AN INVESTIGATION OF THE OXIDATIVE POTENTIAL OF POTASSIUM PERMANGANATE AND CHLORINE DIOXIDE DURING THE OXIDATION OF REDUCED MANGANESE

by

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(ABSTRACT)

This project determined the thermodynamic potentials for various reactions between reduced manganese (Mn$^{+2}$), manganese oxide (MnO$_2$(s)), chlorine dioxide (ClO$_2$), and potassium permanganate (KMnO$_4$). Based on these findings, laboratory analyses were performed to determine if these reactions would occur under simulated water treatment plant conditions. In addition, a speciation procedure was developed to quantify the various species of manganese and chlorine dioxide present in a single sample. The reactions and the speciation procedure were evaluated at TOC concentrations ranging from < 1.0 mg/L to 5.0 mg/L and at pH 6.0 and 8.0. The speciation procedure yielded a reliable measure of Mn$^{+2}$, insoluble manganese, and Mn$^{+7}$; however, the Mn$^{+7}$ evaluation could be disrupted by the presence of free chlorine. The determination of ClO$_2^-$ and ClO$_2^-$ concentrations was also possible; however, the ClO$_2^-$ concentration was subject to error.

The laboratory analyses revealed that ClO$_2$ was unable to oxidize either Mn$^{+2}$ or MnO$_2$(s) to Mn$^{+7}$ under any of the thermodynamically favored conditions. Both KMnO$_4$ and ClO$_2$ selectively oxidized reduced organic material before reducing the concentration of Mn$^{+2}$. When ClO$_2$
and KMnO₄ were added simultaneously, the ClO₂ reacted preferentially with the reduced materials. Only after the ClO₂ concentration was exhausted did the MnO₄⁻ begin to oxidize the reduced species.
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CHAPTER I

INTRODUCTION

The occurrence of manganese in natural water supplies is a common concern within the water treatment industry. Manganese can cause problems such as staining of fixtures and clothes, pipe deposition and clogging, and taste complaints if it is released to a distribution system. Unlike iron, manganese cannot be efficiently removed by aeration and coagulation and must be chemically oxidized. The resulting precipitate is then removed by filtration to effect adequate treatment.

Historically, the oxidants of choice for manganese removal have been free chlorine (HOCl and OCl⁻) and potassium permanganate (KMnO₄). Large doses of HOCl were applied near the beginning of the water treatment scheme and were responsible for disinfection and algal control as well as manganese oxidation. However, concern over the formation of halogenated organic compounds has precluded the use of HOCl as the sole oxidant in many areas.

The use of chlorine dioxide (ClO₂) as an oxidant for control of reduced organic material and manganese oxidation has become common in recent years. ClO₂ is a powerful oxidant that has proven successful for the control of reduced manganese under actual treatment plant conditions.

Ozone (O₃) has also gained prominence as an effective oxidant for the control of reduced organic material and reduced manganese. A
potential problem with O₃, however, concerns its thermodynamic potential to oxidize reduced inorganic species to their highest oxidation states. For example, it has been reported that in actual practice O₃ will oxidize reduced manganese to permanganate (MnO₄⁻).

During the summer of 1985 a study was undertaken by faculty and students in Virginia Tech's Environmental Engineering group within the Department of Civil Engineering to determine the effectiveness of ClO₂ and MnO₄⁻ for the control of reduced organic materials and reduced manganese present in the County of Stafford, Virginia's water supply reservoir. When ClO₂ was used as the oxidant, there were numerous consumer complaints concerning a black precipitate collecting in household fixtures. An explanation proposed for this phenomena was that manganese dioxide (MnO₂(s)) was somehow precipitating within the distribution system and collecting in consumers' homes.

Because of the documentation of the potential of O₃ to oxidize Mn²⁺ to MnO₄⁻, it was hypothesized that perhaps ClO₂ may also have this oxidizing potential. A review of existing literature did not reveal evidence that would prove or disprove this hypothesis; thus, an investigation was undertaken to evaluate the oxidative affect of ClO₂ on Mn²⁺ and MnO₂(s).

To evaluate this hypothesis the following objectives were established:

1. To predict the thermodynamic potential for the oxidation of Mn²⁺ and MnO₂(s) to MnO₄⁻ by ClO₂ based on available thermodynamic information.
2. Develop a speciation procedure which would allow the quantification of Mn$^{2+}$, MnO$_2$(s), MnO$_4^-$, ClO$_2$ and ClO$_2^-$ within a single sample.

3. Determine the potential for ClO$_2$ to oxidize Mn$^{2+}$ or MnO$_2$(s) to MnO$_4^-$ in a laboratory setting under simulated water treatment plant conditions.

The TOC and the pH of the test solutions were varied to evaluate their respective effects on the oxidation-reduction reactions.
CHAPTER II

LITERATURE REVIEW

Natural Occurrence and Distribution of Mn

Manganese, element number 25 on the periodic table, is a transition metal which may be found in many forms in the earth’s lithosphere. In elemental form, at standard temperature and pressure, it occurs as a hard, brittle grey metal; however, it is most commonly found as a constituent of various mineral compounds. Manganese is relatively abundant, comprising approximately 0.1 percent of the earth’s crust, and is widely distributed throughout the world. It is the earth’s 12th most common element and, of the heavy metals, only iron is more abundant. The concentration of manganese in most soils is in the range of 200 – 3000 parts per million (ppm), and it is a required nutrient for nearly all plants and animals (1, 2).

In the aquatic environment, manganese is most often found as the highly soluble, fully reduced, manganous ion (Mn(II)) that is stable under neutral to acidic conditions. It is widely distributed in the earth’s surface waters at concentrations ranging from 0 – 20 mg/L, and in ground water at concentrations of 0 – 50 mg/L. Soluble manganese may also be found in the oceans at a concentration of about 0.002 mg/L (3).

The highest concentrations found in surface waters occur in the hypolimnion of thermally stratified lakes. The low dissolved oxygen concentrations found there promote highly reduced conditions, leading to the reduction and release of manganese from the sediments. Under these reduced conditions, the concentration of manganese in the hypolimnion
may reach 20 mg/L. During the fall thermal destratification, mixing occurs which distributes these high levels of manganese throughout the lake, temporarily increasing the concentration in the meta- and epilimnion (4, 5, 6).

The route of human exposure is almost exclusively through ingestion of plants, animals and water which contain organic or inorganic forms of manganese. Because it is a required nutrient for all plants and animals, the human body is adapted to metabolize the required amount and excrete any excess at all but the most extreme levels of exposure. There are, however, certain exceptions; inhalation of manganese containing dust may cause Parkinson’s-like symptoms, and ingestion of highly oxidized forms of manganese, such as permanganate, may cause serious internal disorders. These, however, are highly uncommon exposures and, under normal circumstances, soluble manganese may be considered of no toxicological importance to humans (3, 7).

Chemistry of Aqueous Manganese

The chemical reactivity of aqueous manganese is based primarily on its position within the periodic table of elements. As the most abundant member of the group VII-A transition metals, it has the potential to exist at several oxidation states: +2, +3, +4, +6, +7. The most stable oxidation state of aqueous manganese is the manganous ion (Mn(II)). In natural systems at neutral pH values it is most commonly found in the hexaquo ionic form \([\text{Mn(H}_2\text{O)}_6]^{+2}\) (2, 3). Manganese in the +3 valence state (Mn(III)) is, in most natural environments, relatively unstable in solution. In the pH range encountered during water treatment processes (5 ≤ pH ≤ 11) Mn(III) will rapidly disproportionate to form Mn(II) or Mn(IV) depending on the pH and redox conditions. In
addition, Mn(III) may be stabilized in the presence of strong complexing agents such as ethylenediamine tetraacetic acid (EDTA), pyrophosphate and oxalate (2, 3).

The chemistry of manganese in the +4 valence state (Mn(IV)) is complex and of significant interest because it is often produced under treatment plant conditions. The most commonly represented form of Mn(IV) is manganese dioxide (MnO₂(s)) which, in its most pure form, is found in the grey-black mineral pyrolusite. The factor which complicates the physical and chemical properties of this compound, however, is its proclivity to form an incompletely oxidized, amorphous colloid in the aqueous environment. Studies by several authors (3, 8, 9) have shown that pH, strength of the oxidant (or reductant) used, ionic strength, presence of divalent cations, and rate of reaction all have a significant effect on the oxidation state of the manganese oxide colloid that is formed. For this reason, the colloidal particle has been represented by the formula MnOₓ(s), where x may be in the range 1.3 to 1.9. Another important physical/chemical property of this colloid is its capacity to reduce the concentration of divalent cations such as calcium, magnesium, and of primary importance, reduced manganese (Mn⁺²) through sorption. In the absence of these divalent cations the MnOₓ(s) particles remain discrete and highly dispersed within the solution; however, as their concentration increases the particles become destabilized and flocculation occurs rapidly. Although this phenomena is not fully understood, Morgan has hypothesized that the mechanisms may be "interpreted as adsorption, as complex formation, or as ion exchange." (3)

The +6 valence state of manganese (Mn(VI)) is of little consequence in natural systems or water treatment due to its instability under conditions normally encountered. If present at all, it will quickly dis-
proportionate to form Mn(IV) or permanganate (Mn(VII))(2).

Manganese in the +7 valence state (Mn(VII)) exists primarily as the permanganate ion (MnO$_4^-$). In the solid form permanganate is usually found as a salt of potassium or sodium (KMnO$_4$ or NaMnO$_4$) and is produced commercially in large quantities for various industrial uses. In solution, these salts rapidly dissociate to release the highly oxidized permanganate ion which may then react with many reduced species present. Although permanganate is thermodynamically unstable with respect to the oxidation of water, the reaction is very slow and, under normal circumstances, permanganate solutions are relatively stable for the duration of most treatment applications (2, 3, 10).

**Chemical Oxidation for Manganese Removal**

The occurrence of manganese in the public water supply, although of little health related significance, is a serious problem in terms of aesthetics. If present in a distribution system, reduced manganese (Mn(II)) will, upon oxygenation or chemical oxidation, form a brown-black precipitate which can collect in pipes and cause staining of fixtures and laundry. In addition, the presence of this manganese oxide precipitate may impart an unpleasant taste to the drinking water (11, 12). For these reasons the United States Environmental Protection Agency (USEPA) has established a secondary (aesthetic related) maximum contaminant level (SMCL) of 0.05 mg/L (13). Although the standard now mandates compliance, public health authorities and the water treatment industry have long recognized the need to limit the amount of manganese in the public water supply.

Early treatment schemes designed for manganese removal relied exclusively on aeration and filtration. This reaction is extremely slow and
is rarely able to remove all reduced manganese. Morgan (3) and Fair, et al. (14) have proposed that the rate of oxidation of Mn(II) by oxygen (aeration) is controlled by the formation of MnO$_2$(s). The rate may be described by the relation;

$$\text{Mn(II)} + \text{O}_2 \xrightarrow{\text{slow}} \text{MnO}_2(s) \quad [2-1]$$

$$\text{Mn(II)} + \text{MnO}_2(s) \xrightarrow{\text{fast}} \text{Mn(II)} \cdot \text{MnO}_2(s) \quad [2-2]$$

$$\text{Mn(II)} \cdot \text{MnO}_2(s) + \frac{1}{2}\text{O}_2 \xrightarrow{\text{very slow}} 2\text{MnO}_2(s) \quad [2-3]$$

and indicates an autocatalytic property of the MnO$_2$(s) particle. Aeration and filtration are often effective for a reduction of very high manganese concentrations but are generally inadequate to meet the finished water standards. In these instances, some form of chemical treatment must generally be performed (10).

The first chemical oxidant used specifically for manganese removal was chlorine or, more accurately, hypochlorous acid (HOCl)(15). Current treatment practice, as presented by White (16), quantifies the doses and conditions conducive to manganese removal with chlorine. The optimum conditions and doses are: A pH of 8.0, an alkalinity of at least 50 mg/L, a free chlorine residual concentration of at least 1.3 mg/L, and a contact time of 2 to 3 hours. It must noted that the "free chlorine residual" mentioned here is in excess of the amount predicted stoichiometrically and is independent of other chlorine demand factors, such as the presence of reduced iron and organic material. The long contact time needed for the complete oxidation of the reduced manganese would almost demand the addition of the chlorine at or near the raw water intake of the treatment plant, unless special contact basins were added. This being the case, the recent concern regarding prechlorination of raw waters containing high concentrations of humic material becomes immediately apparent. The organic material found in these waters has been
found to react with free chlorine to form trihalomethanes (THM's), primarily chloroform (CH₃Cl), which are proven carcinogens in laboratory animals, and are regulated by federal drinking water standards (17, 18). The THM standard has precluded the use of chlorine as a preoxidant in many areas and has added to the list of complications concerning its use as an oxidant for manganese removal.

The reaction chemistry for the oxidation of Mn(II) to Mn(IV) by chlorine is as follows:

**Oxidation:**

\[
\text{Mn}^{+2} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2(s) + 4\text{H}^+ + 2e^- \quad [2.4]
\]

**Reduction:**

\[
\text{HOCl} + \text{H}^+ + 2e^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad [2.5]
\]

**Overall:**

\[
\text{Mn}^{+2} + \text{HOCl} + \text{H}_2\text{O} \rightarrow \text{MnO}_2(s) + \text{Cl}^- + 3\text{H}^+ \quad [2.6]
\]

The use of potassium permanganate (KMnO₄) for the removal of Mn(II) during water treatment has been practiced almost as long as chlorine oxidation (19). The reaction of the permanganate ion (MnO₄⁻) with the reduced manganese present in raw waters has been found to occur very rapidly in the pH range of 5 to 9. The end product of both the MnO₄⁻ reduction and the Mn(II) oxidation is an insoluble manganese oxide particle which can be removed by flocculation and sedimentation or sand filtration (11, 19, 20).

Permanganate has been used in large scale treatment plants since the early 1960's and has proved quite successful. The chemical reactions for the oxidation of Mn(II) to MnO₂(s) by MnO₄⁻ are as follows:

**Oxidation:**

\[
\text{Mn}^{+2} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2(s) + 4\text{H}^+ + 2e^- \quad [2.4]
\]
Reduction:

\[ \text{MnO}_4^- + 4H^+ + 3e^- \rightarrow \text{MnO}_2(s) + 2H_2O \]  \[2.7\]

Overall:

\[ 3\text{Mn}^{+2} + 2\text{MnO}_4^- + 2H_2O \rightarrow 5\text{MnO}_2(s) + 4H^+ \]  \[2.8\]

Using this overall equation it can be seen that 2 moles of MnO_4^- will react stoichiometrically with 3 moles of reduced manganese. The weight reaction ratio is 1.44 mg -MnO_4^- per mg - Mn^{+2} (0.67 mg - Mn^{+7} per mg - Mn^{+2}). This ratio is often not directly applicable in water treatment plants due to the presence of an additional MnO_4^- demand.

Reduced material, such as ferrous iron or naturally occurring organic compounds, may require much higher permanganate doses than predicted by equation [2.8]. A recent study of manganese removal from natural waters containing various concentrations of total organic carbon (TOC) by Knocke, et al. (20), found that permanganate appears to selectively oxidize the organic material before effecting a substantial oxidation of the reduced manganese present. In addition, the manganese oxide produced in this reaction is rarely of the form MnO_2(s) and is more likely an amorphous colloid of the form MnO_x(s) (1.3 < x < 1.9) (3, 8, 9). For these reasons, the permanganate demand of the raw water must be determined in a laboratory or pilot-plant study prior to full-scale application. The most apparent disadvantage of using permanganate for manganese removal is that chemical costs for oxidation will be substantially higher than if chlorine is used. Another concern is that permanganate is not considered a strong disinfectant and, therefore, may allow bacterial and algae growth within the treatment plant (10, 21, 22).

Chlorine dioxide (ClO_2) is a highly reactive yellow-red gas which is readily soluble in water. In water treatment, ClO_2 has been used as an
oxidant for control of taste and odors, THM precursor reduction, disinfection, and manganese removal (16, 23). Due to its reactive, unstable nature, ClO₂ is generated on site, most commonly by the reaction of sodium chlorite (NaClO₂) and chlorine gas (Cl₂):

\[
\text{Cl}_2 + 2\text{NaClO}_2 \rightarrow 2\text{ClO}_2 + 2\text{NaCl}
\]  \[2.9\]

Chlorine dioxide may be used as a preoxidant when prechlorination is not suitable, or added to the finished water for residual disinfection. The aqueous chemistry of ClO₂ is somewhat more complicated than that of permanganate or free chlorine (HOCl) because chlorine may be reduced to chlorite or chloride (Cl⁻) during manganese oxidation. Weber (10) and White (16) present the following redox reactions for the removal of reduced manganese:

**Oxidation:**

\[
\text{Mn}^{+2} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^-
\]  \[2.4\]

**Reduction:**

\[
\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-
\]  \[2.10\]

**Overall:**

\[
2\text{Mn}^{+2} + \text{ClO}_2^- + 2\text{H}_2\text{O} \rightarrow 2\text{MnO}_2(\text{s}) + \text{Cl}^- + 4\text{H}^+
\]  \[2.13\]

Aeita (23), in his review of chlorine dioxide practice, presents the reaction continuing with the reduction of ClO₂⁻ to Cl⁻ as follows:

**Oxidation:**

\[
\text{Mn}^{+2} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^-
\]  \[2.4\]

**Reduction:**

\[
\text{ClO}_2^- + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{Cl}^- + 2\text{H}_2\text{O}
\]  \[2.12\]

**Overall:**

\[
2\text{Mn}^{+2} + \text{ClO}_2^- + 2\text{H}_2\text{O} \rightarrow 2\text{MnO}_2(\text{s}) + \text{Cl}^- + 4\text{H}^+
\]  \[2.13\]

If these two overall reactions are combined, an equation can be formulated for the complete reduction of ClO₂ to Cl⁻ during manganese
oxidation:

\[ 2\text{ClO}_2 + 5\text{Mn}^{+2} + 6\text{H}_2\text{O} \rightarrow 5\text{MnO}_2(s) + 12\text{H}^+ + 2\text{Cl}^- \]  \[ 2.14 \]

There is some controversy over which of the overall equations, \([2.11]\), \([2.13]\) or \([2.14]\), is predominant in water treatment applications. An analysis of the chemical thermodynamics of these reactions is presented in the following section ("Chemical Thermodynamics & Equilibrium Analyses") in an attempt to predict which reaction would be favored under a given set of conditions.

The primary disadvantages with the use of Cl\(_2\)O\(_2\) are high cost and possible toxicity of the by-products chlorite and chlorate. A recent study by Condie (24) of the possible toxicological significance of Cl\(_2\)O\(_2\) and its by-products concluded that the current recommended maximum combined concentration of Cl\(_2\)O\(_2\) and Cl\(_2\)O\(_2^\-) should remain at 1 mg/L. This limitation may be the controlling factor for the Cl\(_2\)O\(_2\) dose that may be applied, and this low dosage may be insufficient to meet the oxidant demand of the raw water. Under these circumstances, it may be necessary to use chlorine dioxide in conjunction with another oxidant such as permanganate in order to effect adequate manganese removal (5, 20).

Another oxidant that is currently gaining favor among water treatment specialists is ozone (O\(_3\)). Ozone has been quite popular in Europe for some time, and, in response to the THM problem, it is also finding much wider application in the U.S. (25, 26, 27). Ozone is an extremely strong oxidant that may be used in water treatment for disinfection, reduction of reduced organic material, taste and odor problems, algal control, and iron and manganese removal.

Disadvantages of this treatment technique include: the ozone must be generated on site; its generation is energy intensive; and the dissolved gas is highly unstable and does not maintain a residual within
the distribution system. Also of concern, and of primary interest in this study, is the potential for \( O_3 \) to oxidize reduced inorganic material to its highest oxidation state \((25, 26)\).

Horvath, et al. (25), postulated such an oxidative pathway for the oxidation of \( Mn(II) \) by ozone:

\[
\begin{align*}
Mn^{+2} + O_3 + 2H_2O & \rightarrow MnO_3^- + O_2 + 4H^+ \\
2MnO_3^- + 3O_3 & \rightarrow 2MnO_4^- + 3O_2 + H_2O \\
2Mn^{+2} + 5O_3 + 3H_2O & \rightarrow 2MnO_4^- + 5O_2 + 4H^+ 
\end{align*}
\]

A review of European treatment practices by Rice, et al. (26), noted this reaction under routine ozone treatment conditions at the Düsseldorf, Germany water works. The plant engineer found that overdosing with ozone produced the distinct pink color of permanganate in the clearwell. This was used as an indication to reduce the applied \( O_3 \) dose.

This tendency toward complete oxidation of manganese under normal treatment plant conditions raises concern about the possible release of permanganate into the distribution system. If any oxidant, whether it be \( ClO_2 \) or \( O_3 \), has the chemical potential to oxidize manganese from \( Mn(II) \) to \( Mn(VII) \) then the initial problem of pipe deposition and laundry or fixture staining has not been solved. Therefore, equilibrium and thermodynamic analyses are required to determine if this complete oxidation is thermodynamically possible under the aqueous conditions routinely present in a water treatment plant. Where the thermodynamic potential appears favorable, laboratory analyses will be required to determine if the kinetics will allow the reaction to occur within the treatment timeframe.
Chemical Thermodynamics and Equilibrium Analyses

The thermodynamic analysis was performed in two parts. First the Gibb's Free Energy of the reaction, denoted $\Delta G^0$, was calculated to obtain a general term for comparison with that of both redox and non-redox relationships. The value was determined from the equation:

$$\Delta G^0 = -nFE^0$$ \[2.18\]

where:
- $n$ = number of electrons
- $F$ = Faraday's Constant ($9.65 \times 10^4$ C/mole)
- $E^0$ = sum of the half-cell redox potentials (V)

A negative value indicates that the reaction will proceed as written, given one molar concentrations of each compound, until equilibrium concentrations are reached. Secondly, an analysis was performed based on the Nernst equation to determine the redox potential of the reaction couple based on concentrations of products and reactants which were used in the experimental procedures. The form of the equation used in this analysis was as follows:

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{(2.003)RT}{nF}\log Q$$ \[2.19\]

where:
- $E_{\text{cell}}$ = cell redox potential at given conditions (V)
- $E_{\text{cell}}^0$ = sum of the half-cell redox potentials at STP (V)
- $R$ = Universal Gas Constant (8.314 J/mole °K)
- $T$ = temperature (°K)
- $n$ = number of electrons transferred
- $F$ = Faraday's Constant ($9.65 \times 10^4$ C/mole)
- $Q$ = Reaction Quotient $\rightarrow$ for an equation of the form $aA + bB \rightarrow cC + dD$

The results of the standard state analyses for the oxidation of Mn(II) to MnO$_2$(s) by the various oxidants are shown in Table 1. Under standard chemical conditions all of the reactions, with the exception of ClO$_2$ to ClO$_2^-$, are favored.

The Nernst equation analyses were completed assuming an initial Mn(II) concentration of 0.50 mg/L - Mn and a pH of 6.0 or 8.0. The
Table 1 - Oxidation of Mn^{2+} to Mn^{4+}

<table>
<thead>
<tr>
<th>Reduction</th>
<th>Equation</th>
<th>$E^0(V)$</th>
<th>(c) $\Delta G^0$(kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HOCl} \rightarrow \text{Cl}^-$</td>
<td>(a) [2.6]</td>
<td>0.260</td>
<td>-1.20</td>
</tr>
<tr>
<td>$\text{MnO}_4^- \rightarrow \text{MnO}_2(s)$</td>
<td>(a) [2.8]</td>
<td>0.455</td>
<td>-21.0</td>
</tr>
<tr>
<td>$\text{ClO}_2 \rightarrow \text{ClO}_2^-$</td>
<td>(b) [2.11]</td>
<td>-0.270</td>
<td>+12.5</td>
</tr>
<tr>
<td>$\text{ClO}_2 \rightarrow \text{Cl}^-$</td>
<td>(a) [2.14]</td>
<td>0.726</td>
<td>-33.5</td>
</tr>
<tr>
<td>$\text{O}_3 \rightarrow \text{O}_2$</td>
<td>(a) [2.17]</td>
<td>0.852</td>
<td>-39.3</td>
</tr>
</tbody>
</table>

**Notes:**

a) $E^0$ values from (28)

b) $E^0$ values from (10)

c) $\Delta G^0$ values are based on 1 molar concentrations of each component at STP
concentrations of the oxidants used in this analysis are representative of the doses used in actual practice. The results presented in Table 2 indicate that under the assumed conditions all of the oxidants in question have the thermodynamic potential to oxidize Mn(II) to MnO₂(s).

The next step in this analysis was to test the potential for ClO₂ to oxidize the MnO₂(s) particle to the soluble MnO₄⁻ ion. The reaction of MnO₂(s) with ozone is also included for comparison because of its reported ability to oxidize manganese to its highest valance state (25, 26). The following redox reactions have been developed to predict this oxidation reaction with respect to ClO₂ and ozone:

\[
\text{MnO}_2(s) + 3\text{ClO}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + 3\text{ClO}_2^- + 4\text{H}^+ \tag{2.20}
\]

\[
\text{MnO}_2(s) + (3/5)\text{ClO}_2 + (4/5)\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + (3/5)\text{Cl}^- + (8/5)\text{H}^+ \tag{2.21}
\]

\[
\text{MnO}_2(s) + (3/2)\text{O}_3 + (1/2)\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + (3/2)\text{O}_2 + \text{H}^+ \tag{2.22}
\]

It should be noted that equations [2.20] and [2.21] differ only in the extent of the reduction of ClO₂. Both are presented and evaluated because it is not clear which is predominant during water treatment processes. The results of the standard state analysis are shown in Table 3 and indicate that only if ClO₂ is fully reduced, does it have the thermodynamic potential to oxidize MnO₂(s) to MnO₄⁻ under these conditions. The Nernst analysis was performed using an initial MnO₂(s) concentration of 0.80 mg/L - Mn and at pH 6.0 and 8.0. The concentrations of the oxidants used in this analysis are consistent with the range used in actual practice. The results are shown in Table 4 and show that ClO₂ does have the thermodynamic potential to oxidize MnO₂(s) to MnO₄⁻ under the assumed conditions. If the ClO₂ to ClO₂⁻ reduction is predominant, however, the manganese oxidation is favored only at a pH > 6.8. If the ClO₂ to Cl⁻ reduction predominates then the oxidation reaction is
Table 2 — Nernst Analysis of the Oxidation of Mn$^{+2}$ to Mn$^{+4}$

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Equation</th>
<th>pH</th>
<th>Dose (mg/L)</th>
<th>$E_{cell}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) HOCl</td>
<td>[2.6]</td>
<td>6.0</td>
<td>1.3</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>&quot;</td>
<td>0.76</td>
</tr>
<tr>
<td>(b) MnO$_4^-$</td>
<td>[2.8]</td>
<td>6.0</td>
<td>0.47 (.215-Mn)</td>
<td>0.513</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>&quot;</td>
<td>0.513</td>
</tr>
<tr>
<td>(c) ClO$_2$</td>
<td>[2.11]</td>
<td>6.0</td>
<td>1.0</td>
<td>0.365</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>1.0</td>
<td>0.601</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td>5.0</td>
<td>0.635</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>5.0</td>
<td>0.601</td>
</tr>
<tr>
<td>(d) ClO$_2$</td>
<td>[2.14]</td>
<td>6.0</td>
<td>1.0</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>1.0</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td>5.0</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>5.0</td>
<td>1.13</td>
</tr>
<tr>
<td>(e) O$_3$</td>
<td>[2.17]</td>
<td>6.0</td>
<td>5.0</td>
<td>1.044</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>5.0</td>
<td>1.162</td>
</tr>
</tbody>
</table>

Notes:

a) [Cl$^-$] assumed 50 mg/L, HOCl at 1.3 mg/L free residual

b) Assumed 10% reaction of MnO$_4^-$ and Mn$^{+2}$

c) Assumed 10% reaction of Mn$^{+2}$, assumed 5% of [ClO$_2$] = [ClO$_2^-$] based on composition of ClO$_2$ stock solution.

d) Assumed 10% reaction of Mn$^{+2}$, [Cl$^-$] assumed 50 mg/L

e) Assumed 10% reaction of Mn$^{+2}$, [O$_2$] assumed 8 mg/L
Table 3 - Oxidation of MnO\(_2\)(s) to MnO\(_4^−\)

<table>
<thead>
<tr>
<th>Reduction</th>
<th>Equation No.</th>
<th>(E^0)(V)</th>
<th>(\Delta G^0)(kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(_2) (\rightarrow) Cl(_2^−) (a)</td>
<td>[2.20]</td>
<td>-0.725</td>
<td>50.1</td>
</tr>
<tr>
<td>Cl(_2) (\rightarrow) Cl(^−) (b)</td>
<td>[2.21]</td>
<td>0.271</td>
<td>-18.7</td>
</tr>
<tr>
<td>O(_3) (\rightarrow) O(_2) (a)</td>
<td>[2.22]</td>
<td>0.397</td>
<td>-27.4</td>
</tr>
</tbody>
</table>

Notes:  
a) \(E^0\) values from (28)  
b) \(E^0\) values from (10)
Table 4 — Nernst Analysis of the Oxidation of MnO$_2$(s) to MnO$_4^-$

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Equation No.</th>
<th>pH</th>
<th>Dose (mg/L)</th>
<th>$E_{cell}(V)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ClO$_2$</td>
<td>[2.20]</td>
<td>6.0</td>
<td>1.0</td>
<td>-0.060</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>8.0</td>
<td>1.0</td>
<td>+0.097</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>6.0</td>
<td>5.0</td>
<td>-0.060</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>8.0</td>
<td>5.0</td>
<td>+0.097</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>10.0</td>
<td>5.0</td>
<td>+0.255</td>
</tr>
<tr>
<td>(b) ClO$_2$</td>
<td>[2.21]</td>
<td>6.0</td>
<td>1.0</td>
<td>+0.551</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>8.0</td>
<td>1.0</td>
<td>+0.615</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>6.0</td>
<td>5.0</td>
<td>+0.560</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>8.0</td>
<td>5.0</td>
<td>+0.623</td>
</tr>
<tr>
<td>(c) O$_3$</td>
<td>[2.22]</td>
<td>8.0</td>
<td>5.0</td>
<td>+0.658</td>
</tr>
</tbody>
</table>

Notes:

a) Assumed 10% reaction of MnO$_2$(s)  
Assumed [ClO$_2^-$] = 5% of [ClO$_2$]; based on composition of stock solution.

b) Assumed 10% reaction of MnO$_2$(s)  
Assumed [Cl$^-$] = 50 mg/L (typ. of natural systems)

c) Assumed 10% reaction of MnO$_2$(s)  
Assumed [O$_2$] = 8 mg/L
favored at pH > 2.2 and the calculated potential is only slightly lower than that of ozone.

The next reaction which was considered was the complete oxidation of reduced Mn(II) to MnO$_4^-$ by ClO$_2$ and O$_3$. The following redox reactions have been developed for use in the thermodynamic analysis:

\[
\begin{align*}
\text{Mn}^{+2} + 5\text{ClO}_2 + 4\text{H}_2\text{O} & \rightarrow \text{MnO}_4^- + 5\text{ClO}_2^- + 8\text{H}^+ \quad [2.23] \\
\text{Mn}^{+2} + \text{ClO}_2 + 2\text{H}_2\text{O} & \rightarrow \text{MnO}_4^- + \text{Cl}^- + 4\text{H}^+ \quad [2.24] \\
\text{Mn}^{+2} + (5/2)\text{O}_3 + (3/2)\text{H}_2\text{O} & \rightarrow \text{MnO}_4^- + (5/2)\text{O}_2 + 3\text{H}^+ \quad [2.25]
\end{align*}
\]

The results of the standard state analysis are presented in Table 5 and reveal that ClO$_2$ does have the thermodynamic potential to fully oxidize reduced manganese if the ClO$_2$ is reduced to Cl$^-$. The Nernst analysis was performed based on an initial Mn$^{+2}$ concentration of 0.50 mg/L - Mn and at pH 6.0 and pH 8.0. The results are presented in Table 6 and reveal that ClO$_2$ has the potential to fully oxidize Mn(II) under each of the given conditions. Further analysis also indicated that the ClO$_2$ to ClO$_2^-$ reduction is possible above pH 4.9 and the ClO$_2$ to Cl$^-$ reaction is favored at any positive pH.

The results presented in Tables 4 and 6 indicate that ClO$_2$ does have the thermodynamic potential to oxidize both Mn(II) and MnO$_2$(s) to MnO$_4^-$ under treatment plant conditions. The redox potential for the ClO$_2$ to ClO$_2^-$ reduction is always lower than that for ClO$_2$ to Cl$^-$, but the reaction is favored in almost all instances. These positive cell potentials, however, are only an indication of the direction of the reaction and in no way address the kinetics or activation energy which may be required to initiate the reaction.
Table 5 - Oxidation of Mn$^{+2}$ to MnO$_4^-$

<table>
<thead>
<tr>
<th>Reduction</th>
<th>Equation No.</th>
<th>$E^\circ (V)$</th>
<th>$\Delta G^\circ$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO$_2$ $\rightarrow$ ClO$_2^-$</td>
<td>(a) [2.23]</td>
<td>-0.553</td>
<td>63.8</td>
</tr>
<tr>
<td>ClO$_2$ $\rightarrow$ Cl$^-$</td>
<td>(b) [2.24]</td>
<td>+0.443</td>
<td>-51.1</td>
</tr>
<tr>
<td>O$_3$ $\rightarrow$ O$_2$</td>
<td>(a) [2.25]</td>
<td>+0.569</td>
<td>-65.7</td>
</tr>
</tbody>
</table>

Notes:  

a) $E^\circ$ values from (28)  
b) $E^\circ$ values from (10)
Table 6 - Nernst Analysis of the Oxidation of Mn$^{+2}$ to MnO$_4^-$

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Equation No.</th>
<th>pH</th>
<th>Dose (mg/L)</th>
<th>Ecell (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ClO$_2$</td>
<td>[2.23]</td>
<td>6.0</td>
<td>1.0</td>
<td>0.101</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>1.0</td>
<td>0.290</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td>5.0</td>
<td>0.101</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>5.0</td>
<td>0.290</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>5.0</td>
<td>0.479</td>
</tr>
<tr>
<td>(b) ClO$_2$</td>
<td>[2.24]</td>
<td>6.0</td>
<td>1.0</td>
<td>0.714</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>1.0</td>
<td>0.808</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td>5.0</td>
<td>0.722</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
<td>5.0</td>
<td>0.817</td>
</tr>
<tr>
<td>(c) O$_3$</td>
<td>[2.25]</td>
<td>8.0</td>
<td>5.0</td>
<td>0.852</td>
</tr>
</tbody>
</table>

Notes:  

a) Assumed 10% reaction of Mn$^{+2}$  
Assumed [ClO$_2^-$] = 5% of [ClO$_2$]; based on composition of stock solution.  

b) Assumed 10% reaction of Mn$^{+2}$  
Assumed [Cl$^-$] = 50 mg/L (typ. of natural systems)  

c) Assumed 10% reaction of Mn$^{+2}$  
Assumed [O$_2$] = 8 mg/L
CHAPTER III

METHODS

Overview

This chapter pertains to the experimental design and the methods and materials used for the investigation of the oxidative effect of ClO₂ on manganese at various oxidation states. The experimental matrix was based on the findings of the thermodynamic calculations and was modeled to simulate treatment plant conditions. The water used in all of the test solutions was deionized/distilled (DI/Dist.) tap water and not from an untreated source. Although this may seem to contradict the premise that the experimental design simulates treatment plant conditions, the underlying goal was to determine if permanganate could be formed. It was important, therefore, to eliminate raw water constituents that might interfere with the analysis procedures. The following paragraphs briefly describe the experimental matrix that was developed and present the conditions common to all of the procedures.

The experimental phase of this investigation was divided into four separate procedures based on the possible combinations of ClO₂ and MnO₄⁻ which might be encountered in a water treatment plant practicing Mn⁺² removal. The four phases developed were as follows:

1) Mn⁺² oxidized by ClO₂ alone.

2) Mn⁺² oxidized by MnO₄⁻ and then immediately dosed with ClO₂. ("Fresh Precipitate Analysis")

3) Mn⁺² rigorously oxidized by MnO₄⁻ and stabilized; then dosed with ClO₂. ("Aged Precipitate Analysis")
4) Mn$^{+2}$ oxidized by the simultaneous addition of MnO$_4^-$ and Cl$_2$. In each of these analyses the concentration of Mn$^{+2}$ was fixed at 0.50 mg/L - Mn by the addition of a prepared stock solution of manganous sulfate (MnSO$_4$) to an aliquot of DI/Dist. tap water. This concentration of reduced manganese is typical of a raw water with a moderate manganese problem.

The parameters which were varied during these analyses were the Cl$_2$ dose, the solution pH, and the total organic carbon (TOC) concentration. The range of these variables will be addressed in the specific experimental descriptions.

Each of the experiments was performed using a standard laboratory jar test apparatus. The tests performed under low TOC (< 1 mg/L) conditions were conducted in 2.8 L, rectangular plastic containers. The tests performed under high TOC (> 4 mg/L) conditions were conducted in 1.8 L, rectangular glass containers. In all cases, the solutions were mixed at approximately 40 revolutions-per-minute (rpm) by a Phipps and Byrd, Inc. (Richmond, VA 23228), model 300, six paddle stirrer.

A phosphate buffer was used to control the pH of the solutions during each of the experiments. The pH of the solutions was monitored throughout the procedures using a Corning (Medfield, MA 02052), model 610-A, pH meter and was adjusted using sodium hydroxide (NaOH) or hydrochloric acid (HCl) as necessary. In each experiment it was deemed important to maintain a similar ionic strength due to its effect on the formation and agglomeration of colloidal particles. For this reason, the amount of phosphate buffer added to each test solution was varied so that the final concentration of phosphate salts was approximately 100 mg/L.
The sampling procedure for the speciation of manganese and chlorine dioxide will be addressed in detail later in this chapter under the heading "Analytical Procedures." During the experiments conducted under low TOC conditions, samples were withdrawn at 20 minutes, 80 minutes and 140 minutes and speciated according to these procedures. Under high TOC conditions, samples were withdrawn at 30 minutes and 150 minutes for speciation.

Experimental Procedures

**Mn**\(^{+2}\) oxidized by Cl\(_2\)O\(_2\) alone.

This analysis was performed in two phases. The first phase was performed using a dose of 1.0 mg/L - Cl\(_2\)O\(_2\) and the second phase utilized a dose of 5.0 mg/L - Cl\(_2\)O\(_2\). In both phases, the TOC concentration was fixed at < 1.0 mg/L - TOC for the low TOC conditions and at 4.6 mg/L for the high TOC conditions. The pH of the test solutions was adjusted to 6.0 or 8.0 during the procedures under low TOC conditions. The pH under high TOC conditions was not varied and was held at 8.0.

The first phase of this experiment was accomplished in the following manner. The test vessel containing the Mn**\(^{+2}\)** and with the pH adjusted appropriately was dosed with 1.0 mg/L - Cl\(_2\)O\(_2\) by the introduction of a measured volume of a prepared Cl\(_2\)O\(_2\) stock solution. This stock solution was evaluated just prior to the procedure to verify its concentration. The reaction time was carefully monitored and the samples were withdrawn as required for the speciation procedures. The procedure under high TOC conditions was performed by adding a measured volume of a stock fulvic acid solution to increase the TOC to approximately 4.6 mg/L - TOC prior to dosing with Cl\(_2\)O\(_2\). This fulvic acid stock solution was evaluated using a Dohrman/Envirotech (Santa Clara, CA), model DC 80, Automated
Laboratory Total Organic Carbon Analyzer. The TOC of the test solutions was also evaluated at the conclusion of the procedures.

The second phase of this experiment was conducted in the same manner, except the volume of the ClO₂ stock solution was increased to achieve a dose of 5.0 mg/L - ClO₂.

\[ \text{Mn}^{+2} \text{ oxidized by MnO}_4^- \text{ and then dosed with ClO}_2. \]

In this experiment \( \text{Mn}^{+2} \) and \( \text{MnO}_4^- \) were combined in solution at concentrations, determined in a preliminary study, which reacted to form an oxide with an approximate composition of \( \text{MnO}_{1.75}(s) \) (i.e. \( \text{Mn}^{+3.5} \)). The \( \text{Mn}^{+2}/\text{MnO}_4^- \) reaction was allowed to proceed for 20 to 30 minutes during which time a colloidal precipitate was formed. The resulting "fresh" precipitate was then immediately dosed with ClO₂.

This experiment was performed using doses of 1.0 mg/L - ClO₂ and 5.0 mg/L - ClO₂. For each ClO₂ dose the TOC concentration was adjusted to < 1.0 mg/L - TOC and to 4.0 to 4.2 mg/L - TOC. Under the low TOC conditions (< 1.0 mg/L - TOC) the pH was adjusted to both 6.0 and 8.0. The pH was not varied under high TOC conditions (4.0 - 4.2 mg/L - TOC) and was fixed at 8.0.

The fresh MnOₓ(s) precipitate was prepared by the combination of a stoichiometric ratio of \( \text{Mn}^{+2} \) and \( \text{MnO}_4^- \) determined in preliminary studies. It was determined that under low TOC conditions, at pH 6.0 or 8.0, that 0.50 mg/L - \( \text{Mn}^{+2} \) would react with 0.215 mg/L - \( \text{Mn}^{+7} \) (0.465 mg/L \( \text{MnO}_4^- \)) to form a precipitate within 20 minutes (see "Results"). Under high TOC conditions (4.0 - 4.5 mg/L - TOC) the ratio increased to 0.65 mg/L - \( \text{Mn}^{+7} \) (1.41 mg/L - \( \text{MnO}_4^- \)) for oxidation of 0.50 mg/L - \( \text{Mn}^{+2} \). In addition, the time required for the reaction to reach equilibrium increased to about 30 minutes.
The experiments were accomplished by first adjusting the TOC concentrations of the test solutions containing the Mn$^{+2}$ to either low (< 1.0 mg/L - TOC) or high (4.0 - 4.2 mg/L - TOC) conditions using the stock fulvic acid solution. The test solutions were then dosed with a measured volume of MnO$_4^-$ stock solution, at 0.215 mg/L - Mn$^{+7}$ or 0.65 mg/L -Mn$^{+7}$ for the low or high TOC conditions respectively. After a 20 minute reaction time for the low TOC solution or a 30 minute reaction time for the high TOC solution, the appropriate ClO$_2$ dose was added by the addition a measured volume of stock solution. The pH of the solutions was monitored and adjusted throughout these procedures as necessary. Samples were withdrawn and speciated as required by the "Analytical Procedures."

Mn$^{+2}$ oxidized rigorously by MnO$_4^-$ and aged prior to dosing with ClO$_2$.

The manganese oxide used in this experiment was prepared by the oxidation of Mn$^{+2}$ by MnO$_4^-$ under very rigorous conditions (see "Preparation of Reagents."). The resulting precipitate was allowed to "age" for more than a week and was then dosed with 5.0 mg/L - ClO$_2$ at pH 6.0 and 8.0 under low TOC (< 1.0 mg/L - TOC) conditions. Because the aged precipitate was found to be unreactive under the most favorable conditions no tests were performed at high concentrations of TOC.

The experiment was performed by the addition of a measured volume of the stock MnO$_X$(s) suspension to an aliquot of DI/Dist. water to achieve an MnO$_X$(s) concentration of approximately 0.75 mg/L - Mn. The test suspension was then dosed with 5.0 mg/L - ClO$_2$ and samples were withdrawn as outlined in "Analytical Procedures."

Mn$^{+2}$ dosed simultaneously with MnO$_4^-$ and ClO$_2$. 
This experiment examined the relationship between ClO₂ and MnO₄⁻ during the oxidation of Mn⁺². The reduced manganese in solution was dosed with the predetermined stoichiometric concentration of MnO₄⁻ and the desired ClO₂ dose simultaneously. The MnO₄⁻ dose was based on the demand exerted by the Mn⁺² present and the TOC concentrations. From this evaluation, the relative rates of MnOₓ(s) formation and oxidant demand may be compared qualitatively to determine which oxidant is more reactive with the reduced manganese present.

The reaction was evaluated for doses of 1.0 mg/L - ClO₂ and 5.0 mg/L - ClO₂. The TOC concentration was adjusted for each dose to 1.0 mg/L - TOC and 5.0 mg/L - TOC by the addition of a measured volume of stock fulvic acid solution. The pH was adjusted to 6.0 and 8.0 for the low TOC conditions. The pH was fixed at 8.0 for the high TOC conditions.

The experiment was conducted by first adjusting the TOC concentration of the test solutions containing Mn⁺² and then introducing the MnO₄⁻ dose and ClO₂ dose by simultaneously adding measured volumes of the respective stock solutions. Sample collection and speciation were performed as previously discussed.

Preparation of Reagents

I. Chlorine Dioxide (ClO₂)

The stock ClO₂ solution was prepared by the reaction of sodium chlorite (NaClO₂) with sulfuric acid (H₂SO₄) according to section 410A., subsection 2a. of Standard Methods (29). The procedure was modified by the utilization of both positive and negative pressure sources (to facilitate air flow through the entire system) and the doubling of the prescribed concentrations of H₂SO₄ and NaClO₂ in the reaction chamber. The ClO₂ solution obtained was stored in a darkened glass reagent bottle with a ground glass stopper and was kept at between 2°C and 6°C during
the generation process and in subsequent storage. The initial ClO₂ concentration was 880 mg/L - ClO₂ with an associated ClO₂⁻ impurity of 54 mg/L - ClO₂⁻ and a chlorine concentration of 48 mg/L - Cl₂.

II. Manganese Sulfate Stock Solution

The manganous sulfate (MnSO₄) stock solution was prepared by dissolving 0.307 grams (g) of MnSO₄ · H₂O in 1 L of DI/Dist. water. The concentration was analyzed by atomic absorption spectrophotometry (Perkin-Elmer, model 703, Norwalk, Connecticut) and was found to be 96.0 mg/L - Mn.

III. Potassium Permanganate Stock Solution

The KMnO₄ stock solution was prepared by dissolving 0.287 g of KMnO₄ in 1 L of DI/Dist. water. The concentration was analyzed by atomic absorption spectrophotometry, and was found to be 97.0 mg/L - Mn. The solution was stored in an opaque glass reagent bottle and kept in the dark when not in use. The concentration of this solution was verified weekly by the speciation procedure.

IV. Manganese Oxide (MnOₓ(s)) Suspension

A solution was prepared which contained an MnSO₄ concentration of approximately 60 mg/L - Mn in DI/Dist. water at a pH of between 10 and 12. Approximately 45 mg/L - Mn of KMnO₄ was added to this solution and the combined reagents continuously stirred overnight. The residual KMnO₄ was reduced to MnOₓ(s) by the addition of several milliliters (mL) of 30 percent hydrogen peroxide (H₂O₂). The resulting MnOₓ(s) suspension was analyzed by both atomic absorption spectrophotometry and the speciation technique outlined in the "Analytical Procedures" sec-
tion. The analysis found that the suspension contained 97.0 mg/L - Mn with an average oxidation state of 3.6 (i.e. MnO\(_{1.8}\)(s)). The concentration of the soluble manganese species in this stock solution were less than 0.01 mg/L.

V. Phosphate Buffers

The pH 6.0 buffer was prepared by combining 61.5 g KH\(_2\)PO\(_4\) with 3.12g Na\(_2\)HPO\(_4\) in one liter of DI/Dist. water and adjusting the pH with concentrated phosphoric acid (H\(_3\)PO\(_4\)). The pH 7.0 buffer was prepared by combining 25.4 g of KH\(_2\)PO\(_4\) with 34.1 g of Na\(_2\)HPO\(_4\) in 1 L of DI/Dist. water and adjusting the pH with concentrated H\(_3\)PO\(_4\) or NaOH as necessary. The pH 8.0 buffer was prepared by combining 9.1 g of KH\(_2\)PO\(_4\) with 46.2 g of Na\(_2\)HPO\(_4\) in 1 L of DI/Dist. water and adjusting the pH with concentrated H\(_3\)PO\(_4\) or NaOH as necessary.

VI. Fulvic Acid (TOC) Stock Solution

For the experiments that were performed at high TOC concentrations it was required that the TOC level be increased without the introduction of a raw water source. This was accomplished by the preparation of a stock solution of dissolved fulvic acid, which had been extracted from a natural source, and had a fixed composition. The fulvic acid extract used was "Suwannee Stream Reference Fulvic Acid" prepared by the United States Geological Service (USGS)(30). The extract was dissolved in 100 mL of organic free water which had been purified by the Milli-Q system (Millipore, Inc., Bedford, Massachusetts). The TOC concentration of this solution was 170 mg/L - TOC.
Analytical Procedures

A major concern in this study was how to measure each species of manganese and chlorine dioxide at any particular time during the experiments. The combination of manganese at +2, +4 and +7 valence states and ClO₂, ClO₂⁻ and Cl₂ in the same sample presented an extremely difficult analytical problem. The speciation of ClO₂, ClO₂⁻ and ClO₃⁻ in solution has been addressed by Arita, et al. (31); however, they noted that oxidized species of manganese interfered in their analytical procedures. The direct amperometric titration of permanganate was addressed by Beck (32); however, this method ignores other oxidized species which are present during the experimental procedures just presented. The methods for determining total manganese and soluble manganese by atomic absorption spectrophotometry are detailed in Standard Methods (29). No method for differentiating between the valences of the soluble manganese forms could be found. It was necessary, therefore, to develop a procedure which combined the principles and methods of several different available techniques in order to accurately speciate the compounds of concern in this study.

The chlorine dioxide speciation method of Arita et al. (31), is based on standard amperometric titration techniques in the presence of potassium iodide (KI) using phenyl arsine oxide (PAO) as the titrant. Because the oxidized forms of manganese interfere in this titration, it was first necessary to quantify their concentrations and then to determine a method for removing their interference from the titration procedure. The series of analyses required to accomplish this task will be detailed in this section and a quantitative evaluation of the methods presented in the "Results" chapter.

Figure 1 is a schematic diagram which represents the complete
Figure 1. Speciation Procedure
speciation procedure. This procedure requires the analysis of four separate samples: one filtered; two untreated after removal from the test vessel; and one purged with nitrogen gas (N₂). The purged sample (steps F. and G.) may be omitted if ClO₂, ClO₂⁻ or Cl₂ are not present in the solution.

The filtration portion of the procedure was performed as follows: Approximately 100 mL of the experimental solution was removed from the test vessel and filtered through an Amicon (Danvers, MA 01923), Diaflo 10 YM 30, 62 mm, ultrafiltration membrane with an approximate pore size of 2.1 nm (33). Approximately 50 mL of the filtrate was collected in a rectangular glass cuvette, with a 4 cm pathlength, and analyzed colorimetrically using a Klett-Summerson (New York, NY) photoelectric colorimeter, model 900-3, utilizing a #52 color filter. The reading obtained was compared to a permanganate standard curve, and the observed MnO₄⁻ (Mn⁷⁺) concentration was recorded for step A. Duplicate 15 mL samples of the filtrate were also collected for analysis by atomic absorption spectrophotometry. Several granules of hydroxyl amine sulfate (HAS), a strong reducing agent, were added to these samples to insure that the manganese remained in a soluble form prior to analysis. The values obtained represented the soluble manganese fraction (Mn²⁺ and Mn⁷⁺) and were recorded for step B.

The analysis of the untreated samples was performed in two parts as follows:

Part 1. - Duplicate 15 mL samples of the experimental solution were withdrawn from the test vessel and fixed for analysis by the addition of several granules of HAS. The samples were analyzed for total manganese (Mn²⁺, Mnₙ⁺ and Mn⁷⁺) using atomic absorption spectrophotometry. The observed concentrations were recorded for step C.
Part 2. - A 200 mL sample of the experimental solution was withdrawn from the test vessel and analyzed by PAO titration at pH 7 and pH 2 in the presence of potassium iodide (KI) as described by Aeita, et al. (31). The titrator used was a Fischer and Porter (Warminster, PA 18974), model 17 T 1010, amperometric titrator. The volume of 0.00564 N PAO titrant required (in mL) was recorded for step D (pH 7) and step E (pH 2).

The N₂ - purged portion of the analysis involved the withdrawal of a 200 mL sample from the test vessel and buffering it to pH 7 with a phosphate buffer solution. Nitrogen gas was then fed into this sample through a diffuser stone for approximately 10 minutes. The sample was then titrated amperometrically with PAO according to the procedure outlined by Aeita et al. (31). The volumes of titrant (mL PAO) required at pH 7 and pH 2 were recorded for steps F and G respectively.

The results obtained from each of the steps described may be summarized as follows:

\[
\begin{align*}
A &= \text{Mn}^{+7} \text{ (filtered)} \\
B &= \text{Mn}^{+2} + \text{Mn}^{+7} \text{ (filtered)} \\
C &= \text{Mn}^{+2} + \text{Mn}^{+x} + \text{Mn}^{+7} \\
D &= \text{ClO}_2 + \text{Cl}_2 + \text{Mn}^{+7} \\
E &= \text{ClO}_2 + \text{ClO}_2^- + \text{Mn}^{+x} \\
F &= \text{Cl}_2 + \text{Mn}^{+7} \\
G &= \text{ClO}_2^- + \text{Mn}^{+x}
\end{align*}
\]

**Evaluation of Speciation Procedures**

In this section an attempt is made to explain, why the particular test was utilized; what modifications to the tests were required; and how the procedure was evaluated.
The ClO2 speciation procedure developed by Aeita et al. (31), was selected due to the speed, accuracy and simplicity with which it could be performed. The speed was particularly critical due to the ongoing reaction between the species present within the samples. The problem with this method, however, was the interference produced by the oxidized manganese. To quantify this interference several concentrations of both permanganate solutions and manganese oxide suspensions were titrated according to the ClO2 titration procedure. The permanganate solutions were prepared by diluting a stock solution in DI/Dist. water at several concentrations. The MnOx(s) suspensions were prepared by two methods. The first method involved the oxidation of approximately 70 mg/L - Mn+2 with excess KMnO4 (50 mg/L as Mn) at an elevated pH while bubbling oxygen through the solution. After 24 hours the excess permanganate was removed by the addition of several milliliters of hydrogen peroxide (H2O2). The second method involved the oxidation of 0.15 mg/L - Mn+2 with KMnO4 at 0.35 mg/L - Mn+7, which are concentrations commonly encountered during water treatment. In both cases samples of the resulting colloidal manganese suspensions were treated with HAS to fully reduce all of the Mn present and analyzed by atomic absorption spectrophotometry.

From the results obtained in these analyses it was possible to determine the number of electron equivalents transferred per mole of oxidized manganese by the following equation:

\[ v = NV/M \]  

where:  
\[ v \] = equivalents transferred/mole  
\[ N \] = normality of the titrant (eq/L)  
\[ V \] = volume of titrant (L)  
\[ M \] = moles of manganese present.
The amperometric titration procedure used yields the following
titration reactions for the oxidized manganese species:

**pH 7 for permanganate:**

\[
\begin{align*}
Mn^{7+} + \frac{Y_1}{2}(I^-) &\rightarrow Mn^{7-} + \frac{Y_1}{2}(I_2) \quad [3-9] \\
\frac{Y_1}{2}(I_2) + \frac{Y_1}{2}(C_6H_5AsO) + \frac{Y_1}{2}(H_2O) &\rightarrow \frac{Y_1}{2}(C_6H_5AsO(OH)_2) + \frac{Y_1}{2}(H^+) + \frac{Y_1}{2}(I^-) \quad [3-10]
\end{align*}
\]

**pH 2 for permanganate:**

\[
\begin{align*}
Mn^{8+} + \frac{Y_2}{2}(I^-) &\rightarrow Mn^{8+} + \frac{Y_2}{2}(I_2) \quad [3-11] \\
\frac{Y_2}{2}(I_2) + \frac{Y_2}{2}(C_6H_5AsO) + \frac{Y_2}{2}(H_2O) &\rightarrow \frac{Y_2}{2}(C_6H_5AsO(OH)_2) + \frac{Y_2}{2}(H^+) + \frac{Y_2}{2}(I^-) \quad [3-12]
\end{align*}
\]

**pH 2 for Colloidal Manganese:**

\[
\begin{align*}
Mn^{8+} + \frac{Y_3}{2}(I^-) &\rightarrow Mn^{8+} + \frac{Y_3}{2}(I_2) \quad [3.13] \\
\frac{Y_3}{2}(I_2) + \frac{Y_3}{2}(C_6H_5AsO) + \frac{Y_3}{2}(H_2O) &\rightarrow \frac{Y_3}{2}(C_6H_5AsO(OH)_2) + \frac{Y_3}{2}(H^+) + \frac{Y_3}{2}(I^-)
\end{align*}
\]

where:

- \( Y_1 \) = Number of electron equivalents transferred for Mn\(^{7+}\) during the pH 7 titration.
- \( Y_2 \) = Number of electron equivalents transferred for Mn\(^{7+}\) during the pH 2 titration.
- \( Y_3 \) = Number of electron equivalents transferred for Mn\(^{8+}\) during the pH 2 titration.

From the water treatment perspective there are only three forms of
manganese of concern:

\[ Mn^{2+} (soluble), Mn^{8+} (colloidal), \text{ and } Mn^{7+} (soluble). \]

A method for the determination of Mn\(^{7+}\) has been developed, which will be
detailed in the "Results" section, that relies on the amperometric
titration steps shown in Figure 1. The method for the speciation of the
other two forms, Mn\(^{2+}\) and Mn\(^{8+}\), is outlined in steps A, B, and C of
Figure 1. In step C the sample was removed from the test vessel,
treated with HAS to fully reduce all manganese species, and then ana-
alyzed by atomic absorption spectrophotometry for total manganese (Mn$^{+2}$, Mn$^{+X}$, Mn$^{+7}$). The samples for analysis according to steps A and B were first filtered through an ultrafiltration membrane to physically separate all particles greater than 2.1 nm in diameter. The filtrate, which contained only soluble manganese (Mn$^{+2}$ and Mn$^{+7}$), was then analyzed colorimetrically for Mn$^{+7}$. The filtrate was also analyzed by atomic absorption spectrophotometry for total soluble species (Mn$^{+2}$ and Mn$^{+7}$). The Mn$^{+7}$ value, determined colorimetrically, could then be subtracted from this value to yield Mn$^{+2}$. The total manganese value determined in step C could then be adjusted by subtracting the Mn$^{+2}$ and Mn$^{+7}$ values to yield Mn$^{+X}$. The mathematical expressions for the determination of each of these species will be presented in the following chapter.
CHAPTER IV

RESULTS

Overview

This chapter contains the results of the speciation evaluation and the four experiments described in the "Methods" chapter. The speciation evaluation first deals with the number of electron equivalents transferred in each step of the amperometric titration procedure and then presents the mathematical formulae derived from this information. Secondly, the results concerning the stoichiometric relationship between Mn$^{+2}$ and Mn$^{+7}$ under the given experimental conditions are presented. Finally, the results of the four experimental phases: 1.) Mn$^{+2}$ with ClO$_2$; 2.) Fresh MnO$_x$(s) precipitate with ClO$_2$; 3.) Aged MnO$_x$(s) precipitate with ClO$_2$; and 4.) Mn$^{+2}$ with Mn$^{+7}$ and ClO$_2$ added simultaneously; are addressed.

Speciation Results

The results of the amperometric titration of several concentrations of potassium permanganate (KMnO$_4$) are listed in Table 7 for each step of the titration procedure. The results are expressed as equivalents of electrons transferred per mole of MnO$_4^-$ (eq/mole) and are the mean of several titrations. The 95 percent confidence limits are shown to the right of each value and the overall means for the entire range of concentrations of KMnO$_4$ are recorded at the bottom of this table. An average interference of 3.5 ± 0.5 eq/mole was found in the pH 7 step of
Table 7 - Equivalents of electrons transferred per mole of permanganate for several concentrations at each pH step of the amperometric titration procedure

<table>
<thead>
<tr>
<th>Permanganate (mg/L as KMnO₄)</th>
<th>Equivalents per Mole</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH-7</td>
<td>pH-2</td>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>0.236</td>
<td>3.8 ± 0.6</td>
<td>1.5 ± 0.6</td>
<td>5.3 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>0.473</td>
<td>3.6 ± 0.2</td>
<td>1.7 ± 0.3</td>
<td>5.3 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>0.940</td>
<td>3.9 ± 0.1</td>
<td>1.5 ± 0.1</td>
<td>5.5 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>0.945</td>
<td>3.5 ± 0.1</td>
<td>1.7 ± 0.1</td>
<td>5.2 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>1.89</td>
<td>3.3 ± 0.1</td>
<td>1.7 ± 0.1</td>
<td>5.0 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>3.31</td>
<td>3.0 ± 0.2</td>
<td>1.9 ± 0.1</td>
<td>4.9 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>3.3 ± 0.5</td>
<td>2.0 ± 0.5</td>
<td>5.3 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>7.81</td>
<td>3.6 ± 0.02</td>
<td>1.4 ± 0.1</td>
<td>5.0 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

Means and 95% Conf. Limits for all Data: 3.5 ± 0.5 | 1.7 ± 0.4 | 5.2 ± 0.3
the titration for the entire range of KMnO₄ concentrations used. If an initial Mn oxidation state of +7 is assumed, then at the end of the pH 7 titration the manganese is at an overall oxidation state of 7.0 - 3.5 ± 0.5 = 3.5 ± 0.5. This value corresponds to the factor Y₁, equation [3.9], and may be used to quantify this interference.

The pH 2 step of the titration yielded an interference of 1.7 ± 0.4 eq/mole for the range of KMnO₄ concentrations evaluated. Assuming a terminal oxidation state of +2 this yields a value of Y₂ = 1.7 ± 0.4 eq/mole for equation [3.11].

The combined interference (Y₁ + Y₂) is then equal to 5.2 eq/mole for the reduction of Mn⁺⁷ to Mn⁺² using this technique. This result is within four percent (4%) of the theoretical value of 5.0 eq/mole and was considered reasonable for the subsequent experimental procedures.

The results of the amperometric titration of MnOₓ(s) suspensions at various concentrations for the pH 2 step of the procedure are shown in Table 8. The pH 7 portion of the procedure was not affected by either form of MnOₓ(s) and, therefore, is not shown. The first two MnOₓ(s) suspensions tested were formed under conditions similar to those at a water treatment plant and differed somewhat from the more vigorously oxidized form (see "Methods" for preparation details). Using a terminal oxidation state of +2, the less rigorously oxidized MnOₓ(s) had an average initial oxidation state of approximately +3.6 while the rigorously oxidized MnOₓ(s) had an average initial oxidation state of approximately +4.0. These results correspond to a Y₃ (equation [3.13]) value ranging from 1.6 to 2.0. In the quantification of the interference, the value chosen for Y₃ was representative of the experimental conditions present in each case.

The filtration of colloidal manganese, prior to steps A and B of the
Table 8 - Equivalents of electrons transferred per mole of manganese oxide (MnO_x(s)) for several concentrations

<table>
<thead>
<tr>
<th>MnO_x(s)(mg/L as Mn)</th>
<th>Equivalents per mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a.)</td>
<td></td>
</tr>
<tr>
<td>0.52</td>
<td>1.6(c)</td>
</tr>
<tr>
<td>0.57</td>
<td>1.5(c)</td>
</tr>
<tr>
<td>(b.)</td>
<td></td>
</tr>
<tr>
<td>2.17</td>
<td>2.0 ± 0.04</td>
</tr>
<tr>
<td>2.40</td>
<td>2.1 ± 0.00</td>
</tr>
<tr>
<td>4.07</td>
<td>2.1 ± 0.04</td>
</tr>
<tr>
<td>5.84</td>
<td>1.7 ± 0.32</td>
</tr>
</tbody>
</table>

Notes:  
(a) Solution prepared under treatment plant conditions. (see "Methods")  
(b) Solution prepared under rigorous oxidizing conditions. (see "Methods")  
(c) Only one titration performed for each initial MnO_x(s) concentration.
speciation procedure, was evaluated by passing samples of the two types of MnOx(s) through a variety of filters. The results of this evaluation are given in Table 9 and reveal additional differences between the two types of MnOx(s). Almost 90 percent of the vigorously oxidized MnOx(s) was removed by a membrane filter with a pore size of 200 nm while only about 3 percent of the stoichiometrically formed MnOx(s) was removed. The ultrafiltration membrane, with an approximate pore size of 2.1 nm (33), was able to remove over 97 percent of either type of MnOx(s) tested.

The mathematical expressions for the speciation process can be developed from these results in the following manner. First, the equations offered by Aeita, et al. (31) for the calculation of the concentrations of the various chlorine species, without the manganese interference, are presented as follows; (Modified to match Figure 1)

\[
\begin{align*}
ClO_2^{(\text{mg/L})} &= \frac{5}{4} \times (E - G) \times N \times 13,500 \text{ mg/eq} \quad [4.1] \\
ClO_2^{(-}\text{mg/L}) &= G \times N \times 16,900 \text{ mg/eq} \quad [4.2] \\
Cl_2^{(\text{mg/L})} &= \left[D - \frac{(E - G)}{4}\right] \times N \times 35,500 \text{ mg/eq} \quad [4.3]
\end{align*}
\]

where: D, E, F and G are mL of titrant used in the corresponding steps of the procedure, as shown in Figure 1, and N is the normality of the titrant.

If the titrant is 0.00564N PAO and the sample volume is 200 mL, the following relationships are obtained;

\[
\begin{align*}
ClO_2^{(\text{mg/L})} &= \frac{(E - G)(95.11)}{(200)} \quad [4.4] \\
ClO_2^{(-}\text{mg/L}) &= \frac{(G)(95.11)}{(200)} \quad [4.5] \\
Cl_2^{(\text{mg/L})} &= \left[D - \frac{(E - G)}{4}\right] \quad [4.6]
\end{align*}
\]

The titration steps D, E, F and G may be modified for the oxidized manganese species in the following manner:

\[
\begin{align*}
D &= ClO_2 + Cl_2 + Y_{1}K MnO_4 \quad [4.7] \\
E &= 4ClO_2 + ClO_2^{-} + Y_{2}K MnO_4 + Y_{3}MnO_\chi(s) \quad [4.8]
\end{align*}
\]
Table 9 - Colloidal manganese retention by various filters

<table>
<thead>
<tr>
<th>Initial Mn conc. (mg/L by AAS)</th>
<th>Filter type (pore size nm)</th>
<th>Filtrate Mn conc. (mg/L by AAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.62, 0.62</td>
<td>glass fiber (300)(a)</td>
<td>0.61, 0.61</td>
</tr>
<tr>
<td>0.62, 0.62</td>
<td>membrane (200)</td>
<td>0.05, 0.09</td>
</tr>
<tr>
<td>0.62, 0.62</td>
<td>molec. sieve (2.1)</td>
<td>0.04, 0.01</td>
</tr>
</tbody>
</table>

Mn$^{2+}$ oxidized by stoichiometric dose of permanganate at pH-7

<table>
<thead>
<tr>
<th>Initial Mn conc. (mg/L by AAS)</th>
<th>Filter type (pore size nm)</th>
<th>Filtrate Mn conc. (mg/L by AAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70, 0.70</td>
<td>membrane (200)</td>
<td>0.65, 0.70</td>
</tr>
<tr>
<td>0.70, 0.70</td>
<td>molec. sieve (2.1)</td>
<td>0.02, 0.02</td>
</tr>
</tbody>
</table>

Notes: (a) Effective pore size based on air filtration
\[ F = \text{Cl}_2 + Y_1\text{KMnO}_4 \tag{4.9} \]
\[ G = \text{ClO}_2^- + Y_2\text{KMnO}_4 + Y_3\text{MnO}_x(s) \tag{4.10} \]

From the substitution of equations [4.8] and [4.10] into equation [4.4] it can be seen that the Mn interferences cancel; thus, the ClO\(_2\) determination should not, theoretically, be affected by the presence of oxidized manganese.

The titration step F of the procedure is comprised of the electron transfer due only to the reduction of Cl\(_2\) and KMnO\(_4\). Because the Cl\(_2\) concentration of the stock ClO\(_2\) solution was generally less than 5 percent of the ClO\(_2\) concentration, it did not affect step F of the titration. It was possible, therefore, to calculate the concentration of MnO\(_4^-\) directly from the volume of titrant used in step F by the following relationship:

\[
\text{MnO}_4^- \text{ (as mg/L - Mn) } = N \times V_1 \times W/Y_1V_2 \tag{4.11}
\]

where:
- \(N\) = normality of titrant (eq/L)
- \(V_1\) = volume of titrant (L)
- \(W\) = gram molecular weight of Mn (54.94 \times 10^3 mg/mole)
- \(Y_1\) = Equivalents Transferred per mole
- \(V_2\) = volume of sample (L)

The concentrations of Mn\(^{+2}\) and Mn\(^{+X}\) in solution were determined by the procedures outlined in steps A, B and C of Figure 1, and described in the "Analytical Procedure" section. These analyses were based on accepted methods and no evaluation of the techniques, other than the filtration evaluation, was necessary.

The final species of concern in this procedural evaluation was ClO\(_2^-\). The concentration of ClO\(_2^-\) is based on the amperometric titration step G (Figure 1) and, as seen in equation [4.10], is directly
affected by the presence of oxidized manganese. This interference may be accounted for by quantifying the volume of titrant required to reduce the manganese present and subtracting this amount from the total volume titrated in step G. The volume of titrant to be subtracted was determined as follows:

1.) Mn$^{+7}$ interference

$$G(Mn^{+7}) = K_1Y_2V/NW$$ \[4.12\]

where:

- $G(Mn^{+7})$ = volume of titrant due to Mn$^{+7}$ (L)
- $K_1$ = concentration of Mn$^{+7}$ (mg/L - Mn)
- $Y_2$ = no. of equivalents trans. at pH 2
- $V$ = volume of sample (L)
- $N$ = normality of sample (eq/L)
- $W$ = gram molecular wt. of Mn ($54.94 \times 10^3$ mg/mole)

2.) Mn$^{+x}$ interference

$$G(Mn^{+x}) = K_2Y_3V/NW$$ \[4.13\]

where:

- $G(Mn^{+x})$ = volume of titrant due to Mn$^{+x}$ (L)
- $K_2$ = concentration of Mn$^{+x}$ (mg/L - Mn)
- $Y_3$ = no. of equiv. trans. at pH 2
- $V$ = volume of sample (L)
- $N$ = normality of titrant
- $W$ = gr. mol. wt. of Mn ($54.94 \times 10^3$ mg/mole)

For the experiments which contained the aged MnO$_x$(s) precipitate (rigorously oxidized) the value of $Y_3$ was estimated to be = 1.9. For the experiments which contained fresh precipitate, the value of $Y_3$ was estimated to be 1.5. These values were then substituted into Equations [4.12] and [4.13] to quantify the volume of titrant required by the Mn$^{+7}$ and Mn$^{+x}$.

Using the titrant volumes determined from equations [4.12] and
[4.13] it was then possible to determine the volume of titrant in step G directly attributable to ClO2− as follows:

\[ G(\text{ClO}_2^-) = G - G(\text{Mn}^{+7}) - G(\text{Mn}^{+x}) \]  

where:  
\[ G(\text{ClO}_2^-) = \text{volume of titrant attributable to ClO}_2^- \text{ (mL)} \]  
\[ G = \text{total volume of titrant from step G (mL)} \]  
\[ G(\text{Mn}^{+7}) = \text{volume of titrant due to Mn}^{+7} \text{ (mL)} \]  
\[ G(\text{Mn}^{+x}) = \text{volume of titrant due to Mn}^{+x} \text{ (mL)} \]

The concentration of ClO2− was then determined as follows:

\[ \text{ClO}_2^-(\text{mg/L}) = G(\text{ClO}_2^-) \times (95.11) \]  

A sample calculation, based on the conditions specific to this investigation, is presented in Appendix B.

\section*{Mn^{+2} and Mn^{+7} - Stoichiometric Balance}

Having developed the methods for the speciation of Mn^{+2}, Mn^{+x}, Mn^{+7}, ClO2 and ClO2− it was then necessary to use these techniques to find the stoichiometric relationship for the oxidation of Mn^{+2} by Mn^{+7} under the experimental conditions. From the information gathered in the procedural evaluation it was determined that the intermediate oxidation state of Mn^{+7} at pH 7 was +3.5 ± 0.5. A stoichiometric relationship was developed using this value and is shown in equation [4.16].

\[ (0.7)\text{Mn}^{+2} + (0.3)\text{Mn}^{+7} \rightarrow \text{Mn}^{+3.5} \]  

Based on an initial reduced manganese concentration of 0.5 mg/L - Mn^{+2} this relationship predicts a permanganate requirement of 0.215 mg/L - Mn^{+7}. The reaction of these concentrations at pH 7 for approximately 20 minutes yielded the following results:

\[ \text{Mn}^{+2} = 0.01 \text{ mg/L} \]
\[ \text{Mn}^{+x} = 0.72 \text{ mg/L} \]
\[ \text{Mn}^{+7} = 0.03 \text{ mg/L} \]
as determined by the speciation procedure. These results were considered acceptable for the experimental procedures and, therefore, these concentrations were used throughout the study. The results of this reaction under the experimental conditions are shown in Table 10. In each experiment noted in this table the combination of Mn$^{2+}$ and Mn$^{7+}$ alone was used as the control to which the experimental results could be compared. The speciation at the 80 minute interval at pH 8.0 was omitted because the reaction was virtually complete after only 20 minutes. The results indicate that the reaction did not proceed to completion after 140 minutes at pH 6.0.

Under high TOC conditions it was necessary to determine the MnO$_4^-$ demand due to the reduced organic material and then add this to the amount of MnO$_4^-$ required for the removal of the reduced manganese. The results of the MnO$_4^-$ oxidation of 4.5 - 5.0 mg/L TOC (fulvic acid) are shown in Table 11 and reveal that the 30 minute MnO$_4^-$ demand was between 0.25 mg/L Mn$^{7+}$ and 0.50 mg/L Mn$^{7+}$. The MnO$_4^-$ demand thus determined was added to the demand due to 0.50 mg/L - Mn$^{2+}$ and yielded an estimate of the total MnO$_4^-$ demand. A range of MnO$_4^-$ doses, corresponding to this estimate, were then tested to determine the 30 minute oxidant demand of both reductants. The results of this analysis, shown in Table 12, indicate that the amount of MnO$_4^-$ required to oxidize 0.50 mg/L Mn$^{2+}$, in the presence of 4.5 - 5.0 mg/L - TOC (fulvic acid) and under the given experimental conditions, was between 0.60 mg/L - Mn$^{7+}$ and 0.70 mg/L - Mn$^{7+}$. A dose of 0.65 mg/L - Mn$^{7+}$ was, therefore, used to form the fresh precipitate during the high TOC experiments.

**EXPERIMENTAL RESULTS**

I. Mn$^{2+}$ oxidized by ClO$_2$ alone

The results of the oxidation of reduced manganese (Mn$^{2+}$) by 1.0 mg/L
Table 10 - Reaction of stoichiometric concentrations of Mn\(^{+2}\) and Mn\(^{+7}\) under experimental conditions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Time (Min)</th>
<th>Species</th>
<th>pH 6.0</th>
<th>pH 8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0(a)</td>
<td>Mn(^{+2})</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn(^{+x})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn(^{+7})</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>Mn(^{+2})</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn(^{+x})</td>
<td>0.54</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn(^{+7})</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>Mn(^{+2})</td>
<td>0.11</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn(^{+x})</td>
<td>0.63</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn(^{+7})</td>
<td>0.02</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>Mn(^{+2})</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn(^{+x})</td>
<td>0.63</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn(^{+7})</td>
<td>0.02</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Notes: (a) Based on initial doses (not speciated)
Table 11 - 30 minute MnO$_4^-$ demand by 4.5 - 5.0 mg/L TOC

<table>
<thead>
<tr>
<th>MnO$_4^-$ dose (mg/L - Mn$^{+7}$)</th>
<th>Mn$^{+X}$ (mg/L - Mn)</th>
<th>Mn$^{+7}$ (mg/L - Mn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.13</td>
<td>0.13</td>
<td>0</td>
</tr>
<tr>
<td>0.25</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.43</td>
<td>0.07</td>
</tr>
<tr>
<td>0.49(a)</td>
<td>0.41</td>
<td>0.08</td>
</tr>
<tr>
<td>1.00</td>
<td>0.53</td>
<td>0.46</td>
</tr>
<tr>
<td>1.57</td>
<td>0.77</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Note: (a.) Repeat of 0.50 mg/L - Mn dose for reliability
Table 12 — 30 minute MnO$_4^-$ demand due to 4.5 - 5.0 mg/L TOC and 0.50 mg/L - Mn$^{2+}$ at pH 6.0 and 8.0

<table>
<thead>
<tr>
<th>MnO$_4^-$ (mg/L - Mn$^{7+}$)</th>
<th>Mn$^{2+}$ (mg/L-Mn)</th>
<th>Mn$^{x}$</th>
<th>Mn$^{7+}$ (mg/L-Mn)</th>
<th>pH 6.0</th>
<th>pH 8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>0</td>
<td>1.19</td>
<td>0</td>
<td>0.03</td>
<td>1.12</td>
</tr>
<tr>
<td>0.70</td>
<td>0</td>
<td>1.25</td>
<td>0.03</td>
<td>0.01</td>
<td>1.18</td>
</tr>
<tr>
<td>0.80</td>
<td>0</td>
<td>1.29</td>
<td>0.08</td>
<td>0.01</td>
<td>1.22</td>
</tr>
</tbody>
</table>
Figure 2. Mn^{+2} oxidized by 1.0 mg/L ClO$_2$ at pH 6.0 with TOC < 1.0 mg/L.
Figure 3. Mn$^{+2}$ oxidized by 1.0 mg/L ClO$_2$ at pH 8.0 with TOC < 1.0 mg/L.
Figure 4. Mn$^{+2}$ oxidized by 1.0 mg/L ClO$_2$ at pH 8.0 with TOC = 4.6 mg/L.
ClO$_2$ are presented in Figures 2 through 4. Figures 2 and 3 represent the low TOC conditions (< 1.0 mg/L) at pH 6 and pH 8 respectively. Figure 4 depicts the results of the high TOC (> 4 mg/L) conditions at pH 8.0.

At the low TOC conditions (Figures 2 and 3) the dose of 1.0 mg/L ClO$_2$ was sufficient to oxidize all of the Mn$^{+2}$ to Mn$^{+x}$ within 20 minutes. There was no increase in Mn$^{+7}$ at any time under these conditions. The concentration of ClO$_2$ was reduced substantially within the first 20 minutes of the reaction with a corresponding increase in the ClO$_2^-$ concentration. The sum of the ClO$_2$ and ClO$_2^-$ concentrations remained at about 1.0 mg/L throughout both the pH 6 and pH 8 phases of this test indicating that little of the ClO$_2$ was lost through volatilization or reduced to Cl$^-$. At the high TOC conditions (Figure 4) only about 50 percent of the Mn$^{+2}$ was oxidized to Mn$^{+x}$ by the 1 mg/L dose of ClO$_2$. The concentration of ClO$_2$ decreased to below detection limits within 30 minutes and no further Mn$^{+2}$ oxidation was observed. There was no indication of Mn$^{+7}$ formation at any time during this test.

The results of the oxidation of Mn$^{+2}$ by the 5 mg/L dose of ClO$_2$ are presented in Figures 5 through 7. Figures 5 and 6 depict the low TOC conditions at pH 6 and 8 respectively while Figure 7 represents the high TOC conditions at pH 8.0.

At the low TOC conditions (Figures 5 and 6) all of the Mn$^{+2}$ was oxidized to Mn$^{+x}$ within 20 minutes by the 5.0 mg/L dose of ClO$_2$. A trace amount (< 0.03 mg/L - Mn) of Mn$^{+7}$ was detected during the amperometric titration portion of the speciation for the pH 6.0 sample after a 140 minute reaction time. Because the filtrate for this sample
Figure 5. Mn$^{+2}$ oxidized by 5.0 mg/L ClO$_2$ at pH 6.0 with TOC $<$ 1.0 mg/L.
Figure 6. Mn$^{+2}$ oxidized by 5.0 mg/L ClO$_2$ at pH 8.0 with TOC < 1.0 mg/L.
Figure 7. Mn\(^{+2}\) oxidized by 5.0 mg/L Cl\(_2\)O at pH 8.0 with TOC = 4.6 mg/L.
contained only 0.01 mg/L soluble manganese, the trace Mn$^{+7}$ measured during the titration was most likely an anomaly due to the high concentrations of the various oxidants which were present in the sample.

The ClO$_2$ concentrations during the low TOC tests decreased rapidly during the first 20 minutes of the reactions. At both pH 6.0 and 8.0 the ClO$_2$ concentration had decreased to about 3 mg/L while the ClO$_2^-$ concentration had increased to approximately 1.5 mg/L prior to the first speciation. Beyond the 20 minute mark the ClO$_2$ levels steadily, but less rapidly, continued to decrease while the ClO$_2^-$ concentrations remained fairly constant. To evaluate the possible loss of the ClO$_2$ to volatilization during the jar test procedures, two concentrations of ClO$_2$ alone were placed in the jar test containers, stirred at the rate established for the experiments, and speciated at 20 minutes, 80 minutes and 140 minutes. The results of this test are presented in Figure 8 and reveal that roughly 30 percent of the initial ClO$_2$ concentration was lost through volatilization for each hour (60 minutes) under these conditions. This would account for the loss of ClO$_2$ with no corresponding increase in ClO$_2^-$ which was found in several of the experiments.

The results of the oxidation of Mn$^{+2}$ under high TOC conditions (Figure 7) reveal that 5 mg/L ClO$_2$ was sufficient to oxidize all of the Mn$^{+2}$ to Mn$^{+7}$ within 20 minutes. Although not indicated on the graph, a significant concentration of Mn$^{+7}$ (0.07 mg/L) was initially detected by amperometric titration in both the 20 minute and 150 minute samples. The filtrate from these samples, however, contained less than 0.01 mg/L Mn which indicated that little or no Mn$^{+7}$ was present. The test was repeated and yielded virtually identical results. It was reasoned, therefore, that chlorine (HOCl) may have been produced during the ClO$_2$ oxidation of the organic material, as proposed by Werdehoff and
Figure 8. ClO$_2$ concentration versus time at pH 7.0. No reductant present.
Singer (34), and was measured as Mn$^{+7}$ during the titration. In addition, no Mn$^{+7}$ was detected at low TOC concentrations under otherwise similar experimental conditions and, therefore, would not be expected to occur where there is an even higher oxidant demand. For these reasons the Mn$^{+7}$ measured was considered an anomaly and was disregarded in this instance.

The ClO$_2$ concentration decreased very rapidly during the first 30 minutes of this test. The ClO$_2$ measured at 30 minutes was approximately 0.5 mg/L with a corresponding ClO$_2^-$ concentration of nearly 3 mg/L. The ClO$_2$ speciation graph appears to indicate that the ClO$_2$ reacted slowly to form chlorite between 30 and 150 minutes. This was most likely not the case. The slope of the line from 30 to 150 minutes is due to the lack of any intermediate data and is in no way an indication of a rate of reaction.

II. Mn$^{+2}$ oxidized by MnO$_4^-$ then dosed with ClO$_2$. (Fresh Precipitate)

The results of the oxidation of the fresh MnO$_x$(s) precipitate by 1.0 mg/L - ClO$_2$ are presented in Figures 9 through 11. The low TOC conditions are presented in Figures 9 and 10 and the high TOC condition is presented in Figure 11.

The manganese speciations, shown in Figures 9 and 10, reveal that the Mn$^{+7}$ dose of 0.215 mg/L - Mn was insufficient to fully oxidize the Mn$^{+2}$ within the first 20 minutes of the tests. The residual Mn$^{+2}$ was, however, oxidized within the first 60 minutes of ClO$_2$ contact. The concentration of Mn$^{+7}$ was near zero within the first 20 minutes at both pH 6 and 8. There was no indication of Mn$^{+7}$ formation at any time during the low TOC tests.

The concentration of ClO$_2$ dropped rapidly during the first hour of
Figure 9. Fresh MnO$_x$(s) precipitate dosed with 1.0 mg/L ClO$_2$ at pH 6.0 with TOC < 1.0 mg/L.
Figure 10. Fresh MnO$_x$(s) precipitate dosed with 1.0 mg/L ClO$_2$ at pH 8.0 with TOC < 1.0 mg/L.
Figure 11. Fresh MnOₓ(s) precipitate dosed with 1.0 mg/L ClO₂ at pH 8.0 with TOC = 4.0 - 4.2 mg/L.
contact with a corresponding increase in ClO$_2^-$.

After 60 minutes the reduction in ClO$_2$ became less rapid and little change in the concentration of ClO$_2^-$ was noted.

The results of the analysis at high TOC conditions are presented in Figure 11 and indicate that the 0.65 mg/L - Mn$^{+7}$ dose was sufficient to oxidize all of the Mn$^{+2}$ to an insoluble oxide within 30 minutes. After the addition of 1.0 mg/L - ClO$_2$ there was no increase in the concentration of Mn$^{+7}$.

The ClO$_2$ speciation reveals that all of the ClO$_2$ was reduced or lost through volatilization within the 120 minute reaction time. The ClO$_2^-$ concentration had reached 0.65 mg/L at the final sampling. Again, because only two data points were available, the slope of the lines between 30 and 150 minutes were not an indication of the rate of ClO$_2$ reduction or ClO$_2^-$ generation. The data simply indicate that at the 150 minute speciation the concentrations of these species had reached these particular levels.

Figures 12 through 14 present the speciation results for the oxidation of fresh MnO$_x$(s) precipitate by the 5.0 mg/L dose of ClO$_2$. The low TOC conditions are depicted in Figures 12 and 13 and the high TOC conditions in Figure 14.

The manganese speciation at 20 minutes for the pH 6.0, low TOC, sample indicated that although the majority of the soluble manganese present had reacted to form MnO$_x$(s), small amounts of both Mn$^{+7}$ and Mn$^{+2}$ remained in solution. After the addition of 5 mg/L - ClO$_2$ the Mn$^{+2}$ was oxidized to Mn$^{+x}$ within 60 minutes. The Mn$^{+7}$ concentration, however, decreased very little throughout the remainder of the test.

The Mn speciation after 20 minutes for the pH 8.0, low TOC sample (Figure 13) revealed that the Mn$^{+7}$ dose was slightly in excess of the
Figure 12. Fresh MnO$_x$(s) precipitate dosed with 5.0 mg/L ClO$_2$ at pH 6.0 with TOC < 1.0 mg/L.
Figure 13. Fresh MnOₓ(s) precipitate dosed with 5.0 mg/L ClO₂ at pH 8.0 with TOC < 1.0 mg/L.
Figure 14. Fresh MnO_x(s) precipitate dosed with 5.0 mg/L ClO_2 at pH 8.0 with TOC = 4.0 - 4.2 mg/L.
amount required to oxidize the Mn$^{+2}$ present. After the addition of ClO$_2$, the level of Mn$^{+7}$ which remained in solution did not change.

The ClO$_2$ concentration decreased steadily throughout both of the tests at low TOC conditions with only a small increase in the ClO$_2^-$ concentration. The majority of this loss was attributed to volatilization of the unreacted ClO$_2$ during the course of the test and was consistent with the rate determined in Figure 8.

The results of the analysis at high TOC conditions are shown in Figure 14. The Mn$^{+7}$ dose was sufficient to meet both the Mn$^{+2}$ and the TOC demand within the first 30 minutes of this test. There was no indication of any Mn$^{+7}$ formation during this test.

The ClO$_2$ concentration decreased below detection limits within the 120 minute duration of the test while the chlorite concentration increased to approximately 3 mg/L. The slope of the ClO$_2$ and ClO$_2^-$ versus time plots are not an indication of a rate of demand or production of these species; only their initial and final concentrations.

III. Mn$^{+2}$ oxidized rigorously by MnO$_4^-$ and aged prior to dosing with ClO$_2$. (Aged Precipitate)

The results of the oxidation of the aged precipitate by 5.0 mg/L ClO$_2$ at pH 6.0 and 8.0 are shown in Figures 15 and 16 respectively. The manganese speciations reveal no changes in any of the Mn species throughout the tests. The ClO$_2$/ClO$_2^-$ speciations indicate a relatively steady decrease in ClO$_2$ concentrations with a slight increase in ClO$_2^-$ levels.

IV. Mn$^{+2}$ dosed simultaneously with MnO$_4^-$ and ClO$_2$.

The results of the oxidation of Mn$^{+2}$ by the simultaneous addition of ClO$_2$ and MnO$_4^-$ are addressed in this section. The MnO$_4^-$ concentration which was used in this experiment was the same dose used to form the
Figure 15. Aged MnO_x(s) precipitate dosed with 5.0 mg/L ClO_2 at pH 6.0 with TOC < 1.0 mg/L.
Figure 16. Aged MnO$_x$(s) precipitate dosed with 5.0 mg/L ClO$_2$ at pH 8.0 with TOC < 1.0 mg/L.
fresh precipitate during the low and high TOC phases of experiment II.

The results of the 1.0 mg/L - ClO₂ dose at low TOC conditions are presented in Figures 17 and 18 for the tests at pH 6.0 and 8.0 respectively. The results of the 1 mg/L - ClO₂, high TOC conditions at pH 8.0 is presented in Figure 19.

At low TOC conditions (Figures 17 and 18) the reduced Mn⁺² was oxidized to MnOₓ(s) within the first 20 minutes of the tests. The Mn⁺⁷, however, was not reduced in this reaction and persisted throughout the 140 minutes of the tests.

The ClO₂ speciations, at low TOC, revealed that the ClO₂ concentration decreased below detection limits within 20 minutes at either pH 6.0 or 8.0. The rapid increase in the concentration of ClO₂⁻ within the first 20 minutes of the procedure to approximately 90 percent of the ClO₂ dose indicated that the ClO₂ was reduced to ClO₂⁻ and not lost through volatilization.

The results of the analysis at high TOC and pH 8.0 are presented in Figure 19. The Mn speciation revealed that the Mn⁺² was oxidized to MnOₓ(s) within 20 minutes. In addition, the higher oxidant demand exerted by the TOC reduced the Mn⁺⁷ to MnOₓ(s) within 20 minutes. No formation of Mn⁺⁷ was seen at any time.

The ClO₂ speciation at the high TOC conditions revealed that none of the ClO₂ remained in solution after 20 minutes. The ClO₂⁻ concentration increased to 0.8 mg/L within 20 minutes and remained at this concentration for the remainder of the test.

The results of the simultaneous addition of 5.0 mg/L - ClO₂ with MnO₄⁻ for the oxidation of Mn⁺² are presented in Figures 20 through 22.

The results at low TOC conditions for pH 6.0 and 8.0 are shown in Figures 20 and 21, respectively. The manganese speciation revealed that
Figure 17. Mn$^{2+}$ dosed simultaneously with 0.22 mg/L Mn$^{7+}$ and 1.0 mg/L ClO$_2$ at pH 6.0 with TOC < 1.0 mg/L.
Figure 18. Mn$^{+2}$ dosed simultaneously with 0.22 mg/L Mn$^{+7}$ and 1.0 mg/L ClO$_2$ at pH 8.0 with TOC < 1.0 mg/L.
Figure 19. Mn\(^{2+}\) dosed simultaneously with 0.65 mg/L Mn\(^{7+}\) and 1.0 mg/L ClO\(_2\) at pH 8.0 with TOC = 4.0 - 4.2 mg/L.
at pH 6.0 a small amount of Mn$^{+2}$ remained in solution at 20 minutes. At pH 8.0 all of the Mn$^{+2}$ had been oxidized within 20 minutes. The Mn$^{+7}$ concentration was, however, unchanged throughout both the pH 6.0 and pH 8.0 phases of this experiment.

The ClO$_2$ concentrations, at both pH conditions, dropped rapidly within the first 20 minutes and were near zero by 80 minutes. The ClO$_2^-$ concentrations increased rapidly to about 3.5 mg/L and then stabilized for the remainder of the experiment. The loss of ClO$_2$ with no corresponding increase in ClO$_2^-$ was attributed to volatilization.

The results of the oxidation of Mn$^{+2}$ by 5.0 mg/L - ClO$_2$ and MnO$_4^-$, at high TOC, are shown in Figure 22. The manganese speciation revealed that the Mn$^{+2}$ was oxidized to MnO$_x$(s) within the first 20 minutes. The Mn$^{+7}$ concentration steadily decreased throughout the 140 minute reaction time to approximately 0.15 mg/L - Mn$^{+7}$.

The ClO$_2$ speciation at high TOC revealed that none of the ClO$_2$ remained in solution after 20 minutes. The ClO$_2^-$ concentration increased to approximately 3.5 mg/L by the 20 minute sampling and remained at this level throughout the remainder of the test.
Figure 20. Mn$^{+2}$ dosed simultaneously with 0.22 mg/L Mn$^{+7}$ and 5.0 mg/L ClO$\textsubscript{2}$ at pH 6.0 with TOC < 1.0 mg/L.
Figure 21. Mn$^{2+}$ dosed simultaneously with 0.22 mg/L Mn$^{7+}$ and 5.0 mg/L ClO$_2$ at pH 8.0 with TOC < 1.0 mg/L.
Figure 22. Mn$^{+2}$ dosed simultaneously with 0.65 mg/L Mn$^{+7}$ and 5.0 mg/L ClO$_2$ at pH 8.0 with TOC = 4.0 - 4.2 mg/L.
CHAPTER V

DISCUSSION

Speciation

The speciation procedure, which was developed to quantify Mn$^{+2}$, Mn$^{+x}$, Mn$^{+7}$, ClO$_2$ and ClO$_2^-$, yielded consistent, reproducible results for the test solutions evaluated during the developmental phase of this investigation. The data presented in Tables 7 and 8 reveal the consistency of the amperometric titration portion of the speciation for both MnO$_4^-$ and MnO$_x$(s) samples tested. The filtration evaluation presented in Table 9 demonstrated the need for ultra-filtration to accurately determine the soluble Mn fraction. This ultra-filtration technique was effective in removing MnO$_x$(s) particles down to a size of 2.1 nm.

The primary purpose of the speciation procedure was to determine if MnO$_4^-$ was produced under any of the experimental conditions studies. The secondary concern was to quantify, as accurately as possible, the other species present to determine the reaction mechanisms. Because the experiments dealt with combinations of highly reactive oxidants, it was impossible to obtain an instantaneous sample or to quantify each constituent at any given moment. In the case of this speciation procedure the samples were tested over a 10 - 15 minute time period; thus, it is probable that some changes took place within the samples. The values obtained, therefore, were not instantaneous but were merely representative of the conditions present at the time of the sampling.
The evaluation of Mn$^{+7}$ was based primarily on the volume of titrant required for Step F (Figure 1) of the speciation procedure. To verify this determination a comparison was made with the soluble Mn$^{+7}$ fraction determined in Step A (Figure 1). Because, in general, a slight loss of MnO$_4^-$ was detected as the sample passed through the ultra-filter, this filtered MnO$_4^-$ value was slightly less than that determined from step F. If a significant discrepancy was found, it was assumed that an interference had been present in the titration step and the value was discounted.

The concentrations of Mn$^{+2}$ and Mn$^{+x}$ were determined as described in the "Methods" chapter and could not be verified by other portions of the speciation procedure.

The determination of the concentration of ClO$_2$ was theoretically unaffected by the presence of manganese. Results obtained during the developmental and experimental phases of this investigation agreed with this theory.

The determination of ClO$_2^-$ concentration was the most involved portion of the speciation procedure. The concentration was determined using equations [4.14] and [4.15] to correct for the presence of MnO$_4^-$ and MnO$_x$(s). In each case, not only was the concentration of the oxidized manganese required for the calculation, but an assumption as to the relative oxidation state was also necessary. There was no method for verifying the ClO$_2^-$ concentration thus determined and it must, therefore, be considered a rough estimate.

The most serious problem with the speciation procedure occurred when free chlorine (HOCl or OCl$^-$) was present in the sample. The presence of free chlorine directly affected the calculation of the Mn$^{+7}$ concentration and when present may have invalidated the test. Care was
taken in preparing and testing the ClO₂ stock solution, used in the experiments, to insure that the free chlorine concentration remained low. If, however, it was formed by the reduction of ClO₂ there would be no way to accurately quantify the Mn⁺⁷.

**Mn⁺² and Mn⁺⁷ - Stoichiometric Balance**

The initial assumption of the intermediate oxidation state of Mn⁺³·₅ was the basis for this stoichiometric evaluation. Once this assumption was made, it was possible to develop equation [4.16] and to predict the amount of Mn⁺⁷ required to oxidize a given amount of Mn⁺². The results of the initial test, at pH 7.0 and TOC < 1.0 shown on page 48, confirmed that a ratio of 0.215 mg/L - Mn⁺⁷ will react with 0.50 mg/L - Mn⁺² to form an insoluble oxide within 20 minutes. Because 0.50 mg/L - Mn⁺² was used throughout the low TOC experiments, the dose of MnO₄⁻ was held at 0.215 mg/L - Mn⁺⁷.

The experimental results presented in Table 10 revealed that the reaction was not complete within 20 minutes at pH 6.0. This may be due to a decrease in the reaction rate or a slight shift in the oxidation state of the MnOₓ(s) particle due to the lower pH. The small residual concentration of Mn⁺², however, did not significantly affect the subsequent experiments. At pH 8.0 the reaction was virtually complete within 20 minutes with only trace amounts of the reactants remaining in solution.

The results for the determination of the concentration of MnO₄⁻ required to oxidize 0.50 mg/L - Mn⁺² in the presence of 4.5 - 5.0 mg/L -TOC were presented in Table 12. This evaluation was required so that the "fresh precipitate" and "simultaneous addition" experiments could be performed under high TOC conditions. This reaction showed less pH dependence and yielded a required dose of 0.65 mg/L - Mn⁺⁷ for use at
Overall, there were few problems encountered in this preliminary evaluation. Because the reaction concerned only Mn$^{+2}$ and Mn$^{+7}$, the reaction path was clearly defined and there were no other oxidants to cause an interference during the speciation procedure.

**Mn$^{+2}$ oxidized by ClO$_2$ alone**

The ClO$_2$ dose of 1.0 mg/L was sufficient to oxidize all of the Mn$^{+2}$ to MnO$_x$(s) within 20 minutes under low TOC conditions at pH 6.0 and 8.0. As shown in Figures 2 and 3, the pH had little effect on either the Mn speciation or the ClO$_2$ speciation under the low TOC conditions. The only noticeable effect was a small ClO$_2$ residual at pH 6.0 for the 20 minute speciation. At both pH 6.0 and 8.0 the ClO$_2^-$ concentration reached approximately 1.0 mg/L within the first 20 minutes, indicating that the entire ClO$_2$ dose was reduced to ClO$_2^-$. There was no evidence of any Mn$^{+7}$ formation at any time for the 1.0 mg/L - ClO$_2$ dose at low TOC conditions.

With the TOC increased to 4.6 mg/L - TOC the dose of 1.0 mg/L ClO$_2$ was not sufficient to oxidize all of the Mn$^{+2}$ in the test solution. As shown in Figure 4, the concentration of ClO$_2$ was exhausted within 20 minutes due to the combined oxidant demand of the Mn$^{+2}$ and reduced organic material. The persistence of the Mn$^{+2}$ indicated that the available ClO$_2$ was consumed more rapidly for the oxidation of the organic matter than for the oxidation of manganese. This same effect was noted by Carlson, et al. (5) in an evaluation of the effectiveness of ClO$_2$ for manganese oxidation in natural waters at various TOC levels. In their analysis, a dose of 3.0 mg/L ClO$_2$ oxidized less than 0.05 mg/L - Mn$^{+2}$ of the initial 0.21 mg/L - Mn$^{+2}$ during the 120 minute analysis at
The ClO₂ dose of 5.0 mg/L was sufficient for the oxidation of all of the Mn⁺² to Mn⁺ₓ within 20 minutes at low TOC conditions. The effects of pH variation on the reaction under the low TOC conditions, as shown in Figures 5 and 6, were minimal. Although a trace of Mn⁺⁷ appears in Figure 7, the value is near the detection limits of the speciation procedure. Also, as mentioned in the "Results" chapter, the soluble manganese concentration was only 0.01 mg/L - Mn; therefore, discounting this value. The Mn⁺⁷ value is shown on the figure only because some soluble manganese was detected and it could not, therefore, be completely dismissed.

The rapid decrease in the ClO₂ concentration from 5.0 mg/L to about 3.0 mg/L during the first 20 minutes of the analyses at low TOC conditions illustrates the oxidant demand exerted by the reduced manganese. Once this demand was met the ClO₂⁻ concentration stabilized at approximately 1.5 mg/L while the ClO₂ concentration continued to decrease. If the ClO₂ was reduced only to ClO₂⁻ and their were no other losses from this system, then the sum of ClO₂ and ClO₂⁻ should remain at approximately 5.0 mg/L. The observed deviation may be accounted for several ways:

1.) The ClO₂ may have been reduced to a species other than ClO₂; most probably Cl⁻.

2.) The measured ClO₂⁻ value, being only an estimate, may not accurately reflect the concentration.

3.) ClO₂ may be lost from the system through volatilization from the open jar test containers.

The first hypothesis, although chemically feasible, was discounted due to the results of the experiments utilizing 1.0 mg/L - ClO₂ at low
TOC. In those tests the ClO₂ reacted rapidly to oxidize the Mn⁴⁺, and in each case the sum of ClO₂ and ClO₂⁻ remained constant at about 1.1 mg/L. When the 5.0 mg/L ClO₂ dose was utilized, approximately the same concentration of ClO₂⁻ (1.5 mg/L) was developed, indicating a similar electron transfer.

The second hypothesis, concerning the accuracy of the ClO₂⁻ evaluation, was also discounted for similar reasons. In the instances where the reaction between ClO₂ and the reduced manganese was rapid and left little or no ClO₂ residual, the combined concentrations of ClO₂ and ClO₂⁻ remained constant. This indicated that the measured ClO₂⁻ concentration was reasonably accurate under the experimental conditions. This problem could not be completely dismissed, however, because there was no available method to independently verify the ClO₂⁻ concentration.

The third hypothesis, ClO₂ loss through volatilization, was addressed by determining the potential rate of loss under the experimental conditions. The results of this analysis were presented in Figure 8 and revealed a potential loss of about 30 percent of the initial dose of ClO₂ per 60 minutes of exposure. Although this rate could not be applied directly to the experimental results, due to the constantly changing ClO₂ concentrations, it was an indication that significant losses occurred through volatilization. Several efforts were made to develop a floating cover to reduce the exposed surface area of the jar test containers. Each of these covers either interfered with sample collection or proved ineffective and they were not used. The solution was simply to accept the volatilization loss as an unavoidable consequence of the procedure. Although this ClO₂ loss was significant over a period of several hours, the reactions which were observed during the investigation were quite rapid; thus, the loss was considered
acceptable. The loss of ClO₂ beyond the point where the ClO₂⁻ concentration became stable was, therefore, considered to be due primarily to volatilization.

The dose of 5.0 mg/L - ClO₂ was found to be sufficient to oxidize all of the Mn²⁺ to Mn⁺² within 30 minutes with a TOC concentration of 4.6 mg/L - TOC. The ClO₂⁻ concentration decreased very rapidly within the first 30 minutes due to the combined demand of the Mn²⁺ and the reduced organic material. There was no preferential oxidation of the organic matter noted at this high oxidant dose.

The ClO₂⁻ concentration increased from 0.25 mg/L to approximately 3.0 mg/L during the first 30 minutes of this reaction. In this instance, the decrease in the combined concentrations of ClO₂ and ClO₂⁻, particularly during the initial 30 minutes of the reaction, was attributed to both a volatilization loss and the possible reduction of ClO₂⁻ to HOCl.

As mentioned in the "Results" chapter, the amperometric titration procedure, which determines the concentration of Mn⁺⁷, indicated the presence of approximately 0.10 mg/L - Mn⁺⁷ for both the 30 minute and 150 minutes samples. The filtrate from these samples, however, contained less than 0.01 mg/L - Mn soluble manganese. The test was repeated and yielded virtually identical results. From this conflicting data it was determined that an interference must have been present during the amperometric titration at pH 7.0. The only other species which could cause such an interference in this evaluation was HOCl. A study by Wedehoff and Singer (34) had proposed the reduction of ClO₂ to HOCl during the oxidation of reduced organic material. This reaction path would explain the anomalous Mn⁺⁷ readings, but only occurred in this one instance. At no other time during this investigation, under
high or low TOC conditions, was this reaction again demonstrated.

\[ \text{Mn}^{+2} \text{ oxidized by MnO}_4^- \text{ then dosed with ClO}_2 \text{ ("Fresh Precipitate") \}

The first portion of this experiment concerned the potential for 1.0 mg/L - ClO\(_2\) to oxidize the fresh MnO\(_x\)(s) precipitate to MnO\(_4^-\) at pH 6.0 and 8.0 under low TOC conditions. The results, which were presented in Figures 9 and 10, indicated that at both pH 6.0 and 8.0 a Mn\(^{+2}\) residual of approximately 0.15 mg/L - Mn remained unreacted during the first 20 minutes of the tests. The presence of this reduced manganese probably exerted a slight demand on the ClO\(_2\) when it was introduced at 20 minutes, but the ClO\(_2\) residual was not significantly affected. During the initial 60 minutes of ClO\(_2\) contact the Mn\(^{+2}\) concentrations were reduced below detection limits at both pH 6 and pH 8. In general, the pH variation had little effect on the ClO\(_2\) or Mn speciation at the low dose, low TOC conditions.

The ClO\(_2\) concentration decreased throughout the 120 minutes test duration but was not exhausted at either pH 6.0 or 8.0. ClO\(_2^-\) concentrations increased to approximately 0.60 mg/L - ClO\(_2^-\) during the initial 60 minutes of the reactions and then stabilized for the remainder of the tests. This increase in the ClO\(_2^-\) concentrations indicated that there was some ClO\(_2\) demand probably due to either the Mn\(^{+2}\) residual or the further oxidation of the MnO\(_x\)(s) particles. The demand from these sources was met relatively quickly as indicated by the stable value of ClO\(_2^-\) beyond the 60 minute sampling.

There was no indication of the formation of Mn\(^{+7}\) at any time during the low dose, low TOC portion of this experiment.

The second phase of this experiment evaluated the potential of 1.0 mg/L - ClO\(_2\) to oxidize the fresh precipitate under high TOC conditions
(4.0 - 4.2 mg/L - TOC). The results, which were presented in Figure 11, indicated that once the precipitate had formed (30 minutes) that the ClO₂ had no effect on the concentration of MnOₓ(s) or MnO₄⁻.

The oxidation of the high level of reduced organic material exhausted the 1.0 mg/L - ClO₂ dose within the 120 reaction time. The loss of ClO₂ from the system, as indicated by the reduction of the sum of ClO₂ and ClO₂⁻, was attributed primarily to volatilization.

The results of the oxidation of fresh MnOₓ(s) precipitate by 5.0 mg/L - ClO₂ under low TOC conditions (Figures 12 and 13) revealed an interesting trend. At pH 6.0 there were residual concentrations of approximately 0.15 mg/L - Mn⁺² and 0.03 mg/L - Mn⁺⁷ after the initial 20 minute reaction time. The ClO₂ was then added and within 60 minutes had oxidized the Mn⁺² residual below detection limits. The Mn⁺⁷ concentration, however, did not decrease over the 120 minute ClO₂ contact time. At pH 8.0 the Mn⁺² and Mn⁺⁷ concentrations were 0.01 mg/L and 0.03 mg/L, respectively, after the initial 20 minutes of the test. Once again, the addition of the ClO₂ decreased the Mn⁺² concentration but did not affect the Mn⁺⁷ concentration throughout the duration of the test. Although the concentration of Mn⁺⁷ appears to change slightly in Figures 12 and 13, this variance was attributed to minor sampling and detection inaccuracies. The trend, however, remained consistent under these experimental conditions.

In both cases, pH 6.0 and 8.0, the ClO₂ concentration decreased fairly steadily throughout the 120 minute contact time, from 5.0 mg/L to about 1 mg/L. The ClO₂⁻ concentration increased, at both pH's, to approximately 1.0 mg/L. This indicated that only a small fraction of the ClO₂ was reduced to ClO₂⁻ and the remainder was most likely lost through volatilization.
The oxidation of the fresh precipitate by 5.0 mg/L ClO₂ under the high TOC conditions (4.0 - 4.2 mg/L - TOC) yielded little additional information. The Mn²⁺/Mn⁷⁺ reaction was virtually complete after 30 minutes; the ClO₂ dose was exhausted during the 120 minute contact time; and the ClO₂⁻ concentration increased to approximately 3.0 mg/L. There was no indication of Mn⁷⁺ formation at any time during this procedure.

\[
\text{Mn}^{+2} \text{ oxidized rigorously by MnO₄}^- \text{ and aged prior to dosing with ClO}_2 \] 
("Aged Precipitate")

The results of the oxidation of the aged precipitate by 5.0 mg/L ClO₂ were presented in Figures 15 and 16. The most apparent trend observed in this experiment was the relatively inert nature of the prepared MnOₓ(s). At no time was there any detectable variance in the concentration of Mn²⁺, Mnˣ⁺ or Mn⁷⁺ throughout the experimental procedures.

Perhaps one significant result of this investigation was the increase in the ClO₂⁻ concentration throughout the tests, particularly at pH 8.0. Although there was no detectable increase in the Mn⁷⁺ concentration, as predicted thermodynamically, the increase in the ClO₂⁻ concentration indicated that a redox reaction was taking place during this procedure. Because there was no detectable Mn²⁺ and the TOC remained below 1.0 mg/L - TOC, the oxidant demand was attributed to the incompletely oxidized MnOₓ(s) particles.

As described in the "Methods" chapter, this MnOₓ(s) suspension was prepared by the oxidation of Mn²⁺ with an excess of Mn⁷⁺ and allowed to react overnight. If the MnOₓ(s) formed by this rigorous oxidation with MnO₄⁻ continued to exert a ClO₂ demand during the experimental procedures, then the precipitate formed by MnO₄⁻ oxidation of Mn²⁺
during water treatment processes would be expected to exert an even stronger demand.

\[
\text{Mn}^{+2} \text{ dosed simultaneously with MnO}_4^- \text{ and ClO}_2
\]

The simultaneous addition of ClO\textsubscript{2} and MnO\textsubscript{4}\textsuperscript{-} revealed a distinct hierarchy of reactivity between these two oxidants for the oxidation of Mn\textsuperscript{+2} at low and high levels of TOC.

Under the low TOC conditions the 1.0 mg/L ClO\textsubscript{2} dose oxidized the 0.50 mg/L - Mn\textsuperscript{+2} within 20 minutes at both pH 6.0 and 8.0 (Figures 17 and 18). The Mn\textsuperscript{+7} (MnO\textsubscript{4}\textsuperscript{-}) concentration remained virtually unchanged at pH 6.0 and decreased only slightly at pH 8.0. The ClO\textsubscript{2} dose was exhausted within the initial 20 minutes of the reaction with a corresponding increase in the ClO\textsubscript{2}\textsuperscript{-} concentration to approximately 0.9 mg/L. The persistence of the Mn\textsuperscript{+7} and the rapid reduction of the ClO\textsubscript{2} indicated that the ClO\textsubscript{2} was responsible for the oxidation of the Mn\textsuperscript{+2} under the low TOC conditions. Although the Mn\textsuperscript{+7} persisted throughout the tests, there was no indication of its formation at any time.

The combination of 1.0 mg/L - ClO\textsubscript{2} and 0.65 mg/L - Mn\textsuperscript{+7} under the high TOC conditions (Figure 19) did not exhibit this tendency probably due to the high overall oxidant demand exerted by the Mn\textsuperscript{+2} and the reduced organic material. In this test, the Mn\textsuperscript{+2} was oxidized within the first 30 minutes, but there was no indication of preferential oxidation by the ClO\textsubscript{2}. Both ClO\textsubscript{2} and Mn\textsuperscript{+7} (MnO\textsubscript{4}\textsuperscript{-}) were exhausted by the first speciation. Again, there was no indication of the formation of Mn\textsuperscript{+7} at any time.

The simultaneous addition of 5.0 mg/L - ClO\textsubscript{2} with 0.215 mg/L - Mn\textsuperscript{+7}, under low TOC conditions (Figures 20 and 21) demonstrated once again the preferential oxidation of Mn\textsuperscript{+2} by ClO\textsubscript{2}. At both pH 6.0 and 8.0 the majority of the Mn\textsuperscript{+2} had been oxidized to MnO\textsubscript{x}(s) within 20 minutes. As
seen in Figures 20 and 21, the ClO\textsubscript{2} concentrations decreased very rapidly during the initial 20 minute reaction period with a concurrent increase in the ClO\textsubscript{2}\textsuperscript{-} concentrations. Because the Mn\textsuperscript{+7} concentrations remained virtually unchanged throughout the tests, it was apparent that the ClO\textsubscript{2} was responsible for the Mn\textsuperscript{+2} oxidation.

The results of the analysis utilizing the 5.0 mg/L - ClO\textsubscript{2} dose, under high TOC conditions (4.0 - 4.2 mg/L - TOC), were presented in Figure 22. In this analysis the majority of Mn\textsuperscript{+2} was oxidized to MnO\textsubscript{x}(s) within 30 minutes. The ClO\textsubscript{2} dose had been exhausted within this 30 minute period with an increase in the ClO\textsubscript{2} concentration of approximately 3.5 mg/L. The Mn\textsuperscript{+7} concentration persisted throughout the experiment, but gradually decreased. These results agree with the preferential ClO\textsubscript{2} oxidation hypothesis. The 5.0 mg/L - ClO\textsubscript{2} dose was quickly reduced to ClO\textsubscript{2}\textsuperscript{-} and the Mn\textsuperscript{+7} (MnO\textsubscript{4}\textsuperscript{-}) then became available for the oxidation of the remaining reduced species.

**Reaction Kinetics**

This section is an attempt to describe, in general terms, the relative rates of the various redox reactions which were observed during this investigation. Although no quantitative kinetic data were collected, a discussion of why certain reactions may have or have not been observed can best be developed by addressing the reaction kinetics in qualitative terms. The reactions for which the kinetics were of concern were as follows:

1.) \[3\text{Mn}^{+2} + 2\text{MnO}_4^{-} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2(s) + 4\text{H}^{+}\] \[2.8\]

2.) \[\text{Mn}^{+2} + 2\text{ClO}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2(s) + 2\text{ClO}_2^{-} + 4\text{H}^{+}\] \[2.11\]

3.) \[\text{MnO}_2(s) + 3\text{ClO}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_4^{-} + 3\text{ClO}_2^{-} + 4\text{H}^{+}\] \[2.20\]

4.) \[\text{Mn}^{+2} + 5\text{ClO}_2 + 4\text{H}_2\text{O} \rightarrow \text{MnO}_4^{-} + 5\text{ClO}_2^{-} + 8\text{H}^{+}\] \[2.23\]
Each of these reactions was evaluated thermodynamically based on the experimental conditions, using the Nernst Equation, in Chapter II. Although each analysis predicted that the reaction was favored under the given conditions, only reactions [2.8] and [2.11] proceeded at a detectable rate.

The reaction between Mn$^{+2}$ and MnO$_4^-$ (Equation [2.8]) has been demonstrated in both laboratory and treatment plant settings for decades. In theory, this relatively straightforward redox reaction occurs rapidly and nearly completely within a pH range of 5 to 9 (11, 19, 20). In this study an experimental relationship was developed in Equation [4.16] which described the observed molar reaction ratio of Mn$^{+2}$ and Mn$^{+7}$ under the prescribed conditions. In the experimental procedures this reaction reached equilibrium rapidly and left only trace concentrations of the reactants. If, however, a ClO$_2$ residual was present the reaction between Mn$^{+2}$ and Mn$^{+7}$ was not observed and the Mn$^{+7}$ remained unreacted in solution.

The reaction between Mn$^{+2}$ and ClO$_2$ to form MnO$_2$(s) (Equation [2.11]) is theoretically rapid and virtually complete. The reaction path has been reported to involve the reduction of ClO$_2$ to Cl$^-$ (23), a transfer of five electrons, but this reaction was not observed during this investigation. The oxidation of Mn$^{+2}$ to MnO$_x$(s) by ClO$_2$ occurred rapidly, under low TOC conditions, during this investigation. The results of the ClO$_2$ speciations during these experiments indicated that the ClO$_2$ was reduced primarily to ClO$_2^-$. Under high TOC conditions the ClO$_2$ appeared to selectively oxidize the reduced organic material before effecting a reduction in the concentration of reduced manganese. This selective oxidation may affect the time required for the complete oxidation of the reduced manganese in solution.
The oxidation of MnO₂(s) to MnO₄⁻ by ClO₂ (Equation [2.20]) was evaluated in two ways during this investigation. The first involved a fresh MnOₓ(s) precipitate and the second involved an aged, stabilized precipitate. The experimental results in both instances, however, were the same. There was no indication of the formation of Mn⁷⁺ (MnO₄⁻) at any time, under any of the experimental conditions. Because of the favorable thermodynamic potential predicted for this reaction, the observed unreactivity was attributed to kinetic limitations and/or the presence of a high activation energy. There are many examples of redox reactions which, although favored thermodynamically, progress at a rate which is negligible from a human perspective. Perhaps the best example is that of graphite reacting spontaneously to form diamonds. Although this reaction is favored to occur based on thermodynamic considerations, the kinetic limitations preclude the observance of its occurrence. The same is apparently true for the formation of Mn⁷⁺ from the ClO₂ oxidation of MnOₓ(s).

The oxidation of Mn²⁺ to Mn⁷⁺ (MnO₄⁻) by ClO₂ (Equation [2.23]) was also not observed during this investigation. Because of the favorable thermodynamic potential, this observed unreactivity was again attributed to kinetic limitations.
The goal of this investigation was to determine whether or not Mn\(^{+2}\) or Mn\(_X\)(s) could be oxidized to MnO\(_4^-\) by various doses of ClO\(_2\) under simulated treatment plant conditions and, if so, would the reaction occur within the water treatment timeframe. To achieve this goal it was first necessary to devise a speciation procedure which could quantify the reactants and products involved in these reactions. In addition, preliminary studies were required to determine the molar reaction ratio between Mn\(^{+2}\) and Mn\(^{+7}\) (MnO\(_4^-\)), at both low and high concentrations of TOC, so that Mn\(_X\)(s) precipitate could be formed and dosed with ClO\(_2\).

The following conclusions were reached from the evaluation of the speciation procedure:

1) The speciation procedure yielded a reliable measure of the Mn\(^{+2}\), Mn\(^{+X}\) (insoluble Mn), and Mn\(^{+7}\) during this investigation.

2) The evaluation of Mn\(^{+7}\) could be disrupted by the presence of free chlorine (HOCl or OCl\(^-\)) in the sample.

3) The determination of ClO\(_2^-\) was not affected by the presence of any form of manganese during this study.

4) The ClO\(_2^-\) determination was affected by both MnO\(_4^-\) and Mn\(_X\)(s).

These manganese species were first quantified so that their interference could be removed. Because of the manipulations required by this interference removal, the ClO\(_2^-\) concentration was viewed as an
approximate value.

The experimental phase of the investigation yielded the following conclusions:

1.) The oxidation of Mn^{+2} or MnO_x(s) to MnO_4^- by 1.0 mg/L or 5.0 mg/L ClO_2 was not observed under any of the experimental conditions during this investigation. Although the reactions were favored thermodynamically, kinetic limitations prevented the reaction from proceeding to a detectable degree during the experimental procedures.

2.) The simultaneous addition of ClO_2 and MnO_4^- to the solutions containing Mn^{+2} and high concentrations of reduced organic material demonstrated the higher reactivity of ClO_2. Only after the ClO_2 concentration was exhausted did the MnO_4^- begin to oxidize the reduced species that were present.

3.) Under high TOC conditions both Mn^{+7} and ClO_2 demonstrated a selective oxidation of reduced organic material before affecting a substantial oxidation of Mn^{+2}. Once the organic demand had been met, the oxidation of Mn^{+2} occurred rapidly.

In terms of actual water treatment practice there are several implications related to this study. First, the organic demand of the raw water must be satisfied before successful manganese removal by ClO_2 or KMnO_4 may be effected. Second, the combination of ClO_2 and KMnO_4 must be monitored closely due to the potential for ClO_2 to keep KMnO_4 from reacting until the ClO_2 concentration is exhausted. If there is insufficient oxidant demand, the KMnO_4 may persist through the treatment plant and reach the clearwell or distribution system before being reduced.
The manganese oxide precipitate ($\text{MnO}_x(s)$), which was produced by various redox reactions and under distinctly different electrochemical conditions (i.e. pH, oxidant concentrations, etc.), varied noticeably in color and consistency during this investigation. This variance was attributed to the rate of formation, relative oxidation state, and the aging characteristics of this oxide particle. Because of the importance of the formation and removal of $\text{MnO}_x(s)$ during water treatment, further study of its physical and chemical structure and the kinetics of its formation during water treatment processes may aid in the design of manganese removal facilities.
A.) Calculation of the standard cell potential

1) Oxidation

\[ \text{Mn}^{+2} + 4\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + 8\text{H}^+ + 5e^- \quad (E^0 = -1.507) \]

11) Reduction

\[ \text{ClO}_2 + e^- \rightarrow \text{ClO}_2^- \quad (E^0 = 0.954) \]

111) Overall

\[ \text{Mn}^{+2} + 5\text{ClO}_2 + 4\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + 5\text{ClO}_2^- + 8\text{H}^+ (E^0 = -0.553) \]

\[ \Delta G^0 = -nF \times E^0 = (-5)(9.65 \times 10^4 \text{F})(-0.553) \]

\[ = 2.67 \times 10^5 \text{ J/mole} = 6.38 \times 10^4 \text{ cal/mole} \]

\[ = 63.8 \text{ kcal/mole} \]

B.) Equilibrium analysis

\[ E_{\text{cell}} = E^0 - \left( \frac{RT}{nF} \right) \ln \frac{[\text{MnO}_4^-] \times [\text{ClO}_2^-]^5 \times [\text{H}^+]^8}{[\text{Mn}^{+2}] \times [\text{ClO}_2^-]^5} \]

Initial Conditions:

\[ E^0 = -0.553 \]

\[ R = 8.314 \text{ J/K} \cdot \text{mole} \]

\[ T = 298 \text{ K} \]

\[ F = 9.65 \times 10^4 \text{ C/mole} \]

\[ [\text{MnO}_4^-] = 0.215 \text{ mg/L} = \text{Mn} = 3.91 \times 10^{-6} \text{M} \]

\[ [\text{ClO}_2^-] = 0.25 \text{ mg/L} = 3.7 \times 10^{-6} \text{M} \]

\[ [\text{H}^+] = 1 \times 10^{-8} \]

\[ [\text{Mn}^{+2}] = 0.5 \text{ mg/L} = 9.1 \times 10^{-6} \text{M} \]

\[ [\text{ClO}_2^-] = 5.0 \text{ mg/L} = 7.41 \times 10^{-5} \text{M} \]

\[ E_{\text{cell}} = (-0.553) - \left( \frac{8.314 \times 298}{5}(9.65 \times 10^4) \right) \ln \left( \frac{(3.91 \times 10^{-6})(3.7 \times 10^{-6})^5(1 \times 10^{-8})^8}{(9.1 \times 10^{-6})(7.41 \times 10^{-5})^5} \right) \]

\[ E_{\text{cell}} = 0.285 \]
A.) Raw Experimental Data

1) **Amperometric Titration** (mL of titrant)

   - Step D = 1.38
   - Step F = 0.57
   - Step E = 10.80
   - Step G = 8.00

ii) **Atomic Absorption Analysis**

   - Total = 0.73 mg/L - Mn
   - Filtered = 0.19 mg/L - Mn

iii) **Klett-Summerson Colorimeter Reading**

   - Reading = 12.5 Klett Units

B.) **Calculations**

   - Total Mn(Mn$^{+2}$, Mn$^{+x}$, Mn$^{+7}$) = 0.73 mg/L
   - Mn$^{+7}$ = (0.57)(.443) = 0.25 mg/L [4.11]
   - Mn$^{+2}$ = (0.19 - 0.25) = 0 [3.2]
   - Mn$^{+x}$ = 0.73 - 0.25 - 0 = 0.48 mg/L [3.3]
   - ClO$_2$ = (10.80 - 8.00)(95.11/200) = 1.33 mg/L [4.4]
   - ClO$_2^-$ = [8.00 - (.97)(.25 + .48)](95.111/200)
   - 3.47 mg/L [4.14, 4.15]
### Mn^{+2} dosed with ClO₂ alone with TOC < 1 mg/L

<table>
<thead>
<tr>
<th>Elapsed Time</th>
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<th>pH 8.0</th>
</tr>
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<tbody>
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<td></td>
<td>0 mg L ClO₂</td>
<td>1.0 mg L ClO₂</td>
</tr>
<tr>
<td>0 min (Initial Dose)</td>
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</tr>
<tr>
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**Notes:** Dash indicates species not detected. Blank indicates species not sampled.
### Fresh precipitate dosed with ClO₂ and TOC < 1.0 mg/L

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<td>0.03</td>
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<td>0.86</td>
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<td>0.63</td>
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**Notes:**
- Dash indicates species not detected.
- Blank indicates species not sampled.
- ¹ClO₂ added after 20 minute sampling.
Mn\(^{+2}\) dosed with ClO\(_2\) alone and TOC = 4.6 mg/L

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<tr>
<th>Elapsed Time</th>
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<th>1.0 mg/L ClO(_2)</th>
<th>5.0 mg/L ClO(_2)</th>
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</thead>
<tbody>
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<td>0 min (Initial Dose)</td>
<td>Mn(^{+2})</td>
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</tr>
<tr>
<td></td>
<td>Mn(^{+X})</td>
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</tr>
<tr>
<td></td>
<td>Mn(^{+7})</td>
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<td>--</td>
</tr>
<tr>
<td></td>
<td>ClO(_2)</td>
<td>1.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>ClO(_2)(^{-})</td>
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<td>0.25</td>
</tr>
<tr>
<td>30 min</td>
<td>Mn(^{+2})</td>
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<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Mn(^{+X})</td>
<td>0.24</td>
<td>0.40</td>
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<td></td>
<td>Mn(^{+7})</td>
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<td>0.08</td>
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<td>ClO(_2)</td>
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<tr>
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<td>ClO(_2)(^{-})</td>
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<tr>
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<td>Mn(^{+X})</td>
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<td>0.42</td>
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<td>0.07</td>
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Notes: Dash indicates species not detected. Blank indicates species not sampled.
Fresh Precipitate dosed with ClO₂ and TOC = 4.0 - 4.2 mg/L

<table>
<thead>
<tr>
<th>Elapsed Time (Initial Dose)</th>
<th>Species</th>
<th>0 mg/L ClO₂</th>
<th>1.0 mg/L ClO₂</th>
<th>5.0 mg/L ClO₂</th>
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<tbody>
<tr>
<td>0 min</td>
<td>Mn⁺²</td>
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<td>0.50</td>
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<tr>
<td></td>
<td>Mn⁺⁷</td>
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<tr>
<td></td>
<td>ClO₂⁻</td>
<td>0.65</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>ClO₂⁺</td>
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</tr>
</tbody>
</table>

| 30 min²                     | Mn⁺²    | 0.03        | 0.04          | 0.03          |
|                             | Mn⁺⁷    | 1.12        | 1.04          | 1.05          |
|                             | ClO₂⁻   | 0.01        | 0.06          | 0.06          |
|                             | ClO₂⁺   | --          | --            | --            |

| 150 min                     | Mn⁺²    | --          | 0.01          | 0.01          |
|                             | Mn⁺⁷    | 1.12        | 1.12          | 1.12          |
|                             | ClO₂⁻   | 0.02        | 0.07          | 0.07          |
|                             | ClO₂⁺   | --          | 0.65          | 2.88          |

Notes: Dash indicates species not detected. Blank indicates species not sampled. Preliminary Study. ClO₂ added after 30 minute speciation.
<table>
<thead>
<tr>
<th>Elapsed Time</th>
<th>Species</th>
<th>pH 6.0</th>
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<th>pH 8.0</th>
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<td>1.0 mg/L ClO₂</td>
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<tr>
<td>20 min</td>
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<td>0.01</td>
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<tr>
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<td>Mn⁺⁺⁺</td>
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<td>0.77</td>
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<td>Mn⁺⁺</td>
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Notes: Dash indicates species not detected. Blank indicates species not sampled.
Mn$^{+2}$ dosed simultaneously with MnO$_4^-$ and ClO$_2$ with TOC < 1.0 mg/L

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<td>mg L</td>
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<td>Mn$^{+x}$</td>
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Notes: Dash indicates species not detected. Blank indicates species not sampled.
Mn$^{+2}$ dosed simultaneously with MnO$_4^-$ and ClO$_2$ with TOC = 4.0 - 4.2

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<td>0.03</td>
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</tbody>
</table>

Note: Dash indicates species not detected. Blank indicates species not sampled. Preliminary Study.
REFERENCES


The vita has been removed from the scanned document