

**The Effect of Various Oxidants on Water Treatment Processes**

by

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**(ABSTRACT)**

The effects of four oxidants upon water treatment process parameters were investigated. The four oxidants under consideration were ozone, chlorine dioxide, potassium permanganate, and chlorine. Experimentation was directed towards the impact of these oxidants upon turbidity, TOC, and color removal, as well as reduced manganese oxidation. Studies were conducted with an experimental water with enhanced TOC levels. Experimentation was accomplished by a series of jar tests in which solution pH, coagulant dose, and oxidant dose were varied.

Results show that, in general, oxidant application had either no impact or a negative impact upon TOC, turbidity, and color removal. Further deterioration of finished water quality was observed with increasing oxidant dose. Reduced manganese was oxidized by both potassium permanganate and chlorine dioxide. Ozone effectively oxidized reduced manganese in waters of low initial TOC, while chlorine was an ineffectual oxidant.

Additionally, particle counts were conducted. Results show that the application of an oxidant increased the number of smaller particles present after settling. However, this increase of particles did not significantly alter settled turbidity levels.

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# Chapter 1

## Introduction

The objective of water treatment is to provide a safe, unobjectionable water of consistent quality. In order to meet this goal, objectionable contaminants must be either removed completely or rendered innocuous by chemical, biological or physical methods. Currently, chemical oxidation of contaminants is a cornerstone for water treatment technology. The target contaminants are of both an organic and inorganic nature and include taste-and-odor compounds, reduced metals, color-causing compounds, and a variety of other man-made and natural contaminants. The most commonly utilized chemical oxidants are chlorine, potassium permanganate, chlorine dioxide and ozone. Research has indicated that the application of chlorine, when in contact with naturally occurring organics, has resulted in the formation of carcinogenic trihalomethanes. This finding has spawned new research emphasis aimed at investigating the efficacy of alternate oxidants for the oxidation of organic and inorganic species from water.

The Abel Lake treatment facility provides potable water for the residents of Stafford County, Virginia. The plant is of a conventional design with two million gallons of finished water produced daily. Seasonally, the plant encounters difficulties meeting regulations imposed for trihalomethanes (THMs). In an effort to abate this problem, pre chlorination was discontinued and chlorination was then applied prior to filtration. While this aided in controlling THMs, high levels

of dissolved metals and taste and odor problems persisted without the application of a pre-oxidant. These problems gave impetus for the need to research the efficacy of suitable alternative oxidants to be used in place of chlorine.

Implementation of alternative oxidants relies on further investigation. Particularly necessary are studies researching the impacts of the aforementioned oxidants upon reduced metal oxidation and impacts upon the coagulation process. That is, will the use of an alternate oxidant enhance or inhibit the removal of color and turbidity from raw water? In an effort to address these questions, the following research objectives were proposed:

1. To determine the effect of the alternative oxidants upon the oxidation and removal of dissolved manganese.
2. To assess the effects of the alternative oxidants upon color removal, TOC removal, and turbidity removal.
3. To assess the role of pH upon the performance of these alternative oxidants.

## Chapter 2

# Literature Review

In order to focus research efforts and analyze experimental results, a literature review of past studies was undertaken. Of special interest were studies investigating the use of alternate oxidants upon the removal of manganese and impacting effects upon turbidity and color removal. After a review of sources, it became clear that only a limited amount of literature had been published, especially regarding the effect of oxidants on the removal of color and turbidity from surface waters. Currently, ozone is being widely investigated regarding its impact upon the coagulation process, unlike the other three oxidants. The following section reviews pertinent literature concerning topics to be addressed in this study. Each oxidant will be addressed initially in a general manner with subsequent discussion being more specific. For further information concerning each oxidant, the reader is referred to the bibliography for pertinent references.

### *Oxidant chemical characteristics and manganese removal*

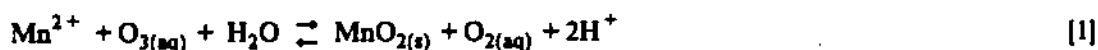
#### **Ozone**

Ozone has been employed successfully for various applications in water treatment. Rice *et al.* (1) have presented an excellent discussion of the benefits and drawbacks of ozonation along with a review of its recent uses. Currently, ozone is utilized in over 1,000 European municipalities with

primary being the major application. The inactivation of microbes is reportedly assured when a residual of 0.3 mg/L O<sub>3</sub> is maintained for a minimum a four minutes (2). Further uses of ozone include removal of taste and odors, reduced metal oxidation, and algal control. Maier (3) reported that ozone acts as a microfloculant, which may reduce the requirement for metal ion coagulants. Of further interest to water purveyors is that ozone will not react with organics to form trihalomethanes (THMs). Major concerns that may limit ozone use are generation cost and the lack of residual after application. Studies have shown that the half-life of ozone in drinking water is twenty minutes at 20°C (4).

Ozone is a highly reactive and unstable gas at room temperature. Therefore due to its instability it must be generated on-site. Self-decomposition of ozone is accelerated in aqueous solution, with the rate being dependent upon the presence of catalyzing hydroxide ions. The oxidation of organic compounds is believed to be accomplished by two reaction pathways, a direct and an indirect reaction (5). Directly, ozone reacts with organics to form ozonides and peroxides which subsequently split at the double bond. Simpler compounds such as ketones and aldehydes are by-products of this cleavage. The indirect reaction sequence is initiated by the decomposition of ozone to by-products such as the OH and HO<sub>2</sub> radicals. These radicals are highly reactive, promoting the degradation of organics. The effect of this pathway seems to be greatly influenced by radical scavengers such as bicarbonate and chloride.

Manganese(II) oxidation by ozone may be described by the following reaction:



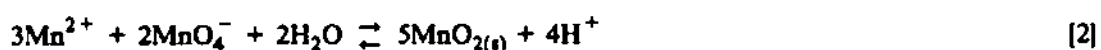
The theoretical ozone requirement is .88 mg O<sub>3</sub> per mg Mn(II). The oxidation of Mn(II) by ozone occurs rapidly with increasing pH. Under conditions of excessive ozonation, MnO<sub>2</sub>(s) may be further oxidized to permanganate (6). In addition, oxidation of organic-metal complexes is accomplished by ozonation. Stoebner (7) and Rollag observed that the application of 4 mg/L O<sub>3</sub> decreased the soluble Mn(II) concentration from 0.65 mg/L to less than 0.1 mg/L. In addition, reaction time had no impact upon Mn(II) oxidation as intervals from 5 to 30 minutes gave similar results. Weissenhorn (6) reported that 0.5-1.0 mg/L Mn(II) in Reine River water could be oxidized

to acceptable levels upon the application of 3 mg/L ozone. Furthermore, the author reported the formation of permanganate under excess ozone dosing conditions was found to aid in the removal of organics and turbidity. It was postulated that as permanganate contacted the filters it was reduced to insoluble  $MnO_2$ . Organic constituents were subsequently adsorbed onto this precipitate.

## Potassium Permanganate

Permanganate has been used successfully in water treatment for a myriad of reasons, including iron and manganese removal, phenol oxidation, control of taste and odors and algae control. Currently, of those utilities concerned with manganese removal, one-third employ permanganate (7). In addition, Cleasby (8) reported that permanganate is an effective disinfectant. Among its other attributes include ease of application and resistance to forming trihalomethanes. Drawbacks to the use of permanganate include its relatively high unit cost and the formation of an insoluble species upon reduction. This precipitate however, may be removed by the coagulation-sedimentation-filtration process.

Dissolved manganese oxidation by permanganate occurs according to the following reaction:



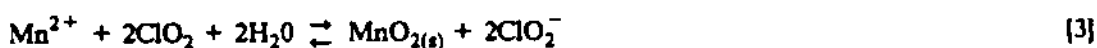
When applied as potassium permanganate, the theoretical requirement for manganese oxidation is 1.92 mg  $KMnO_4$  per mg  $Mn(II)$ . This reaction occurs over a wide pH range (pH 5 to 10), with increased efficiency noted under alkaline conditions. Studies by Kotter (9) have shown that at the higher pH range, dissolved manganese may be adsorbed onto manganous oxides, resulting in less than the stoichiometric amount of permanganate being required for manganese oxidation. Griffin (10) reported that permanganate reacts rapidly with  $Mn(II)$ , with complete oxidation within five minutes. Knocke *et al.* (11) found that 0.25 mg/L of  $Mn(II)$  was oxidized to a level below .05 mg/L with a dose of 0.7 mg/L  $KMnO_4$  using a water source with an initial TOC of 1-2 mg/L. In contrast, a raw water with an initial TOC of 8-10 mg/L needed 2.2 mg/L of  $KMnO_4$  to oxidize  $Mn(II)$  below 0.5 mg/L. This illustrates the competitive oxidant demand that organics may exert on permanganate.

## Chlorine Dioxide

Recently chlorine dioxide has been the focus of many research efforts investigating its application in water treatment. Aieta and Berg (12) offer an extensive literature review on the subject. Interest in chlorine dioxide application is due mainly to its strong disinfectant capacity and capability to effectively oxidize organic and inorganic species (1). Unlike ozone, chlorine dioxide is relatively stable and is capable of maintaining a residual within the distribution system. In addition, Masschelein (13) reported that chlorine dioxide is capable of micelle formation in a manner similar to ozone. However, use of chlorine dioxide may be limited by reported health concerns. Currently, it is recommended that chlorine dioxide and its reaction by-product chlorite ( $\text{ClO}_2^-$ ), not exceed 1 mg/L in treated water released to the consumer. Additionally, chlorine dioxide has been implicated in producing objectionable taste and odors, especially when in contact with hydrocarbons (14).

Chlorine dioxide is currently being utilized by many utilities within the U.S. for non-disinfection applications (1). Control of taste and odor compounds is the predominant usage, with its use being found in nearly forty water treatment facilities. It is particularly effective in the destruction of phenolic compounds and those responsible for fishy and musty odors (1).

Manganese(II) oxidation by chlorine dioxide can be described by the following two reactions:



The stoichiometry of Reaction (3) predicts that 2.44 mg  $\text{ClO}_2$  are necessary to oxidize 1 mg Mn(II). Aieta and Berg (12) proposed Reaction (4), showing that chlorite is capable of oxidizing Mn(II), with chloride being the ultimate reaction product of chlorine dioxide. The theoretical requirement of  $\text{ClO}_2$  being .49 mg 1 mg Mn(II). In addition, this reaction is known to occur over a wide pH range (12). Studies conducted by Knocke *et al.* (11) showed that at pH 5.5, 2 mg/L  $\text{ClO}_2$  as  $\text{Cl}_2$  were needed to oxidize Mn(II) below .05 mg/L using a water source with a TOC of 1-2 mg/L.

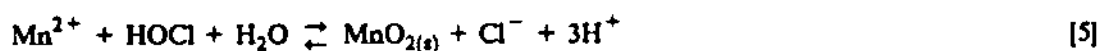


Conversely, 4 mg/L ClO<sub>2</sub> as Cl<sub>2</sub> were needed to oxidize Mn(II) below .05 mg/L with a water source containing 8-10 mg/L TOC.

## Chlorine

Chlorine, far and away, has been the most widely utilized oxidant among water utilities. Important reasons for this include its potent disinfection capability and low cost. Recently, however, chlorine usage has decreased due to its reactivity with organics, resulting in trihalomethane formation. Even so, chlorine is still utilized by nearly two-thirds of the municipalities that target manganese removal (15).

Manganese (II) oxidation with chlorine proceeds slowly, even at an elevated pH, with one to two hours necessary for complete oxidation (15). The reaction may be described as follows:



When applied stoichiometrically, .95 mg HOCl is necessary to oxidize 1 mg Mn(II). Knocke *et al.* (11) found that an initial concentration of .16 mg/L Mn(II) was decreased to .05 mg/L by an application of 2 mg/L chlorine at pH 8.0; however when the pH was decreased to 6.0, efforts to oxidize Mn(II) were unsuccessful.

## *Role of Oxidants in Coagulation*

### **Turbidity and Organics Removal by Coagulation**

Metal ion coagulation is used extensively in water treatment for the removal of soluble, suspended and colloidal materials responsible for color and turbidity. Stumm and O'Melia (16) present an excellent discussion of this topic. However, due to the scope of this project, only specific aspects concerning turbidity and color removal by alum coagulation will be addressed.

Removal of natural color and turbidity by alum coagulation is accomplished by two mechanisms, (a) charge neutralization for adsorption and (b) enmeshment by sweep floc. Parameters affecting these mechanisms include coagulant dosage, pH and initial concentration of organic compounds and turbidity. Removal by charge neutralization is accomplished by the destabilization of negatively charged particles by the adsorption of hydrolyzed aluminum species. Destabilized

particles are then agglomerated during flocculation and ultimately removed during sedimentation. In addition, stoichiometric relationships of coagulant requirements to achieve destabilization of colloids have been shown to exist (17). That is, more alum is needed to achieve destabilization as the concentration of colloids increases. However, an overdosing of alum can lead to the restabilization of colloids. Charge neutralization for the removal of humic acids by alum is targeted over a narrow pH range, normally within the 5-5.5 pH range. Finally, lower amounts of coagulant are generally necessary to achieve charge neutralization than to attain enmeshment by sweep floc.

The second mechanism, sweep floc, achieves contaminant removal by the action of an aluminum precipitate. Humic acid removal is optimized within the pH range from 6-8, whereas optimal turbidity removal occurs within the 7-8 pH range (18). Turbidity is removed from suspension as particulates become entrapped within the precipitate. Color-causing compounds are thought to be removed by an adsorptive reaction (18). That is, electrostatic forces between the precipitate and humic acids lead to the adsorption of the humic acid. Overall, doses of coagulant required to affect removal by sweep floc are somewhat inversely related to the colloid concentration. This is due to the effect of colloids acting as nuclei for the formation of the precipitate (17).

## Ozone

Microflocculation has been identified as a beneficial effect of ozonation, resulting in greater turbidity removals, lower sludge volumes, and longer filter runs. Reckhow *et al.* (19) have presented an exhaustive review of past studies on this topic. Essentially, microflocculation is described as the shifting of particle size ranges from smaller to larger. Although not fully understood, it is believed that ozone acts to convert organic colloids into negatively charged compounds which agglomerate into larger particles (20). These particles are felt to be more amenable to removal by polyvalent cations. Particle count studies conducted by Jekel (21) showed ozonation had the effect of decreasing particle concentration in the 1-3  $\mu\text{m}$  size range while increasing the total number of particles greater than 3  $\mu\text{m}$ . Overall, an ozone dose of 2.4 mg/L decreased total particle counts by 44% for raw water. Solution turbidity also decreased from 3.4 FTU to 2.8 FTU. Saunier *et al.* (22) found that ozone increased turbidity removal from 32% to 43% when using 1.2 mg/L  $\text{O}_3$  in conjunction with 15 mg/L alum. Also, a dose of 0.8 mg/L ozone added along with

15 mg/L alum resulted in the same turbidity removal as a dose of 30 mg/L alum with no ozone. Likewise, Jekel (21) found that ozone enhanced turbidity removal when the desired finished turbidities were between 0.5 and 1.0 FTU. However, pre-ozonation was of no benefit if finished turbidities under 0.5 FTU were desired. Optimal ozone doses were found to lie between 1-2 mg/L for raw water with an initial turbidity of 3.4 FTU.

It should be noted the above studies represent cases in which the effects of microfloculation were shown to occur. Reckhow *et al.* (19) also listed several researchers have observed either an anti-flocculation phenomena or no effect at all upon the application of ozone. The authors postulated that the nature of the raw water is critical to observe the effects of microfloculation. Waters of high organic content are believed to be more amenable to microfloculation.

Several studies have investigated optimal ozone doses for the removal of turbidity and organics. Kuhn *et al.* (23) observed for a raw water with 5 mg/L humic acid that an ozone dose of 2.5 mg O<sub>3</sub>/mg humic acid resulted in the optimal removal of turbidity. This study also pointed out that ozone application could result in increased turbidity. Doses of ozone at 1.0 mg O<sub>3</sub>/mg humic acid resulted in a two-fold turbidity increase after settling. In addition, Jekel (21) observed that optimum removal of humic acids was found to range from .25-.60 mg O<sub>3</sub>/mg dissolved organic carbon (DOC). Furthermore, high ozone applications were found to promote the formation of soluble complexes which were difficult to remove by coagulation. In summary, optimum ozone dose appears to be a critical parameter for the removal of turbidity and organics.

## **Potassium Permanganate**

Literature sources suggest that permanganate is reactive with certain organic compounds. For instance, phenols and certain taste and odor compounds may be removed with permanganate. Brodeur *et al.* (24) observed that color derived from lignins and tannins could be decreased from 57 Pt-Co units to 27 Pt-Co units upon the addition of 8 mg/L KMnO<sub>4</sub>. Colthurst and Singer (25) also noted the reactivity of permanganate with organics, observing that a small portion of TOC was oxidized completely to carbon dioxide upon the addition of 4 mg/L KMnO<sub>4</sub>. Furthermore, with 40 mg/L Ca<sup>2+</sup> present, the addition of permanganate and subsequent reduction to MnO<sub>2</sub>(s)

resulted in a decrease of 54% of the initial TOC. The authors believed that divalent calcium acts to bridge negatively charged manganese dioxide with negatively charged organics. In this way, permanganate may be thought of as a coagulant aid.

## **Chlorine Dioxide**

An EPA survey indicated that chlorine dioxide is being used on a limited basis for color removal, with at least three European utilities using chlorine dioxide for turbidity reduction (1). Brodeur *et al.* (24) studied  $\text{ClO}_2$  for treating a water with both lignins and tannins. They observed that a 3mg/L dose  $\text{ClO}_2$  reduced color from 22 Pt-Co units to 13 Pt-Co units. Studies conducted by Hildebrand *et al.* (26) evaluated the effect of  $\text{ClO}_2$  upon filtered water turbidity and color removal. Five separate water sources were investigated. The authors found one instance of enhanced removal, one instance of decreased removal, while the remaining three studies were inconclusive. They concluded that the effects of  $\text{ClO}_2$  upon coagulation were site specific. Although haloforms were not generated, the formation of total organic halides was noted.

## **Chlorine**

Chlorine has been shown to be highly reactive with certain organics. Of special interest is the reaction with humics, producing haloforms. Sontheimer (27) proposed that the magnitude of THM formation may be decreased by a step-wise application of chlorine, making certain that free chlorine was not present. Regarding color removal, Brodeur *et al.* (24) observed that an initial color of 46 Pt-Co units imparted by lignins and tannins was decreased to 15 Pt-Co units with application of 20 mg/L chlorine and a contact time of 30 minutes. Further studies with a settled water showed a color reduction from 35 Pt-Co units to 23 Pt-Co units upon dosing 12.7 mg/L chlorine.

## ***Uses of Particle Enumeration***

Particle counting is an analytical technique being utilized to evaluate the performance of unit operations used in the purification of drinking water. Beard and Tanaka (28) reported that particle counting is a more sensitive technique than nephelometry for the measurement of suspended solid concentrations. Results of their studies showed correlations between particle numbers and turbidity if the pool of data was sufficiently large. However, attempting to compare

discrete data points was of no benefit. Tate and Russell (29) likewise have investigated the applications of particle counters for use in water treatment. They propose that particle counters may be employed to optimize unit processes. By doing so, savings in treatment costs may be realized. However, one of the most comprehensive applications of particle counting has been advanced by Lawler *et al.* (30). In this study, models were developed for each unit process based upon the results of particle counting. From this, it was hoped that performance of the treatment train may be predicted by relating characteristics of the raw water.

## Chapter 3

### Methods and Materials

#### *Experimental Water*

This study attempted to quantify the effects of various oxidants upon the water treatment processes at the Abel Lake treatment facility in Stafford, Virginia. Unfortunately, due to the inconvenience and impractical nature of transporting raw water from Stafford to Blacksburg, a more accessible source of water was needed. After considering possible local water sources, New River water was chosen for use. This water was collected from the raw water inlet at the Blacksburg-Christiansburg-VPI water treatment facility and transported to the Virginia Tech Environmental Engineering laboratory for testing.

Certain chemicals were added to New River water in order to better simulate the water quality of Abel Lake. First, a prepared humic substance (CH-9470 Buchs, Fluka Chemical Corp., Hauppauge, N.Y.) was added to enhance levels of TOC, and color in certain studies. In addition, dissolved manganese levels were enhanced by introducing a stock solution of manganous sulfate. This was done to increase reduced manganese levels to those observed levels during overturn at Abel Lake. The experimental water was stirred for a period of at least three hours prior to testing to ensure uniformity. Table 1 presents typical ranges of the water quality parameters of the

experimental water prior to chemical enhancement and after chemical enhancement. (Note: Low values of color and TOC for experimental water, in the majority of the samples, were not enhanced by the addition of supplemental chemicals.)

## ***Experimental Procedure***

Jar tests were conducted under a wide range of conditions. over a wide range of conditions. Parameters which were varied included alum and oxidant dosages, system pH, and initial TOC of the test water. Essentially all jar tests were conducted in a similar manner. Testing was initiated by introducing a 1.5 L volume of experimental water into one of six rectangular Plexiglas jar reactors. The samples were then rapidly mixed with a Phipps and Bird (Richmond, Virginia) jar test apparatus for one minute as alum and oxidant were added. In the case of potassium permanganate, a ten minute reaction period was utilized prior to alum addition, simulating treatment operations at the Abel Lake facility. The method of application of ozone was slightly different and will be subsequently discussed. Oxidant doses ranged from 0 to 4 mg/L, while alum doses ranged from 15 to 60 mg/L. In addition, during rapid mixing, the pH of the system was adjusted with either hydrochloric acid or sodium bicarbonate. Coagulation pHs of 6.0 and 7.5 were chosen for this study. Following rapid mixing, the samples were flocculated for a 20 minutes at a mixing speed of 20 rpm. At the end of the flocculation period, samples of approximately 100 mL were collected from each reactor to for particle analysis. Ultimately, after a sedimentation period of 40 minutes, a battery of tests was conducted upon the settled water. These are described in the following sections.

## ***Experimental Analyses***

*Particle Counts:* Collected samples of approximately 100 mL were analyzed with either a HIAC HR-120 HC or HIAC CHM-300 Particle Counter (Menlo Park, California). Each unit is capable of enumerating the number of particles within twelve distinct size ranges; the former unit enumerates particles between 2 to 120  $\mu\text{m}$ , while the latter enumerates particles between 5 and 300  $\mu\text{m}$ . Enumeration of particles is accomplished by passing the sample fluid through a calibrated light source that impinges upon a photodiode. As the suspension passes, particles obscure the path of

**Table 1. Water Quality Parameters of Collected and Sample Water**

<b>Water Quality Parameters</b>	<b>Collected Water (New River)</b>	<b>Sample Water (Enhanced)</b>
pH	7.0-7.3	6.0, 7.5*
TOC (mg/L)	1.4-3.0	1.4-5.3**
Turbidity (NTU)	1.0-3.0	1.0-6.2
Color (Pt-Co Units)	7-22	7-162**
Reduced Mn (mg/L)	< .01	.16-.40***

\* adjusted with either sodium bicarbonate or hydrochloric acid

\*\* enhanced with humic acid

\*\*\* enhanced with manganous sulfate



the light, with the degree of light attenuation being proportional to the number of particles in suspension.

*Soluble Manganese, Mn(II)*: Samples of settled and raw water were analyzed for reduced, soluble manganese by filtering a portion through a 0.2  $\mu\text{m}$  Metrical membrane filter (Gelman Sciences Inc., Ann Arbor Michigan). Filtered samples were preserved with a concentrated solution of nitric acid and subsequently analyzed by atomic adsorption spectrophotometry (Perkin-Elmer Model 703, Norwalk, Connecticut).

*Total Organic Carbon (TOC)*: Raw and treated water samples were filtered through a Type A/E filter (Gelman Sciences, Inc., Ann Arbor Michigan) and preserved with concentrated phosphoric acid. Samples were refrigerated before being analyzed for TOC with a Dohrmann DC-80 Carbon Analyzer (Santa Clara, California).

*Turbidity*: The turbidity of raw and settled water samples were measured with a HACH Model 2100A turbidimeter (Ames, Iowa).

*Apparent Color*: Unfiltered samples of both raw and settled water were analyzed by photoelectric colorimetry, using a #42 filter in a Klett-Summerson colorimeter (Klett-Summerson, New York, N.Y.). Color determinations were based upon a technique outlined in *Standard Methods* (31), section 204.

*Residual Permanganate*: A modified technique from *Standard Methods* (31), section 314B, was used for this analysis. Initially, a standard curve was developed for permanganate employing photoelectric colorimetry. Permanganate concentrations were then determined by referring to this standard curve. Interferences due to turbidity were masked by introducing 0.5 mL of 30% hydrogen peroxide to the sample after an initial reading for color. The difference between the color readings before and after peroxide addition was a direct function of the amount of permanganate present.

## ***Preparation Of Oxidants***

### **Chlorine Dioxide**

A chlorine dioxide stock solution was generated by the Iodometric Method described in *Standard Methods* (31), section 410C. Chlorine Dioxide was generated by the addition of

concentrated hydrochloric acid to a solution of sodium chlorite. The generated chlorine dioxide gas was trapped in an opaque, sealed bottle filled with distilled water. The stock solution was then refrigerated until it was needed, at which time it was pipetted into the sample. Determination of the concentration of chlorine dioxide was made by using a method described by Aieta *et al.* (32). This was done by amperometric titration using phenylarsine oxide as a titrant.

## Chlorine

A stock solution of chlorine was prepared by diluting bleach with distilled water. The concentration of chlorine was determined by amperometric titration using phenylarsine oxide as a titrant. This method was found in *Standard Methods* (31), section 408C.

## *Ozone Application and Determination*

Ozone, being a highly reactive and unstable gas, cannot be applied in a manner similar to the other oxidants, thus necessitating an alternative application methodology. Ozone was generated onsite in the laboratory by passing an electrical current through air. An Airox Ozonator (Pollution Control Industries, Inc., Stamford, Connecticut) was utilized for ozone generation. Ozone was applied by introducing it through a porous diffuser at the same point the water sample was introduced. Ozonated water was collected in a glass vessel. Unreacted ozone was trapped in the head space above the water level purged with air, and collected in a solution of indigo. The indigo solution was used to aid in quantifying the actual amount of ozone which remained in the water sample. During the study it was found that the amount of unreacted ozone was negligible in comparison to the applied dose.

Ozone concentration determinations were made by using a method developed by Bader and Hoigne (33). This method is based upon the decoloration of indigo trisulfonate in the presence of ozone under acidic conditions. Ozone concentrations were calculated from measurements of solution absorbance at 600 nm before and after ozonation using the following relationship:

$$O_3 \text{ (mg/L)} = \frac{\Delta A(100)}{0.42(b)(V)} \quad [6]$$

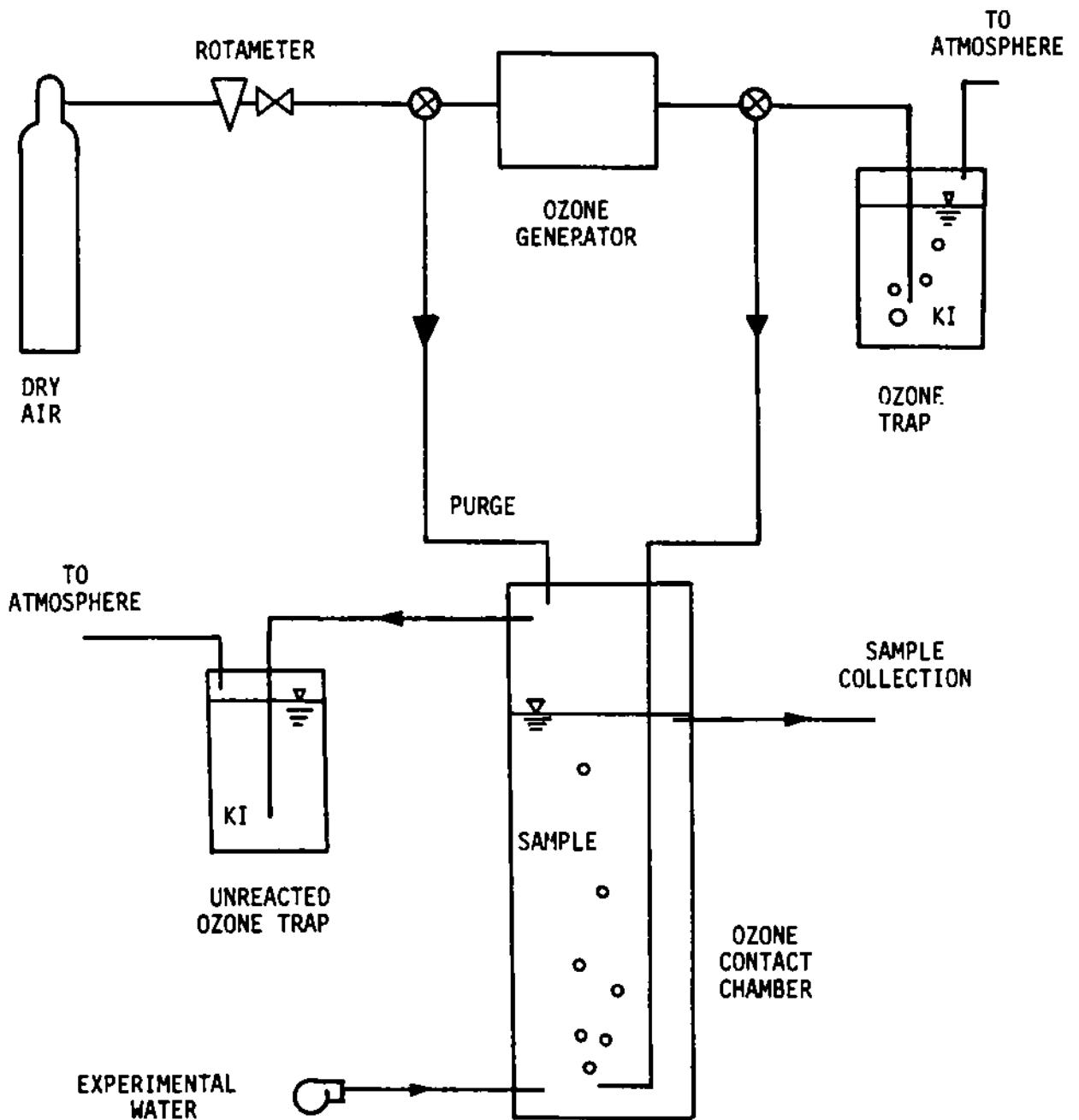


Figure 1. Ozone Application Diagram

where:  $\Delta A$  = difference in absorbance between sample and blank  
b = pathlength of cuvette, cm  
V = sample volume, mL

According to Bader and Hoigne, manganese oxides can cause interferences in the procedure. During the course of this study, a comparison of samples containing manganous oxides and those without showed no difference in absorbance readings. Therefore, interferences due to manganous oxides were deemed to be insignificant.

Calibration of the ozonator was accomplished by operating the system in a continuous-flow mode. Indigo was introduced directly into the ozone contact chamber. By varying conditions such as ozone flow rate or liquid flow rate, distinct ozone doses could be achieved. After the generator was calibrated, the test water was ozonated. Test water was pumped through the ozonator at a rate of 0.88 L/min., resulting in a contact time of 1.5 minutes. Different ozone doses were achieved by varying the ozone flow rate through the diffuser. The ozonated effluent was collected in a separate vessel, from which the water was immediately transferred to the jar-test apparatus. At this point, testing proceeded in the same manner as previously described.

## Chapter 4

### Results

In this section, experimental results are presented. The effects of the four oxidants investigated are addressed in four separate sub-sections. Within each sub-section, results pertaining to the removal of Mn(II), color, TOC, and turbidity are also presented.

#### *Oxidant Effects Upon Mn(II) Removal and Coagulation*

##### **Ozone**

*Turbidity Removal:* Results presented in Figure 2 indicate that the solution pH affected the removal of turbidity in ozonated samples. Both trials conducted at pH 7.5 showed enhanced turbidity removal; however, the opposite effect was noted at pH 6.0 where increasing oxidant dose led to increasing residual turbidity levels. The effect of alum upon turbidity removal was different for both pHs investigated.

*TOC Removal:* Results summarizing the effect of ozone on TOC removal are found in Figure 3. Lower ozone doses had little effect upon TOC removal. Higher doses of ozone, however, inhibited TOC removal. Removal of TOC was found to be better at the lower pH condition of 6.0.

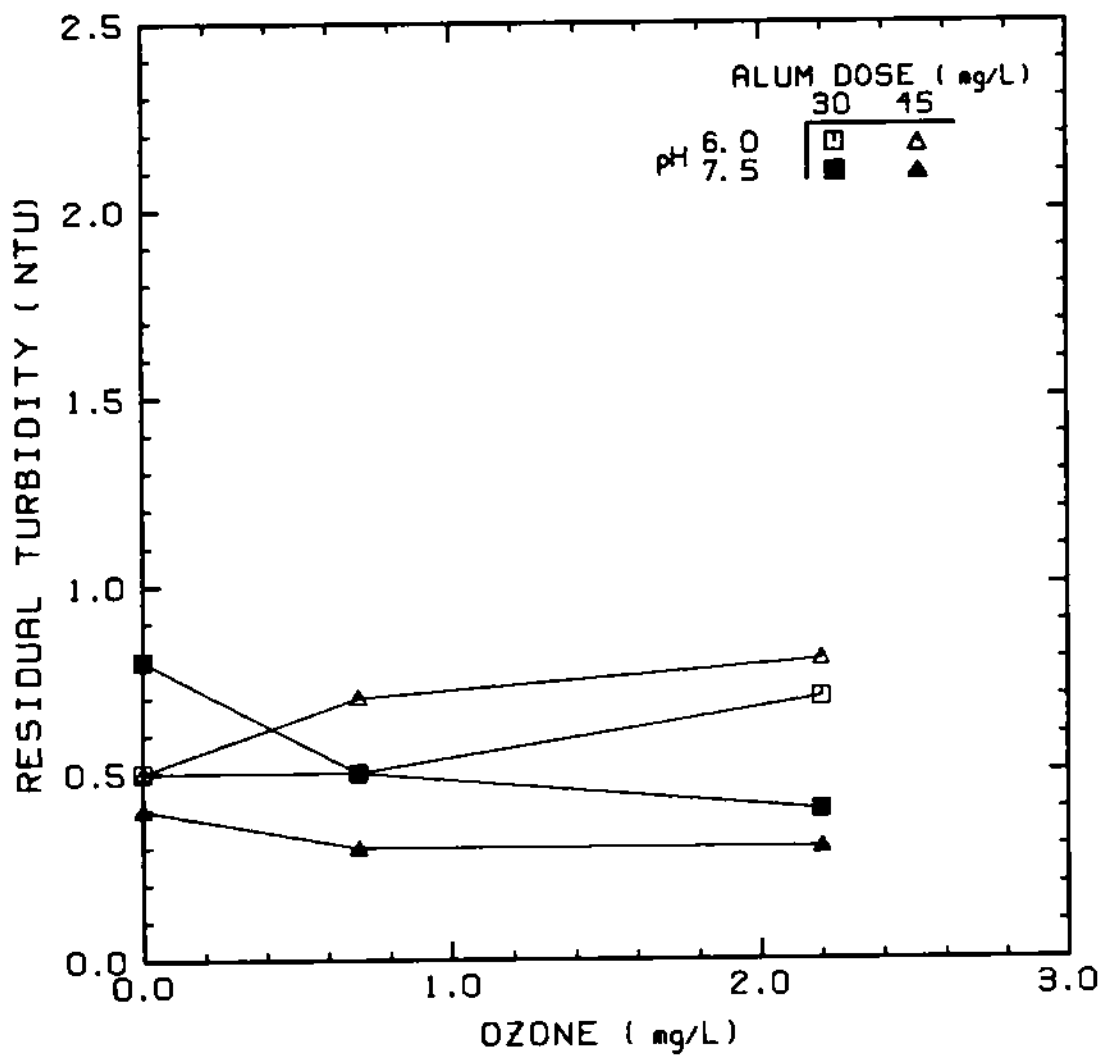


Figure 2. The Effect of Ozone Upon Turbidity Removal (Initial Turbidity: 3.0 NTU at pH 7.5, 2.5 NTU at pH 6.0).

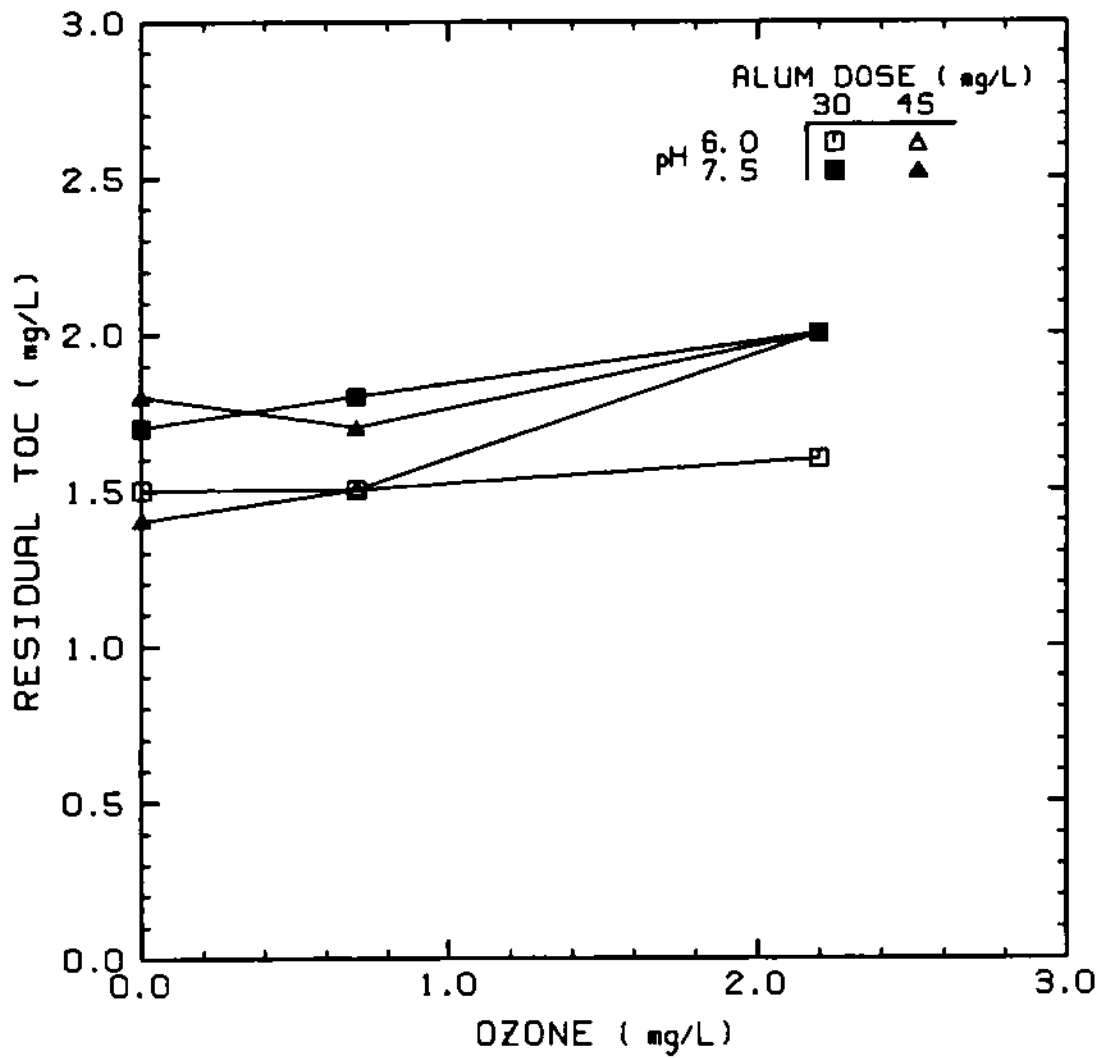


Figure 3. The Effect of Ozone Upon TOC Removal (Initial TOC: 2.7 mg/L at pH 6.0, 2.4 mg/L. at pH 7.5).

*Color Removal:* Figure 4 presents data showing the effects of ozone upon color removal. Solution pH appeared to have a role in color removal, especially under conditions of high ozone application. The inhibition of color removal was noted at a solution pH of 6.0, while enhanced color removal was evident at pH 7.5. Lower ozone doses tended to have little effect upon color removal. Finally, the higher alum dose of 45 mg/L at pH 6.0 apparently was inhibitory to color removal. (Note: It should be pointed out that color is reported as apparent color as opposed to true color.)

*Manganese(II) Removal:* Ozone dose had a significant impact upon Mn(II) removal as reported in Figures 5 and 6. Under both pH conditions, increased Mn(II) removal was observed with increasing ozone dose. Results presented in Figure 5 indicate that initial TOC inhibited the effectiveness of ozone for Mn(II) oxidation.

## **Potassium Permanganate**

*Turbidity Removal:* Figures 7 and 8 summarize the effects of potassium permanganate upon turbidity removal. Results presented in Figure 7 show the effectiveness of potassium permanganate may be related to initial turbidity levels. Turbidity removal was much better when the initial turbidity was > 6 NTU. However, turbidity removal from samples with initial turbidities below 4 NTU was inhibited by the application of potassium permanganate. Figure 8 presents results indicating that solution pH had no apparent effect upon turbidity removal.

*TOC Removal:* The effects of potassium permanganate upon TOC removal are presented in Figures 9 and 10. Potassium permanganate did not affect the removal of TOC at dosages up to 2 mg/L.

*Color Removal:* Increasing oxidant dose tended to inhibit color removal as may be seen in Figures 11 and 12. Results shown in Figure 11 indicate that the application of potassium permanganate in a treated water sample on occasion resulted in increased unfiltered color levels than were initially present in the raw water. Results from Figure 12 indicate that alum dose had little impact upon color removal. In addition, higher doses of potassium permanganate were found to increase residual apparent color levels.



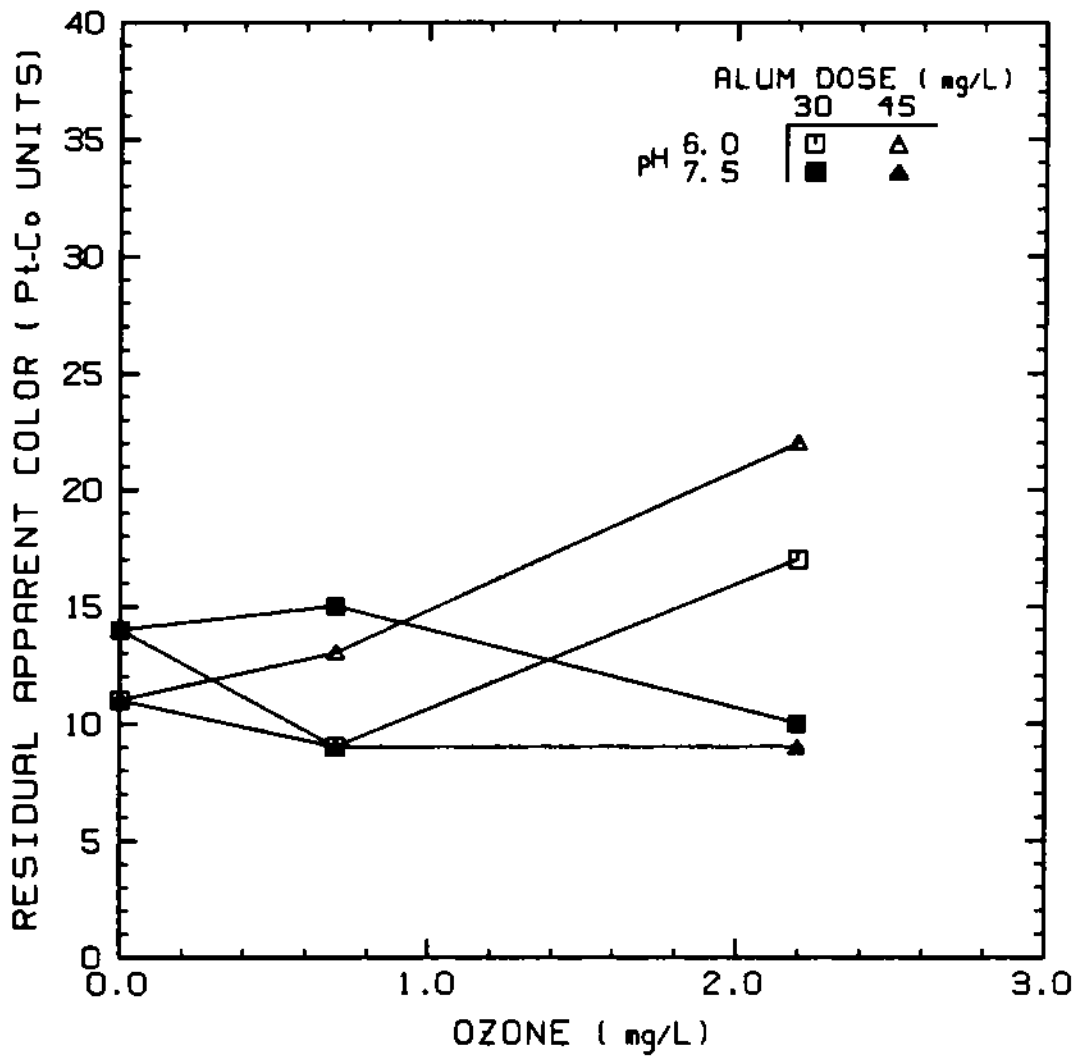


Figure 4. The Effect of Ozone Upon Color Removal (Initial Color: 100 Pt-Co Units at pH 6.0, 74 Pt-Co Units at pH 7.5).

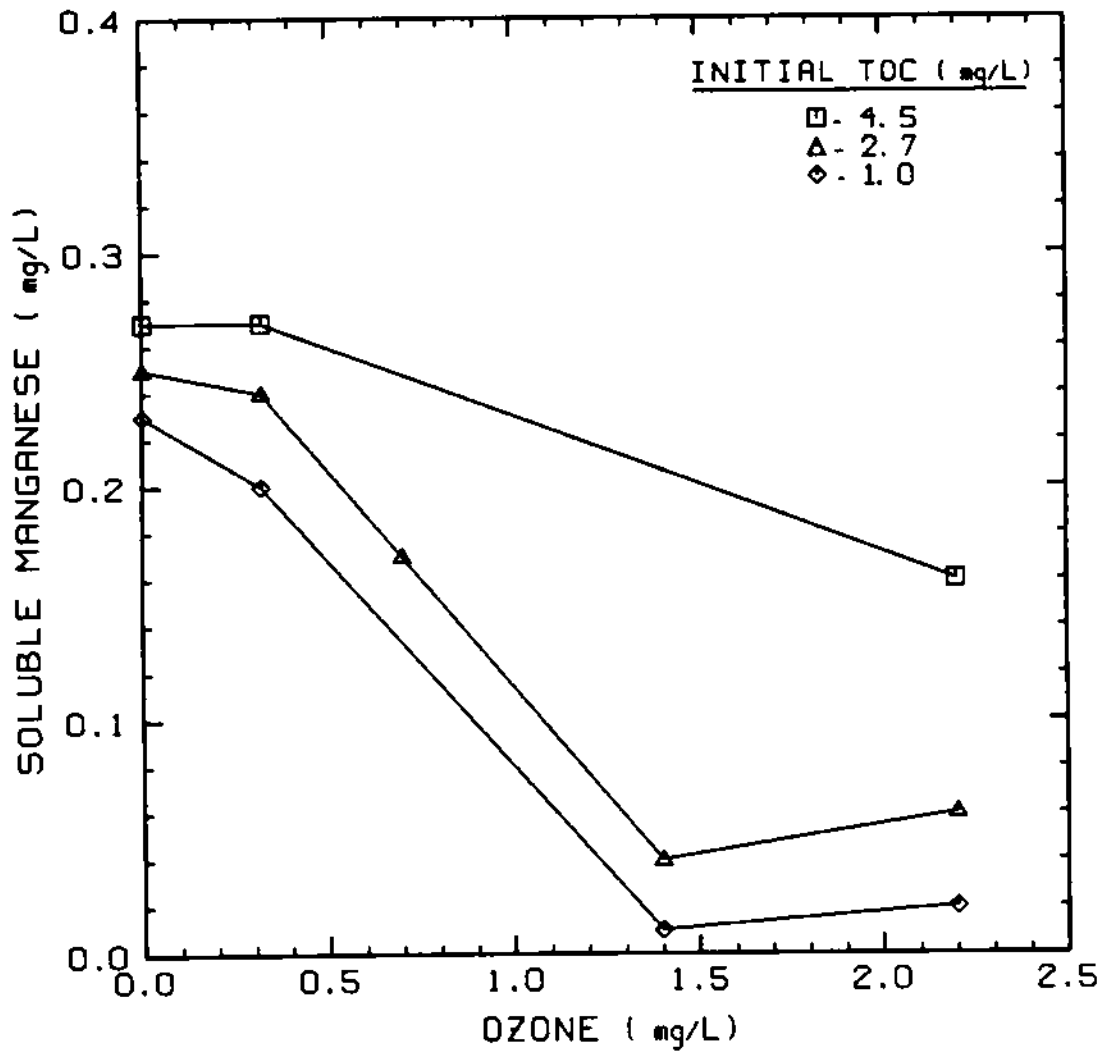


Figure 5. The Effect of Ozone Upon Reduced Manganese Removal Coagulated at pH 6.0.

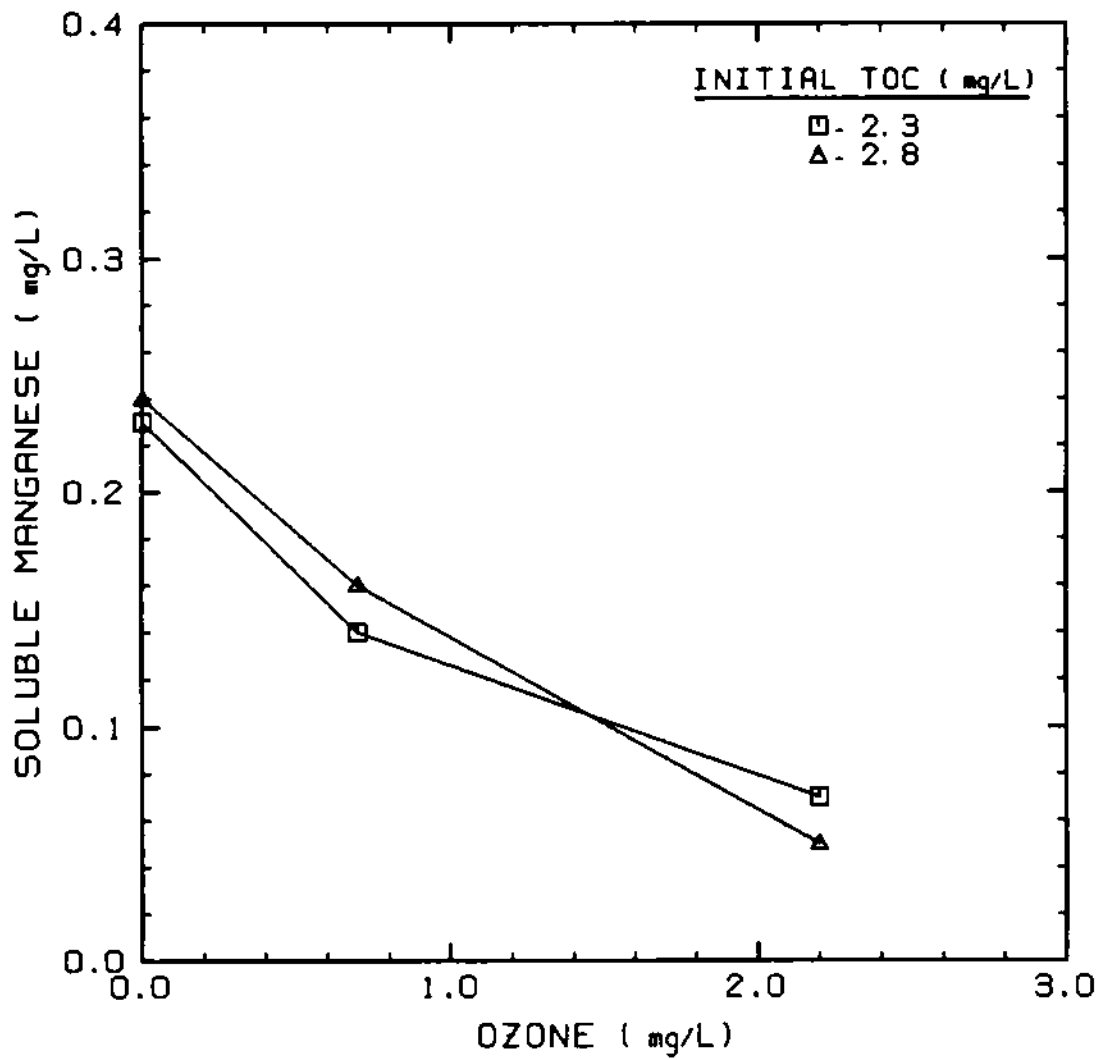


Figure 6. The Effect of Ozone Upon Reduced Manganese Removal Coagulated at pH 7.5.

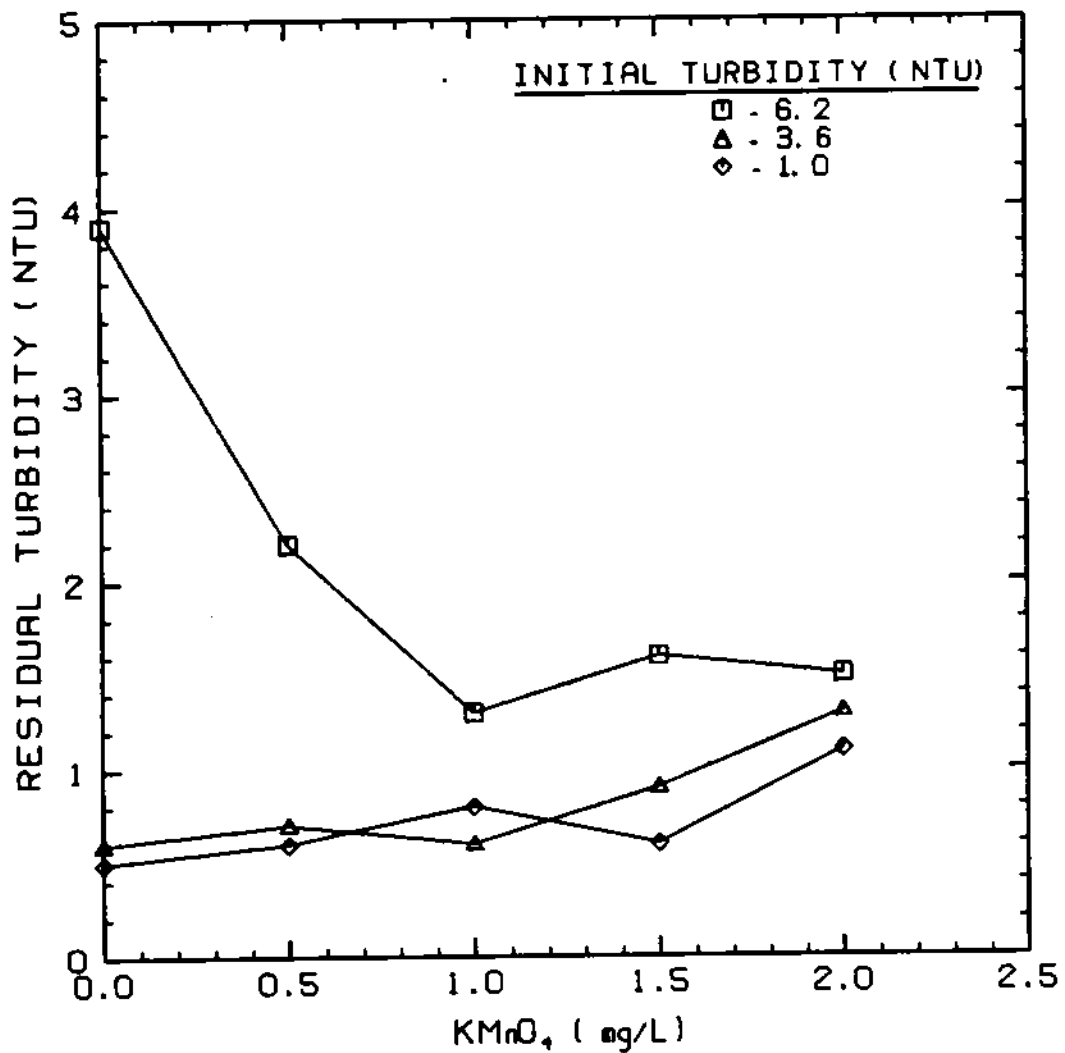


Figure 7. The Effect of Potassium Permanganate Upon Turbidity Removal Coagulated at pH 6.0 with 30 mg/L Alum.

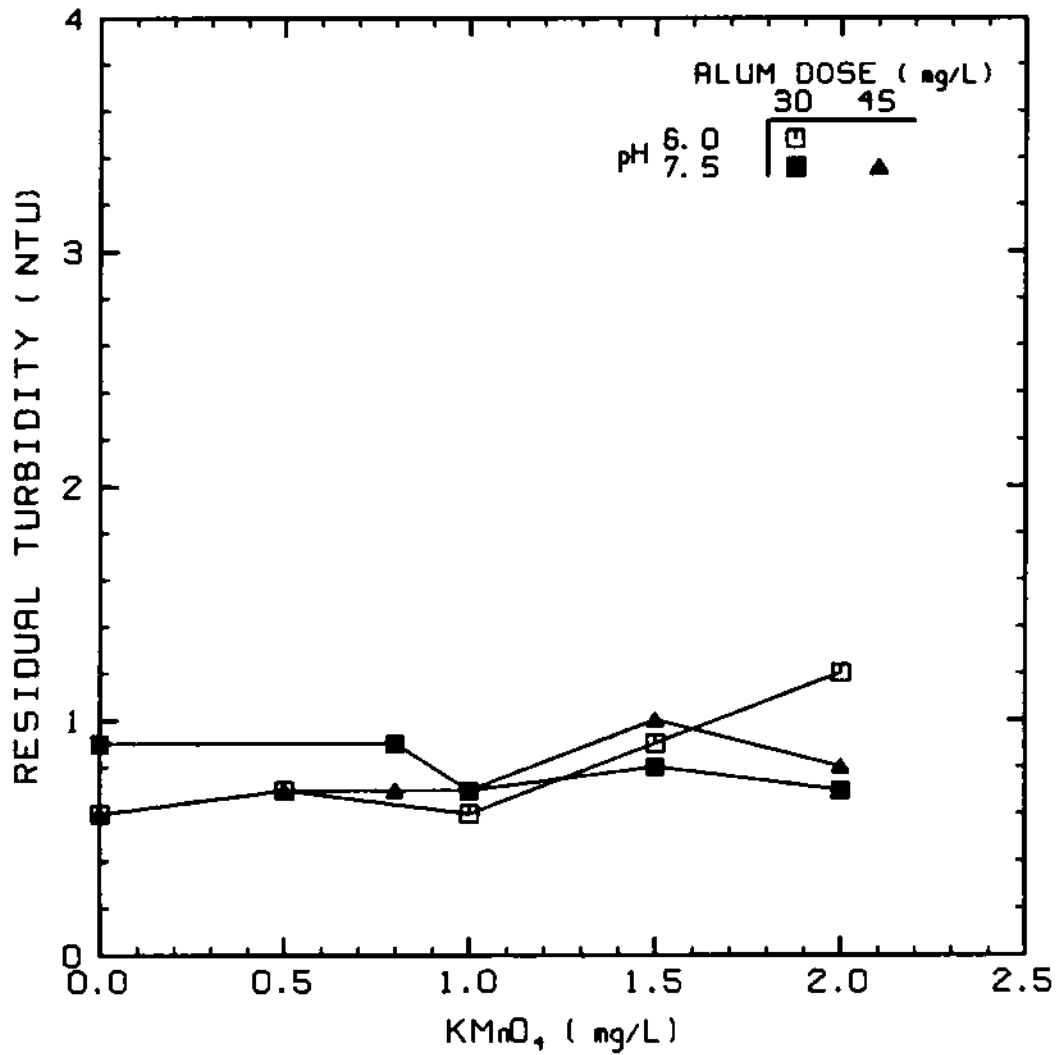


Figure 8. The Effect of Potassium Permanganate Upon Turbidity Removal with Various Alum Doses and pH (Init. Turb.: 3.9 NTU at pH 7.5 and 30 mg/L alum, 3.0 NTU at pH 7.5 and 45 mg/L alum, 1.0 NTU at pH 6.0).

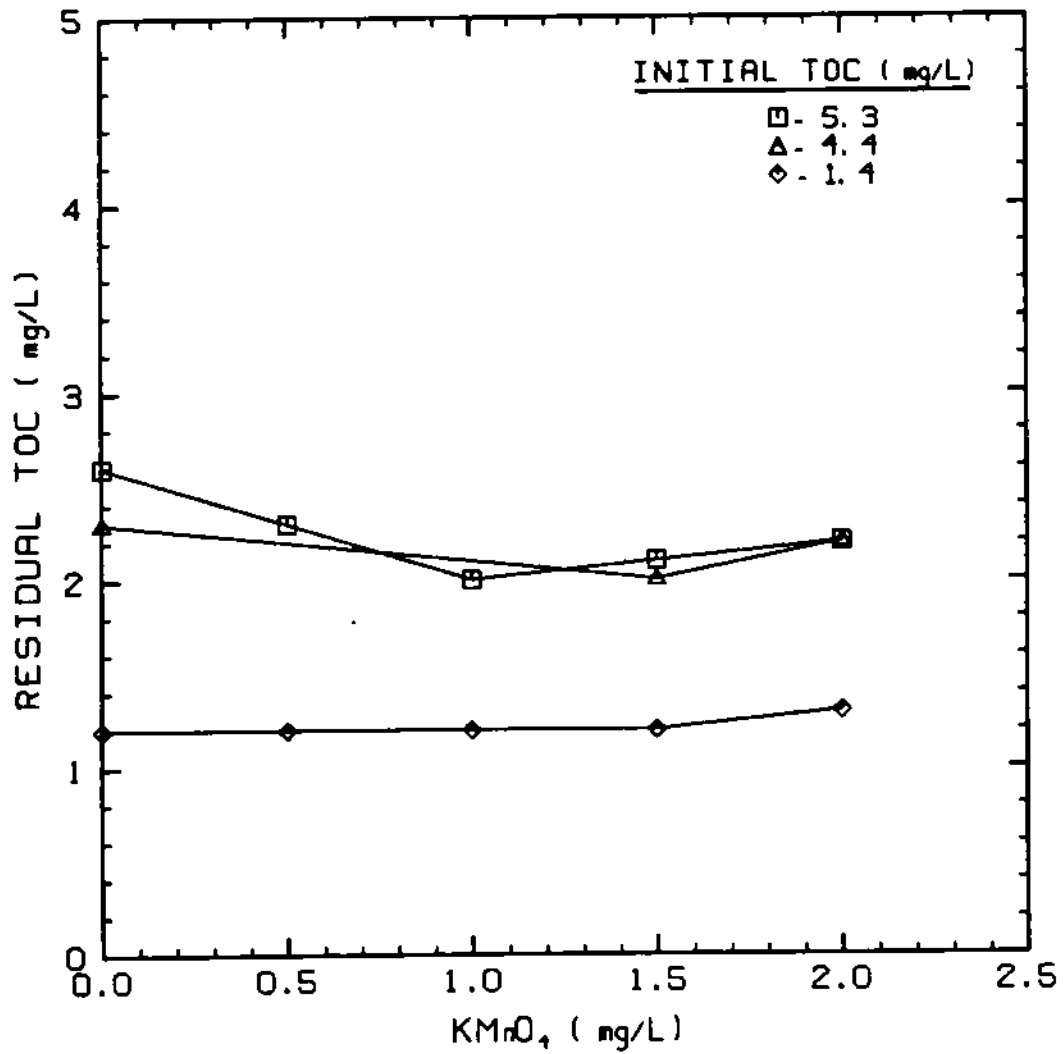


Figure 9. The Effect of Potassium Permanganate Upon TOC Removal Coagulated at pH 6.0 with 30 mg/L Alum.

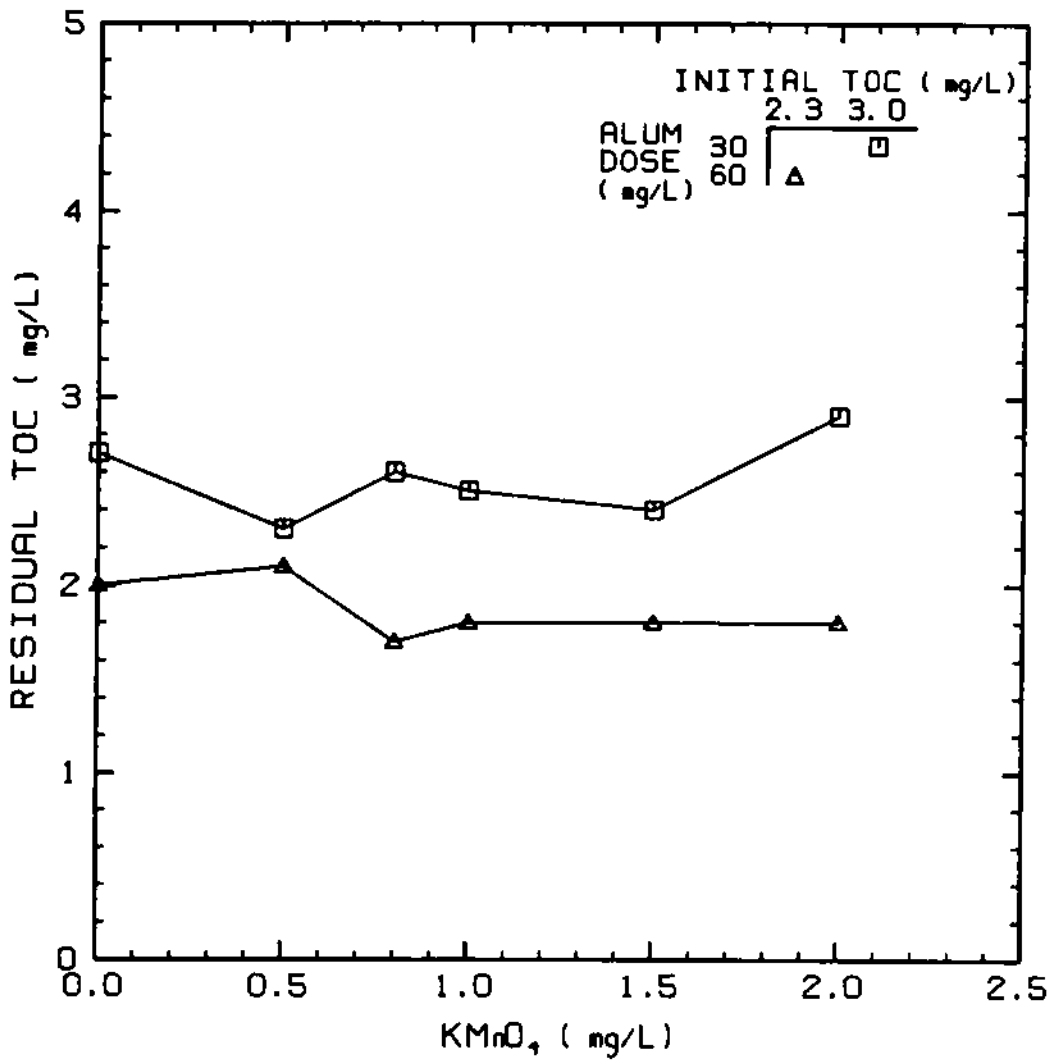


Figure 10. The Effect of Potassium Permanganate Upon TOC Removal at pH 7.5.

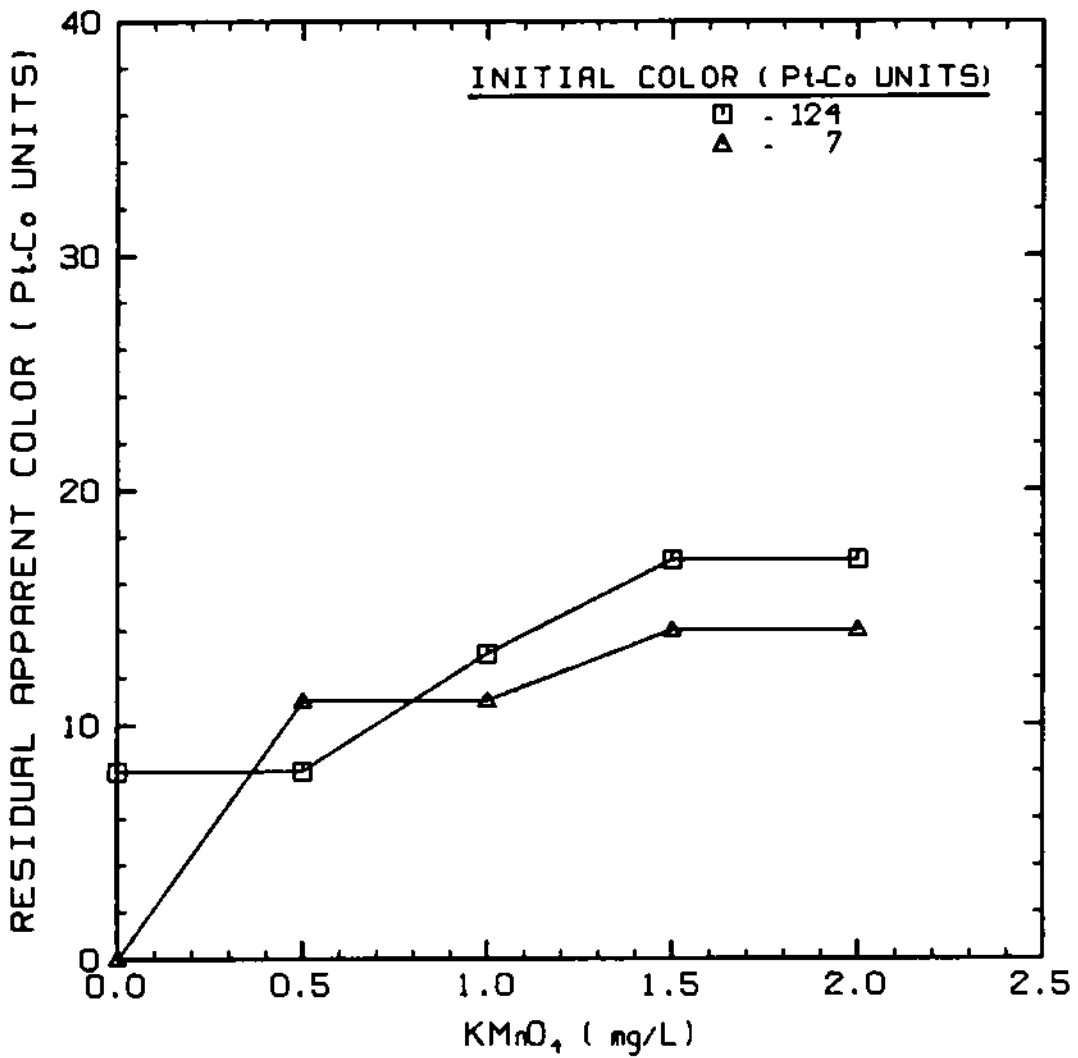


Figure 11. The Effect of Potassium Permanganate Upon Color Removal Coagulated at pH 6.0 with 30 mg/L Alum.



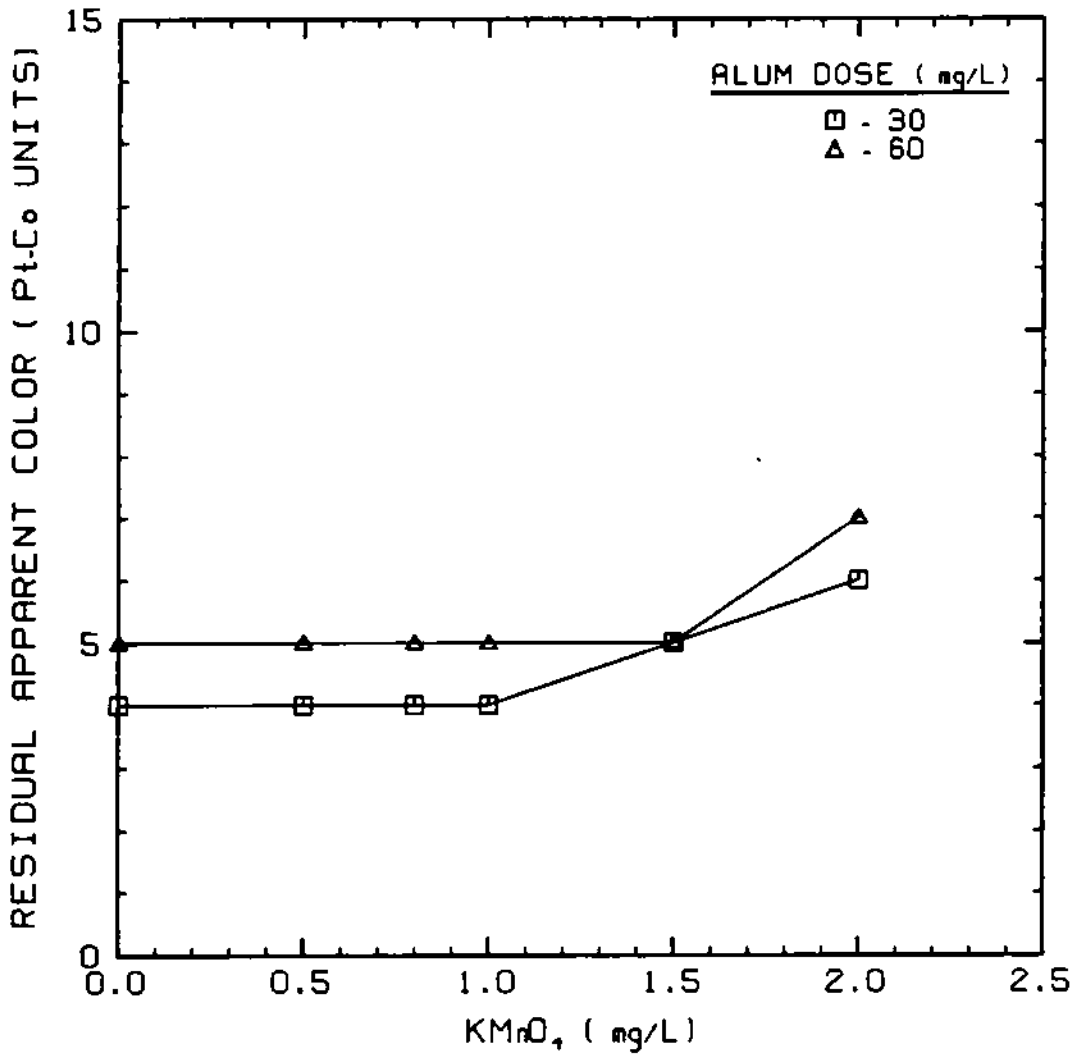


Figure 12. The Effect of Potassium Permanganate Upon Color Removal Coagulated at pH 7.5 (Average Initial Color: 90 Pt-Co Units).

*Manganese Removal:* Figure 13 and Figure 14 summarize the effects of potassium permanganate upon Mn(II) oxidation. Under both pH conditions, potassium permanganate was observed to effectively oxidize Mn(II). Figure 13 presents the impact of initial TOC upon Mn(II) removal. In the case of low initial TOC, an increase in soluble manganese was noted when the oxidant application exceeded 1.5 mg/L. This was likely due to excess potassium permanganate that remained unreacted.

## **Chlorine Dioxide**

*Turbidity Removal:* Figure 15 summarizes the effects of chlorine dioxide upon turbidity removal. Results indicated that chlorine dioxide either did not affect or slightly inhibited turbidity removal.

*TOC Removal:* No apparent trends were noted relating chlorine dioxide and TOC removal as reported in Figure 16. TOC removal was favored at pH 6.0.

*Color Removal:* Figure 17 summarizes the effects of chlorine dioxide upon color removal. Results indicated that chlorine dioxide dosages up to 2mg/L inhibited color removal under conditions of low initial color. This effect was to be minimal under conditions of extremely high initial color. In addition, increased color removal occurred in the cases in which a solution pH of 6.0 was investigated.

*Manganese(II) Removal:* Chlorine dioxide was found to be effective for Mn(II) oxidation under both pH conditions studied as shown in Figure 18. Slightly better Mn(II) removal was observed at pH 7.5. Results also indicated that increased initial TOC inhibited Mn(II) oxidation.

## **Chlorine**

*Turbidity Removal:* No conclusive trends were observed relating the effect of chlorine upon turbidity removal as illustrated in Figure 19. In general, turbidity removal was unaffected by the addition of varying doses of chlorine up to 4 mg/L.

*TOC Removal:* Figure 20 illustrates the effects of chlorine upon TOC removal. Results show that chlorine did not affect TOC removal under the conditions investigated.

*Color Removal:* The effects of chlorine upon color removal are summarized in Figure 21. Results show that chlorine had no apparent impact upon color removal.

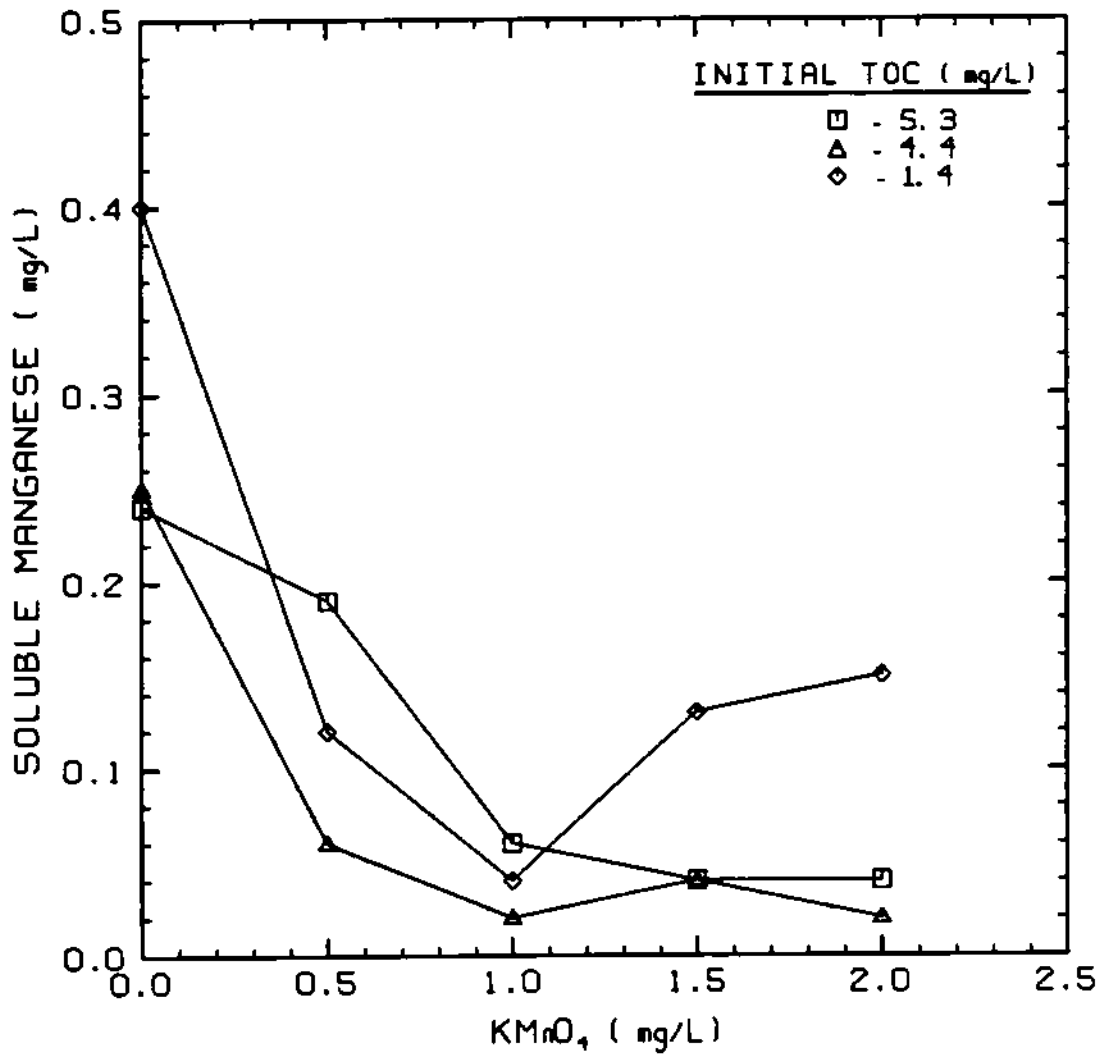


Figure 13. The Effect of Potassium Permanganate Upon Reduced Manganese Removal at pH 6.0.

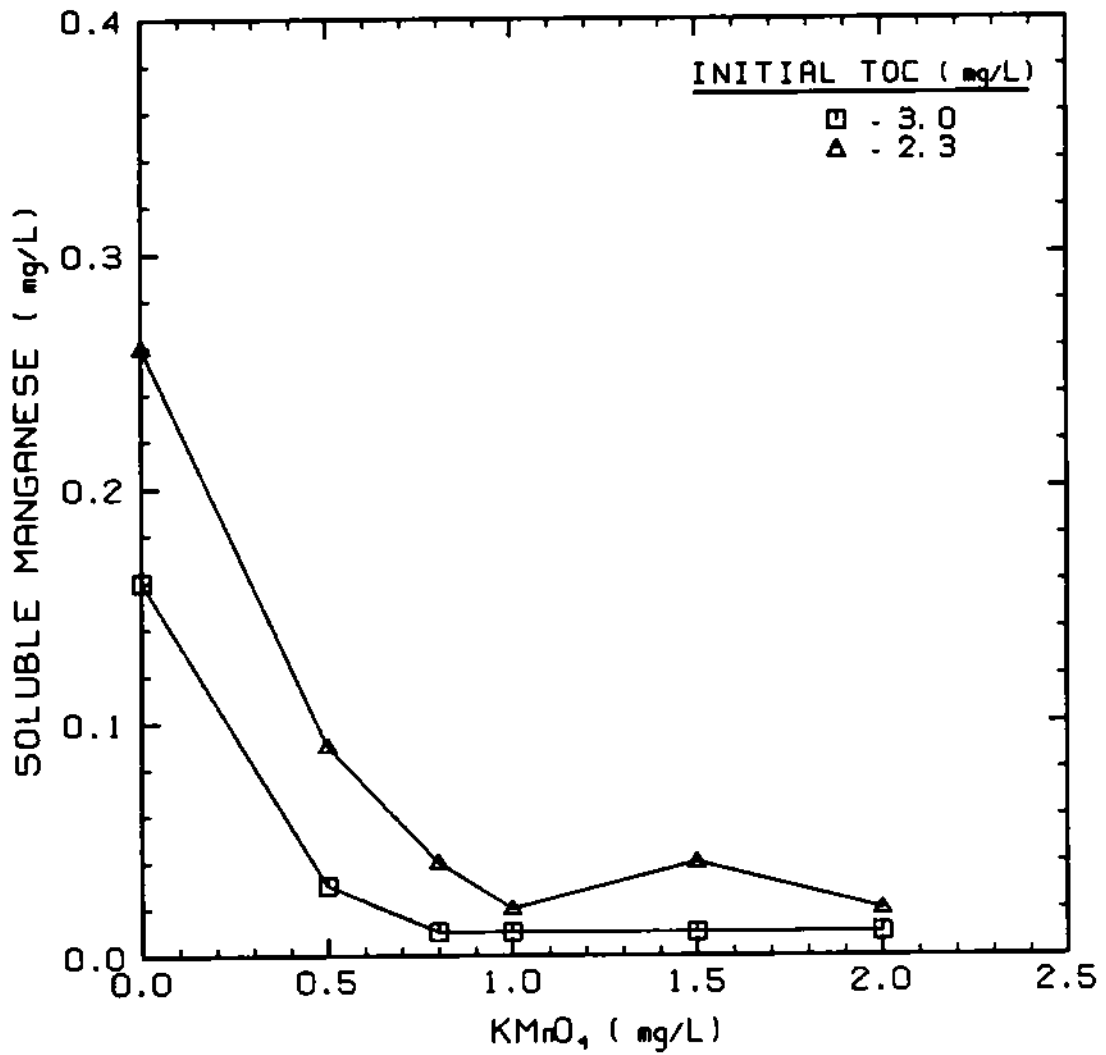


Figure 14. The Effect of Potassium Permanganate Upon Reduced Manganese Removal at pH 7.5.

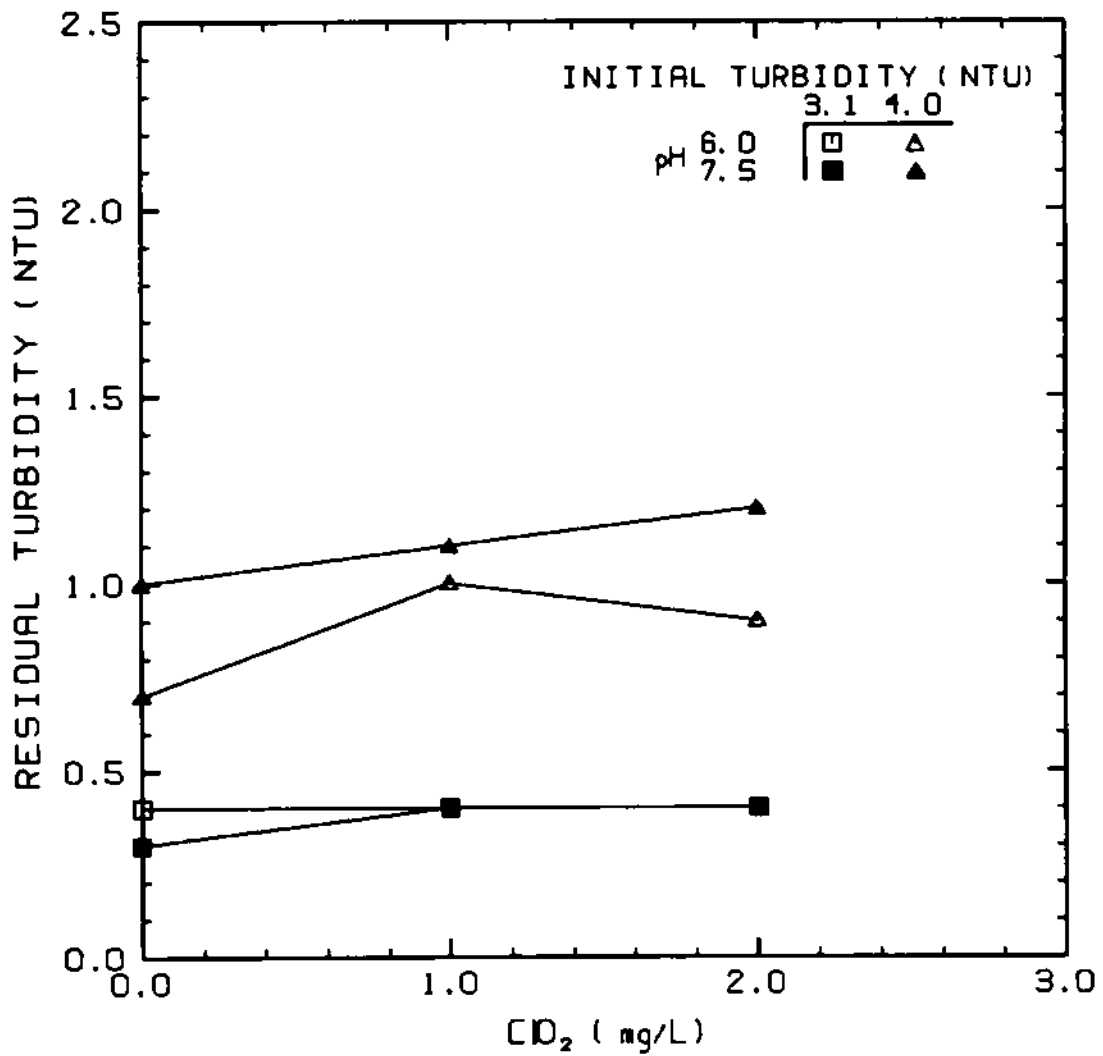


Figure 15. The Effect of Chlorine Dioxide Upon Turbidity Removal Coagulated with 30 mg/L Alum.

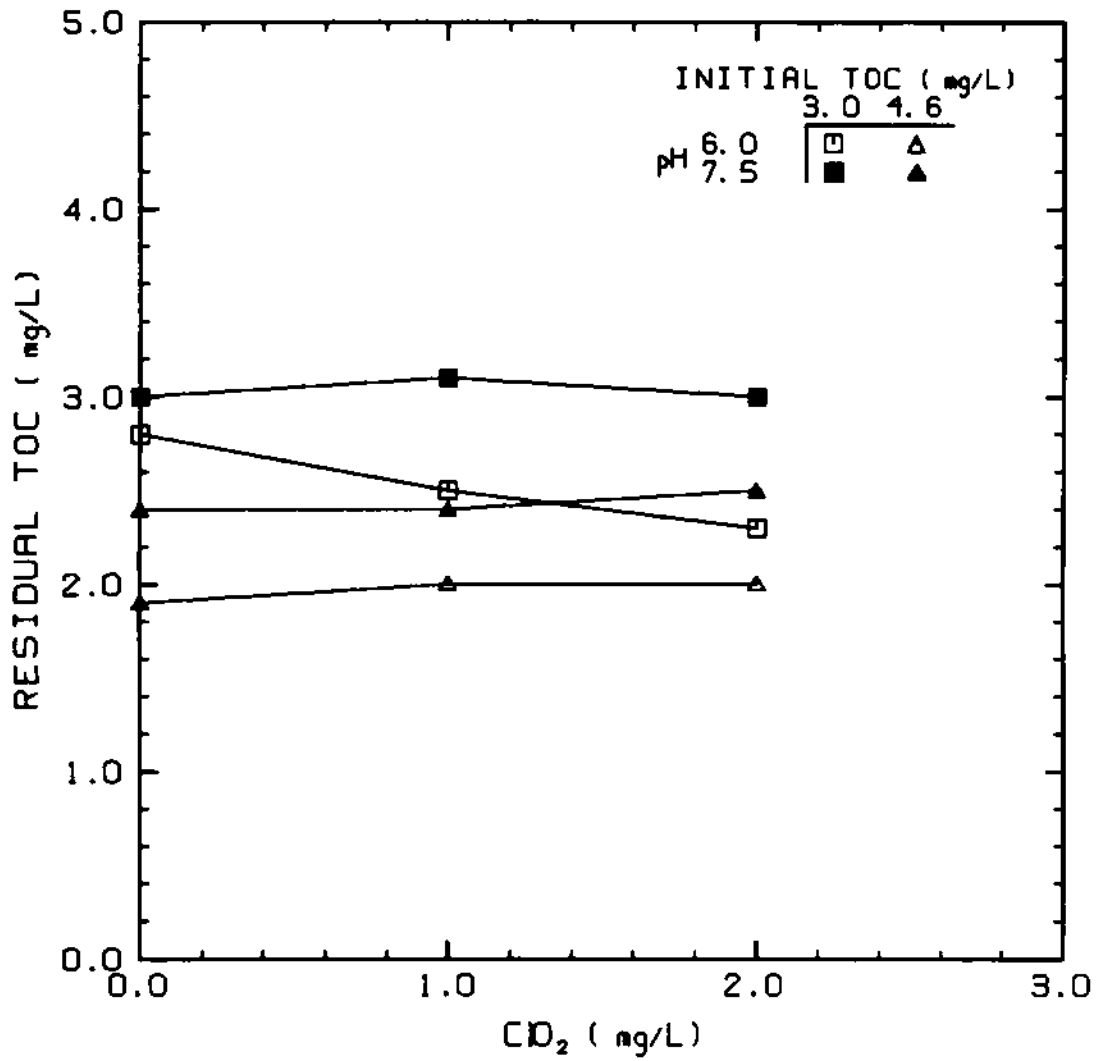


Figure 16. The Effect of Chlorine Dioxide Upon TOC Removal Coagulated with 30 mg/L Alum.

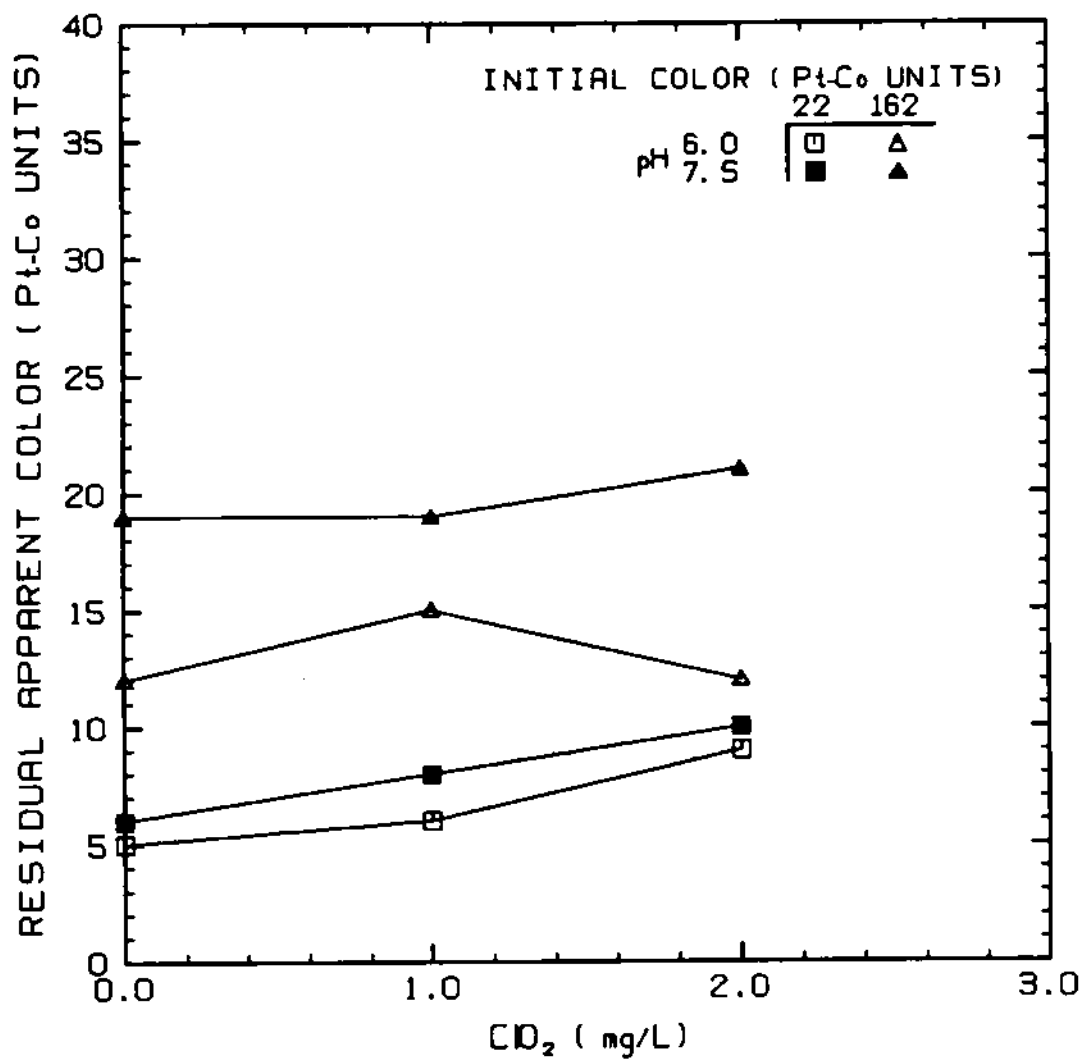


Figure 17. The Effect of Chlorine Dioxide Upon Color Removal Coagulated with 30 mg/L Alum.

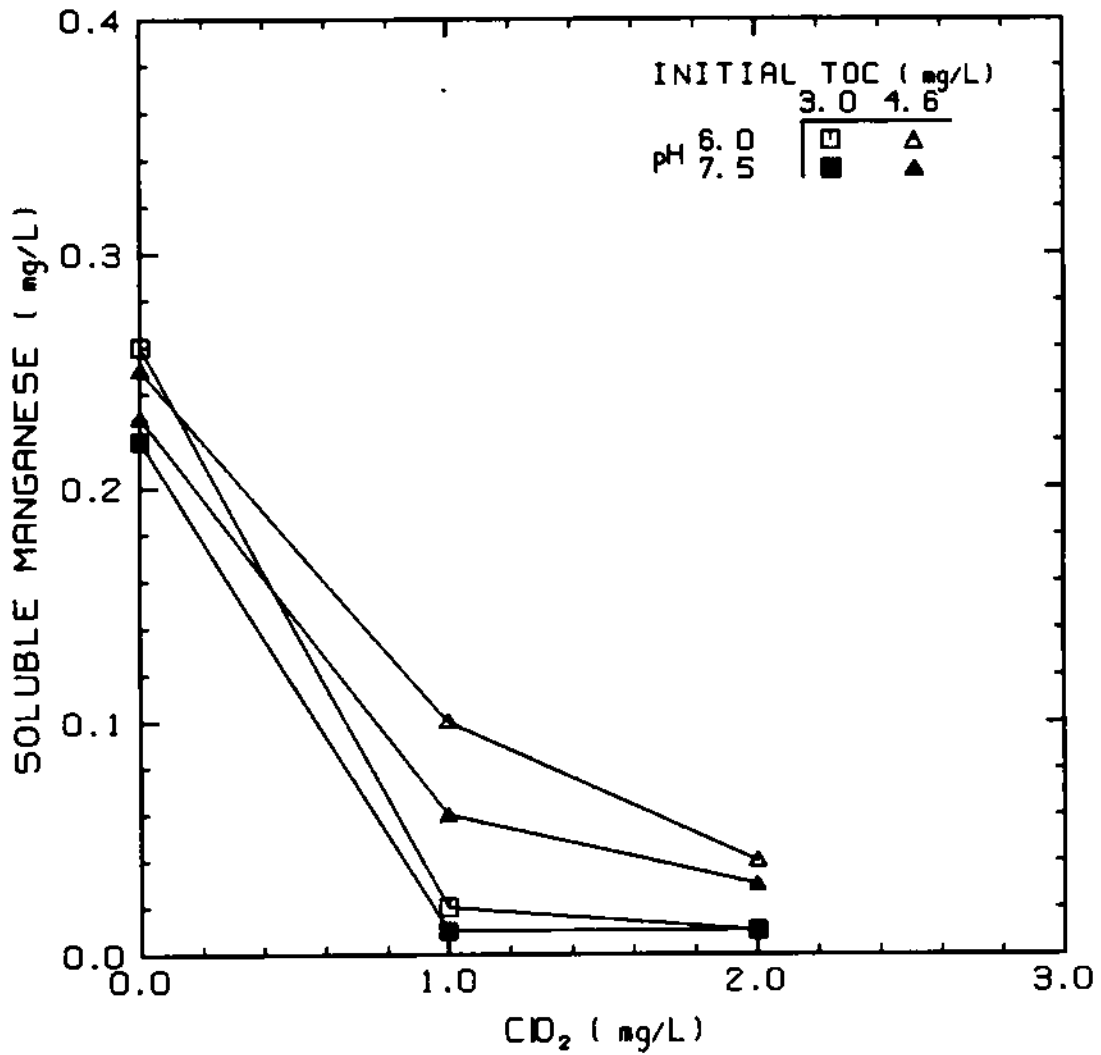


Figure 18. The Effect of Chlorine Dioxide Upon Reduced Manganese Removal Coagulated with 30 mg/L Alum.



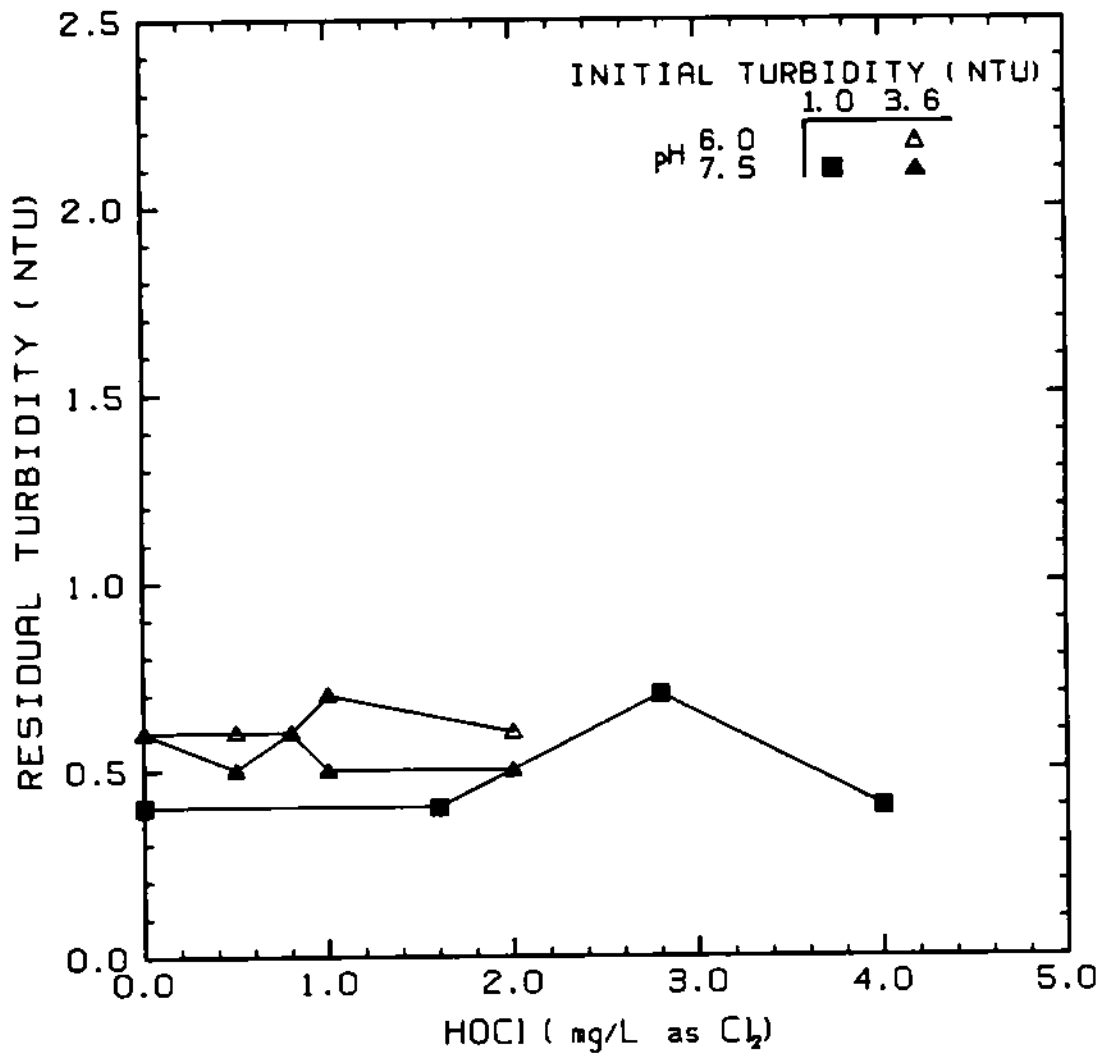


Figure 19. The Effect of Chlorine Upon Turbidity Removal Coagulated with 30 mg/L Alum.

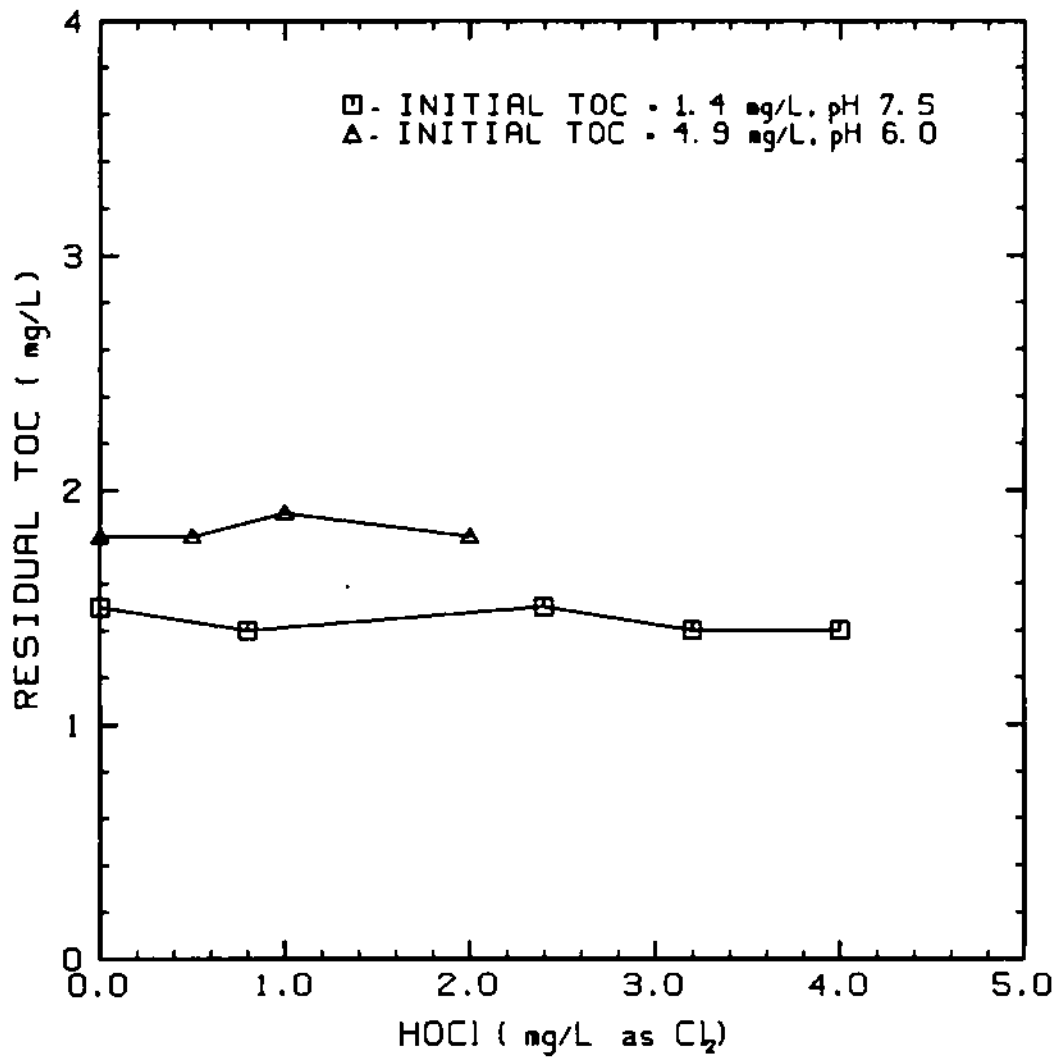


Figure 20. The Effect of Chlorine Upon TOC Removal Coagulated with 30 mg/L Alum.

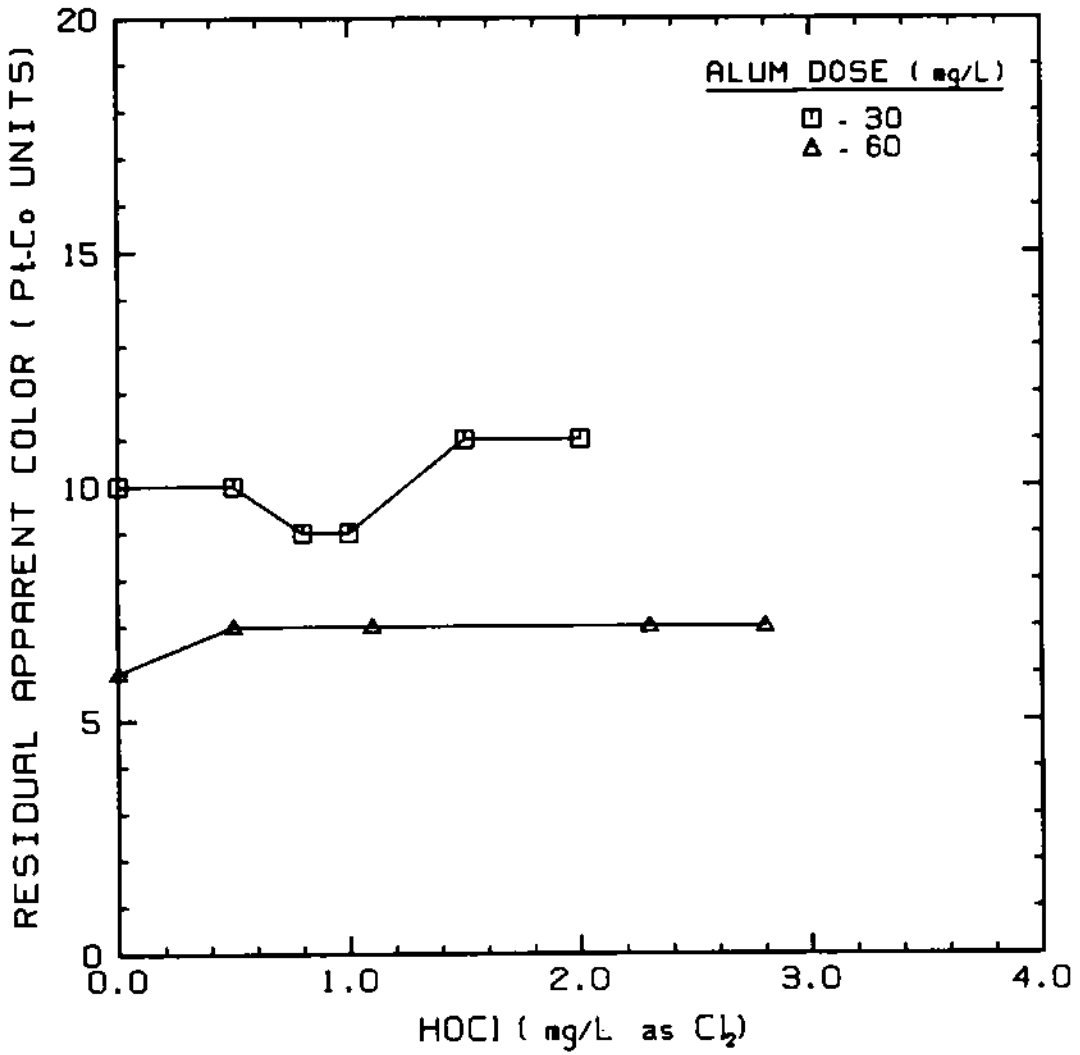


Figure 21. The Effect of Chlorine Upon Color Removal Coagulated at pH 7.5 (Average Initial Color: 115 Pt-Co Units).

*Manganese(II) Removal:* Solution pH had a significant impact upon the efficiency of Mn(II) oxidation with chlorine. Figure 22 shows that enhanced Mn(II) removal, in general, was found with increasing pH. Even so, significant oxidation of Mn(II) was not observed for doses up to 3 mg/L to effectively control reduced manganese.

## ***Particle Size Distribution Studies***

### **Studies Without Coagulant**

Attempts were made to verify that microfloculation occurs when water is dosed with ozone. Figure 23 illustrates the results of a time study conducted with raw water and 2.2 mg/L O<sub>3</sub>. A raw water with a high initial turbidity of 12 NTU was chosen in hopes of better identifying the effects of microfloculation. As can be seen over the time period, microfloculation was not observed. Monitoring residual turbidity over the study period showed that no net changes in turbidity resulted from the application of ozone.

Figure 24 presents the temporal effects of potassium permanganate upon the size distribution of particles in raw water. Results show that the contact with potassium permanganate for 30 minutes shifted particles from the smaller ranges toward the larger ranges. A net decrease in particle concentration was observed below an average mean diameter of 18.8  $\mu\text{m}$ , while an increase in particles was noted above this size.

Figure 25 illustrates the results of a time study performed with 2 mg/L HOCl as Cl<sub>2</sub> upon particle size distributions. Results indicate that the presence of chlorine had the effect of breaking-up larger particles into smaller particles. A significant reduction of particles above 12  $\mu\text{m}$  was observed after a 15 minute reaction period had elapsed, while an increase in particle concentrations was noted below 5  $\mu\text{m}$ .

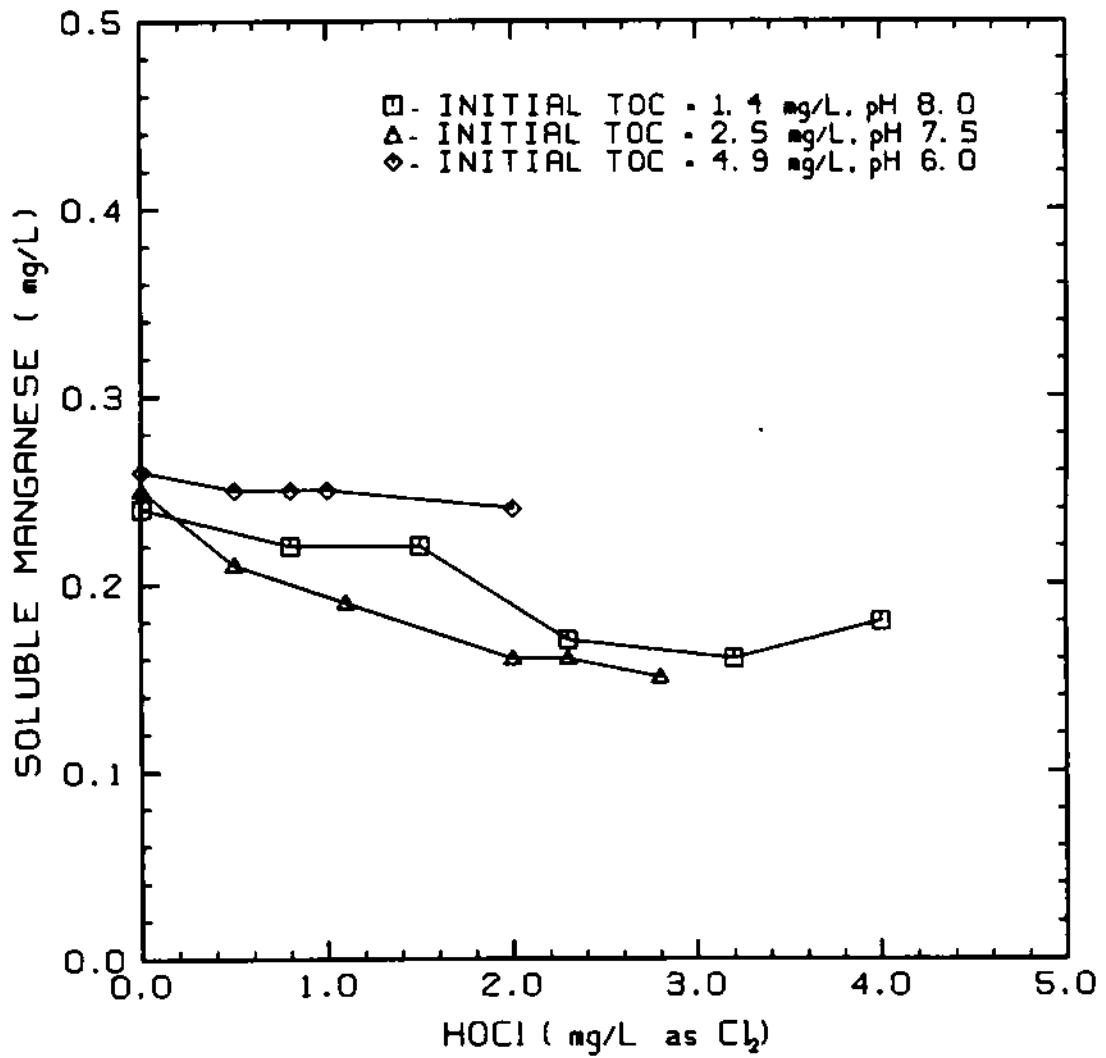


Figure 22. The Effect of Chlorine Upon Reduced Manganese Removal.

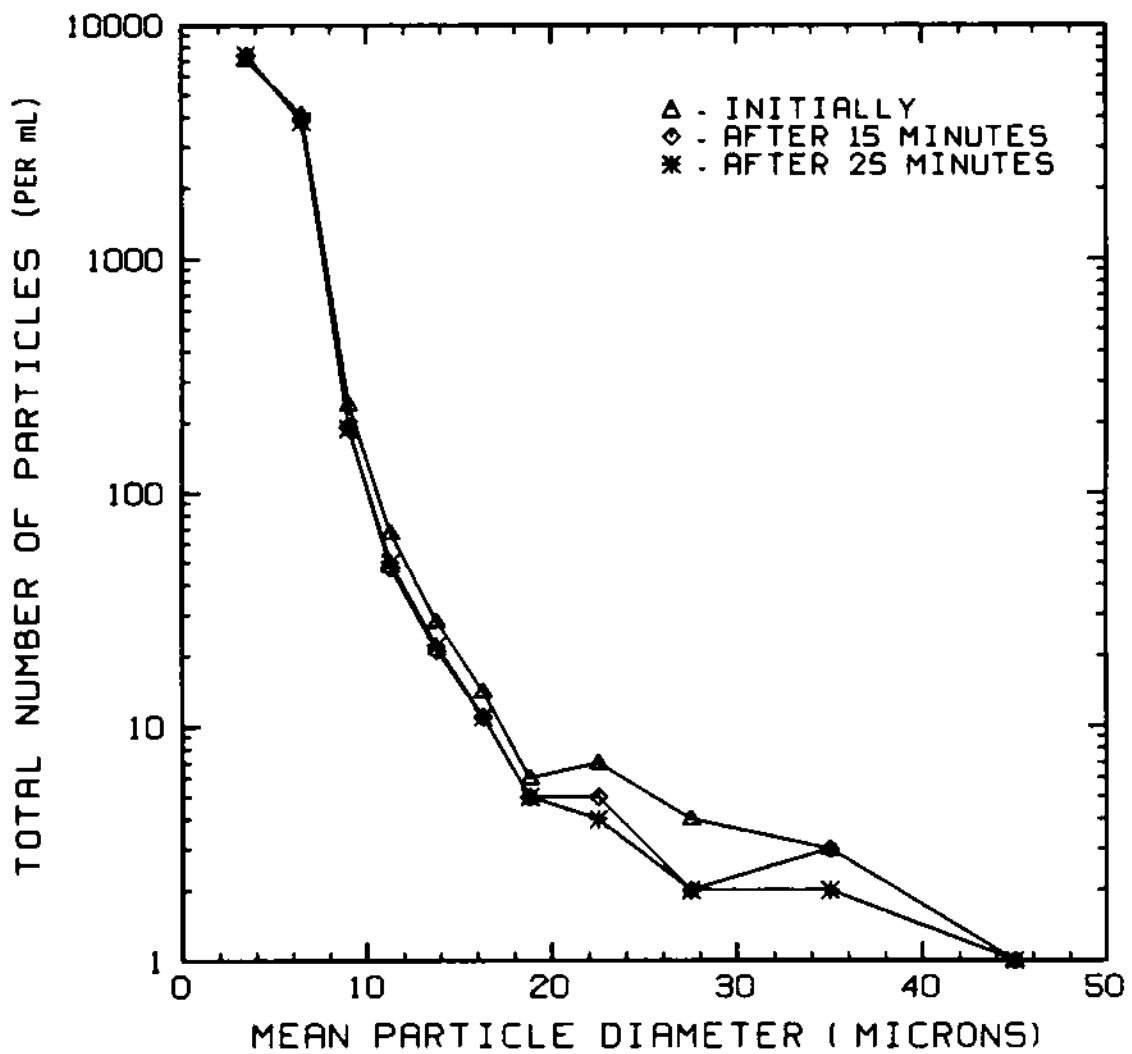


Figure 23. The Effect of 2.2 mg/L Ozone Upon Particle Size Distribution.

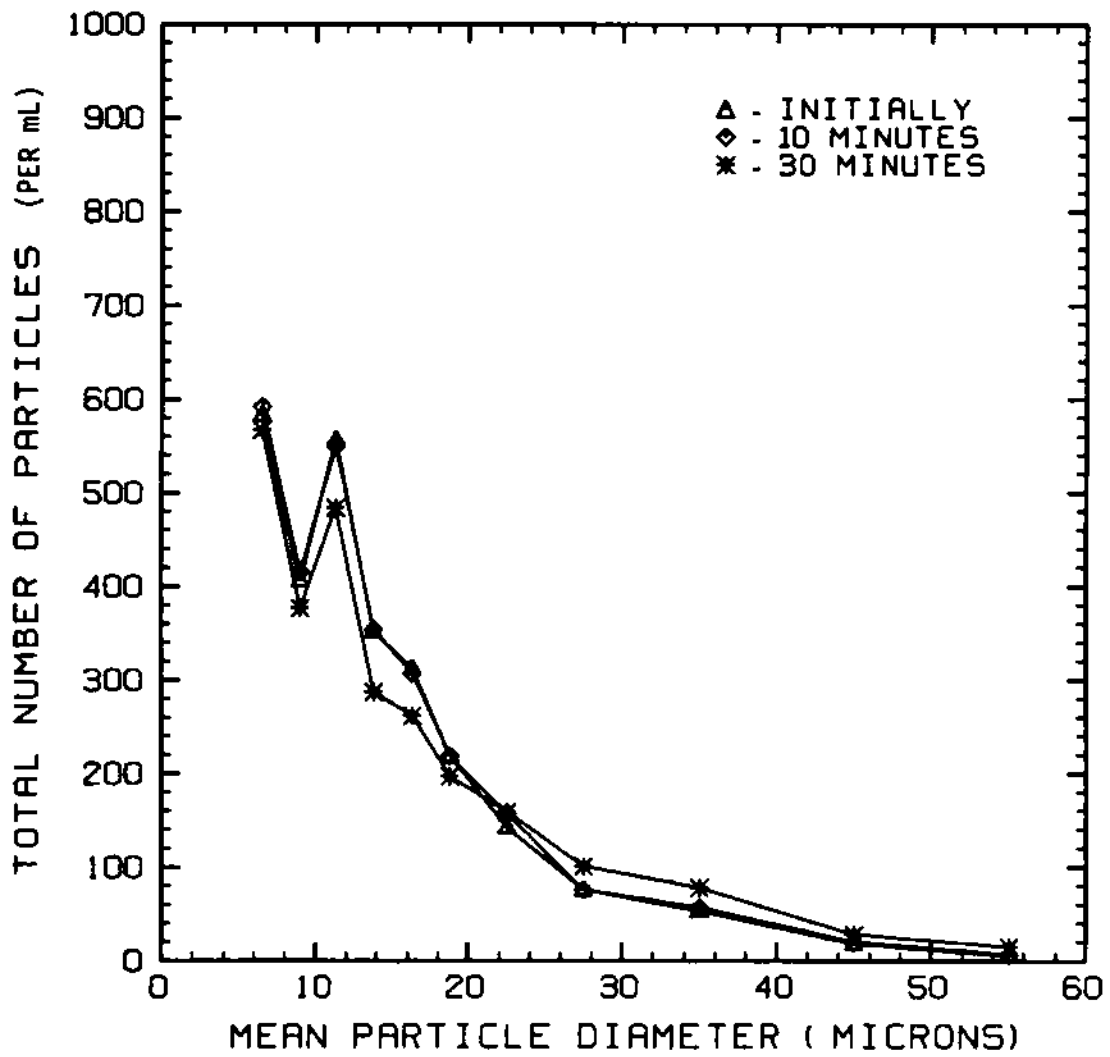


Figure 24. The Effect of 2.0 mg/L Potassium Permanganate Upon Particle Size Distribution.

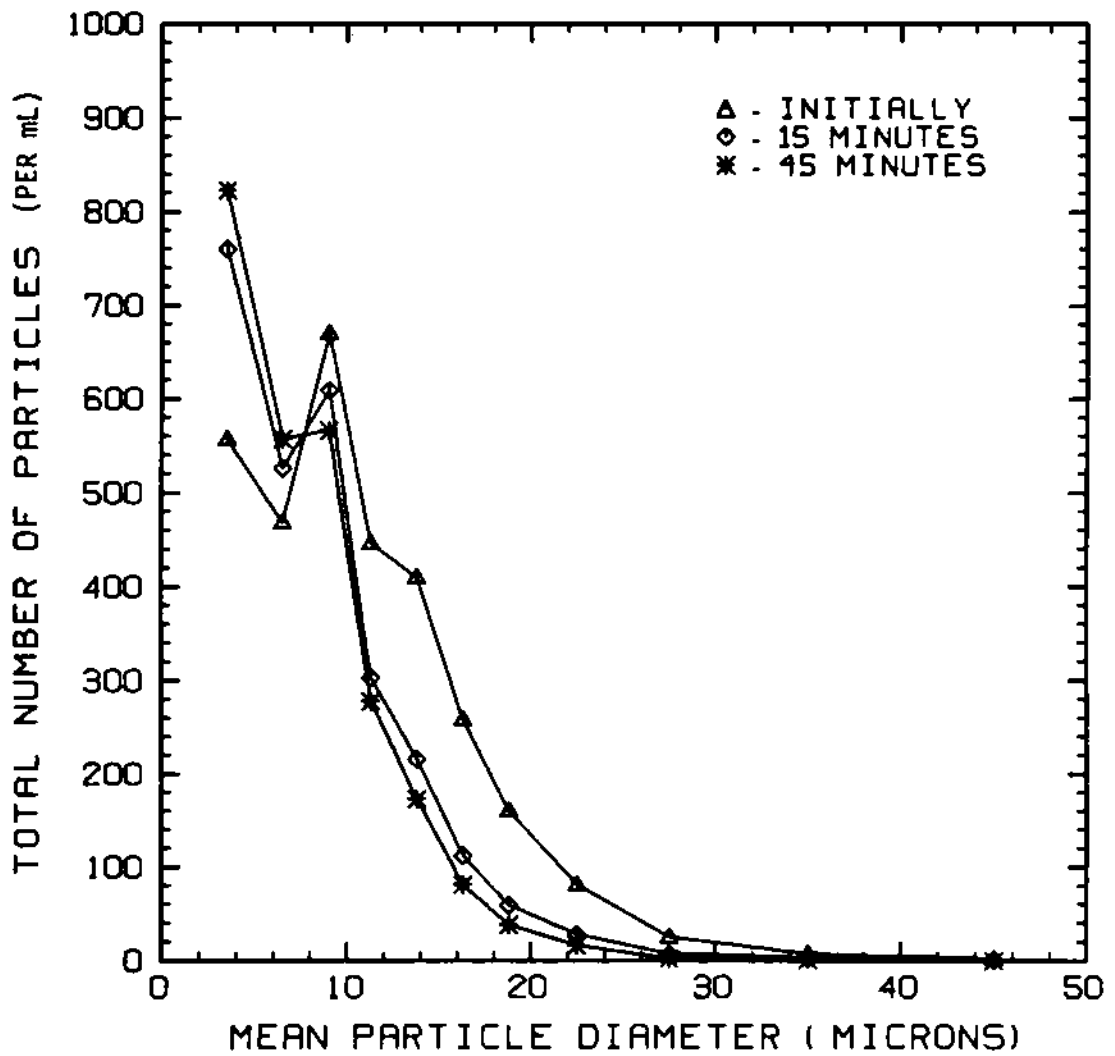


Figure 25. The Effect of 2.0 mg/L Chlorine as  $Cl_2$  Upon Particle Size Distribution.



## Studies With Coagulant

### *Ozone*

Figures 26 and 27 present the results of the effects of ozone upon particle size distributions during water treatment studies conducted at pH 6.0. Results of flocculated particle distribution studies shown in Figure 26 indicate that ozone increased particle counts within the smaller size ranges. Figure 27 indicates that particles within the smaller size ranges did not settle completely. A slight increase in settled turbidity was noted in the sample dosed with ozone.

### *Potassium Permanganate*

The effects of potassium permanganate upon particle distributions after flocculation and settling at pH 6.0 are shown in Figures 28 and 29. Figure 28 shows that after flocculation the majority of the particles were between 25  $\mu\text{m}$  and 45  $\mu\text{m}$ . Comparing particle size distributions from Figure 29 show that flocculation in the smaller size ranges continued during settling as can be seen in the cases of potassium permanganate application. Interestingly, residual turbidities may be partially explained by these particle distributions. Comparing data from Figure 29 show that the case in which potassium permanganate was not applied, particle concentrations were less than the other two cases in all size ranges. This suggests an explanation for it also having the lowest residual turbidity. Analyzing the other two cases in which potassium permanganate was applied revealed that particle concentrations were greater, leading to increased residual turbidities. A case may be made for a higher residual turbidity resulting from the higher dosing conditions due to an increase in particles over the entire range of sizes.

Figures 30 and 31 present the impacts of potassium permanganate upon particle distributions after flocculation and settling at pH 7.5. Comparing both graphs shows that flocculation during settling was observed. This result was most obvious in the case of the highest applied

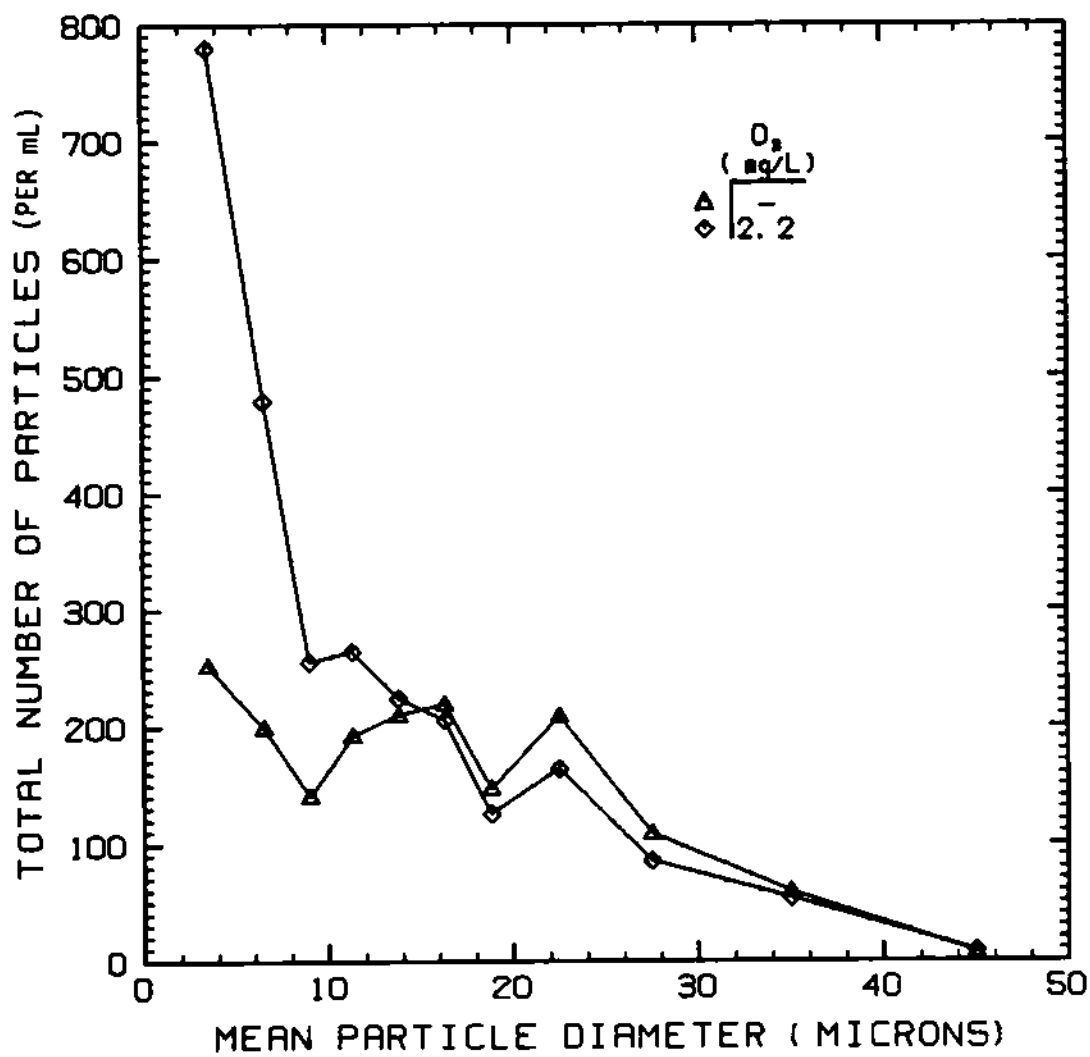


Figure 26. The Effect of Ozone Upon Flocculated Particle Size Distribution at pH 6.0.

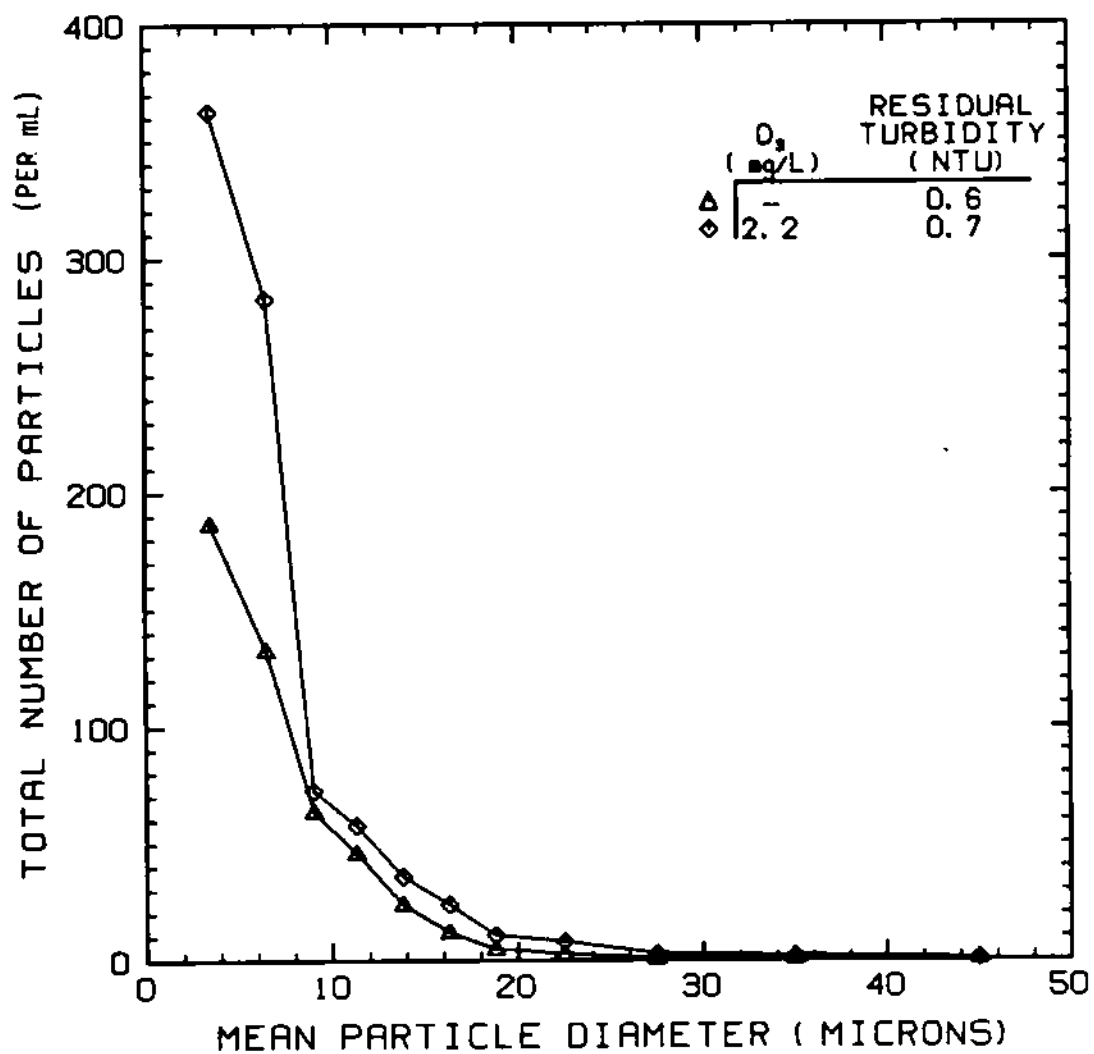


Figure 27. The Effect of Ozone Upon Settled Particle Size Distribution at pH 6.0.

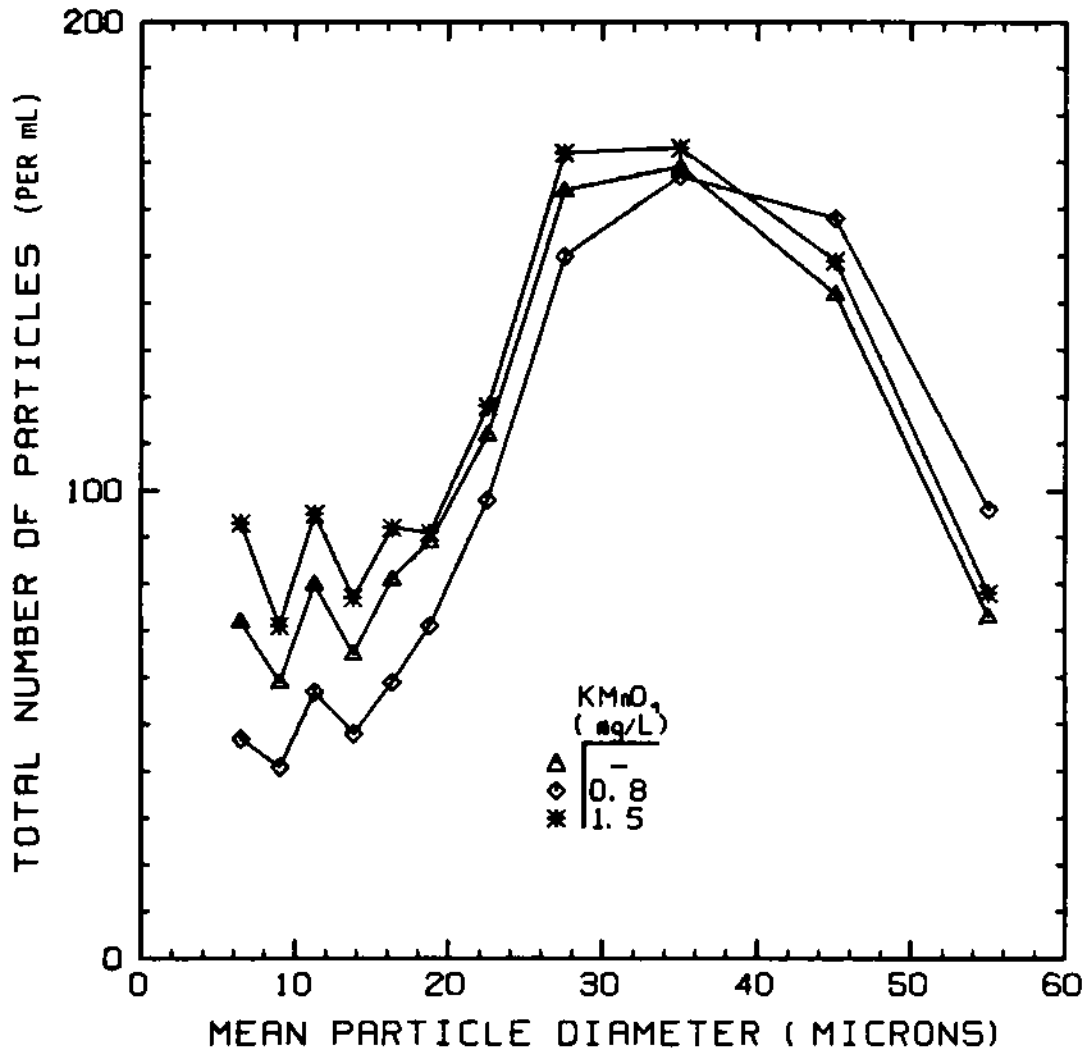


Figure 28. The Effect of Potassium Permanganate Upon Flocculated Particle Size Distribution at pH 6.0.

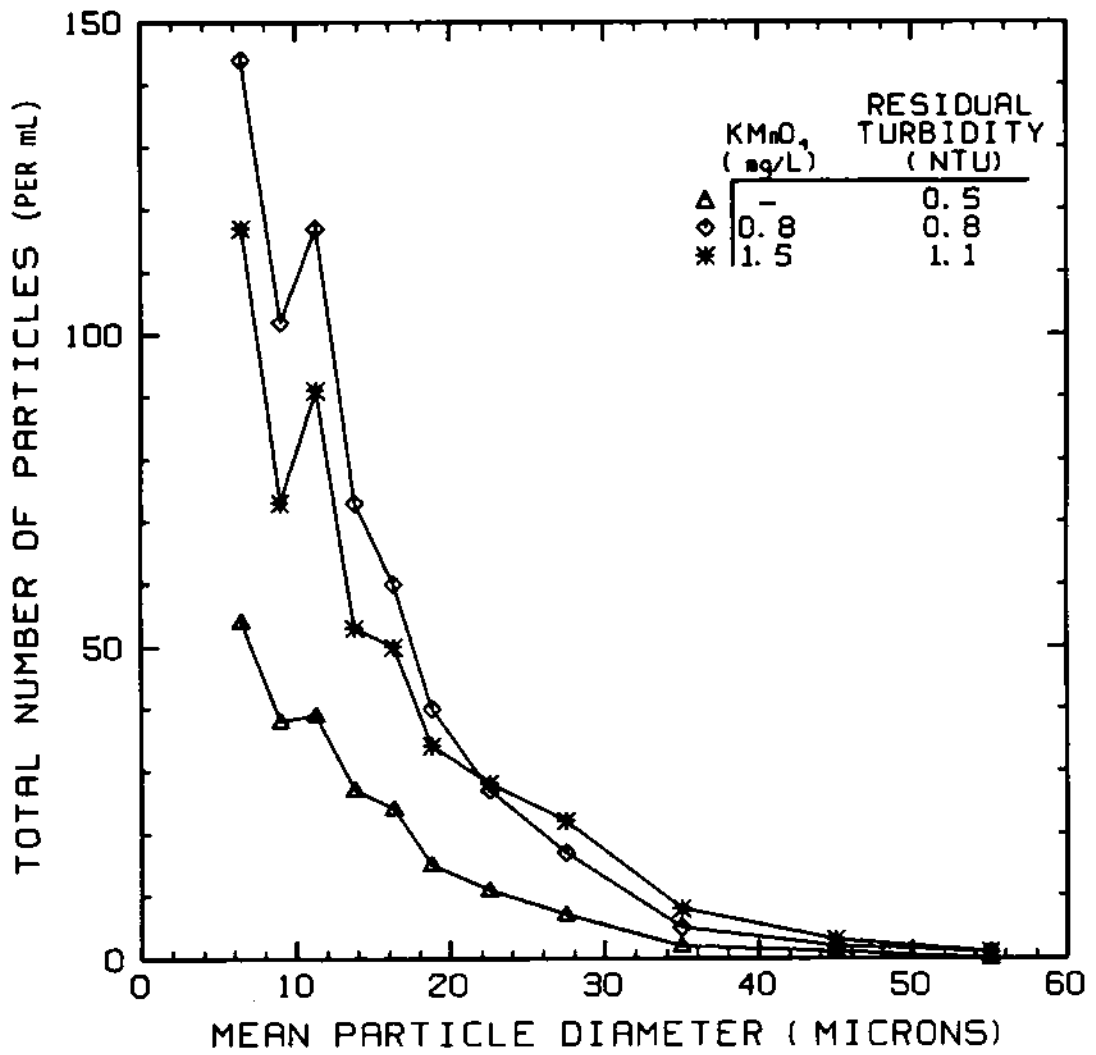


Figure 29. The Effect of Potassium Permanganate Upon Settled Particle Size Distribution at pH 6.0.

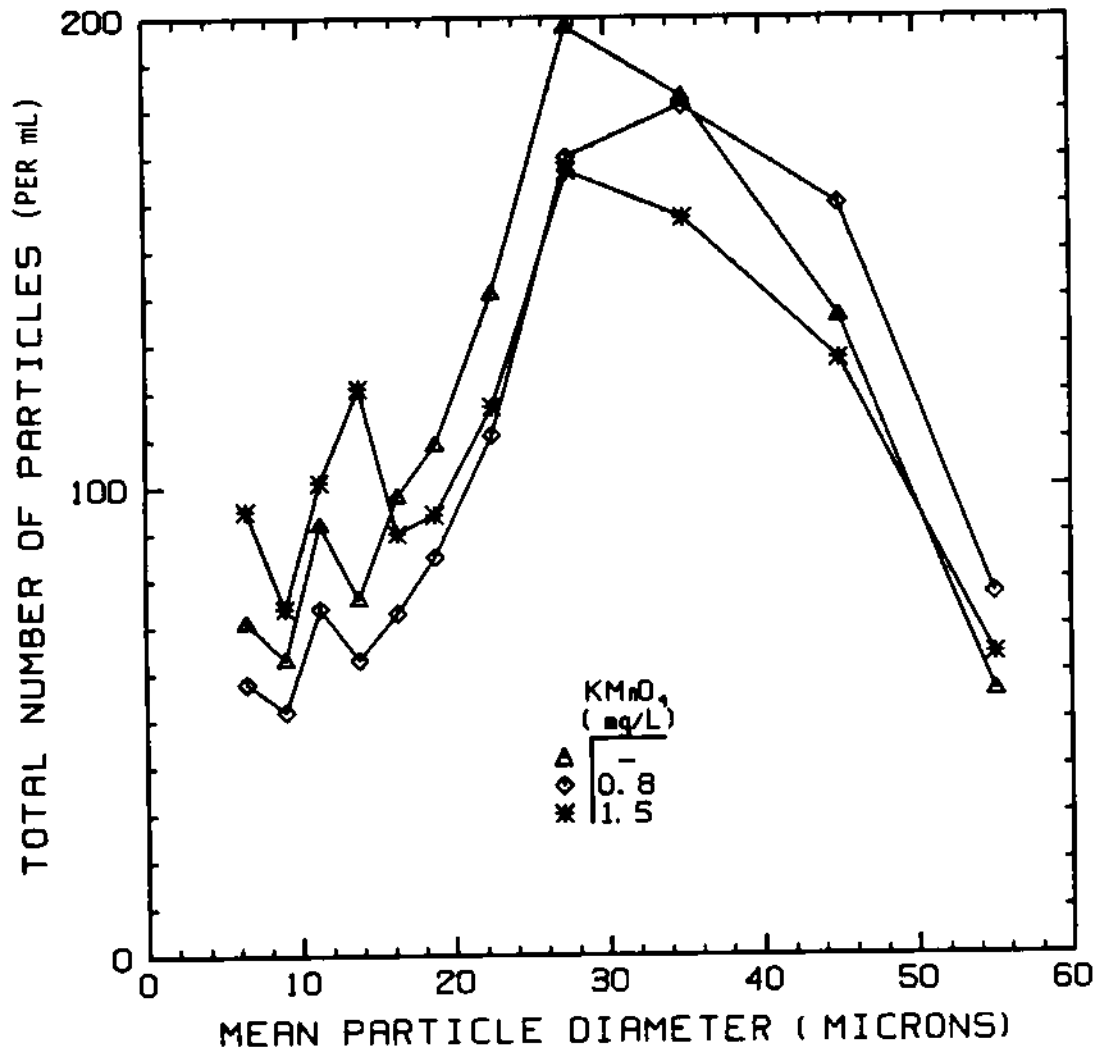


Figure 30. The Effect of Potassium Permanganate Upon Flocculated Particle Size Distribution at pH 7.5.

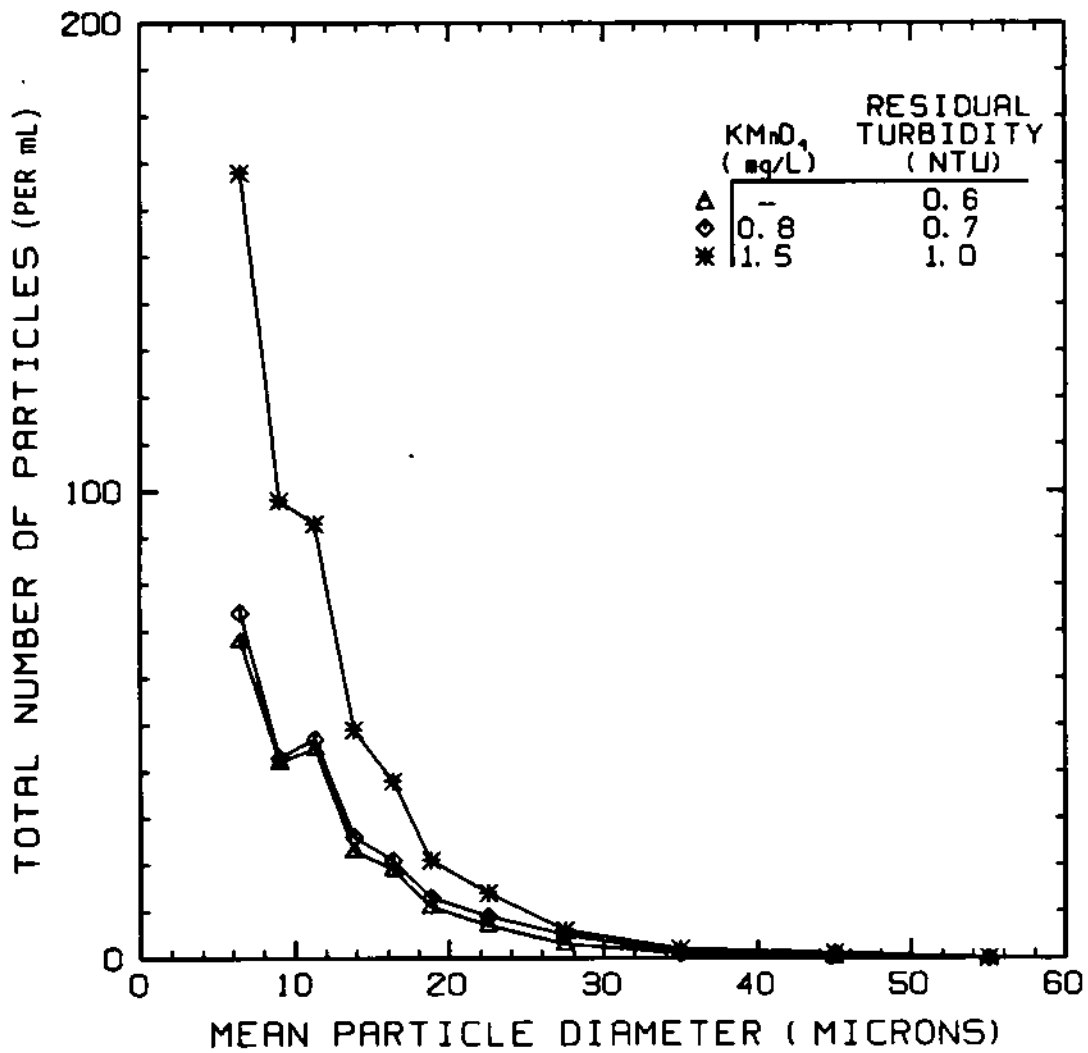


Figure 31. The Effect of Potassium Permanganate Upon Settled Particle Size Distribution at pH 7.5.

potassium permanganate dose. Residual turbidities seemed to increase in a similar manner as particle concentrations increased.

### *Chlorine Dioxide*

Figures 32 and 33 summarize the effect of chlorine dioxide upon water treatment studies conducted at pH 6.0. From Figure 32 the data indicate that the application of chlorine dioxide produced greater particle concentrations within the smaller size ranges. Results of the settled particle distributions are shown in Figure 33. Indications are that during settling, particle flocculation was occurring in the smaller size ranges in all three cases. Highest particle counts were noted in those cases in which chlorine dioxide was applied.

The effects of chlorine dioxide upon particle size distributions for water treatment studies conducted at pH 7.5 are presented in Figures 34 and 35. Data found in Figure 34 suggest that the application of chlorine dioxide produced more particles within the size ranges up to 35  $\mu\text{m}$ . The most significant increase in particles was observed to be within the smallest size ranges. Results from settled particle studies shown in Figure 35 indicate that flocculation continued during settling. Particle concentrations within the smaller size ranges increased after settling in all cases, although greater concentrations were noted in those samples dosed with chlorine dioxide.

### *Chlorine*

Figures 36 and 37 present data collected pertaining to the effect of chlorine upon water treatment studies conducted at pH 6.0. Results from Figure 36 suggest that those cases in which chlorine was added, fewer particles were produced during flocculation. However, Figure 37 shows that during settling, particle concentrations within the smaller size ranges increased in the water in all three jars. The most extreme shift in particle concentration was noted in the water that received the highest applied chlorine dose. Increased particle numbers in settled samples were accompanied by increases in turbidity.



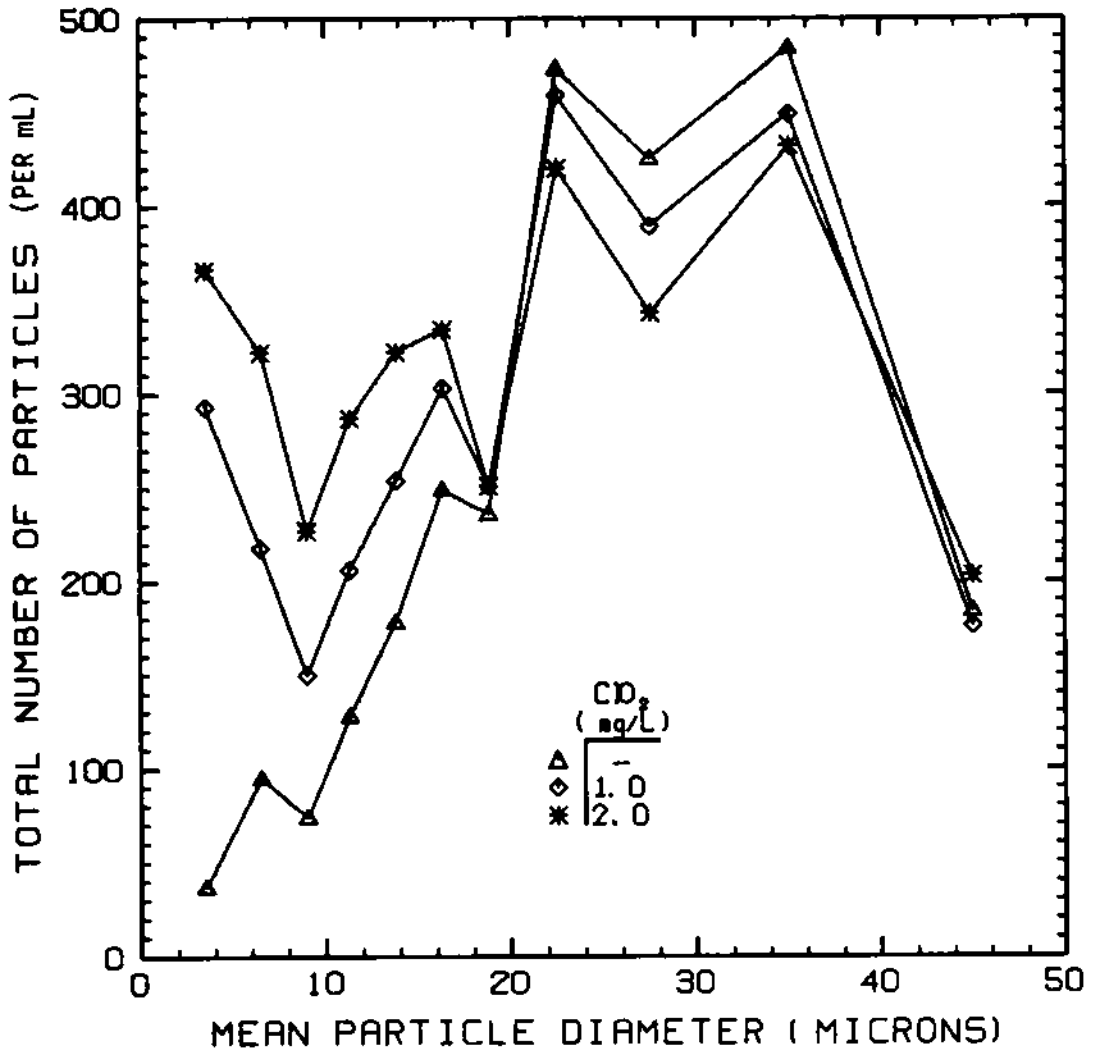


Figure 32. The Effect of Chlorine Dioxide Upon Flocculated Particle Size Distribution at pH 6.0.

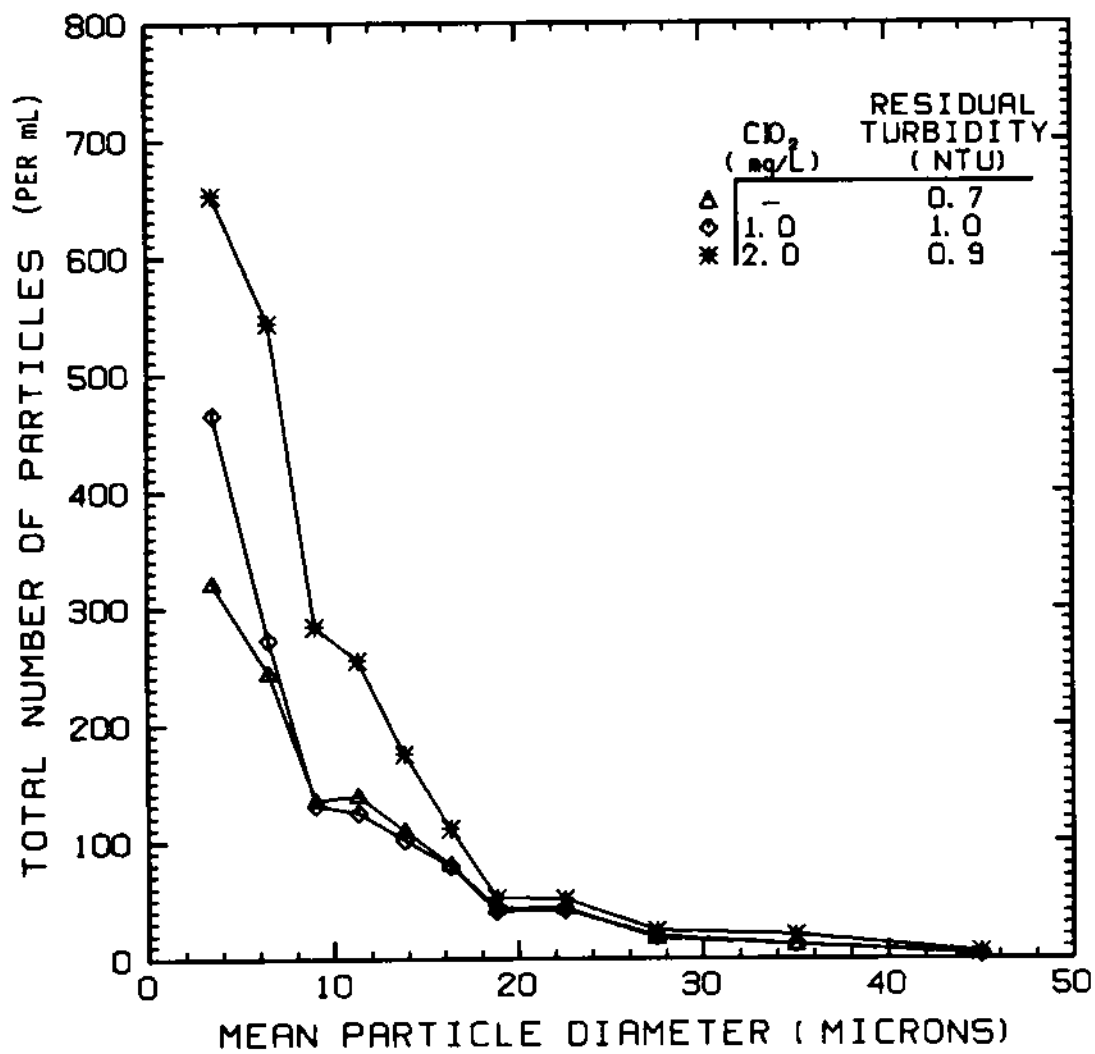


Figure 33. The Effect of Chlorine Dioxide Upon Settled Particle Size Distribution at pH 6.0.

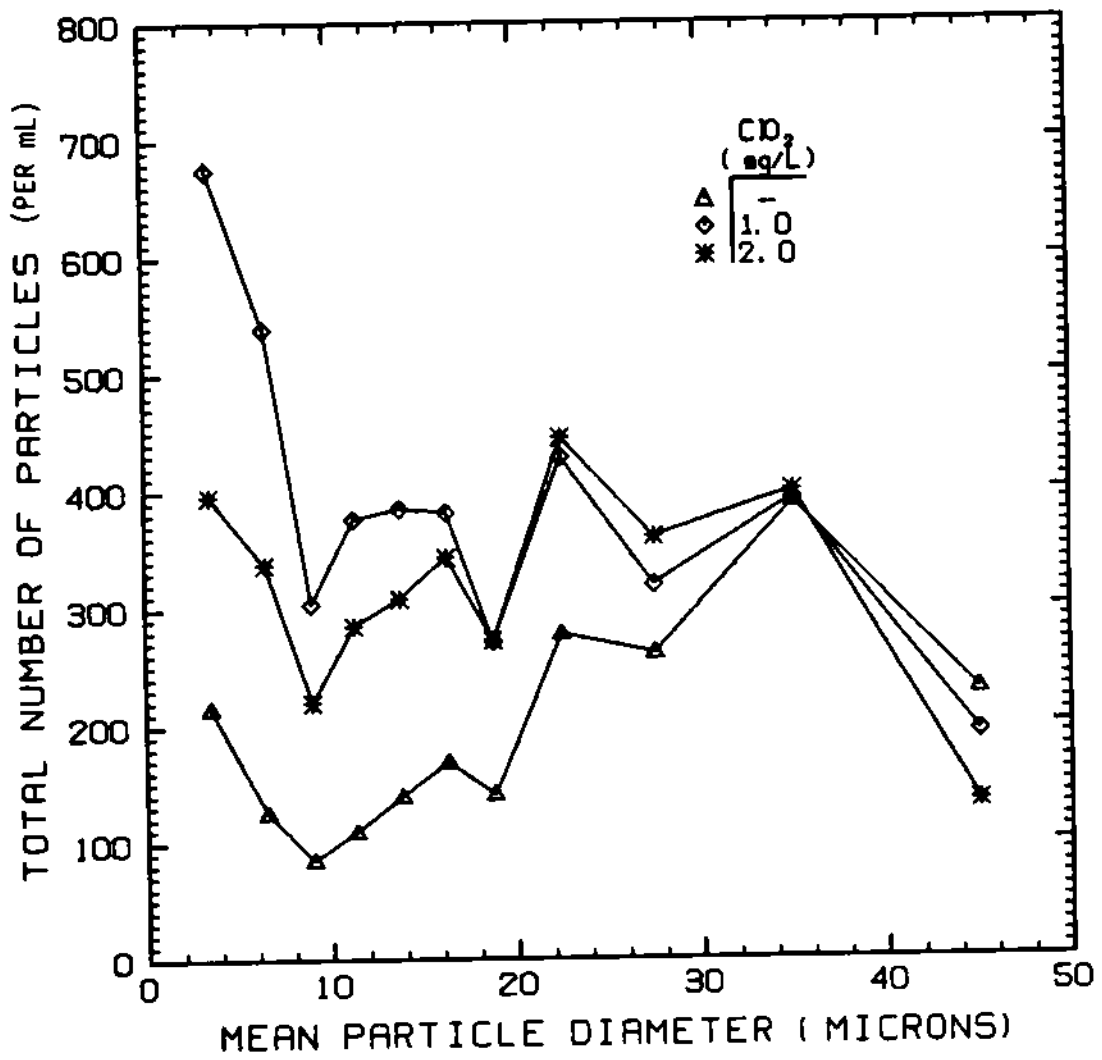


Figure 34. The Effect of Chlorine Dioxide Upon Flocculated Particle Size Distribution at pH 7.5.

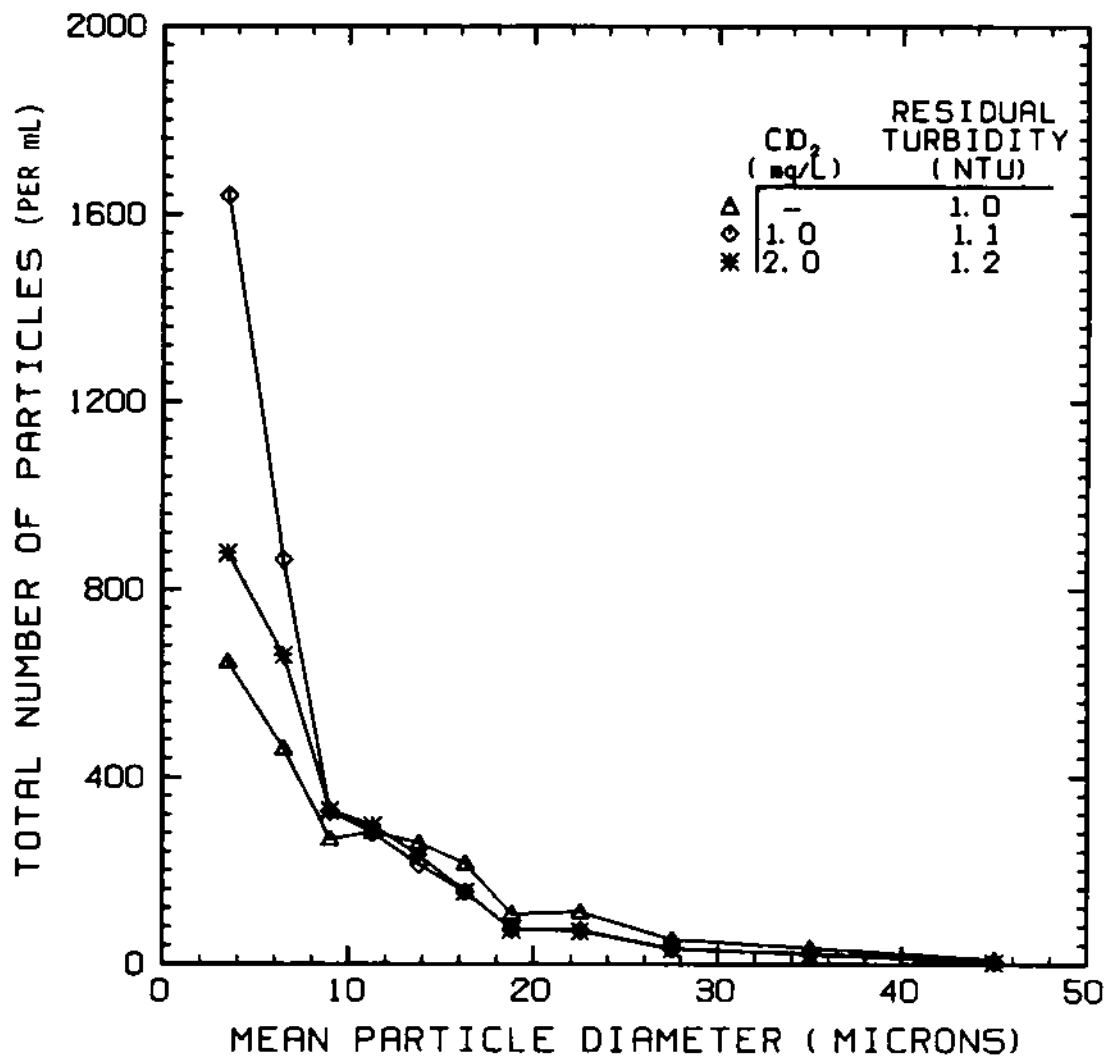


Figure 35. The Effect of Chlorine Dioxide Upon Settled Particle Size Distribution at pH 7.5.

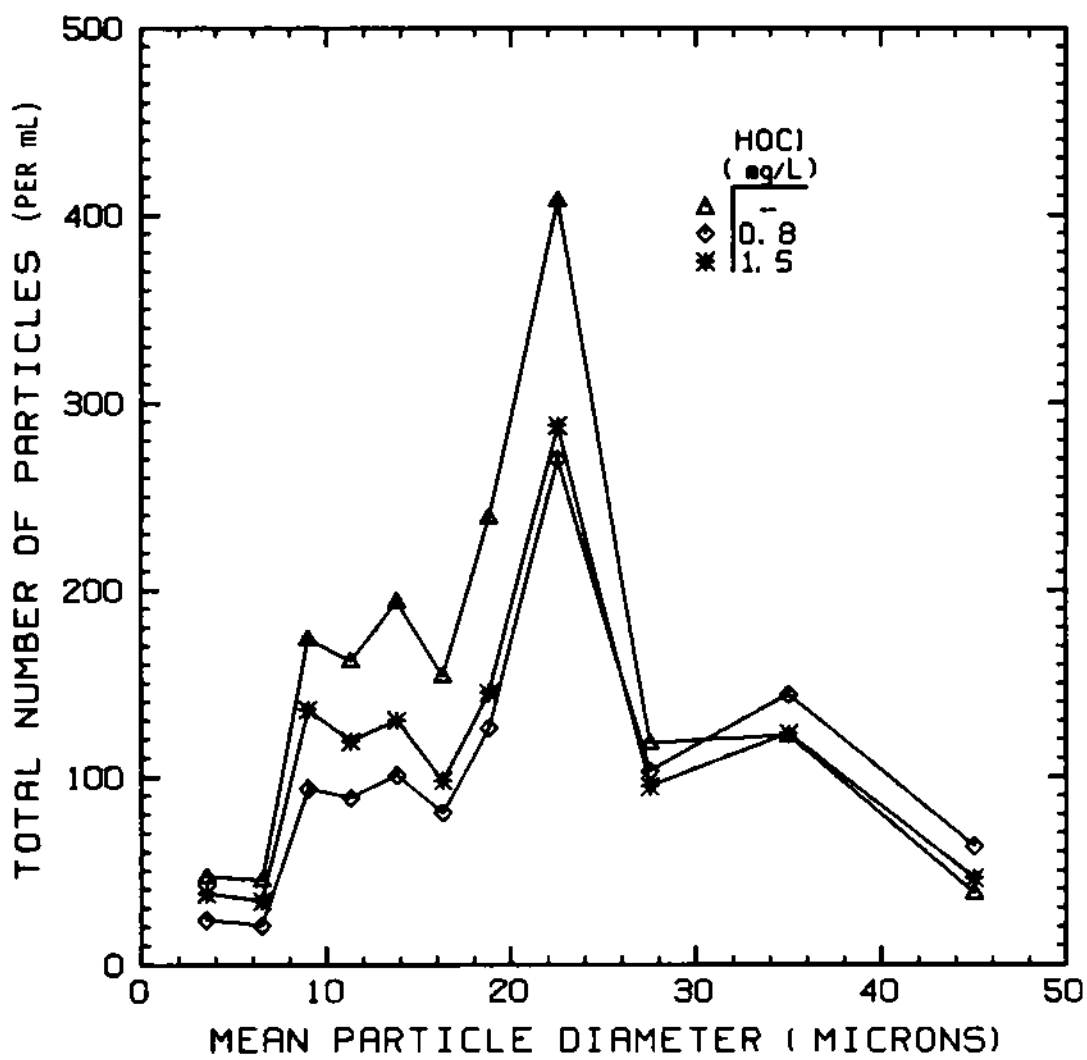


Figure 36. The Effect of Chlorine Upon Flocculated Particle Size Distribution at pH 6.0.

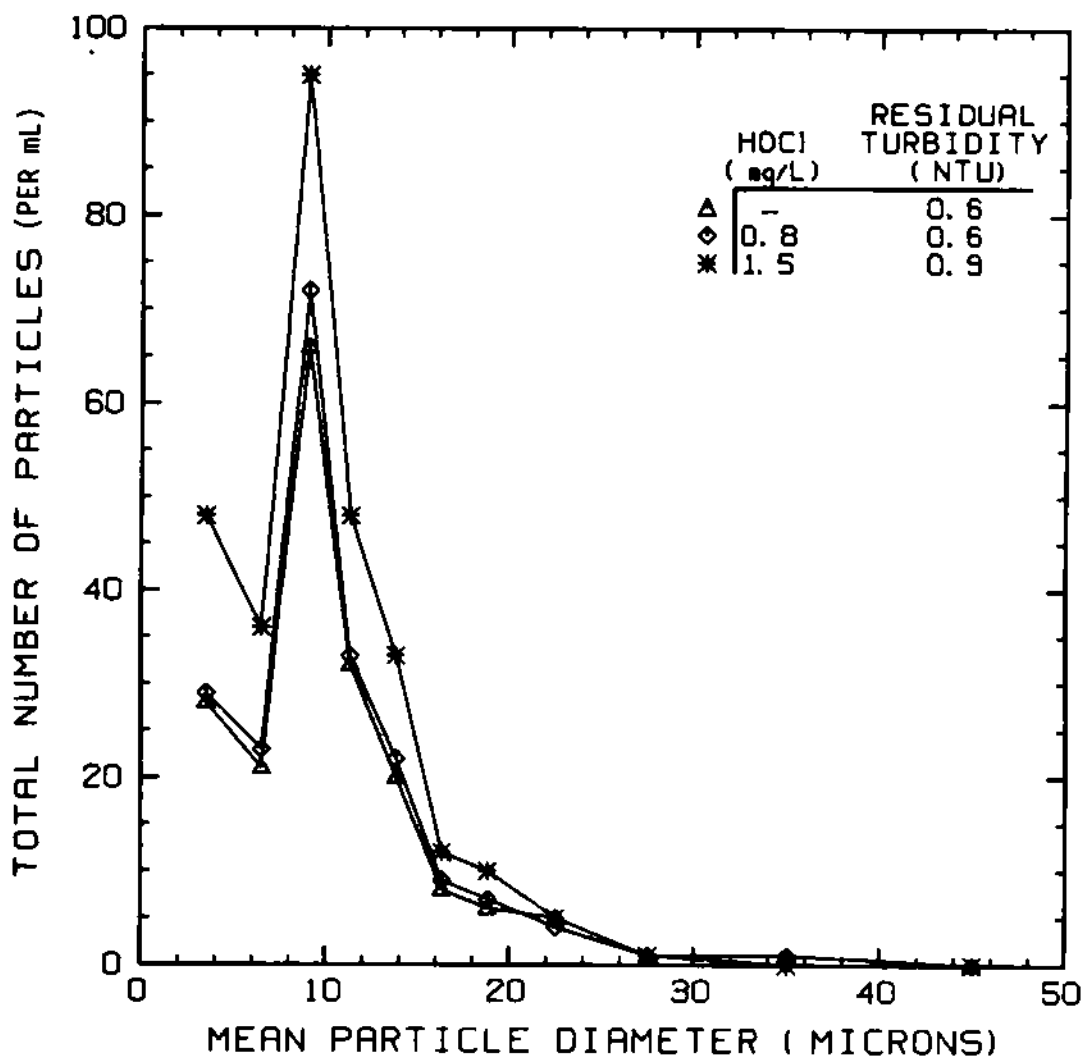


Figure 37. The Effect of Chlorine Upon Settled Particle Size Distribution at pH 6.0.

Figures 38 and 39 summarize the effects of chlorine upon particle-size distributions during water treatment studies conducted at pH 7.5. Figure 38 presents the data collected pertaining to particle distributions after flocculation. The lowest particle concentrations were observed in the smallest size ranges in the samples that received the highest applied chlorine dose. Figure 39 shows that settled particle concentrations increased with chlorine dose. Increased particle numbers in settled samples were accompanied by increases in turbidity.

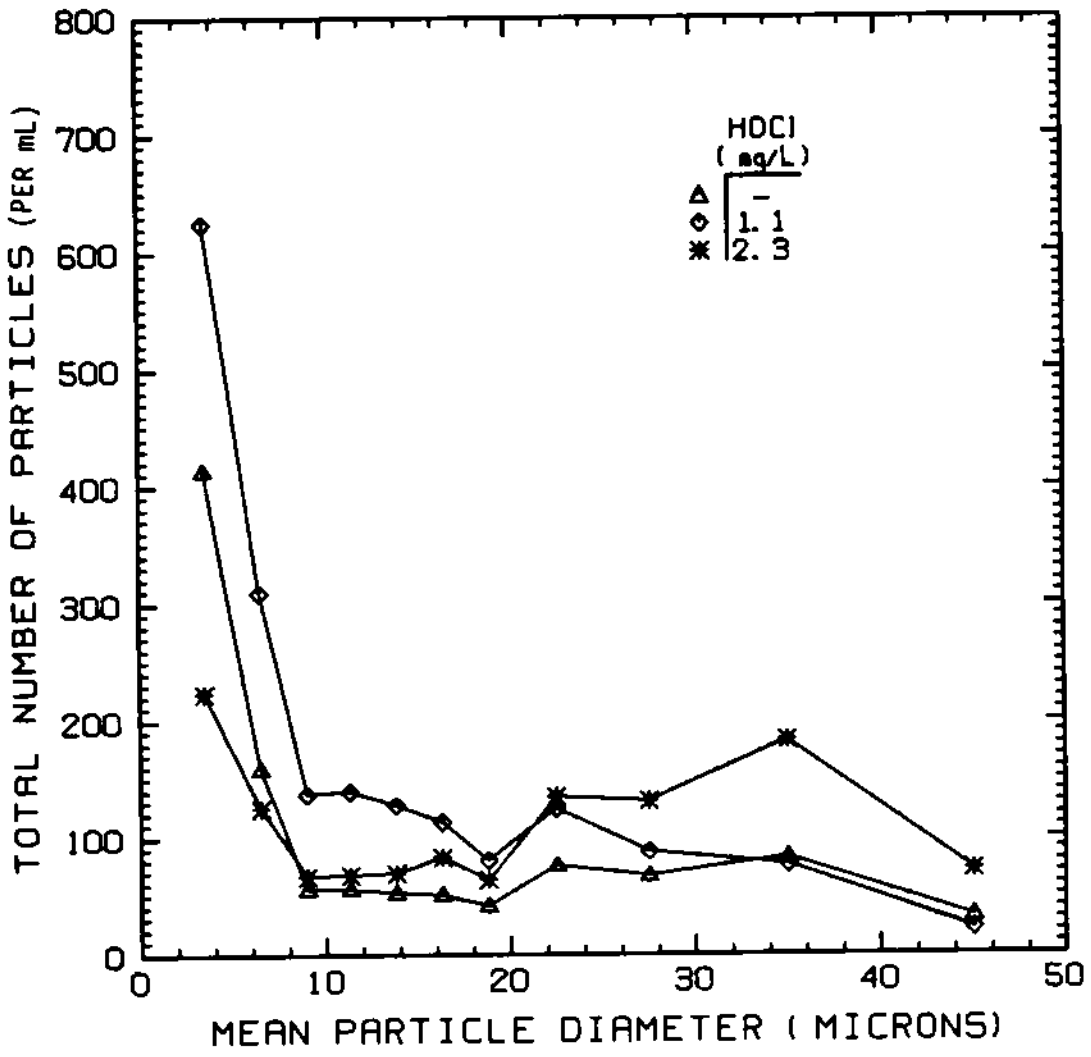


Figure 38. The Effect of Chlorine Upon Flocculated Particle Size Distribution at pH 7.5.



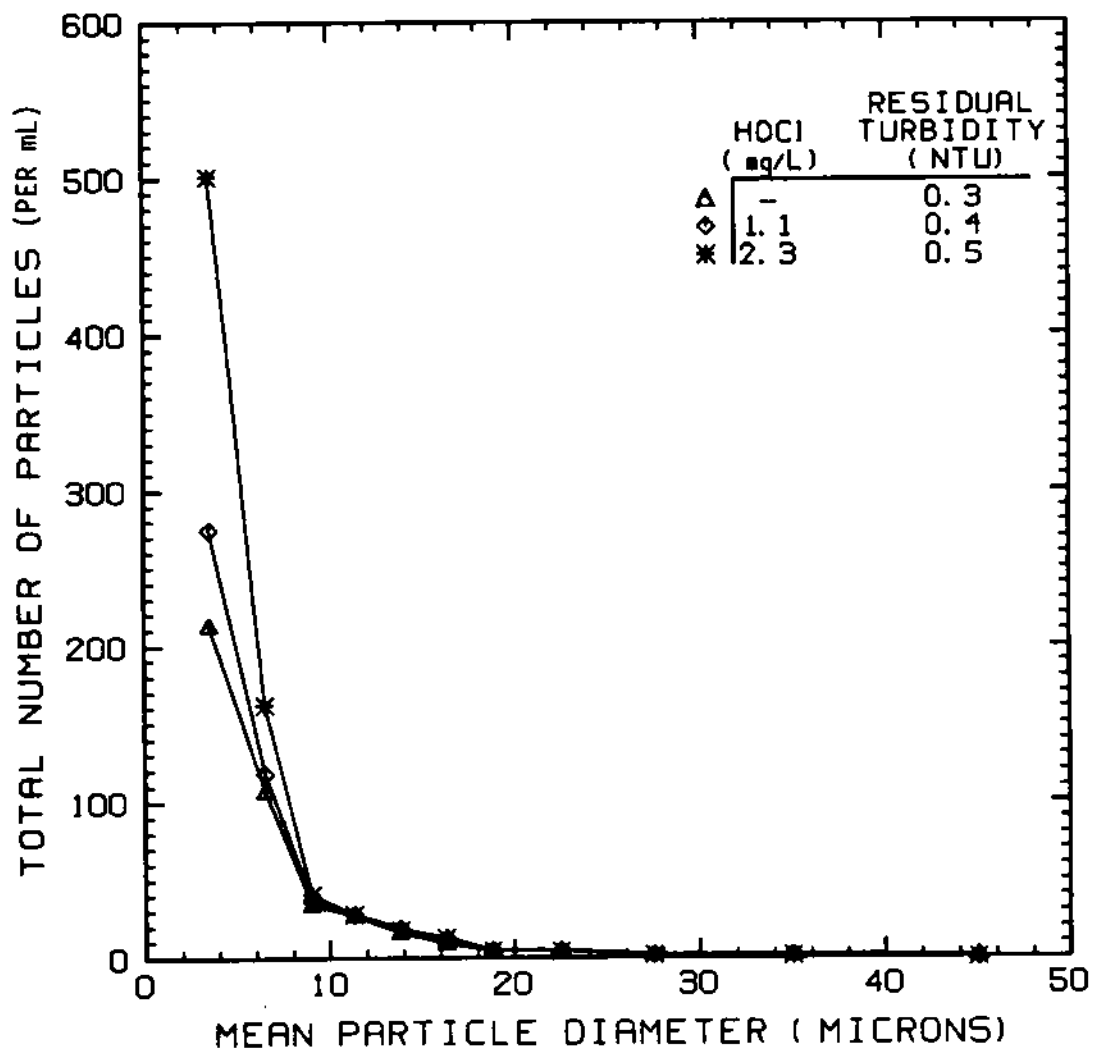


Figure 39. The Effect of Chlorine Upon Settled Particle Size Distribution at pH 7.5.

## **Chapter 5**

### **Discussion**

The following chapter summarizes the effects of the four oxidants upon each water quality characteristic examined in this study. In the interest of brevity, this summary focuses particularly on those cases conducted at a solution pH of 6.0.

#### ***Oxidant Effects Upon Targeted Parameter***

##### **Turbidity Removal**

Results show that each of the four oxidants exerts a somewhat negative effect upon turbidity removal. These results are consistent with those of Van Breeman *et al.* (34) who found that settled turbidity levels increased when ozone and chlorine were applied as pre-oxidants. Moreover, Hildebrand *et al.* (26) concluded that chlorine dioxide application also resulted in increased turbidity levels after settling. Potassium permanganate, in particular, was observed to be detrimental to turbidity removal under high doses. However, it should be noted that under all conditions, except one, residual turbidity levels after settling were below 1.0 NTU.

##### **TOC Removal**

Results indicate that all oxidants except potassium permanganate were found to either have no effect or slightly inhibit TOC removal. Similar observations were reported by Van Breeman *et*

*al.* (34) in which both chlorine and ozone had no impact upon TOC removal. Potassium permanganate, conversely, may enhance TOC removal under certain conditions. This observation was also made in the work of Colthurst and Singer (25). In summary, no real significant effects can be noted either positive or negative.

## **Color Removal**

Figure 40 summarizes the effects of the four oxidants upon color removal at pH 6.0. In all cases, color removal was shown to be either slightly or severely inhibited by the presence of an oxidant. These findings are consistent with studies conducted by Van Breeman *et al.* (34) who found that color removal was inhibited by the presence of ozone and chlorine. Most notably, potassium permanganate adversely affected color quite severely. Under conditions of high dosing, both potassium permanganate and ozone produced settled water with color levels above 15 Pt-Co Units. The extent of color removal inhibition by chlorine and chlorine dioxide, on the other hand, probably would not preclude their selection as a suitable oxidant.

It should be reiterated that these residual color levels represent apparent color (without filtration) as opposed to true color (filtered). Most likely, subsequent filtration of settled water would reduce final color levels. It is difficult to speculate whether an applied oxidant would ultimately affect true color.

## **Reduced Manganese Removal**

A summary of the impacts of the four oxidants upon reduced manganese removal are found in Figure 41. Results show that both potassium permanganate and chlorine dioxide were capable of oxidizing 0.25 mg/L Mn(II) below the recommended MCL of .05 mg/L Mn(II). Conversely, chlorine was observed to be completely ineffectual for Mn(II) removal under conditions of this study. Surprisingly, ozone was unable to remove Mn(II) below the MCL. Since the removal of Mn(II) removal with ozone was by the levels of TOC (Figure 5), its use may be applicable under more suitable conditions. These results were similar to those observed by Knocke *et al.* (11).

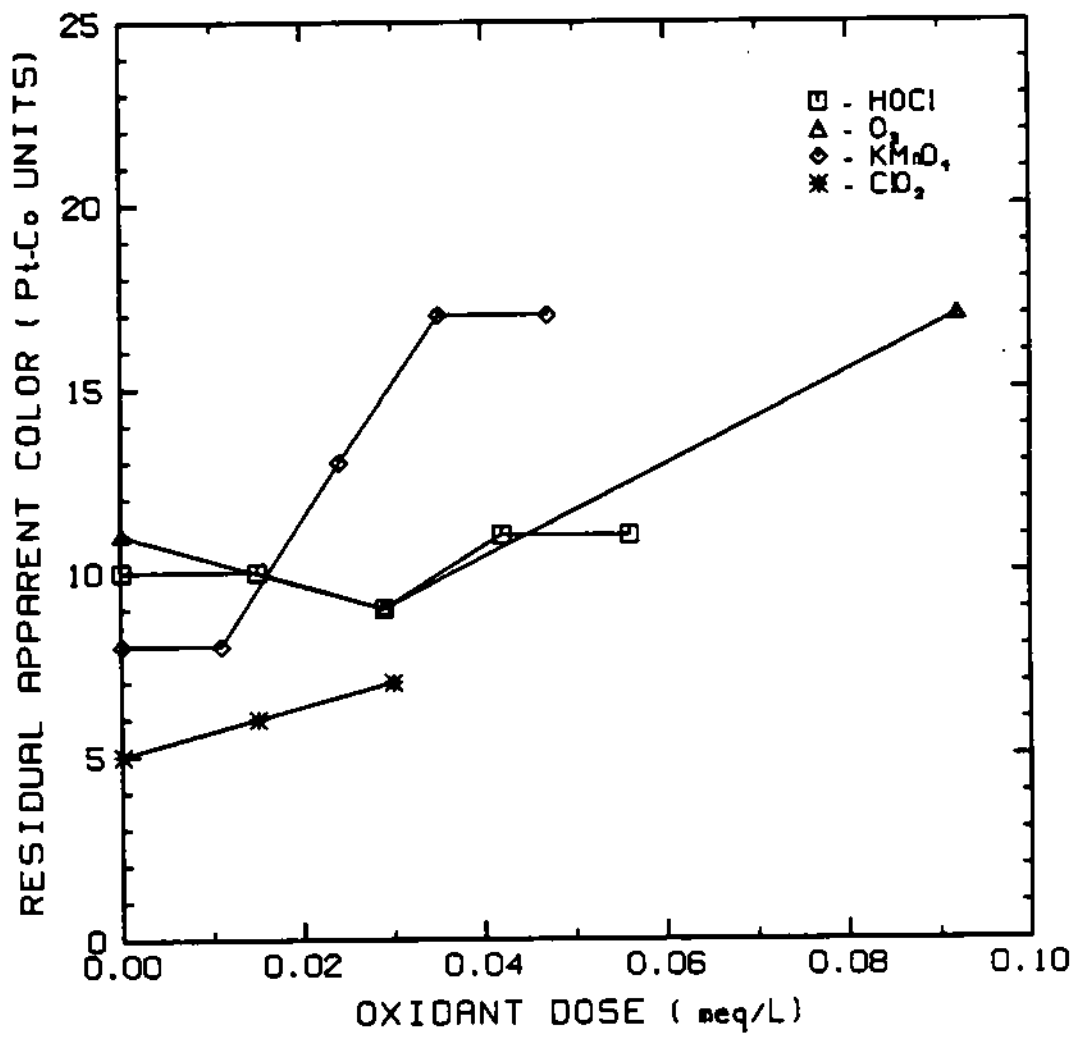


Figure 40. The Effect of Various Oxidants Upon Color Removal Coagulated With 30 mg/L Alum at pH 6.0.

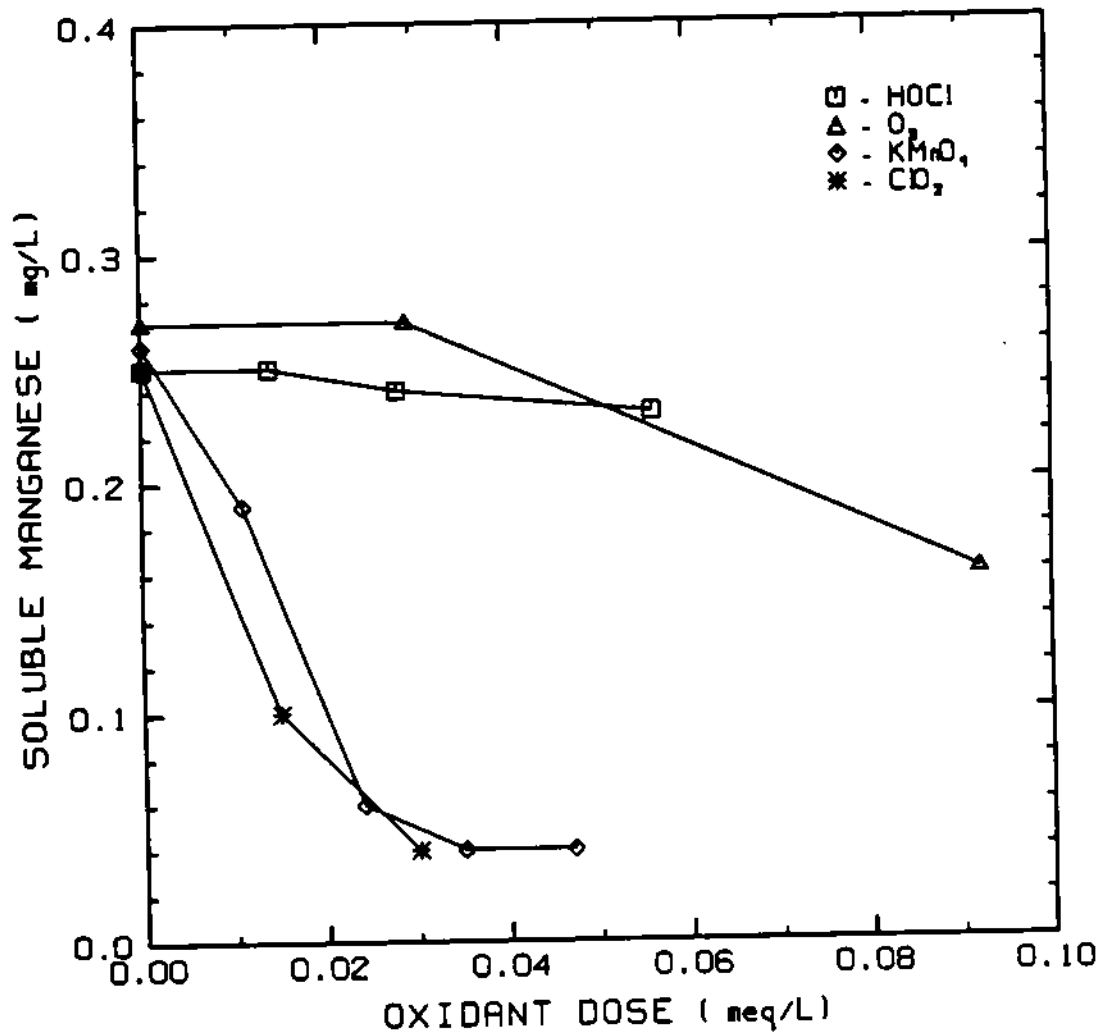


Figure 41. The Effect of Various Oxidants Upon Soluble Manganese Removal Congulated at pH 6.0 (Initial background TOC: 4.8 mg/L; average of the four studies).

## ***Particle Counting Considerations***

### **Microflocculation Studies With Ozone**

Recent literature has been replete with studies supporting or refuting the microflocculation effects of ozone. As of yet, no definitive explanation has been forthcoming to account for these differing results. Implications of ozone use as a microflocculant are interesting, if not profound. The most notable reported benefits include turbidity reduction and increased filter performance. Most of the current research, however, has investigated ozone application without an accompanying coagulant. This area will be addressed in the following discussion.

One phase of this study involved additions of ozone without a coagulant to investigate possible microflocculation effects (Figure 23). As can be seen, no flocculation benefits occurred. In fact, a shift of particles from the larger ranges to the smaller ranges was observed when 2.2 mg/L ozone was applied. This observation was also made by several other investigators (19). Jekel (21) ozonated a water with an initial particle concentration of 53,400 particles per mL ( $> 1 \mu\text{m}$ ) and observed microflocculation. Saunier *et al.* (22) confirmed microflocculation after ozonating a raw water containing 260,000 particles per mL ( $> 1 \mu\text{m}$ ). The failure to observe microflocculation during this study may have been because the water had an initial particle concentration of only 11,400 particles per mL ( $> 2 \mu\text{m}$ ). Despite the inability to ascertain the number of particles between 1 and 2  $\mu\text{m}$ , it is reasonable to assume that high particle concentrations were present initially in the aforementioned studies. Based upon parallels of coagulation theory that particle agglomeration is influenced by particle concentration, it may be postulated that microflocculation responds in a like manner. That is, microflocculation may be influenced by high initial particle concentrations.

While a majority of the literature regards microflocculation with ozone in conjunction with direct filtration, the broader picture must focus upon ozone application within the framework of conventional alum coagulation. Figure 42 and Figure 43 present findings of alum coagulation after ozonation. Figure 42 indicates that 0.7 mg/L ozone caused continued flocculation during settling, but only a slight increase in total particles was found. Differences in residual turbidity levels were not significant. Figure 43 illustrates the effects of a higher dose of ozone upon alum coagulation.

Results show that the higher dose had a more dramatic effect upon particle concentrations, producing nearly twice as many particles than the control study in the smallest size ranges. This result supports the work of Albert (35) who observed that ozone application was decidedly detrimental to flocculation. Even though particle numbers increased, residual turbidity levels were similar.

### *Studies of Other Oxidants*

Figures 44 through 46 present typical results of flocculated and settled particle concentration studies with oxidants other than ozone. By comparing particle distributions obtained after flocculation, the effects of an oxidant upon particle numbers within distinct size ranges may be determined. In the case of potassium permanganate, an increase in particle numbers was observed in the smaller ranges, while the larger ranges did not increase. The most dramatic shift in particle size distributions was experienced in the case of chlorine dioxide application. The data suggest that smaller particles were generated at the expense of larger particles.

Data from the above studies indicate that larger particles settled quickly in relation to smaller particles. In general, particles greater than 30  $\mu\text{m}$  settled during the forty-minute quiescent period. Regarding the studies with chlorine dioxide and potassium permanganate, particle concentrations after settling were indirectly related to particle size. Although this result was not observed with chlorine at pH 6.0, a similar relationship was noted at pH 7.5 (Figure 39). The implication of this observation is that in order to facilitate settling, larger flocculated particles ( $> 30 \mu\text{m}$ ) are desirable. In short, by the removal of these particles during settling, fewer particles will ultimately be loaded onto the filter.

### *Implications of Particle Count Studies*

Over the course of this study, particle concentrations within the lower size ranges were observed to increase after settling in comparison to concentrations prior to settling (after flocculation). This phenomenon may be explained by (1) continued flocculation during settling, whereby those particles too small to be counted ( $< 2 \mu\text{m}$ ) before settling agglomerated into particles of measurable size ( $> 2 \mu\text{m}$ ); and/or (2) the settling of smaller particles was somehow inhibited

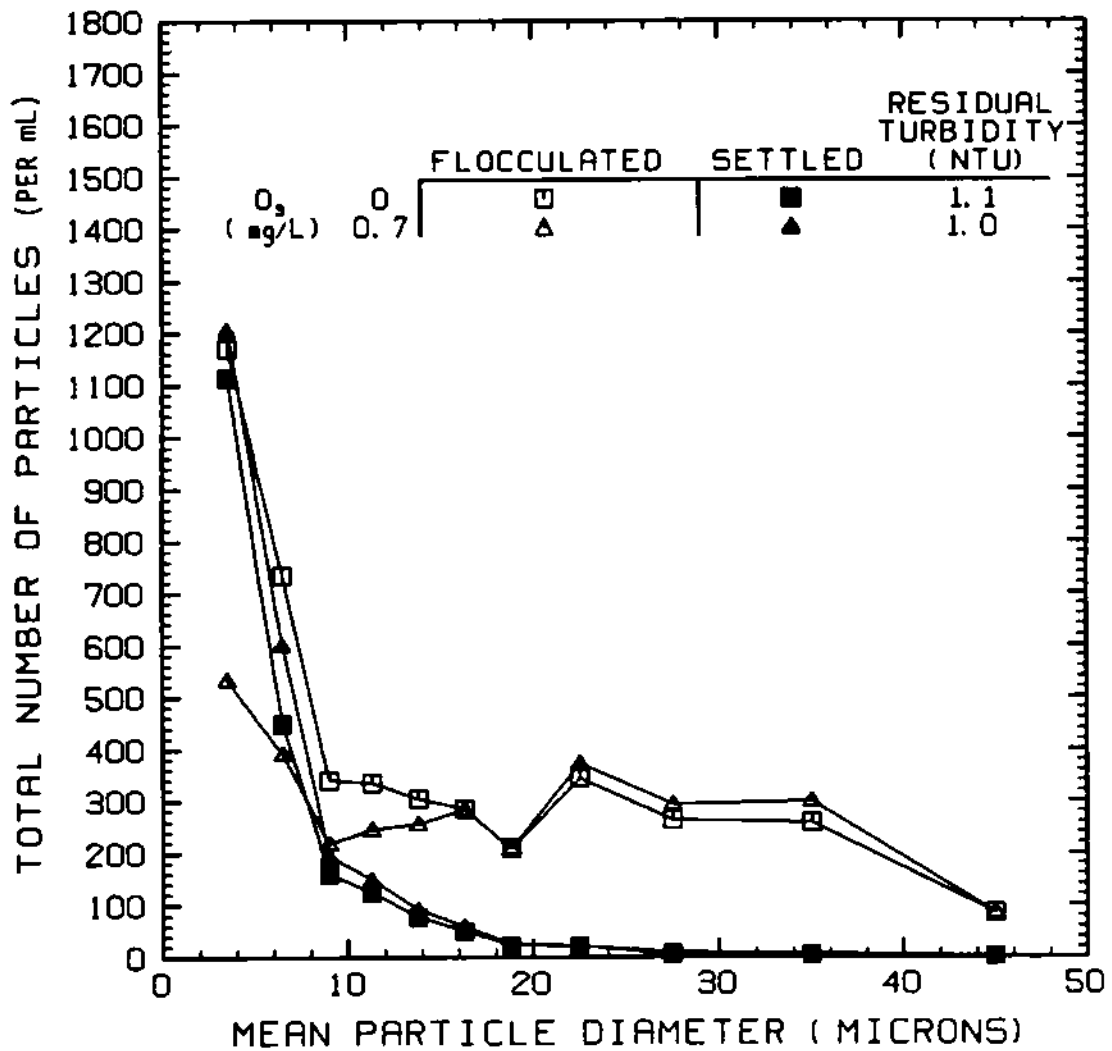


Figure 42. The Effect of Ozone Upon Settled and Flocculated Particle Size Distributions at pH 6.0.



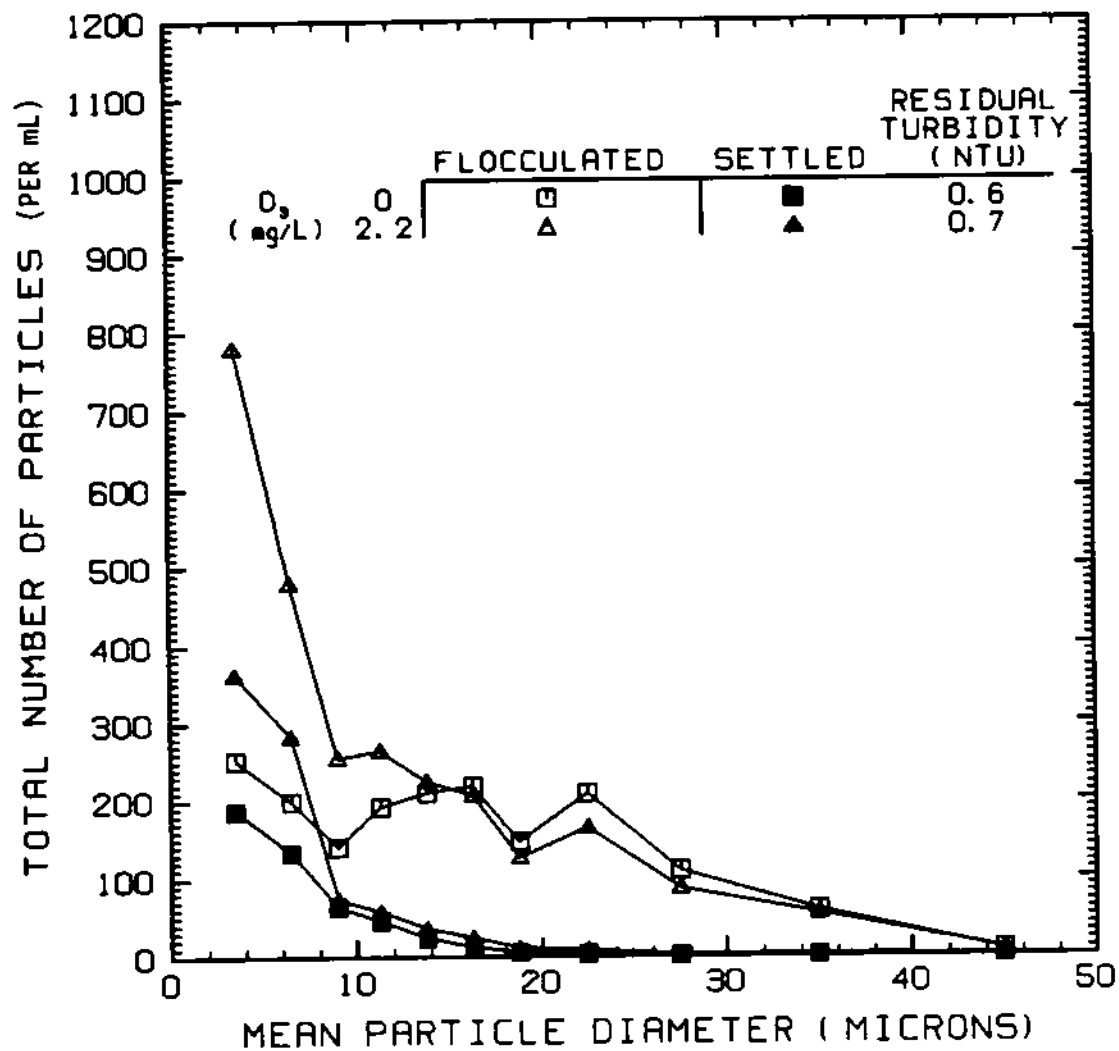


Figure 43. The Effect of Ozone Upon Settled and Flocculated Particle Size Distributions at pH 6.0.

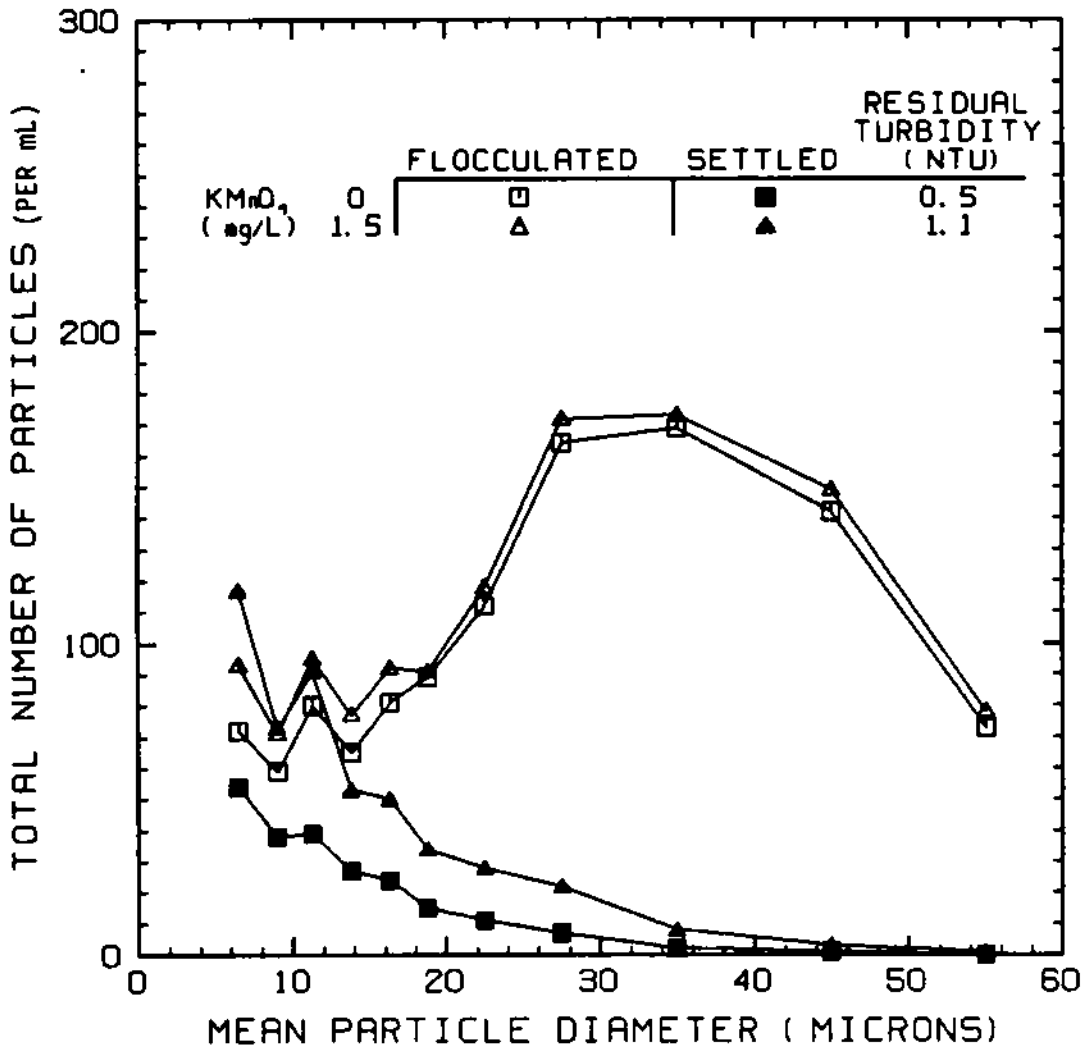


Figure 44. The Effect of Potassium Permanganate Upon Settled and Flocculated Particle Size Distributions at pH 6.0.

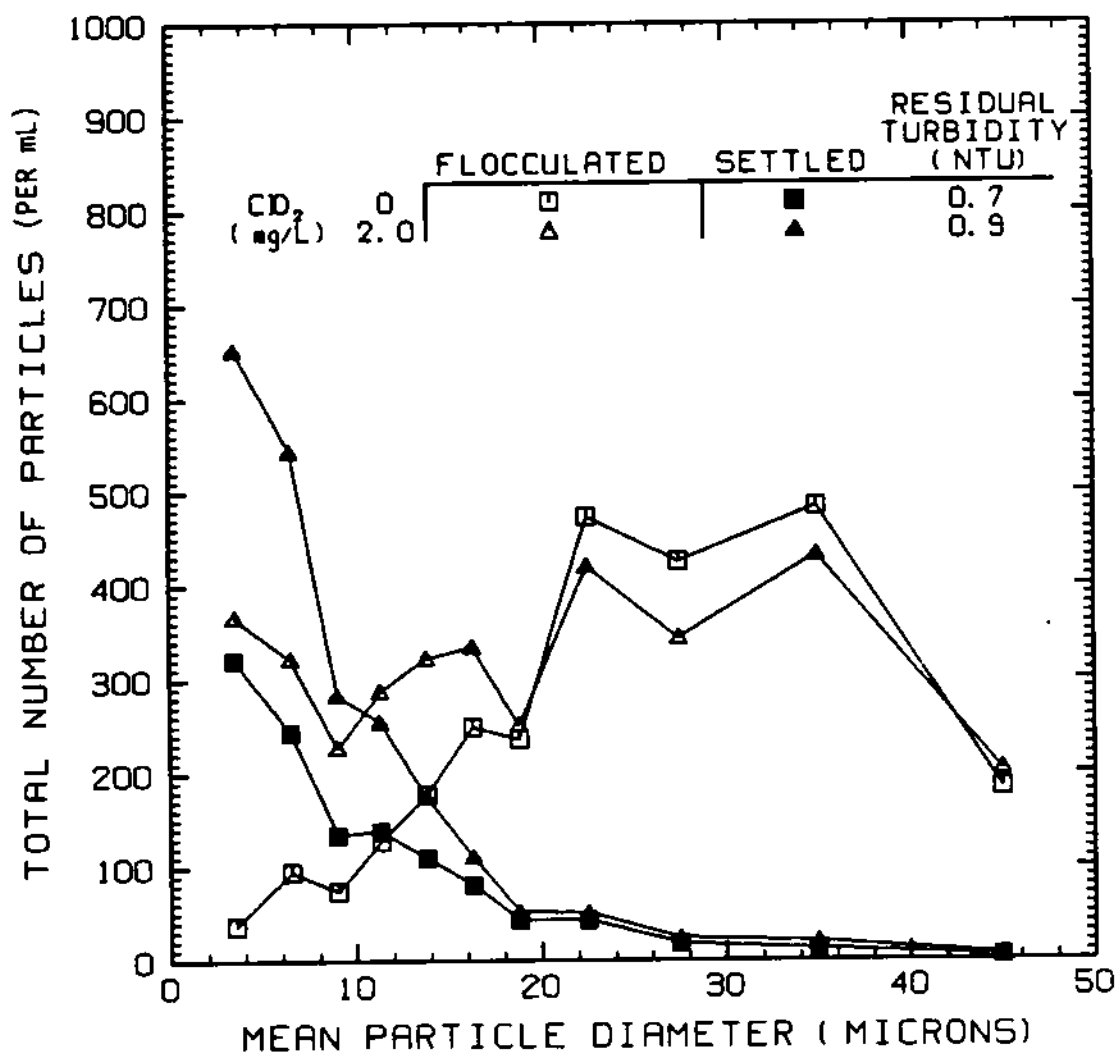


Figure 45. The Effect of Chlorine Dioxide Upon Settled and Flocculated Particle Size Distributions at pH 6.0.

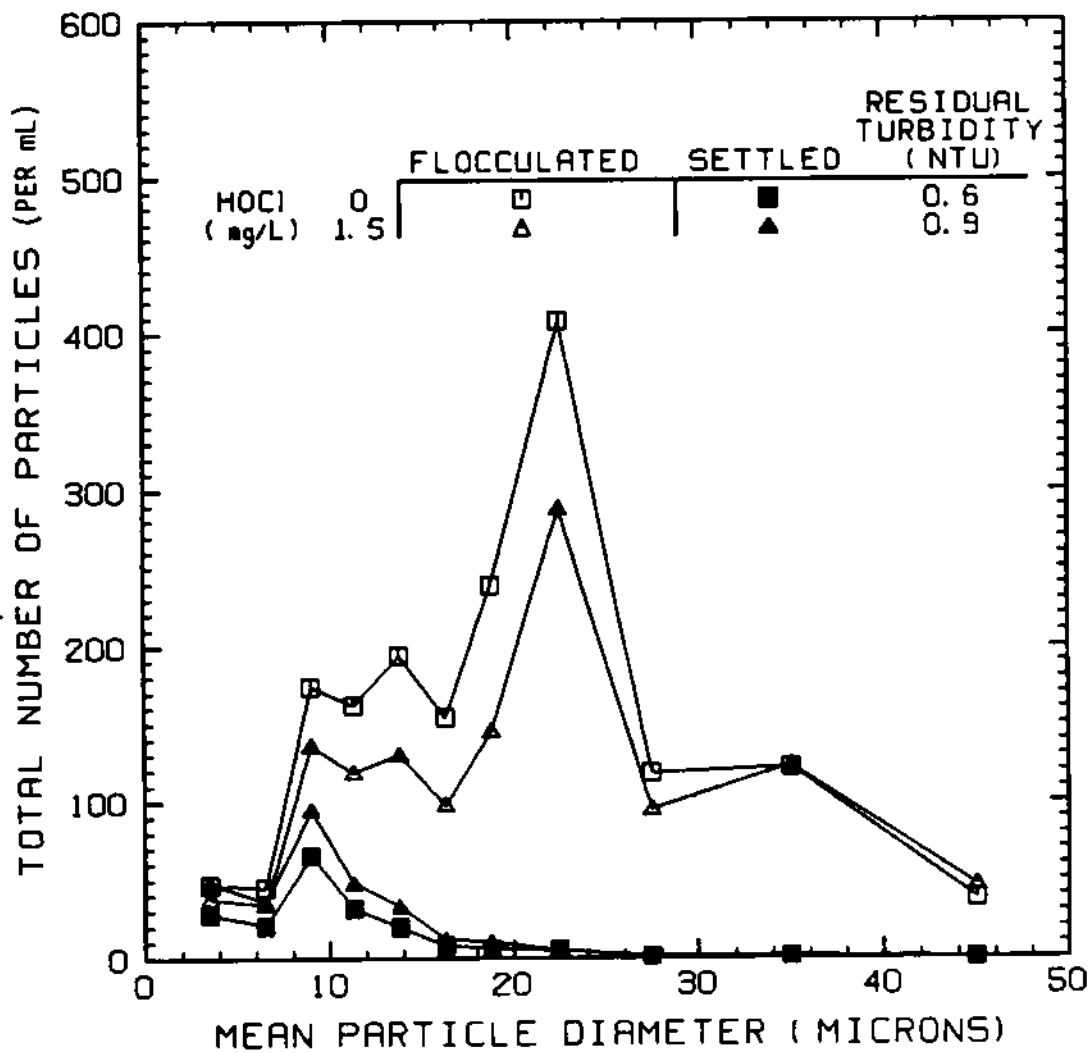


Figure 46. The Effect of Chlorine Upon Settled and Flocculated Particle Size Distributions at pH 6.0.

by the presence of an oxidant. Table 2 presents data from this study pertaining to increased particle concentrations after settling. However, even with an increase of particles, residual turbidity levels did not always increase.

The preceding section illustrated that oxidant addition during alum coagulation produced greater settled particle concentrations, particularly within the smaller size ranges investigated. Accompanying residual turbidity levels were generally somewhat increased. In a conventional water treatment facility, however, filtration follows quiescent settling. This being the case, it would be appropriate to postulate as to the effect of increased particle concentrations upon filtration and filter performance.

Yao *et al.* (36) researched critical parameters affecting filter efficiency. Figure 47 presents a graph depicting the predicted theoretical particle removal efficiency as a function of suspended particle size. When considering Yao's filtration model, particles between 0.1 and 10  $\mu\text{m}$  are subject to decreased removal efficiencies, with particles of 1  $\mu\text{m}$  being the most difficult to remove by filtration. The implication being, that in the analysis of the particle data collected in this study, greater attention is given to this size range ( $< 10 \mu\text{m}$ ), because this is the particle size range most likely to escape filtration and impact final turbidity.

## ***Recommendations***

Over the course of this study, observations were made to determine the effects of the alternate oxidants upon certain water quality characteristic. In general, no particular oxidant was found to enhance coagulation; the use of an oxidant to aid either TOC, color, or turbidity removal could not be justified based on the results of this study. For example, a treatment plant experiencing no problems with neither THMs nor reduced metals, probably would not benefit by switching from chlorine to another oxidant.

The effectiveness of each one of the oxidants was shown to be influenced by raw water quality and operating pH. Of particular concern are initial TOC, initial particle counts and reduced metals. The use of potassium permanganate and chlorine dioxide were the most effective for the oxidation of reduced manganese. A particular benefit to a treatment facility was that both of these oxidants were effective under both pHs conditions investigated. This implies that a facility would

**Table 2. Cases In Which Particle Numbers Were Observed to Increase After Settling**

oxidant	number of cases	number of cases of increased particle counts	percentage of cases of increased particle counts*	percentage of cases in which increased particle counts led to increased turbidity**
none	24	9	38%	
$O_3$	20	15	75%	50%
$KMnO_4$	22	18	82%	55%
HOCl	20	14	70%	64%
$ClO_2$	8	4	50%	100%

\* represents cases in which flocculation continued during settling; that is, particle numbers were greater after settling than prior to settling.

\*\* represents cases in which increased particle numbers after settling due to an applied oxidant led to greater settled turbidity levels in comparison to a sample with no applied oxidant.

not be limited by pH for manganese removal and could adjust it to optimize either turbidity or organics removal. Conversely, ozone effectiveness appeared to be limited by initial background TOC. Because it reacts with organics, ozone may be best suited for waters with a background TOC level below 3 mg/L.

Applied oxidant dose impacted treated water quality. Under lower dosing conditions, overall detrimental effects were minimized; however, higher doses severely inhibited color and turbidity removal in the cases of potassium permanganate and ozone. Of those oxidants applied at high doses, chlorine dioxide had the least negative impact upon treated water quality. Even though past studies have suggested that ozone may aid flocculation, preliminary investigations are advised. Raw waters containing high particle concentrations ( $> 40,000$  above 1  $\mu\text{m}$ ) may be the most amenable to microfloculation. If this criterion is met, a study to determine optimal ozone dose can then be initiated.

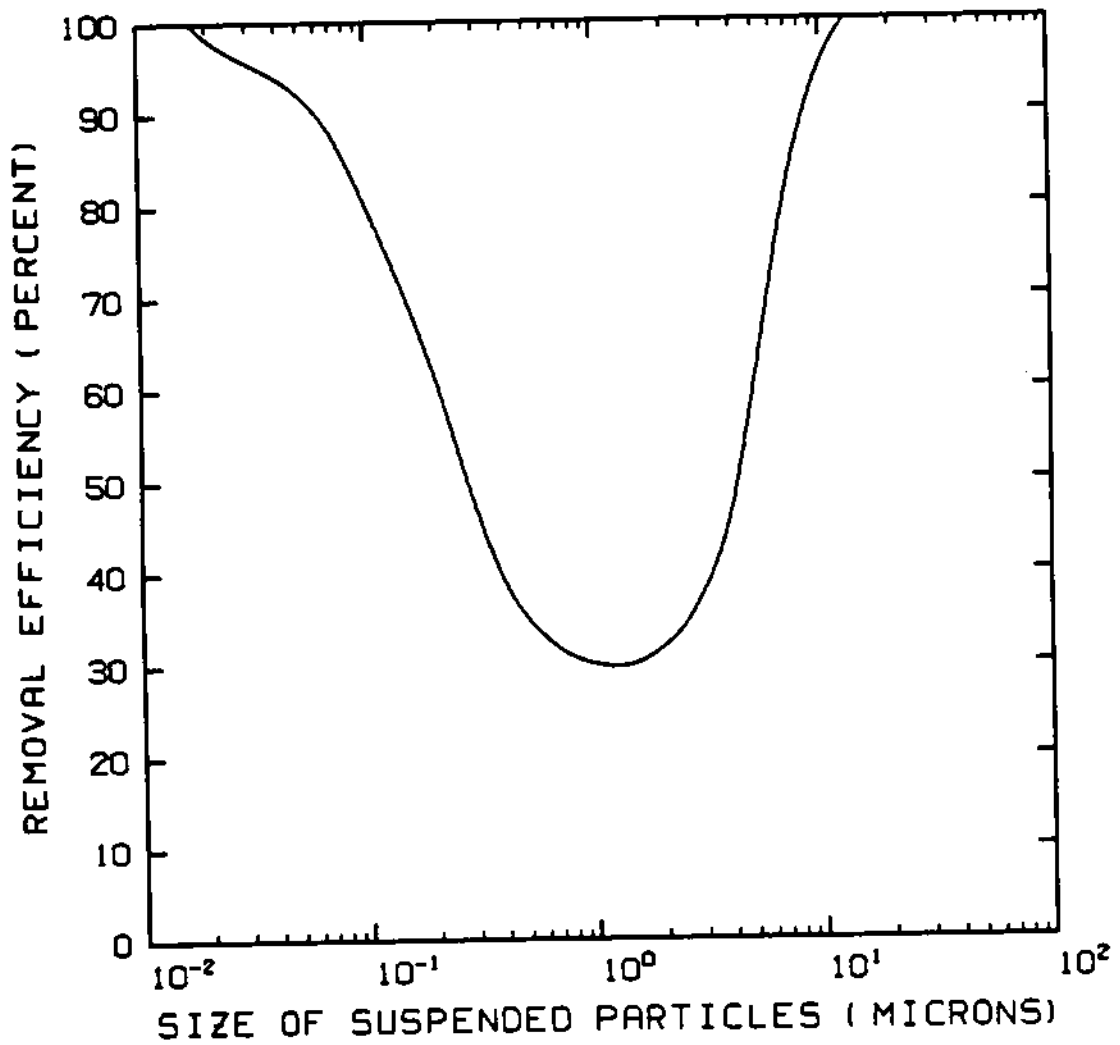


Figure 47. A Theoretical Filtration Model of Particle Removal Efficiency as a Function of Particle Size. (After Yao, Habibian, and O'Melia, 1971)



## **Chapter 6**

### **Summary and Conclusions**

This study was initiated to investigate the effects of alternate oxidants upon water quality treatment parameters. In addition, particle counts were performed to determine oxidant effects upon particle distributions. Further studies were undertaken in order to determine the microfloculant properties of ozone. Overall, this research emphasized the effects upon the treatment of low turbidity, colored waters when pre-oxidants were applied. Based on the results of this investigation, the following conclusions were reached:

1. TOC, turbidity, and color removal were not enhanced by the application of an oxidant. While oxidants in low dosages may be applied to oxidize reduced manganese, their use to improve the removal of TOC, turbidity, and color by the coagulation-sedimentation-filtration process, cannot be justified.
2. In low TOC waters, chlorine dioxide, potassium permanganate, and ozone were effective oxidants for the removal of reduced manganese at both pH 6.0 and pH 7.5. Chlorine was not an effective oxidant at either pH value.

3. Initial TOC concentrations inhibited the removal of reduced manganese by the oxidants investigated. In the cases of chlorine dioxide and potassium permanganate, increased dosing of oxidants led to the removal of reduced manganese below the MCL (.05 mg/L). However, increased ozone doses were unable to remove reduced manganese to acceptable levels in waters with high initial TOC concentration ( $> 4$  mg/L).
4. The removal of reduced manganese was better at pH 7.5 than at pH 6.0. Color, and TOC removal were better at pH 6.0, while turbidity removal did not vary with pH.
5. The application of an oxidant resulted in an increase of particles within the smaller ranges ( $< 10$   $\mu\text{m}$ ). However, this did not result in a significant increase in settled turbidity values.

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