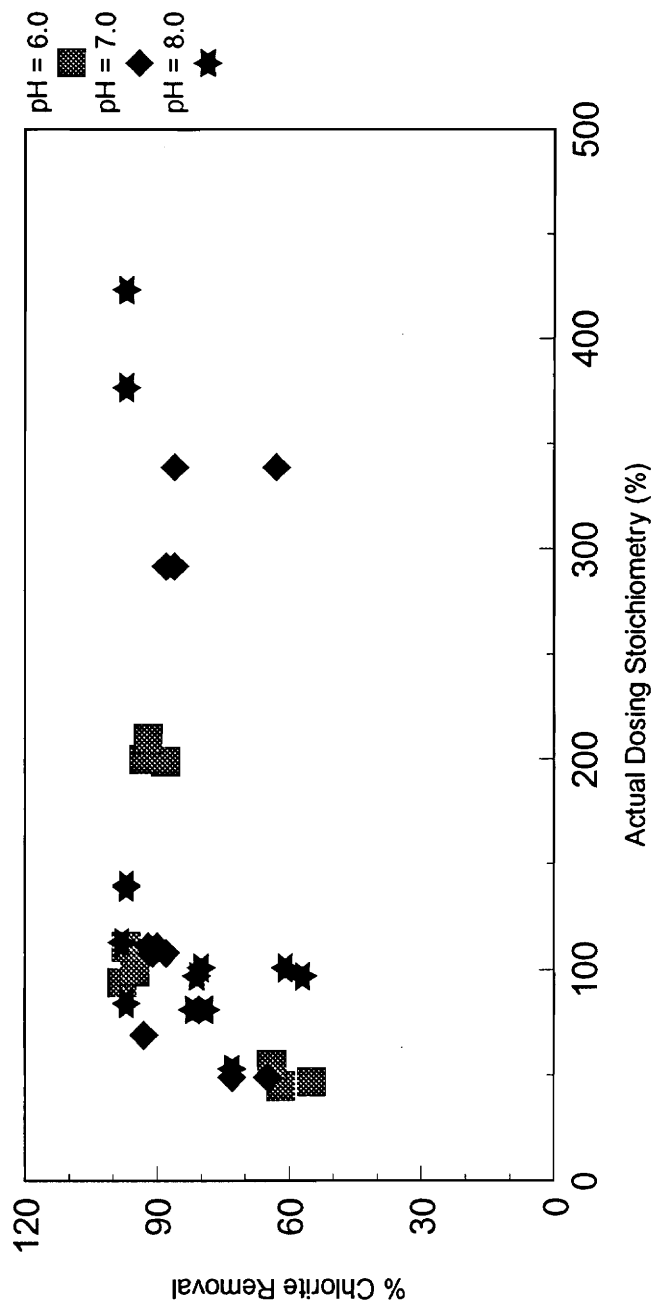
Figure 4: Impacts of Fe(II) Dosing on Chlorite Removal in Low Dissolved Oxygen Solutions with pH Values of 6, 7, and 8.
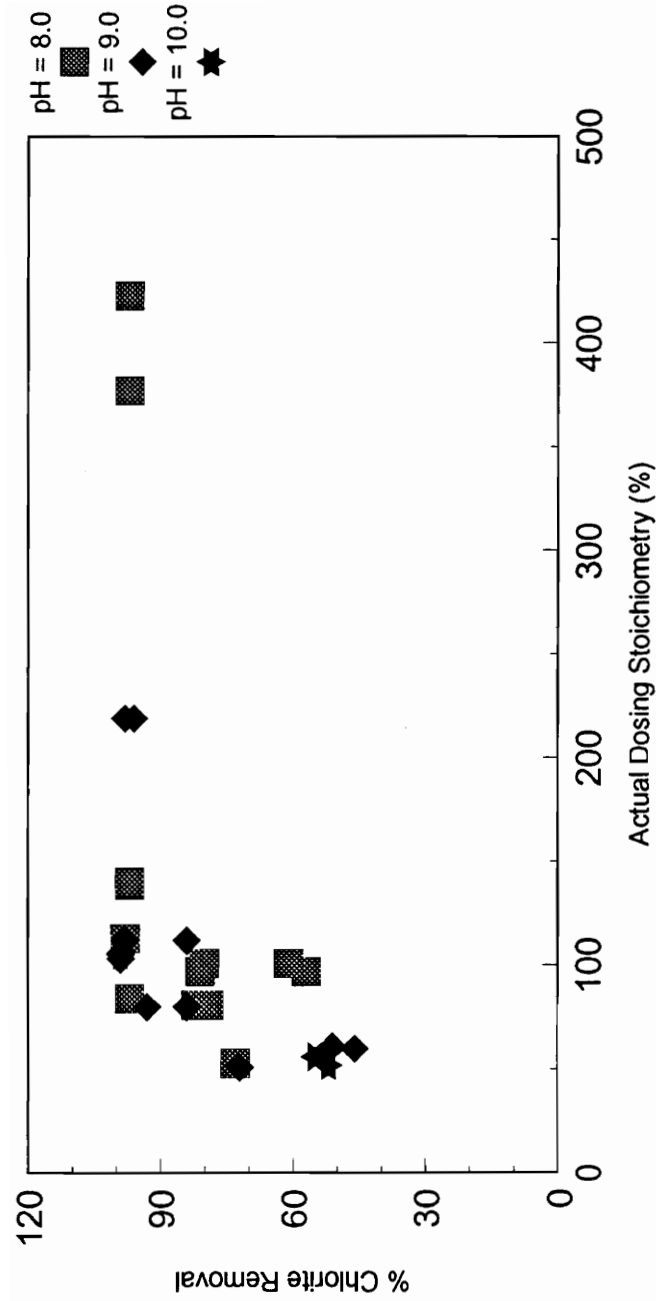
Figure 5: Impacts of Fe(II) Dosing on Chlorite Removal in Low Dissolved Oxygen Solutions with pH Values of 8, 9, and 10.
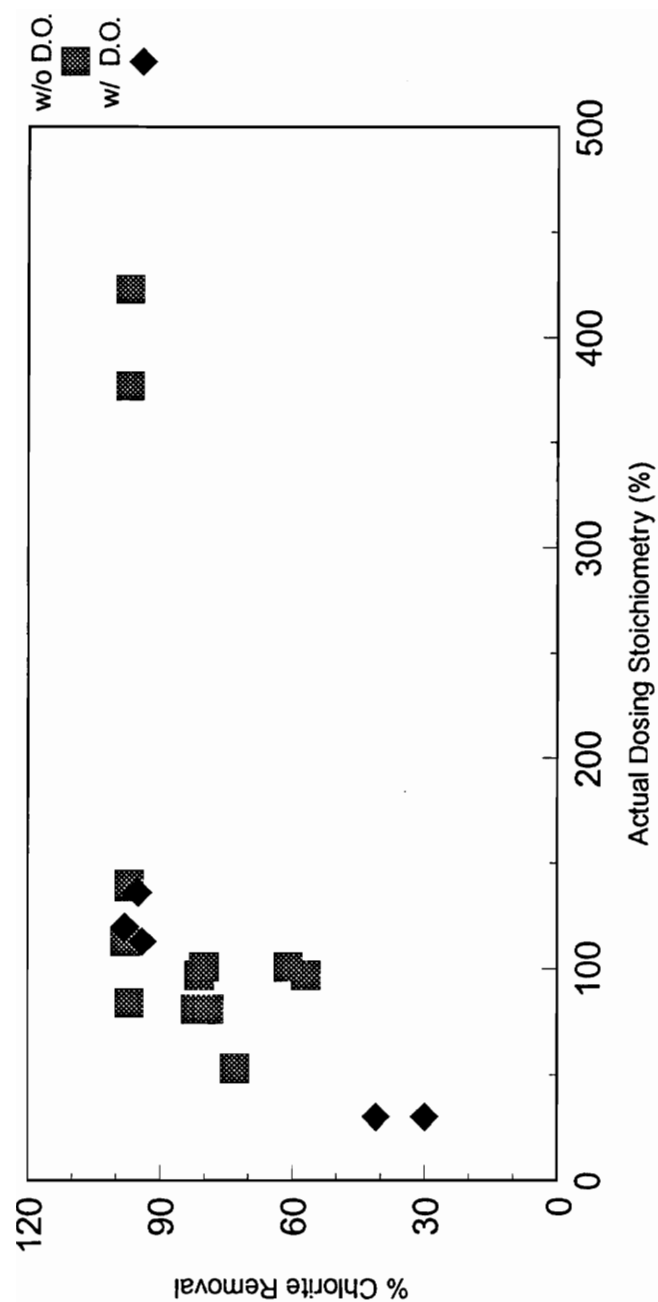
Figure 6: Effects of Aqueous Oxygen on the Removal of Chlorite by Fe(II) in Solutions with pH of 8.0.
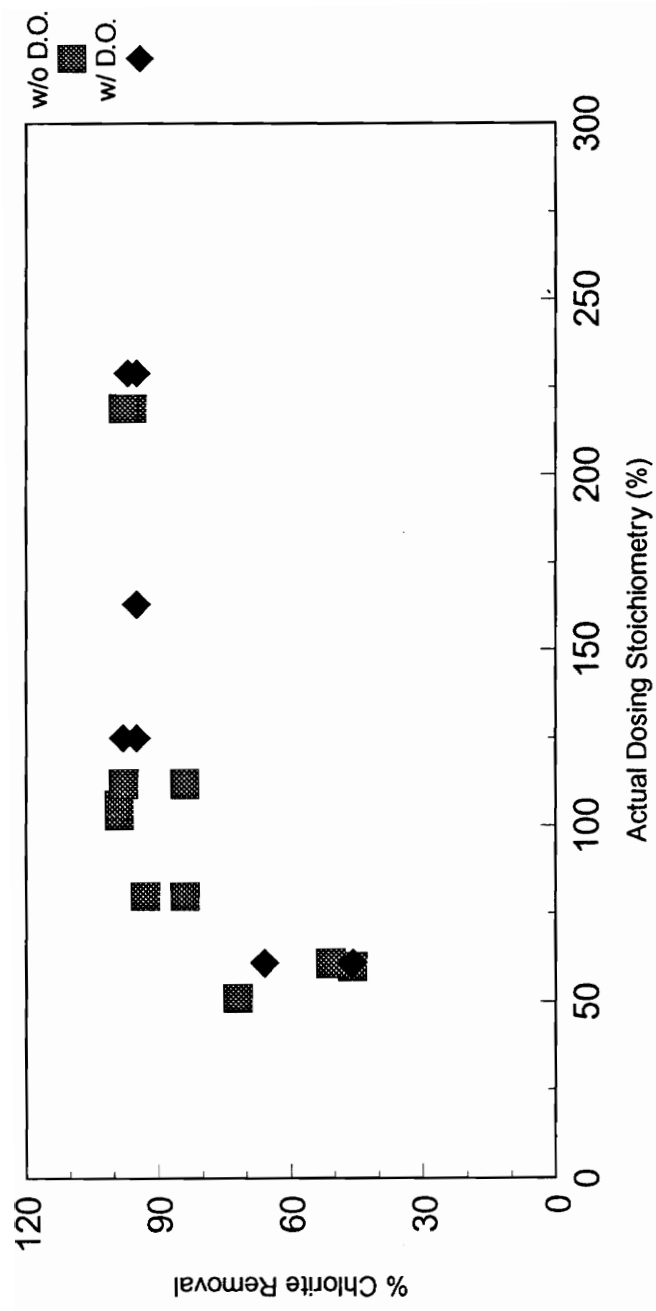
Figure 7: Effects of Aqueous Oxygen on the Removal of Chlorite by Fe(II) in Solutions with a pH of 9.0.
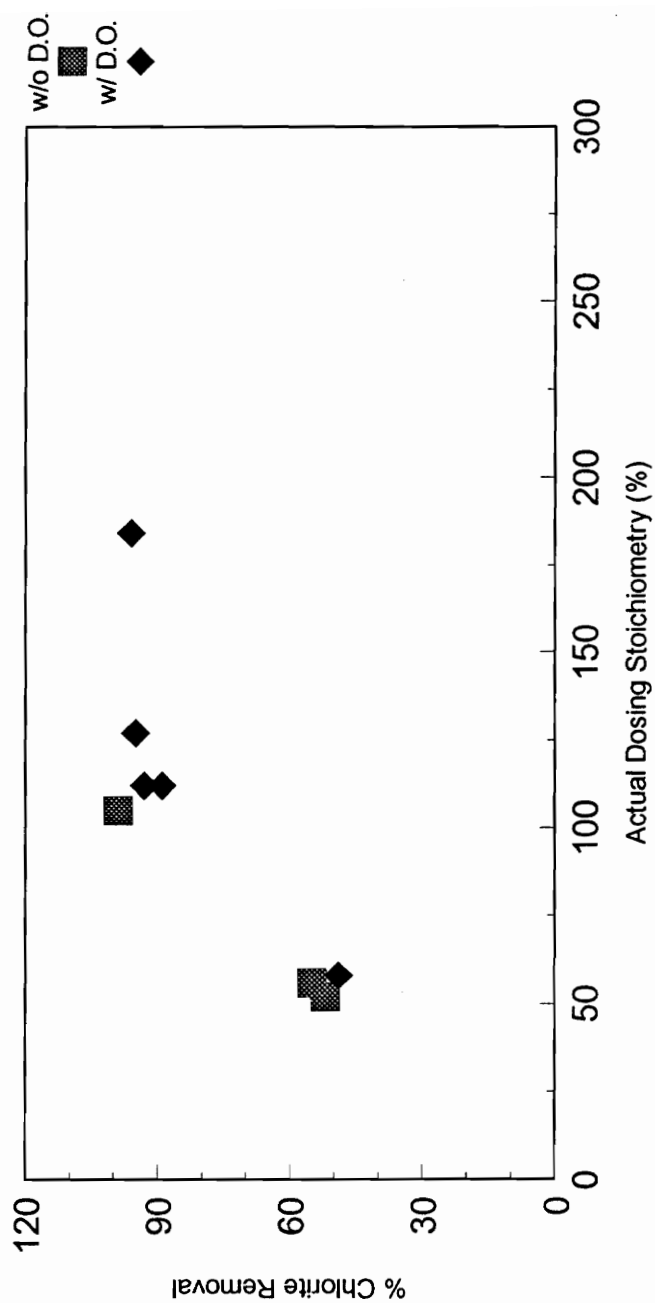
Figure 8: Effects of Aqueous Oxygen on the Removal of Chlorite by Fe(II) in Solutions with a pH of 10.0.

Chlorate Analysis

One of the major concerns associated with the use of ClO_2 in water treatment facilities is the production of disinfection-by-products. Therefore, not only was it essential to study the removal of ClO_2^- by Fe(II), but it was also necessary to investigate the possibility of a ClO_3^- residual which may result from the Fe(II):ClO_2^- reaction at elevated solution pH. Analysis for ClO_3^- concentrations was performed on samples collected during the stoichiometric tests (low and high O_2(aq) concentrations) at pH values equal to or greater than 8.0.

Table 9 presents the ClO_3^- data collected during the stoichiometric tests. The studied pH range (ie. 8 to 10) revealed insignificant fluctuations between the initial and final ClO_3^- concentrations. There was no evidence of ClO_3^- formation under these test conditions. It can be noted that initial ClO_3^- concentrations seem to be associated with impurities within the $NaClO_2$ utilized in the preparation of ClO_2^- solutions. As is evident from the data presented in Table 9, increases in initial ClO_3^- concentrations correspond to increases in the initial ClO_2^- residual. For example, at pH 8, an initial ClO_2^- concentration of 7.1 mg/L resulted in an initial ClO_3^- concentration of 0.06 mg/L, while at an initial ClO_2^- concentration of 4.6 mg/L the initial ClO_3^- concentration was 0.04 mg/L.

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Table 9 : Evaluation of the Formation of Chlorate
as a By-Product of the Fe(II)/ Chlorite
Reaction at Solution pH Values of 8, 9,
and 10.

	Chlorite, mg/L		Chlorate, mg/L		Actual %
pH	Initial	Final	Initial	Final	Stoich. Dosing
8.0	4.6	2.7	0.04	0.04	30
8.0	7.5	2.0	-----	0.07	53
8.0	7.1	<0.1	0.06	0.07	113
8.0	3.5	0.2	0.04	0.04	113
8.0	4.4	0.2	0.04	0.04	136
8.9	6.7	3.6	0.11	0.10	60
8.9	6.7	3.3	0.11	0.10	61
8.9	4.5	0.7	0.04	0.05	80
9.1	7.5	<0.1	0.06	0.08	106
9.0	4.9	0.8	0.03	0.04	112
9.0	4.3	0.2	0.07	0.07	125
9.0	4.0	0.2	0.06	0.07	163
8.9	4.7	0.2	0.04	0.04	219
9.0	4.7	0.1	0.04	0.04	219
9.0	3.7	0.1	0.07	0.07	229
10.1	4.3	2.2	0.07	0.08	58
10.0	7.6	0.1	0.08	0.06	105
10.0	5.7	0.2	0.10	0.10	112
10.0	4.3	0.2	0.07	0.07	127
10.0	4.6	0.2	0.10	0.09	184

Note : Actual % Stoich. dosing based on 3.3 mg Fe(II)/ mg Chlorite
Conducted during stoichiometric testing

Mass Balance of Oxychlorine Species for the Fe(II)/ClO$_2^-$ Reaction

Mass balance experiments were conducted in order to determine the by-products of the reduction of ClO$_2^-$ by Fe(II). Equation #11 proposes that ClO$_2^-$ is reduced to Cl$^-$ by Fe(II), but as outlined in the literature review, previous studies have identified other mechanisms which might occur and subsequently result in the production of other oxychlorine species. During these tests, analysis was conducted to determine the possible occurrence of chlorine dioxide, chlorite, chlorate, chlorine, and chloride.

The target pH range for this testing was 8 to 10, with variations in the dosing stoichiometry of 50 and 100 percent. Table 10 presents the data collected with respect to pH and dosing stoichiometry.

At solution pH values ranging from 8 to 10 and Fe(II) dosing at 100 percent, samples of the initial test solution revealed ClO$_2^-$, ClO$_3^-$, and Cl$^-$ residuals. Trace amounts of a ClO$_2$ by-product were detected at each of the pH values studied, while Cl$_2$ was only detected at pH 8.0. The sum of the final residual divided by the sum of the initial concentration of the oxychlorine species (expressed on a molar basis) of concern indicate that approximately 10 percent of the initial concentration was not accounted for by the final speciation. These results also indicate that

Table 10: Evaluation of the Mass Balance for the Fe(II)/Chlorite Reaction at Solution pH Values of 8, 9, and 10: Comparisons based on the oxychlorine species detectable by the methods presented in this research thesis.

pH	Dosing Stoich.	Initial Conc., uM					Final Conc., uM					Sum Final Conc./ Sum Initial Conc.
		ClO2	ClO2-	ClO3-	Cl2	Cl-	ClO2	ClO2-	ClO3-	Cl2	Cl-	
8	100%	< 0.7	105	0.71	< 1.0	15.2	1.5	1.0	0.89	2.4	104	0.91
9	100%	< 0.7	112	0.70	< 1.0	18.1	2.1	1.0	0.91	< 1.0	114	0.90
10	100%	< 0.7	113	0.90	< 1.0	16.6	3.0	1.0	0.72	< 1.0	108	0.86
8	50%	< 0.7	111	0.71	< 1.0	18.6	1.0	29.8	0.89	3.4	92	0.97
10	50%	< 0.7	115	---	< 1.0	21.7	1.5	54.6	---	< 1.0	76	0.97
10	50%	< 0.7	105	---	< 1.0	16.4	1.0	47.4	---	< 1.0	79	1.05

Note: Reaction vessel was set-up to provide for a closed system

Cl^- is not the only by-product of the $Fe(II)/ClO_2^-$ reaction in certain instances.

At solution pH values ranging from 8.0 to 10.0 and $Fe(II)$ dosing at 50 percent, samples of the initial test solution revealed ClO_2^-, ClO_3^-, and Cl^- residuals. Trace amounts of ClO_2 residuals were detected for each test, while Cl_2 residuals were detected only at a solution pH value of 8.0. The absence of initial and final ClO_3^- concentrations for the tests conducted at pH 10 was due to sample contamination which prevented complete analysis. The sum of the final residual divided by the sum of the initial concentration of the oxychlorine species of concern, indicates that approximately 97 percent of the oxychlorine by-products are accounted for at solution pH values of 8 and 10.

Table 11 indicates approximately 84 percent Cl^- recovery (ie. based on Equation 11) for pH values ranging from 8 to 10 and $Fe(II)$ dosing at 100 percent. When the $Fe(II)$ dosing was reduced to 50 percent of the theoretical requirement, 96 percent Cl^- recovery was realized.

Impacts of DOC on the Removal of ClO_2^- by $Fe(II)$

The impacts of DOC on the $Fe(II)/ClO_2^-$ reaction were studied at solution pH values ranging from 8 to 10. The testing involved varying the DOC concentrations from 0 to 15

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Table 11: Comparative Analysis Between the Theoretical and Actual Chloride Production of the Fe(II)/Chlorite Reaction at Solution pH Values of 8, 9, and 10.

pH	Dosing Stoich.	Diff. btw. Initial & Final Conc.,uM		Theoretical Cl- Production	Actual Cl- Prod. Theo. Cl- Prod.
		ClO2-	Cl-		
8	100%	104	88.8	104	85
9	100%	111	95.9	111	86
10	100%	112	91.4	112	82
8	50%	81.2	73.4	81.2	90
10	50%	60.4	54.3	60.4	90
10	50%	57.6	62.6	57.6	109

Note: Theo. Cl- determined using Equation # 11

mg/L, while utilizing constant initial ClO_2^- and Fe(II) concentrations. This section will review the data collected from these tests.

Table 12 presents the data collected at pH 8.0 with an initial ClO_2^- concentration of 8.3 mg/L and an Fe(II) dosing of 117 percent of the theoretical amount required for ClO_2^- reduction. Initial DOC concentrations for the six test solutions were varied from 0.3 to 12.8 mg/L. Residual ClO_2^- concentrations varied from 0.07 to 0.18 mg/L, and minimal amounts of residual Fe(II) were detected.

Figure 9 illustrates the adsorptive capacity (q) of the iron for the organic material present in solution versus the DOC residual after the five minute reaction period. The adsorptive capacity (q) was determined by utilizing the following equation,

$$q = [(DOCi - DOCf)/(Fe(II)i - Fe(II)f)]$$

Over the range of DOC concentrations studied, it was evident that increases in the DOC residual were representative of an increasing q value, a result typical of a physical adsorption process.

Table 13 presents the data collected at pH 9.0 with an initial ClO_2^- concentration of 8.0 mg/L and an Fe(II) dosing of 120 percent. Initial DOC concentrations for the six test solutions were varied from 0.8 to 13.1 mg/L. It should be noted that the ClO_2^- residuals detected for test solutions

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Table 12: Impacts of Solution DOC on the Fe(II)/Chlorite Reaction with pH of 8.0.

Chlorite, mg/L		Fe(II), mg/L				DOC, mg/L			q
Initial	Final	Initial	Final '	Final "	Diff.	Initial "	Final "	Diff.	
8.26	0.2	31.9	2.7	0.04	31.86	0.3	0.27	0.05	< 0.01
8.26	0.1	31.9	1.0	0.03	31.87	1.1	0.50	0.64	0.02
8.26	0.1	31.9	1.0	0.03	31.87	3.7	0.81	2.90	0.09
8.26	< 0.1	31.9	2.1	0.03	31.87	6.2	1.40	4.83	0.15
8.26	< 0.1	31.9	2.5	0.03	31.87	8.6	2.02	6.57	0.21
8.26	0.2	31.9	1.2	0.04	31.86	12.8	3.19	9.61	0.30

Note: pH = 8.05
    ' sample filtered thru a 0.45 um filter
    " sample filtered thru a 30K ultrafiltration cell
    Actual % Stoich. Dosing = 117%
    q = mg DOC adsorbed / mg Iron

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Figure 9: Impacts of Solution DOC on the Fe(II) Dosed for Chlorite Removal: Fe(II) dose of 117% and solution pH of 8.0.

Table 13: Impacts of Solution DOC on the Fe(II)/Chlorite Reaction with pH of 9.0

Chlorite, mg/L		Fe(II), mg/L				DOC, mg/L			q
Initial	Final	Initial	Final '	Final "	Diff.	Initial "	Final "	Diff.	
8	0.2	31.7	0.03	------	31.67	0.8	0.80	0.01	< 0.01
8	< 0.1	31.7	0.03	------	31.67	1.3	0.80	0.48	0.02
8	0.6	31.7	0.04	------	31.66	3.7	1.63	2.11	0.07
8	0.2	31.7	0.03	------	31.67	6.3	2.73	3.61	0.11
8	0.5	31.7	0.06	------	31.64	8.8	4.05	4.75	0.15
8	0.3	31.7	0.17	------	31.53	13.1	6.32	6.81	0.22

Note: pH = 8.98
    ' sample filtered thru a 0.45 um filter
    " sample filtered thru a 30K ultrafiltration cell
    Actual % Stoich. Dosing = 120%
    q = mg DOC adsorbed / mg Iron

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with initial DOC concentrations greater than 3.7 mg/L were more significant than those for the testing conducted at pH 8.0.

Figure 10 illustrates the adsorptive capacity (q) of the iron for the organic matter present in solution versus the DOC residual after the five minute reaction period. Increases in the residual DOC were associated with an increasing q value, but the data produced a plot which was significantly less steep than that produced by the data collected at pH 8.0.

Table 14 presents the data collected at pH 10.0 with an initial ClO_2^- concentration of 8.6 mg/L and an Fe(II) dosing of 112 percent. Initial DOC concentrations were varied from 0.5 to 12.0 mg/L. ClO_2^- residuals ranged from 0.7 to 2.0 mg/L, with the higher concentrations being associated with increased DOC content.

Figure 11 illustrates the plot of q versus the final DOC content for the testing at pH 10.0. Once again the data illustrate increasing q values with associated increases in residual DOC. These data also produce a plot which was considerably less steep than that achieved with the data collected at pH 8.0.

Table 15 presents the data collected at pH 9.9 with an initial ClO_2^- concentration of 8.1 mg/L and an Fe(II) dose of 158 percent of the theoretical requirement. Initial DOC

Figure 10: Impacts of Solution DOC on the Fe(II)
Dosed for Chlorite Removal: Fe(II) dose of 158%
and solution pH of 9.0.

Table 14: Impacts of Solution DOC on the Fe(II)/Chlorite Reaction with pH of 10.0.

| Chlorite, mg/L | | Fe(II), mg/L | | | | DOC, mg/L | | | q |
Initial	Final	Initial	Final '	Final "	Diff.	Initial "	Final "	Diff.	
8.58	0.7	31.7	0.03	0.03	31.67	0.5	0.29	0.16	0.01
8.58	0.8	31.7	0.04	0.03	31.67	1.0	0.51	0.51	0.02
8.58	1.1	31.7	0.05	0.03	31.67	3.5	1.37	2.14	0.07
8.58	1.6	31.7	0.09	0.03	31.67	6.1	2.41	3.72	0.12
8.58	1.9	31.7	0.1	0.03	31.67	8.6	3.67	4.90	0.15
8.58	2.0	31.7	0.16	0.04	31.66	12.0	6.07	5.90	0.19

Note: pH = 9.96
' sample filtered thru a 0.45 um filter
" sample filtered thru a 30K ultrafiltration cell
Actual % Stoich. Dosing = 112%
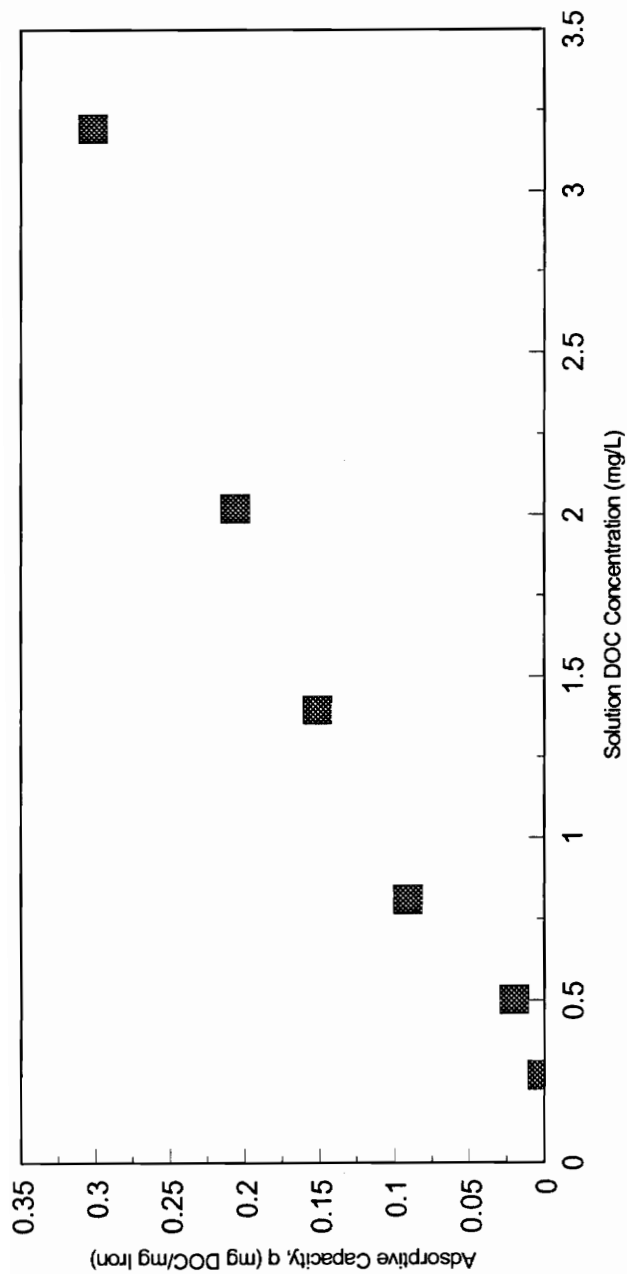q = mg DOC adsorbed / mg Iron

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Figure 11: Impacts of Solution DOC on the Fe(II)
Dosed for Chlorite Removal: Fe(II) dose of 112%
and solution pH of 10.0.

Table 15: Impacts of Solution DOC on the Fe(II)/Chlorite Reaction with pH of 10.0.

| Chlorite, mg/L | | Fe(II), mg/L | | | | DOC, mg/L | | | q |
Initial	Final	Initial	Final '	Final "	Diff.	Initial "	Final "	Diff.	
8.09	0.3	42.2	0.05	0.04	42.16	0.7	0.36	0.29	0.01
8.09	0.2	42.2	0.05	0.04	42.16	1.2	0.55	0.64	0.02
8.09	0.6	42.2	0.05	0.04	42.16	3.7	1.35	2.37	0.06
8.09	0.7	42.2	0.07	0.04	42.16	6.7	2.31	4.39	0.10
8.09	0.8	42.2	0.15	0.04	42.16	9.4	3.51	5.85	0.14
8.09	1.0	42.2	0.37	0.04	42.16	13.4	5.26	8.10	0.19

Note: pH = 9.92
' sample filtered thru a 0.45 um filter
" sample filtered thru a 30K ultrafiltration cell
Actual % Stoich. Dosing = 158%
q = mg DOC adsorbed / mg Iron

concentrations ranged from 0.7 to 13.4 mg/L. Due to the
increased Fe(II) dosing, the ClO_2^- residuals were less than
those obtained during the previous test at pH 10.0; but the
residuals were still significantly higher than those
detected at pH 8.0 and 9.0.

Figure 12 illustrates the plot of q versus the final
DOC content for the testing at pH 9.9. Increasing values of
q were associated with increases in final DOC
concentrations.

Figure 13 presents an overlay of the plots illustrated
in Figures 9, 10, 11, and 12. From this overlay one can see
the marked difference between the adsorptive capacity at pH
8.0 and those produced at pH values of 9.0, 9.9, and 10.0.
It is also evident that the adsorptive capacity of iron for
the organics was relatively consistent at pH values of 9.0,
9.9, and 10.0.

The impacts of DOC on the Fe(II)/ClO_2^- reaction were
also studied with respect to the presence of dissolved
oxygen in solution. Table 16 presents the results of the
studies conducted, which involved initial ClO_2^- doses of 8.2
mg/L, Fe(II) dosing at 117 percent, solution pH of 10.0, and
DOC concentrations of 1.4 and 12.6 mg/L. The test solutions
were aerated and the reaction was conducted in a closed
system. As outlined in Table 16, the ClO_2^- residual for the
test solution containing an initial DOC concentration of

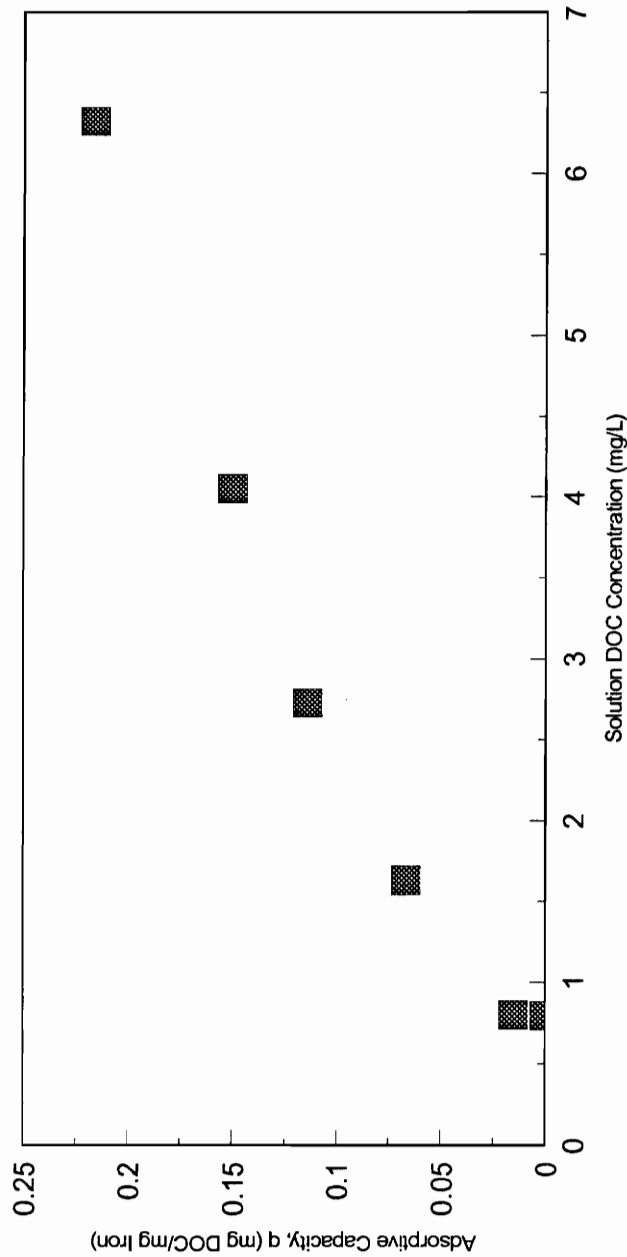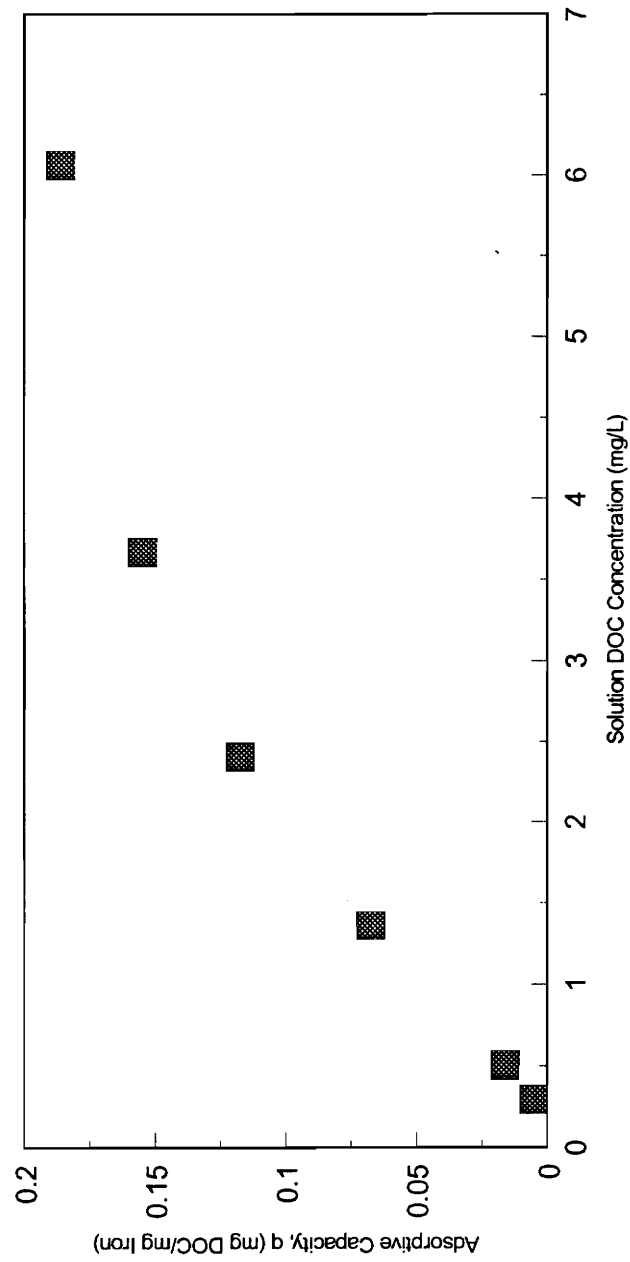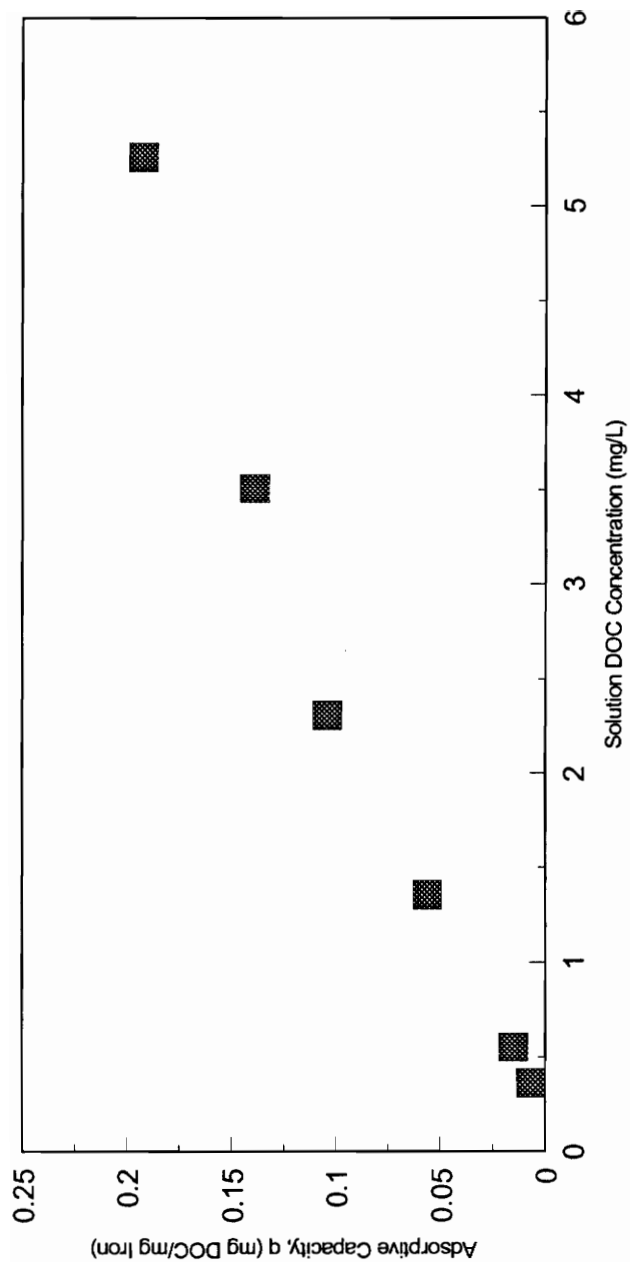Figure 12: Impacts of Solution DOC on the Fe(II) Dosed for Chlorite Removal: Fe(II) dose of 158% and solution pH of 9.9.
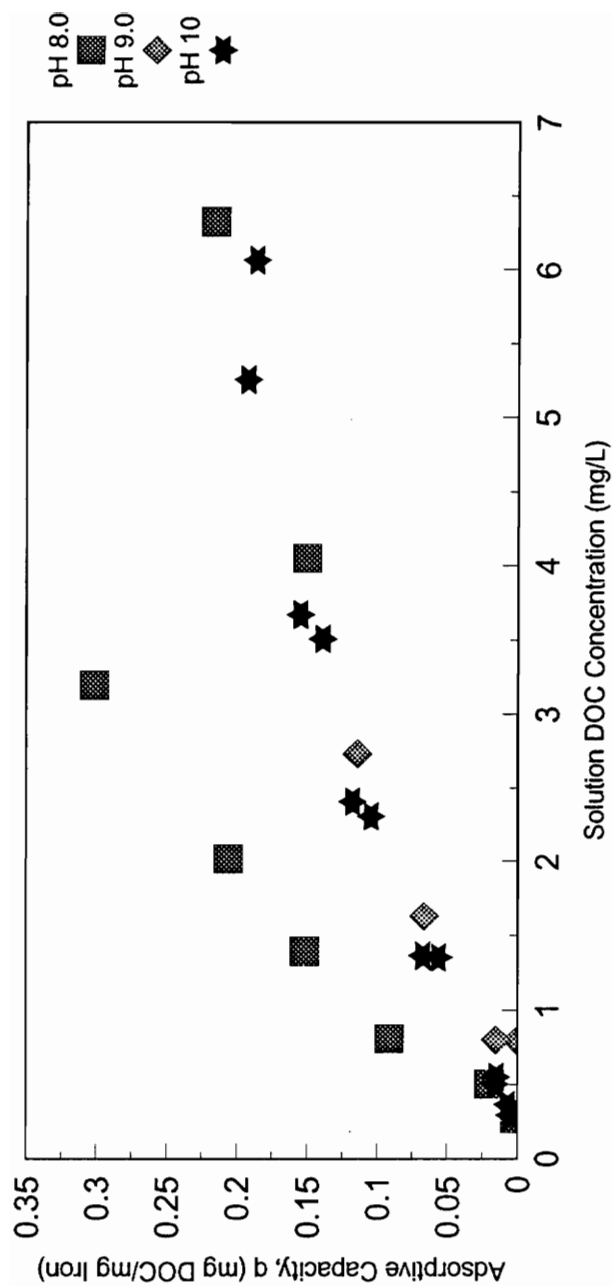
Figure 13: Impacts of Solution DOC on the Fe(II) Dosed for Chlorite Removal: Solution pH values of 8, 9, and 10.

Table 16: Impacts of DOC Concentration on the Fe(II)/ Chlorite Reaction in an Oxygenated Solution

Chlorite, mg/L		Fe(II), mg/L				DOC, mg/L			q
Initial	Final	Initial	Final '	Final "	Diff.	Initial "	Final "	Diff.	
8.2	2.0	31.8	0.04	0.05	31.75	1.4	0.88	0.55	0.02
8.2	4.3	31.8	0.14	0.05	31.75	12.6	5.32	7.29	0.23

Note: pH = 9.98

Dosing Stoichiometry = 117%

Reaction conducted in a closed system

Study solution aerated for approximately 15 min. prior to test

' sample filtered thru a 0.45 um filter

" sample filtered thru a 30K ultrafiltration cell

q = mg DOC adsorbed / mg Iron

12.6 mg/L was significantly higher than that for the test solution having the lower DOC content.

Figure 14 presents the dissolved oxygen concentration as a function of time with respect to the DOC content of the test solutions. From these presentations, it is evident that the oxygen consumption in the test solution containing the higher DOC content was approximately 1.3 mg/L greater than that of the test solution containing the lesser amount of DOC. The adsorptive capacities determined through these tests were consistent with the previous findings.

Further testing was conducted involving an initial ClO_2^- dose of 8.32 mg/L, Fe(II) dosing at 117 percent, initial DOC concentrations of 16.5 and 13.6 mg/L, and dissolved oxygen levels less than 0.5 and greater than 5.0 mg/L. Table 17 presents the data associated with these tests at a solution pH of 10.0. These data indicate that solutions containing lower dissolved oxygen concentrations result in lower ClO_2^- residuals. The reported adsorptive capacities for these tests were relatively similar. Figure 15 contains the data obtained by monitoring the dissolved oxygen concentration during the five-minute reaction period.

Figure 16 graphically represents residual ClO_2^- as a function of initial DOC concentration for solution pH values of 8, 9, and 10. From this plot one can see that initial DOC concentration produced minimal interferences with ClO_2^-
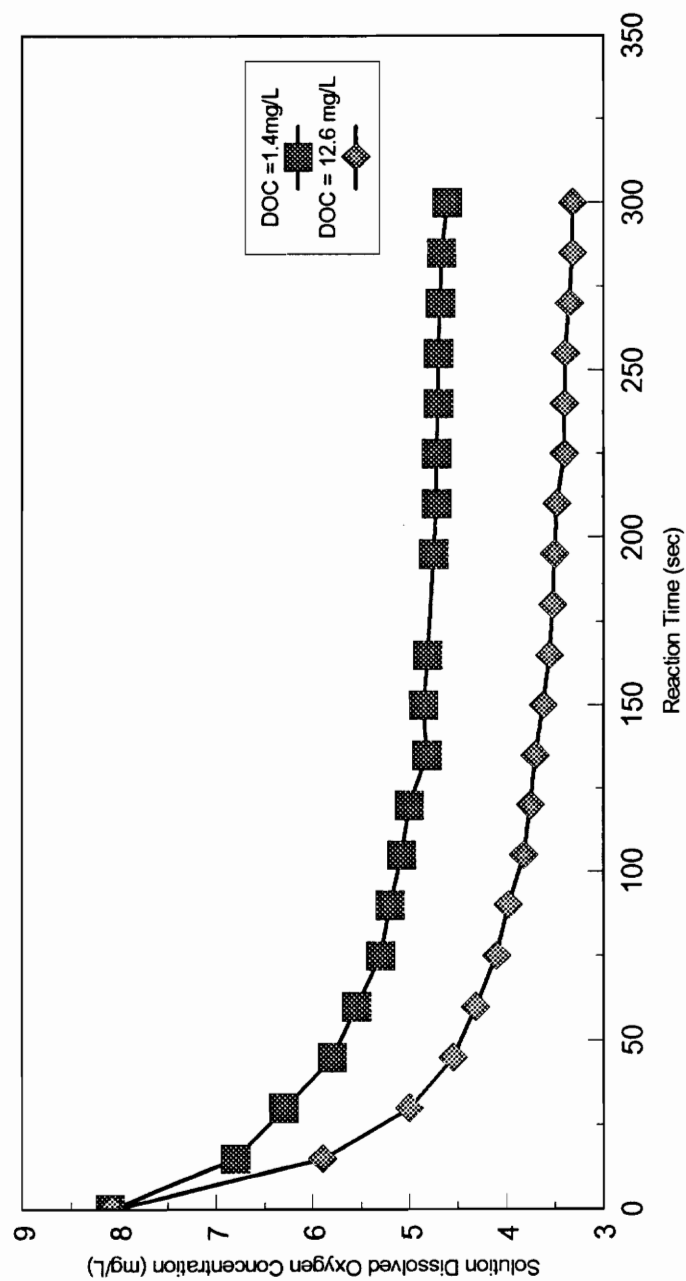
Figure 14: Impacts of the Fe(II)/Chlorite Reaction on Aqueous Oxygen with Respect to Time (DOC varied, pH of 10, dose of 117%).

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**Table 17: Impacts of Solution DOC and Aqueous Oxygen Concentrations
on the Fe(II) / Chlorite Reaction**

Chlorite, mg/L		Fe(II), mg/L				DOC, mg/L			q
Initial	Final	Initial	Final '	Final "	Diff.	Initial "	Final "	Diff.	
8.32 '''	0.3	32.1	0.05	0.05	32.05	16.5	6.68	9.84	0.31
8.32 ''''	2.8	32.1	0.06	0.05	32.05	13.6	5.02	8.58	0.27

Note: pH = 9.98
    Dosing Stoichiometry = 117%
    Reaction conducted in a closed system
    ' sample filtered thru a 0.45 um filter
    " sample filtered thru a 30K ultrafiltration cell
    ''' Study solution deaerated by bubbling with nitrogen for approximately 15 min. prior to test
    '''' Study solution aerated for approximately 15 min. prior to test
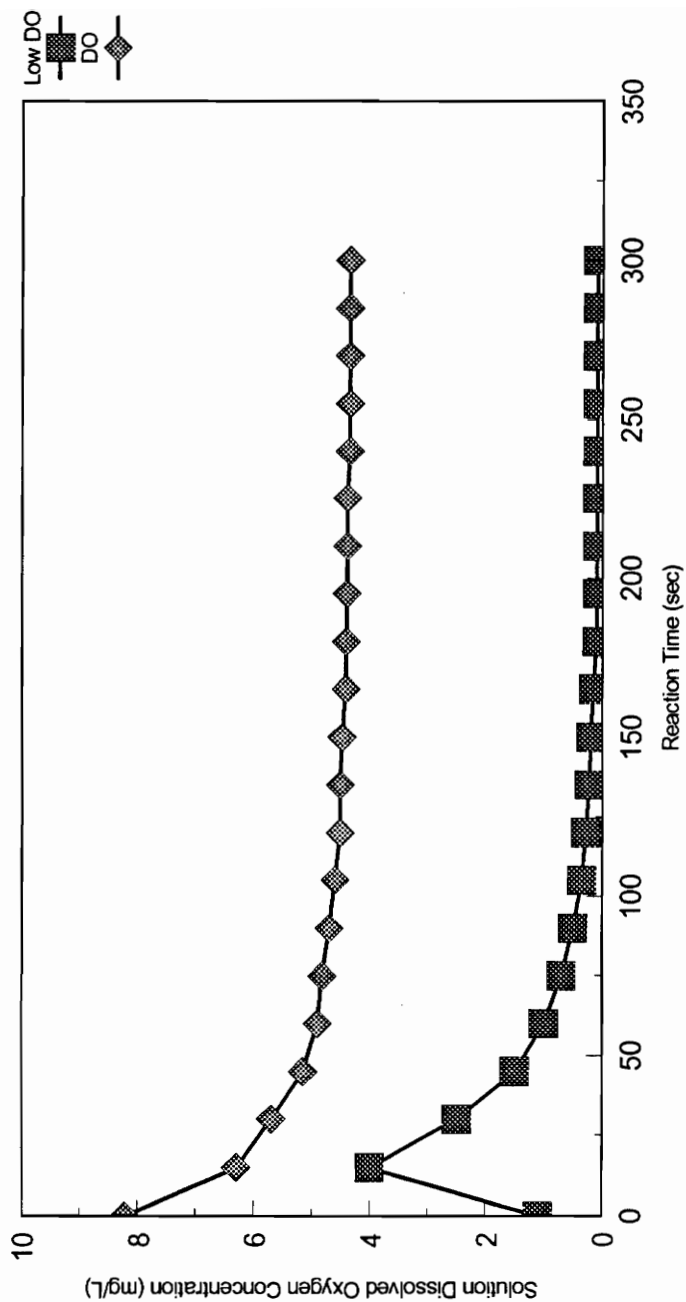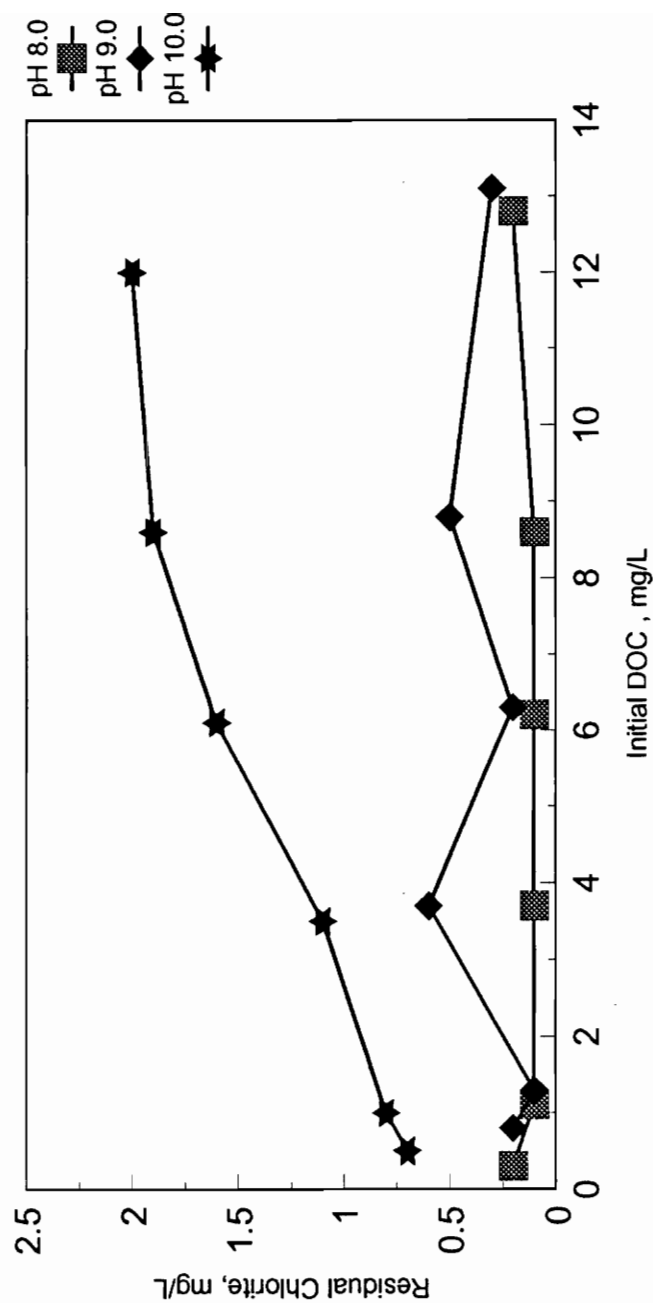   q = mg DOC adsorbed / mg Iron

Figure 15: Impacts of the Fe(II)/Chlorite Reaction on Aqueous Oxygen with respect to Time (varied oxygen, pH of 10, dose of 117%).

Figure 16: Impact of Initial DOC Concentration on Residual Chlorite for Solution pH Values of 8, 9, and 10 (stoichiometric dose of 120%).

removal at a solution pH of 8.0. However, an increase in solution pH (ie. pH 9 and 10) produced a trend in which increasing DOC concentrations resulted in greater amounts of residual ClO_2^-. From Figure 17 it was evident that increases in the Fe(II) dosing stoichiometry (ie. 120% to 160%) enhanced the removal of ClO_2^- associated with increasing initial DOC concentrations.

During the tests conducted to observe the effects of organic material on the Fe(II)/ClO_2^- reaction, samples were also collected and analyzed for ClO_3^-. Table 18 presents the data obtained with respect to ClO_3^- formation. The results obtained during these tests were consistent with previous findings in that insignificant changes between initial and final ClO_3^- concentrations were noticed. Thus, there was again no evidence of ClO_3^- formation as a result of the interaction between Fe(II) and ClO_2^-.
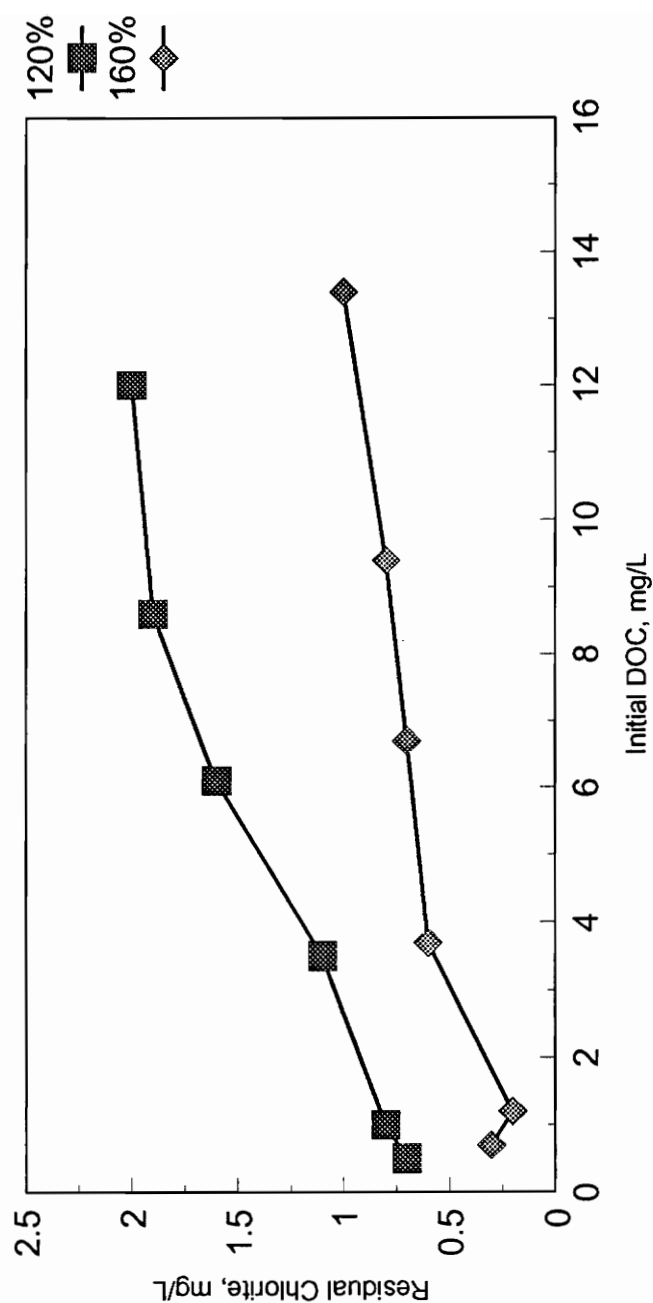
Figure 17: Impact of Initial DOC Concentration on Residual Chlorite for Stoichiometric Doses of 120 and 160% (pH of 10.0).

Table 18: Impacts of Solution DOC and pH on the Formation of Chlorate as a By-Product of the Ferrous Iron/ Chlorite Reaction

| pH | Chlorite, mg/L | | Chlorate, mg/L | | Actual % | DOC, mg/L |
	Initial	Final	Initial	Final	Stoich. Dosing	Initial
8.0	8.3	0.2	0.07	0.07	117	0.3
8.0	8.3	0.1	0.07	0.08	117	8.6
8.0	8.3	0.2	0.07	0.08	117	12.8
9.0	8.0	0.2	0.06	0.07	120	0.8
9.0	8.0	0.1	0.06	0.06	120	1.3
9.0	8.0	0.6	0.06	0.06	120	3.7
9.0	8.0	0.2	0.06	0.07	120	6.3
9.0	8.0	0.5	0.06	0.06	120	8.8
9.0	8.0	0.3	0.06	0.06	120	13.1
10.0	8.6	0.7	0.08	0.07	112	0.5
10.0	8.6	0.8	0.08	0.07	112	1.0
10.0	8.6	1.1	0.08	0.08	112	3.5
10.0	8.6	1.6	0.08	0.07	112	6.1
10.0	8.6	1.9	0.08	0.07	112	8.6
10.0	8.6	2.0	0.08	0.08	112	12.0
10.0	8.1	0.3	0.06	0.07	158	0.7
10.0	8.1	0.2	0.06	0.06	158	1.2
10.0	8.1	0.6	0.06	0.06	158	3.7
10.0	8.1	0.7	0.06	0.06	158	6.7
10.0	8.1	0.8	0.06	0.06	158	9.4
10.0	8.1	1.0	0.06	0.06	158	13.4

Note : Actual % Stoich. dosing based on 3.3 mg Fe(II)/ mg Chlorite

CHAPTER V

DISCUSSION

Introduction

This chapter contains a discussion of the results accumulated during the course of the study. The issues to be addressed are separated into the following sections: the stoichiometry of the $Fe(II)/ClO_2^-$ reaction at elevated pH; occurrence of a ClO_3^- residual due to the reaction of ClO_2^- with $Fe(II)$; mass balance of the oxychlorine residuals associated with the $Fe(II)/ClO_2^-$ reaction, and the impacts of DOC on the $Fe(II)/ClO_2^-$ reaction.

Stoichiometry of the $Fe(II)/ClO_2^-$ Reaction at Elevated pH

Stoichiometric tests utilizing solutions with low (< 0.5 mg/L) $O_2(aq)$ were conducted in order to describe the reaction stoichiometry between $Fe(II)$ and ClO_2^- at elevated pH with minimal $O_2(aq)$ interference. Over the pH range of 6.0 to 7.0, a stoichiometric ratio of 3.3 mg $Fe(II)$ per mg ClO_2^- resulted in minimal ClO_2^- residuals, which reflects the stoichiometry described by equation #11. Iatrou and Knocke (1992) studied the $Fe(II)/ClO_2^-$ reaction over a pH range of 5.0 to 7.0 and reported that a dosing stoichiometry of 3.1 mg $Fe(II)$ per mg ClO_2^- provided for efficient ClO_2^- removal.

Data presented in Tables 1 and 2 reflect the increased
kinetics of the oxidation of Fe(II) by O_2(aq) with related
increases in pH. Comparison of the Fe(II) residuals
detected at solution pH values of 6 and 7 and dosing
stoichiometries in excess of 100 percent reveals
significantly lower residual Fe(II) concentration for the
tests conducted at pH 7. The theoretical stoichiometry of
0.14 mg O_2(aq) per mg Fe(II) indicates that the minimal
amount of O_2(aq) remaining after solution deaeration and the
subsequent transfer of the solution to the test bottle,
which could have allowed for additional aeration, was still
significant enough to allow for the oxidation of Fe(II) by
O_2(aq). Iatrou and Knocke (1992) also reported noticeable
increases in the oxidation of Fe(II) by O_2(aq) at pH 7.

Stoichiometric ratios of 3.3, 3.4, and 3.4 mg Fe(II)
per mg ClO_2^- were found to effectively eliminate ClO_2^-
residuals at pH values of 8, 9, and 10, respectively.
Fe(II) residuals, as reported in Tables 3 - 5, were
consistently found to be equal to or less than 0.3 mg/L,
even when testing involved the use of Fe(II) doses as high
as 377 percent of the theoretical amount predicted by
equation # 11. Figure 2 illustrates increasing
stoichiometric ratios with respect to dosing stoichiometries
greater than 3.3 mg Fe(II) per mg ClO_2^- (ie. 100 percent of
stoichiometric dose). This trend was common for all tests
conducted over the pH range of 8.0 to 10.0. The increases

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in the observed stoichiometry reflect the oxidation of excess Fe(II) by O_2(aq) for the reported pH values. Although increases in the kinetics of the Fe(II)/O_2(aq) reaction were noticed due to the minimal amount of O_2(aq) in solution, sufficient ClO_2^- removal was still accomplished. Studies conducted by Stumm and Lee (1961) also reported increased oxygenation of Fe(II) with increases in solution pH.

Test solutions were also aerated in order to determine if significant amounts of O_2(aq) would inhibit the reduction of ClO_2^- by Fe(II). Dissolved oxygen concentrations ranging from 8 to 10 mg/L were utilized for these tests. Stoichiometric ratios of 3.9, 3.9, and 4.0 mg Fe(II) per mg ClO_2^- were found to effectively reduce ClO_2^- concentrations at solution pH values of 8, 9, and 10, respectively. Slight increases were noticed when compared to the stoichiometric ratios reported for the tests conducted with low O_2(aq) concentrations. The differences were related to the increases in the initial O_2(aq) concentration in the test solution, thereby allowing for greater Fe(II) oxidation by O_2(aq) with associated influences upon the observed Fe(II)/ClO_2^- reaction stoichiometry.

Fe(II) residuals were found to be less than or equal to 0.22 mg/L for all testing conducted with solutions containing high O_2(aq) concentrations (Tables 6 - 8). Fe(II) doses as high as 229 percent of the theoretical

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amount described by equation #11 were utilized for these tests. Figure 3 illustrates trends for the aerated tests which are similar to those reported by Figure 2 for the tests with low $O_2(aq)$ concentrations, thereby illustrating increases in the observed stoichiometric ratio with Fe(II) dosing stoichiometries in excess of 100 percent (ie. 3.3 mg Fe(II) per mg ClO_2^-).

Although the data presented in this section indicate a significant increase in the rate of Fe(II) oxidation by $O_2(aq)$ in accordance with increases in solution pH, the rate of reaction between Fe(II) and ClO_2^- was still proceeding rapidly enough to prevent the presence of $O_2(aq)$ from inhibiting ClO_2^- removal efficiencies as can be seen on the overlays presented in Figures 6, 7 and 8. Due to the observed increases in the reaction rate of Fe(II) and $O_2(aq)$ over the pH range of 8 to 10, it would be possible for water utilities to utilize excess amounts of Fe(II) for the removal of ClO_2^- with minimal concerns about exceeding the recommended residual iron concentration of 0.3 mg/L. Likewise, the results indicate that only a slight increase in Fe(II) stoichiometric dosing will be needed to compensate for $O_2(aq)$ under alkaline pH conditions.

Chlorate Analysis

Analysis of samples collected prior to the reaction of ClO_2^- with Fe(II) indicated the significance of the ClO_3^-

impurities associated with the $NaClO_2$ utilized to prepare ClO_2^- solutions. Table 9 presents the data which illustrate the relationship between initial ClO_2^- and ClO_3^- concentrations. Increases in the initial ClO_2^- concentrations used for testing corresponded with detected increases in initial ClO_3^- concentrations.

Over the range of pH values studied (8 to 10) insignificant fluctuations when comparing initial and final ClO_3^- concentrations were observed. These results correspond to data presented by both Iatrou and Knocke (1992) and Griese et al (1991), wherein both studies showed no evidence of ClO_3^- as a by-product of the $Fe(II)/ClO_2^-$ reaction. From these results, it is apparent that the removal of ClO_2^- by Fe(II) can likewise be achieved at elevated pH values (8 to 10) without significant production of ClO_3^-.

Mass Balance of Oxychlorine Species for the $Fe(II)/ClO_2^-$ Reaction

Equation #11 is based on the assumption that the reaction of Fe(II) with ClO_2^- results in complete reduction of the ClO_2^- to Cl^-. Although a significant amount of the reaction by-products detected during the mass balance testing was attributed to the Cl^- ion, it was evident that complete reduction of ClO_2^- to Cl^- was not occurring at pH values ranging from 8 to 10, as depicted by Table 10. At

Fe(II) dosing stoichiometries of 100 percent, the residual oxychlorine species detected were ClO_2, ClO_2^-, ClO_3^-, Cl_2, and Cl^-. These residuals accounted for over 90 percent of the species present in solution prior to the reaction (Figures 9 and 10). Tests involving Fe(II) doses of 50 percent showed similar trends, although residual species accounted for approximately 97 percent of the initial concentrations.

As previously stated, equation #11 assumes the Cl^- ion to be the only by-product of the Fe(II)/ClO_2^- reaction, but the data presented by this study indicate that several oxychlorine species are detected as reaction by-products. These oxychlorine by-products can be accounted for by the many side-reactions which have been identified during previous studies conducted by Gordon et al. Ondrus and Gordon (1972) proposed the side reactions presented by Equations 6 - 9, and Fabian and Gordon (1992) identified the side reactions represented by equations 20 - 22, which were discussed in the literature review and experimental methods and materials. These side reactions account for the possibility of reaction by-products such as HOCl, [Cl(II)] intermediate, ClO^-, and ClO_2. Due to the limitations of the laboratory equipment available during the study, only those oxychlorine species listed in Table 10 could be detected.

From the data collected during this study, it appears that as the Fe(II) dosing approaches 100 percent of the theoretical amount predicted by equation #11, the

accountability of the residual oxychlorine species decreases, as indicated by the 10 percent difference in initial and final concentrations shown in Table 10. One explanation for these differences would be the production of the highly volatile [Cl(II)] intermediate species, HOCl, or ClO$^-$ as a consequence of the Fe(II)/ClO$_2^-$ reaction at elevated pH, therefore preventing accurate detection of all the oxychlorine by-products associated with the reaction. From these results, it can be demonstrated that the Fe(II)/ClO$_2^-$ reaction produces several oxychlorine by-products in addition to the Cl$^-$ ion, but it must be pointed out that the species other than Cl$^-$ are only present in trace amounts. The data presented in Table 10 indicates that at stoichiometric dosing of 100 percent Cl$^-$ accounts for approximately 95 percent of the detected by-products.

Impacts of DOC on the Removal of ClO$_2^-$ by Fe(II)

As outlined in the results chapter, the impact of DOC on the removal of ClO$_2^-$ by Fe(II) was studied under several different conditions such as: variations in initial DOC concentration (0 -15 mg/L), variations in the O$_2$(aq) concentration of the test solutions, and pH values ranging from 8 to 10. These tests were conducted in order to determine if DOC would interfere with the removal of ClO$_2^-$ by Fe(II) (ie. complexation of the Fe(II) by the DOC,

thereby hindering the ability of the Fe(II) to react with the ClO_2^-).

Tables 12 through 15 present the results of the testing with respect to pH and initial DOC variations. The adsorptive capacity (q) of the iron-oxide solids for the DOC was calculated as discussed in the results chapter. It is apparent from these data that increases in the solution pH produce decreased q values. These findings can be explained by examining the surface charge of the iron-oxide solids. Dependent upon solution pH, the surface of the iron-oxide solids is going to be more negatively charged (pH greater than 9) or more positively charged (pH less than 9). Culp et al, 1986, reported a zero point of charge for iron-oxides of approximately 9.0. At pH values less than 9 (ie. more positive iron-oxide surface charge), the q value will increase due to the negative surface charge associated with the DOC particles; but as the data indicate, increases in solution pH relate to decreasing q values due to the surface of the iron-oxide solids becoming more negatively charged. Knocke et al (1994) also reported increased q values being associated with decreases in solution pH in the range of 6.5 to 5.5. The data were collected from tests involving the oxidation of complexed Fe(II) by the application of free chlorine and ClO_2.

Adsorption isotherms, illustrating the relationship between residual DOC concentration and q were developed for

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the range of pH values studied. The isotherms presented in Figure 13 were developed according to the Freundlich model, which is represented as follows:

$$q_e = KC_e^{(1/n)} \qquad [30]$$

where:

q_e = adsorption capacity, mg DOC/mg Fe(II)

C_e = residual DOC concentration, DOC mg/L

K, n = constants

As illustrated by the overlay of the isotherms for the studied pH range, increased q values were associated with both decreases in solution pH and increases in initial DOC concentration.

From Figure 16 it was evident that increases in initial DOC concentration produced significantly higher ClO_2^- residuals at a solution pH value of 10.0. At a solution pH of 10.0 and Fe(II) dosing at 112 percent, significant ClO_2^- residuals were noticed. Increases in initial DOC concentrations also provided for increasing ClO_2^- residuals at pH 10.0. Tests conducted at pH 10.0, with an Fe(II) dose of 158 percent, also revealed significant ClO_2^- residuals, although less than those reported at the Fe(II) dosing of 112 percent (Figure 17).

These findings led to tests which involved the utilization of a closed system in order to monitor oxygen consumption during the Fe(II)/ClO_2^- reaction. The results previously presented in Table 16 and Figure 14 indicated a

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significant difference in the amount of oxygen consumed between the test solution containing a low DOC content (1.4 mg/L) and the one containing a high DOC content (12.6 mg/L). From these results, it was evident that an increase in solution DOC content caused the increased oxygenation of Fe(II). As noted in Figure 14, the test solution whose DOC content was 12.6 mg/L consumed approximately 1.3 mg/L more O_2(aq) than the test solution with the lower DOC content. Recalling the theoretical stoichiometry of 0.14 mg O_2(aq) per mg Fe(II), it is evident that this difference could be attributed to the increased ClO_2^- residual (4.3 mg/L) noticed for the test pertaining to the higher DOC content. This suggests that increased DOC content provides for a mechanism by which Fe(II) oxidation by O_2(aq) competes favorably with the reaction between Fe(II) and ClO_2^-.

Additional tests involved the incorporation of a high DOC content with variations in the initial dissolved oxygen concentration. These results were presented in the previous chapter (Table 17 and Figure 15). These tests were conducted in order to determine if ClO_2^- removal would improve for solutions containing significant levels of DOC and minimal amounts of O_2(aq). From Table 17, it is apparent that more efficient ClO_2^- removal occurred for testing conducted with minimal O_2(aq) concentrations (1.1 mg/L) even in the presence of a significant amount of DOC (16.5 mg/L). Once again, the test involving high DOC

content in an aerated solution ($O_2(aq)$ = 8.22 mg/L)
exhibited inefficient ClO_2^- removal (ie. ClO_2^- residual = 2.8
mg/L). One explanation of these results would be that the
DOC acts as a catalyst for the oxidation of Fe(II) by
$O_2(aq)$; therefore, increases in the DOC content would force
increased Fe(II) oxygenation while preventing the complete
reduction of ClO_2^- at solution pH values of approximately
10.

As illustrated in Table 18, DOC content had no effect
upon ClO_3^- residuals with results similar to those collected
during the stoichiometric tests.

Applicability of Results to Water Treatment

Iatrou and Knocke (1992) reported that Fe(II) dosing at
100 percent of the stoichiometric requirement would
effectively reduce ClO_2^- residuals within the scheme of
water treatment processes operated over the pH range of 5.0
to 7.0. Results gathered from the stoichiometric tests
conducted for this study indicate significant increases in
the kinetics of the Fe(II)/$O_2(aq)$ reaction over the pH range
of 8.0 to 10.0. In order to integrate the removal of ClO_2^-
by Fe(II) into the treatment schemes of water utilities that
operate unit processes at elevated pH conditions it would be
necessary to utilize Fe(II) doses in excess of the
stoichiometric requirement (ie. 3.3 mg Fe(II) per mg ClO_2^-
). This dosing would be sufficient for treatment processes

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that operate with significant concentrations of $O_2(aq)$. Due to the increased kinetics of the $Fe(II)/O_2(aq)$ reaction $Fe(II)$ residuals in excess of 0.3 mg/L would not be expected.

DOC-laden waters may pose a greater challenge for the removal of ClO_2^- by reaction with $Fe(II)$, especially under higher pH conditions (ie. pH 10.0). Insufficient ClO_2^- removal was observed for solutions with pH values of approximately 10.0 and significant DOC concentrations. The poor removal efficiency was related to the catalyst effect caused by the DOC, whereby an increased reaction rate between $Fe(II)$ and $O_2(aq)$ was noticed. Therefore it would be more feasible for utilities that operate unit processes over the pH range of 8.0 to 10.0 to incorporate DOC removal prior to dosing with $Fe(II)$ for the removal of ClO_2^-, or to simply dose at a higher stoichiometry.

CHAPTER VI

CONCLUSIONS

The primary objective of this project was to study the removal of ClO_2^- by reaction with Fe(II) under alkaline pH conditions. The stoichiometry of the reaction was evaluated within the pH range of 6.0 to 10.0. The stoichiometric experiments were conducted under both aerated and deaerated conditions in order to describe the possible effects that the presence of $O_2(aq)$ might have upon the stoichiometry of the Fe(II)/ClO_2^- reaction. Further emphasis was directed toward the speciation of the oxychlorine residuals associated with the reduction of ClO_2^-. Other possible interferences, such as, the DOC content of the source water were also investigated.

As stated earlier, there was no evidence of the formation of a significant ClO_3^- residual as a result of the Fe(II)/ClO_2^- reaction during the course of the original study. During this study, tests that were conducted at pH values greater than 7.0 were analyzed for the possibility of a ClO_3^- by-product. This was an essential component of the research due to the possible health risks associated with ClO_3^- in drinking water.

Based upon the data collected during the study, the following conclusions were formulated:

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(1) Fe(II) dosing from 10 to 20 percent in excess of the theoretical amount required (3.3 mg Fe(II) per mg ClO_2^-) will provide for sufficient ClO_2^- removal under alkaline pH conditions (pH 7.0 to 10.0). The increased stoichiometries described in this study are attributed to the increasing competiveness $O_2(aq)$. Trace $O_2(aq)$ doses present a competing reaction over the pH range of 7.0 to 10.0, thereby creating increases in the Fe(II)/ClO_2^- stoichiometry.

(2) There was no evidence found to suggest the occurrence of a ClO_3^- by-product due to the reduction of ClO_2^- by Fe(II) over the pH range of 7.0 to 10.0.

(3) There was no significant impact of DOC content upon the Fe(II)/ClO_2^- reaction for solution pH values ranging from 8.0 to 9.0.

(4) Increases in solution DOC content at pH 10.0 provided a mechanism which resulted in increasing reaction rates between Fe(II) and $O_2(aq)$, thereby preventing the efficient removal of ClO_2^-. Solutions containing minimal amounts of $O_2(aq)$ revealed more efficient ClO_2^- removal. Future investigation is recommended.

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(5) Theoretically, the reaction between Fe(II) and ClO_2^- results in the complete reduction of ClO_2^- to Cl^-. This study detected several oxychlorine residuals, which included, ClO_2, Cl_2, and Cl^-. Although several oxychlorine species were detected during analysis approximately 95 percent of the residual was attributed to Cl^-.

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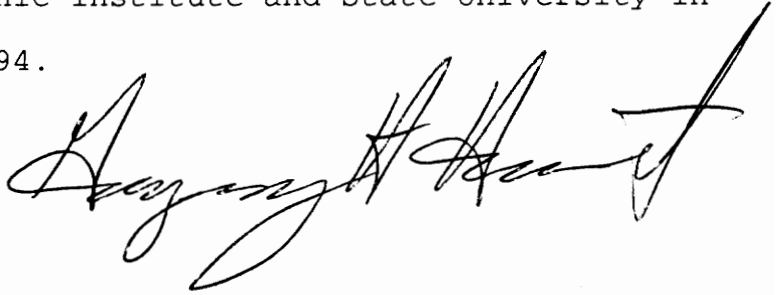
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