

**Evaluation of Different Powdered Activated Carbons
in The Control of Chlorite Ion**

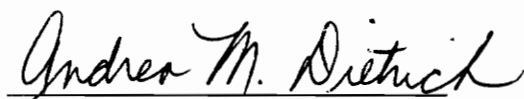
by

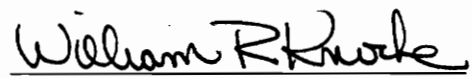
Robert M. Mitchell

Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
Master of Science
in
Environmental Engineering

APPROVED:


Dr. Robert C. Hoehn, Chairman


Dr. Andrea M. Dietrich


Dr. William R. Knocke

C.2

5655
V855
1993
M583
C.2

EVALUATION OF DIFFERENT POWDERED ACTIVATED CARBONS IN THE CONTROL OF CHLORITE ION

by

Robert M. Mitchell
Dr. Robert C. Hoehn, Chairman
Environmental Engineering

(ABSTRACT)

Twelve different powdered activated carbons (PACs) were screened under laboratory conditions to determine their performance in the removal of chlorite ions (ClO_2^-) and in the production of chloride ions (Cl^-) and chlorate ions (ClO_3^-) during that removal. All screenings were conducted in reagent water, at $\text{pH } 7.0 \pm 0.2$ pH units, with a standard concentration of 20 mg/liter of powdered activated carbon (PAC) added in each case, and with the process and samples protected from light. One set of screening experiments was conducted with both ClO_2^- and chlorine added with the PAC, while the other set contained only ClO_2^- and PAC. The chlorine and ClO_2^- were added to concentration levels which might be expected in disinfection practice in water treatment plants.

Periodic samples were drawn as the mixtures were stirred over a 24 hour period. Each sample was analyzed for Cl^- , ClO_2^- , and ClO_3^- concentrations utilizing ion chromatography. All PACs were found to reduce ClO_2^- to Cl^- , and ClO_3^- was never detected when chlorine was absent. The data provided no consistent significant evidence of ClO_3^- formation even when chlorine was present. The rate of ClO_2^- removal was most rapid in the first two hours of contact, but slowed to rates below 6 percent per hour after 4 hours of contact. Rates of ClO_2^- removal varied with PAC type. The overall rate of ClO_2^- removal was also slower, with the total percentage of ClO_2^- removal less, when chlorine was present in the mixture.

ACKNOWLEDGEMENTS

The author would like to express his most sincere appreciation to Dr. Robert C. Hoehn for all his cheerful advice, assistance, and expert suggestions throughout. The patience, the many thoughtful answers (to my not always so thoughtful questions) and the superb moral support provided always by Dr. Andrea Dietrich, by Julie Petruska, by Marilyn Grender, and by Dianna Rashash is most deeply appreciated

TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS.....	iii
I. INTRODUCTION.....	1
II. LITERATURE REVIEW	4
Background	4
The Chemistry of Chlorine Dioxide	9
Physical Properties	9
Generation and Measurement of Chlorine Dioxide	11
Reactions of Chlorine Dioxide With Other Compounds	14
Aqueous Reactions	14
Reactions With Hydrocarbons, Alcohols, Acids	15
Reactions With Inorganics	16
Biological Properties of Chlorine Dioxide	17
Disinfection.....	17
Health Effects of Chlorine Dioxide, Chlorite, and Chlorate	18
Removal/Reduction of Oxychlorine Residuals From Drinking Water	22
Powdered Activated Carbon.....	25
History of Powdered Activated Carbon (PAC)	25
PAC manufacture, characteristics, and use	27
Porosity of carbon.....	33
Ion chromatography.....	37

III. METHODS AND MATERIALS	41
Reagents.....	41
Powdered Activated Carbons (PACs) Screened.....	41
Glassware.....	44
Instrumentation	44
Ion Chromatography	44
Amperometric Titration	46
Other Instruments and Equipment.....	47
Analysis of Metals Associated With PAC	47
Laboratory protocol.....	49
Precision of the Ion Chromatographic Analyses	52
IV. RESULTS.....	59
Chlorite Ion Removal by PAC in Laboratory Studies	59
Analysis of Acid Extracted Metals	71
V. DISCUSSION.....	74
Chlorite Ion Removal by PAC in Laboratory Studies	74
Removal of Chlorite Ion With Chlorine Present.....	76
Correlation Between Removal Efficiency and PAC Characteristics.....	77
Acid extracted metals	77
Particle Diameter	79
Carbon Raw Material	80
Porosity of the Carbon	80

VI. SUMMARY AND CONCLUSIONS82

 Summary82

 Conclusions84

REFERENCES88

Appendix A. Raw Data From Experiments118

Appendix B. Individual Plots for each PAC176

Appendix C. Data and Plots Comparing the PACs.....201

LIST OF FIGURES

Figure 1. Pore distributions of active carbons for three different source materials.	30
Figure 2. Chloride ion standards (mg/L) versus measured peak height in centimeters for the Dionex Ion Chromatograph.....	53
Figure 3. Chlorate ion standards (mg/L) versus measured peak height in centimeters for the Dionex Ion Chromatograph.....	54
Figure 4. Chlorite ion standards (mg/L) versus measured peak height in centimeters for the Dionex Ion Chromatograph.....	55
Figure 5. Percent of ClO_2^- removed by various PAC over a 4 hour period from reagent water containing only PAC and ClO_2^- at pH 7.	64
Figure 6. Percent of ClO_2^- removed by various PAC over a 4 hour period from reagent water containing only PAC and ClO_2^- at pH 7.	65
Figure 7. Percent of ClO_2^- removed by various PAC over a 4 hour period from reagent water containing chlorine, PAC and ClO_2^- at pH 7.	66
Figure 8. Percent of ClO_2^- removed by various PAC over a 4 hour period from reagent water containing chlorine, PAC and ClO_2^- at pH 7.	67
Figure 9. Rate of removal of ClO_2^- by each of the tested PACs after 15 minutes contact time.	68
Figure 10. Total metal (aluminum, boron, iron, magnesium, manganese, and zinc) versus mg ClO_2^- removal after 1 hour contact time.....	73

LIST OF TABLES

Table 1. Properties of activated carbons from several raw materials	29
Table 2. Reagents used in the laboratory research	42
Table 3. Known characteristics of PACs screened	43
Table 4. ICP detection limits for metals analyzed	48
Table 5. Summary of statistics for replicate samples resulting from a six jar test of CECA 20 B PAC at 20 mg/L, starting with 2.40 mg/L ClO_2^-	56
Table 6. Comparison of the actual concentration of standards with the results determined by ion chromatograph analysis for standard samples created by an independent analytical chemist.....	58
Table 7. Chlorite ion removal by 12 PACs during 24-hour contact when chlorine was absent.....	60
Table 8. Chlorite ion removal by 12 PACs during 24-hour contact when chlorine was present	61
Table 9. Rate of removal (in percent per hour) of chlorite ion by 12 PACs during 24 hour contact when chlorine was absent	62
Table 10. Rate of removal (in percent per hour) of chlorite ion by 12 PACs during 24 hour contact when chlorine was present.....	63
Table 11. Results of analysis by VPI & SU Soil Testing and Plant Analysis Laboratory	72

Chapter I

INTRODUCTION

For over seventy years chlorine has been the potable water disinfectant of choice in the United States, with over 99 percent of all municipal water plants eventually selecting this chemical. In 1972, chlorination was associated with the formation of trihalomethanes (THMs), which are organic compounds with three substituted halogens that are formed by reactions between chlorine and certain organics present in the raw water. These findings, coupled with many other reports of THMs and other chlorinated by-products in drinking water, were major contributors to the Safe Drinking Water Act of 1974. Later, in 1976, the National Cancer Institute found that chloroform, one of the THMs, was carcinogenic in laboratory animals.

The United States Environmental Protection Agency (USEPA) responded by regulating THMs. The maximum allowable concentration of total THMs (TTHMs) in finished drinking water is currently 0.10 mg/liter (mg/L). The USEPA further recommended that those water treatment plants utilizing raw water with high organic content consider the use of an alternate disinfectant.

Chlorine dioxide (ClO_2) was recommended as an effective water disinfectant which did not produce THMs. The EPA further advised that ClO_2 could be used as a pre oxidant, alternative disinfectant, or supplemental disinfectant to chlorine. It soon became obvious, however, that ClO_2 was not without its own problems. During the water treatment process, ClO_2 was discovered to produce chlorite ion

(ClO_2^-), chlorate ion (ClO_3^-), and chloride ion (Cl^-). This led researchers to investigate potential health effects of ClO_2^- and the known by-products.

Several potential health effects of concern have been demonstrated in laboratory animals, the most serious of which involve hemolytic anemia and thyroid effects (Condie, 1986). The few human studies referenced in this paper stated that no significant health effects had been discovered. The USEPA, apparently not agreeing with this perception, has acted upon the advice of the National Academy of Sciences Safe Drinking Water Committee to currently recommend that the combined total residuals of ClO_2 , ClO_2^- , and ClO_3^- not exceed 1 mg/L in finished water (Pfaff and Brockhoff, 1990). Action to lower these limits much further is currently in process (Zavalata, 1992).

If ClO_2 dosages exceed about 1.5 mg/L this current limit cannot be met (Gordon *et al.*, 1990). With even more restrictive limits on oxychlorine residuals expected in the near future, the utilization of ClO_2 as a drinking water disinfectant will prove difficult unless other actions are taken to remove some or all of these constituents (Regli, 1991). Previous studies by Oehler and Schuttler (1986), Orr (1990) and Grabeel (1991) all suggested that treatment with PAC would be a viable technique to remove ClO_2^- from water.

This study focused on three major objectives. The first of these was to determine the ClO_2^- -reduction capability of twelve powdered activated carbons. The second objective was to evaluate the effects of chlorine on ClO_2^- reduction and ClO_3^- formation. The final major objective was to evaluate several properties of the carbons with a view toward possible explanations regarding the level of effectiveness of each carbon in the removal of ClO_2^- . The removal of ClO_2^- by PAC was of major interest, since some 70 percent of ClO_2 is oxidized to ClO_2^-

during the water treatment process (Gordon *et al.*, 1990). Any resulting production of ClO_3^- during the process was also important, since the removal of ClO_3^- is not possible by conventional treatment techniques.

The approach to meet these objectives was first to observe the removal of ClO_2^- and the production of ClO_3^- and Cl^- in a well-stirred jar of reagent water containing ClO_2^- , at $\text{pH } 7 \pm 0.2$ pH units, with 20 mg/L PAC added in each case. The next step repeated the experiment with chlorine added but all other conditions held the same. The results of these two sets of experiments were then used to screen the twelve different PACs under each of the above conditions to allow comparison of the capability of several types of activated carbon. The final step involved comparison of a number of PAC chemical and physical properties with the ClO_2^- removal capability of each PAC to determine if a correlation could be suggested from the experimental data.

Chapter II

LITERATURE REVIEW

Background

Waterborne disease was a dire, ubiquitous health problem throughout the world until the turn of the century when disinfection was first introduced to the treatment of municipal drinking water (Bryant, *et. al*, 1992). In the United States, disinfection was probably the single most important factor in the control of typhoid fever (National Academy of Sciences, 1987). The chemical initially used for drinking water disinfection in this country was chlorine, with the first successful installation at the Bubbly Creek Filter Plant in Chicago in 1908 to provide safe water to the Chicago stockyards. Because of its oxidizing powers, chlorine was also found to serve other useful purposes in water treatment, such as taste and odor control, prevention of algal growths, maintenance of clean filter media, removal of iron and manganese, destruction of hydrogen sulfide, color removal, control of slime growths in distribution systems and main sterilization. Chlorine was also found to be reasonably inexpensive, easy to apply, measure and control, and fairly persistent (White, 1986).

In the seventy years which followed, chlorine became by far the predominant method used for drinking water disinfection because of its potency and range of effectiveness as a biocide, with over 95 percent of all municipal water supplies being disinfected with chlorine. Even in countries where ozone is preferred,

chlorination has been almost universally employed in practice as an adjunct to the ozone (White, 1986).

This state of affairs persisted without health concerns until the early 1970s, when speculation about the effect of chlorination upon organic materials in drinking water began to surface in the literature. In Europe, Kleopfer et al. (1972), Novak et al. (1973), Friloux (1971), Grob and Grob (1974), Bellar et al. (1974), and Rook (1974, 1976) reported the presence of organohalides in finished waters. Rook (1974) and Bellar (1974) found that the chlorination of Rhine River water brought about the formation of the trihalomethanes (THMs) chloroform, bromoform, dibromochloromethane, and dichlorobromomethane, all chemicals which had not been present in the raw water.

The U.S. EPA (1972) reported on the industrial pollution of the lower Mississippi River and disclosed the presence of chloroform (a suspected carcinogen) in the New Orleans potable water supply. The Safe Drinking Water Act (SDWA) of 1974 was prompted, in part, by these reports.(Gilbert & Calabrese, 1992). [Research since that date has found many additional chlorine byproducts in drinking water, both volatile and nonvolatile, some of which are carcinogens and some mutagens (Rechow & Singer, 1990)]. In 1976 the National Cancer Institute confirmed that chloroform had been found to be carcinogenic in rats. When this was followed in November 1979 by the promulgation of the 0.10 mg/L maximum contaminant level for total THMs, the search for alternatives to chlorination was intensified (White, 1986). The alternatives were found to be:

- a. remove the organic precursors from raw water prior to chlorination.
- b. remove the trihalomethanes from the water after they formed.
- c. use an alternate disinfectant which did not produce THMs.

- d. Optimize coagulation to improve THM-precursor reduction prior to chlorination.

The use of alternate disinfectants was determined to be the most rapidly implemented and least costly of the four choices. The other disinfectants considered included ClO_2 , ozone (O_3), chloramines, potassium permanganate, and ultraviolet radiation (Bryant *et al.*, 1992). One of the alternative disinfectants proposed, which received the recommendation of the U.S. EPA and a good deal of interest, was ClO_2 .

Sir Humphrey Davey first produced ClO_2 in 1811 when he mixed hydrochloric acid with potassium chlorate and observed the evolution of a greenish-yellow gas with a pungent aroma, which he named "euchlorine." This gas was later found to be a mixture of ClO_2 and chlorine (White, 1986). White (1986) also reports that Watt and Burgess recognized in 1854 the bleaching action of ClO_2 on wood pulp. Today, large quantities of ClO_2 are produced in the United States, with the primary application being the bleaching of wood pulp; however, it is also used in the textile industry for bleaching and dye stripping, with additional use in bleaching flour, fats, oils, and waxes (Gall, 1978).

The first United States use of ClO_2 in water treatment was in 1944 at the Niagara Falls Plant Number 2 to control phenolic tastes and odors which had been produced by algae, decaying vegetation, and industrial waste contamination (Sussman and Rauh, 1978). Granston and Lee (1958) reported on a survey of U.S. water treatment plants believed to be using ClO_2 . A large majority (56) of the plants responding reported using ClO_2 for taste and odor control, with seven plants using it for algae control, three for iron and manganese control, and only fifteen plants using ClO_2 for disinfection (White, 1986). In 1978, 84 plants in the U.S.

were using ClO_2 , but only the Hamilton, Ohio plant reported using the chemical solely for disinfection (Miller, *et al.*, 1978). A Wallace and Tiernan survey in 1981 recorded 260 installations in the U.S. which were using ClO_2 for potable water (White, 1986). Sussman (1978) confirmed that the primary use of ClO_2 was for taste and odor control in the U.S., but found that it was used mainly for disinfection in England, Italy, and Switzerland.

The AWWA Water Industry Data Base (WIDB), (with data for those utilities which serve over 50,000 people collected in 1989-1990, and with utilities serving 10,000-50,000 people surveyed 1991-1992), contains information regarding 1097 utilities, of which 703 use surface water, and 590 use ground water as a raw water source. Of the 703 plants which use surface water, 69 use ClO_2 for pre-disinfection/pre-oxidation, and another 16 use ClO_2 for post-disinfection. Of the 590 plants with ground water as a source, only three use ClO_2 as a pre disinfectant/pre oxidant and only one uses it for post-disinfection (AWWA, 1993).

Chlorine dioxide is a strong oxidizing agent which reacts by electron extraction from many organic and inorganic substances dissolved in water to produce primarily ClO_2^- and Cl^- ions (Rav Acha, 1984). Chlorine dioxide produces a spectrum of oxidized products in the water, not the chlorinated products like those produced when chlorine is used, and produces virtually no THMs (Symons *et al.*, 1981). When ClO_2 is used in company with chlorine to treat water, the ClO_2 greatly decreases the amount of THMs formed by the chlorine (Miltner, 1976; Symons *et al.*, 1981).

Chlorine dioxide rapidly kills most bacteria, viruses and algae present in water (Ridenour and Armbruster, 1949; Rav-Acha, 1984). It does not react with phenols to form chlorophenols or other compounds present in water which may

produce an unpleasant taste or odor (Aieta and Berg, 1986). Chlorine dioxide also oxidizes iron and manganese ions in drinking water (Katz, 1980; Knocke *et al.*, 1987). Average dosages of ClO_2 in the United States range from 0.10 to 1.5 mg/L, depending on whether the oxidant is used for pre treatment (removal of algae, Fe, Mn, etc.) or for final treatment (disinfection) (Miller *et al.*, 1978). The average dosage in Europe ranges from 0.10 to 0.5 mg/L (Miller *et al.*, 1978). Chlorine dioxide does not readily react with ammonia, as does chlorine, but many waters can exert a ClO_2 demand that results from the presence of background organic matter or inorganic substances such as iron, manganese, and sulfides (Bryant *et al.*, 1992).

White (1986) summarized the advantages of ClO_2 for drinking water treatment as follows:

1. "It is at least as effective a bactericide as chlorine, and in many cases is superior."
2. "It is far superior as a viricide."
3. It does not react with ammonia.
4. It does not react with oxidized materials to form THMs.
5. "It reacts to destroy up to 30 percent of THM precursors present in raw water."
6. Its efficiency as a disinfectant is unaffected by pH in the range 6-10.
7. It is specific for the destruction of phenols and can destroy chlorophenols.
8. It does not react with water as other halogens do.
9. "It is superior at removing manganese and iron, particularly with complexed compounds."
10. It has been used successfully in removal of taste and odor problems.
11. Its residuals persist longer than those of chlorine in the distribution system.

Most of these are discussed more thoroughly in the following sections of the literature review.

While there are many advantages, ClO_2 use is not without its disadvantages. The following have been identified:

1. Both ClO_2 and its inorganic by-products have a number of potential adverse health effects, as have been previously discussed.
2. Chlorine dioxide must be made on-site, due to its unstable, explosive nature.
3. It can produce several disagreeable odors at point of use (Dietrich *et al.*, 1992; Hoehn *et al.*, 1990).
4. Some production processes may produce free chlorine and thus the potential for the formation of THMs.
5. The cost for water treatment is about five times the cost of chlorine.
6. If dosage is greater than 6 lb/Mgal, ClO_2 can produce a metallic taste in water.
7. There are no reliable, rapid and practical tests for utility personnel to use to evaluate and differentiate the three chemicals in treated water.

The Chemistry of Chlorine Dioxide

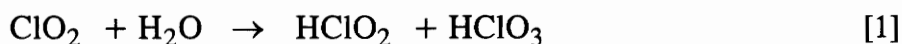
Physical properties

At room temperature, ClO_2 is as a yellowish-green gas which approaches orange-red as its concentration increases. It is soluble in water as a true gas to a concentration of 2.9 grams per liter at 22° C, but in chilled water its solubility increases to 7 grams per liter (Gall, 1978). Gordon *et al.* (1972) indicates a solubility as high as 70 grams per liter. It is normally used as an aqueous solution. The melting point of ClO_2 is -59° C and its boiling point is 11° C. The density of

ClO_2 in the liquid form is 1.64, and at 0°C it exerts a vapor pressure of 500 torr. Chlorine dioxide exists as a permanent free-radical monomer, with the chlorine-oxygen bonds showing predominantly double bond characteristics (Gordon *et al.*, 1972). Chlorine dioxide is paramagnetic, and this feature allows it to be differentiated from sodium chlorite in the process stream (Masschelein, 1979).

Chlorine dioxide in its liquid form is very unstable. It may explode in the presence of bright light, physical impact, or upon coming into contact with organic compounds. In the gaseous form, it is explosive above 10 percent in air if a spark or other source of ignition is present (Masschelein, 1979). Chlorine dioxide is quite safe in aqueous solution, although it remains a strong oxidizing agent.

Chlorine dioxide is a mixed anhydride of chlorous acid (HClO_2) and chloric acid (HClO_3):



In neutral aqueous solution the dissociation constant is small:

$$\frac{[\text{HClO}_2][\text{HClO}_3]}{[\text{ClO}_2]} = 1.2 \times 10^{-7} \text{ (at } 20^\circ \text{C)} \quad [2]$$

Therefore, most of the ClO_2 remains in the undissociated form in a neutral aqueous solution.

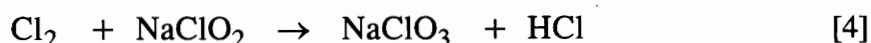
Chlorine dioxide is light sensitive, reacting with light to generate other free radicals which react through a variety of pathways to produce chlorine, Cl^- , ClO_2^- , and ClO_3^- (Masschelein, 1979; Gordon *et al.*, 1972). Even in the dark, solutions of ClO_2 at room temperature will decompose at a rate of 2-10 percent per day while

slowly becoming more acidic. If the solution is kept in a dark refrigerator at 2° C, the rate decreases to less than 1 percent per day (Ingols and Ridenour, 1948).

Generation and Measurement of ClO₂.

Chlorine dioxide can be generated by several methods, the choice of which depends on the volume and purity needed (Gordon, *et al.*, 1972). Large production units for bleaching of paper and textiles generate ClO₂ from sodium chlorate (NaClO₃), while in most water treatment plants, ClO₂ is produced by the addition of either a chlorine solution or chlorine gas to aqueous sodium chlorite (NaClO₂). The reaction between acid (either hydrochloric or sulfuric) and ClO₂⁻ is sometimes used to generate ClO₂ in smaller installations, and in the laboratory, with sulfuric acid, to produce high purity ClO₂ (White, 1986).

The first system, in which theoretical maximum efficiency reaches 100 percent, utilizes chlorine to oxidize chlorite to ClO₂ in one of the following reactions, the second of which produces the undesirable by-product chlorite (Aieta and Berg, 1986):



During the reaction shown by the first equation, 1.34 lb of pure NaClO₂ will react with 0.5 lb of chlorine to produce 1.0 lb of ClO₂. The technical grade NaClO₂ usually used in this process is only about 80 percent pure, so that 1.68 lb would be required if 100 percent yield is achieved (White, 1986). If the chemicals were

reacted stoichiometrically, the resulting pH would be close to 7, but the reaction proceeds more favorably at a pH of less than 4.0. Excess chlorine is used to lower the pH and drive the process further toward completion, but this can impact upon the purity of the final solution, as can be seen from equation [4], which demonstrates the production of the undesired ClO_3^- ion (White, 1986).

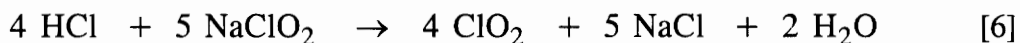
The concentration of reactants determines whether more ClO_2 or ClO_3^- will be formed. High concentrations of NaClO_2 and either hypochlorous acid (HOCl) or molecular chlorine will enhance the formation of ClO_2 . Feeding two to three times the stoichiometric requirements of chlorine will result in high yields, but if too much excess chlorine is added, the pH will be depressed and ClO_3^- concentration will be increased. The presence of chlorine in the disinfectant solution is also undesirable because this chlorine will produce THMs if organics are present (Aieta and Berg, 1986; Huebner, 1988).

The purity (P) of the production process is defined as the ratio of ClO_2 to the total of all oxidative chlorine compounds (White, 1986):

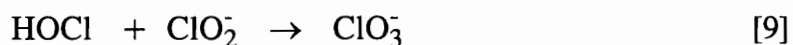
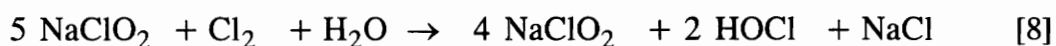
$$P = \frac{\text{ClO}_2}{\text{ClO}_2 + \text{Cl}_2 + \text{NaClO}_2 + \text{NaClO}_3} \times 100\% \quad [5]$$

The second type of system, not as common in practice, adds acid to NaClO_2 , and conditions are developed that encourage a disproportionation reaction. The theoretical maximum efficiency of this system, however, is only about 80 percent. Essentially, 20 percent of the chlorite is sacrificed to oxidize the remaining

chlorine to ClO_2 (Huebner, 1988). The following equations describe the reactions involved in this system:



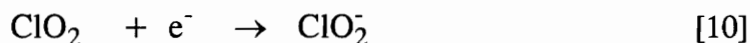
Other side reactions may also take place (Ingols and Ridenour, 1948; Katz, 1980; Gordon *et al.*, 1972).



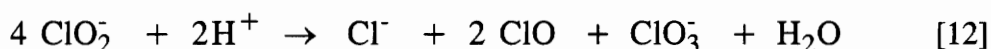
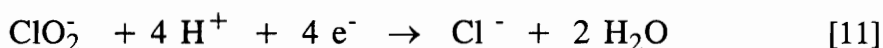
The only other factor which should affect the performance of a ClO_2 generator is pH. A pH below 4 is essential for a rapid and complete reaction, and pH is normally adjusted with HCl to be in the range 2 to 3. The acidic conditions shift the equilibrium of the chlorine solution to favor hypochlorous acid (HOCl) and Cl_2 . A lower pH would cause equation [6] to be the predominant reaction of ClO_2 formation, with the maximum theoretical conversion of only 80 percent (Masschelein and Rice, 1979). A higher pH results in the OCl^- ion form of chlorine, which does not react rapidly to produce good yields. In addition, high pH values or low reaction rates may cause the formation of ClO_3^- (Gordon, *et al.*, 1990).

Reactions of Chlorine Dioxide With Other Compounds

Aqueous reactions. Chlorine dioxide can disproportionate in water to yield HClO_2 and HClO_3 , although the degree is very limited at neutral pH. These compounds can then dissociate liberating ClO_2^- and ClO_3^- ions as well as hydrogen ions, which lowers the pH (Gordon *et al.*, 1972). Due to its strong oxidizing ability, ClO_2 can acquire electrons and be directly reduced to chlorite (Gordon *et al.*, 1972).



At low pH, the chlorite ion may react according to the following equations:

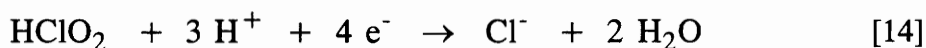


to yield chloride ions as one of the reaction products (Masschelein, 1979).

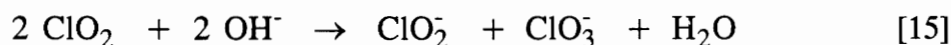
Chlorous acid may also disproportionate by:



Where HClO_3 is chloric acid. It may be reduced according to the equation.:



to yield chloride ions. In strongly alkaline solutions, ClO_2 may disproportionate according to the essentially irreversible equation (Masschelein, 1979; Gordon *et al.*, 1972; Rosenblatt, 1978).



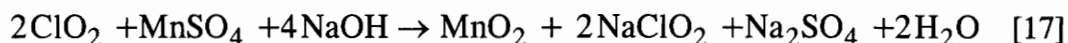
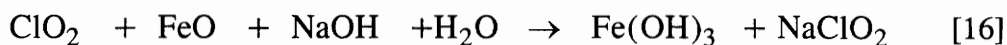
In summary, in aqueous solution of ClO_2 , chlorite ions, chlorate ions, and chloride ions are the major products, their relative abundance determined by the pH of the water and the presence of oxidizable substances.

Reactions with hydrocarbons, alcohols, carboxylic acids and phenols. Most aliphatic and aromatic hydrocarbons do not react with ClO_2 under normal water-treatment conditions unless they contain specific reactive groups (Stevens, 1978). Alcohols are resistant at neutral pH, but under conditions of very low pH, high temperatures, or high ClO_2 concentrations, they can react to produce their corresponding aldehydes or carboxylic acids (Rav Acha, 1984). Phenol reacts rapidly with ClO_2 . The reaction rate is first order with respect to each reactant (Gordon *et al.*, 1972).

Rav-Acha (1984) found that ClO_2 reacted with humic acids and fulvic acids in one water supply to produce quinones and hydroquinones in the finished water, while Guttnam-Bass *et al.* (1987) found the end products of the reactions to be primarily aldehydes and ketones in another water supply. Rav-Acha (1984) also found ClO_2 reacting with phenols to produce quinones. When insufficient ClO_2 is present to destroy the phenols, the reaction will produce chloroquinones, chlorohydroquinones, and chlorophenols, which may impart a strong medicinal taste to the water (White, 1986). In these instances, chlorine substitutes on the precursor compound, which is rare.

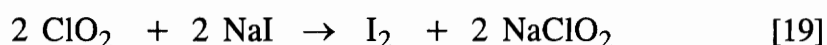
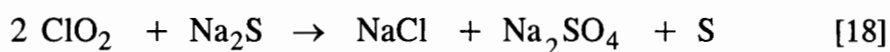
Reactions With Inorganics.

Iron and manganese are oxidized by the following reactions with ClO_2 :

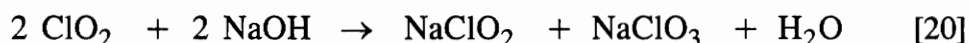


The reaction of ClO_2 with these metals is the basis of their removal from water sources.

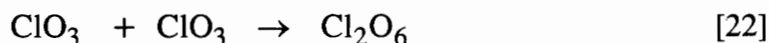
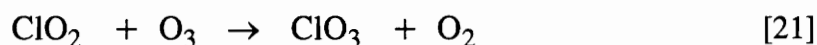
Chlorine can also oxidize sulfides and iodide by the following reactions:



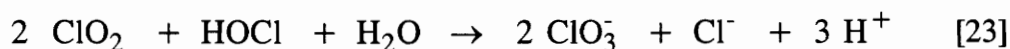
In aqueous, base solutions, ClO_2^- and ClO_3^- are produced:



Chlorine dioxide reacts also with other oxidants commonly used during the treatment of drinking water. It reacts with ozone to form chlorine hexoxide (Cl_2O_6) by two reactions:



If aqueous chlorine is present as HOCl , at low pH, ClO_2 can be oxidized to ClO_3^- by the following reaction:



Biological Properties of Chlorine Dioxide

Disinfection

White (1986) cited three studies conducted by Ridenour *et al.* concerning the disinfection capabilities of ClO_2 : Ridenour and Ingols (1947) concluded that ClO_2 was at least as effective as chlorine, and that it was relatively unaffected by pH values from 6 to 10, unlike chlorine. Ridenour and Armbruster (1949) found that ClO_2 destroyed several common water pathogens. Ridenour and Ingols (1949) reported that ClO_2 was clearly superior to chlorine in the destruction of spores .

Bernarde *et al.* (1965, 1967) noted that the germicidal efficiency of chlorine results from its hydrolysis in aqueous solutions to form hypochlorous acid, which is the disinfectant constituent. In contrast, ClO_2 does not hydrolyze in aqueous solutions and therefore, the ClO_2 molecule appeared to be the bactericidal agent. This investigation further determined that the mechanism of kill occurred through the disruption of protein synthesis and not enzyme inactivation which earlier studies had postulated (Gall, 1978). Contact time tests with *E. coli* demonstrated that at pH of 6.5 chlorine was somewhat more effective, but that ClO_2 was dramatically more effective at pH 8.5 (Bernarde, 1965).

White (1986) related that a Hettche and Ehlbeck (1953) investigation found the action of ClO_2 against poliomyelitis virus to be more effective than either ozone or chlorine. Chlorine dioxide also functions as an algacide, and has been shown to be effective in controlling musty and fishy tastes and odors that are characteristic of algae such as *Anabaena*, *Asterionella*, *Synura*, and a protozoan, *Vorticella* (Katz, 1980).

In summary, ClO_2 has been found to be a strong primary disinfectant that is effective for bacterial, viral, and protozoan pathogens. In case of the removal of *Giardia*, CT levels are less than half those required for free chlorine, with the reduction even greater under most pH conditions. For the removal of virus, free chlorine is given higher "CT credit," but ClO_2 is still more effective (Bryant, *et al.*, 1992). As has been noted previously, the disinfecting effectiveness of ClO_2 is not seriously affected over the pH range of 6 to 9, and, in addition, ClO_2 does not react readily with ammonia, a chemical which exerts an appreciable chlorine demand.

Health Effects of Chlorine Dioxide, Chlorite, and Chlorate.

When ClO_2 was selected in the U.S. as an alternative drinking water disinfectant, it became apparent that little was known about the possible health hazards of ClO_2 or its reaction by-products (Condie, 1986). Since that time, numerous studies have been conducted with ClO_2 , ClO_2^- , and ClO_3^- . Toxicological effects were first associated with the hemopoietic (blood producing) system and studies indicated that ClO_2^- produced hemolytic anemia in animals, which was associated with oxidative damage to the red blood cell membrane (Condie, 1986). Additional studies extended these findings to ClO_3^- and to ClO_2 itself, although ClO_2^- remained the most potent in effect in several animal species.

Bercz *et al.* (1982) evaluated hematological effects in monkeys, with the disinfectant in the drinking water being increased in stepwise fashion. Hematological effects were noted with ClO_2^- and ClO_3^- , but not with ClO_2 . In addition, the researchers detected decreases in serum thyroxin levels at a dose of 9 mg/kg/day. This hypothyroid effect was unique to ClO_2 , because the metabolite ions did not

produce any observable effect, even at much higher exposure levels. It was not surprising that developing rats exposed to ClO_2 exhibited delayed brain development and behavior, because thyroid function is intimately involved with the control of neurobehavioral development. Daniel *et al.* (1990) conducted subchronic toxicity studies in which Sprague-Dawley rats were exposed to ClO_2 (at concentrations of 25, 50, 100, and 200 mg/L) in their drinking water for 90 consecutive days. No premature deaths were noted, but ClO_2 produced decreased weights and nasal lesions at all doses.

Reproductive and developmental studies were also conducted with ClO_2 . Female mice exposed to ClO_2 in drinking water from breeding to weaning delivered pups with lower growth rates and body weights at the time of weaning (Moore and Calabrese, 1982). In another study, dams exposed to "extreme" levels of ClO_2 experienced smaller litter sizes and an increase in stillbirths (Couri *et al.*, 1982). Couri *et al.* (1982) reported an increased percentage of abnormal sperm in male rats exposed to drinking water containing ClO_2 at a concentration of 500 mg/L, while yet another study did not detect sperm-head abnormalities in mice exposed to ClO_2 , ClO_2^- , or ClO_3^- (Meier *et al.*, 1985).

The mutagenic potential of all three chemicals was evaluated in the mouse micronucleus assay, the mouse bone marrow chromosomal aberration assay, and the mouse sperm-head abnormality assay (Meier, *et al.*, 1985). No evidence of mutagenic activity was detected. Chlorite ion at 100 mg/L was utilized in a carcinogen test on Sencar mice (Kurokawa *et al.*, 1984). No tumors were detected in the complete carcinogenicity test. A renal carcinogenesis bioassay of rats with sodium chlorate and potassium chlorate reported by the same team in 1985 did not demonstrate a carcinogenic effect

Because of the extensive use of ClO_3^- as a weed killer, there are a number of reports of chlorate-poisoning in humans, with doses as high as 3400 mg/kg, the lowest lethal doses being about 220 mg/kg in adults and about 250 mg/kg in children. Reported effects of ClO_3^- ingestion include cyanosis, methemoglobinemia, renal failure, congested kidneys, hypothermia, convulsions, coma, and death (Condie, 1986).

Lubbers et al. (1981, 1982, 1983) provided human volunteers increasing doses of ClO_2 , ClO_3^- and ClO_2^- in drinking water for one day, in Phase I of a clinical evaluation. In Phase II, volunteers ingested for twelve weeks water which had been disinfected with 5 mg/L ClO_2 . There were no detectable alterations in blood parameters, serum or urine chemistry values and no adverse physical symptoms. During Phase III, the same drinking water was provided to "potentially at-risk glucose-6-phosphate dehydrogenase deficient subjects" who may be expected to be especially susceptible to oxidative stress. The conclusion reached was "by absence of detrimental physiological response within the limits of this study, the relative safety of oral ingestion of ClO_2 and its metabolites was demonstrated" (Lubbers, *et al.*, 1982).

An epidemiological study of a community was conducted in a rural village in which ClO_2 (at an average addition concentration of 5 mg/L) was used as a drinking water disinfectant for 12 weeks. A total of 198 persons was exposed to the drinking water for the entire period, while a control group of 118 was not exposed. Final adult exposure ranged from 0.25 to 1.1 mg/L for ClO_2 , 3.2 to 7 mg/L for ClO_2^- , and 0.87 to 1.8 mg/L for ClO_3^- . No consistent changes were observed in any of the measured clinical parameters, and "an ANOVA test failed to identify any significant exposure related effects" (Michael, *et al.*, 1981).

Tuthill et al. (1982) examined a population that had drunk water disinfected with ClO₂ in the 1940s and compared mortality and morbidity with a neighboring community. The only significant difference was a greater postnatal weight loss by infants in the exposed population.

In summary, ClO₂ produces hematological effects in both laboratory animals and humans. The mechanism is suspected to be related to the oxidizing properties of ClO₂ and its aqueous reaction products, ClO₂⁻ and ClO₃⁻. Laboratory animals have also demonstrated thyroid and developmental neurological effects. Chlorite's thyroid effects are thought to be caused by its oxidation of iodine in the GI tract, which binds the oxidized iodine to food or tissue and prevents absorption. The mechanisms of the neurological effects are unknown (National Academy, 1987).

The Safe Drinking Water Committee (1987) determined that investigators have demonstrated a no-observed-effect-level (NOEL) of 3.0 mg/kg per day for ClO₂ and used this number in combination with an uncertainty factor of 100 to determine a suggested-no-adverse-reaction-level (SNARL); calculated as follows:

$$\frac{3\text{mg/kg body weight/day} \times 70\text{ kg} \times 0.2}{100 \times 2\text{ liters}} = 0.21\text{ mg/liter}$$

The standard assumptions of body weight and liters per day water consumed are coupled with an assumption that only 20 percent of the ClO₂ ingested each day is provided by the drinking water (National Academy, 1987). The possible source(s) of the remaining 80 percent of daily ingested ClO₂ are not identified by the National Academy.

Removal/Reduction of Oxychlorine Residuals From Drinking Water

Because of the numerous studies which have focused on potential toxicological effects associated with the use of ClO_2 and its inorganic by-product species ClO_2^- and ClO_3^- , all three substances are included on the drinking water priority list for disinfectants and disinfectant by-products and are targeted for future regulatory consideration by EPA (Griese, *et al.*, 1991). As was mentioned earlier, the EPA established in 1983 a recommended limit of 1 mg/L for the combined residuals of ClO_2 , ClO_2^- and ClO_3^- in finished water (Dixon, *et al.*, 1991). Vogt and Regli (1981) suggested that the MCL should be less than 0.5 mg/L combined oxidants, but Zavaleta (1992) reported that the USEPA is considering MCLG's of 0.8mg/L for ClO_2 and 0.3 mg/L for ClO_2^- . The toxicological basis for establishing a limit for ClO_3^- is poorly developed; therefore, no MCLG was recommended. When a regulation is actually issued by the USEPA, it may well include a limit lower than 1 mg/L. In fact, Zavaleta (1992) suggested an MCLG of 0.8 mg/L for the sum of ClO_2 and its by products.

Aieta and Berg (1986) and Werdehoff and Singer (1987) reported that during water treatment, between 50 percent and 70 percent of the reacted ClO_2 will immediately appear as ClO_2^- and the remainder will appear as Cl^- . The residual ClO_2^- will continue to degrade to Cl^- in the distribution system. They stated that under these conditions no ClO_3^- is found. Thus, if ClO_2 is to continue as a viable disinfectant for drinking water, a method must be found to eliminate the ClO_2^- or further reduce it to Cl^- without the introduction of additional objectionable residuals (Gordon, *et al.*, 1990; Iatrou and Knocke, 1992).

Gordon *et al.* (1990) conducted a study on the use of sulfur dioxide to remove ClO_2^- , and found that some 90 percent was removed in less than 15 minutes; however, Dixon and Lee (1991) stated that this procedure led to the formation of ClO_3^- in significant amounts when the water contained dissolved oxygen. Griesse *et al.* (1991) also reported ClO_3^- formation when either metasilfite or sulfur dioxide was used. Sodium thiosulfate effectively reduced ClO_2^- with little ClO_3^- formation, yielding sulfate and Cl^- ions. The required doses, however, make sodium thiosulfate impractical for the removal of chlorite. Bryant *et al.* (1992) reports that, under some conditions, ClO_3^- seems to be a major end product when granular activated carbon is used to remove ClO_2 and ClO_2^- . Dixon and Lee (1991) found this to be true at one utility where water containing both ClO_2^- and free chloride (HOCl) passed through GAC columns.

Iatrou and Knocke (1992) reported the successful use of ferrous iron $[\text{Fe(II)}]$ to reduce ClO_2^- concentrations with no evidence of ClO_3^- forming as a by-product of the reaction. They also found the reaction rate to be rapid at pH values of 5 and above and the interference from dissolved oxygen to be minimal. Ondrus and Gordon *et al.* (1972) and Aieta and Roberts (1985) also found that $[\text{Fe(II)}]$ would remove ClO_2^- under slightly acid conditions, but found slight production of ClO_3^- , with the formation of even more ClO_3^- when the water pH was less than 5. The use of Fe(II) was not effective in reducing concentrations of ClO_3^- (Griesse, *et al.*, 1992).

Orr (1990) reported the results of an investigation into the cause of odors in customer homes and into potential water treatment methods to mitigate these odors when ClO_2^- was used to disinfect drinking water. She determined that "a high level of PAC (50 mg/L) was required to effect good removal." Orr (1990) also investigated the use of a simulated floc-blanket clarifier to remove ClO_2^- at levels

>5 mg/L from drinking water. The PAC enmeshed in the floc at high concentrations effectively removed these levels of ClO_2^- over a 12 hour period.

Grabeel (1991) reported research into the chlorite-removal capability of two PACs, evaluated in both laboratory and pilot-scale studies. Grabeel determined that ClO_2^- removal decreased with increasing pH over a range from pH 5.5 to pH 7.5. Grabeel also determined that ClO_2^- was reduced to Cl^- over that same pH range and that ClO_3^- was additionally formed at pH 5.5 to pH 6.0. The pilot plant study, conducted at a municipal water works in Virginia, evaluated ClO_2^- removal by PAC enmeshed in a floc blanket in a pulsed-bed clarifier. A PAC dose of 10 mg/L removed just over 25 percent of the ClO_2^- , while a PAC dose of 20 mg/L removed nearly 60 percent of the ClO_2^- .

The research cited suggested that more study was needed into the removal of ClO_2^- using PAC at pH and dose levels which could be expected in municipal plants. The result was this study, which evaluates the removal of ClO_2^- by twelve different PACs at a pH of 7 and a PAC dose of 20 mg/L.

Powdered Activated Carbon

History of Powdered Activated Carbon (PAC)

Sontheimer *et al.* (1988) discusses the work of Place (1905), who indicated in a notice from India that old medical scripts in Sanskrit (ca. 2000 BC) gave the following prescription: "It's a good idea to keep water in copper kettles, to expose it to sunlight, and to filter it through charcoal" Although the application of charcoal in water treatment was thus proposed approximately 4000 years ago, charcoal was not used for water treatment in an organized fashion until the late 18th century (Hassler, 1974). Hassler (1974) also reported other interesting historical facts about PAC. In the time of Hippocrates wood chars were used to treat various ailments. The earliest date at which adsorptive powers were definitely recognized was 1773 when Scheele described experiments with gases. In 1785, Lowitz called attention to decolorizing effects of charcoal on solutions; and in 1786, he performed experiments demonstrating the decolorizing of solutions as well as water treatment (Baker, 1949). Kehl in 1793 discussed the use of char for removal of odors from gangrenous ulcers (Hassler, 1974).

A few years later, wood char was employed to purify cane sugar, and in 1808 was applied to the then infant beet-sugar industry (Hassler, 1974). Figuers' discovery in 1811 of greater decolorizing power of bone char led to its almost immediate adoption by the sugar refiners. At first, pulverized bone char was applied on a single use and discard basis, but limited supplies made regeneration necessary (Hassler, 1974).

Hassler (1974) also reports on work by Ostrejko, patented in 1900 and 1901, which led to the development of modern commercial activated carbons. Early interest was stimulated by a belief that a large potential market existed in the cane sugar industry. Some early studies seemed to indicate that PAC could be applied for decolorization directly to the raw cane juice; however, this hope was not realized. The intermediate stage of raw sugar was still necessary. The use of chlorine gas in WW I stimulated rapid progress in developing effective methods of production of granular carbons, which were used in gas masks.

In the early 20th century, activated carbon, which was employed in a few food-processing factories for decolorization, was combined with the removal of taste and odor. Powdered activated carbon was used for taste-and-odor control in drinking water for the first time in Chicago by Baylis (1929) and in 1931 by Spalding (Sontheimer, *et al.*, 1988). The main problem substances were thought to be chlorophenols that impart unpleasant tastes and odors to drinking water at concentrations as low as 5 mg/cubic meter (micrograms per liter), and are formed by the chlorination of phenol in the water treatment process (Sontheimer, *et al.*, 1988). By 1932, only a few years after the first published results on the use of carbon for water treatment had appeared, about 400 waterworks in the USA were adding PAC to their water to improve taste and odor, at least periodically (Baker, 1949). By 1943, 1200 waterworks in the USA were using PAC, and by 1970 the number of waterworks which used either PAC or GAC columns for water treatment was estimated at 10,000 worldwide (Sontheimer, *et al.*, 1988).

The 1980 world production of activated carbon was approximately 400,000 tons per year, of which only about 20 percent was used in water treatment (Sontheimer *et al.*, 1988, quoting von Kienle and Bader, 1980). The advantage of

activated carbon over other adsorbents is that it removes a wide range of compounds, whereas others are more limited. Numerous water treatment plants that must rely on contaminated surface water as their source now use either PAC or GAC primarily for safety reasons. Moreover, in recent years, some water utilities utilizing ground water have had to employ activated carbon treatment to remove halogenated hydrocarbons. For more than 70 years, PAC has been used in water treatment plants all over the world (Sontheimer *et al.*, 1988).

Powdered Activated Carbon Manufacture, Characteristics and Use

Activated carbon can be made from a number of raw materials having a high carbonaceous content. The principal ones used by producers whose products are sold in the United States are:

1. Lignite
2. Bituminous coal
3. Sub bituminous coal
4. Coconut Shell
5. Charcoal
6. Pulp mill waste
7. Peat (outside of the United States)
8. Sawdust

All of these raw materials yield satisfactory activated carbons, are in good supply, and are relatively inexpensive except for coconut shell. Additional materials which are used as source materials for activated carbon include rice hulls, nut shells, coconut timber, olive pits, fruit pits, cereals, coffee beans, corncobs, hardwoods, softwoods, molasses, cottonseed hulls, sugarcane juice foam, fish, bones, animal flesh, blood, asphalt, carbon black tars, pitches, graphite, oil shale and many others (Sorrento, 1993; Hassler, 1974).

As stated earlier, the raw material determines to a large degree what the pore structure of an activated carbon will be. Figure 1 compares the pore size distributions of activated carbons made from three source materials; lignite, coal, and coconut shell. Table 1 lists some important properties for activated carbons produced from wood, coconut, coal and lignite. Lignite is a "low-ranked" coal; that is, a young coal which possesses a high content of volatiles that are lost during carbonization (Sorrento, 1993). The remaining fixed carbon has a low fraction of graphitic (crystalline) carbon and a high amorphous carbon fraction. The amorphous carbon is easily reacted with steam as well as oxygen and carbon dioxide (American Norit, 1989). The activated carbon made from lignite possesses a low volume of micropores suggesting an overriding effect of the exothermic reaction (DeJohn, 1975). The fact is that the rate of the reaction is so fast that large pores are created with steam alone (Sorrento, 1993).

Table 1. Properties of activated carbons from several raw materials.

Source	Wood	Lignite	Coal	Coconut
Surface area (m ² / gram)	500-1700	500-700	900-1100	900-1200
Apparent density (g/ml)	0.2-0.35	0.3-0.44	0.45-0.52	0.48-0.55
Iodine no. (mg/g)	500-1000	500-675	900-1200	900-1050
Molasses no.	200-400	300-600	200-300	<200
Abrasion no.	30-50	60-70	70-95	75-95
% Moisture	10	8	2	2
% Ash	1-10	20	7-15	2-10
Mean pore radius (Angstroms)	25-40	30	15	15-20

(after Sorrento, 1993, and modified by Rester, 1993)

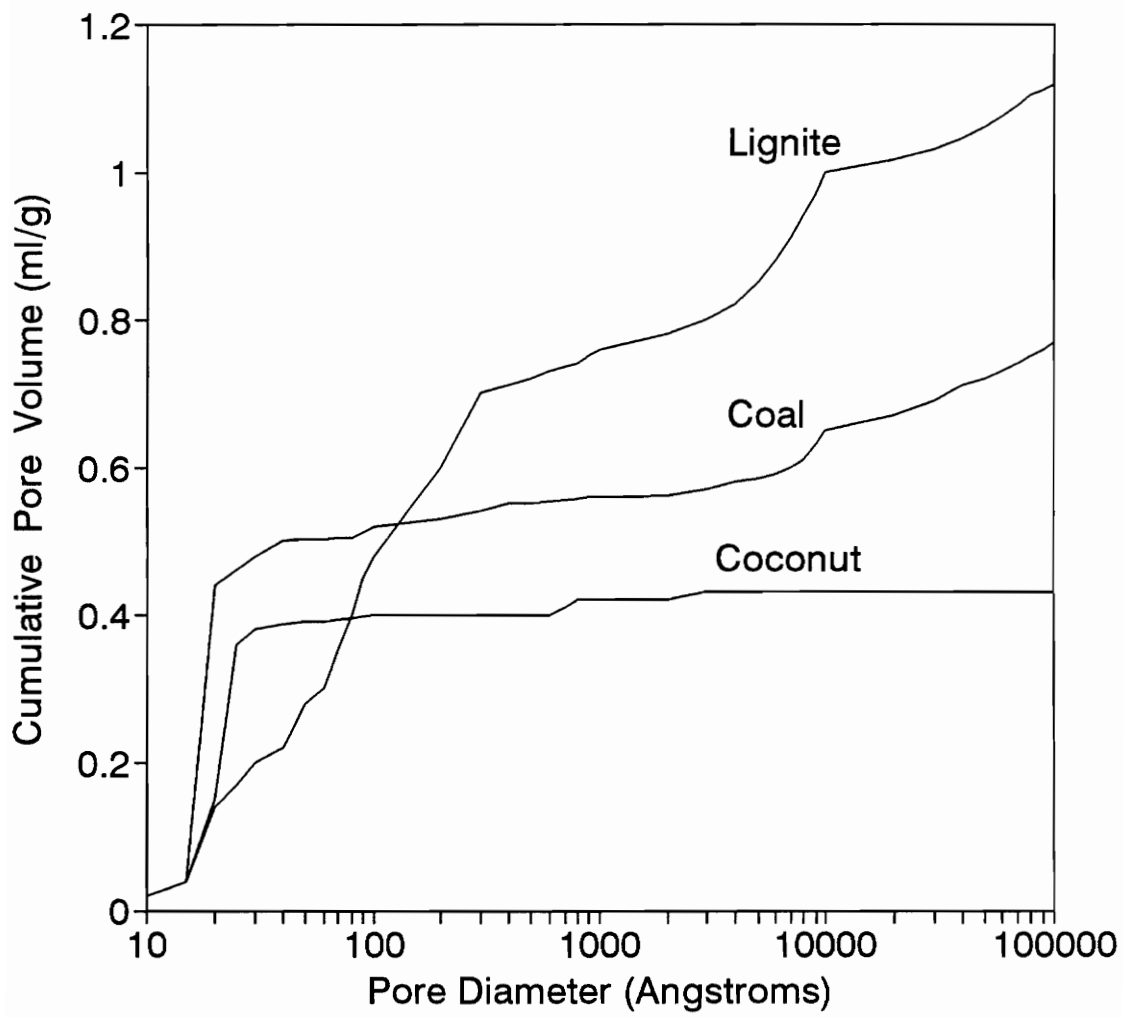


Figure 1. Pore distributions of active carbons for three different source materials.
(Sorrento, 1993).

Coconut shell, on the other hand, contains a low volatiles content and a high fraction of graphitic carbon in the fixed carbon mass. It is slow to react with steam. Because the surface resists oxidation, it can be permitted a long reaction time with steam resulting in the creation of a high-developed micropore network (Sorrento, 1993). When coal is used as the base material, it is possible to obtain a wide range of pore sizes as shown in Figure 1. Coals vary in rank (age) which affects the volatiles content, fixed carbon, and other parameters responsible for mechanical and physical properties in the activated carbon (Sorrento, 1993; DeJohn, 1975). The selection of a coal for use in the manufacture of activated carbon is further complicated by the balance of economics of production and desired properties (DeJohn, 1975).

Because coal is heterogeneous in nature and possesses numerous natural fracture points, it is generally pulverized, compacted, and crushed to size before carbonization and activation (Hassler, 1974; DeJohn, 1975). The coal is pulverized to speed the oxidative charring portion of the process (Rester, 1993). A number of different processes may be used, but the material must be formed into "briquettes" either before or after activation. The American Norit Company separates the process into 3 stages in 3 furnaces so they may isolate and collect at will (Thomas, 1993)

The two principal methods for treating these carbonaceous materials to produce activated carbon are thermal and chemical (Sontheimer *et al.*, 1988; Hassler, 1974). Thermal activation involves heating the raw material to a high temperature in the presence of an oxidizing gas, the most common being steam. Chemical activation consists of heating at an elevated temperature a mixture of the raw material and a dehydrating agent. After the raw material is carbonized and

activated, the dehydrating agent is leached out and concentrated for reuse (Sontheimer *et al.*, 1988; Hassler, 1974).

As an example of the process for coal feed material, the following steps are used (Hassler, 1974):

1. The raw coal feed material is ground to a 100 to 325 mesh size.
2. This ground material is thoroughly mixed and then compacted into briquettes.
3. The briquettes are crushed and sized (4 mesh x 50 mesh).
4. The material enters the oxidizer for 10 min. to 1 hour at 400-700°F.
5. The following step is the carbonization step at 1000-1200°F.
6. The final step is activation at 1650-1950°F, using steam or other oxygen containing gas.

Adsorption is a complex process involving at least three steps (Sontheimer *et al.*, 1988):

1. Bulk transport of the solute from the solution to the surface of the activated carbon by means of diffusion.
2. Intraparticle diffusion into the pores.
3. Adsorption onto the internal surface of the pores.

Traditionally, the adsorption has been categorized as physical adsorption and chemisorption. Since adsorption is the result of forces acting at a surface, the goal is to produce the maximum amount of surface and pore volume possible consistent with suitable pore sizes for the intended application (Sontheimer *et al.*, 1988; Hassler, 1974). "An activated carbon might be described as a solid foam of extremely high internal areas." (Atlas Chemical Industries, 1968). For liquid phase

carbons used in water treatment the area will generally range from 450-1800 square meters per gram and a pore volume of 0.7 to 1.8 ml per gram. In addition, it is desired to achieve a distribution of this area and pore volume among pores of the proper size so that the area will be available for adsorption and an element of selectivity will be created.

Porosity of carbon.

Three types of pores can be defined :

a. **Macropores** are defined as pores greater than 10,000 Angstroms (Å) (CECA, 1985) in diameter [Hassler, 1974 uses 1000 Angstroms and North American Norit uses 500 (Thomas, 1993)]. These pores do not play a particularly important role in the adsorption process.

b. **Mesopores or Transition pores** range from 100 to 10,000 (CECA, 1985) Angstroms (Å) [North American Norit uses 20 Å-500 Å (Thomas, 1993)] in diameter, and also are negligible contributors to the adsorption process. They are, however, significant in the kinetic process as pores of this size act as entrance avenues for the micropores.

c. The **micropores**, the pores of adsorption, are those which are less than 100 (Å) (CECA, 1985) in diameter [North American Norit uses <20 Å in diameter (Thomas, 1993)].

Sontheimer *et al.* (1988) reports on a recently (1982) proposed and IUPAC accepted set of criteria for activated carbon pore distribution:

<u>Pore Nomenclature</u>	<u>Diameter of Pores</u>
Micropores	pores < 2 nm
Mesopores	2 nm to 50 nm
Macropores	pores > 50 nm

Another method which has been used is to define the BET (Brunauer, Emmett, and Teller) surface area of the carbon which measures the amount of low temperature nitrogen absorbed by the carbon at various pressures and plots the results as a Freundlich isotherm, but this yields only a very general result which does not give a precise indication of the possibilities of the capability of the carbon of interest (CECA, 1985; Hassler, 1974)

One type of molasses test requires 20 to 60 grams of molasses dissolved in water, depending upon the type of molasses. The "color" of this mixture is measured by spectrophotometer, then a small amount of carbon is added to this one liter solution. This mixture is filtered, and the color again measured by spectrophotometer. This process is continued until 70 to 90 percent of the original color has been removed. The number of mg of carbon required to accomplish this color removal is known as the molasses index (Hassler, 1974; Sontheimer *et al.*, 1988). The iodine number is the mg of iodine adsorbed by 1.0 gram of carbon at a residual concentration of 0.02N as defined by the AWWA (1974, 1978) (Sontheimer *et al.*, 1988). The methylene blue test measures percentage color removal from a solution of 0.80 g/L of the dye and 0.50 g/100 ml of the carbon (Hassler, 1974).

The description of the pore size distribution characteristics of activated carbon, and the "scientific" measurement of those characteristics is seen to vary from one manufacturer to another and from one reference book to another. Hassler (1974) provides a list of chemicals which may be used in pore structure tests to characterize activated carbon pore distribution. This list of chemicals includes iodine, potassium permanganate, methylene blue, erythrosine red, phenol, aniline blue, malachite green, alcohol, zinc chloride, calcium chloride, carbon dioxide, and molasses (among others). North American Norit, in their publication *Norit Testing Methods* (undated) lists methylene blue, iodine, benzene, phenol, and molasses as the chemicals to use in determining adsorptive properties of activated carbon. Sontheimer *et al.* (1988) suggests the use of mercury, nitrogen, argon, krypton, benzene, water, and microscopy to determine pore size distribution.

Even the widely used "Molasses Number" (or the associated "Molasses Removal Efficiency") appears flawed as a method for comparing activated carbon adsorption capability among several manufacturers, because many companies do not even have a stable molasses (Thomas, 1993). Sontheimer *et al.* (1988) notes that this test is valid only if a "standard" molasses is used (or a "standard" dose of "standard" carbon is used to allow comparison). Hassler (1967) uses a different test in which diluted solutions of molasses have added different amounts of carbon. He then compares carbon dosage required to achieve a 90 to 95 percent color removal with the same results for a "standard" carbon and reports the result as "relative efficiency."

"When PAC is used in the dechlorination of water, it is the total surface of the carbon which is to be taken into account, essentially the micro porosity." (CECA, 1985). Rester (1993) states that dechlorination depends upon the external

surface area, i.e. carbon particle size. The only reliable method to determine the efficiency of PAC appears to be testing a number of different PACs under conditions most nearly those expected.

One of the difficulties in the use of PAC in water plants is the high cost which results mainly from the nature of PAC use. The time of contact between the carbon and the water containing undesired materials has often been on the order of one hour or less, requiring a much higher dose of PAC to achieve the concentration-time product needed for removal. If the PAC is added just prior to the filter, it is retained within the filter for longer times, resulting in improved adsorption capacity and effectiveness. However, the complete penetration of the filter must be carefully avoided to prevent PAC in the distribution system, with attendant bacterial re-growth problems (Sontheimer, *et al.*, 1988). The filter time between backwash evolutions may also be reduced due to PAC clogging effects. Sontheimer *et al.* (1988) reported a 10 percent to 20 percent reduction in filter run time due to PAC addition during tests completed in 1967. Several interesting alternate processes have been investigated to permit these problems to be circumvented, .

Sontheimer, *et al.* (1988) reports that Hamann *et al.* (1986) applied PAC to the influent of a solids contact clarifier. The PAC was incorporated in the floc and could be retained in the floc blanket for few hours to a few days, depending on the characteristics of the floc particles and the clarifier. Improved adsorption efficiency was obtained due to the long contact times. Kassam, *et al.* (1991) discussed the accumulation and adsorption capacity of PAC in a slurry recirculating clarifier in which they found that very high concentrations of PAC (>4000 mg/L) could be maintained. They felt that PAC could then be an efficient alternative to GAC, particularly for those plants where only intermittent removal by carbon is required.

Hoehn *et al.* (1984) reported on the evaluation of the Roberts-Haberer process to remove THM precursors from settled water at a water treatment plant. Hoehn *et al.* (1987) also discussed the use of PAC for THM precursor control in a pulsed-bed, solids-contact clarifier. Najm *et al.* (1989) measured PAC retention times of from nine hours to two days in a study of the addition of PAC to a bench-scale floc-blanket reactor.

PAC has been the most common choice of the water treatment industry for the removal of tastes and odors from water supplies (McCreary and Snoeyink, 1977). PAC has been chosen over GAC where problems are primarily seasonal (Najm, 1991) because PAC is more economical to use overall in these conditions. An additional advantage of PAC is its ease of use since it can be easily added to various points in the plant without the need for expensive or sophisticated equipment or training.

Ion Chromatography.

Methods currently used to analyze inorganic disinfection by-products are predominantly titrimetric and colorimetric in nature (Pfaff and Brockhoff, 1990). The disadvantage of these methods is that they are subject to interference and contamination. Some methods lack the ability to determine the chlorate ion (Aieta, *et al.*, 1984; Gordon, 1982). Some of the tests which do detect and determine the chlorate ion are somewhat laborious, requiring extensive practice and the ability to visually detect endpoints (Pfaff and Brockhoff, 1990). The use of ion chromatography seems a preferable method for these analyses because of its current

acceptance by USEPA for the analysis of other ions in drinking waters and because of its use to speciate other types of anions.

Ion chromatography is the result of the merging of two major technologies, chromatography and ion exchange. It relies upon the ability of certain ion-exchange resins to separate a mixture of anionic species (Small, 1989). Separation occurs in this case because of different affinities of the components of the analyzed mixture for the stationary phase and, therefore, is due to different transport velocities along the column (Shpigun and Zolotov, 1988).

A liquid mobile phase (eluent) is used to carry the sample through the system. The stationary phase is the ion exchanger. Isocratic elution requires use of the same eluent throughout the run, whereas gradient elution implies variation of the eluent concentration or flow rate. After separation of species has been achieved, the individual anions are measured by some form of detector. The detectors currently available include ultraviolet or visual spectrophotometry or fluorescence (Pfaff and Brockhoff, 1990; Small, 1989).

Chromatography of inorganic substances was comparatively moribund from the early days of the technology until late 1971 when the Dow Chemical Company finally started research which led to the conductrometric detector as a universal means of quantifying inorganic ions (Small, 1989). The detector response is used to determine the species of ion by the time each anion remains on the column and to determine the concentration of each ion present by the magnitude of the detector output signal (Shpigun and Zolotov, 1988).

The other breakthrough in the science was announced by Dow in 1975. This was the novel addition of a second column, later called the "suppressor," which essentially removed the conductivity of the background eluent but allowed the

analytes to remain, usually with enhanced conductivity. This allowed the detection of small quantities of electrically conducting analytes against a background of highly conducting mobile phase. During the same year, Dow licensed the Dionex Corporation to manufacture instruments that embodied both the new detector and the suppressed conductivity approach; these were the first ion chromatographs (Small, 1989).

Ledder (1991) and Dietrich *et al.* (1992) have shown that the ion chromatograph is accurate and effective for the measurement of ClO_2^- and ClO_3^- in drinking water and in reagent water, applying a modification of USEPA Method 300.0B with a Dionex Ion Chromatograph 2010i (Sunnyvale, CA) utilizing a conductivity detector, AS 9 analytical column, AG 9 guard column, 50 micro liter injection loop, and an eluent which consisted of 2.8 mM bicarbonate and 0.4 mM carbonate at a pumping rate of 2 mL/minute. The suppressor used with this carbonate eluent was 0.025 N H_2SO_4 with a flow rate of 4.0 mL/minute. Using other eluents, Pfaff and Brockhoff (1990) and Hautman and Bolyard (1992) successfully used ion chromatographs for analysis of drinking water to determine the oxyhalide anions of chlorine and bromine as well other anions. Pfaff and Brockhoff (1990) were able to determine, in a single run of about 25 minutes duration, Cl^- , ClO_2^- , ClO_3^- , NO_2^- , NO_3^- , and SO_4^- with a data system utilized to analyze the conductivity output of their ion chromatograph. The 95 percent method detection limits in drinking water were 0.03 mg/L for ClO_2^- and 0.02 mg/L for ClO_3^- . The values were even lower in de ionized water.

Ion chromatography is currently acceptable to the USEPA for NO_3^- in drinking water, and continuing laboratory use of this instrument for the detection and analysis of disinfection by-products should extend this EPA acceptance to them

as well. The use of the ion chromatograph, with the ability to accurately measure very low concentrations of Cl^- , ClO_2^- , and ClO_3^- in a short length of time, is vital to the laboratory study of the disinfection by-products of ClO_2 and the study of the use of PAC to reduce or eliminate one or more of these ions from water.

CHAPTER III

METHODS AND MATERIALS

This chapter reports the details of the experiments performed for the screening of the performance of various types of powdered activated carbon (PAC), both with and without the presence of chlorine in the water, in the removal of chlorite ions (ClO_2^-) from water, and the affect of this removal action on the concentration of chloride ions (Cl^-) and chlorate ions (ClO_3^-).

Reagents:

The reagents used during this study are described in Table 2.

Powdered Activated Carbons (PACs) Screened

The known characteristics for the twelve PACs screened during this research are reported in Table 3. Review of this table reveals several gaps. Some of the gaps result from the fact that several of the characteristics, such as "Molasses Number" and "Molasses Decolorizing Index" are either no longer used by all manufacturers or were not yet in use when that PAC was characterized. Some of the characteristics, such as pH, have not ever been measured (or at least not recorded in any location currently known) by the manufacturer for some of the PACs listed because these characteristics were not of interest to large volume buyers. Other data for characteristics is blank because the information is proprietary.

Table 2. Reagents used in the laboratory research.

Supplier	Chemical Name	CAS number	Remarks
Fisher Scientific	Sodium Bicarbonate	144-55-8	
Fisher Scientific	Sodium Carbonate	497-19-8	
Fisher Scientific	Potassium Iodide	7681-11-0	
Fisher Scientific	Potassium Chlorate	3811-04-9	
Fisher Scientific	Sodium Hypochlorite	7681-52-9	
Fisher Scientific	Calcium Hypochlorite	7778-54-3	
Fisher Scientific	Hydrochloric Acid	7647-01-0	
Fisher Scientific	Phenylarsine oxide	637-03-6	Standardized 0.00564 Normal.
Fisher Scientific	Anhydrous ethylene diamine	107-15-3	
Novatek	Ultra pure sodium chlorite	1314-56-3	Stored over phosphorous pentoxide in a desiccator.
Millipore	reagent water	"Milli-Q" water	Glass distilled water demineralized by passing through several ion exchangers and carbon filters with a final 0.45 micron paper filter. (Millipore Corp. Norwalk, CT)

Table 3. Known characteristics of PACs screened.

Brand Name	PAC	Typical Adsorption Properties (Molasses Number and Index based on various test methods. Not valid to compare among manufacturers.)	Moisture Percent (max. % as packed)	Ash Content (max. %)	Iodine No. (mg/g)	pH	Compact. Density (g/mL)	BET Surface Area (m ² /g)	Screen Analysis (325 mesh)	Remarks
Acticarb	L2S	Molasses No.(MN) = 400 Molasses Decolorizing Index (MDI) = 120	10.0	1.5	985	> 4.5	0.37-0.41	1100	80 %	Imported from France wood based
CECA	20B	MN = 190 min. MDI = 40	3.0	2.0 or less	800 min.		0.48-0.52	900	50 % min.	Coal based (sub bituminous) between lignite & bituminous
CECA	20C	MN = 200 min.	2.0		900 min.				50-85 %	No longer manufactured Coal based.
NUCHAR	S-A	MDI = 14.0 min.	10.0	3-6	900 min.	4-6	0.38	1400-1800	65-85 %	Soft wood based, activated by phosphoric acid. High activity
NUCHAR	Aqua S	MDI = 9.0 min.	5.0		800 min.		0.64	550-650	90 %	soft wood based, high temperature steam activated, no longer manufactured.
Calgon	WPL	MN = 220-240	5.0	6	600 min.		0.74	950-1050	90 %	Bituminous coal based, high temperature steam activated.
Calgon	WPH	MN = 220-240	3.0	6			0.54	950-1050	90% min.-98 % typ.	Bituminous coal based, high temperature steam activated.
Darco	G-60	Methylene blue adsorption 15.0 g/100 g of PAC	12.0	5.5		7.0	0.40 (25 lb/ft ³)	750-800	50 %	Acid solubles 1 % Maximum iron 200 mg/L
Darco	KB-B	Molasses Removal Efficiency (R.E). = 185 min. MN = 400 R.E. = 95 min.	33.0	3.0		5.0	0.45 (28 lb/ft ³)	1500	70 %	Hardwood based, Chemically activated, high purity carbon Large pore volume
Darco	S-51		10.0			5.0	0.51 (32 lb/ft ³)	650	70 %	Lignite coal, acid washed, steam activated
Darco	HDB	MN = 450 R.E. = 90 Tannin value = 200 ppm R.E. = 5	5.0		500 min.		0.50 (31 lb/ft ³)		97 %	Lignite coal, Steam activated (more micropores)
Watercarb ("Husky" brand)			7.5	1.5	560		0.45-0.51		86 %	Soft wood or fly ash based, Chemically activated

Glassware

Prior to first use, all glassware and sample bottles were soaked in 50 percent nitric acid for greater than 72 hours, thoroughly rinsed with Milli-Q water (reagent water), and dried in a drying oven at 105 degrees Celsius. The same method was utilized prior to each subsequent use of the equipment, except that 10 percent nitric acid was used instead of 50 percent, the acid-soak period was 24-48 hours, and the glassware was not always dried between reagent water rinsing and use.

Instrumentation

Ion chromatography was utilized to determine the concentrations of Cl^- , ClO_2^- , and ClO_3^- by EPA Method 300.0 B except that the eluent concentration had been modified from that in the method. The Amperometric Titration Methods of Section 4500 of the 18th edition of *Standard Methods for the Examination of Water and Wastewater* (1992) were used to determine total chlorine and chloride. The Amperometric Titration Method II (PROPOSED) of Section 4500E of *Standard Methods* was used to determine ClO_2^- , ClO_3^- , and chlorine.

Ion Chromatography (IC)

The Dionex Model 2010i Ion Chromatograph with an AS-9 analytical column, an ASG-9 guard column, AMMS1 suppressor, 50 microliter (μL) injection loop, a conductivity detector and Dionex 4270 integrator was used to analyze for ClO_3^- , ClO_2^- , and Cl^- for every experiment. The output level scales used were 3

microsiemens (μS) and 10 μS to allow improved accuracy while reducing the effects of excess detector and system noise. The method selected was a modification of EPA method 300.0 B (Pfaff *et al.*, 1989), with the eluent concentration changed to 0.4 mM Na_2CO_3 and 2.8 mM NaHCO_3 and the eluent flow rate modified to 2.0 mL/min. for all analyses instead of the 1.0 mL/min. specified in the method.

This modification to the eluent composition provided good separation, allowed resolution of the fluoride ion and ClO_2^- peaks, and reduced analysis time (Ledder, 1991; Dietrich *et al.*, 1992). The suppressant selected was a 0.025 N H_2SO_4 solution, with a 4.0 mL/min. flow rate. The approximate retention times observed for the ions of interest were as follows:

<u>Ion</u>	<u>Approximate Retention Time</u>
F^-	1.1 minutes*
ClO_2^-	1.4 minutes
Cl^-	1.8 minutes
ClO_3^-	3.4 minutes

*Fluoride (approximately 0.5-1.0 mg/L) was sometimes added to the standards and samples just prior to analysis to increase the separation between the "water dip" peak and the chlorite ion peak.

Manual peak height measurements were usually used instead of the peak area or peak height recorded by the Dionex 4270 integrator. As with Ledder (1991) most peaks were found to be relatively low even on the 3 μS scale with many of the sample concentrations being low. Lower output scales were attempted to magnify these peaks, but the resulting noise made the baselines unstable. Although manual peak height measurements were used throughout, the integrator peak heights for Cl^-

and ClO_3^- often corresponded well. The ClO_2^- peak heights, which were skewed either by the "water dip" or sometimes by fluoride that had been added in an attempt to eliminate the effect of the water dip, seldom matched the values obtained through manual peak height measurement, and these ClO_2^- peak heights were not used.

For ClO_2^- and Cl^- , five standard solutions were analyzed and the peak height versus concentration calibration curve regression used to quantify unknown concentrations. In the case of ClO_3^- , eight solutions were used, with five of them at 0.5 mg/L or less since the ClO_3^- concentrations being measured were quite low in comparison with the other two ions. Method detection limits reported for Method 300.0b were 0.01 mg/L for ClO_2^- and 0.003 mg/L for ClO_3^- . Ledder (1991), using the same equipment and same carbonate eluent as was used in this research, found limits of detection of 0.03 mg/L for ClO_2^- and 0.11 mg/L for ClO_3^- .

Amperometric Titration

The amperometric titration methods of Section 4500 in the 18th edition of *Standard Methods for the Examination of Water and Wastewater* (1992) was used to analyze for chlorine, ClO_3^- , and ClO_2^- . The analysis was conducted on a Fisher Scientific (Springfield, N.J.) Model 450 computer aided titrimeter. Periodically a Fischer-Porter Model 17T2012A (Fischer and Porter, Warminster, PA.) was used to measure chlorine. Both electrodes on both instruments were platinum instead of copper and platinum. The titrant was standardized 0.00564 Normal phenylarsine oxide. The stock chlorine solutions used for standards and for addition to the experimental mixtures were analyzed on the computer aided titrimeter, with at least three laboratory replicates of each sample for standardization.

Other Instruments and Equipment

Solution pH was determined by a Model 610A Fisher Scientific Accumet® pH meter. Iron measurements were conducted on a Perkin Elmer (Norwalk, CT.) Model 703 Flame Absorption (FAA) Spectrophotometer. Measurements of iron, boron, aluminum, magnesium, manganese, and zinc were conducted by the analytical chemist in the Virginia Polytechnic Institute and State University Soil Testing and Plant Analysis Laboratory utilizing an Inductively Coupled Plasma (ICP) Spectrometer. The ICP system consists of a simultaneous spectrometer (Jarrell-Ash ICAP 9000) and a sequential (scanning) spectrometer (Jarrell-Ash Atomscan 2400). The detection limits for the ICP for the metals of interest are shown in Table 4. The six paddle jar stirrer was a Phipps and Bird (Richmond, Virginia) Model Number 300, while the magnetic stirrers were Corning Laboratory Stirrers, Model PC-353 (Corning Glass Works Corning, New York).

Analysis of Metals Associated with PAC

Metals were extracted from triplicate samples of each PAC by the procedure utilized by Orr (1990) [and recommended to her by Snoeyink (1990)]. The carbon samples were dried at 104^o C weighed to 1.000 grams, then ashed at 550^o C for one hour. The ash was then cooled in a desiccator for one hour and added to 10.0 ml of 1:1 concentrated HCl. The ash-acid slurry was filtered through a # 42 Whatman filter that had been prewashed with the acid. Iron concentrations were determined by an atomic absorption (AA) spectrophotometer and iron, boron, magnesium, manganese, aluminum and zinc were determined by ICP, as previously discussed.

Table 4. ICP detection limits for metals analyzed.

Element	Analytical Range*(mg/L)
Aluminum	0.025-5000
Boron	0.006-150
Iron	0.005-150
Magnesium	0.010-350
Manganese	0.001-150
Zinc	0.004-150

* "Analytical ranges were compiled from published values and may not reflect actual ICP performance. Detection limits will vary somewhat depending on sample matrix." (VPI&SU soil testing and plant analysis memo dated January 4, 1991)

Laboratory Protocol

Chlorine-demand-free water was prepared by placing 7 L of Milli-Q water into a 9-L glass jar with chlorine added to a concentration of 0.2-0.3 mg/L. This jar of water was then exposed to ultraviolet light for 7-23 days, until no further drop in chlorine concentration was observed. The chlorine level was not ever observed to lower below 0.15 mg/L, with 0.10 mg/L considered the lowest reliable level of detection for chlorine. In one case, no decrease in chlorine had been observed for the entire 23 day period and the jar was then exposed to direct sunlight for three additional days. No measurable change in chlorine concentration was observed over that 3 day period. For each sample series, this 7 L of chlorine-demand-free reagent water remained in the 9-L glass jar until chemicals had been added and the solution well mixed by agitation.

The water was adjusted to pH 7.0 with the phosphate buffer solution specified in *Standard Methods* and checked with at least two pH meters. The pH of water in each jar was measured periodically during the 24-hour experimentation period to ensure that it remained within the band $\text{pH } 7.0 \pm 0.2$ pH units. During those experiments in which chlorine was not added, this buffer maintained the pH easily within the desired band; but when chlorine levels of greater than 1.0 mg/L were used, the pH decreased below pH 6.8 unless KOH was added also. This discovery led to some retesting of solutions which did not contain chlorine, with the KOH being added instead of the pH 7 buffer. No significant variation in results was discovered.

The entire research was conducted with pH 7, except for one experiment in which pH meter failure led to a pH of 9.5, and 20 mg/L PAC in order to provide

data which would reflect conditions found in typical municipal water treatment plants. The results of the experiment at pH 9.5, reported in Tables A11 and A12, demonstrated no removal. Grabeel (1991) conducted similar research for Ceca 20B and Nuchar SA at several other conditions of PAC loading and pH.

The ClO_2^- standard solution and, if applicable, the chlorine standard solution were then added to the jar by transfer pipette to achieve the desired concentration. An entire series of experiments was conducted with initial ClO_2^- concentration targeted to be 2 mg/L (as ClO_2^-) and with free chlorine targeted to be 2 mg/L (as measured by titrimeter). When the experimental results for ClO_3^- concentration appeared to be erratic, the entire set of experiments was repeated with initial ClO_2^- concentration targeted to be 2.4 mg/L (as ClO_2^-) in hope that higher initial concentrations would result in increased ClO_3^- concentrations, which could more easily distinguished from the background level on the ion chromatograph. The results of these further experiments did not always display a consistent pattern for ClO_3^- .

The ClO_2^- was always added first, with the chlorine solution following within one minute. After the solution had been well mixed for about 30 seconds, three field replicate samples were immediately withdrawn for analysis. One liter of the solution was then added to each of four 1-L jars, then dosed with PAC to provide a concentration of 20 mg/L PAC. A fifth 1-L solution was used as a control; no PAC was added. The sixth jar, also used as a control, contained 1 L of chlorine-demand-free reagent water and 20 mg/L PAC, but no ClO_2^- .

After an initial sample had been withdrawn from each of the jars, the stirrer was started at maximum speed, and PAC (20 mg/L) was added to the four jars which contained the solution of reagent water and ClO_2^- (or ClO_2^- and chlorine) and

to the control jar which contained only reagent water. Another set of samples was immediately taken from each jar. Each sample was protected from light until it had been analyzed.

Additional samples were then taken from each bottle at 15-minute intervals during the first two hours, and again after 4, 8, 12, and 24 hours. All samples were analyzed within four hours of being withdrawn, with most being analyzed within one hour. Some samples were analyzed again after they had been stored under fluorescent light for 48-54 hours, and the data were compared with concentrations in samples that had been stored in darkness for the same time interval, to investigate degradation of sample concentration in reagent water,. No statistically significant variations in Cl^- , ClO_2^- , or ClO_3^- concentration were observed when the concentrations were compared to those from the original analysis.

The contents of each sample jar were sampled by dedicated sampling equipment and filters to preclude cross-contamination. The samples were filtered through Gelman Sciences Metrical membrane filters (model GN-6) into a Teflon-capped bottle which was stored in the dark until analysis. At the injection point into the ion chromatograph, an installed Gelman Ionchrom Acrodisk 0.45 micrometer (μM) filter provided an additional stage of filtration.

During each analysis session, standards were analyzed in triplicate prior to and after each set of samples was analyzed. During the analysis sequence, standards were analyzed after every 15-20 samples had been analyzed. At least one set of triplicate laboratory samples were analyzed during each experiment in addition to the normal set of field replicate samples. The peak heights of all replicate samples were measured and compared at the instrument prior to injection of further samples as a quick check that conditions were proper for correct analysis of the samples.

The results of these replicate samples were later reviewed in more detail and were later subjected to statistical analysis, particularly analysis of variance (ANOVA).

Precision of the Ion Chromatographic Analyses

Prior to the first set of experiments, a set of standards for each ion was analyzed, and the peak heights were measured and recorded. The results of these measurements were plotted with a linear regression for use in comparing the results of all future standards analyses. The plotted curves are provided as Figures 2, 3, and 4. The different slopes of the three curves are reflective of the relative sensitivity of the instrument for the three ions. Prior to each experiment, a triplicate set of standards for each ion were analyzed and compared to these curves. Standards were also injected after each 15-20 samples and at the end of each experiment. The peak heights of all replicate samples were measured and compared at the instrument prior to injection of further samples as a quick check of proper operation and calibration. The results of these replicate samples were later reviewed in more detail and subjected to statistical analyses, particularly analysis of variance (ANOVA). In all cases, the measured peak heights of these standards were within one standard deviation of the original standard curves.

A six jar test was conducted with six jars of test solution containing CECA 20 B PAC to ensure reproducibility. At the beginning of the experiment, triplicate samples were withdrawn and analyzed. Additional replicate samples were withdrawn and analyzed during the course of the 24-hour experiment. The data from these replicate samples was statistically analyzed with computer software Microsoft Excel, Version 4.0. A summary of the statistics is provided in Table 5.

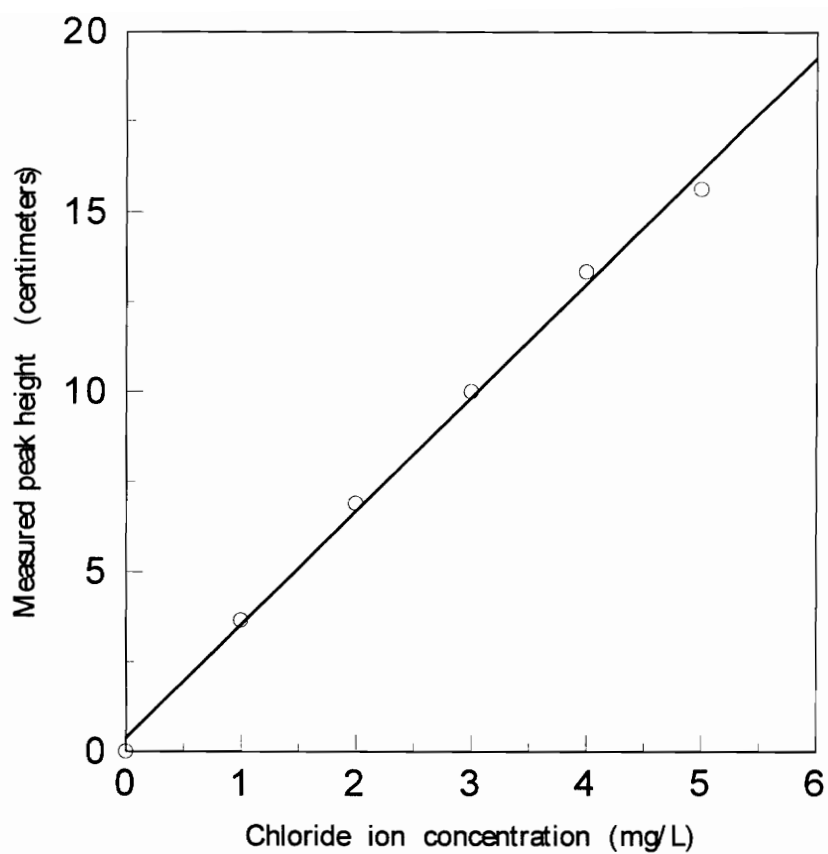


Figure 2. Chloride ion standards (mg/L) versus measured peak height in centimeters for the Dionex Ion Chromatograph. ($R^2 = 0.99495$)

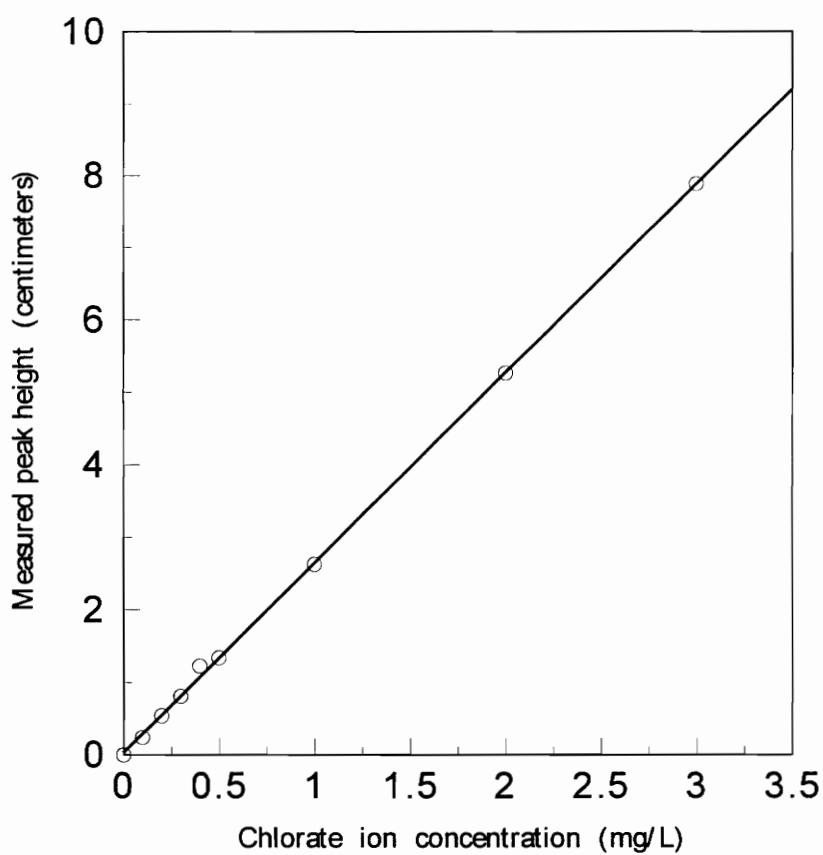


Figure 3. Chlorate ion standards (mg/L) versus measured peak height in centimeters for the Dionex Ion Chromatograph. ($R^2 = 0.999525$)

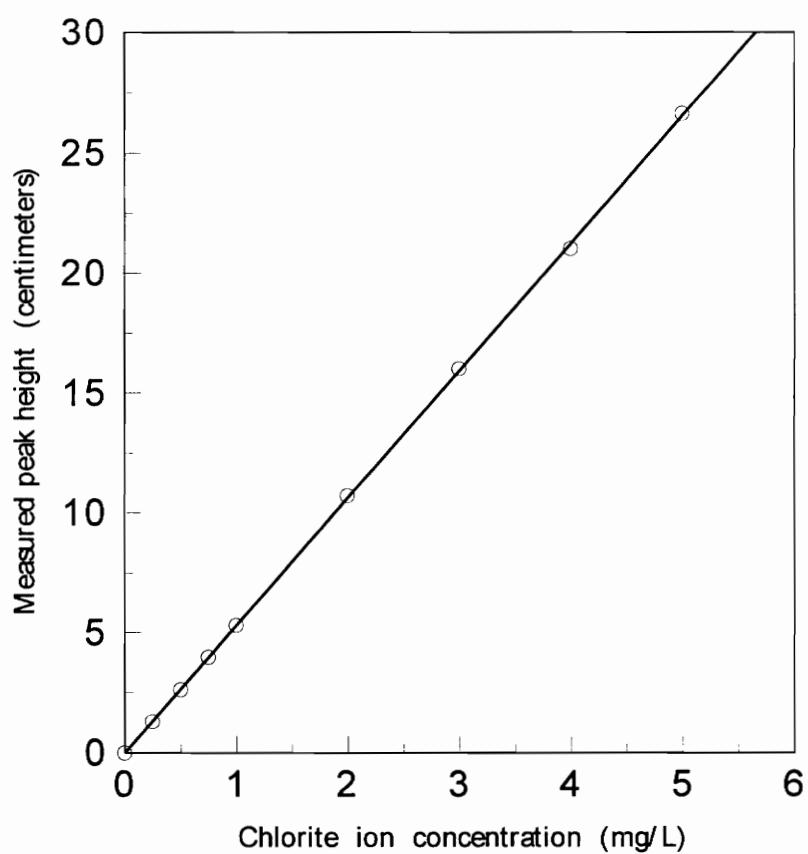


Figure 4. Chlorite ion standards (mg/L) versus measured peak height in centimeters for the Dionex Ion Chromatograph. ($R^2 = 0.999902$)

Table 5. Summary of statistics for replicate samples of CECA 20 B PAC at 20 mg/L, starting with 2.40 mg/L ClO_2^- and 1.5 mg/L HOCl. All the replicate samples were taken at time zero.

Ion	Mean value	Standard Deviation	Variance	Number of Samples, n*
chlorite ion	2.39	0.0249	0.00062	17
chloride ion	1.28	0.0133	0.00018	9
chlorate ion	0.27	0.00894	8E-05	8

* Several field replicate samples taken from each jar at the same time and analyzed for ClO_2^- . Some of these field replicates were also analyzed for Cl^- and ClO_3^- as well.

A series of ten standard solutions was prepared by an independent analytical chemist and analyzed for the three ions of interest. After the results of the analysis had been delivered to the chemist, the actual value of the standards was revealed and a comparison was made. In all cases the ClO_2^- and ClO_3^- concentrations were well within one standard deviation of the value of the standards. The values for Cl^- were not as accurate during the first set of comparisons because the column had become saturated with Cl^- ions. This problem had been noticed during analysis of the first set of samples, but the decision was made to complete all analyses since the results for the other two ions appeared to be normal. The Cl^- concentrations determined after the column problem was resolved proved to be within one standard deviation of the concentration of the standards. The results of this comparison are provided in Table 6.

Table 6. Comparison of the actual concentration to concentration determined by ion chromatography for standard samples created by an independent analytical chemist.

Standard Set	Actual Concentration of Standards			Concentration Determined by Ion Chromatograph		
	ClO_2^-	Cl^-	ClO_3^-	ClO_2^-	Cl^-	ClO_3^-
1	1.8	2.3	0.42	1.82	2.37*	0.45
2	0.8	0.7	0.16	0.80	0.93*	0.16
3	<MDL**	1.0	<MDL	<MDL	1.16*	<MDL
4	2.4	<MDL	<MDL	2.40	<MDL	0.02
5	<MDL	<MDL	0.35	<MDL	<MDL	0.35
6	0.8	1.2	0.5	0.81	1.2	0.5
7	<MDL	<MDL	0.3	<MDL	<MDL	0.28
8	2.2	<MDL	<MDL	2.21	<MDL	0.02
9	1.2	0.8	0.20	1.21	0.78	0.20
10	<MDL	2.1	<MDL	<MDL	2.10	<MDL

* Instrument malfunction for chloride ion readings detected by analyst during analysis because of erratic replicate samples. Results recorded for the record. Column difficulties were later resolved and all readings were then within one standard deviation of the actual value.

**<MDL is the abbreviation for "less than Method Detection Limits". Ledder (1991), using the same equipment, methods, and carbonate eluent as was used in this research, found Method Detection Limits of 0.03 mg/L for ClO_2^- and 0.11 mg/L for ClO_3^- .

Chapter IV

RESULTS

This chapter contains two major sections that present data concerning the removal of ClO_2^- in laboratory studies and the results of the analysis of acid-extracted metal contents for the twelve PACs screened.

Chlorite Ion Removal by PAC in Laboratory Studies

The raw data for all experiments are provided in Appendix A and a separate plot for each of the PACs under each of the two conditions may be found in Appendix B. Data and plots linking and comparing the performance of all 12 PACs are provided in Appendix C. Appendix C also contains bar plots of ClO_2^- removal performance for each PAC over the 24 hour period overlaid with a line plot depicting the results of metal content analysis performed as part of this research.

Table 7 reports the results of experiments to determine ClO_2^- removal with chlorine absent for all 12 PACs screened. Table 8 reports the results of these tests when chlorine was present. The Table 7 data for the first 4 hours of contact time are presented graphically in Figures 5 and 6, and the Table 8 data for the same period are presented in Figures 7 and 8. Tables 9 and 10 provide the calculated rate of removal for each PAC over the 24 hour contact periods utilized for each experiment. Figure 9 is a plot of all the removal rate data after 15 minutes contact time. Similar plots for 30 minutes, 1 hour, 2 hours, and 4 hours of contact time are provided in Appendix C.

Table 7. Chlorite ion removal by 12 PACs during 24-hour contact when chlorine was absent.

TIME (hours)	Percent Chlorite Ion Removed, by PAC											
	C 20 B	20 C	WPH	WPL	SA	AQUA S	L 2 S	HUSKY	S-51	G-60	KBB	HDB
0.00	0	0	0	0	0	0	0	0	0	0	0	0
0.25	23	18	7	29	23	43	61	49	37	51	15	35
0.50	39	37	47	50	39	52	68	55	51	65	23	45
0.75	47	44	52	57	47	66	71	58	53	68	23	48
1.00	54	53	59	64	54	71	74	60	56	70	23	50
1.25	60	59	63	68	57	74	76	62	58	71	23	51
1.50	64	65	68	71	60	76	78	63	59	73	24	52
1.75	67	67	70	73	62	78	79	64	60	74	24	53
2.00	71	68	72	75	64	79	81	65	62	76	24	53
4.00	82	77	81	81	67	83	83	68	72	88	26	64
8.00	89	84	87	87	71	97	89	72	82	100	33	78
12.00	100	87	89	87	82	100	99	80	90	100	38	88
24.00	100	89	89	91	94	100	100	81	92	100	50	100

Table 8. Chlorite ion removal by 12 PACs during 24-hour contact when chlorine was present.

TIME (hours)	Percent Chlorite Ion Removed, by PAC											
	C 20 B	20 C	WPH	WPL	SA	AQUA S	L 2 S	HUSKY	S-51	G-60	KBB	HDB
0.00	0	0	0	0	0	0	0	0	0	0	0	0
0.25	42	6	40	42	9	29	20	21	37	43	28	43
0.50	51	14	54	51	18	40	27	27	47	53	33	53
0.75	53	21	58	55	27	44	31	29	58	59	36	56
1.00	55	27	61	59	37	48	35	31	61	66	38	61
1.25	60	30	63	61	38	51	36	31	64	68	39	62
1.50	64	31	65	64	40	55	36	32	67	70	40	62
1.75	69	33	66	66	42	55	37	32	69	73	40	63
2.00	74	35	67	68	43	55	38	32	70	75	41	64
4.00	79	39	73	77	48	64	42	33	78	85	46	68
8.00	81	43	78	80	49	68	54	34	84	94	49	73
12.00	86	46	81	83	50	70	59	35	86	95	51	74
24.00	96	48	86	87	52	76	88	47	91	100	52	79

Table 9. Rate of removal (in percent per hour) of chlorite ion by 12 PACs during 24-hour contact when chlorine was absent.

TIME (hours)	Rate of Chlorite Ion Removal (%/hour), by PAC											
	C 20 B	20 C	WPH	WPL	SA	AQUA S	L 2 S	HUSKY	S-51	G-60	KBB	HDB
0.00												
0.25	92	72	28	116	92	172	244	196	148	203	60	139
0.50	64	76	160	84	64	36	28	24	56	56	32	40
0.75	32	28	20	28	32	56	12	12	8	12	0	12
1.00	28	36	28	28	28	20	12	8	12	8	0	8
1.25	24	24	16	16	12	12	8	8	8	4	0	4
1.50	16	24	20	12	12	8	8	4	4	8	4	4
1.75	12	8	8	8	8	8	4	4	4	4	0	4
2.00	16	4	8	8	8	4	8	4	8	8	0	0
4.00	5.5	4.5	4.5	3	1.5	2	1	1.5	5	6	1	5.5
8.00	1.8	1.8	1.5	1.5	1	3.5	1.5	1	2.5	3	1.8	3.5
12.00	2.8	0.8	0.5	0	2.8	0.8	2.5	2	2	0	1.2	2.5
24.00	0	0.2	0	0.3	1	0	0.1	0.1	0.2	0	1	1

Table 10. Rate of removal (in percent per hour) of chlorite ion by 12 PACs during 24-hour contact when chlorine was present.

TIME (hours)	Rate of Chlorite Ion Removal (%/hour), by PAC											
	C 20 B	20 C	WPH	WPL	SA	AQUA S	L 2 S	HUSKY	S-51	G-60	KBB	HDB
0.00												
0.25	166	26	159	167	37	114	81	84	147	- 169	114	170
0.50	37	29	57	37	35	46	27	26	42	41	20	41
0.75	9	27	13	16	37	15	14	6.9	42	25	8.4	14
1.00	9.4	27	12	16	37	15	19	7	10	26	10	17
1.25	18	8.6	8.9	10	6.8	14	2.5	1.9	14	8.2	3.4	3.2
1.50	17	6.9	8.4	10.7	6.8	14	2.5	1.3	14	11	2.5	3.4
1.75	21	8.6	4	7.7	6.8	0	2.5	1.3	5.1	10	2.5	3.4
2.00	20	6.9	3	7	6.8	0	2.5	0.4	5.1	10	3.4	3.7
4.00	2.3	2	3	4.7	2.3	4.8	2.2	0.4	4.2	4.6	2.3	2.1
8.00	0.4	0.9	1.4	0.7	0.1	0.8	2.9	0.4	1.4	2.3	0.8	1.2
12.00	1.2	0.9	0.7	0.6	0.4	0.7	1.4	0.2	0.5	0.3	0.4	0.3
24.00	0.8	0.1	0.4	0.4	0.2	0.4	2.4	1	0.4	0.4	0.1	0.4

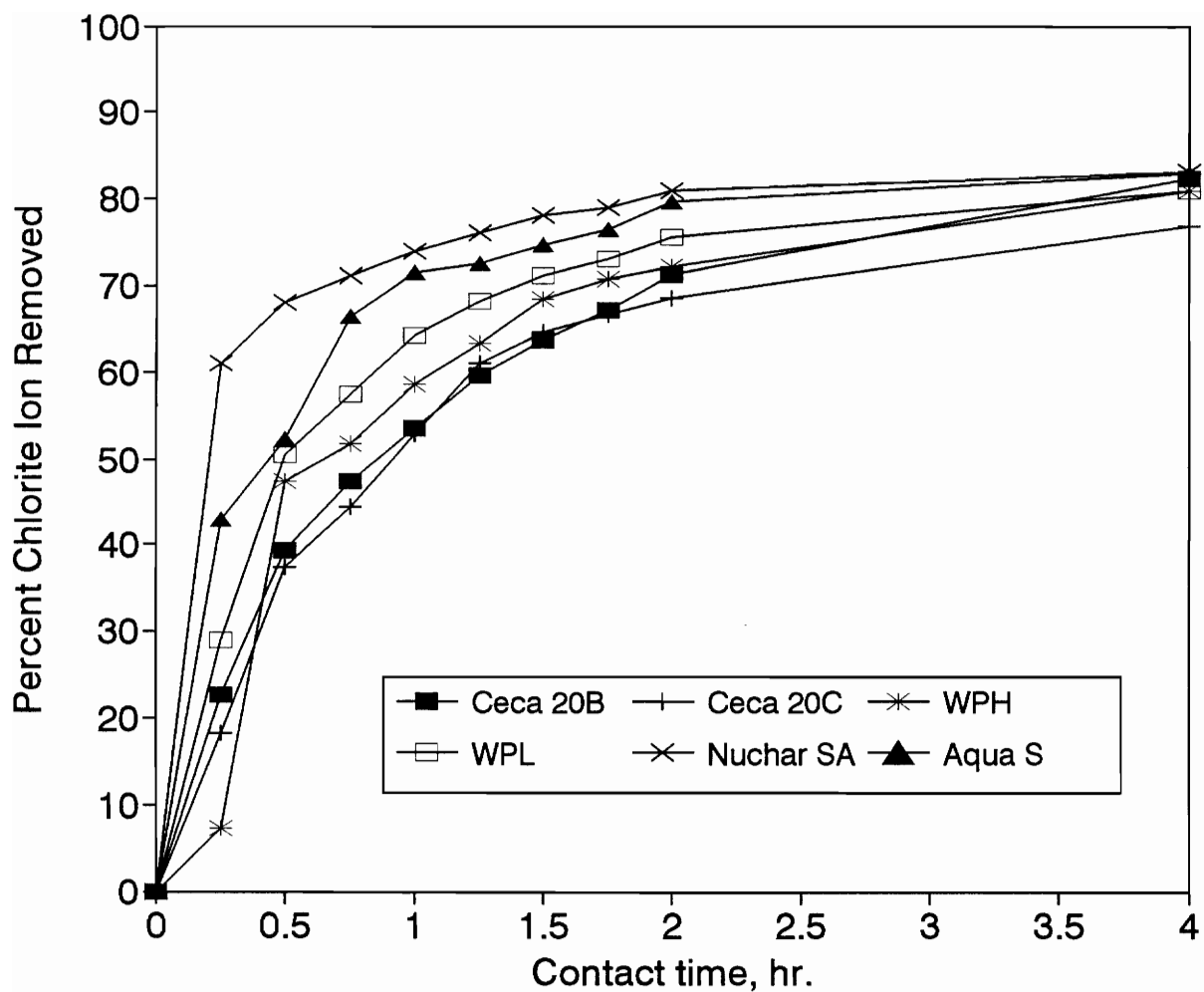


Figure 5. Percent of ClO_2^- removed by various PAC over a 4 hour period from reagent water containing only PAC and ClO_2^- at pH 7.

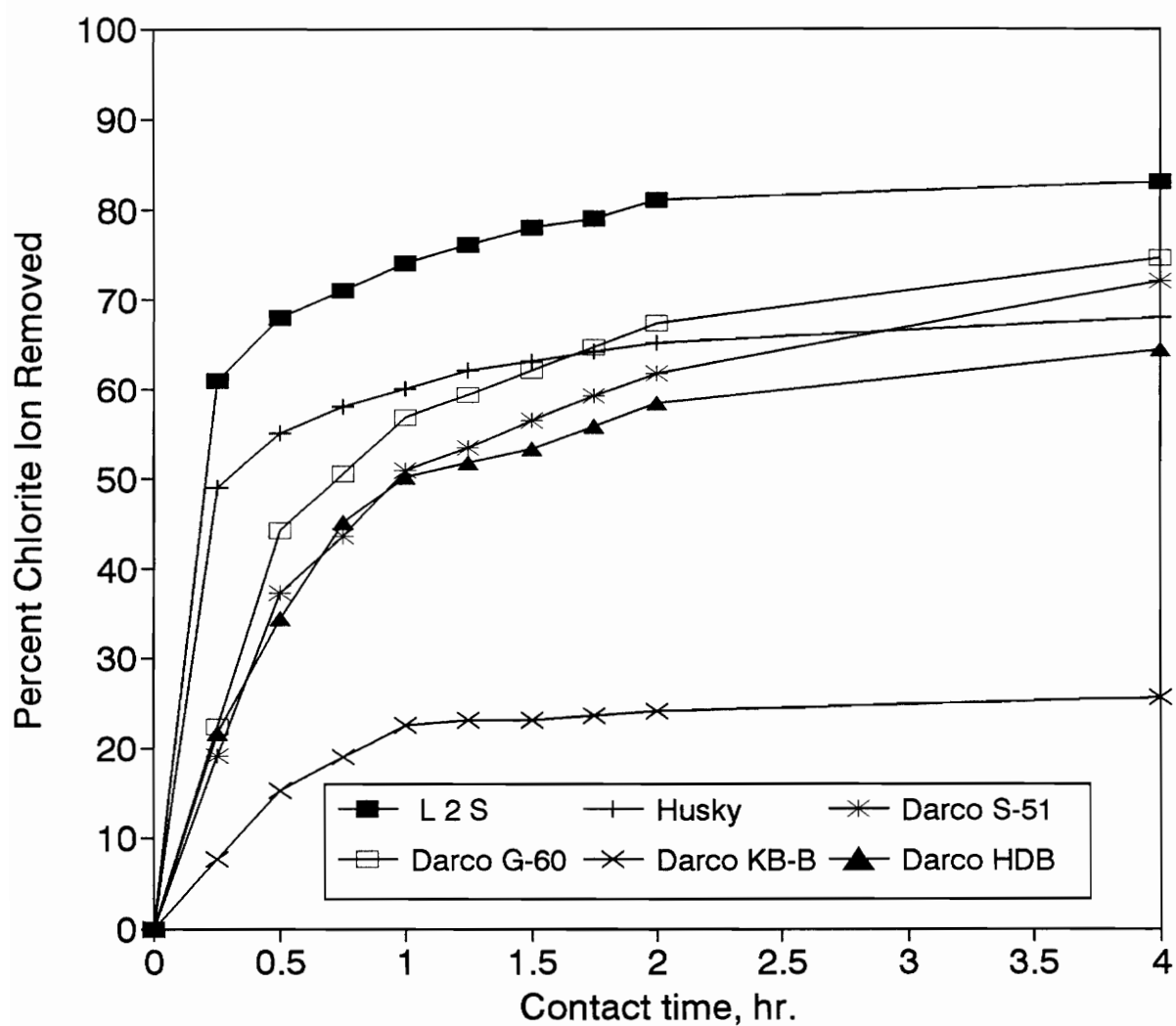


Figure 6. Percent of ClO_2^- removed by various PAC over a 4 hour period from reagent water containing only PAC and ClO_2^- at pH 7.

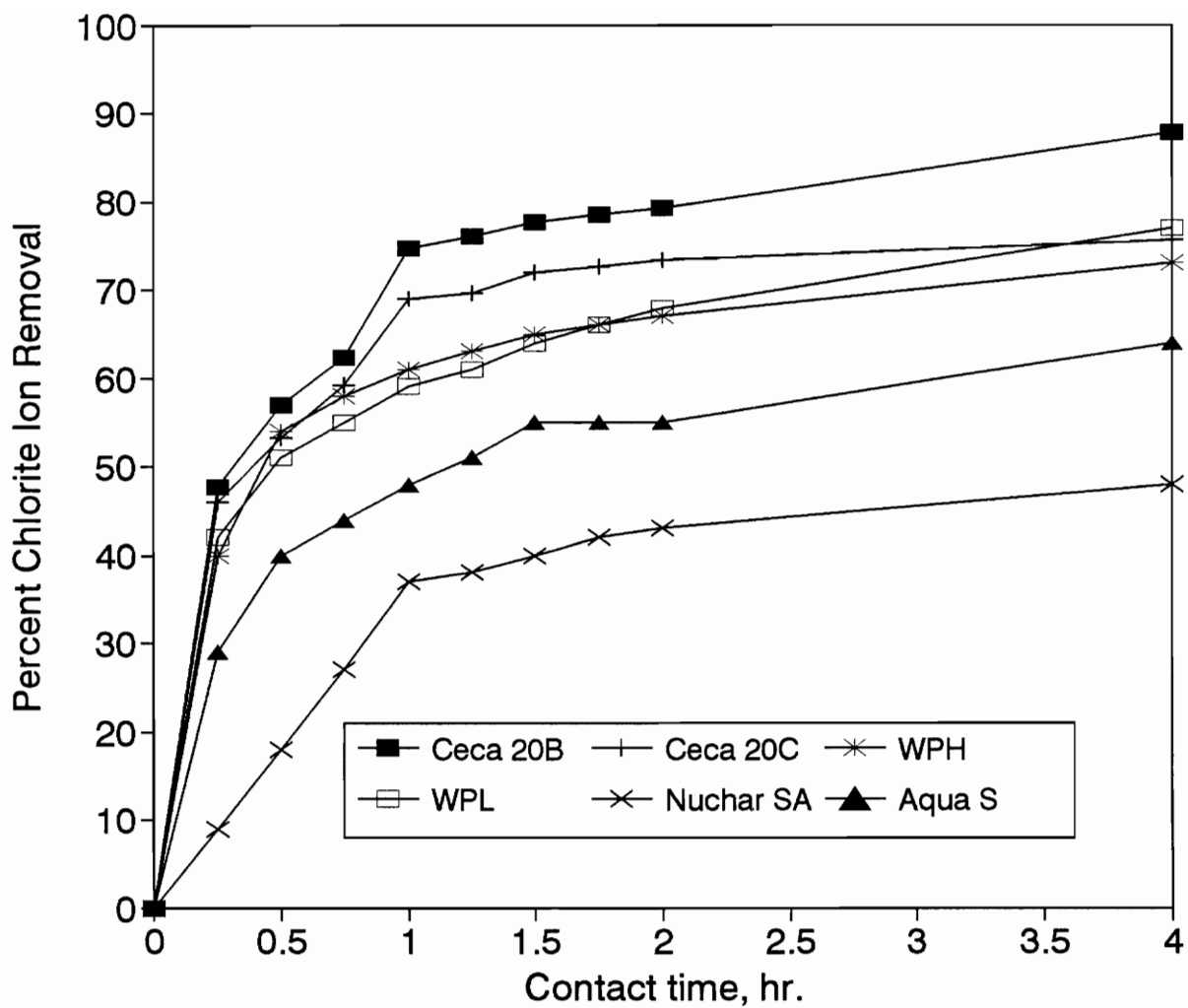


Figure 7. Percent of ClO_2^- removed by various PAC over a 4 hour period from reagent water containing chlorine, PAC and ClO_2^- at pH 7.

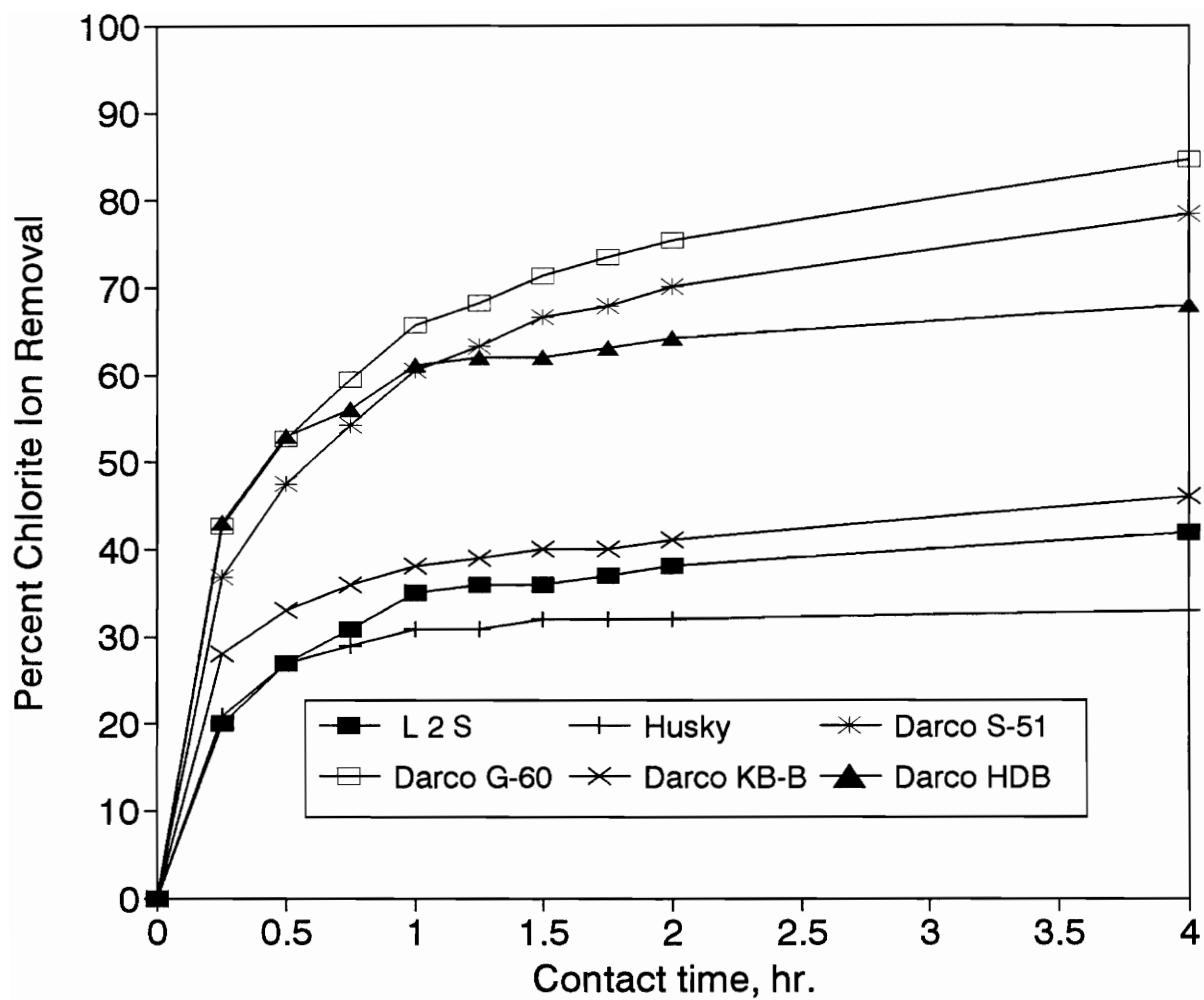


Figure 8. Percent of ClO_2^- removed by various PAC over a 4 hour period from reagent water containing chlorine, PAC and ClO_2^- at pH 7.

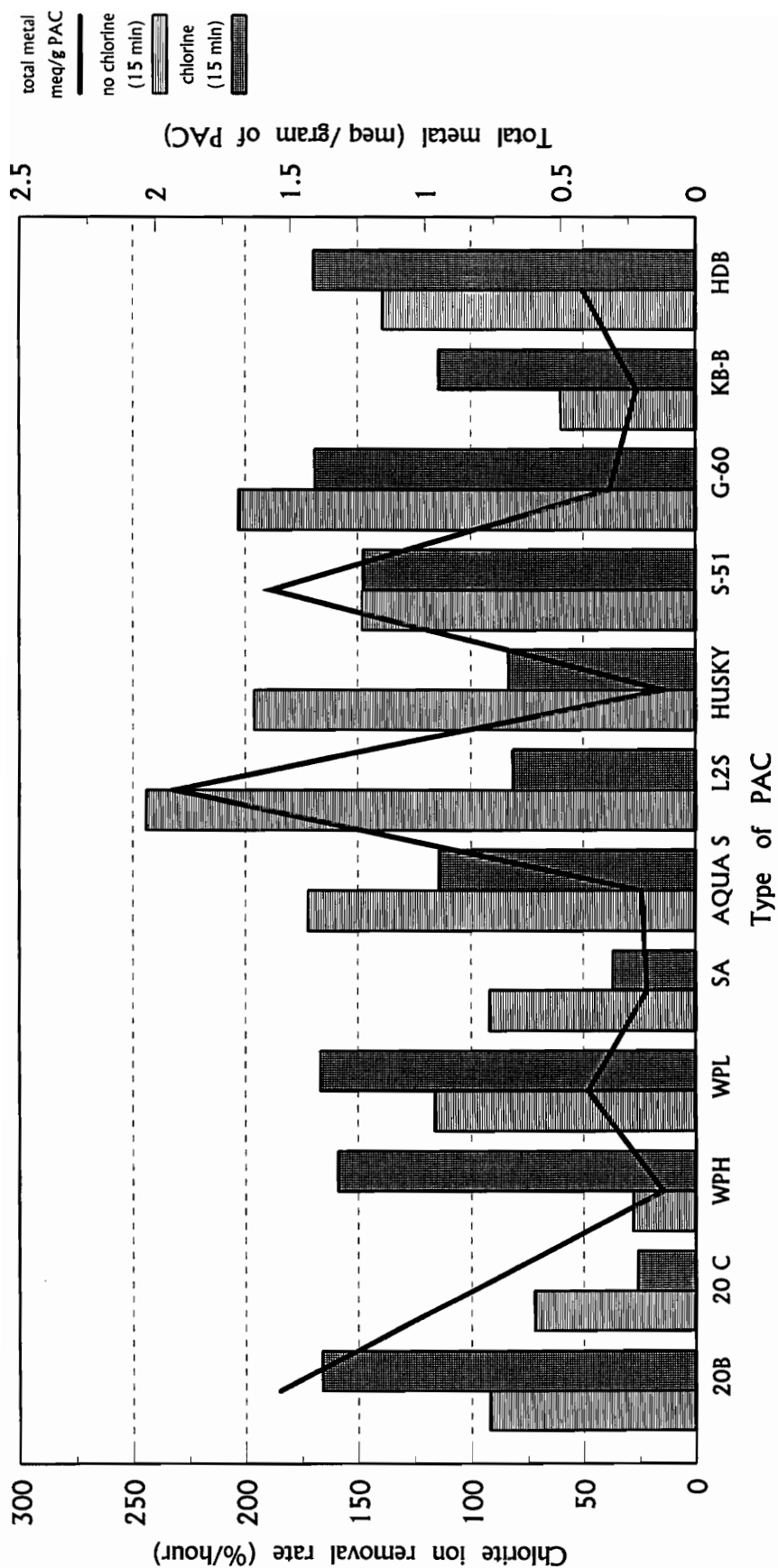


Figure 9. Rate of removal of ClO_2^- by each of the tested PACs after 15 minutes contact time.

Several important points should be noted during the review of these results :

1. Initial ClO_2^- removal rates were very rapid for all PACs.

a. During the first 15 minutes, four of the PACs (Aqua S, L2S, Husky and G-60) removed over 40 percent of the ClO_2^- when chlorine was absent. In the presence of chlorine, five of the PACs (20B, WPH, WPL, G-60, and HDB) removed 40 percent or more of the ClO_2^- during the same period. Removal rates for six of the PACs (Aqua S, L2S, Husky, S-51, G-60, and HDB) exceeded 140 percent per hour when chlorine was absent. In the case where chlorine was present, six PACs (20B, WPH, WPL, S-51, G-60, and HDB) exceeded 148 percent per hour ClO_2^- removal rate.

b. After a contact time of 30 minutes, the percentage of ClO_2^- removal for eight of the PACs was 45 percent or greater in the absence of chlorine. With chlorine present, five of the PACs had removed over 50 percent of the ClO_2^- . The removal rates had been reduced compared to those after 15 minutes of contact time. The only rate in excess of 100 percent per hour was WPH with chlorine absent.

c. During the first hour, when chlorine was absent, all PACs except KBB reduced ClO_2^- at least 50 percent, and removals by three of the PACs (Aqua S, L2S, and G-60) were at 70 percent or more. With chlorine present, these removal rates were lower when 20 C, WPL, SA, Aqua S, L2S, and Husky PAC were used. The presence of chlorine increased the ClO_2^- removal rates during the first hour when S-51, G-60, KBB, and HDB PAC were used.

The removal rates with 20 B, WPH, and G-60 remained nearly the same as those observed when chlorine was absent.

d. After two hours of PAC contact, the ClO_2^- removal rates among the PACs had become more uniform. When chlorine was present, six PACs (20B, WPH, WPL, S-51, G-60, and HDB) had removed over 60 percent of the ClO_2^- , while removals by the other six were lower. When chlorine was absent, the disparity was much less, and ClO_2^- removal by all PACs except KBB and HDB exceeded 64 percent.

2. After the first 4 hours of contact, the rate of reduction of ClO_2^- had decreased to a rate of six percent per hour or less for all PACs under both conditions. After 8 hours, the rate had fallen to 3 percent per hour or less except for HDB and Aqua S in the absence of chlorine, which were both at 3.5 percent per hour.

3. No ClO_3^- was detected during any tests conducted in the absence of chlorine. In those tests where chlorine had been added, ClO_3^- was always present, but the concentration sometimes lowered for four of the PACs (Ceca 20C, Nuchar SA, Nuchar Aqua S, and Husky), although there is no known mechanism which would produce this result. Overall, for those four PACs, the data provides no significant evidence of ClO_3^- formation and does not substantiate such formation at this pH and chemical concentration. The amount of ClO_3^- did increase for the other eight PACs.

Analysis of Acid Extracted Metals

The acid extraction of metal ions and the subsequent analysis to determine the concentrations of aluminum, boron, iron, magnesium, manganese, and zinc were completed as described in Methods and Materials. The purpose of this investigation was to look for correlation between ClO_2^- removal efficiency and metal content for the twelve carbons screened. The results of the analysis of metal concentrations are reported in Table 11, and the results are further displayed, to allow improved comparison of all twelve carbons versus metal content, in plots in Appendix C.

Table 11 and the plots demonstrate no obvious correlation between ClO_2^- removal efficiency and the concentrations of aluminum, boron, iron, magnesium, manganese, and zinc for any of the 12 PACs which were screened. The "best performing" PAC, G-60, displayed a low concentration of each of the metals tested, as did the "worst performing" PAC, KB-B. An in-depth discussion of this topic is found in the Discussion chapter.

The concentration of each metal was also converted to milli-equivalents (meq) of metal per gram of PAC, and added together to provide a total metal content (in meq) for those metals analyzed for each PAC. These results are plotted versus ClO_2^- removal rate in Figure 9 and also versus ClO_2^- removal and removal rate in Appendix C. These several plots display no apparent correlation between total metal content and PAC performance. Figure 10 plots total metal content (meq/gram of PAC) versus mg of ClO_2^- removed after 1 hour contact time. At total metal levels greater than 0.4 mg/gram PAC the results group between 1.0 and 1.1 mg chlorite ion removed. Additional plots of this type for different contact times are provided in Appendix C, however they do not appear to demonstrate correlation.

Table 11. Results of analysis by VPI & SU Soil Testing and Plant Analysis Laboratory.

PAC Type	Metal Concentration, mg/g PAC					
	Boron	Iron	Aluminum	Magnesium	Manganese	Zinc
CECA 20 B	0.177	1.78	9.67	4.07	0.059	0.0036
CECA 20 C	0.174	3.18	3.91	2.33	0.095	0.0057
NUCHAR SA	0.002	0.016	1.01	0.058	0.015	0.0008
Nuchar Aqua S	0.026	3.56	1.72	0.182	0.024	0.0015
Calgon WPL	0.009	1.91	0.663	0.065	0.034	0.0005
Calgon WPH	0.018	2.04	0.708	0.068	0.006	0.0008
Darco HDB	0.402	4.71	9.06	7.14	0.214	0.0128
Darco KB-B	0.002	0.069	1.05	0.013	0.002	<MDL*
Darco S-51	0.013	1.53	12.90	0.659	0.024	0.001
Darco G-60	0.003	0.152	2.43	0.528	0.005	<MDL
Acticarbonyl L2S	0.008	3.32	0.198	0.204	0.016	0.001
HUSKY	0.025	1.59	1.92	1.29	0.327	0.004
1:1 HCl	0.001	0.005	0.033	0.001	0.000	<MDL

Mean values for each PAC from 3 separate field replicate samples except for Darco G-60, which had 4 separate field replicate samples.

*<MDL is the abbreviation for "less than method detection limit" (see Table 4 for values).

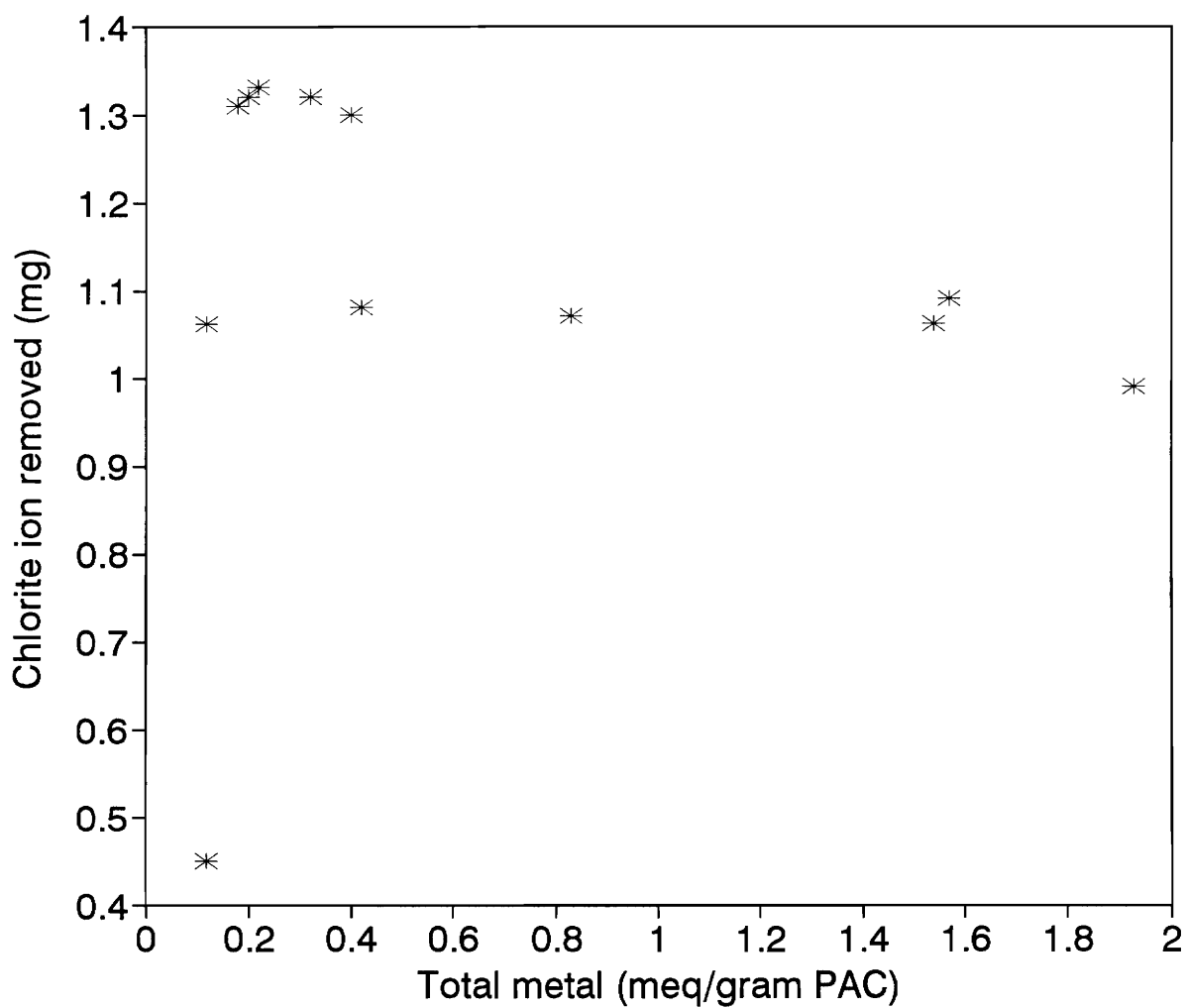


Figure 10. Total metal (aluminum, boron, iron, magnesium, manganese, and zinc) versus mg chlorite ion removal after 1 hour contact time.

Chapter V

DISCUSSION

This chapter presents analysis of the data contained in Chapter 4.

Chlorite Ion Removal by PAC in Laboratory Studies

Chlorite ion, which has been found to be the predominant by-product of ClO_2 used as a water disinfectant, was successfully removed by PAC in previous studies by Grabeel (1992), Orr (1990), and Oehler and Schuttler (1986). The concentrations of both ClO_2^- and PAC used in these studies were higher than would be expected in actual water treatment facilities. These higher doses were used to ensure that ions of interest would be well within the detection limits of the analytical instruments (Grabeel, 1992). The experiments conducted during this project were planned to utilize chemical concentrations that would be expected in municipal water treatment plants, and the PAC screening builds upon the work of Grabeel (1992), who investigated two of the same PACs, but under various conditions of pH and PAC concentration.

Grabeel (1992) felt that this ClO_2^- removal occurred in two stages, and reported that Dixon and Lee (1991) felt that GAC removed ClO_2^- in two stages, namely adsorption and chemical reduction. Although it would be equally easy to classify the rates discussed above into either two stages or three, it also appears that the shape of the removal curves in this paper could closely fit a standard exponential rate curve which could be explained by effects of PAC loading.

Grabeel (1992) conducted several other experiments, in which she demonstrated that the addition of new virgin PAC to the process restored the high rate at a time when removal rate was low. The conclusion was that neither product/reactant ratio nor the concentrations of these chemicals present was the cause of rate decline, but that the PAC itself was the agent.

Gallagher *et al.* (1993) discussed Grabeel's 1992 work, in which PAC which was in contact with ClO_2^- for four hours, then removed from contact and water washed. When this PAC was returned to contact, it did remove ClO_2^- , but not as much and at a slower rate. "In fact, the total ClO_2^- removed by the PAC both before and after washing was the same as that removed by PAC that remained in the test solution for the same length of time (8 hours)" (Gallagher, *et al.*, 1993). These data suggest that the removal of ClO_2^- alters the surface of the PAC, and that the surfaces cannot be restored by water washing.

The PAC may have acted as a catalyst, both in a reaction that reduced ClO_2^- to Cl^- , and in an oxidation reaction that yields ClO_3^- when chlorine is present in reagent water at neutral pH. The reactions are most probably a surface phenomenon that relies on sites on the carbon surface, although the plot provided in Appendix C demonstrates no obvious correlation with BET surface area itself. The more likely correlation probably lies within the micropore distribution characteristics, which were not available. More study is needed in this area, particularly as the rules for disinfection by-products become ever more limiting.

Whatever the mechanism or mechanisms involved, the ClO_2^- ions present are reduced to Cl^- ions. Grabeel (1992) was able to account for 86 to 117 percent of the chloride species as chloride ion. The Dionex Ion Chromatograph cannot detect OCl^- ions and ClO_2^- can react to form ClO_2 (also not detectable on the instrument,

and sample volume much too small to permit titrimeter analysis), as shown in equations [6] and [7], which would account for most of this variation.

Removal of Chlorite Ion With Chlorine Present

The removal of ClO_2^- by PAC was also affected by the presence of chlorine in the water. The summary of PAC performance is demonstrated most clearly in Table 8. In ten experiments with different PACs, the total removal of ClO_2^- was higher when chlorine was absent, and in several cases the removals were substantially higher. Darco G-60 PAC removed all of the ClO_2^- under both conditions, and, in contrast, Darco KB-B removed more ClO_2^- when chlorine was present.

No ClO_3^- was detected during any tests conducted in the absence of chlorine. In those tests where chlorine had been added, ClO_3^- was always present, but the concentration sometimes lowered for four of the PACs (Ceca 20C, Nuchar SA, Nuchar Aqua S, and Husky), although there is no known mechanism which would produce this result. Overall, for those four PACs, the data provides no significant evidence of ClO_3^- formation and does not substantiate such formation at this pH and chemical concentration. The amount of ClO_3^- did increase for the other eight PACs. The reviewed literature supports the contention that ClO_2 will not form ClO_3^- without the actions of other agents, such as chlorine or catalysts, at or near neutral pH, which was the pH during this investigation. This research provided no consistent evidence of ClO_3^- formation under the experimental conditions for four of the PACs.

The recovery of any of the three ions of concern is further complicated by the addition of chlorine in the form of either calcium hypochlorite or sodium hypochlorite. The ClO_2^- may react as previously discussed and may, in addition, react with HOCl to form ClO_2 . The total recovery of chloride species as chloride ion under either the presence or absence of chlorine was 77 percent to 115 percent in this investigation. The range of reduction in ClO_2^- was from 0.35 mg/L to 2.4 mg/L when chlorine was absent and from 1.25 mg/L to 2.39 mg/L when chlorine was present. The gain in Cl^- was from 0.35 mg/L to 1.06 mg/L when chlorine was absent and from 0.33 mg/L to 1.97 mg/L when chlorine was present. The gain in ClO_3^- was zero when chlorine was absent and from 0 mg/L to 0.54 mg/L when chlorine was present; however, the beginning concentration of ClO_2^- and the beginning concentration of Cl^- was not the same for all experiments, and that is why percentage removals are used at most points in this report.

Correlation Between Removal Efficiency and PAC Characteristics

Acid Extracted Metals

The acid extraction process conducted on the twelve different PACs screened in this research was followed by an analysis of the concentrations of aluminum, boron, iron, magnesium, manganese, and zinc. The results were reported in Table 11 of the Results chapter and plotted versus ClO_2^- -removal percentages in Appendix C. These investigations were conducted to determine whether a linkage could be found between concentrations of certain metals and the ability of PAC to remove

ClO_2^- . Since Iatrou and Knocke (1991) demonstrated that reduced iron could rapidly reduce ClO_2^- to Cl^- in drinking water, it was the metal of primary interest.

The iron content of the twelve carbons screened was reported in Table 9 and plotted versus ClO_2^- removal in Appendix C. Review of the data demonstrates that the Darco G-60 PAC, the best performer in ClO_2^- removal, contained only 0.15 mg iron per gram of PAC. The worst performing PAC, Darco KB-B, did have a lower iron content of 0.069 mg iron per gram of PAC, but the PAC with the lowest iron content (Nuchar SA) demonstrated good removal in the absence of chlorine. The highest value of iron measured was 4.71 mg per gram of PAC, extracted from Darco HDB carbon. This carbon did remove 100 percent of the ClO_2^- in the absence of chlorine, but fell below 80 percent removal when chlorine was added. The Ceca 20 C contained 3.18 mg iron per gram of PAC, yet it and "Watercarb" (also known as "Husky brand") removed the least ClO_2^- . The data demonstrates no obvious relationship between iron content and ClO_2^- removal.

A series of linear regressions were computed to determine correlation between metal content and ClO_2^- removal when chlorine was absent for each of the PACs and each of the metals. The highest correlation (with an R^2 of only 0.209) was for iron. The lowest correlation (with an R^2 of 0.000183) was for manganese. None of the PACs had a significant correlation between metal content and ClO_2^- removal for aluminum, boron, iron, magnesium, manganese, or zinc. These results are not surprising considering the low species concentrations. The details are provided in Tables A46 through A51 in Appendix A.

Particle Diameter

Carbon manufacturers often specify PACs by the percentage which will pass through screens of 100 mesh, 200 mesh, and 325 mesh. For the twelve PACs screened in this research, the only value available for the majority of the carbons was the percentage passing through a 325 mesh screen; therefore, that characteristic was utilized for comparison in this paper, with the tabular information reported in Table 3 and the summary plot provided in Appendix C. The carbon that was reported to have the largest percentage smaller than 325 mesh was Calgon WPH, at a "typical" value of 98 percent and a specification value of 90 percent. The other PACs tested which have a specification of 90 percent for this mesh are Calgon WPL, Nuchar Aqua S, and Watercarb. A minimum value of 50 percent is listed in the specifications for Ceca 20 B and Darco G-60, and a band of 50 percent to 85 percent is listed for Ceca 20 C. Values for the other PACs lie in bands between the two extreme values.

The two Calgon PACs have been noted to be good performers for ClO_2^- removal and they, particularly the WPH, contain the smallest size particles of the twelve. However, the top performer, Darco G-60, passes only 50 percent through the 325 mesh screen by specification, as does the number two PAC, Ceca 20 B. The data does not demonstrate any obvious linkage between ClO_2^- removal efficiency and particle diameter, as measured by percentage passing through a 325 mesh screen.

Carbon Raw Material

The raw source material of the different PACs screened has been reported in Table 3, and is summarized in a plot of ClO_2^- removal efficiency annotated with PAC source found in Appendix C. Review of these data reveals several interesting facts. The PACs which were manufactured from sub-bituminous coal and peat demonstrated the best overall ClO_2^- removal characteristics. The carbons produced from sub-bituminous coal, bituminous coal, and peat display the smallest degradation in ClO_2^- removal when chlorine is added. The performance of coal-based carbons is exceeded by the peat-based, lignite-based, and the sub-bituminous based carbons. Two of the three soft wood PACs and the one hard wood PAC removed the least ClO_2^- , only about 50 percent, in those tests where chlorine had been added. The one hard wood PAC was the only one of the twelve PACs screened which removed more ClO_2^- with chlorine present. No clear relationship was discovered between ClO_2^- removal and carbon raw material.

Porosity of the Carbon

The micro porosity of the PAC is best quantified by the measure "iodine index", which indicates the degree of "mini-micro porosity" of the carbon, essentially the total surface area of the carbon, including the smallest passages which can be measured with current technology. When the iodine index is plotted versus the percentage of ClO_2^- removed (see Appendix C), it is obvious that this carbon characteristic also does not correlate with ClO_2^- removal capability.

Another general measurement of carbon porosity, the BET surface area, is plotted against ClO_2^- removal in Appendix C. This plot certainly reveals a pattern different from the iodine index curve; but like the iodine index, it does not display any correlation with ClO_2^- removal. The final figure of this series plots the carbon density versus ClO_2^- removal percentages. This physical characteristic of the PAC, which is also linked to the porosity of the PAC, shows no apparent correlation to the ClO_2^- removal performance of the PACs screened.

Chapter VI

SUMMARY AND CONCLUSIONS

The major objectives of this study were to:

- 1) determine the ClO_2^- reduction capability of twelve powdered activated carbons (PACs).
- 2) evaluate the effects of chlorine on ClO_2^- reduction and ClO_3^- formation, which had been demonstrated by other research.
- 3) evaluate several properties of the carbons with a view toward possible explanations regarding the level of effectiveness of each carbon in the removal of ClO_2^- .

Summary

The approach to meet these objectives was to observe the removal of ClO_2^- and the production of ClO_3^- and Cl^- in a well stirred jar of reagent water containing ClO_2^- , at $\text{pH } 7.0 \pm 0.2$ pH units, with 20 mg/L of powdered activated carbon (PAC) added in each case. The next step was to repeat the same experiment with chlorine added and observe the removal of ClO_2^- and the production of ClO_3^- and Cl^- . The results of these two sets of experiments were then used to screen the twelve different PACS under each of the above conditions to allow comparison of the capability of

several types of carbons. The final step was to analyze several known PAC physical or chemical properties in a search for possible explanations regarding the level of effectiveness of each PAC for removing ClO_2^- .

The water samples were analyzed by ion chromatograph with the results recorded and plotted. The performance of each PAC in the removal of ClO_2^- from water and the concurrent production of Cl^- and ClO_3^- in the process were plotted and compared. The significance of the presence or absence of chlorine upon the above performance was also plotted and compared. No ClO_3^- levels above background were detected during any tests conducted in the absence of chlorine. In those tests where chlorine had been added, ClO_3^- was always present, but the concentration sometimes lowered for four of the PACs (Ceca 20C, Nuchar SA, Nuchar Aqua S, and Husky), although there is no known mechanism which would produce this result. Overall, for those four PACs, the data provided no significant evidence of ClO_3^- formation and did not substantiate such formation at this pH and chemical concentration.

An extensive literature search, coupled with liaison with the technical experts of several different carbon companies, was utilized to assemble information on certain physical and chemical characteristics of the PACs tested. This information was supplemented with a laboratory analysis of the concentration of certain metals present in the acid extract of the ash of each PAC. This assemblage of information was reported, plotted, and evaluated to determine if any of these PAC characteristics could be correlated with their ability to remove ClO_2^- from water.

Conclusions

1. Initial ClO_2^- removal rates were very rapid for all PACs.

a. During the first 15 minutes, four of the PACs (Aqua S, L2S, Husky and G-60) removed over 40 percent of the ClO_2^- when chlorine was absent. In the presence of chlorine, five of the PACs (20B, WPH, WPL, G-60, and HDB) removed 40 percent or more of the ClO_2^- during the same period. Removal rates for six of the PACs (Aqua S, L2S, Husky, S-51, G-60, and HDB) exceeded 140 percent per hour when chlorine was absent. In the case where chlorine was present, six PACs (20B, WPH, WPL, S-51, G-60, and HDB) exceeded 148 percent per hour ClO_2^- removal rate.

b. After a contact time of 30 minutes, the percentage of ClO_2^- removed for eight of the PACs was 45 percent or greater in the absence of chlorine. With chlorine present, five of the PACs had removed over 50 percent of the ClO_2^- . The removal rates had been reduced compared to those after 15 minutes of contact time. The only rate in excess of 100 percent per hour was WPH with chlorine absent.

c. During the first hour, when chlorine was absent, all PACs except KBB reduced ClO_2^- at least 50 percent, and removals by three of the PACs (Aqua S, L2S, and G-60) were at 70 percent or more. With chlorine present, these removal rates were lower when 20 C, WPL, SA, Aqua S, L2S, and Husky PAC were used. The presence of chlorine increased the ClO_2^- removal rates during the first hour when S-51, G-60, KBB, and HDB

PAC were used, while the removal rates with 20 B, WPH, and G-60 remained nearly the same as those observed when chlorine was absent.

d. After two hours of PAC contact, the ClO_2^- removal among the PACs had become more uniform. When chlorine was present, six PACs (20B, WPH, WPL, S-51, G-60, and HDB) had removed over 60 percent of the ClO_2^- , while removals by the other six were lower. When chlorine was absent, the disparity was much less, and ClO_2^- removal by all PACs except KBB and HDB exceeded 64 percent.

2. After the first 4 hours of contact, the rate of reduction of ClO_2^- had decreased to a rate of six percent per hour or less for all PACs under both conditions. After 8 hours, the rate had fallen to 3 percent per hour or less except for HDB and Aqua S in the absence of chlorine, which were both at 3.5 percent per hour.

3. No ClO_3^- was detected during any tests conducted in the absence of chlorine. In those tests where chlorine had been added, ClO_3^- was always present, but the concentration sometimes lowered for four of the PACs (Ceca 20C, Nuchar SA, Nuchar Aqua S, and Husky), although there is no known mechanism which would produce this result. For those four PACs, the data provides no significant evidence of ClO_3^- formation and does not substantiate such formation at this pH and chemical concentration. The amount of ClO_3^- did increase for the other eight PACs.

4. The extent of ClO_2^- removal was **not** related to:

- a) The acid extracted metal content (aluminum, boron, iron, magnesium, manganese, or zinc) or the total metal content.
- b) The percentage of PAC passing through a 325 mesh screen.
- c) The raw material from which the PAC was manufactured.
- d) The iodine index of the carbon; which is an indicator of the total surface area of the PAC, including the smallest passages.
- e) The BET surface area, a less accurate surface area measurement.
- f) The density of the powdered activated carbon.

5. The PAC performance in the removal of ClO_2^- from reagent water may not fully mirror the removal of ClO_2^- in drinking water, all other conditions being equal, because organics and other materials present in the drinking water may block pores of the PAC which would otherwise have provided surface area for ClO_2^- . The PACs to be screened for use in water treatment plant must be pilot plant tested using the waters which will actually be treated, under the exact same conditions to be found in the plant.

6. Some of the PACs screened may not prove economically viable for full scale use in water treatment plants, although several of them have been so used. It may be necessary to test other, less expensive PACs for actual plant use.

7. The required PAC loading of several of the carbons screened should prove to be less than the 20 mg/L which was chosen for all the experiments, depending upon the available contact time permitted in the water treatment plant, and the nature of the water to be treated. This loading would also require in-situ testing.

8. Powdered activated carbon should provide a viable alternative for the removal of ClO_2^- in a water treatment plant. The required dose, and thus the economic feasibility, will vary with the composition of the raw water, the amount of contact time permitted, the ClO_2^- concentration permitted by regulations, and the particular carbon used.

REFERENCES

- Abdel-Rahman, M.S., Couri, D. and Bull, R.J. "Metabolism and Pharmokinetics of Alternate Drinking Water Disinfectants." *Environmental Health Perspectives*, 46: 19-23. (1982)
- Abdel-Rahman, M.S., Couri, C. and Bull, R.J. "Effect of Exogenous Glutathione, Glutathione Reductase, Chlorine Dioxide and Chlorite on Osmotic Fragility of Rat Blood in Vitro." *Journal of the American College of Toxicology*, 3(4): 269-275 (1984).
- Abdel-Rahman, M.S., Couri, C. and Bull, R.J. "Kinetics of ClO_2^- and Effects of ClO_2 , ClO_2^- , and ClO_3^- in Drinking Water on Blood Glutathione and Hemolysis in Rat and Chicken" *Journal of Environmental Pathology and Toxicology* 3: 431-449 (1979).
- Abdel-Rahman, M. S. (1985). "Pharmokinetics of Chlorine Obtained From Chlorine Dioxide, Chlorine, Chloramine, and Chloride" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L.. Jolley, Richard. Bull, William P., Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 281-294
- Abdel-Rahman, M.S., Couri, C. and Jones, J. D. "Chlorine Dioxide Metabolism in Rat" *Journal of Environmental Pathology and Toxicology* 3: 421-430 (1980).
- Aharoni, C. "Kinetics of Adsorption in the S-Shaped Z-T Plot." *Adsorption Science and Technology*, 1: 1-29 (1984)
- Aieta, E.M., Roberts, P. V. and Hernandez, M. "Determination of Chlorine Dioxide, Chlorine, Chlorite and Chlorate in Water." *Journal of the American Water Works Association*, 76(6): 64-70 (1984).
- Aieta, E. M., and Berg, J.D. "A Review of Chlorine Dioxide in Drinking Water Treatment." *Journal of the American Water Works Association*, 78(6): 62-72 (1986).

- Aieta, E.M. and Roberts, P.V. (1985). "The Chemistry of Oxo-Chlorine Compounds Relevant to Chlorine Dioxide Generation" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 783-796.
- Akin, E.W., Hoff, J. C., and Lippy, E. C. "Waterborne Outbreak Control: Which Disinfectant?" *Environmental Health Perspectives*, 46: 7-12 (1982).
- Akin, E.W. and Hoff, J. C. (1985). "Microbiological Risks Associated with Changes in Drinking Water Disinfection Practices" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard. Bull, William P., Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 99-130.
- American Norit Company (1989). "Introduction to Activated Carbon" Atlanta, Georgia. 17pp.
- American Norit Company (1989). "Information on Lignite versus Coal in Potable Water Treatment" Atlanta, Georgia. 23pp.
- American Norit Company (1989). "Norit [Carbon] Testing Methods" Amersfoort Holland. 22pp.
- American Norit Company (1989). "Purification of Gases and Liquids Using Norit GAC" Atlanta, Georgia. 11pp.
- American Norit Company. "Measuring the Adsorption Capacity of Powdered Activated Carbon" Atlanta, Georgia.
- American Norit Company. "Granular Activated Carbon Evaluation" Atlanta, Georgia.
- American Norit Company. "Dechlorination With Activated Carbon" Atlanta, Georgia.
- American Norit Company. "Dechlorination Efficiency Test Procedure" Atlanta, Georgia.

American Norit Company. "Carbon Selection Chart" Atlanta, Georgia.

American Public Health Association, American Water Works Association, American Pollution Control Federation (1989). *Standard Methods for the Examination of Water and Wastewater*, 17th edition.

American Public Health Association, American Water Works Association, American Pollution Control Federation (1992). *Standard Methods for the Examination of Water and Wastewater*, 18th edition.

American Water Works Association (1993). "Water Industry Data Base (WIDB): Utility Profiles Report." Denver, Colorado.

Ames, R.G. and Stratton, J.W. "Effect of Chlorine Dioxide Water Disinfection on Hematologic and Serum Parameters of Renal Dialysis Patients." *Archives of Environmental Health*, 42(5) : 280-285, (1987).

Amoore, J.E. and Hautala, E. "Odor as an Aid to Chemical Safety: Odor Thresholds Compared with Threshold Limit Values and Volatilities for 214 Industrial Chemicals in Air and Water Dilution." *Journal of Applied Toxicology*, 3(6): 272-289 (1983).

Atlas Chemical Industries, Inc. (1963) "Measuring Adsorptive Capacity of Activated Carbons for Liquid Purification." Wilmington, Delaware.

Atlas Chemical Industries, Inc. (1968) "A Symposium on Activated Carbon" 80 pp. Wilmington, Delaware.

ATOCHEM North America, Inc. "Activated Carbon Evaluation and Selection" 33 pp. Pryor, Oklahoma.

Bean, E.L., "Taste and Odor Control at Philadelphia." *Journal of the American Water Works Association*, 49(2): 205-216.(1957).

Bellar, T.A., Lichtenberg, J.J. and Kroner, R.C. "The Occurrence of Organohalides in Chlorinated Drinking Waters." *Journal of the American Water Works Association*, 66: 703 (1974).

- Bercz, J.P., Jones, L., Garner, L., Murray, D., Ludwig, D.A., and Boston, J. "Subchronic Toxicity of Chlorine Dioxide and Related Compounds in Drinking Water in the Nonhuman Primate." *Environmental Health Perspectives*, 46: 47-55 (1982).
- Bercz, J.P., Jones, L., Harrington, R.M., Bawa, R. and Condie, L. "Mechanistic Aspects of Ingested Chlorine Dioxide on Thyroid Function: Impact of Oxidants on Iodide Metabolism" *Environmental Health Perspectives*, 69: 249-255 (1986).
- Bernard, M.A., Snow, W.B., Olivieri, V.P. and Davidson, B., "Kinetics and Mechanism of Bacterial Disinfection by Chlorine Dioxide," *Applied Microbiology*, 15: 2,257 (1967).
- Bernard, M.A., Isreal, B.M., Olivieri, V.P. and Granstrom, M.L., "Efficiency of Chlorine Dioxide as a Bactericide," *Applied Microbiology*, 13: 776-780 (Sept. 1965).
- Bernard, M.A., Snow, W.B. and Olivieri, V.P., "Chlorine Dioxide Disinfection Temperature Effects," *Journal of Applied Bacteriology* 30: 159 (April, 1967).
- Boeining, P.H., Beckmann, D.D., and Snoeyink, V.L. "Activated Carbon Versus Resin Adsorption of Humic Substances." *Journal of the American Water Works Association*, 72(1): 54-59 (1980).
- Briley, K.F., Williams, R.F., Longley, K.E. and Sorber, C.E. "Trihalomethane Production from Algae Precursors." in *Water Chlorination: Environmental Impact and Health Effects*, vol 3. R. Jolley, W. Brungs, and R. Cummings, eds. Ann Arbor Science, Ann Arbor, Michigan. pp. 117-130 (1980).
- Bryant, E.A., Fulton, G.P. and Budd, G.C. (1992). *Disinfection Alternatives for Safe Drinking Water*. Van Nostrand Reinhold, New York, NY, 518 p.
- Bull, R.J. "Health Effects of Alternate Disinfectants and Their Reaction Products." *Journal of the American Water Works Association*, 72(5): 299-303 (1980).
- Bull, R.J. "Toxicological Problems Associated with Alternative Methods of Disinfection." *Journal of the American Water Works Association*, 74(12): 642-648 (1982).

- Bull, R.J. (1983). "Health Risks of Drinking Water Disinfectants and Disinfection By-products" in: *Water Chlorination: Environmental Impact and Health Effects, Volume 4*, Robert L. Jolley, William A. Brungs, Joseph A. Cotruvo, Robert B. Cumming, Jack S. Mattice and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 1401-1416.
- Bull, R. J. and McCabe, L.J. (1985). "Risk Assessment Issues in Evaluating the Health Effects of Alternate Means of Drinking Water Disinfection." in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 111-132.
- Calabrese, E.J. and Gilbert, C.E. (1989). "Drinking Water Quality and Water Treatment Practices: Charting the Future." in: *Safe Drinking /Water Act: Amendments, Regulations and Standards*, Lewis Publishers, Chelsea, Michigan.
- Cantor, K.P. "Epidemiological Evidence of Carcinogenicity of Chlorinated Organics in Drinking Water." *Environmental Health Perspectives*, 46: 187-195 (1982).
- Cantor, K.P. (1983). "Epidemiological Studies of Chlorination By-products in Drinking Water: An Overview." in: *Water Chlorination: Environmental Impact and Health Effects, Volume 4*, Robert L. Jolley, William A. Brungs, Joseph A. Cotruvo, Robert B. Cumming, Jack S. Mattice and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 1381-1400.
- Carlton, B.D. and Smith, M. K. (1985). "Reproductive Effects of Alternate Disinfectants and Their By-Products." in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 295-306.

Carswell, J.K., Clark, R.M., Dorsey, P., Geldrich, E.E., Heffernan, W.P., Hoff, J.C., Love, O.T..Jr., McCabe L.J. and Stevens, A.A. (1978) Ozone, Chlorine Dioxide and Chloramines as Alternatives to Chlorine for Disinfection of Drinking Water. in: *Water Chlorination: Environmental Impact and Health Effects*, Vol. 2, R.L. Jolley, H. Gorchev, and D.H. Hamilton, eds., Ann Arbor Science, Ann Arbor, Michigan, pp. 555-560 .

CECA, INC. "Activated Carbon Applications" Tulsa, Oklahoma.

CECA, INC. (1985)"Use of Activated Carbon in Water Treatment" Tulsa, Oklahoma.

CECA, INC. (1973) "Activated Carbon Evaluation and Selection" 33 pp. Tulsa, Oklahoma.

Chen, A.S.C., Larson, R.A. and Snoeyink, V.L. "Reactions of Chlorine Dioxide with Hydrocarbons: Effects of Activated Carbon." *Environmental Science and Technology.*, 16(5): 268-273 (1982)

Cheremisinoff, P.N. and Ellerbusch, R. (1980). *Carbon Adsorption Handbook*. Ann Arbor Science, Ann Arbor, Michigan, 1054 p.

Chudyk, W.A., Snoeyink, V.L., Beckmann, D., and Temperly, R.J. "Activated Carbon Versus Resin Adsorption of 2-Methylisoborneol and Chloroform." *Journal of the American Water Works Association*, 71(9): 529-538 (1979)

Chlorine Dioxide Panel. "A Review of the Uses, Chemistry, and Health Effects of Chlorine Dioxide and the Chlorite Ion (1st Draft)" The Chemical Manufacturer's Association (undated).

City of Elgin. "October 1988 PAC Evaluation" Elgin, Illinois.

City of Philadelphia Water Department Organics Laboratory. "Evaluation of Four Powdered Activated Carbons for Geosmin Removal for Laboratory Adjusted Water" Philadelphia, Pennsylvania.

Condie, L. "Toxicological Problems Associated with Chlorine Dioxide." *Journal of the American Water Works Association*, 78(6): 73-78 (1986).

- Condie, L.W. and Bercz, J. P. (1985). "Target Organ Effects of Disinfectants and Their By-Products" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 345-354.
- Cooper, R.S. and Liberman, D.A. "Fixed-Bed Adsorption Kinetics with Pore Diffusion Control." *Industrial Engineering Chemical Fundamentals*, 3(4): 620-623 (1970).
- Costa, E., Calleja, G. and Marijuan, C. "Adsorption of Phenol and P-nitrophenol on Activated Carbon: Determination of Effective Diffusion Coefficients." *Absorption Science and Technology*, 4: 1-29 (1987)
- Cotruvo, J.A. "Introduction: Evaluating the Benefits and Potential Risks of Disinfectants in Drinking Water Treatment." *Environmental Health Perspectives*, 46: 1-6.(1982).
- Cotruvo, J.A. (1983). "Drinking Water Perspective" in: *Water Chlorination: Environmental Impact and Health Effects, Volume 4*, Robert L. Jolley, William A. Brungs, Joseph A. Cotruvo, Robert B. Cumming, Jack S. Mattice and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 1417-1422.
- Cotruvo, J. A. and Vogt, C. D. (1985). "Regulatory Aspects of Disinfection" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 91-98.
- Couri, D., Abdel-Rahman, M.S. and Bull, R. "Toxicological Effects of Chlorine Dioxide, Chlorite and Chlorate." *Environmental Health Perspectives*, 46: 13-17.(1982),
- Couri, D., Abdel-Rahman, M.S. "Effect of Chlorine Dioxide and Metabolites on Glutathione Dependent System in Rat, Mouse, and Chicken Blood" *Journal of Environmental Pathology and Toxicology* 3: 451-459 (1979).

- Couri, D., Miller, C.H., Bull, R.J., Delphia, J. M., and Ammar, A.M.
 "Assessment of Maternal Toxicity, Embryotoxicity and Teratogenic Potential of Sodium Chlorite in Sprague-Dawley Rats." *Environmental Health Perspectives*, 46: 25-30. (1982).
- Craun, G. F. (1985). "Epidemiologic Considerations for Evaluating Associations Between the Disinfection of Drinking Water and Cancer in Humans" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard. Bull, William P., Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, Michigan, 133-143.
- Cronier, S., Scarpino, P.V. and Zink, M.L. (1978). "Chlorine Dioxide Destruction of Viruses and Bacteria in Water." in: *Water Chlorination: Environmental Impact and Health Effects*, Vol. 2, R.L. Jolley, H. Gorchev, and D.H. Hamilton, eds., Ann Arbor Science, Ann Arbor, Michigan, 651-658.
- Culp, G. (1984) *Control of Trihalomethanes Using Alternative Oxidants and Disinfectants*. Noyes Publications, Park Ridge, New Jersey. .
- Dallas Water Company East Side Plant. (1992) "Laboratory Evaluation of Hydrodarco B and Watercarb in Taste and Odor Removal." Dallas, Texas 10 pp.
- Daniel, F.B., Condie, L.W., Robinson, M., Stober, J.A., York, G.A. , Olson, G.R., and Wang, S. "Comparative Subchronic Toxicity Studies of Three Disinfectants." *Journal of the American Water Works Association*, 82(10): 61-69. (1990).
- Davis, Mac. L., and Cornwell, D.A. (1991). *Introduction to Environmental Engineering*, Second Edition. MacGraw-Hill, Inc., New York, New York, 822 p.
- DeJohn, P.B., "Carbon From Lignite or Coal: Which is Better?" reprint from *Chemical Engineering*, April 28, 1975. 113-116 (1975).
- De Zuane, J. *Handbook of Drinking Water Quality Standards and Control* (1990). Van Nostrand Reinhold, New York, New York, 523 p.

- Di Giano, F.A. and Weber, W.J. "Sorption Kinetics in Finite Bath Systems." *Journal of the Sanitary Engineering Division Proceedings of the American Society of Civil Engineers*, 98(SA6): 1021-1036 (1973).
- Di Giano, F.A. and Weber, W.J. "Sorption Kinetics in Infinite-Bath Systems." *Journal of Water Pollution Control Federation*, 45(4): 713-725 (1973).
- Dietrich, A., Ledder, T, Gallagher, D., Grabeel, M., and Hoehn, R. "Analysis of Chlorite and Chlorate in Chlorinated and Chloraminated Drinking Water by Flow Injection Analysis and Ion Chromatography." *Analytical Chemistry*, submitted Aug. 1991.
- Dietrich, A.M., Orr, M.P., Gallagher, D.C., Hoehn, R.C., "Tastes and Odors Associated with Chlorine Dioxide." *Journal of the American Water Works Association*, 84(6): 82-88 (1992).
- Dietrich, A., Ledder, T., Gallagher, D., Grabeel, M., and Hoehn, R. "Determination of Chlorite and Chlorate in Chlorinated and Chloraminated Drinking Water by Flow Injection Analysis and Ion Chromatography." *Analytical Chemistry* 64(5): 496-502 (1992).
- Dietrich, A.M., Orr, M.P., Gallagher, D.C., Hoehn, R.C. "Current Chlorine Dioxide Practice and Problems in the USA." *Proceedings of the Annual Conference of the American Water Works Association*, Cincinnati, Ohio, June 17-21(1990).
- Dionex Corporation (1983). Basic Ion Chromatography Training Manual. Dionex Corporation, Sunnyvale, CA.
- Dixon, K.L. and Lee, R.G. "The Effect of Sulfur-Based Reducing Agents and GAC Filtration on Chlorine Dioxide by-Products." *Journal of the American Water Works Association*, 83(5): 48-55 (1991).
- Dowling, L. T. "Chlorine Dioxide in Potable Water Treatment." *Water Treatment and Examination* 23 (2): 190-204 (1974).
- Edeskuty, F.J. and Amundson "Mathematics of Adsorption. IV. Effect of Intraparticle Diffusion in Agitated Static Systems." *The Journal of Chemical Physics*, 56: 148-152 (1950).

Elf Atochem North America, Inc. (1988) "Technical Bulletin Free Chlorine Removal With CECACARBON Granulated Activated Carbon." Pryor, Oklahoma.

Federal Register, vol. 44, no. 231, R, 68624-68707, 11/29/79.

Foley, J.P. and Dorsey, J.G. " Clarification of the Limit of Detection in Chromatography." *Chromatographia*, 18(9): 503-511(1984).

Gall, R.J. (1978) "Chlorine Dioxide: An Overview of its Preparation, Properties, and Uses." in: *Ozone/Chlorine Dioxide Oxidation Products of Organic Materials*. R.G. Rice and J. A. Contruvo, Eds. Ozone Press International: Cleveland, OH. pp. 356-382 .

Gallagher, D.L, Hoehn, R.C. and Dietrich, A.M. (1993). "Sources, Occurrence, and Control of Chlorine Dioxide By-Product Residuals in Drinking Water" The AWWA Research Foundation and the American Water Works Association. Denver, Colorado.

Gates, D. "A Two-Step Method for Determining Residual Oxidants in the Presence of Other Chlorine Species in Finished Water." *Proceedings, Water Quality Technology Conference*, St. Louis, Missouri, November 13-17 1988. 689-701.

Gilbert, C.E., and Calabrese, E.S. (eds.), (1992). *Regulating Drinking Water Quality*. Lewis Publishers, Ann Arbor, Michigan, 328 p.

Gordon, G., Cooper, W.J., Rice, R.G. and Pacey, G. (1987). *AWWARF Report, Disinfectant Residual Measurement Methods*. American Water Works Association Research Foundation, American Water Works Association, Denver, CO.

Gordon, G., Cooper, W.J., Rice, R.G. and Pacey, G. "Methods of Measuring Disinfectant Residuals." *Journal of the American Water Works Association*, 80(9): 94 (1988).

Gordon, G. and Ikeda, Y. " Lower Detection Limits Found for Chlorine Dioxide Contaminants. " *Journal of the American Water Works Association*, 76(7): 98-101.(1984).

- Gordon, G., Kieffer, R.G. and Rosenblatt, D.H. (1972). "The Chemistry of Chlorine Dioxide. in: *Progress in Inorganic Chemistry*." Volume 15, Wiley-Interscience Publishers, New York, NY, 488 p.
- Gordon, G., Sootmaekers, B., Tachiyashiki, S. and Wood, D. "Minimizing Chlorite Ion and Chlorate Ion in Drinking Water Treated with Chlorine Dioxide." *Journal of the American Water Works Association*, 82(4): (1990).
- Gordon, G. and Tachiyashiki, S. " Kinetics and Mechanism of Formation of Chlorate Ion from Hypochlorous Acid/Chlorite Ion Reaction at pH 6-10.", *Environmental Science and Technology*, 25: 468-474. (1991).
- Gordon, G., Yoshino, K., Themelius, D.G., Wood, D.W. and Pacey, G.E. "Utilization of Kinetic Based Flow Injection Analysis Methods for the Determination of Disinfection Species." *Analytica Chimica Acta*, 224: 383-391 (1989).
- Grabeel, M.N. "Chlorine Dioxide By-Products in Drinking Water and Their Control by Powdered Activated Carbon." M.S. Thesis. Virginia Polytechnic Institute and State University; Blacksburg, Virginia (1992).
- Granstrom, M.L. and Lee, G.F. "Generation and Use of Chlorine Dioxide in Water Treatment," *Journal of the American Water Works Association*, 50: 53-58 (1958).
- Griese, M.H., Hauser, K., Berkemeire, M. and Gordon G. "Using Reducing Agents to Eliminate Chlorine Dioxide and Chlorite Ion Residuals in Drinking Water." *Journal of the American Water Works Association*, 83(5): 56-61 (1991).
- Griese, M.H., Kaczur, J. J. and Gordon, G. "Combining Methods for the Reduction of Oxychlorine Residuals in Drinking Water." *Journal of the American Water Works Association*, 84(11): 69-77 (1992).
- Grisham, M.B., Jefferson, M.M. and Thomas, E.L. " Role of Monochloramine in the Oxidation of Erythrocyte Hemoglobin by Stimulated Neutrophils" *The Journal of Biological Chemistry* 259 (11): 6766-6772 (1984).
- Grob, K. and Grob, G. "Organic Substances in Potable Water and its Precursor" *Journal of Chromatography* 90 (2): 303-313 (1974).

- Grzywna, Z.J. and Petropoulos, J.H. "Transient Diffusion Kinetics in Media Exhibiting Axial Variation of Diffusion Properties Part I Sorption Kinetics." *Journal of the Chemical Society*, 79: 571-583 (1982).
- Grzywna, Z.J. and Petropoulos, J.H. "Transient Diffusion Kinetics in Media Exhibiting Axial Variation of Diffusion Properties Part 2. Permeation Kinetics." *Journal of the Chemical Society*, 79: 585-596 (1982).
- Guttman-Bass, N., Bairey-Albuquerque, M., Ulitzur, S., Chartrand, A., and Raq-Acha, C. "Effects of Chlorine and Chlorine Dioxide on Mutagenic Activity of Lake Kinnereth Water." *Environmental Science and Technology*, 21(3): 252-260 (1987).
- Hammer, M.J. *Water and Waste Water Technology*. (1975). John Wiley and Sons, New York, New York, 502 p.
- Hand, D.W., Crittenden, J.C. and Thacker, W.E. "Simplified Models for Design of Fixed-Bed Adsorption Systems." *Journal of Environmental Engineering*, 110(2): 440-457 (1984).
- Harakeh, M.S., Hoff, J. C. and Matin, A. (1985). "Response of Chemostat-Grown Bacteria to Chlorine Dioxide" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 615-618.
- Harriott, P.O. "Mass Transfer to Particles: Part 1 Suspended in Agitated Tanks." *American Institute of Chemical Engineers Journal* 1: 1-29 (1984).
- Hass, C.N. (Chairman) Water Quality Diversion Disinfection Committee. "Survey of Water Utility Disinfection Practices," *Journal of the American Water Works Association*, 84(9): 121-128 (1992).
- Hassler, J. W. (1974). *Activated Carbon*. Chemical Publishing Co., Inc., New York, NY, 390 p.
- Hautman, D. and Bolyard, M. (1991). "Analysis of Inorganic Disinfection By-Products Using Ion Chromatography." Paper presented at the Water Quality Technology Conference, American Water Works Association, Orlando, FL, November 10-15 pp. 1043-1059.

- Hautman, D. and Bolyard, M. "Using Ion Chromatography to Analyze Inorganic Disinfection By-Products." *Journal of the American Water Works Association*, 84(11): 88-93 (1992).
- Heffernan, W.P., Guion, C. and Bull, R.J. . "Oxidative Damage to the Erythrocyte Induced by Sodium Chlorite in Vitro." *Journal of Environmental Pathology and Toxicology*, 2: 1487-1499 (1979a).
- Heffernan, W.P., Guion, C. and Bull, R.J. . " Oxidative Damage to the Erythrocyte Induced by Sodium Chlorite in Vivo." *Journal of Environmental Pathology and Toxicology*, . 2: 1501-1510 (1979b).
- Hettche, O. and Ehlbeck, H.W.S., "Epidemiology and Prophylaxes of Poliomyelitis in Resptct of the Role of Water in Transfer," *Arch. Hyg. Berlin* 137: 440 (1953).
- Hoehn, R.C., Barnes, D.B., Thompson, B.C., Randall, C.W., Grizzard, T.J. and Shaffter, P.T.B. "Algae as Sources of Trihalomethane Precursors." *Journal of the American Water Works Association*, 72(6): 344-350 (1980).
- Hoehn, R.C., Dietrich, A.M., Farmer, W.S., Orr, M.P., Lee, R.G., Aieta, E.M., Wood, D.W. and Gordon, G. "Household Odors Associated with the Use of Chlorine Dioxide." *Journal of the American Water Works Association*, 80(4): 166-172 (1990).
- Hoehn, R.C., Lavinder, S.R., Hamann, C., Jr., MeElroy, J. and Snyder, E.G. "THM-Precursor Control with Activated Carbon in a Pulsed-Bed, Solids-Contact Clarifier." *Proceedings of the American Water Works Association*, Kansas City MO. 657-676 (1987).
- Hoehn, R.C., Johnson, P.E., Kornegay, B.H. and Rogenmuser, K.P. (1984) A Pilot Scale Evaluation of the Roberts-Haberer Process for Removing Trihalomethane Precursors From Surface Water With Powdered Activated Carbon. *Proceedings, 1984 Annual Conference*, Dallas, Texas, June 10-14, 1984.
- Hoff, J.C. and Geldrich, E.E. "Comparison of the Biocidal Efficiency of Alternative Disinfectants." *Journal of the American Water Works Association*, 71(1): 40-44 (1981).

- Howland, R.G. and Wallace, C.J., (1978). "Chlorine and Activated Carbon Treatment for Removal of Toxic Substances From Water." in: *Water Chlorination: Environmental Impact and Health Effects*, Vol. 2, R.L. Jolley, H. Gorchev, and D.H. Hamilton, eds., Ann Arbor Science, Ann Arbor, Michigan, 659-674.
- Huebner, W. "Improvements in Equipment for Chlorine Dioxide Generation." *American Water Works Association Annual Conference*, Orlando, FL (1988).
- Iatrou, A. and Knocke, W.R. "Chlorite Removal by the Addition of Ferrous Iron." *Journal of the American Water Works Association*, 84(11): 63-68 (1992).
- Ingols, R.S. and Ridenour, G.M. "Chemical Properties of Chlorine Dioxide." *Journal of the American Water Works Association*, 40: 1207 (1948)
- Jackson, D.E., Larson, R.A. and Snoeyink, V.L., "Reaction of Chlorine and Chlorine Dioxide with Resorcinol in Aqueous Solution and Adsorbed on Granular Activated Carbon." *Water Research*, 21(7): 849-857 (1987).
- Jensen, J.N. and Johnson, J.D. . "Interferences by Monochloramine and Organic Chloramines in Free Available Chlorine Methods. 1. Amperometric Titration." *Environmental Science and Technology*, 24: 981-985 (1990a).
- Jensen, J.N. and Johnson, J.D. "Interferences by Monochloramine and Organic Chloramines in Free Available Chlorine Methods. 2. N,N-Diethyl-p-phenylenediamine." *Environmental Science and Technology*, 24: 985-990 (1990 b).
- Jolley, R. J. (1985). "Basic Issues in Water Chlorination: A Chemical Perspective" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 19-38.
- Johnson, J.D., Christman, R.F., Norwood, D.L. and Millington, D.S. "Reaction Products of Aquatic Humic Substances With Chlorine." *Environmental Health Perspectives*, 46: 63-72 (1982).
- Kassam, K., Huck, P. M., Van Roodselnor, A. and Shariff, R., "Accumulation of Adsorption Capacity of PAC in a Slurry Recirculating Clarifier." *Journal of the American Water Works Association*, 83(2): 69-78 (1991).

- Katz, J. (ed).(1980). "Chlorine Dioxide." in: *Ozone and Chlorine Dioxide Technology for Disinfection of Drinking Water*. Noyes Data Corp., Park Ridge, New Jersey. pp. 7-75 and pp. 268-379.
- Keith, L. H., ed., (1991). *Compilation of E.P.A.'s Sampling and Analysis Methods* Lewis Publishers, Inc. Boca Raton, Florida, 803 p.
- Kepinski, A. and Kepinski W. (1987). *Water Supply and Waste Water Disposal International Almanac Vol. 8*. Zoetermeer, The Hague Netherland, 342 p.
- Kleffman, D. "Health Research Needed to Resolve Scientific Issues Surrounding Drinking Water Disinfection" *Environmental Health Perspectives* 69: 285-286 (1986).
- Kleopfer, R. D. and Fairless, B. J., "Characterization of Organic Components in a Municipal Water Supply" *Environmental Science and Technology* 6 (12): 1036-1037 (1972).
- Kolthoff, I.M. and Sandell, E.B. (1952). *Textbook of Quantitative Inorganic Analysis*, Third Edition, New York, NY, p. 585.
- Komorita, J.D. and Snoeyink, V.L. "Technical Note: Monochloramine Removal From Water by Activated Carbon" *Journal of the American Water Works Association*, 77 (1): 62-64 (1985).
- Kool, H.S., van Kreijl, C.F. and Hrubec, J. (1985). "Mutagenic and Carcinogenic Properties of Drinking Water Chlorination." in: *Environmental Impact and Health Effects. Volume 5*, R.SJ. Jolley (ed). Ann Arbor, Michigan, Ann Arbor Science Publishers, 187-205.
- Kotiacho, T., Hayward, M.J. and Cooks, R.C. . "Direct Determination of Chlorination Products of Organic Amiones using Membrane Introduction Mass Spectrometry." *Analytical Chemistry*, 63: 1794-1801 (1991).
- Knocke, W.R., Hoehn, R.C. and Sinsabugh, R.L. "Using Alternative Oxidants to Remove Dissolved Manganese from Waters Laden with Organics." *Journal of the American Water Works Association*, 79(3): 75-79 (1987).
- Kumar , K., Day, R.A. and Margerum, D.W. "Atom Transfer Redox Kinetics: General-Acid-Assisted Oxidation of Iodide by Chloramines and Hypochlorite." *Inorganic Chemistry*, 25: 344-4350 (1986).

- Kurokawa, Y. "Lack of Promoting Effect of Sodium Chlorate and Potassium Chlorate in Two-Stage Rat Renal Carcinogenesis" *Journal of the American College of Toxicology* 4: 331-335 (1985).
- Lalezary, S., Pirbazare, M. and McGuire, M.J. "Oxidation of Five Earthy-Musty Taste and Odor Compounds." *Journal of the American Water Works Association*, 78(3): 62-69 (1986).
- Lalezary, S., Pirbazare, M. and McGuire, M.J. "Evaluating Activated Carbons for Removing Low Concentrations of Taste and Odor-Producing Organics." *Journal of the American Water Works Association*, 78(11): 76-82 (1986).
- Lalezary-Craig,, S. Pirbazari, M., Dale, M., Tanaka, T. and McGuire, M. "Optimizing the Removal of Geosmin and 2-Methylisoborneol by Powdered Activated Carbon." *Journal of the American Water Works Association*, 80(3): 73-79 (1988).
- Lauer, W.C., Lohman, S.R. and Rogers, S.E. . "Experience with Chlorine Dioxide at Denver's Reuse Plant." *Journal of the American Water Works Association*, 71(6): 79-87 (1986).
- Ledder, T. "Comparison of Ion Chromatography and Flow Injection Analysis Methods for Monitoring Chlorite and Chlorate Ion in Drinking Water." M.S Thesis. Virginia Polytechnic Institute and State University; Blacksburg, VA (1991).
- Lee, M.C. Crittenden, J.C. Snoeyink, V.L. and Ari, M. "Design of Carbon Beds to Remove Humic Substances." *Journal of Environmental Engineering*, 107(3): 631-645 (1982).
- Liles, A.W. and Geankoplis, C.J. "Axial Diffusion of Liquids in Packed Beds and End Effects." *American Institute of Chemical Engineers Journal*, 6(4): 591-595 (1960).
- Limoni, B., Choshen (Goldstein), E. and Rav-Acha, C. "Determination of Oxidants. Formed Upon the Disinfection of Drinking Water with Chlorine Dioxide." *Journal Of Environmental Science and Health*, vol. A19(8): 943-57. (1984).

- Long, G. and Winefordner, J.D. . "Limit of Detection: A Closer Look at the IUPAC Definition." *Analytical Chemistry*, 55(7): 712A-724A.(1983).
- Lubbers, J.R., Chauhan, S. and Bianchine, J.R. . "Controlled Clinical Evaluations of Chlorine Dioxide, Chlorite and Chlorate in man." *Environmental Health Perspectives*, 46: 57-62 (1982)
- Lubbers, J.D., Bianchine, J.B. and Bull, R.J. (1983). "Safety of Oral Chlorine Dioxide, Chlorite, and Chlorate Ingestion in Man." in: *Water Chlorination: Environmental Impact and Health Effects, Volume 4*, Robert L. Jolley, William A. Brungs, Joseph A. Cotruvo, Robert B. Cumming, Jack S. Mattice and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 1335-1354.
- Lubbers, J. R. and Bianchine, J.R. "Effect of Acute Rising Dose Administration of Chlorine Dioxide, Chlorate and Chlorite to Normal Healthy Male Volunteers." *Journal of Environmental Pathology, Toxicology and Oncology*, 5:215-228, (1984a).
- Lubbers, J.R., Chauhan, S., Miller, Jk. and Bianchine, J.R. "The Effects of Chronic Administration of Chlorine Dioxide Chlorite, and Chlorate to Normal Healthy Adult Male Volunteers." *Journal of Environmental Pathology , Toxicology and Oncology*, 5:229-238 (1984b).
- Lubbers, Jr.R., Chjauhan, S. Miller, J.K. and Bianchine, J.R. The Effects of Chronic Administration of Chlorite to Glucose-6-Phosphate Dehydrogenase Deficient Healthy Adult Male Volunteers. *Journal of Environmental Pathology , Toxicology and Oncology* 5:239-242 (1984c).
- Lykins, B. W. and Griesse, H.G. . "Using Chlorine Dioxide for Trihalomethane Control." *Journal of the American Water Works Association*, 71(6): 88-93 (1986)
- Lykins, B. W., Koffskey, W.E. and Miller, R.C., "Chemical Products and Toxicological Effects of Disinfection." *Journal of the American Water Works Association*, 78(11): 66-75 (1986).
- Lykins, B. W., Goodrich, J.A., Koffskey, W.E. and Griesse, M.H. (1991) "Controlling Disinfection By-products With Alternative Disinfectants." *Proceedings, AWWA Annual Conference, Philadelphia, Pennsylvania, June 23-27, 1991*. 897-911.

- Manatee County Public Works Department "Comparison of Various Powdered Activated Carbons for the Removal of Geosmin and 2-MIB in Selected Water Conditions" Bradenton, Florida.
- Marx, J. L. "Drinking Water: Another Source of Carcinogens." *Science*, 188:809-812 (1974).
- Masamune, S. and Smith, J. "Adsorption Rate Studies-Interaction of Diffusion and Surface Processes." *American Institute of Chemical Engineers Journal* 11(1): 34-39 (1965).
- Masschelein, W.J. and Rice, R.G. (1979) *Chlorine Dioxide Chemistry and Environmental Impact of Oxychlorine Compounds*. Ann Arbor Science, Ann Arbor, Michigan.
- Masschelein, W.J. (1979). *Chlorine Dioxide: Chemistry and Environmental Impact of Oxychlorine Compounds*. Ann Arbor Science Publishers, Ann Arbor, Michigan, 190 p.
- Masschelein, W.J., Denis, M. and Ledent, R. . "Determination of Chlorite Ion in Dilute Solutions by Pulse Polography." *Analytica Chimica Acta*, 107: 383-386. (1979).
- Masschelein, W.J., "Experience wiith Chlorine Dioxide in Brussels: Generation of Chlorine Dioxide." *Journal of the American Water Works Association*, 76(1): 70-76 (1984).
- Masschelein, W.J., "Experience wiith Chlorine Dioxide in Brussels, Part 2: Methods for Controlling Chlorine Dioxide Operation." *Journal of the American Water Works Association*, 76(3): 80-87 (1984).
- Masschelein, W.J., "Experience wiith Chlorine Dioxide in Brussels, Part 3: Operational Case Studies." *Journal of the American Water Works Association*, 77(1): 73-80 (1985).
- McCreary, J.J. and Snoeyink, V.L. "Granular Activated Carbon in Water Treatment." *Journal of the American Water Works Association*, 69(8): 437 (1977).

- McCreary, J.J. and Snoeyink, V.L. "Reaction of Free Chlorine with Humic Substances Before and After Adsorption on Activated Carbon." *Environmental Science and Technology*, 15(2): 193-197 (1981).
- McGuire, M.J. and Suffet, I.H. "Aqueous Chlorine/Activated Carbon Interactions." *ASCE Journal of Environmental Engineering*, 110(3): 629-645 (1984).
- McGuire, J.J., Davis, M.K., Tate, CH., Aieta, E.M., Howe, E.W. and Crittenden, J.C. "Evaluating GAC for Trihalomethane Control." *Journal of the American Water Works Association*, 83(8): 57-63 (1991).
- McGhee, T.J. (1991). *Water Supply and Sewage Sixth Edition*. McGraw-Hill, Inc., New York, New York, 602 p.
- Meier, J. R. and Bull, R. J. (1985). "Mutagenic Properties of Drinking Water Disinfectants and By-Products." in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 207-220.
- Michael, G.E., Miday, R.K., Bercz, J.P., Miller, R.G., Greathouse, D.G., Kraemer, D.F. and Lucas, J.B. "Chlorine Dioxide Water Disinfection: A Prospective Epidemiology Study." *Archives of Environmental Health*, 36(1): 20-27. (1981).
- Miller, K.G., Pacey, G.E. and Gordon, G. "Automated Iodometric Method for Determination of Trace Chlorate Ion Using Flow Injection Analysis." *Analytical Chemistry*, 57: 734-737. (1985).
- Miller, G.W., Rice, R.G., Robson, C.M., Scullin, R.L., Kuhn, W. and Wolf, H. *An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies*. EPA-600/2-78-147. Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. (1978).
- Miltner, R. J., "Measurement of Chlorine Dioxide and Related Products." in: *Proceedings, AWWA Water Quality Technology Conference, San Diego, Dec. 6-7, 1976*. American Water Works Association, Denver, 1977, paper 2A-5.

- Montgomery, J. (1985). *Water Treatment Principles and Design*. John Wiley and Sons, New York, NY.
- Moore, G.S., Calabrese, E.J. and Ho, S.C. "Groups at Potentially High Risk from Chlorine Dioxide Treated Water." *Journal of Environmental Pathology and Toxicology*, 4-2, 3: 465-470 (1980).
- Moore, G.S. and Calabrese, E.J. "Toxicological Effects of Chlorite in the Mouse." *Environmental Health Perspectives*, 46: 31-38 (1982).
- Morris, R.D., Audet, A.M., Angelillo, I. F., Chalmers, T.C. and Mosteller, F. "Chlorination, Chlorination By-products, and Cancer: A Meta-analysis." *American Journal of Public Health*, 82(7): 955-963 (1992).
- Morris, J. C., Christman, R.F., Glaze, W.H., Helz, G.R., Hoehn, R.C. and Jolley, R.L. "The Chemistry of Disinfectants in Water: Reactions and Products." in: *Drinking Water and Health*, National Academy of Sciences, Washington, D.C., 1980, pp.139-249.
- Munson, A.E., Sain, L.E., Sanders, V.M., Kauffmann, B.M., White, K. L., Page, D.G., Barnes, D.W. and Borzelleca, J. F., "Toxicology of Organic Drinking Water Contaminants: Trichloromethane, Bromodichloromethane, Dibromochloromethane and Tribromomethane" *Environmental Health Perspectives*, 46: 117-126 (1982).
- Myers, G.L. and Thompson, A.L. "Controlling Taste and Odor with Chlorine Dioxide." *Southwest and Texas Water Works Journal*, 4-10 (1986).
- Myhrstad, J.A. and Somdal, J.E. "Behavior and Determination of Chlorine Dioxide." *Journal of the American Water Works Association*, 61(4): 205-208 (1969).
- Najm, I. N., Snoeyink, V.L. and Richards, Y. "Effect of Initial Concentration of a SOC in Natural Water on Its Adsorption by Activated Carbon." *Journal of the American Water Works Association*, 83(8):. 57-63 (1991).
- Najm, I.N. "Effect of Particle Size and Background Organics on the Adsorption Efficiency of PAC." *Journal of the American Water Works Association*, 82(1): 65 (1991).

Najm, I.N., Snoeyink, V.L., Lykins, B.W. and Adams J.Q. "Using Powdered Activated Carbon: A Critical Review." *Journal of the American Water Works Association*, 83(1): (1991).

National Academy of Sciences, National Research Council, Commission on Life Sciences, Board on Environmental Studies and Toxicology, Safe Drinking Water Committee (1977). "Toxicity of Selected Drinking Water Contaminants". In: *Drinking Water and Health*, National Academy Press, Washington, DC, 939 pp.

National Academy of Sciences, National Research Council, Commission on Life Sciences, Board on Environmental Studies and Toxicology, Safe Drinking Water Committee (1980a). "Toxicity of Selected Drinking Water Contaminants". In: *Drinking Water and Health Volume 2*, National Academy Press, Washington, DC, 393 pp.

National Academy of Sciences, National Research Council, Commission on Life Sciences, Board on Environmental Studies and Toxicology, Safe Drinking Water Committee (1980b). "Toxicity of Selected Drinking Water Contaminants". In: *Drinking Water and Health Volume 3*, National Academy Press, Washington, DC, 193-200.

National Academy of Sciences, National Research Council, Commission on Life Sciences, Board on Environmental Studies and Toxicology, Safe Drinking Water Committee (1982). "Toxicity of Selected Inorganic Contaminants in Drinking Water." in: *Drinking Water and Health Volume 4*, National Academy Press, Washington, DC, 174-178.

National Academy of Sciences, National Research Council, Commission on Life Sciences, Board on Environmental Studies and Toxicology, Safe Drinking Water Committee, Subcommittee on Disinfectants and Disinfectant By-products (1987). *Drinking Water and Health, Volume 7, Disinfectants and Disinfectant By-products*, National Academy Press, Washington, DC, 207 p.

National Cancer Institute, Washington, D.C. *Report on the Carcinogenesis Bioassay of Chloroform*. NTIS PB264018/AS (1976).

Neely, J.W. and Isacoff, E.G. (1982) *Carbonaceous Adsorbents for the Treatment of Ground and Surface Waters*. Marcel Dekker, Inc., New York, NY, 228 p.

- Noack, M.G. and Doerr, R.L. (1978). "Reactions of Chlorine, Chlorine Dioxide and Mixtures Thereof with Humic Acid: An Interim Report." in: *Water Chlorination: Environmental Impact and Health Effects*, Vol. 2, R.L. Jolley, H. Gorchev, and D.H. Hamilton, eds., Ann Arbor Science, Ann Arbor, Michigan, 47-58.
- Noss, C.J., Dennis, W.H. and Olivieri, V.P. (1983). "Reactivity of Chlorine Dioxide with Nucleic Acids and Proteins" in: *Water Chlorination: Environmental Impact and Health Effects, Volume 4*, Robert L. Jolley, William A. Brungs, Joseph A. Cotruvo, Robert B. Cumming, Jack S. Mattice and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 1077-1086.
- Novak, J. "Analysis of Organic Constituents Present in Drinking Water" *Journal of Chromatography* 76 (1): 45-50 (1973).
- Novatek. (1990) "The Determination of Low Level Chlorite Ion and Chlorate Ion." Method C9-01001. Novatek, Miami, OH. .
- Oehler, V.K.E. and Schuttler, A. "Entfernung von Chlorit durch Wasseraufbereitungs-Verfahren." *Z. Wasser-Abwasser-Forsch*, 19: 98-102 (1986).
- Oehler, V.K.E, Kohler, A. and Schuttler, A. "Formation of Chlorite During Raw Water Treatment with Chlorine Dioxide and the Removal of Chlorite by Water Treatment." *Water Supply*, vol.4:127-139 (1986).
- Olivieri, V. P. (1985). "Human Pathogens, Disinfection, and Chlorine." in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 5-18.
- Olivieri, V.P., Hauchman, F.S., Noss, C.I. and Vasl, R. (1985). "Mode of Action of Chlorine Dioxide on Selected Viruses" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 619-634.

- Ondrous, M.G. and Gordon, G. "The Oxidation of Hexaquoiron (II) by Chldorine (III) in Aqueous Solution" *Inorganic Chemistry*, 11(5): 985-989 (1972).
- Orr, M.P. "Reduction of Odors Associated with Chlorine Dioxide Applications to Drinking Water." M.S. Thesis. Virginia Polytechnic Institute and State University; Blacksburg, VA (1990).
- Oxenford, J.L. and Lykins, B.W. "Conference Summary: Practical Aspects of the Design and Use of GAC." *Journal of the American Water Works Association*, 83(1): (1991).
- Palin, A.T. "The Determination of Free and Combined Chlorine in Water by the Use of Diethyl -p-phenylene Diamine." *Journal of the American Water Works Association*, 49: 873-880 (1957).
- Palin, A.T. "Analytical Control of Water Disinfection with Special Reference to Differential CDP Methods for Chlorine, Chlorine Dioxide, Bromine, Iodine and Ozone". *Journal of the Institute of Water Engineers*, 28: 139-154 (1974).
- Palin, A.T. "Methods for the Determination, in Water, of Free and Combined Available Chlorine, Chlorine Dioxide and Chlorite, Bromine, Iodine, and Ozone Using Diethyl-p-Phenylene Diamine (DPD)." *Journal of the Institute of Water Engineers*, 21: 537-47 (1976).
- Palin, A.T. (1983). *Chemistry and Control of Modern Chlorination*, Second Edition Lamotte Chemical Product Company, Maryland, USA.
- Pereira, M.A., Lin, L.H.C., Lippitt, H. M. and Herren, S.L., "Trihalomethanes as Initiators and Promoters of Carcinogenesis." *Environmental Health Perspectives*, 46: 151-156 (1982).
- Pfaff, J.D. and Brockhoff, C.A. "Determining Inorganic Disinfection By-Products by Ion Chromatography." *Journal of the American Water Works Association*, 82(4): 192-195 (1990).
- Pfaff, J.D., Brockhoff, C.A. and O'Dell J.W. "Test Method: The Determination of Inorganic Anions in Water by Ion Chromatography-Method 300.0 A & B." United States Environmental Protection Agency Environmental Monitoring and Systems Laboratory, Cincinnati, OH (1989).

- Pirbazare, M. and McGuirte M.J. "Oxidation of Taste and Odor Compounds" *Proceedings of the American Water Works Association Annual Conference*. Dallas, TX (1984) pp. 1587-1609.
- Pontius, F.W. ed. (1990) *Water Quality and Treatment. Fourth Edition*. AWWA/McGraw-Hill, Inc., New York, New York, 1194 p.
- Ram, N.M. and Malley, J.P. "Chlorine Residual Monitoring in the Presence of N-Organic Compounds." *Journal of the American Water Works Association*, 76.(9): 74-81 (1984).
- Rav-Acha, C. "The Reactions of Chlorine Dioxide with Aquatic Organic Materials and Their Health Effects." *Water Res.*, 18(11): 1329-1341 (1984).
- Rav-Acha, C., Serri, A., (Goldstein) Chosen, E. and Limoni, B. "Disinfection of Drinking Water Rich in Bromide with Chlorine and Chlorine Dioxide, While Minimizing the Formation of Undesirable By-Products." *Water Science and Technology*, 17: 611-621 (1984).
- Reckhow, D.A. and Singer, P.C. "Chlorination By-Products in Drinking Waters: From Formation Potentials to Finished Water Concentrations." *Journal of the American Water Works Association*, 80(4): 174-181 (1990).
- Regli, S. "United States Environmental Protection Agency Status Report on Development of Regulations for Disinfectants and Disinfection By-Products", Washington, DC, June, 1991.
- Rester, D. Technical Services Manager, American Norit Company Inc.; Marshall, Texas; Personal Communication, 1993.
- Ridenour, G. M. and Armbruster, E. "Bactericidal Properties of Chlorine Dioxide." *Journal of the American Water Works Association*, 39: 561 (1947).
- Ridenour, G. M. and Ingols, R.S. "Bactericidal Effects of Chlorine Dioxide." *Journal of the American Water Works Association*, 41: 537-550 (1949).
- Ridenour, G. M., Ingols, R.S. and Armbruster, E. H. "Sporicidal Properties of Chlorine Dioxide." *Water Works Sewage*, 96: 276 (1949).
- Rook, J. J. "Formation of Haloforms During Chlorination of Natural Waters." *Water Treatment and Examination*, 23: 234-243 (1974).

- Rook, J. J. "Haloforms in Drinking Water" *Journal of the American Water Works Association*, 68: 168-172 (1976).
- Rosen, J.B. "Kinetics of a Fixed Bed System for Solid Diffusion into Spherical Particles." *The Journal of Chemical Physics*, 20(3): 387-394 (1951).
- Rosenblatt, D.H. (1978) "Chlorine Dioxide: Chemical and Physical Properties." In *Ozone/Chlorine Dioxide Oxidation Products of Organic Materials*. Rice, R.G., and Cotruvo, J.A., Eds. Ozone Press: Cleveland, OH, pp. 332-43.
- Ruzicka, J. and Christian, G. "Flow Injection Analysis and Chromatography: Twins or Siblings?" *Analyst*, 115: 475-486 (1990).
- Seidel, A., Reschke, S., Friedrich, S. and Gelbin, D. " Equilibrium Adsorption of Two-Component Organic Solutes from Aqueous Solutions on Activated Carbon." *Absorption Science and Technology*, 3: 189-199 (1986)
- Shpigun, O. A. and Zolotov, Yu. A. (1988). *Ion Chromatography in Water Analysis*. John Wiley and Sons, New York, New York, 188 p.
- Singer, P.C. (1989). *Complying with Trihalomethane Reduction Requirements in Water Treatment Facilities*. Noyes Data Corporation, Park Ridge, New Jersey, 285 p.
- Singer, P.C. and O'Neil, W.K. "Technical Note: The Formation of Chlorate from the Reaction of Chlorine and Chlorite in Dilute Aqueous Solution." *Journal of the American Water Works Association*, 79(11): 75-76 (1987).
- Sjodin, A. and Sundqvist, U. "Advances in Flow Injection Analysis." *American Laboratory*, 21(1): 63-67. (1989).
- Small, H. (1989) *Ion Chromatography*. Plenum Press, New York, NY, 276 p.
- Smith, J. Renner, R., Heg, B. and Bende, J.(1991). *Upgrading Existing or Designing New Drinking Water Treatment Facilities*. Noyes Data Corp. Park Ridge, New Jersey, 384 p.
- Snoeyink, V.L. and Jenkins, D. (1980). *Water Chemistry*. John Wiley and Sons, New York, New York, 463 p.

- Snoeyink, V.L., McCreary, J.J. and Murin, C.J. "Activated Carbon Adsorption of Trace Organic Compounds." Environmental Protection Agency-600/2-77-223 (1977).
- Sontheimer, H., Crittenden, J. C. and Summers, S. (with contribution of Hubele, Roberts, Snoeyink and Zimmer) (1988). *Activated Carbon for Water Treatment, Second Edition in English*. DVGW-Faorschungsstelle Engler-Bunte-Institut Universitat Karlsruhe, Federal Republic of Germany, 722 p.
- Sorrento, L. J., (1993) *Activated Carbon Treatment* Ceca Division of ATOCHEM, Inc, Pryor, Oklahoma.
- Steinbergs, C.Z., "Removal of By-products of Chlorine and Chlorine Dioxide at a Hemodialysis Center." *Journal of the American Water Works Association*, 78(6): 94-98 (1986).
- Stevens, A.A., "Reaction Products of Chlorine Dioxide" *Environmental Health Perspectives*, 46: 101-110 (1982).
- Suh, D.H., Abdel-Rahman, M.S. and Bull, R.J. "Effect of Chlorine Dioxide and Its Metabolites in Drinking Water of Fetal Development in Rats." *Journal of Applied Toxicology*, 3:75-169 (1983).
- Summers, R.S. and Roberts, P.V. "Simulation of DOC Removal in Activated Carbon Beds." *Journal of Environmental Engineering*, 110: 73-92 (1984).
- Sussman, S. and Rauh, J.E. (1978) "Use of Chlorine Dioxide in Water and Wastewater." in: *Ozone/Chlorine Dioxide Oxidation Products of Organic Materials*. Rice, R.G., and Cotruvo, J.A., eds. Ozone Press, Cleveland, OH, pp. 344-55
- Symons, J., Stevens, A., Clark, R., Geldreich, E., Love, O. and DeMarco, J. "Treatment Techniques for Controlling Trihalomethanes in Drinking Water." *USEPA-600/2-81-156* (1981).
- Synan, J.F., MacMahon, J. D. and Vincent, G. P. "Chlorine Dioxide - A Development in Treatment of Potable Water" *Water Works and Sewer*, 91: 423-426. (1944).

- Synan, J.F., MacMahon, J. D. and Vincent, G. P. "A Variety of Water Problems Solved by Chlorine Dioxide Treatment." *Journal of the American Water Works Association* 37: 869-875 (1945).
- Tate, C.H. and Arnold, K.F. "Health and Aesthetic Aspects of Water Quality." *Journal of the American Water Works Association*, (1990)
- Taylor, D. T. and Pfohl, R.J. (1985). "Effects of Chlorine Dioxide on Neurobehavioral Development of Rats" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 355-364.
- Themelis, D.G., Wood, D. W. and Gordon, G. "Determination of Low Concentrations of Chlorite and Chlorate Ions by Using a Flow-Injection System." *Analytica Chimica Acta*, 225: 437-441 (1989).
- Thomas, Bob. Project Manager, Water Applications, American Norit Company, Inc., Atlanta, Georgia, Personal Communication, 1993.
- Thompson, A.L., Matthew, N.O., Mittl, A.J. and Owen, D.M. "Chlorite and Chlorate Residuals in the Distribution System." *Proceedings, Water Quality Technology Conference: Advances in Water Analysis and Treatment*, November, 13-17,1988, St. Louis, American Water Works Association, Denver, CO. pp. 305-326.
- Trihalomethanes in Drinking Water (Sampling, Analysis, Monitoring and Compliance). USEPA 570/9-83-002. USEPA (1983).
- Troyan, J.S. and Hansen, S.P. eds. (1989). *Treatment of Microbial Contaminants in Potable Water Supplies*. Noyes Data Corporation, Park Ridge, New Jersey.
- Trussell, R.R. and Umphres, M.D. "The Formation of Trihalomethanes" *Journal of the American Water Works Association*, 70: 604-612 (1978).
- Tuthill, R. W., Giusti, R.A., Moore, G.S. and Calabrese, E. "Health Effects Among Newborns After Prenatal Exposure to ClO₂-Disinfected Drinking Water." *Environmental Health Perspectives*, 46: 39-45 (1982).

- United States Environmental Protection Agency. "Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater." J. Longbottom and J. Lichtenberg, editors. *EPA-600/4-82-057*, July 1982. pp. A1-A4.
- United States Environmental Protection Agency. "An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies." G.W. Miller, R.G. Rice, C.M. Robson, W. Kuhn, and H. Wolf *EPA-600/2-78-147*, August 1978 . pp. 179-290.
- United States Environmental Protection Agency. "Interim Treatment Guide for Controlling Organic Contamination in Drinking Water Using GAC." James M. Symons, editor. January 1978.
- Van Vliet, B.M., Weber, W.J. and Itozumi, H., "Modeling and Prediction of Specific Compound Adsorption by Activated Carbon and Synthetic Adsorbents." *Water Research*, 14(12): 1719-1728 (1979).
- Varma, M.M., Torrence, G., Chawla, R.C. and Okrend, H. (1985). "Relative Disinfection Potentials of Chlorine and Chlorine Dioxide in Drinking Water." in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 635-650.
- Vogt, C. and Regli, S. "Controlling Trihalomethanes While Attaining Disinfection." *Journal of the American Water Works Association*, 73(1): 33-40 (1981).
- Voudrais, E.A., Larson, R.A. and Snoeyink, V.L. "Effects of Activated Carbon on the Reactions of Free Chlorine with Phenols." *Environmental Science and Technology*. 19(5): 441-449 (1985).
- Voudrais, E.A., Larson, R.A. and Snoeyink, V.L. "Importance of Surface Free Radicals in the Reactivity of Granular Activated Carbon Under Water Treatment Conditions." *Carbon*, 25(4): 503-515 (1987).
- Voudrais, E.A., Larson, R.A. and Snoeyink, V.L. "Effects of Activated Carbon on the Reactions of Combined Chlorine with Phenols." *Water Research*, 19(7): 909-915 (1984).

- Vondraiss, E.A., Dielmann, L. M., Snoeyink, V.L., Larson, R. A., McCreary, J.J. and Chen, A.S.C. "Reactions of Chlorite with Activated Carbon and with Vanillic Acid and Indan Adsorbed on Activated Carbon." *Water Research*, 17(9): 1107-1114 (1983).
- Walker, G.S., Lee, F.P. and Aieta, E.M. "Chlorine Dioxide for Taste-and-Odor Control." *Journal of the American Water Works Association*, 79(9): 107-133 (1987).
- Watts, C.D., Crathorne, B., Fielding, M. and Killops, S.D. "Nonvolatile Organic Compounds in Treated Waters" *Environmental Health Perspectives* 46: 87-89 (1982).
- Werdehoff, K.S. and Singer, P.C. "Chlorine Dioxide Effects on THMFP, TOXFP, and the Formation of Inorganic By-Products." *Journal of the American Water Works Association*, 79(9): 107-133 (1987).
- White, G.C. (chairman) Disinfection: Committee Report. *Journal of the American Water Works Association*, 70(4): 219-222 (1978).
- White, G.C., (1986). *Handbook of Chlorination, Second Edition* Van Nostrand Reinhold Co., New York, NY, 1070 p.
- Wolfe, R.L., Ward, N.R. and Olson, V.B.H. "Interference in the Bacterial Properties of Inorganic Chloramines by Organic Nitrogen Compounds. " *Environmental Science and Technology*, 19 (12): 1192-1195 (1985).
- Wood, D.W. "Determination of Disinfectant Residuals in Chlorine Dioxide Treated Water Using Flow Injection Analysis." Ph.D. Thesis. Miami University; Miami, OH (1990).
- Yehaskel, A. (1978). *Activated Carbon Manufacture and Regulation*. Noyes Data Corporation, Park Ridge, New Jersey, 329 p.
- Yen, C. and Singer P.C. "Competitive Adsorption of Phenols on Activated Carbons." *Journal of Environmental Engineers*, 110(5): 976-989 (1984).
- Zavelata, J. O., "Chlorine Dioxide Risk Assessment for Drinking Water," pp. 53-69 in: *Chlorine Dioxide: Drinking Water Issues*, 2nd International Symposium, Houston, Texas; May 7-8, 1992.

Zika, R.G., Moore, C.A., Gidel, L.T. and Cooper, D. G. (1985). "Sunlight-Induced Photodecomposition of Chlorine Dioxide" in: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 5*, Robert L. Jolley, Richard J. Bull, William P. Davis, Sidney Katz, Morris H. Roberts, Jr. and Vivian A. Jacobs, eds., Lewis Publishers, Inc., Chelsea, Michigan, 1041-1054.

Zoeteman, B.C., Hrubec, J., de Greef, E. and Kiil, H.J. "Mutagenic Activity Associated With By-Products of Drinking Water Disinfection by Chlorine, Chlorine Dioxide, Ozone, and UV-Irradiation." *Environmental Health Perspectives*, 46: 196-206 (1982).

APPENDIX A
Raw Data From Experiments

Table A1. Raw data from experiment number one, a jar test with Ceca 20 B at a concentration of 20 mg/L and pH 7. Ethylene diamine was also added due to operator error, invalidating the results for comparison with other carbons.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)*	Cl ⁻ (mg/L)**
0	2.25	0
0.25	1.80	0.12
0.5	1.18	0.13
0.75	1.49	0.13
1	1.47	0.12
1.25	1.18	0.34
1.5	1.27	0.38
1.75	1.22	0.47
2	1.25	0.54
4	1.21	0.65
8	1.07	0.82
12	1.02	0.89
24	1.00	0.98

* mg/L ClO₂⁻ as ClO₂⁻ throughout this Appendix.

** mg/L Cl⁻ as Cl⁻ throughout this Appendix.

Table A2. Raw data from experiment number two, a jar test with Ceca 20 B at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₂ ⁻ REMOVED (PERCENT)
0	1.13	0	0
0.25	1.05	0	6.7
0.5	1.04	0	8.0
0.75	0.85	0	24.6
1	0.68	0	39.4
1.25	0.47	0.18	58.4
1.5	0.23	0.26	79
2	0.23	0.89	79
4	0.23	0.93	80
8	0.22	0.94	81
12	0.21	0.92	81
24	0.19	0.94	83

Table A3. Raw data from experiment number three, a jar test with Ceca 20 B at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₂ ⁻ REMOVED (PERCENT)
0	1.98	0.22	0
0.25	1.53	0.40	22.7
0.5	1.20	0.33	39.3
0.75	1.04	0.43	47.5
1	0.92	0.47	53.5
1.25	0.80	0.52	59.6
1.5	0.72	0.57	63.6
1.75	0.65	0.66	67.2
2	0.57	0.58	71.2
4	0.35	0.66	82.2
8	0.21	0.72	89.4
12	0.00	0.73	100
24	0.00	0.86	100

Table A4. Raw data from experiment number four, a jar test with Ceca 20 B at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₂ REMOVED (PERCENT)
0	1.98	0.03	0
0.25	1.53	0.4	2.9
0.5	1.20	0.33	9.8
0.75	1.04	0.43	19.3
1	0.92	0.47	22.2
1.25	0.80	0.52	25.9
1.5	0.72	0.57	28.5
1.75	0.65	0.66	29.2
2	0.57	0.67	31.5
4	0.35	0.68	38.1
8	0.21	0.72	40.2
12	0	0.73	47.5
24	0	0.86	53.1

Table A5. Raw data from experiment number three, a jar test with Nuchar SA at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₂ ⁻ REMOVED (PERCENT)
0	1.98	0.03	0
0.25	1.53	0.40	2.88
0.5	1.20	0.33	9.76
0.75	1.04	0.43	19.3
1	0.92	0.47	22.2
1.25	0.80	0.52	25.9
1.5	0.72	0.57	28.5
1.75	0.65	0.66	29.2
2	0.57	0.67	31.5
4	0.35	0.68	38.3
8	0.21	0.72	40.2
12	0	0.73	47.5
24	0	0.86	53.1

Table A6. Raw data from experiment number five control jar with no PAC added, just chlorite and Milli-Q water at pH 7.

TIME (HOURS)	ClO ₂ (mg/L)	Cl ⁻ (mg/L)
0	1.9	0.13
0.25	1.76	0.06
0.5	1.77	0.00
0.75	1.72	0.22
1	1.74	0.05
1.5	1.75	0.05
2	1.72	0.06
4	1.68	0.04
7	1.70	0.06
12	1.67	0.06
24	1.68	0.21

Table A7. Raw data from experiment number five, a jar test with Ceca 20 C at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)
0	2.23	0.14
0.25	1.52	0.35
0.5	1.14	0.42
0.75	0.95	0.49
1	0.80	0.48
1.5	0.57	0.57
2	0.46	0.58
4	0.25	0.68
7	0.12	0.76
12	0.04	0.78
24	0	0.77

Table A8. Raw data from experiment number five, a jar test with Calgon WPH at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)
0	2.05	0.12
0.25	1.76	0.06
0.5	0.95	0.44
0.75	0.81	0.52
1	0.59	0.55
1.5	0.4	0.62
2	0.29	0.66
4	0.17	1.02
7	0.06	1.01
12	0.00	1.11
24	0.00	1.26

Table A9. Raw data from experiment number five, a jar test with Calgon WPL at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)
0	2.04	0.12
0.25	1.31	0.52
0.5	0.86	0.75
0.75	0.69	0.62
1	0.57	0.64
1.5	0.44	0.68
2	0.32	0.65
4	0.17	0.86
7	0.06	0.75
12	0.03	0.76
24	0.00	0.86

Table A10. Raw data from experiment number five, a jar test with Darco HDB at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)
0	1.92	0.12
0.25	1.86	0.12
0.5	1.76	0.15
0.75	1.71	0.19
1	1.58	0.24
1.5	1.43	1.12
2	1.31	1.12
4	1.23	0.80
7	1.10	1.11
12	0.95	0.79
24	0.85	0.55

Table A11. Raw data from experiment number six a jar test with Nuchar Aqua S at a concentration of 20 mg/L and pH 9.5. (NOTE error in pH).

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)
0	1.82	0.07
0.25	1.83	0.08
0.5	1.70	0.09
0.75	1.75	0.10
1	1.73	0.13
1.5	1.76	0.11
2	1.75	0.09
4	1.75	0.08
7	1.75	0.10
12	1.76	0.08
24	1.75	0.09

Table A12. Raw data from experiment number six, a jar test with Darco HDB at a concentration of 20 mg/L and pH 9.5. (NOTE error in pH).

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)
0	1.82	0.07
0.25	1.74	0.25
0.5	1.80	0.29
0.75	1.74	0.20
1	1.72	0.20
1.5	1.76	0.18
2	1.76	0.18
4	1.74	0.19
7	1.77	0.35
12	1.75	0.29
24	1.76	0.31

Table A13. Raw data from experiment number seven, a jar test with Nuchar Aqua S at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)
0	1.82	0.13
0.25	1.04	0.23
0.5	0.87	0.40
0.75	0.61	0.49
1	0.52	0.86
1.5	0.43	0.81
2	0.37	0.68
4	0.31	0.77
8	0.05	1.02
12	0.00	0.69
24	0.00	0.71

Table A14. Raw data from experiment number seven, a jar test with Darco HDB at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ (mg/L)	Cl ⁻ (mg/L)
0	1.82	0.13
0.25	1.67	0.11
0.5	1.61	0.14
0.75	1.53	0.18
1	1.48	0.20
1.5	1.36	0.23
2	1.34	0.27
4	1.23	0.27
8	0.97	0.31
12	0.84	0.39
24	0.67	0.43

Table A15. Raw data from a control jar for experiment number eight, a jar test at pH 7 with only chlorite and chlorine added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	0.71	2.36	0.32
1	1.09	2.33	0.08
2	0.95	2.30	0.35
4	0.51	3.18	0.23
8	0.98	1.95	0.15
12	1.01	1.89	0.13
24	1.04	1.84	0.13

Table A16. Raw data from experiment number eight, a jar test at pH 7 with Ceca 20 B at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	1.06	2.03	0.46
0.25	0.56	2.27	0.37
0.5	0.46	2.23	0.29
0.75	0.40	2.21	0.04
1	0.27	2.42	0.09
1.25	0.30	2.47	0.30
1.5	0.24	2.42	0.26
1.75	0.23	2.56	0.13
2	0.22	2.42	0.25
4	0.13	2.54	0.27
8	0.06	2.58	0.29
12	0.00	2.60	0.18
24	0.00	2.64	0.07

Table A17. Raw data from experiment number eight, a jar test at pH 7 with Nuchar SA at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ (mg/L)
0	1.01	1.99	0.51
0.25	0.74	3.02	0.08
0.5	0.57	2.12	0.09
0.75	0.57	2.01	0.19
1	0.62	1.94	0.26
1.25	0.61	2.42	0.29
1.5	0.69	2.44	0.29
1.75	0.66	2.43	0.29
2	0.61	2.73	0.32
4	0.59	2.48	0.28
8	0.57	2.53	0.12
12	0.55	2.61	0.28
24	0.54	2.70	0.29

Table A18. Raw data from experiment number nine, a jar test over a 96 hour period at pH 7 with both chlorite and chlorine added, but with no stirring occurring due to operator error.

Jar Number	Contents (in water)	Time (hours)	mg/L chlorite ion	mg/L chlorine	mg/L chlorate ion
1	chlorine only	0	0	1.03	0.03
1	chlorine only	24	0	1.03	0.08
1	chlorine only	48	0	0.98	0.08
1	chlorine only	72	0	1.06	0.05
1	chlorine only	96	0	1.04	0.09
2	chlorite only	0	2.01	0.15	0.06
2	chlorite only	24	1.92	0.22	0.96
2	chlorite only	48	1.95	0.10	0.03
2	chlorite only	72	1.97	0.13	0.96
2	chlorite only	96	2.00	0.15	1.13
3	chlorine & chlorite	0	2.03	1.05	0.06
3	chlorine & chlorite	24	1.77	0.95	0.15
3	chlorine & chlorite	48	1.71	0.94	0.19
3	chlorine & chlorite	72	1.71	1.04	0.26
3	chlorine & chlorite	96	1.65	1.09	0.26
4	Ceca 20 B	0	2.02	1.03	0.07
4	Ceca 20 B	24	1.16	0.72	0.14
4	Ceca 20 B	48	0.98	0.52	0.04
4	Ceca 20 B	72	0.21	0.78	0.13
4	Ceca 20 B	96	0.07	0.80	0.05
5	Nuchar SA	0	2.01	1.02	0.06
5	Nuchar SA	24	0.50	0.64	0.13
5	Nuchar SA	48	0.37	0.78	0.13
5	Nuchar SA	72	0.38	0.61	0.05
5	Nuchar SA	96	0.12	0.49	0.12

Table A19. Raw data from experiment number ten, a jar test over a 72 hour period at pH 7 with Nuchar SA at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ (mg/L)
0	2.33	2.15	0.20
1	1.50	3.18	0.21
3	1.34	3.28	0.19
4	1.23	3.27	0.19
8	1.22	3.47	0.39
24	1.12	3.48	0.22
48	1.04	3.44	0.23
72	0.94	3.50	0.21

Table A20. Raw data from experiment number ten, a jar test over a 72 hour period at pH 7 with Ceca 20 B at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.33	2.37	0.23
1	1.05	3.15	0.55
3	0.60	4.16	0.68
4	0.49	3.73	0.70
8	0.33	3.52	0.71
24	0.09	3.97	0.72
48	0.00	3.77	0.78
72	0.00	3.99	0.77

Table A21. Raw data from experiment number ten, a jar test over a 72 hour period at pH 7 with both chlorite and chlorine added. This data is from a control jar with only chlorine and chlorite.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.35	2.16	0.21
1	2.28	2.22	0.24
3	2.30	2.14	0.26
4	2.36	2.06	0.22
8	2.19	2.14	1.02
24	2.01	2.21	0.74
48	1.67	2.31	0.73
72	1.41	2.31	0.99

Table A22. Raw data from experiment number ten, a jar test over a 72 hour period at pH 7 with both chlorite and chlorine added. This data is from a control jar with only chlorite.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.54	0.80	0.00
1	2.48	0.61	0.00
3	2.41	1.34	0.00
4	2.34	0.81	0.01
8	2.35	0.80	0.00
24	2.45	0.14	0.00
48	2.47	0.33	0.02
72	2.50	0.57	0.01

Table A23. Raw data from experiment number ten, a jar test over a 72 hour period at pH 7 with both chlorite and chlorine added. This data is from a control jar with only chlorine.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	0.00	2.12	0.2
1	1.23	2.13	0.18
3	0.00	2.24	0.21
4	0.00	2.06	0.20
8	0.00	2.19	0.20
24	0.00	2.10	0.19
48	0.00	2.55	0.16
72	0.00	2.70	0.21

Table A24. Raw data from experiment number eleven, a jar test over a 48 hour period at pH 7 with both chlorite and chlorine added. This data is from a control jar with only chlorite and chlorine.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	1.79	2.57	0.80
0.25	1.73	2.47	0.81
0.5	1.60	2.40	0.78
1	1.55	2.75	0.82
4	1.62	2.84	0.82
8	1.33	2.52	0.84
24	1.61	2.56	0.78
48	1.58	2.68	0.85

Table A25. Raw data from experiment number eleven, a jar test over a 48 hour period at pH 7 with Acticarbene L2S and both chlorine and chlorite added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	1.62	2.63	0.60
0.25	1.29	2.82	0.63
0.50	1.18	3.41	0.65
1	1.05	2.85	0.61
2	1.01	3.16	0.71
4	0.94	3.18	0.74
8	0.75	3.26	0.74
12	0.66	3.29	0.73
24	0.19	3.46	0.76
48	0.19	3.46	0.79

Table A26. Raw data from experiment number eleven, a jar test over a 24 hour period at pH 7 with Husky Brand and both chlorine and chlorite added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	1.79	2.57	0.68
0.25	1.25	2.76	0.69
0.5	1.15	3.04	0.69
1	1.15	2.74	0.69
2	1.09	2.76	0.70
4	1.07	2.87	0.72
8	1.06	2.81	0.71
12	1.06	2.95	0.72
24	1.03	2.90	0.72
48	1.01	3.04	0.70

Table A27. Raw data from experiment number eleven, a jar test over a 48 hour period at pH 7. This data is from a control jar with only Husky Brand PAC and Milli-Q water present.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	0.00	0.00	0.00
1	0.00	0.00	0.00
3	0.00	0.00	0.00
4	0.00	0.00	0.00
8	0.00	0.00	0.00
24	0.00	0.00	0.00
48	0.00	0.00	0.00
72	0.00	0.00	0.00

Table A28. Raw data from experiment number twelve, a jar test at pH 7 with Acticarbne L2S at a concentration of 20 mg/L, with both chlorite and chlorine added. This test took a large number of samples prior to the one hour point to investigate the initial chlorite reduction curve.

TIME (HOURS)	ClO_2^- (mg/L)	Cl^- (mg/L)	ClO_3^- (mg/L)
0	2.4	2.08	0
0.08	1.97	1.97	0.46
0.17	1.93	2.31	0.51
0.25	1.79	2.19	0.51
0.33	1.75	2.20	0.51
0.42	1.67	2.86	0.51
0.50	1.60	2.26	0.50
0.75	1.5	2.39	0.51
1.0	1.4	2.38	0.52
1.25	1.32	2.64	0.53
1.5	1.28	2.51	0.51
2	1.25	2.68	0.52
2.5	1.19	2.71	0.53
3	1.18	2.59	0.52
3.5	1.16	2.57	0.53
4	1.13	2.64	0.53
20	0.95	2.80	0.54

Table A29. Raw data from experiment number thirteen, a jar test with Darco S-51 at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)
0	1.93	0.25
0.5	1.21	0.92
1.0	0.95	0.95
1.5	0.84	0.95
2.0	0.74	0.91
4.0	0.54	1.00
6.5	0.42	1.00
10	0.34	1.15
23	0.19	1.23
24	0.15	1.26

Table A30. Raw data from experiment number thirteen, a jar test with Darco HDB at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ (mg/L)	Cl ⁻ (mg/L)
0	1.97	0.45
0.5	1.29	0.67
1.0	1.08	0.70
1.5	0.98	0.75
2.0	0.92	0.72
4.0	0.70	0.82
6.5	0.62	0.91
10	0.44	1.00
23	0.23	1.10

Table A31. Raw data from experiment number thirteen, a jar test with Darco KB-B at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)
0	1.95	0.45
0.5	1.65	0.54
1.0	1.51	0.59
1.5	1.50	0.64
2.0	1.48	0.65
4.0	1.45	0.67
6.5	1.35	0.63
10	1.31	0.69
23	1.20	0.80

Table A32. Raw data from experiment number thirteen, a jar test with Darco G-60 at a concentration of 20 mg/L and pH 7.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)
0	1.92	0.37
0.5	1.07	0.67
1.0	0.83	0.91
1.5	0.73	0.92
2.0	0.63	0.96
4.0	0.49	1.07
6.5	0.35	1.11
10	0.26	1.17
23	0.00	1.32

Table A33. Raw data from experiment number fourteen, a jar test over a 24 hour period at pH 7 with Darco S-51 at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.36	2.09	0.21
0.25	1.49	2.77	0.20
0.5	1.24	2.99	0.24
1	0.93	3.17	0.27
2	0.71	3.58	0.27
4	0.51	3.76	0.34
6	0.44	3.75	0.34
9	0.38	3.79	0.36
10.75	0.33	3.82	0.35
24	0.21	3.90	0.35

Table A34. Raw data from experiment number fourteen, a jar test over a 24 hour period at pH 7 with Darco HDB at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.39	2.01	0.22
0.25	1.37	3.04	0.20
0.5	1.13	3.28	0.24
1	0.94	3.40	0.28
2	0.86	3.58	0.30
4	0.76	3.70	0.31
6	0.70	3.71	0.30
9	0.65	3.65	0.30
10.75	0.62	3.61	0.29
24	0.49	3.76	0.29

Table A35. Raw data from experiment number fourteen, a jar test over a 24 hour period at pH 7 with Darco KB-B at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.39	2.11	0.23
0.25	1.71	2.80	0.24
0.5	1.59	2.81	0.22
1	1.48	2.91	0.22
2	1.41	3.14	0.23
4	1.30	3.29	0.24
6	1.30	3.35	0.23
9	1.22	3.35	0.23
10.75	1.18	3.59	0.23
24	1.14	3.82	0.25

Table A36. Raw data from experiment number fourteen, a jar test over a 24 hour period at pH 7 with Darco G-60 at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.39	2.14	0.22
0.25	1.37	2.78	0.23
0.5	1.13	3.00	0.26
1	0.82	3.35	0.30
2	0.59	3.54	0.34
4	0.37	3.69	0.38
6	0.27	3.81	0.40
9	0.15	4.11	0.41
10.75	0.12	3.89	0.41
24	0.00	4.11	0.44

Table A37. Raw data from experiment number fifteen, a jar test over a 24 hour period at pH 7 with both chlorite and chlorine added. This data is from a control jar containing only chlorine and chlorite.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.05	2.20	0.33
2	2.17	2.15	0.33
5	2.05	2.35	0.29
8	2.15	2.14	0.32
11	1.90	2.17	0.35
22	1.90	2.28	0.42
24	1.96	2.17	0.41

Table A38. Raw data from experiment number fifteen, a jar test over a 24 hour period at pH 7 with Nuchar Aqua S at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.10	2.13	0.32
0.25	1.50	2.77	0.27
0.5	1.26	2.82	0.29
1	1.10	2.99	0.27
1.5	0.95	3.02	0.31
2	0.95	3.09	0.28
5	0.75	3.31	0.32
8	0.68	3.49	0.35
10	0.60	3.43	0.37
11	0.57	3.76	0.32
22	0.48	3.53	0.34
24	0.51	3.41	0.32

Table A39. Raw data from experiment number fifteen, a jar test over a 24 hour period at pH 7 with Calgon WPL at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ (mg/L)
0	2.08	2.23	0.26
0.25	1.27	2.89	0.25
0.5	1.07	3.11	0.27
1	0.90	3.18	0.31
1.5	0.78	3.32	0.37
2	0.70	3.31	0.42
5	0.49	3.41	0.44
8	0.43	3.47	0.42
10	0.41	3.66	0.41
11	0.34	3.44	0.39
22	0.28	3.59	0.41
24	0.28	3.69	0.41

Table A40. Raw data from experiment number fifteen, a jar test over a 24 hour period at pH 7 with Calgon WPH at a concentration of 20 mg/L, with both chlorite and chlorine added.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.06	2.57	0.34
0.25	1.24	3.07	0.29
0.5	0.94	3.23	0.30
1	0.81	3.68	0.32
1.5	0.72	3.68	0.38
2	0.68	3.61	0.39
5	0.56	3.91	0.42
8	0.44	3.71	0.43
10	0.39	3.86	0.40
11	0.36	4.03	0.39
22	0.29	3.81	0.41
24	0.28	3.87	0.45

Table A41. Raw data from experiment number sixteen, a jar test over a 24 hour period at pH 7 with Ceca 20 B at a concentration of 20 mg/L, with both chlorite and chlorine added, in a replicate test for this PAC.

TIME (HOURS)	ClO ₂ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ (mg/L)
0	2.40	0.54	0.06
0.5	1.61	0.54	0.05
0.75	1.31	0.70	0.10
1	1.14	0.74	0.11
2	0.96	1.08	0.13
4	0.65	1.24	0.20
8	0.38	1.49	0.24
12	0.17	1.54	0.27
24	0.00	1.59	0.28

Table A42. Raw data from experiment number sixteen, a jar test over a 24 hour period at pH 7 with Ceca 20 B at a concentration of 20 mg/L, with both chlorite and chlorine added, in a replicate test for this PAC.

TIME (HOURS)	ClO ₂ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ (mg/L)
0	2.39	0.15	0.06
0.5	1.60	0.55	0.06
0.75	1.32	0.63	0.10
1	1.15	0.74	0.11
2	0.96	1.09	0.13
4	0.67	1.25	0.20
8	0.39	1.46	0.24
12	0.19	1.48	0.27
24	0.00	1.57	0.29

Table A43. Raw data from experiment number sixteen, a jar test over a 24 hour period at pH 7 with Ceca 20 B at a concentration of 20 mg/L, with both chlorite and chlorine added, in a replicate test for this PAC.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.41	0.19	0.05
0.5	1.53	0.61	0.08
0.75	1.29	0.57	0.09
1	1.11	0.65	0.14
2	0.93	0.97	0.15
4	0.63	1.26	0.21
8	0.34	1.48	0.26
12	0.16	1.53	0.27
24	0.00	1.61	0.28

Table A44. Raw data from experiment number sixteen, a jar test over a 24 hour period at pH 7 with Ceca 20 B at a concentration of 20 mg/L, with both chlorite and chlorine added, in a replicate test for this PAC. This data is from control jar number one, which contained no PAC.

TIME (HOURS)	ClO ₂ ⁻ (mg/L)	Cl ⁻ (mg/L)	ClO ₃ ⁻ (mg/L)
0	2.44	0.19	0.06
0.5	2.41	0.22	0.06
0.75	2.40	0.23	0.04
1	2.36	0.19	0.05
2	2.39	0.17	0.05
4	2.41	0.21	0.05
8	2.37	0.18	0.07
12	2.39	0.19	0.06
24	2.40	0.17	0.06

Table A45. Raw data from experiment number sixteen, a jar test over a 24 hour period at pH 7 with Ceca 20 B at a concentration of 20 mg/L, with both chlorite and chlorine added, in a replicate test for this PAC. This data is a sample of the type of data normally recorded, including peak height and centimeter measurements and their comparisons for each of the ions.

TEST NUMBER 16 CONDUCTED ON DECEMBER THE twenty first											
DECEMBER TWENTY FIRST											
WITH THREE JARS WITH CECA 20 B PAC PLUS CONTROL JAR PROTECTED FROM LIGHT.								CONTROL IN JAR 1 AT 24.2 DEGREES C AND AT pH 7.0			
JAR 1 CONTROL											
TIME (HRS)	BOTTLE	CM CLO2	PKHT	PPM CLO2 (CM)	PPM PKHT	CM CL	PKHT CL	PPM CL (CM)	PPM PKHT	CLO3 PKHT	PPM CLO3 (PKHT)
0	22	12.91	791072	2.44	2.36	1.52	124379	0.14	0.19	8345	0.06
0.5	23	12.77	791176	2.41	2.36	2.12	148853	0.19	0.22	8452	0.06
0.75	24	12.72	787309	2.40	2.35	2.15	151888	0.19	0.23	6118	0.04
1	25	12.48	782901	2.36	2.33	1.76	127419	0.16	0.19	7848	0.05
2	26	12.66	788564	2.39	2.35	1.68	111989	0.15	0.17	7667	0.05
4	28	12.74	789688	2.41	2.35	1.89	138529	0.17	0.21	7763	0.05
8	29	12.56	787045	2.37	2.35	1.59	116804	0.14	0.18	10251	0.07
12	22	12.65	788554	2.39	2.35	1.78	128431	0.16	0.19	8431	0.06
24	30	12.68	789651	2.40	2.35	1.68	111999	0.15	0.17	8944	0.06
0	32	13.33		2.52		2.64	176979	0.24	0.27	8521	0.06
0	32	13.32		2.52		2.28	158776	0.20	0.24	8130	0.05
0	32	13.47		2.55		2.14	150403	0.19	0.23	7795	0.05
0	33	13.26		2.51		2.44	166176	0.22	0.25	7996	0.05
0	33	13.21		2.50		2.58	174064	0.23	0.26	7887	0.05
0	33	13.72		2.59		2.78	178766	0.25	0.27	7857	0.05
0	32	13.12	827896	2.48		2.48	168085	0.22	0.25	7337	0.05
0	32	13.36	836520	2.53		2.61	169045	0.23	0.25		

Table A45 Continued.

JAR NUMBER TWO CECA 20 B				TEST NUMBER 16							
TIME	BOTTLE	CM CLO2	PKHT	PPM CLO2	PPM	CM CL	PKHT	PPM CL	PPM	CLO3	PPM CLO3
(HRS)				(CM)	PKHT	CL		(CM)	PKHT	PKHT	(PKHT)
0	1	12.71	787257	2.40	2.35	1.76	358104	111899	0.54	8553	0.06
0.5	2	8.52	564927	1.61	1.68	5.86	358104	0.52	0.54	8138	0.05
0.75	3	6.92	461341	1.31	1.37	7.66	463587	0.68	0.70	15333	0.10
1	5	6.02	411876	1.14	1.23	6.96	495444	0.72	0.74	16296	0.11
2	6	5.09	338452	0.96	1.01	6.66	719658	1.05	1.08	18982	0.13
4	7	3.44	234587	0.65	0.70	9.46	829788	1.20	1.24	29103	0.20
8	8	2.02	136751	0.38	0.41	9.81	995458	1.44	1.49	35607	0.24
12	9	0.91	68585	0.17	0.20	10.62	1026895	1.49	1.54	40353	0.27
24	11	0	0	0.00	0.00	14.24	1059828	1.58	1.59	42108	0.28
JAR NUMBER THREE CECA 20 B				TEST NO. 16							
TIME	BOTTLE	CM CLO2	PKHT	PPM CLO2	PPM	CM CL	PKHT	PPM CL	PPM	CLO3	PPM CLO3
(HRS)				(CM)	PKHT	CL		(CM)	PKHT	PKHT	(PKHT)
0 A		12.66		2.39		1.68	112347	0.15	0.17	8837	0.06
0.5 B		8.48		1.60		6.02	366768	0.54	0.55	9214	0.06
0.75 C		6.96		1.32		7.42	421171	0.66	0.63	14987	0.10
1 D		6.09		1.15		8.32	495605	0.74	0.74	15975	0.11
2 E		5.06		0.96		12.29	727005	1.10	1.09	18667	0.13
4 F		3.54		0.67		14.11	832968	1.26	1.25	30115	0.20
8 G		2.04		0.39		16.37	996747	1.46	1.50	36157	0.24
12 H		1.01		0.19		16.61	1044800	1.48	1.57	40500	0.27
24 I		0	0	0.00	0.00	5.29	225240	1.57	1.11	42751	0.29

JAR NUMBER FOUR CECA 20 B				TEST NUMBER 16							
TIME	BOTTLE	CM CLO2	PKHT	PPM CLO2	PPM	CM CL	PKHT	PPM CL	PPM	CLO3	PPM CLO3
(HRS)				(CM)	PKHT	CL		(CM)	PKHT	PKHT	(PKHT)
0 M		12.75	790051	2.41	2.35	1.85	125684	0.16	0.19	7985	0.05
0.5 N		8.12	538064	1.53	1.60	6.58	405960	0.59	0.61	11529	0.08
0.75 O		6.85	439472	1.29	1.31	7.32	379627	0.65	0.57	14049	0.09
1 P		5.85	377925	1.11	1.13	8.19	433011	0.73	0.65	20129	0.14
2 Q		4.91	341979	0.93	1.02	12.19	643789	1.09	0.97	22378	0.15
4 R		3.32	240252	0.63	0.72	14.18	833147	1.26	1.26	30623	0.21
8 S		1.82	137240	0.34	0.41	15.86	982678	1.41	1.48	38985	0.26
12 T		0.87	70973	0.16	0.21	16.58	1015972	1.48	1.53	40588	0.27
24 U		0	0	0.00	0.00	5.34	328627	1.59	1.61	40813	0.28

Table A45 Continued.

STANDARD NUMBER TWO											
TIME	BOTTLE	CM CLO2	PKHT	PPM CLO2	PPM	CM CL	PKHT	PPM CL	PPM	CLO3	PPM CLO3
(HRS)				(CM)	PKHT	CL		(CM)	PKHT	PKHT	(PKHT)
		6.14		1.16		638131			0.96	18948	0.13
		6.15		1.16		673429			1.01	18479	0.12
		6.14		1.16		636605			0.95	18057	0.12
		5.96		1.13		703733			1.06	16139	0.11
		5.96		1.13		853243			1.28	15797	0.11
		6.06		1.15		597368			0.90		
		5.99		1.13		636757			0.96		
		5.96	406080	1.13	1.22	14.76	846779	1.32	1.27	16212	0.11
		6.03	417531	1.14	1.25	14.82	869480	1.32	1.30	18223	0.12
		6.16	440093	1.16	1.32	14.98	917459	1.34	1.38		
		6.19	419563	1.17	1.26	10.63	626227	0.95	0.94	24913	0.17
		6.18	419029	1.17	1.26	11.17	666901	1.00	1.00		
		5.92	426067	1.12	1.28		853243		1.28	15797	0.11
		5.98	422907	1.13	1.27		703733		1.06		

Table A46. Data from analysis of acid extracted boron along with linear regression to test correlation with ClO_2^- removal for each of the 12 PACs.

PAC type	ClO_2^- removal (percent)	BORON mg/g of PAC
Ceca 20 B	100	0.177
Ceca 20 C	89	0.174
Calgon WPH	89	0.018
Calgon WPL	91	0.009
Nuchar SA	94	0.002
Nuchar Aqua S	100	0.026
Acticarb L2S	100	0.008
Watercarb (Husky)	81	0.025
Darco S-51	92	0.013
Darco G-60	100	0.003
Darco KB-B	50	0.002
Darco HDB	100	0.402

Regression Output	Boron
Constant	-0.14537
Std. Error of Y Estimated	0.122892
R Squared	0.077284
Number of Observations	12
Degrees of Freedom	10
X Coefficient(s)	0.002397
Std. Error of Coefficient	0.002619

Table A47. Data from analysis of acid extacted iron along with linear regression to test correlation with ClO₂⁻ removal for each of the 12 PACs.

PAC type	ClO ₂ ⁻ removal (percent)	Iron mg/g of PAC
Ceca 20 B	100	1.78
Ceca 20 C	89	3.18
Calgon WPH	89	2.04
Calgon WPL	91	1.91
Nuchar SA	94	0.016
Nuchar Aqua S	100	3.56
Acticarbhone L2S	100	3.32
Watercarb (Husky)	81	1.59
Darco S-51	92	1.53
Darco G-60	100	0.152
Darco KB-B	50	0.069
Darco HDB	100	4.71

Regression Output	Iron
Constant	-2.37185
Std. Error of Y Estimated	1.390311
R Squared	0.209034
Number of Observations	12
Degrees of Freedom	10
X Coefficient(s)	0.048176
Std. Error of Coefficient	0.029635

Table A48. Data from analysis of acid extracted aluminum along with linear regression to test correlation with ClO_2^- removal for each of the 12 PACs.

PAC type	ClO_2^- removal (percent)	Aluminum mg/g of PAC
Ceca 20 B	100	9.67
Ceca 20 C	89	3.91
Calgon WPH	89	0.708
Calgon WPL	91	0.663
Nuchar SA	94	1.01
Nuchar Aqua S	100	1.72
Acticarbhone L2S	100	0.198
Watercarb (Husky)	81	1.92
Darco S-51	92	12.9
Darco G-60	100	2.43
Darco KB-B	50	1.05
Darco HDB	100	9.06

Regression Output	Aluminum
Constant	-3.41603
Std. Error of Y Estimated	4.341875
R Squared	0.068563
Number of Observations	12
Degrees of Freedom	10
X Coefficient(s)	0.079403
Std. Error of Coefficient	0.092548

Table A49. Data from analysis of acid extacted magnesium along with linear regression to test correlation with ClO_2^- removal for each of the 12 PACs.

PAC type	ClO_2^- removal (percent)	Magnesium mg/g of PAC
Ceca 20 B	100	4.07
Ceca 20 C	89	2.33
Calgon WPH	89	0.068
Calgon WPL	91	0.065
Nuchar SA	94	0.058
Nuchar Aqua S	100	0.182
Acticarb L2S	100	0.204
Watercarb (Husky)	81	1.29
Darco S-51	92	0.659
Darco G-60	100	0.528
Darco KB-B	50	0.013
Darco HDB	100	7.14

Regression Output	Magnesium
Constant	-2.72882
Std. Error of Y Estimated	2.188823
R Squared	0.086656
Number of Observations	12
Degrees of Freedom	10
X Coefficient(s)	0.045445
Std. Error of Coefficient	0.046655

Table A50. Data from analysis of acid extacted manganese along with linear regression to test correlation with ClO_2^- removal for each of the 12 PACs.

PAC type	ClO_2^- removal (percent)	Manganese mg/g of PAC
Ceca 20 B	100	0.059
Ceca 20 C	89	0.095
Calgon WPH	89	0.006
Calgon WPL	91	0.034
Nuchar SA	94	0.015
Nuchar Aqua S	100	0.024
Acticarbhone L2S	100	0.016
Watercarb (Husky)	81	0.327
Darco S-51	92	0.024
Darco G-60	100	0.005
Darco KB-B	50	0.002
Darco HDB	100	0.214

Regression Output	Manganese
Constant	0.077154
Std. Error of Y Estimated	0.10578
R Squared	0.000183
Number of Observations	12
Degrees of Freedom	10
X Coefficient(s)	-9.7E-05
Std. Error of Coefficient	0.002255

Table A51. Data from analysis of acid extacted zinc along with linear regression to test correlation with ClO_2^- removal for each of the 12 PACs.

PAC type	ClO_2^- removal (percent)	Zinc mg/g of PAC
Ceca 20 B	100	0.0036
Ceca 20 C	89	0.0057
Calgon WPH	89	0.0008
Calgon WPL	91	0.0005
Nuchar SA	94	0.0008
Nuchar Aqua S	100	0.0015
Acticarbhone L2S	100	0.0010
Watercarb (Husky)	81	0.0040
Darco S-51	92	0.0010
Darco G-60	100	0
Darco KB-B	50	0
Darco HDB	100	0.0128

Regression Output	Zinc
Constant	-0.00296
Std. Error of Y Estimated	0.003727
R Squared	0.057333
Number of Observations	12
Degrees of Freedom	10
X Coefficient(s)	6.19E-05
Std. Error of Coefficient	7.94E-05

Table A52. Summary data from spreadsheet listing percent ClO₂ removal for each of the 12 PACs.

GRAND TOTAL SUMMARY OF ALL TWELVE PACS. PERCENT CHLORITE ION REMOVED VERSUS TIME IN HOURS																			
ONE GROUP WITH CHLORITE ION ONLY ADDED.						SECOND GROUP WITH BOTH CHLORITE ION AND CHLORINE ADDED													
(TOP GROUP IS WITH ONLY CHLORITE ION ADDED).																			
TIME (HOURS)	C 20 B		20 C		WPH	WPL	SA	AQUA S		L 2 S	HUSKY		S-51	G-60		KBB		HDB	
	Percent	Removed	Percent	Removed	Percent	Percent	Percent	Percent	Removed	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	
	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	(percent)	
0.00	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
0.25	23	18	7	29	23	43	61	49	37	51	15	35							
0.50	39	37	47	50	39	52	68	55	51	65	23	45							
0.75	47	44	52	57	47	66	71	58	53	68	23	48							
1.00	54	53	59	64	54	71	74	74	60	56	23	50							
1.25	60	59	63	68	57	74	76	62	58	71	23	51							
1.50	64	65	68	71	60	76	78	63	59	73	24	52							
1.75	67	67	70	73	62	78	79	64	60	74	24	53							
2.00	71	68	72	75	64	79	81	65	62	76	24	53							
4.00	82	77	81	81	67	83	83	68	72	88	26	64							
8.00	89	84	87	87	71	97	89	72	82	100	33	78							
12.00	100	87	89	87	82	100	99	80	90	100	38	88							
24.00	100	89	89	91	94	100	100	81	92	100	50	100							

Table A52, continued:

(THIS GROUP HAS BOTH CHLORITE ION AND CHLORINE ADDED.)																								
TIME (HOURS)	20 B		20C		WPH		WPL		S A		AQUA S		L 2 S		HUSKY		S-51		G-60		KB-B		HDB	
	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)	Percent Removed (percent)
0.00	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.25	42	6	40	42	9	29	20	21	37	43	28	43												
0.50	51	14	54	51	18	40	27	27	47	53	33	53												
0.75	53	21	58	55	27	44	31	29	58	59	36	56												
1.00	55	27	61	59	37	48	35	31	61	66	38	61												
1.25	60	30	63	61	38	51	36	31	64	68	39	62												
1.50	64	31	65	64	40	55	36	32	67	70	40	62												
1.75	69	33	66	66	42	55	37	32	69	73	40	63												
2.00	74	35	67	68	43	55	38	32	70	75	41	64												
4.00	79	39	73	77	48	64	42	33	78	85	46	68												
8.00	81	43	78	80	49	68	54	34	84	94	49	73												
12.00	86	46	81	83	50	70	59	35	86	95	51	74												
24.00	96	48	86	87	52	76	88	47	91	100	52	79												

Table A53. PACs demonstrating increase in ClO₃ over the full 24 hours of contact.

PAC Type	Initial ClO ₃ ⁻ (mg/L)	Final ClO ₃ ⁻ (mg/L)	Increase in ClO ₃ ⁻ (mg/L)
Ceca 20 B	0.23	0.77	0.54
L 2 S	0.60	0.79	0.19
L 2 S	0	0.54	0.54
S-51	0.25	1.26	1.01
HDB	0.45	1.10	0.65
KBB	0.45	0.80	0.35
G-60	0.37	1.32	0.95
WPL	0.26	0.41	0.15
WPH	0.34	0.45	0.11
CECA 20 B	0.06	0.28	0.22
CECA 20 B	0.06	0.29	0.23
CECA 20 B	0.05	0.28	0.23

Table A54. Results of replicate sample testing for CECA 20B PAC.

TIME	JAR 2	JAR 3	JAR 4		JAR 2	JAR 3	JAR 4	JAR 2	JAR 3	JAR 4
(HRS)	mg/L CLO2	mg/L CLO2	mg/L CLO2		mg/L CL	mg/L CL	mg/L CL	mg/L CLO3	mg/L CLO3	mg/L CLO3
0	2.40	2.39	2.41		0.18	0.15	0.16	0.06	0.06	0.05
0.5	1.61	1.60	1.53		0.52	0.54	0.59	0.05	0.06	0.08
0.75	1.31	1.32	1.29		0.68	0.66	0.65	0.10	0.10	0.09
1	1.14	1.15	1.11		0.72	0.74	0.73	0.11	0.11	0.14
2	0.96	0.96	0.93		1.05	1.10	1.09	0.13	0.13	0.15
4	0.65	0.67	0.63		1.20	1.26	1.26	0.20	0.20	0.21
8	0.38	0.39	0.34		1.44	1.46	1.41	0.24	0.24	0.26
12	0.17	0.19	0.16		1.49	1.48	1.48	0.27	0.27	0.27
24	0.00	0.00	0.00		1.58	1.57	1.59	0.28	0.29	0.28

APPENDIX B

Individual Plots For Each PAC

of

Concentration Versus Time

During the Removal of ClO_2^- by PAC

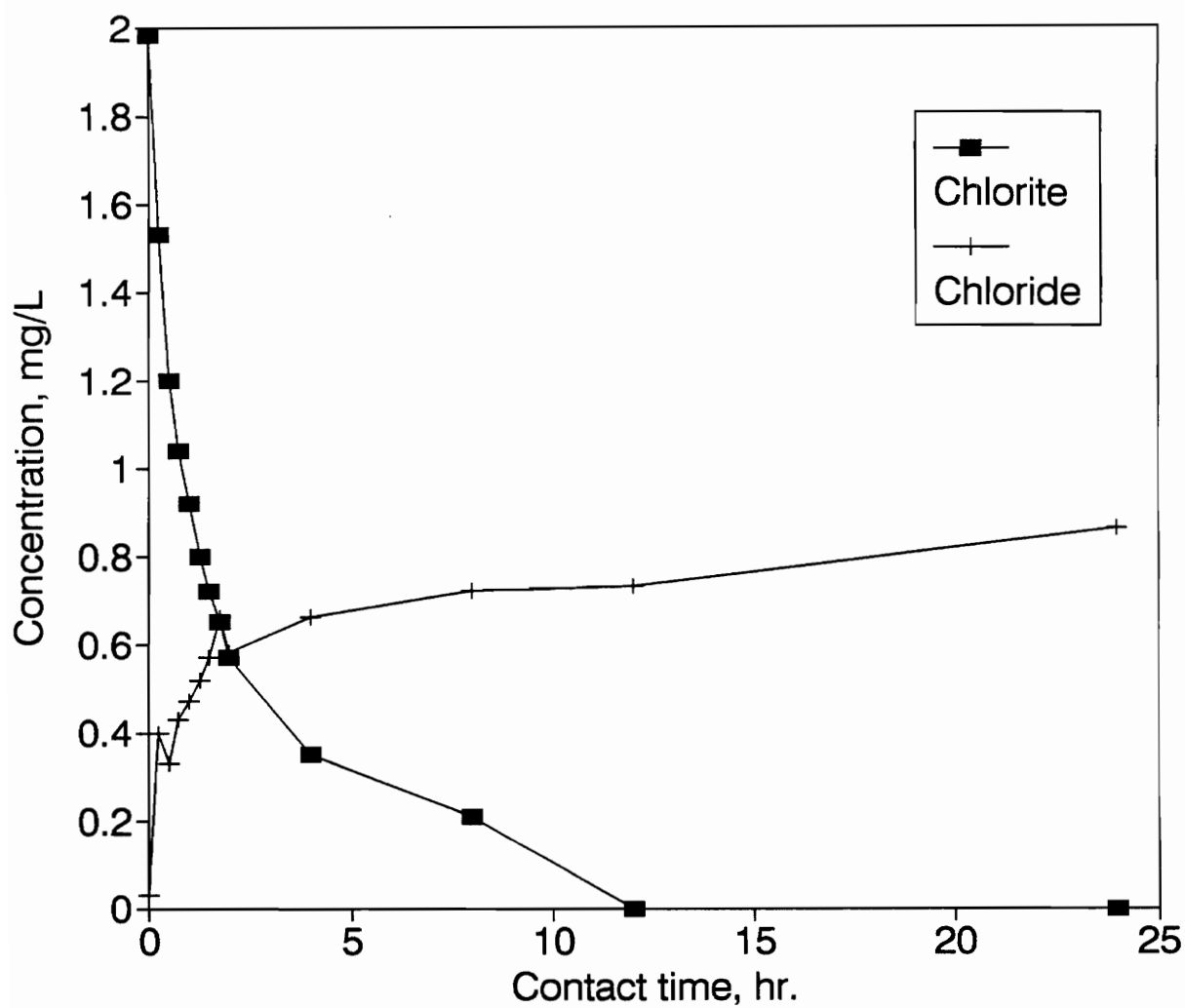


Figure B1. Concentration versus time during the removal of ClO_2 by Ceca 20 B PAC (20 mg/L) at pH 7, without chlorine added.

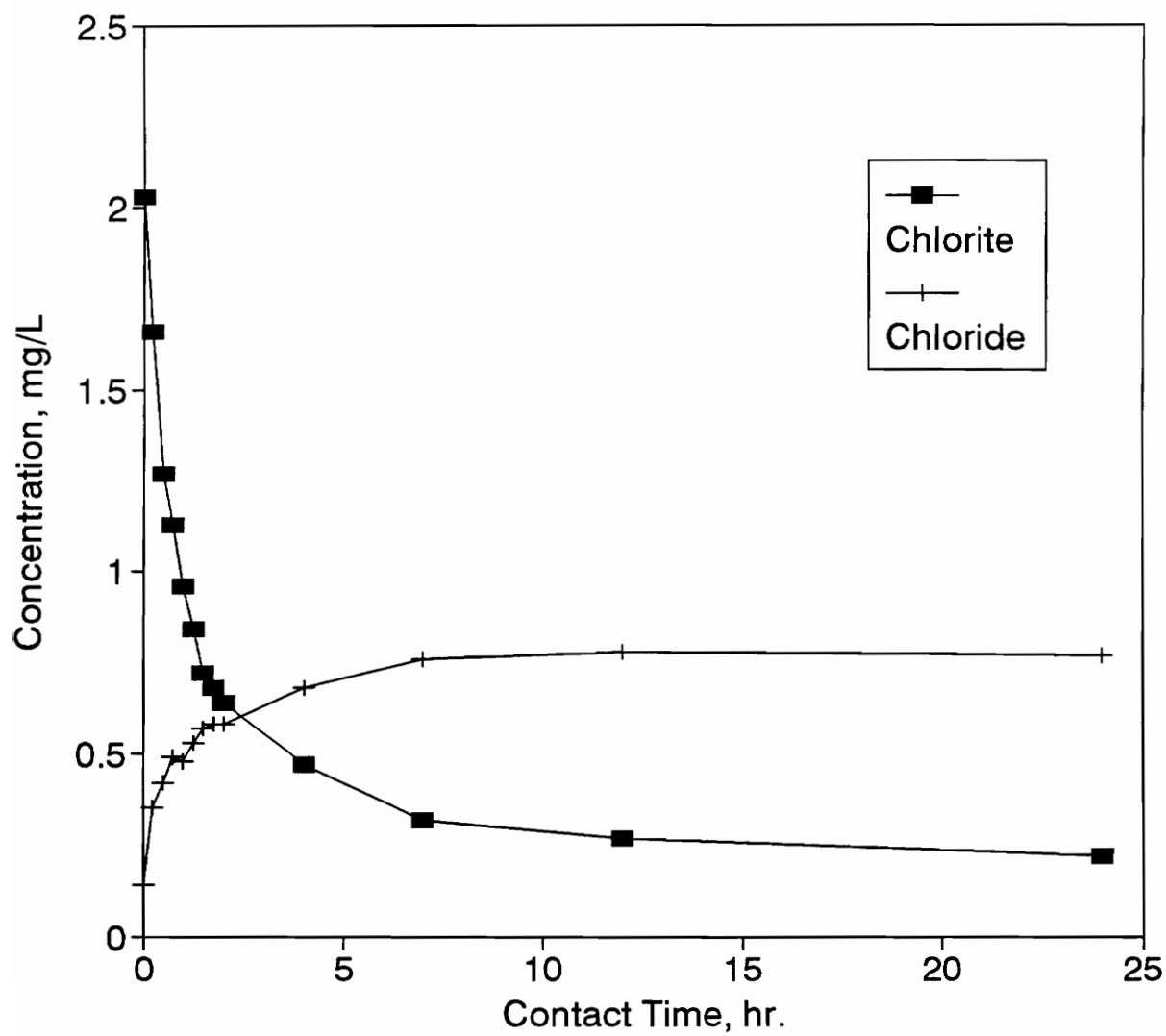


Figure B2. Concentration versus time during the removal of ClO_2^- by Ceca 20 C PAC (20 mg/L) at pH 7, without chlorine added.

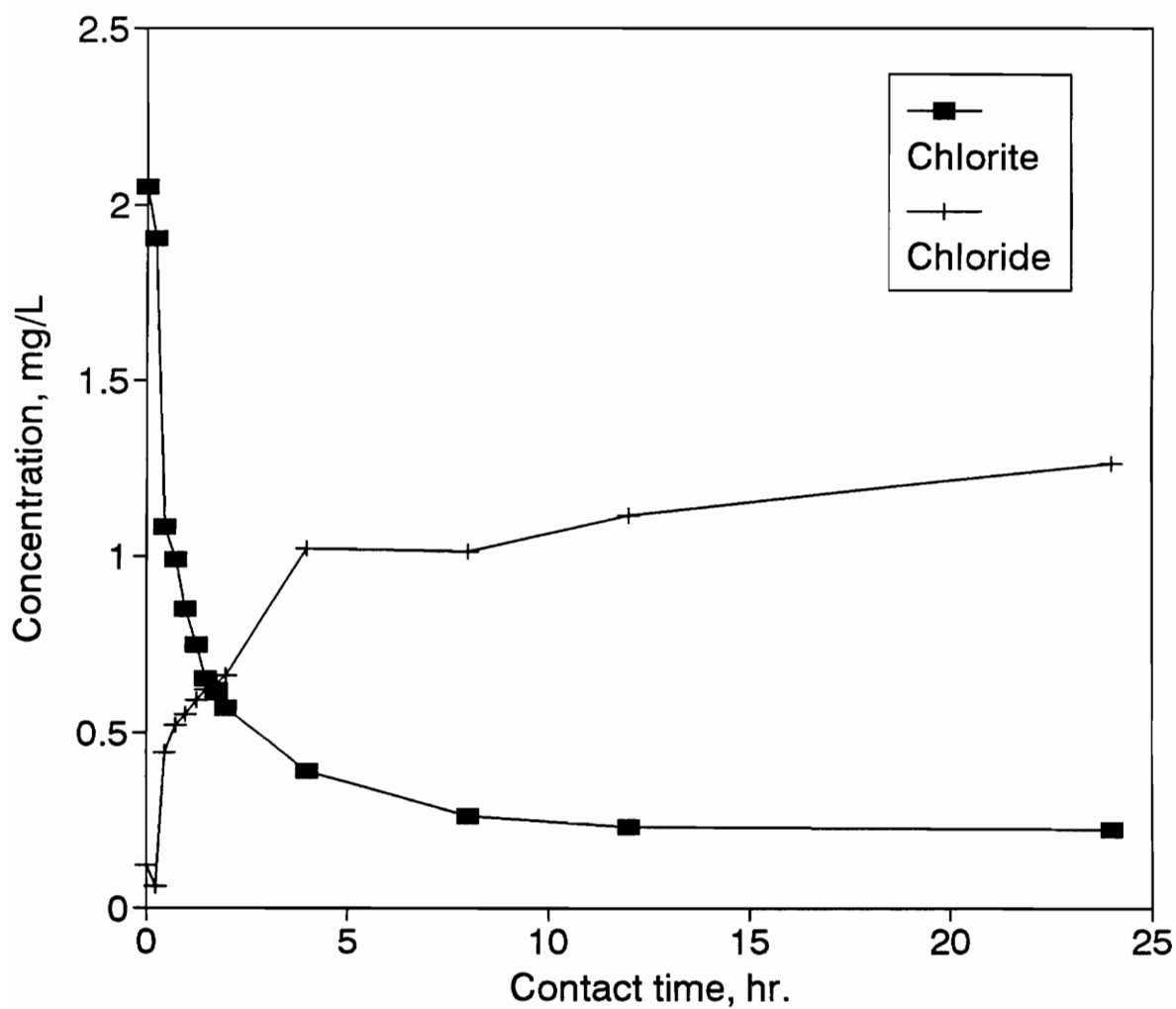


Figure B3. Concentration versus time during the removal of ClO_2^- by Calgon WPH PAC (20 mg/L) at pH 7, without chlorine added.

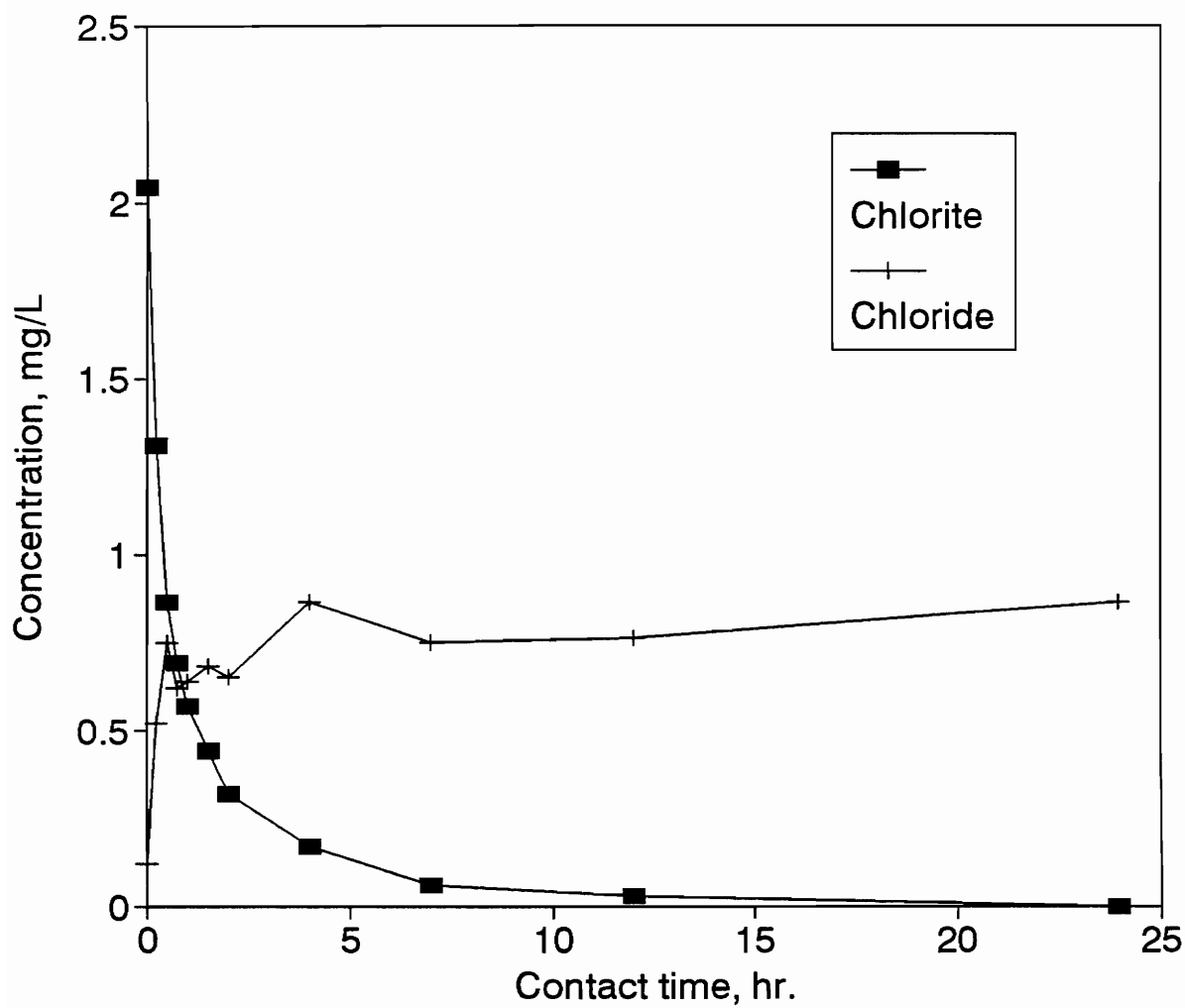


Figure B4. Concentration versus time during the removal of ClO_2 by Calgon WPL PAC (20 mg/L) at pH 7, without chlorine added.

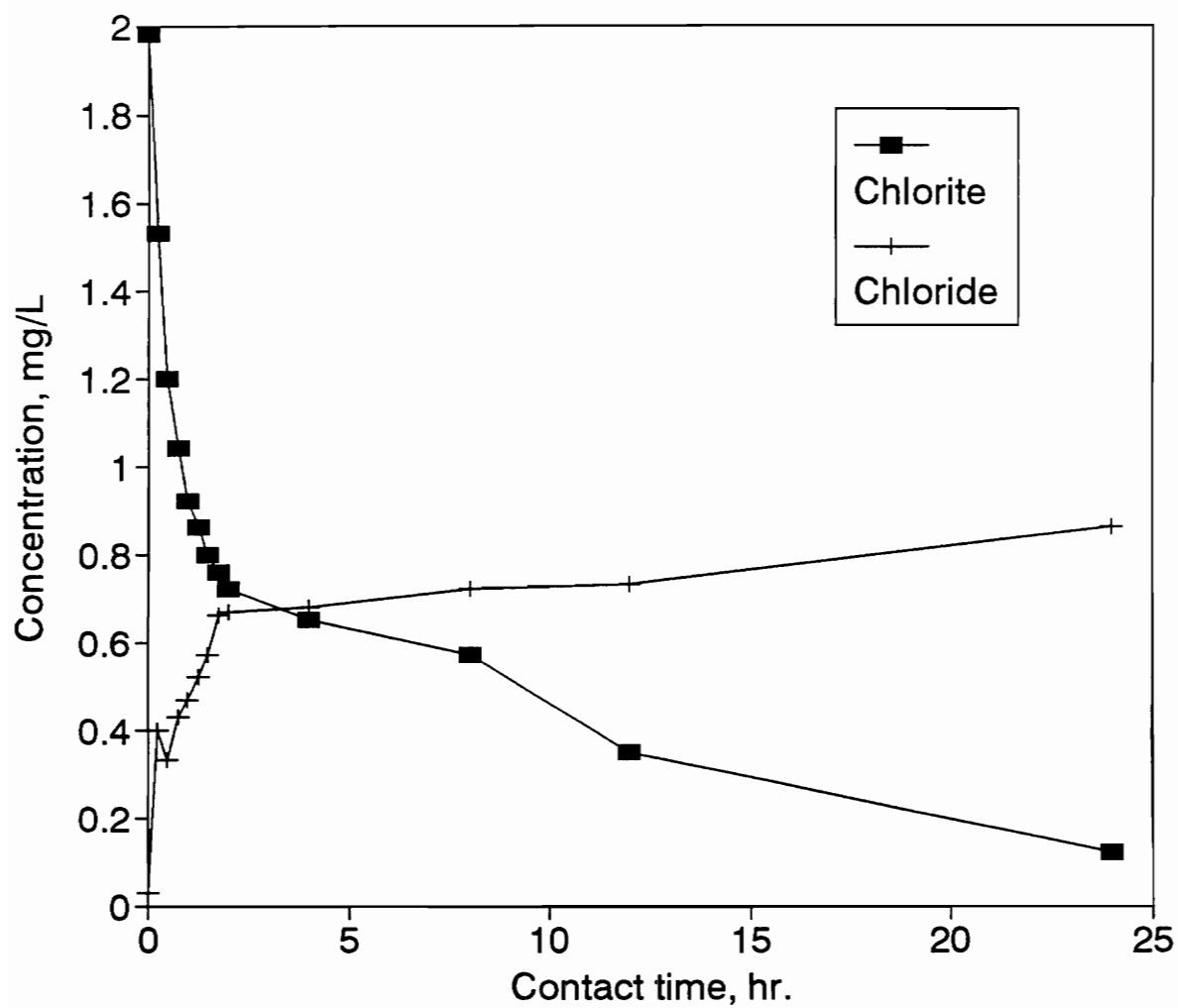


Figure B5. Concentration versus time during the removal of ClO_2 by Nuchar SA PAC (20 mg/L) at pH 7, without chlorine added.

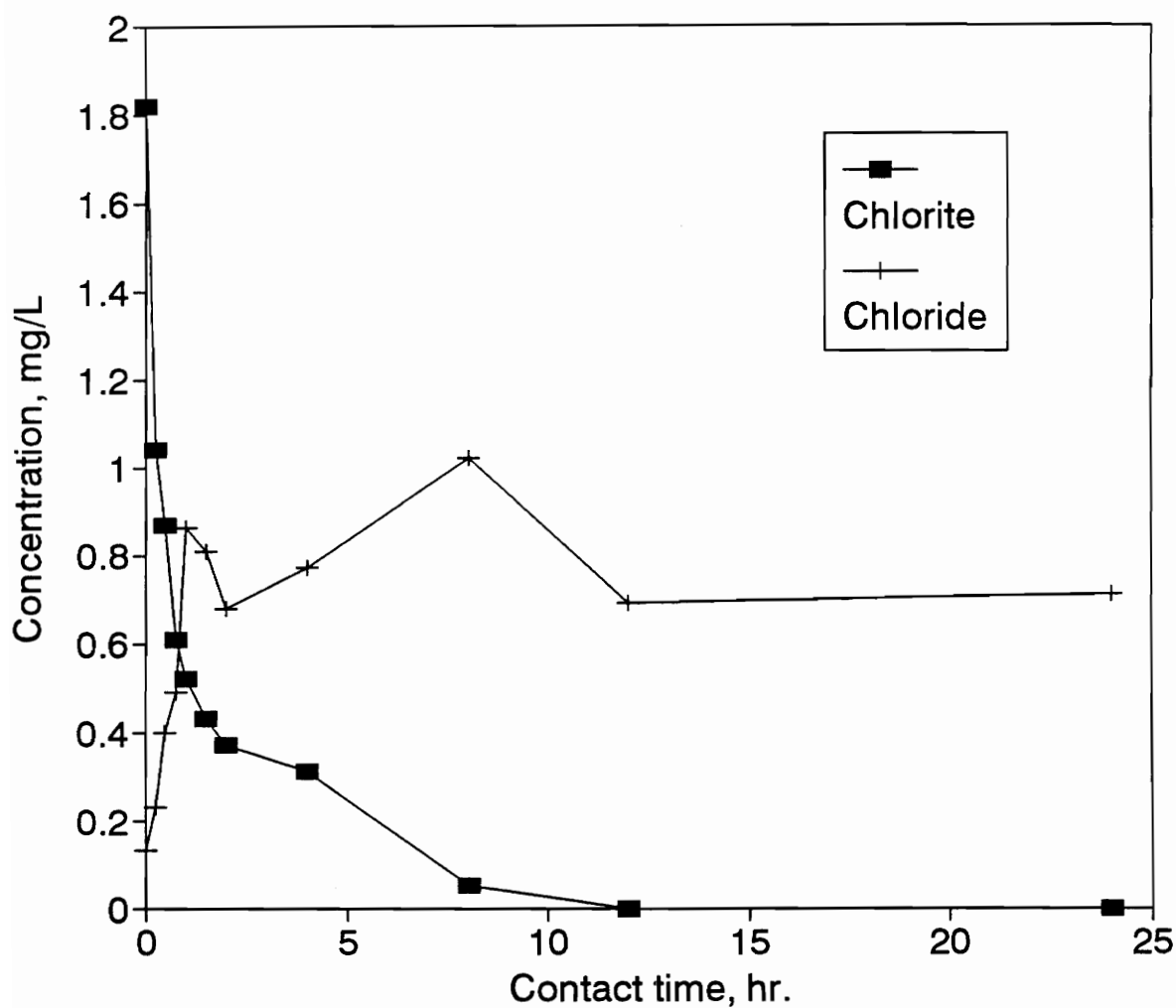


Figure B6. Concentration versus time during the removal of ClO_2^- by Nuchar Aqua S PAC (20 mg/L) at pH 7, without chlorine added.

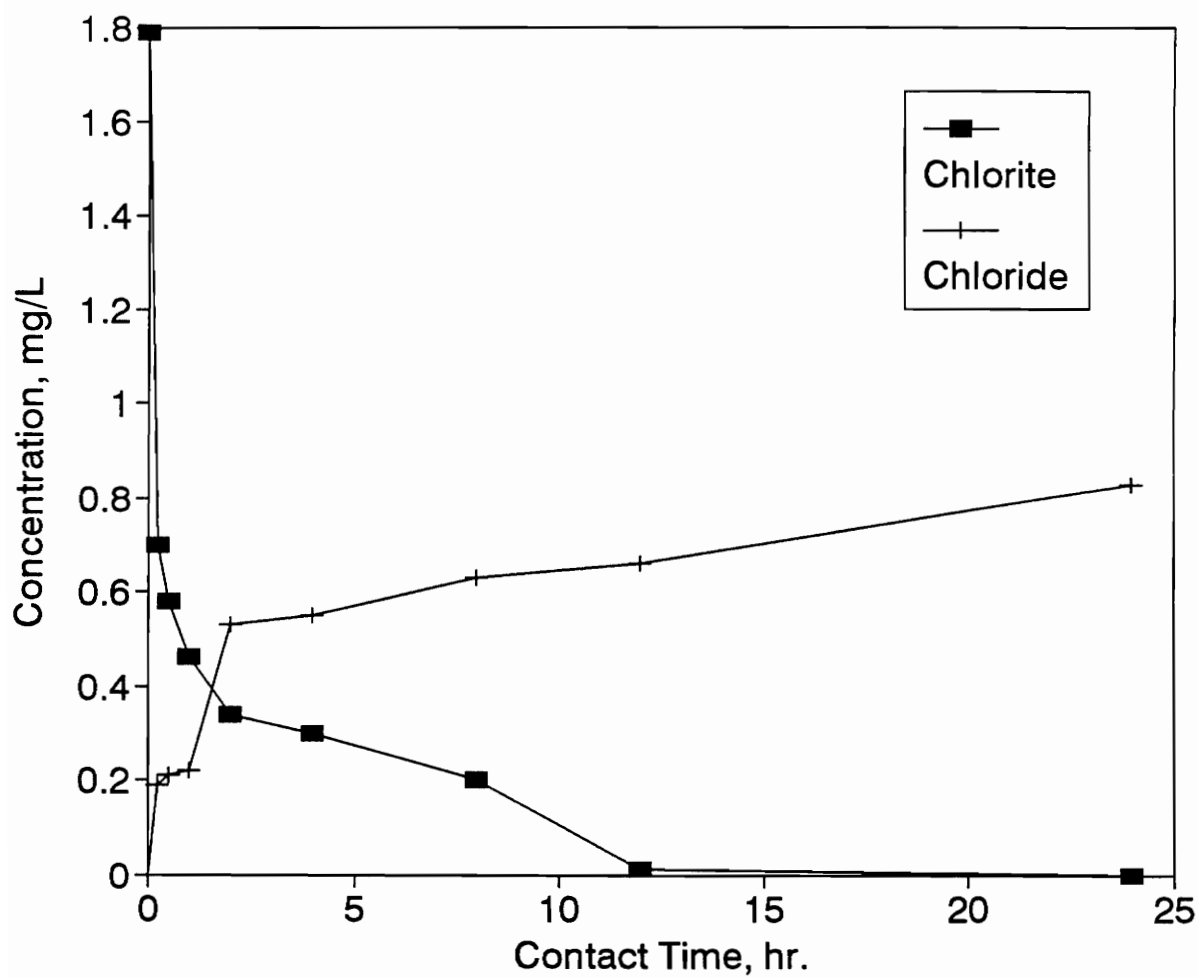


Figure B7. Concentration versus time during the removal of ClO_2^- by Acticarbhone L2S PAC (20 mg/L) at pH 7, without chlorine added.

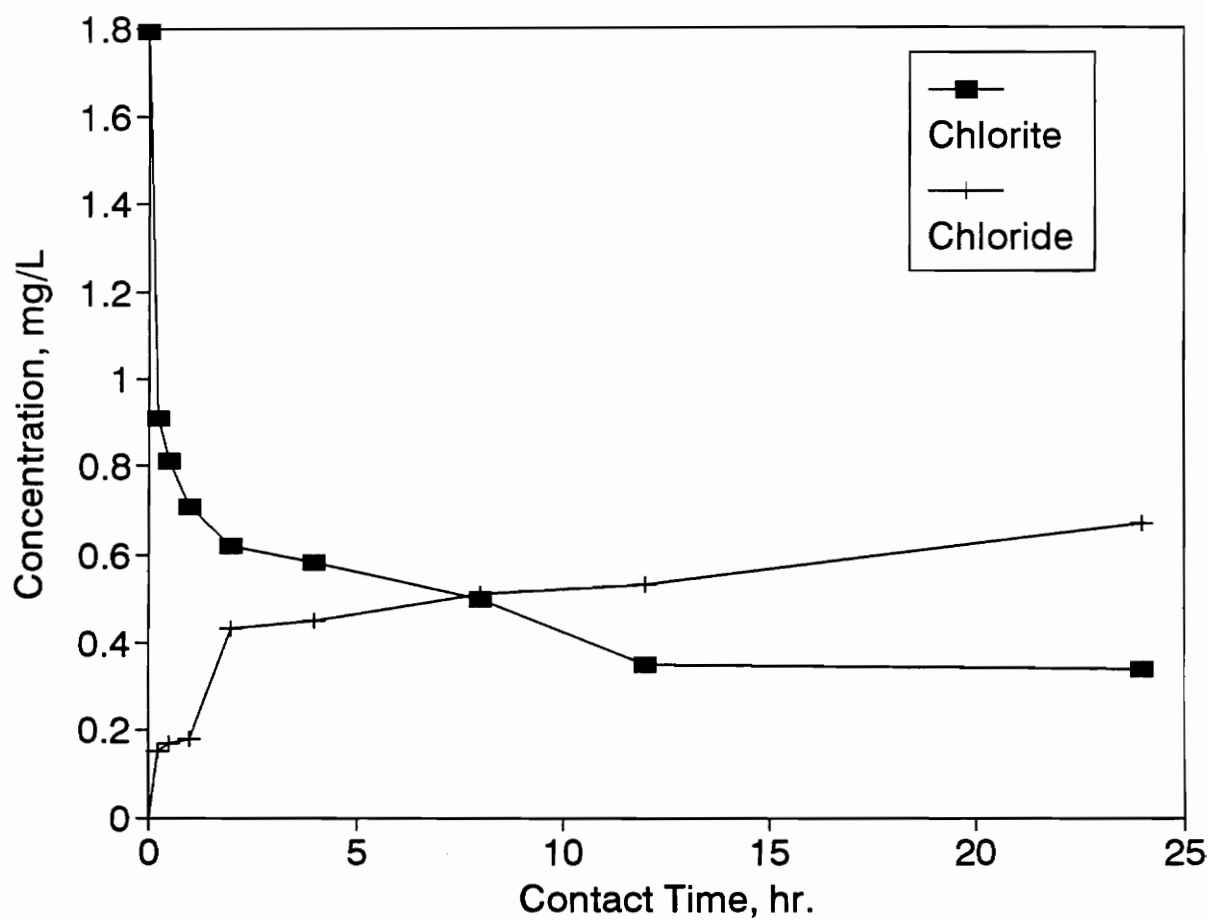


Figure B8. Concentration versus time during the removal of ClO_2^- by Husky (Watercarb) PAC (20 mg/L) at pH 7, without chlorine added.

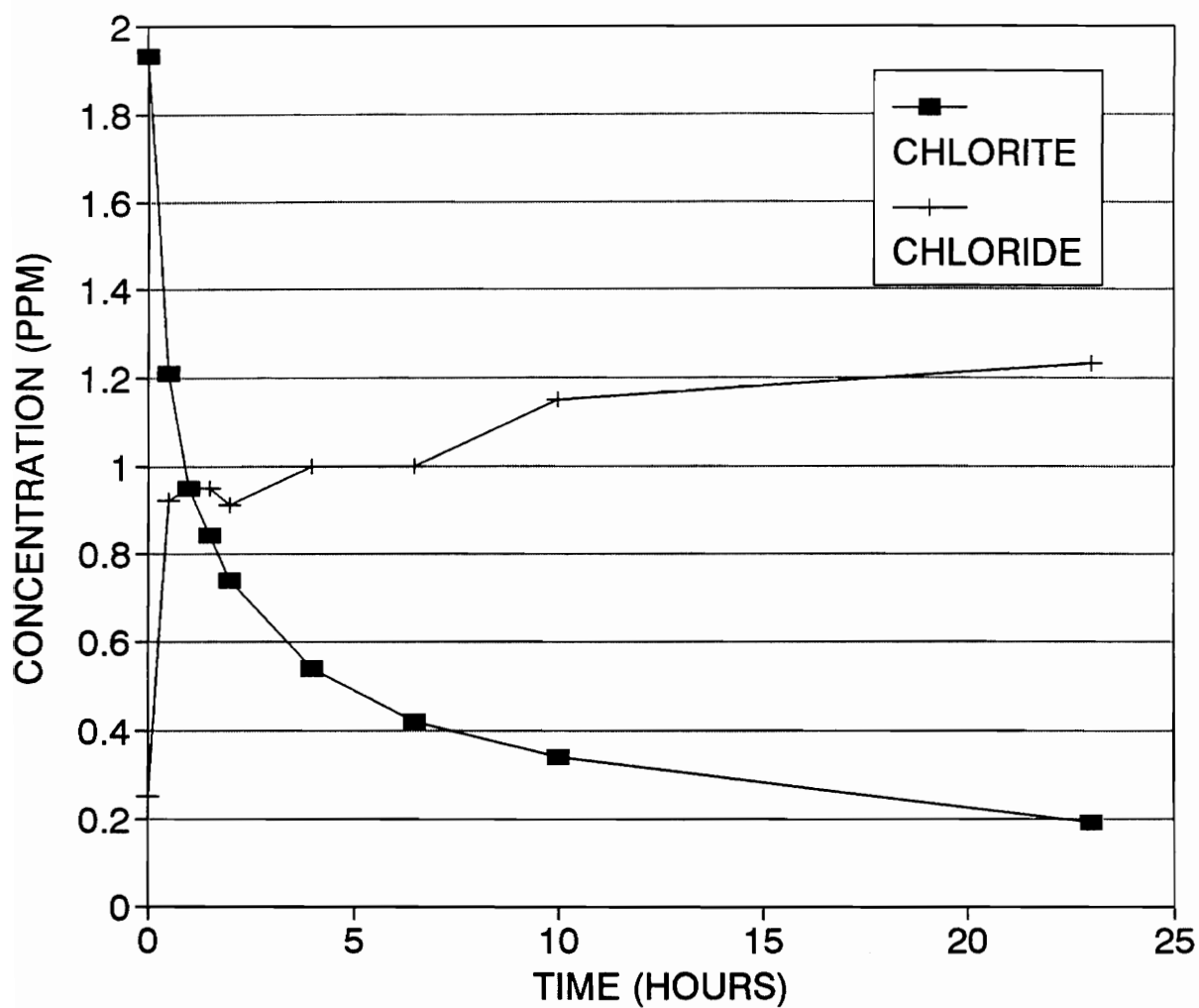


Figure B9. Concentration versus time during the removal of ClO_2 by Darco S-51 PAC (20 mg/L) at pH 7, without chlorine added.

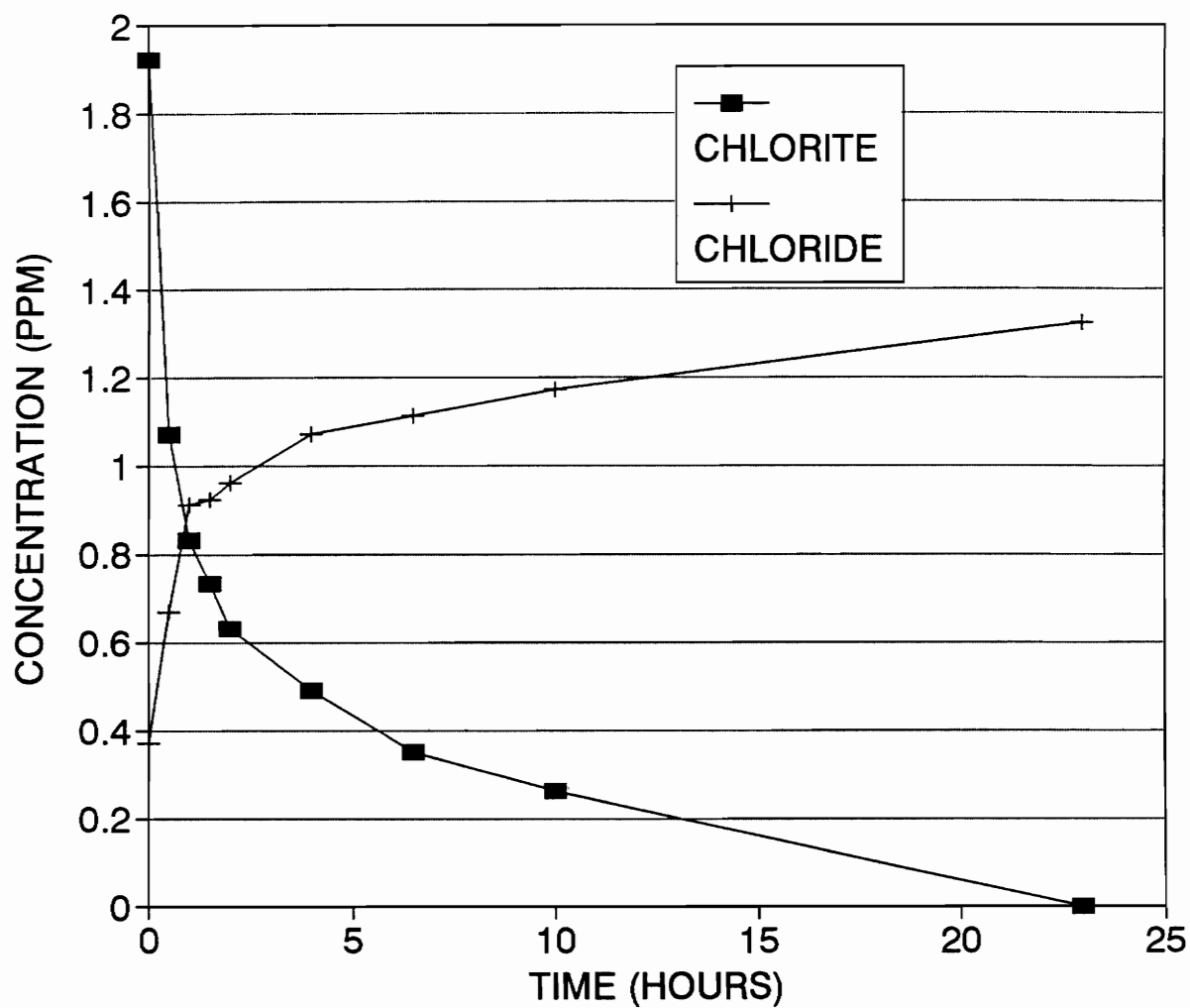


Figure B10. Concentration versus time during the removal of ClO_2^- by Darco G-60 PAC (20 mg/L) at pH 7, without chlorine added.

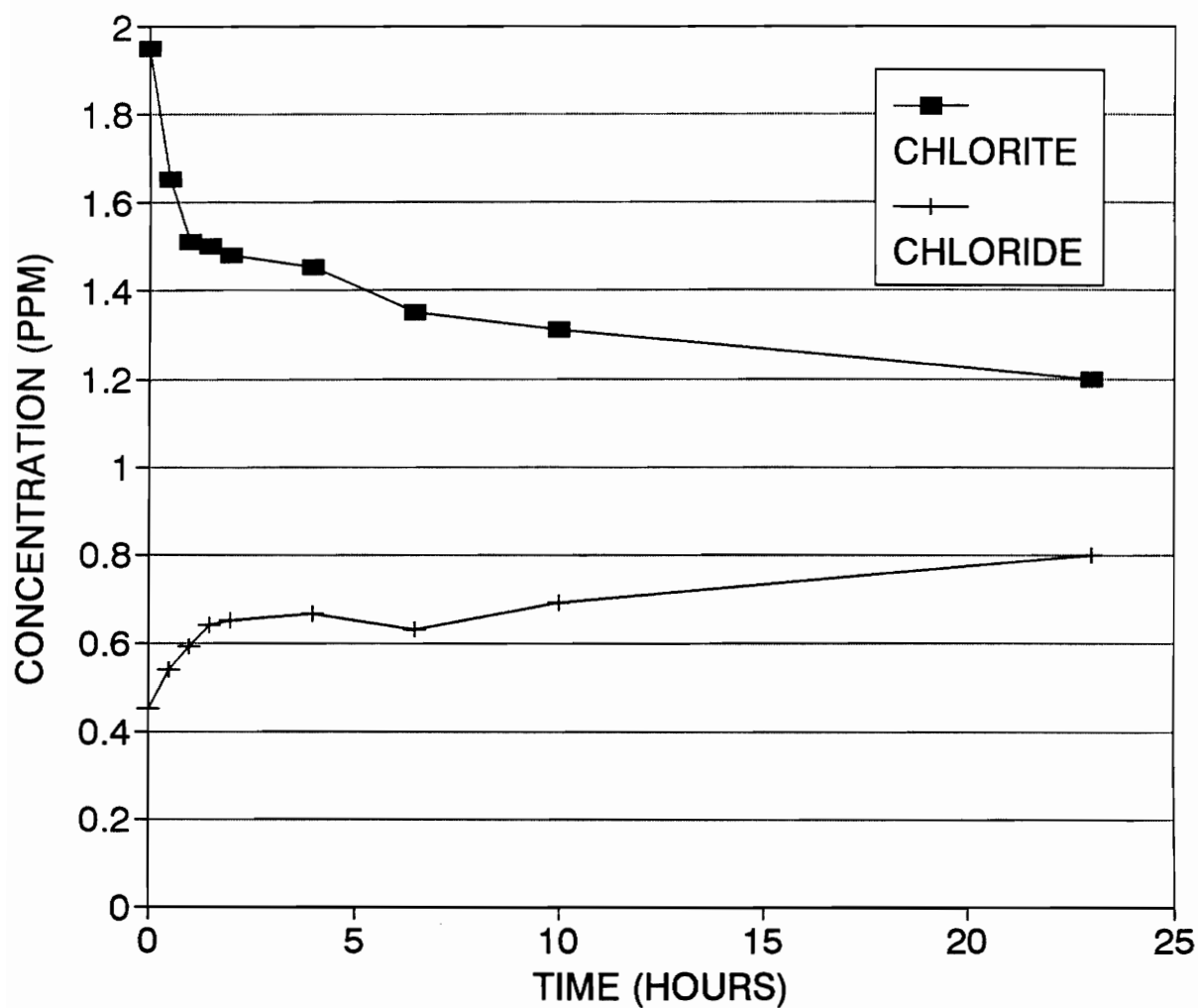


Figure B11. Concentration versus time during the removal of ClO_2 by Darco KB-B PAC (20 mg/L) at pH 7, without chlorine added.

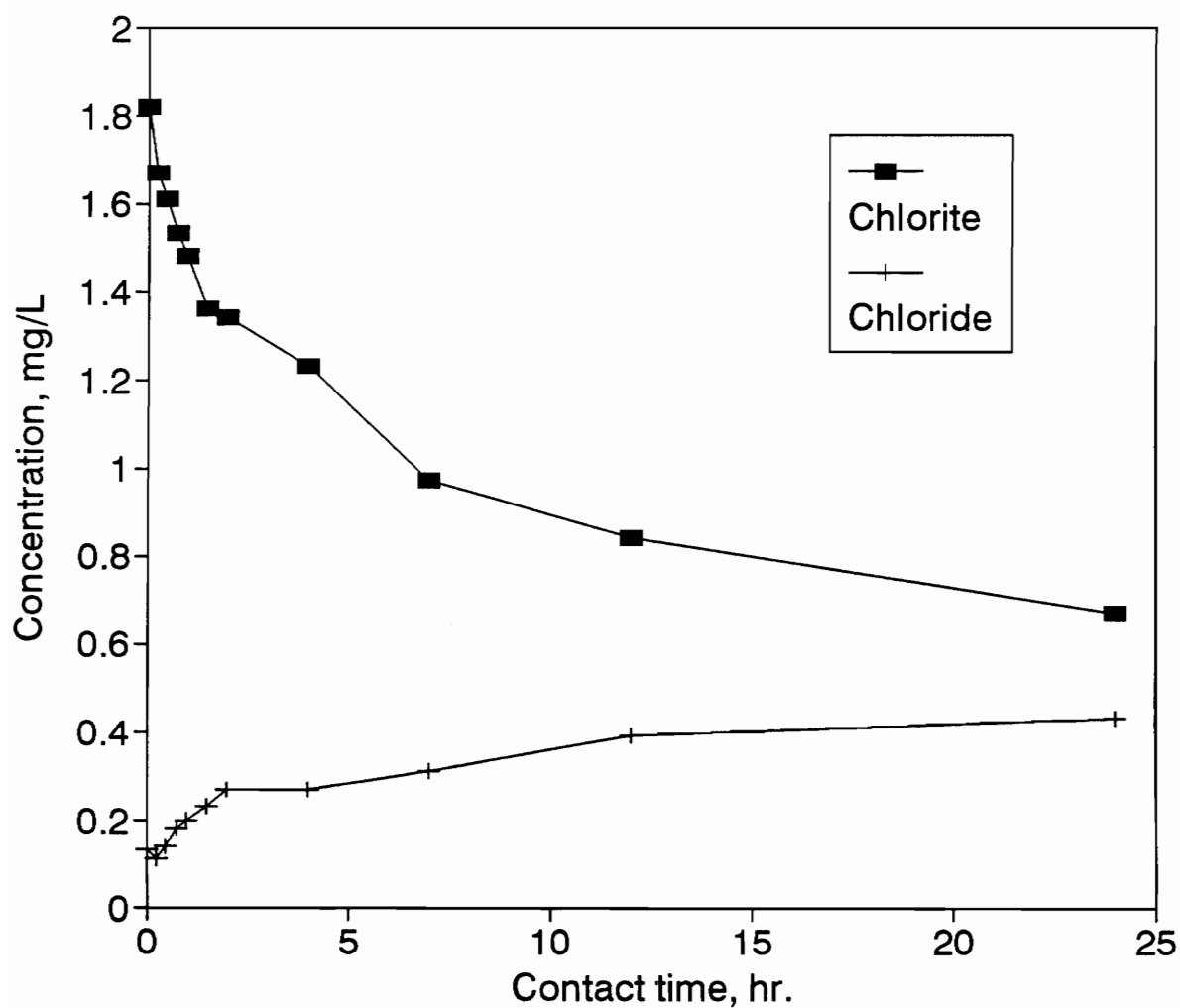


Figure B12. Concentration versus time during the removal of ClO_2^- by Darco HDB PAC (20 mg/L) at pH 7, without chlorine added.

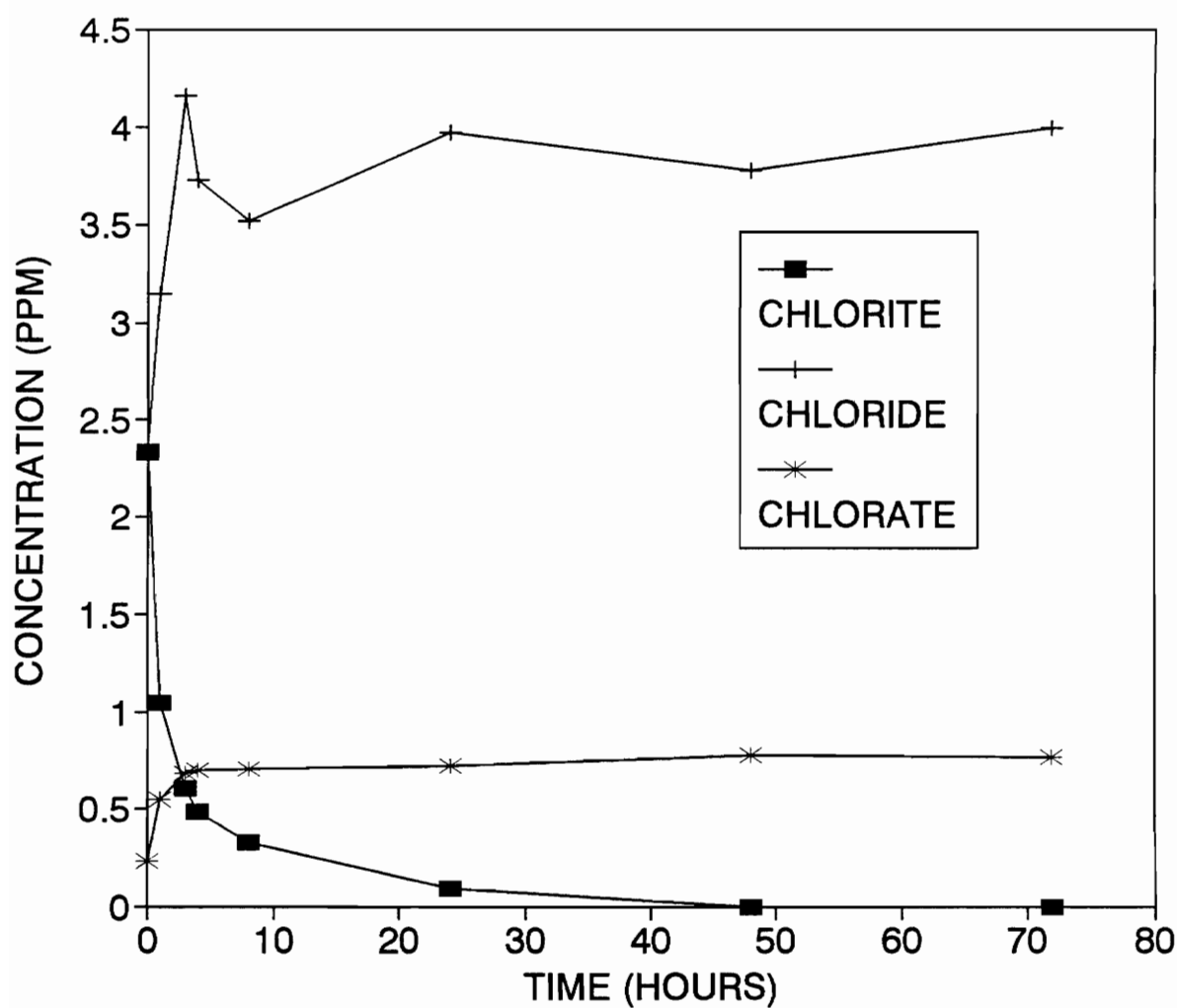


Figure B13. Concentration versus time during the removal of ClO_2 by Ceca 20 B PAC (20 mg/L) at pH 7, **with** chlorine added.

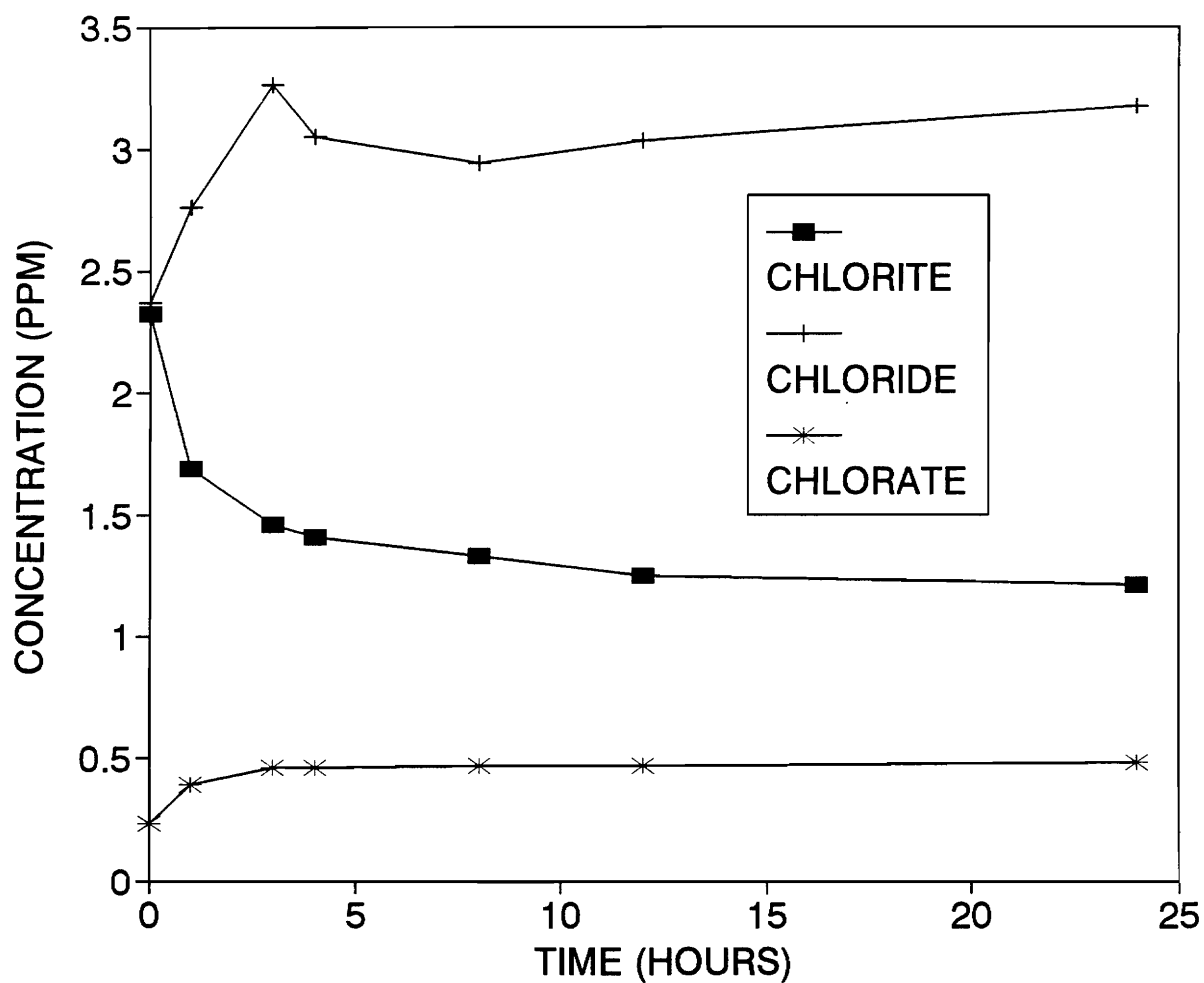


Figure B14. Concentration versus time during the removal of ClO_2 by Ceca 20 C PAC (20 mg/L) at pH 7, **with** chlorine added.

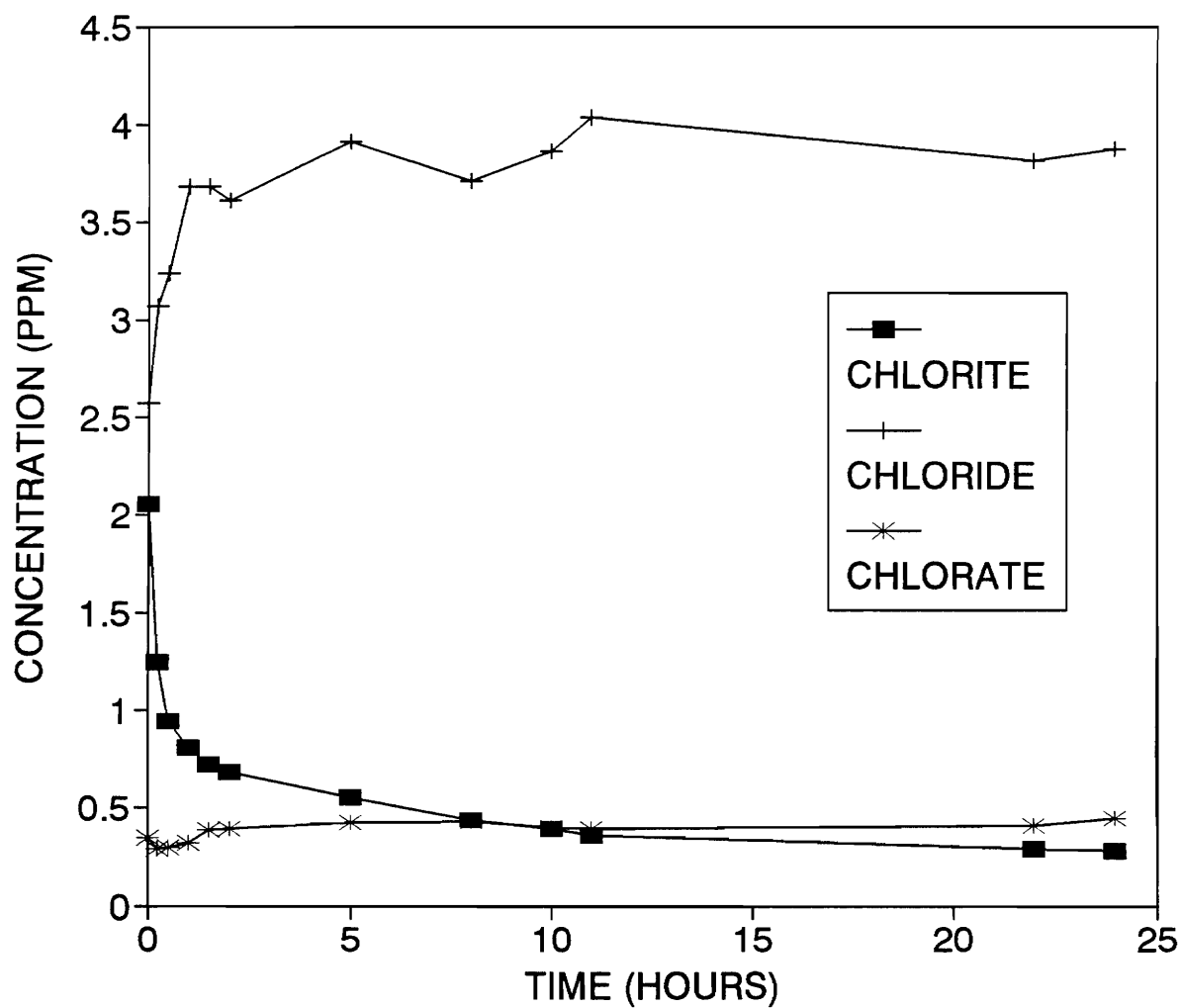


Figure B15. Concentration versus time during the removal of ClO_2 by Calgon WPH PAC (20 mg/L) at pH 7, with chlorine added.

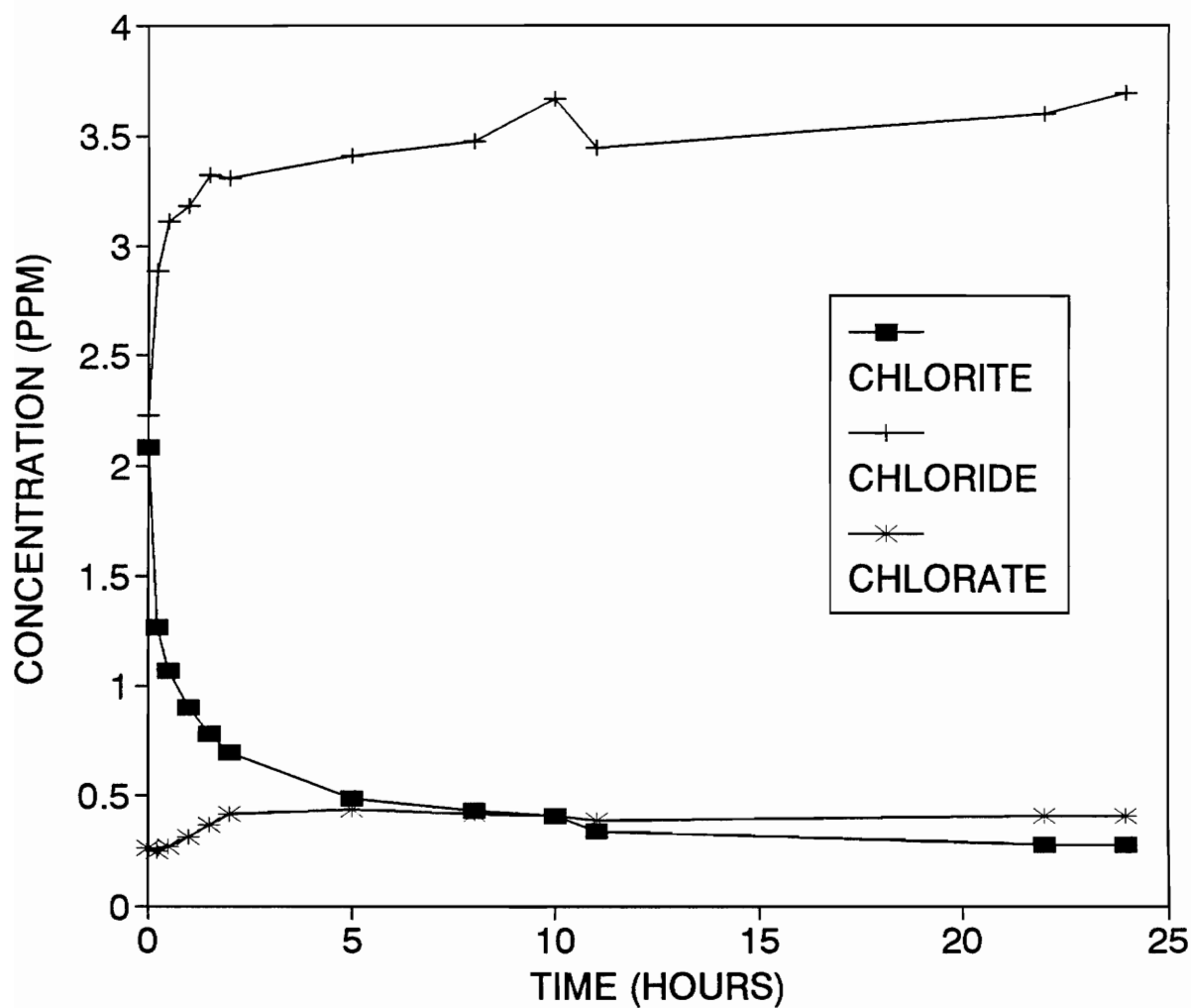


Figure B16. Concentration versus time during the removal of ClO_2 by Calgon WPL PAC (20 mg/L) at pH 7, **with** chlorine added.

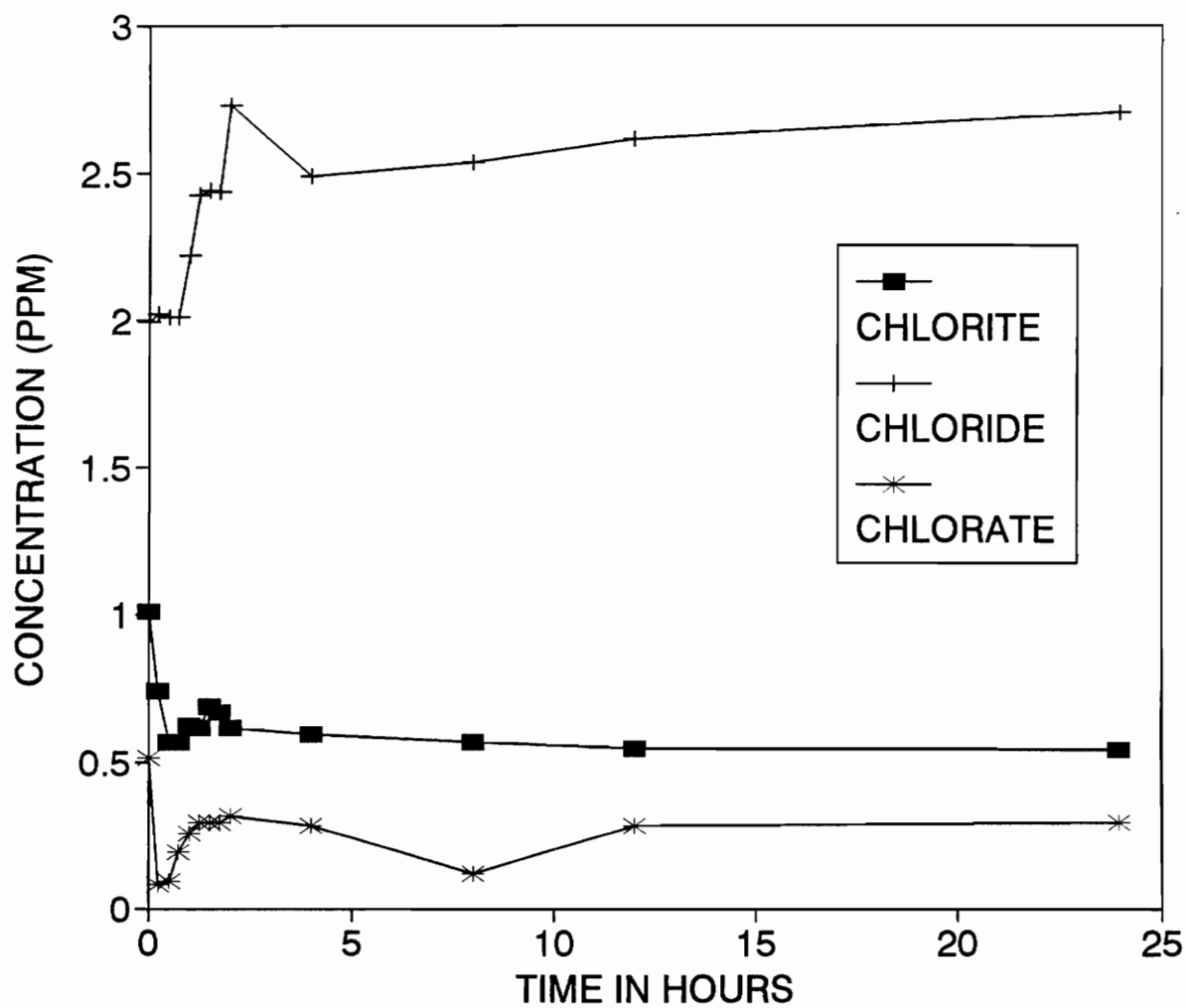


Figure B17. Concentration versus time during the removal of ClO_2 by Nuchar SA PAC (20 mg/L) at pH 7, **with** chlorine added.

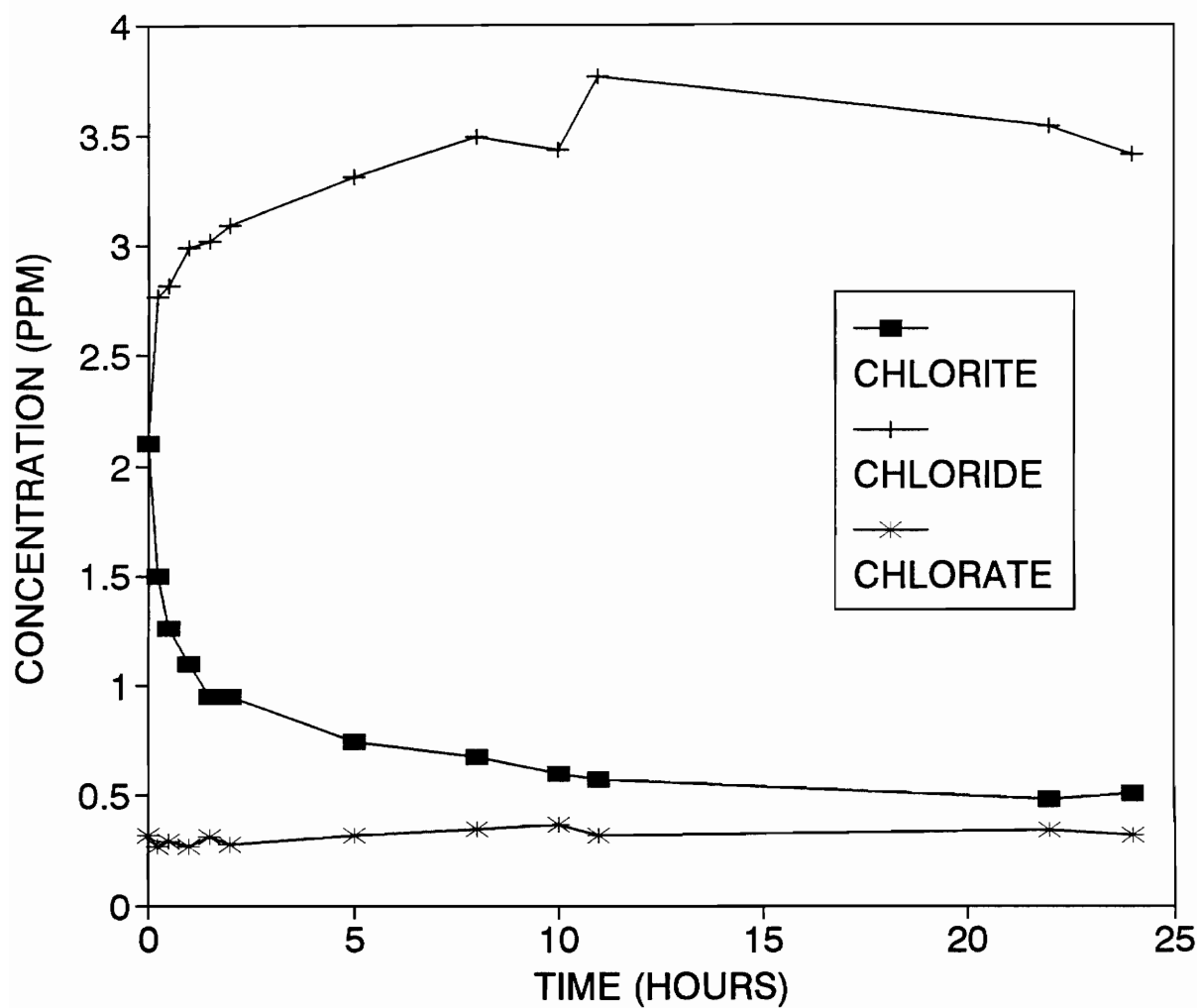


Figure B18. Concentration versus time during the removal of ClO_2 by Nuchar Aqua S PAC (20 mg/L) at pH 7, **with** chlorine added.

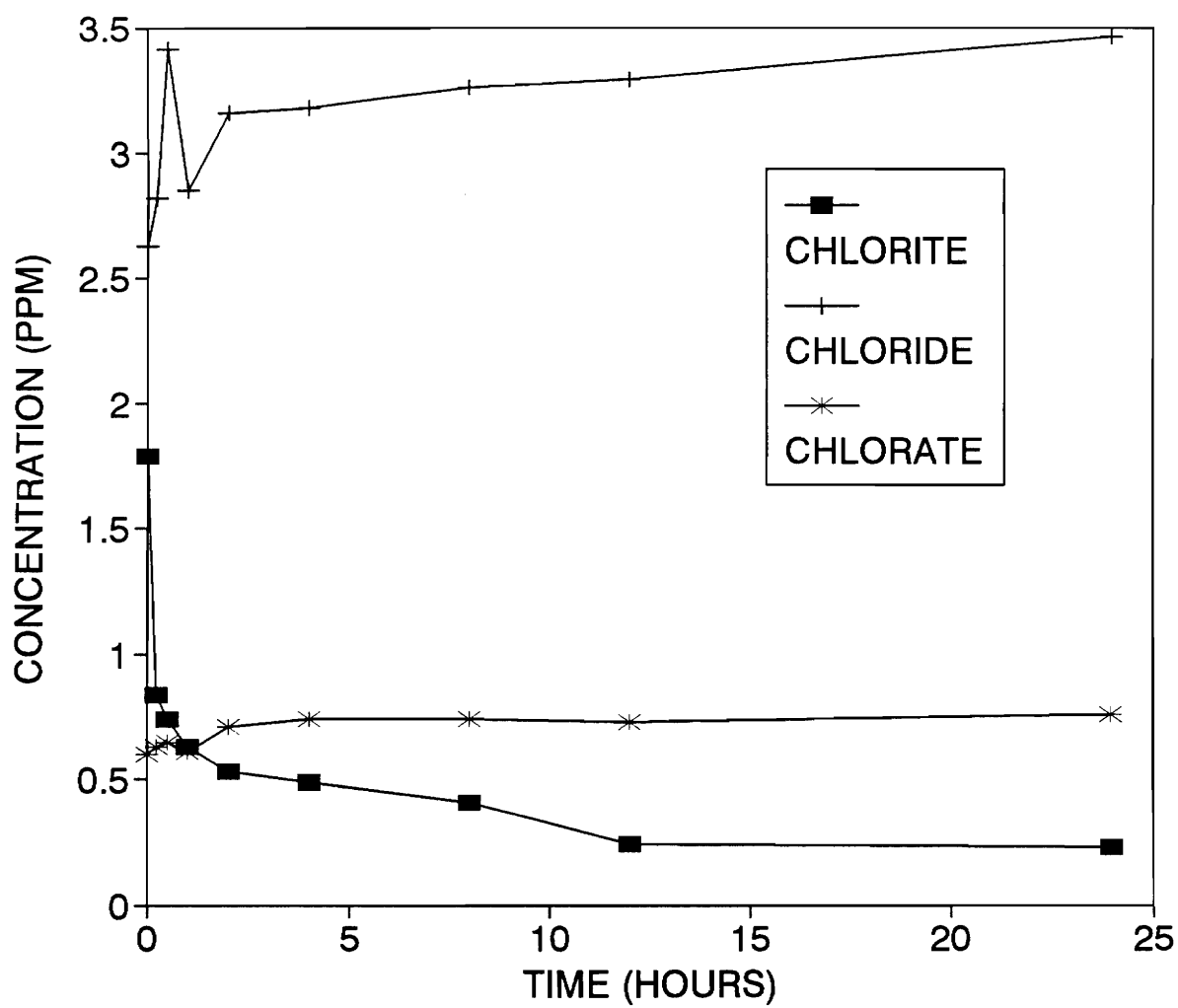


Figure B19. Concentration versus time during the removal of ClO_2 by Acticarbone L2S PAC (20 mg/L) at pH 7, with chlorine added.

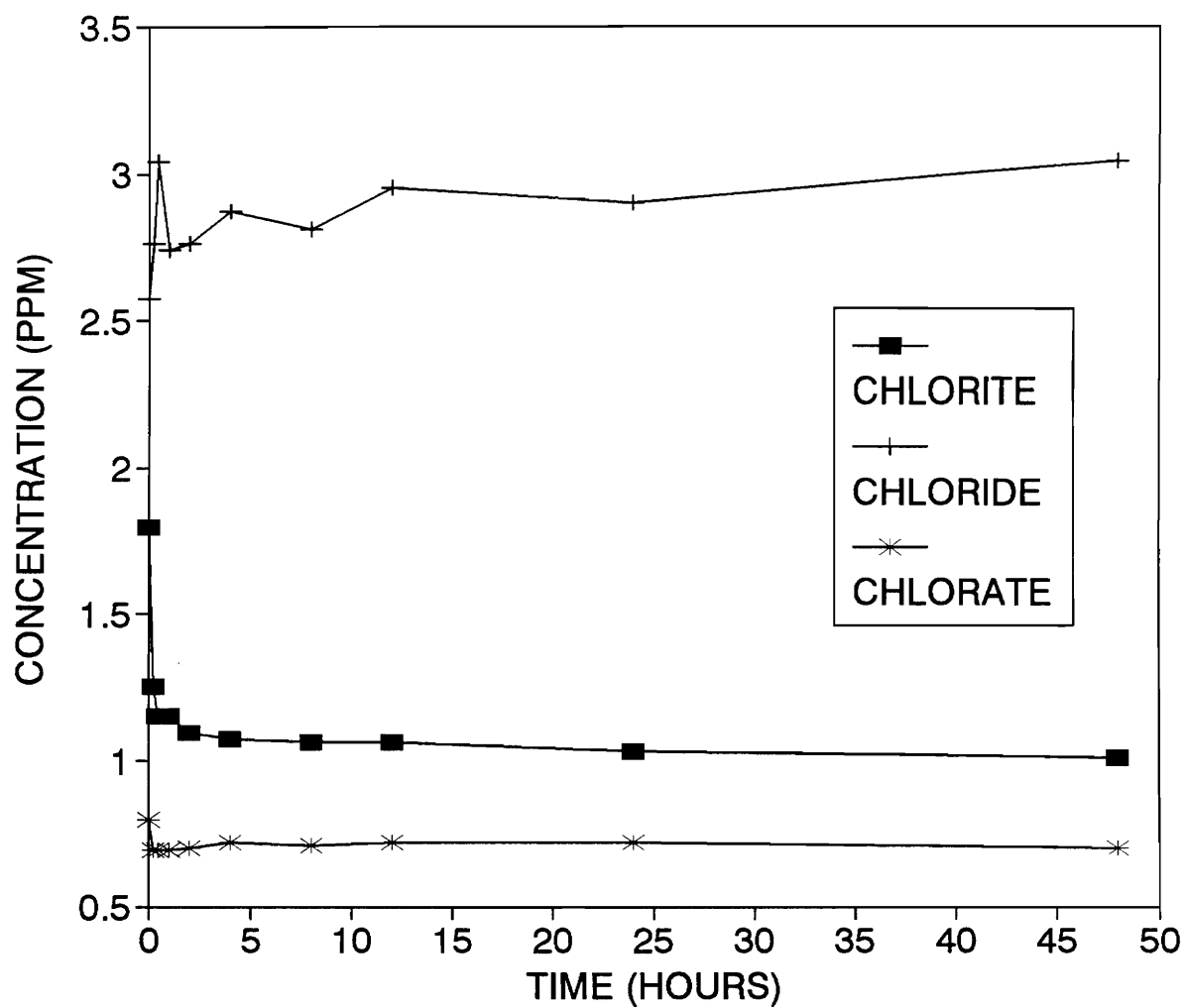


Figure B20. Concentration versus time during the removal of ClO_2 by Husky (Watercarb) PAC (20 mg/L) at pH 7, **with** chlorine added.

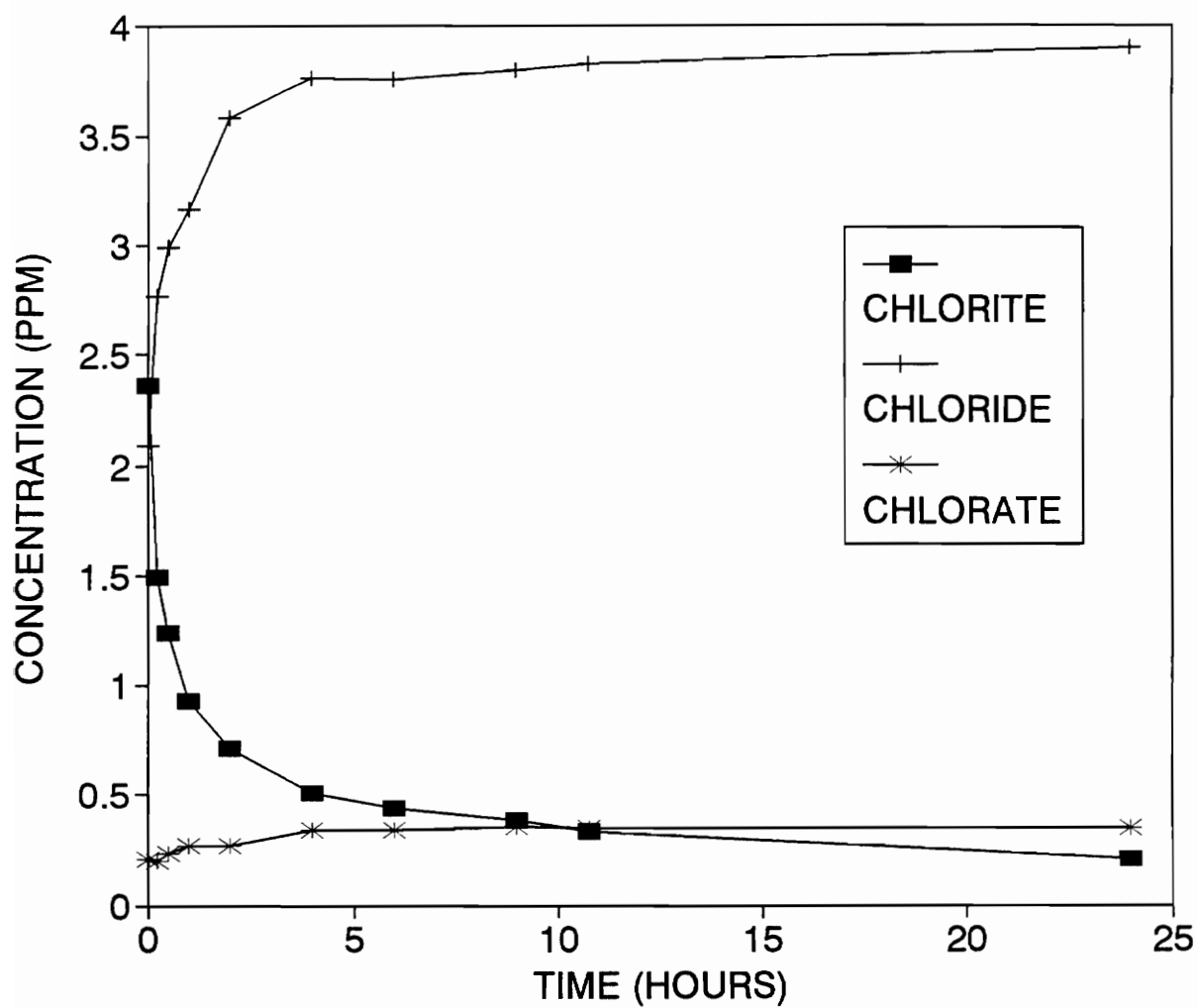


Figure B21. Concentration versus time during the removal of ClO_2 by Darco S-51 PAC (20 mg/L) at pH 7, **with** chlorine added.

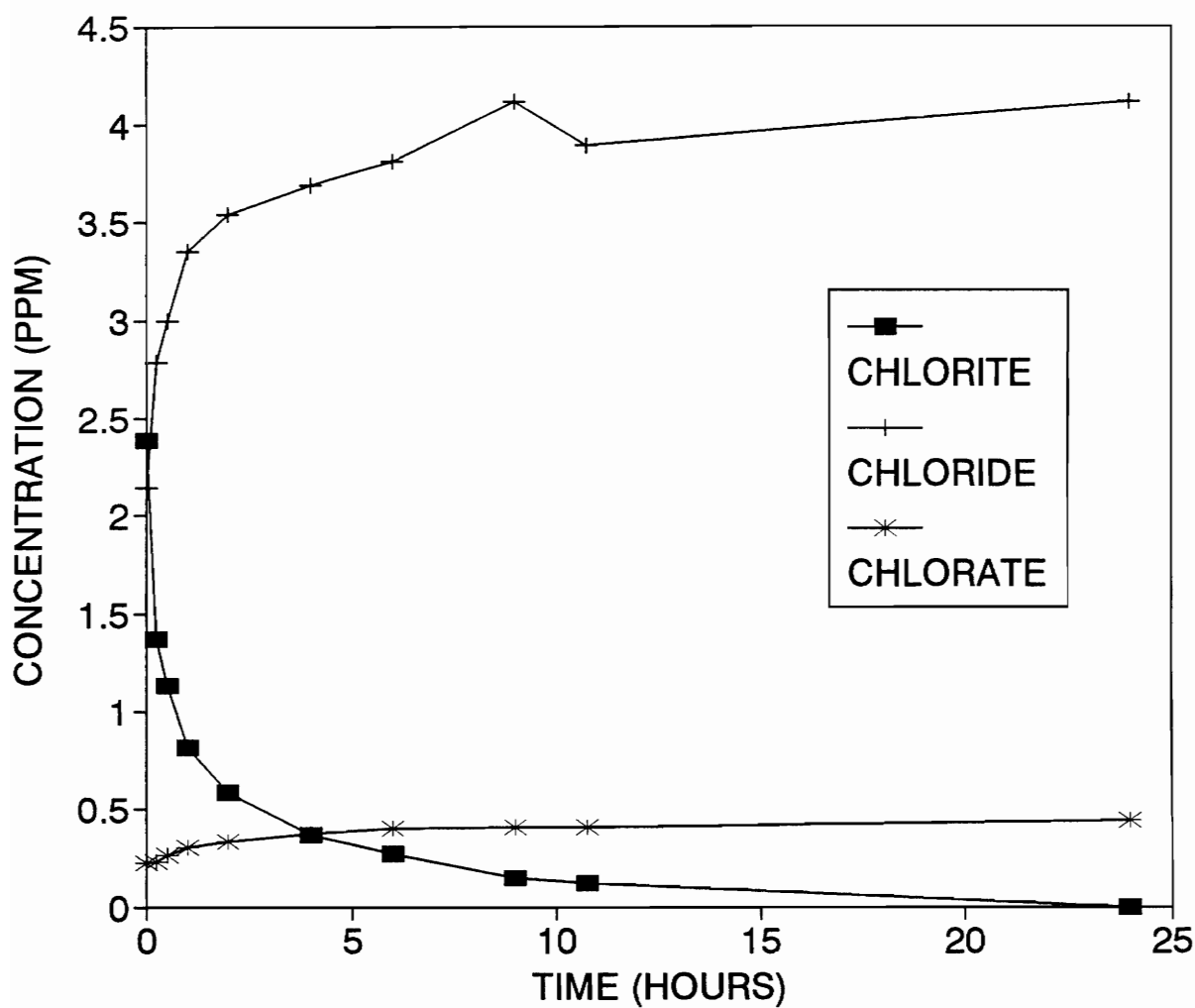


Figure B22. Concentration versus time during the removal of ClO_2 by Darco G-60 PAC (20 mg/L) at pH 7, **with** chlorine added.

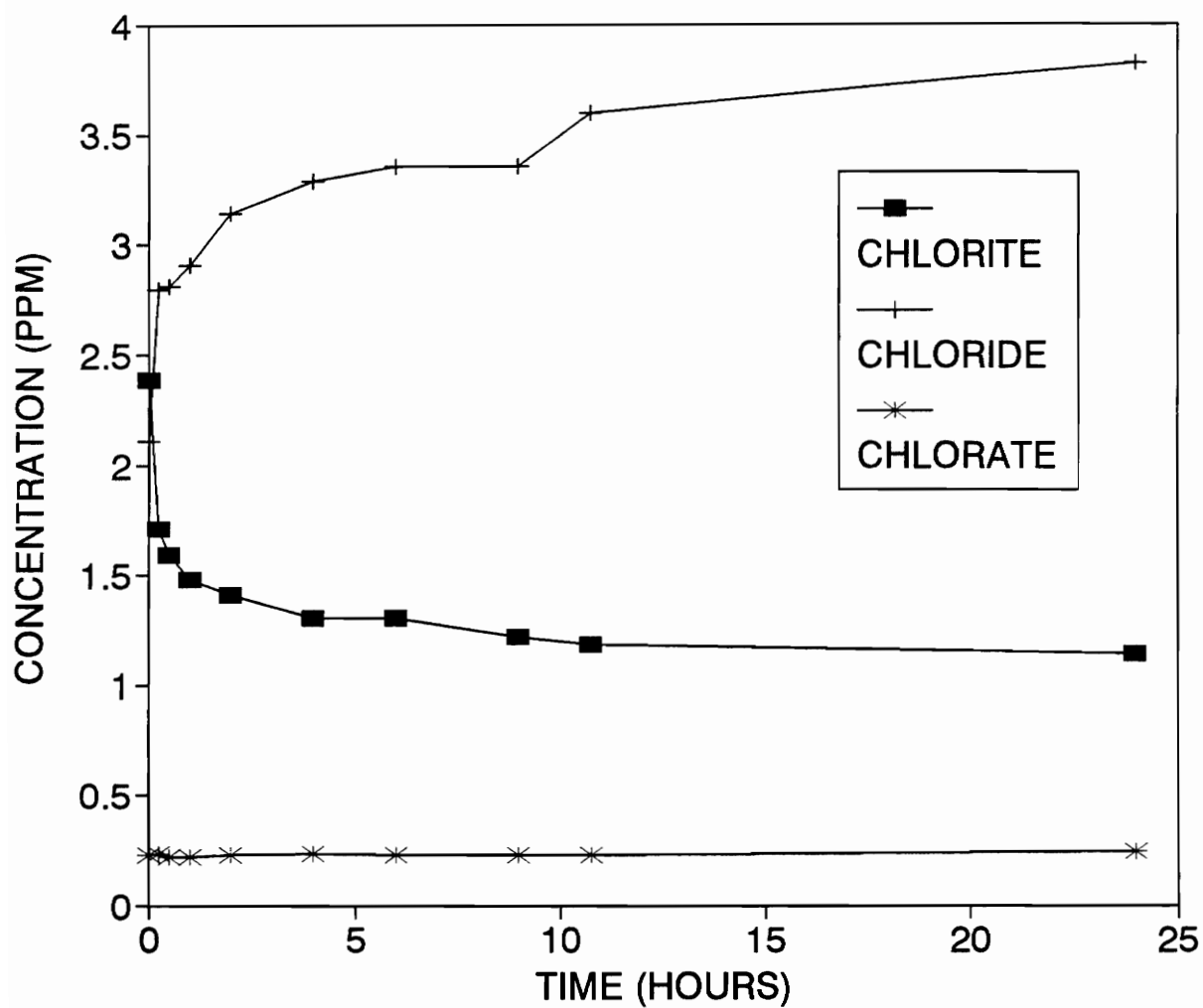


Figure B23. Concentration versus time during the removal of ClO_2 by Darco KB-B PAC (20 mg/L) at pH 7, with chlorine added.

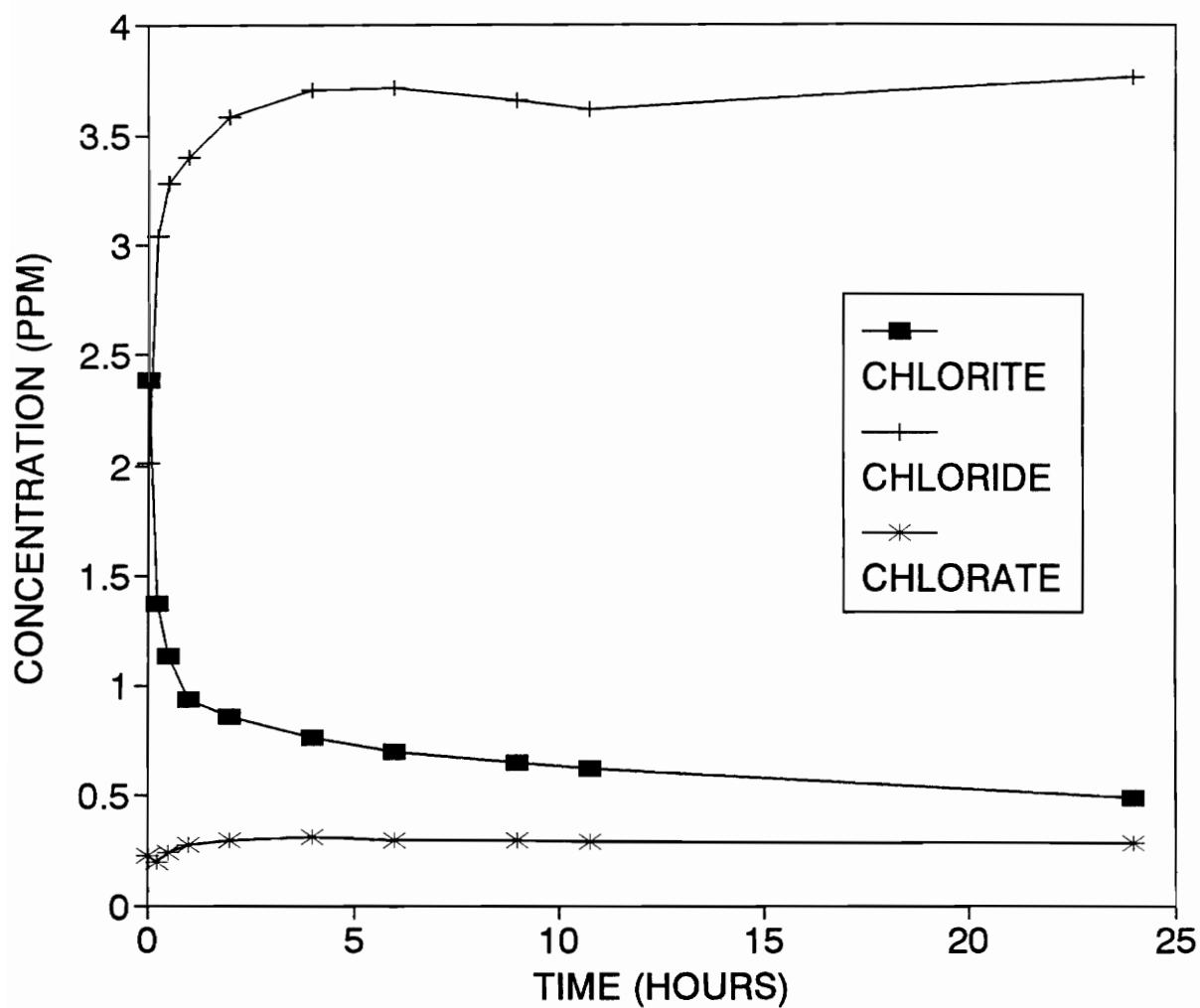


Figure B24. Concentration versus time during the removal of ClO_2 by Darco HDB PAC (20 mg/L) at pH 7, **with** chlorine added.

APPENDIX C
DATA AND PLOTS
COMPARING THE PACS

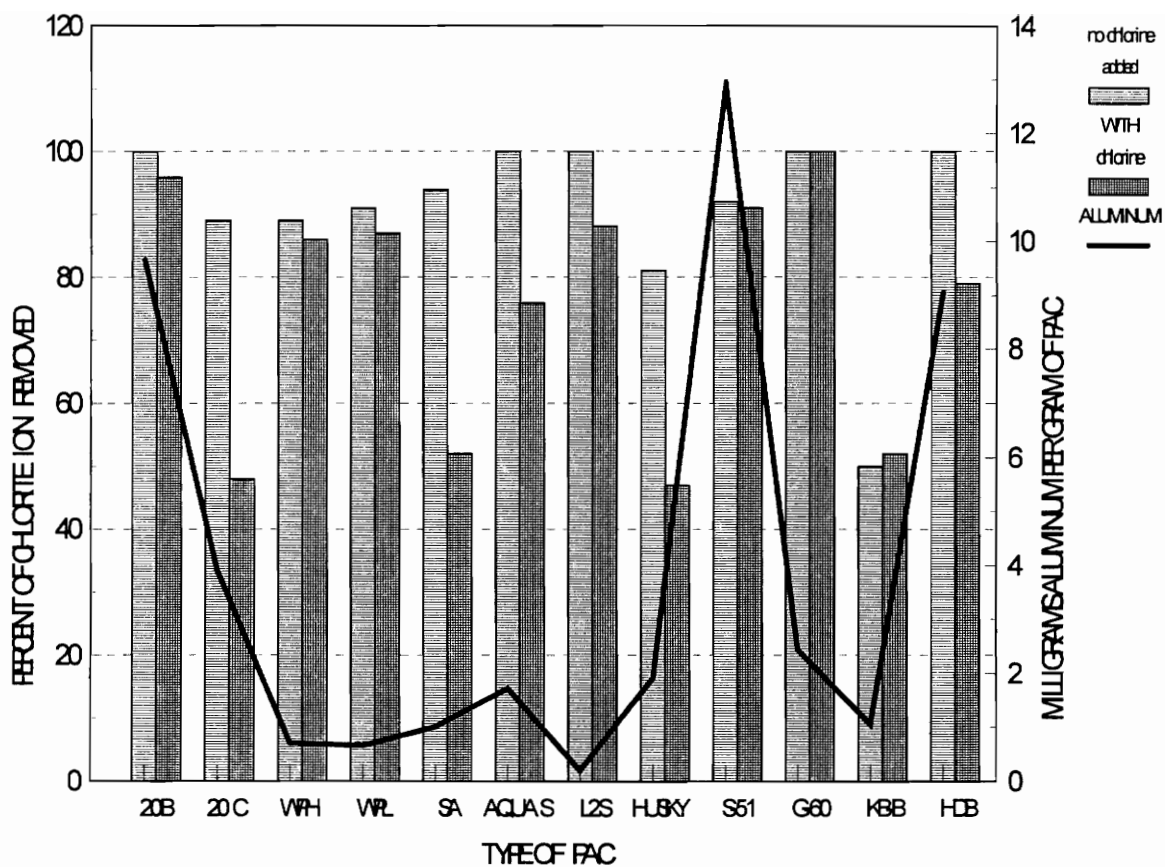


Figure C1. Summary of performance of twelve PACs in the removal of ClO_2^- versus milligrams of aluminum per gram of PAC after 24 hours contact.

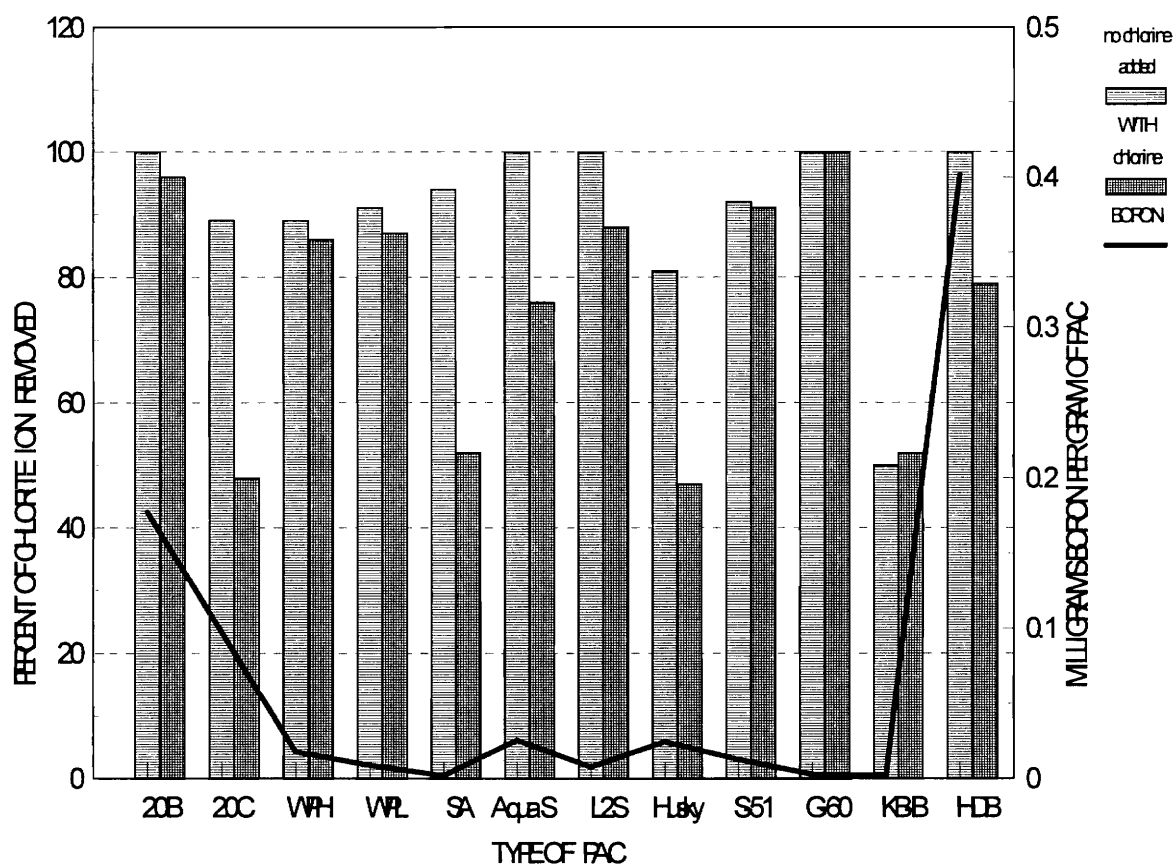


Figure C2. Summary of performance of twelve PACs in the removal of ClO_2^- versus milligrams of boron per gram of PAC after 24 hours contact.

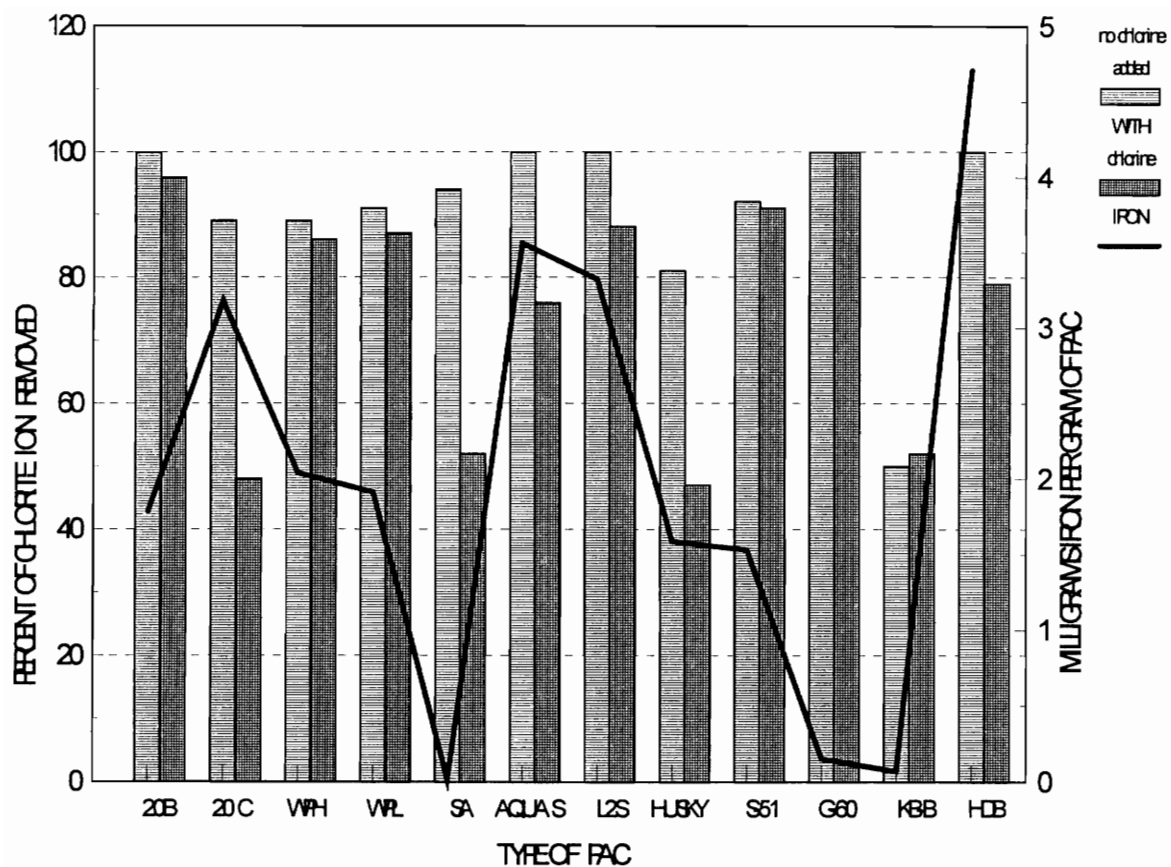


Figure C3. Summary of performance of twelve PACs in the removal of ClO_2^- versus milligrams of iron per gram of PAC after 24 hours contact.

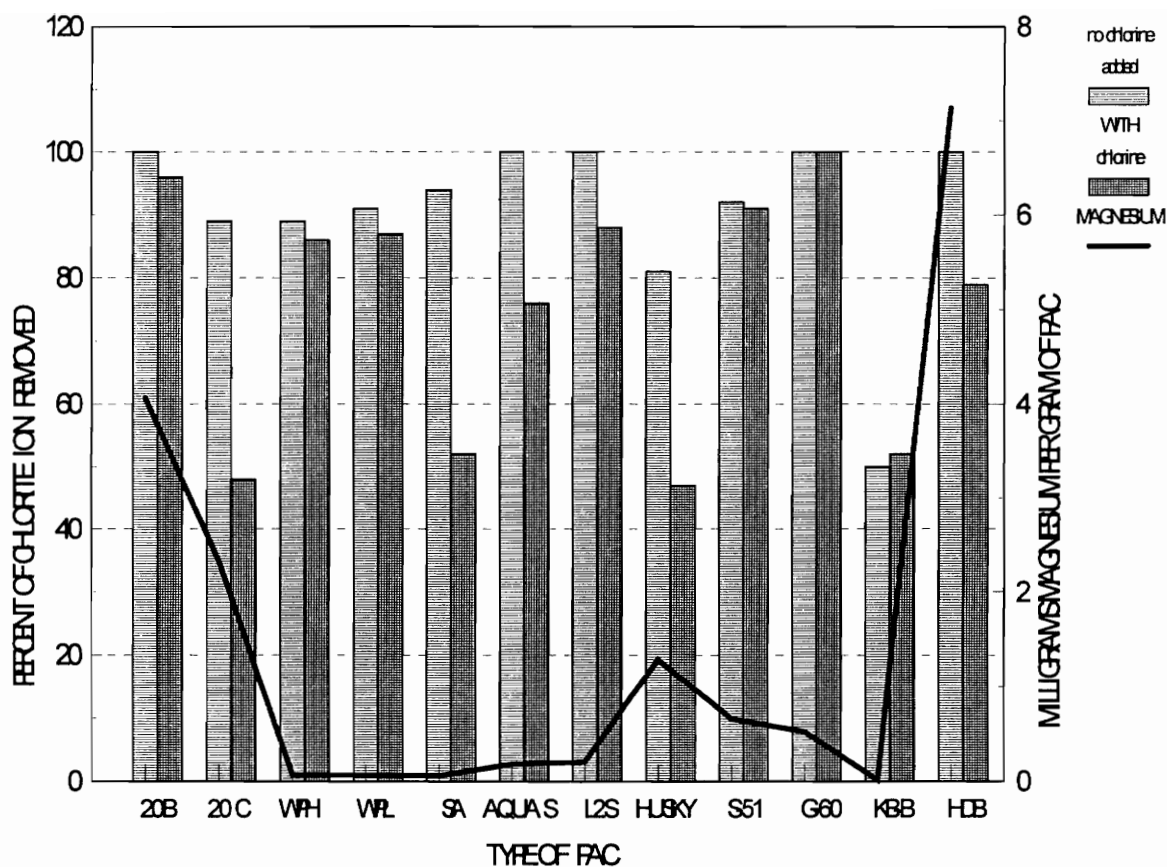


Figure C4. Summary of performance of twelve PACs in the removal of ClO_2^- versus milligrams of magnesium per gram of PAC after 24 hours contact.

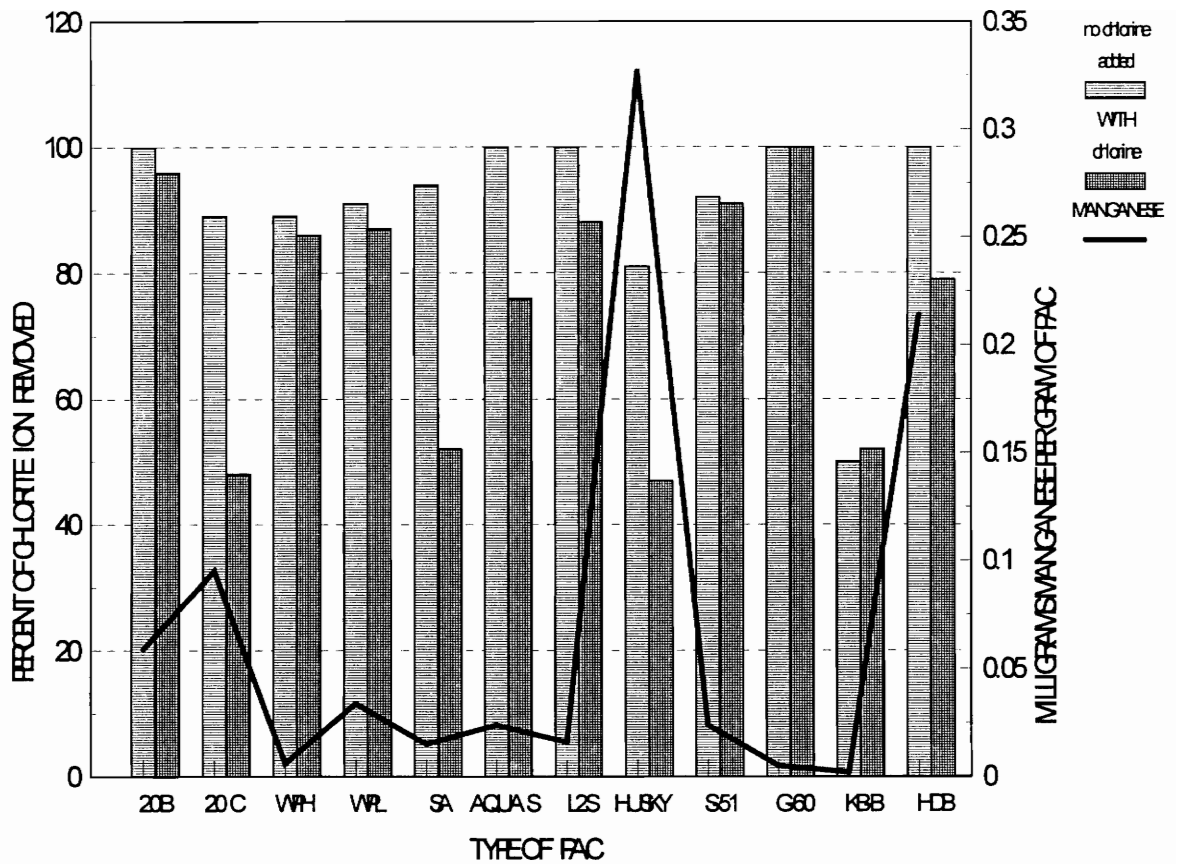


Figure C5. Summary of performance of twelve PACs in the removal of ClO_2^- versus milligrams of manganese per gram of PAC after 24 hours contact.

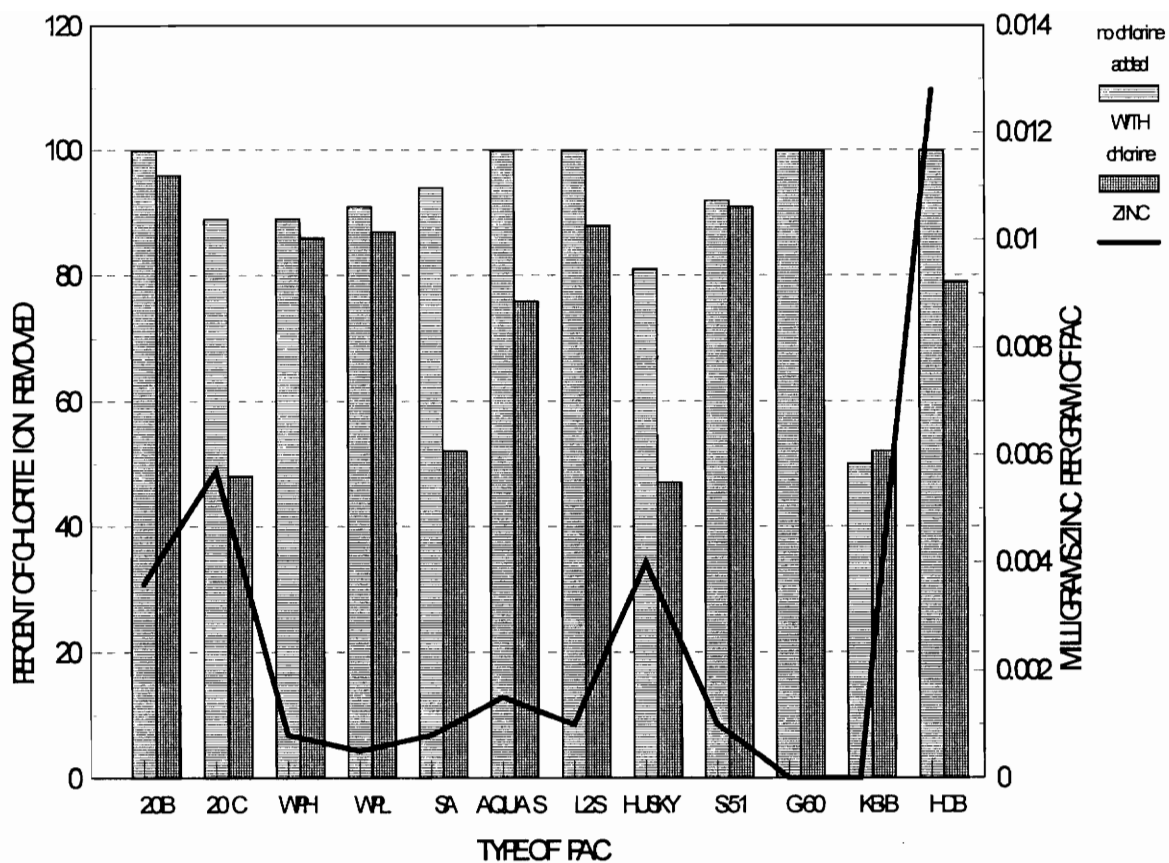


Figure C6. Summary of performance of twelve PACs in the removal of ClO_2^- versus milligrams of zinc per gram of PAC after 24 hours contact.

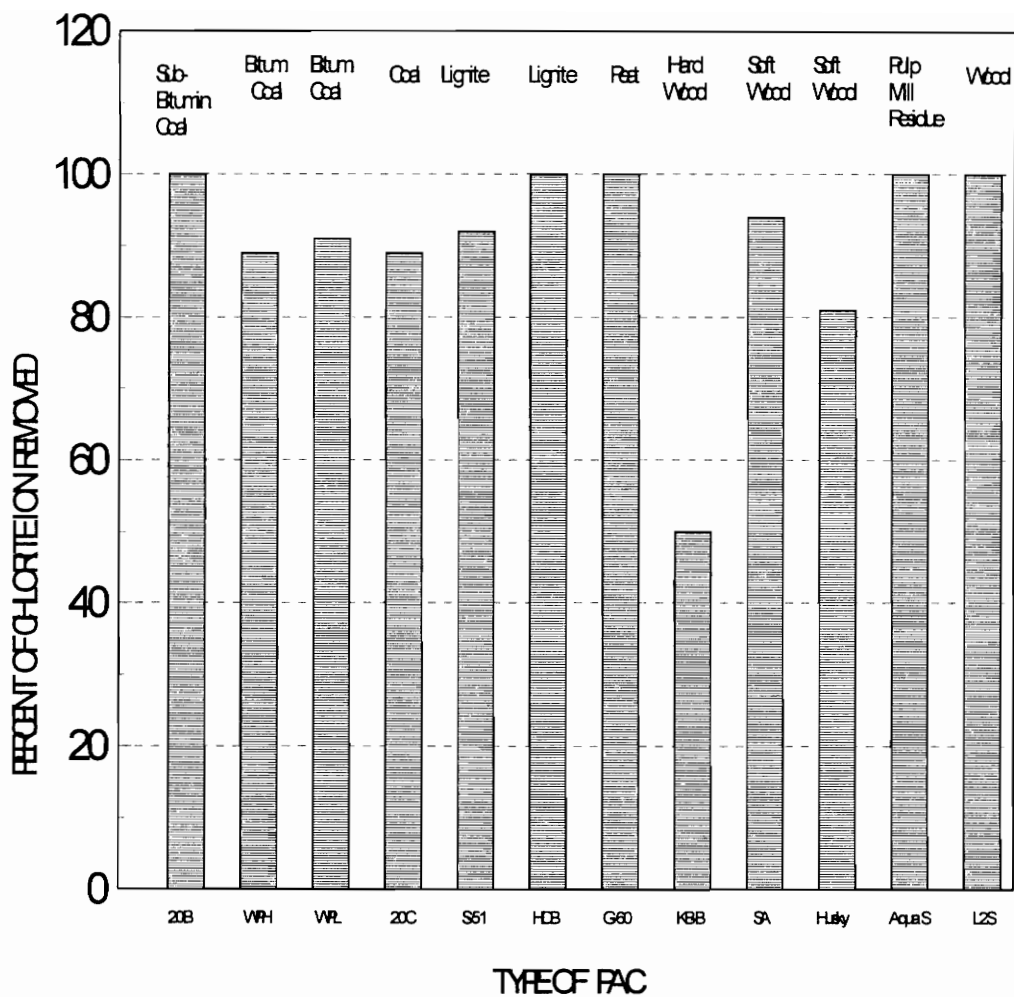


Figure C7. Raw material sources for PAC versus ClO_2^- removal percentages after 24 hours contact.

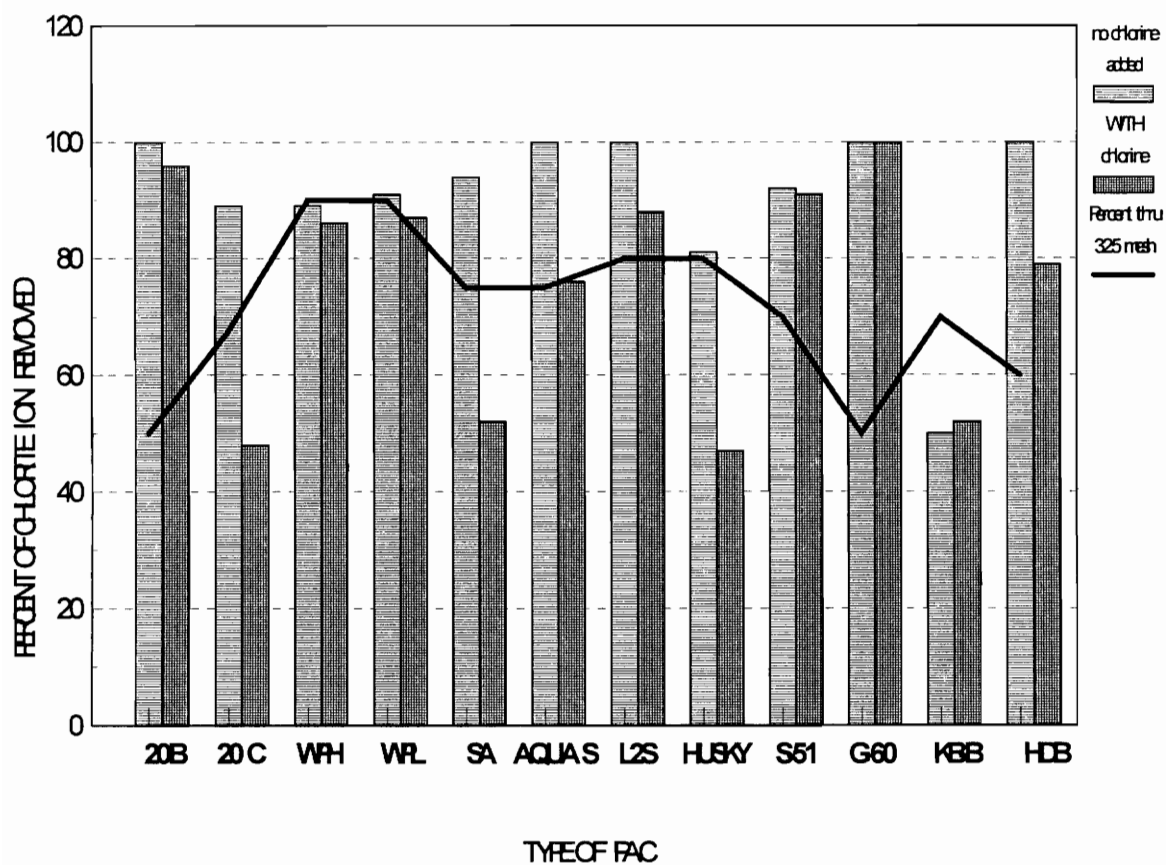


Figure C8. Percent of PAC passing through a 325 mesh screen versus ClO_2^- removal percentages after 24 hours contact.

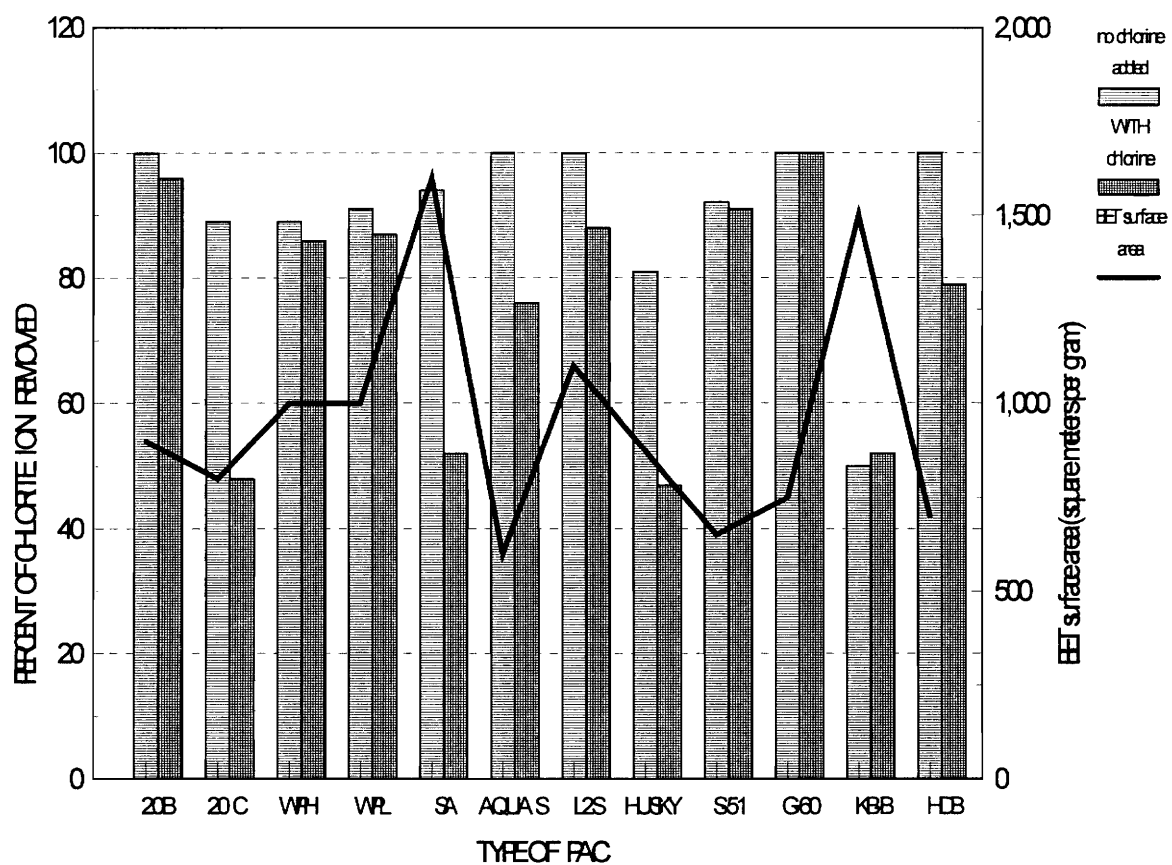


Figure C9. BET surface area versus ClO_2^- removal percentages for twelve PACs after 24 hours contact.

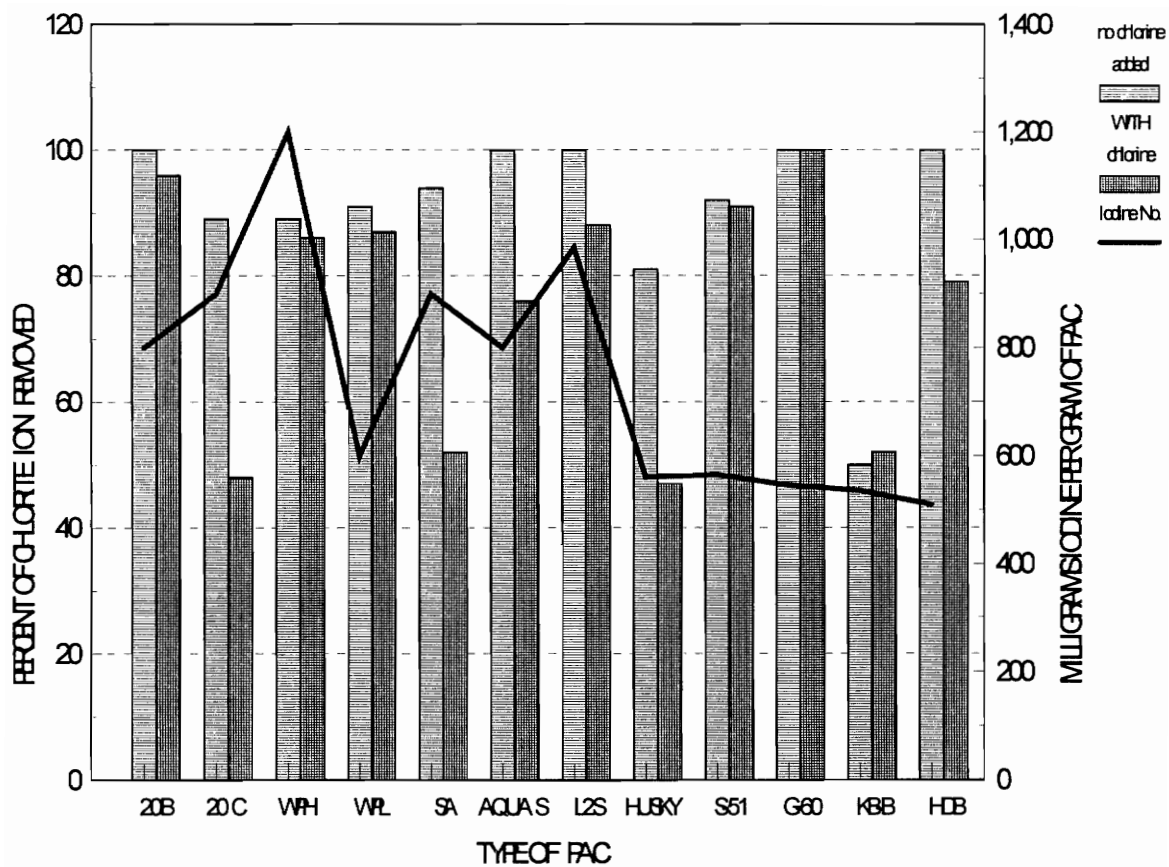


Figure C10. Iodine Number versus ClO_2 removal percentages for twelve PACs after 24 hours contact.

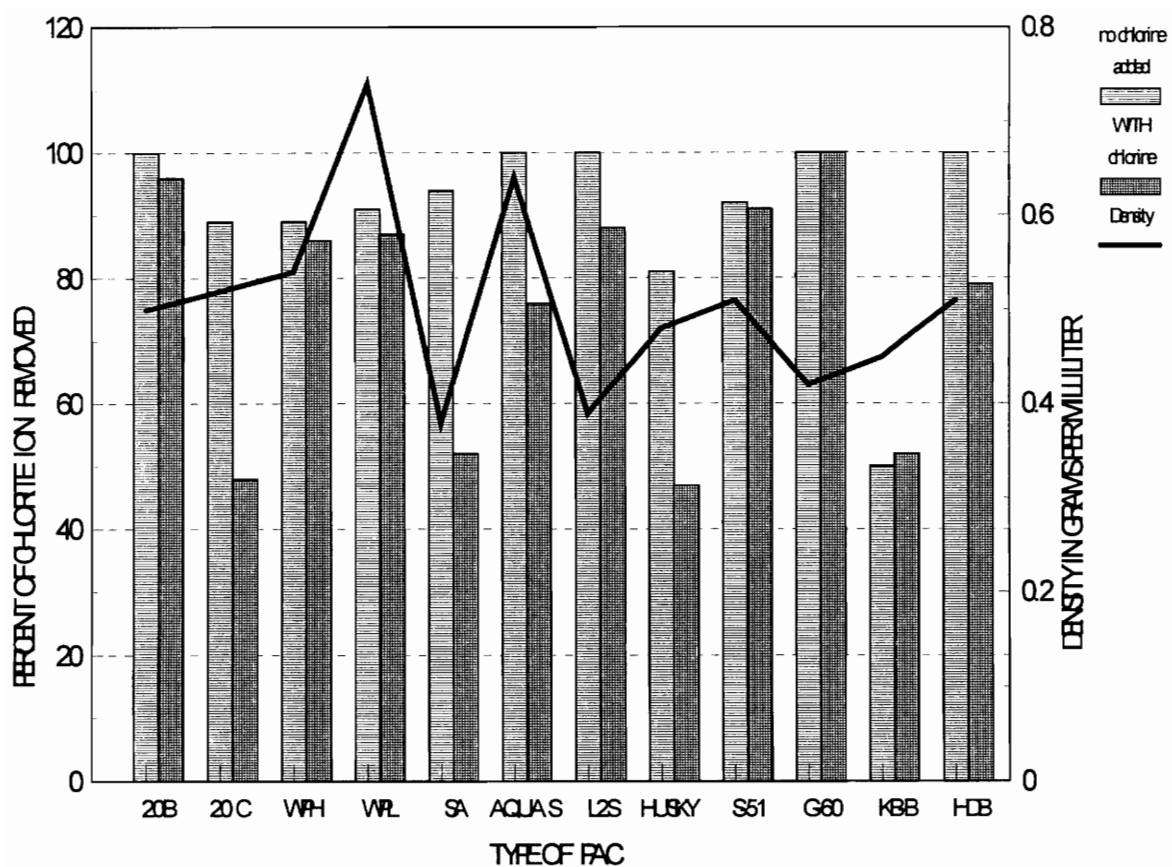


Figure C11. PAC Density versus ClO_2^- removal percentages for twelve PACs after 24 hours contact.

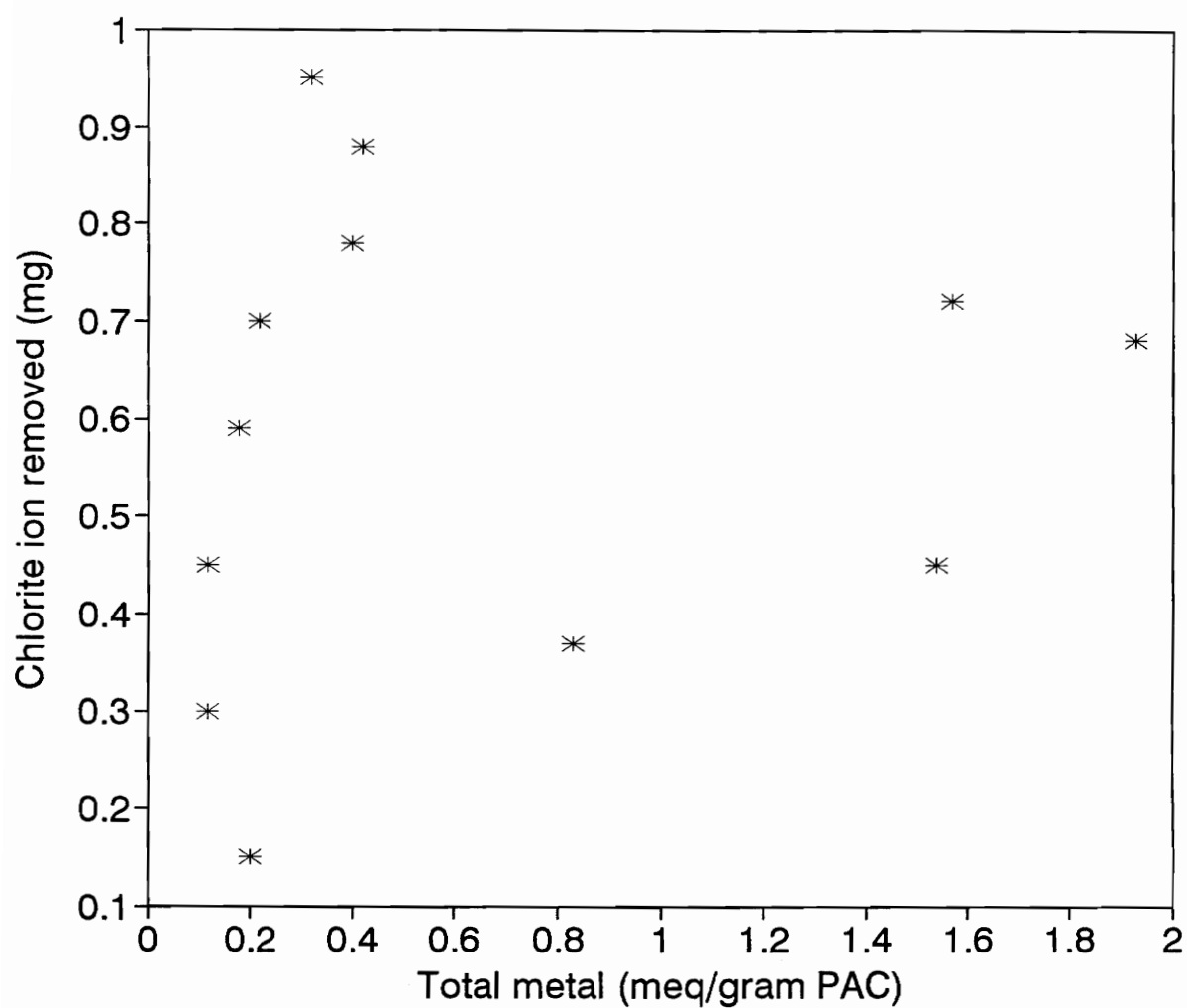


Figure C12. Total metal (aluminum, boron, iron, magnesium, manganese, and zinc) versus mg chlorite ion removal after 15 minutes contact time.

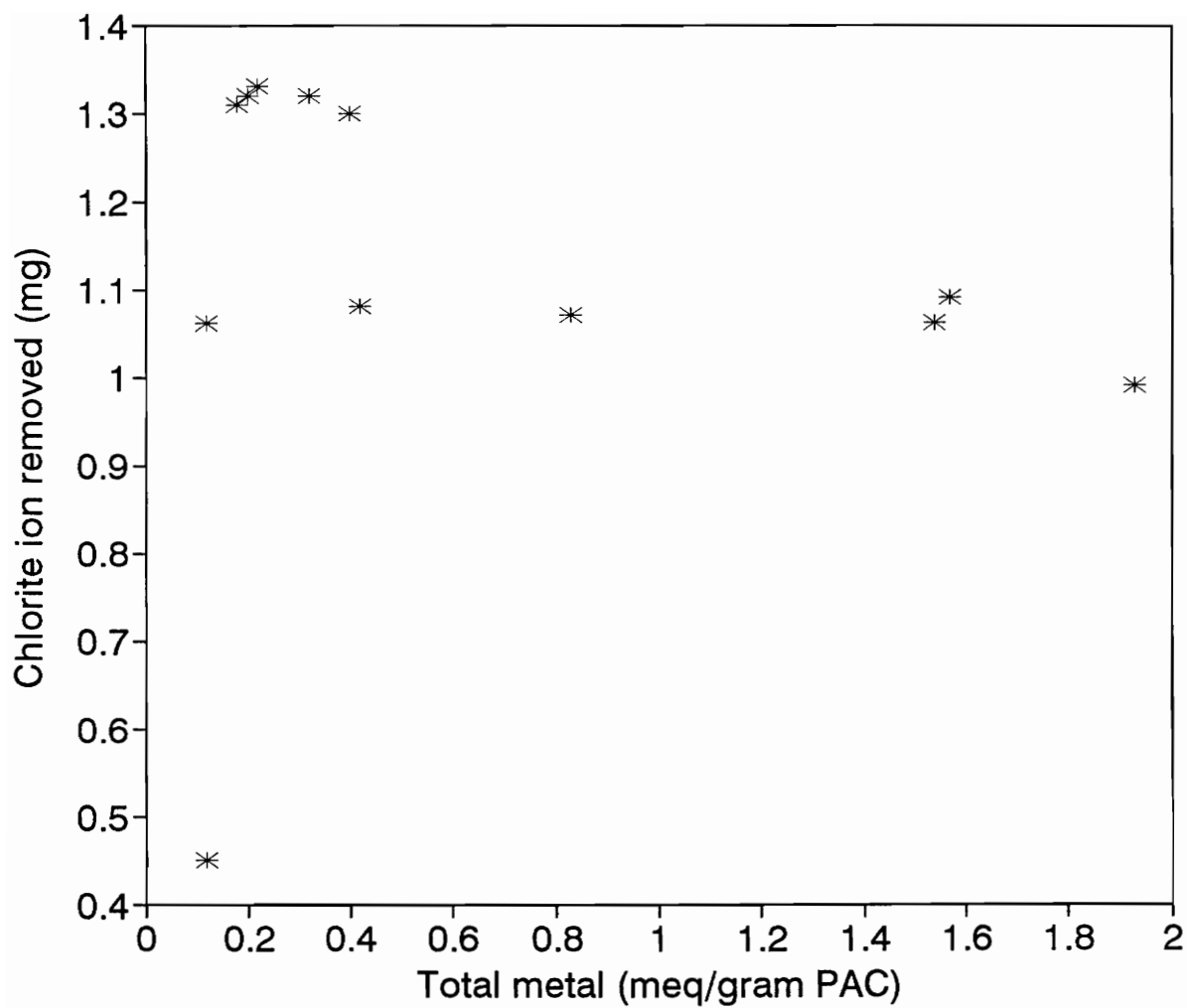


Figure C13. Total metal (aluminum, boron, iron, magnesium, manganese, and zinc) versus mg chlorite ion removal after 1 hour contact time.

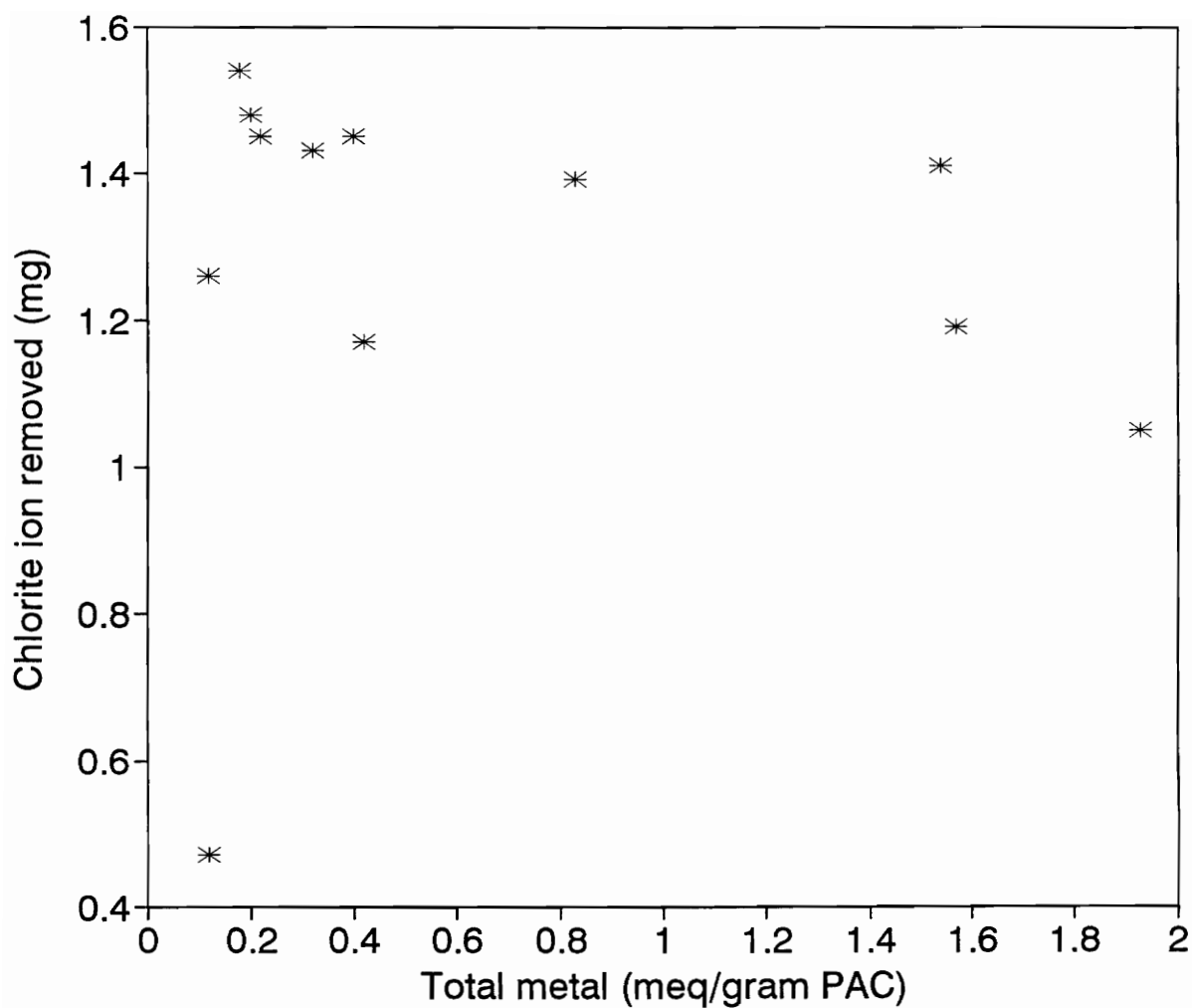


Figure C14. Total metal (aluminum, boron, iron, magnesium, manganese, and zinc) versus mg chlorite ion removal after 2 hours contact time.

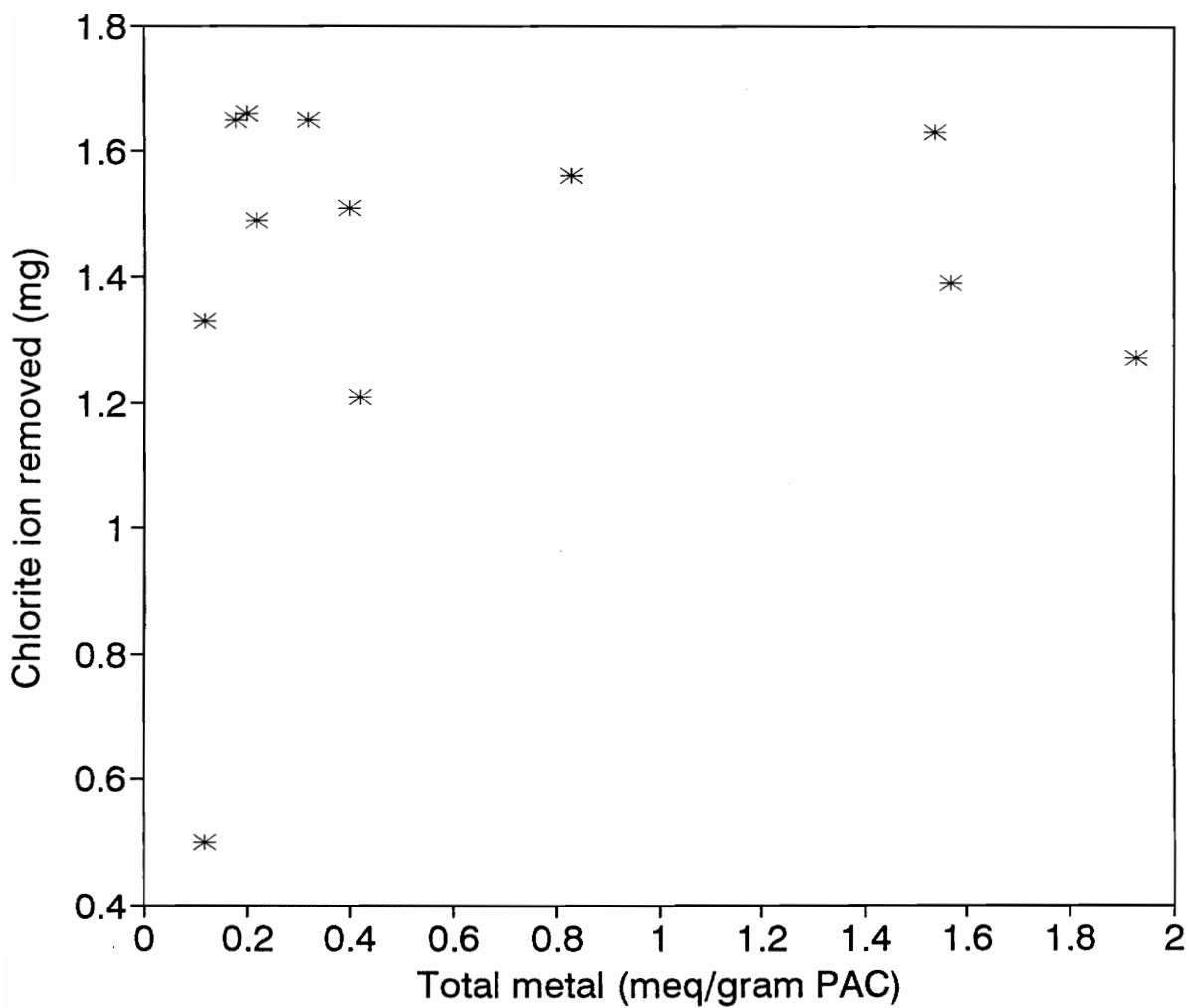


Figure C15. Total metal (aluminum, boron, iron, magnesium, manganese, and zinc) versus mg chlorite ion removal after 4 hours contact time.

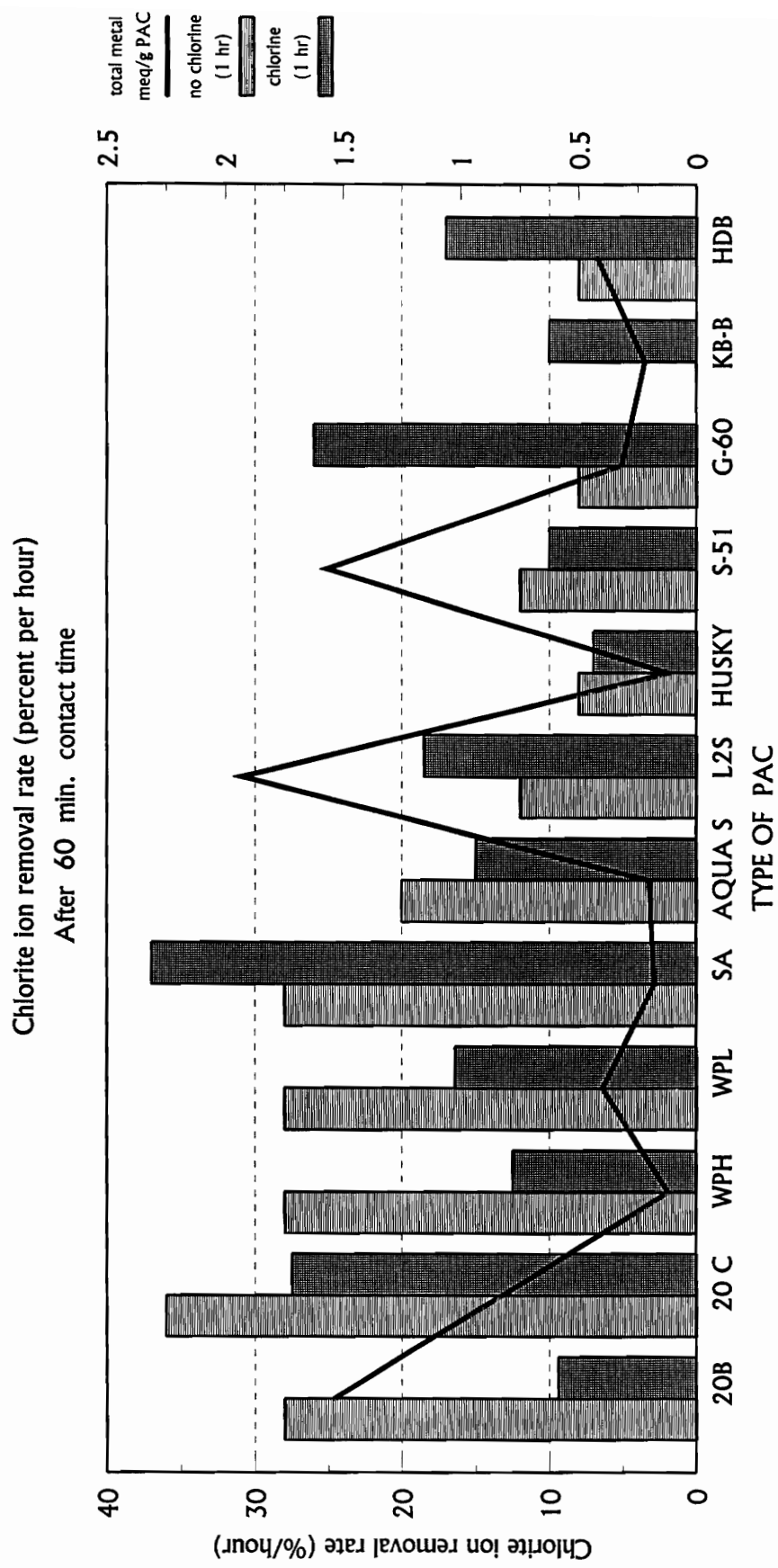


Figure C14. Rate of removal of ClO_2^- by each of the tested PACs after 1 hour contact time.

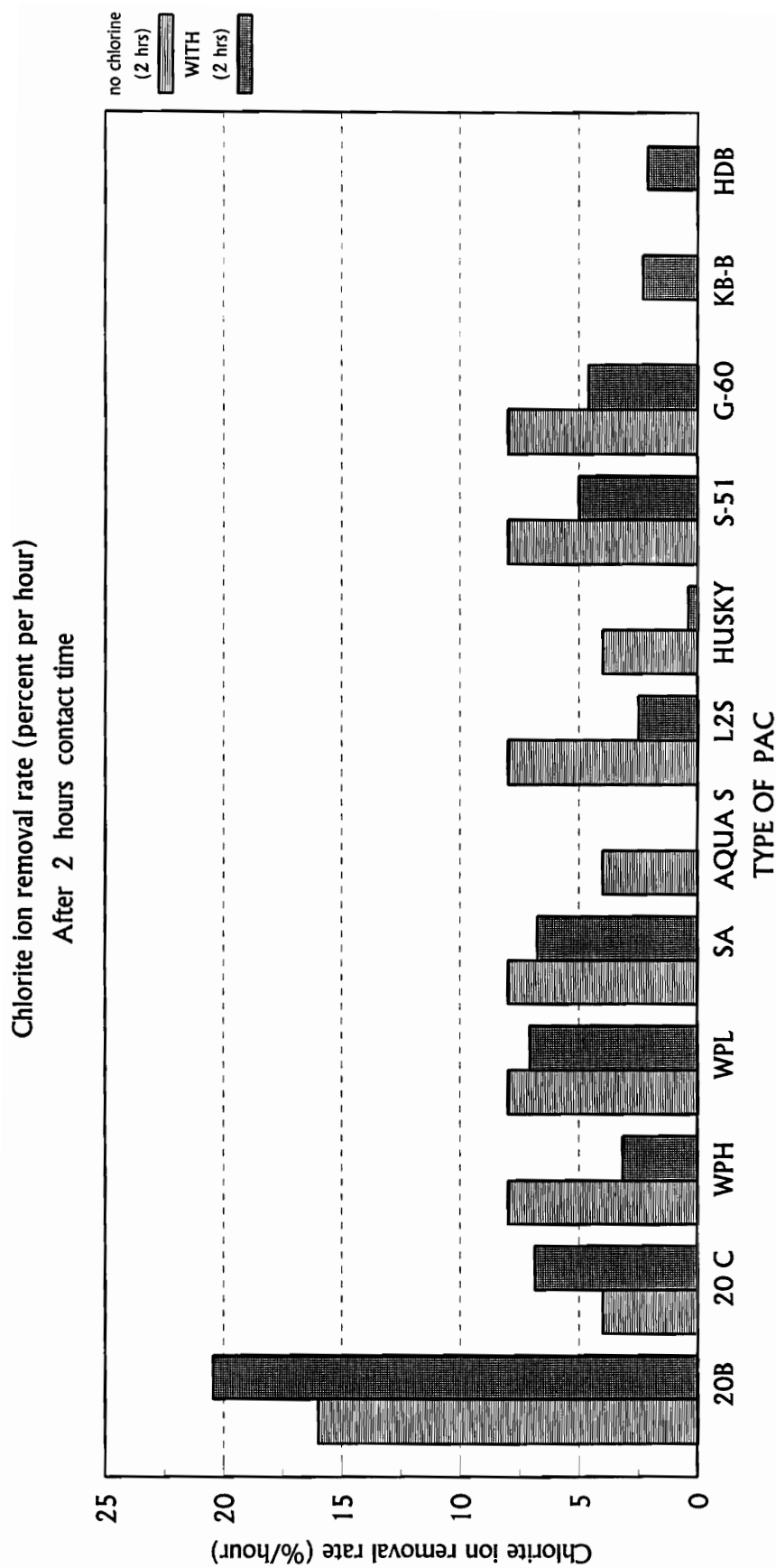


Figure C15. Rate of removal of ClO_2^- by each of the tested PACs after 2 hours contact time.

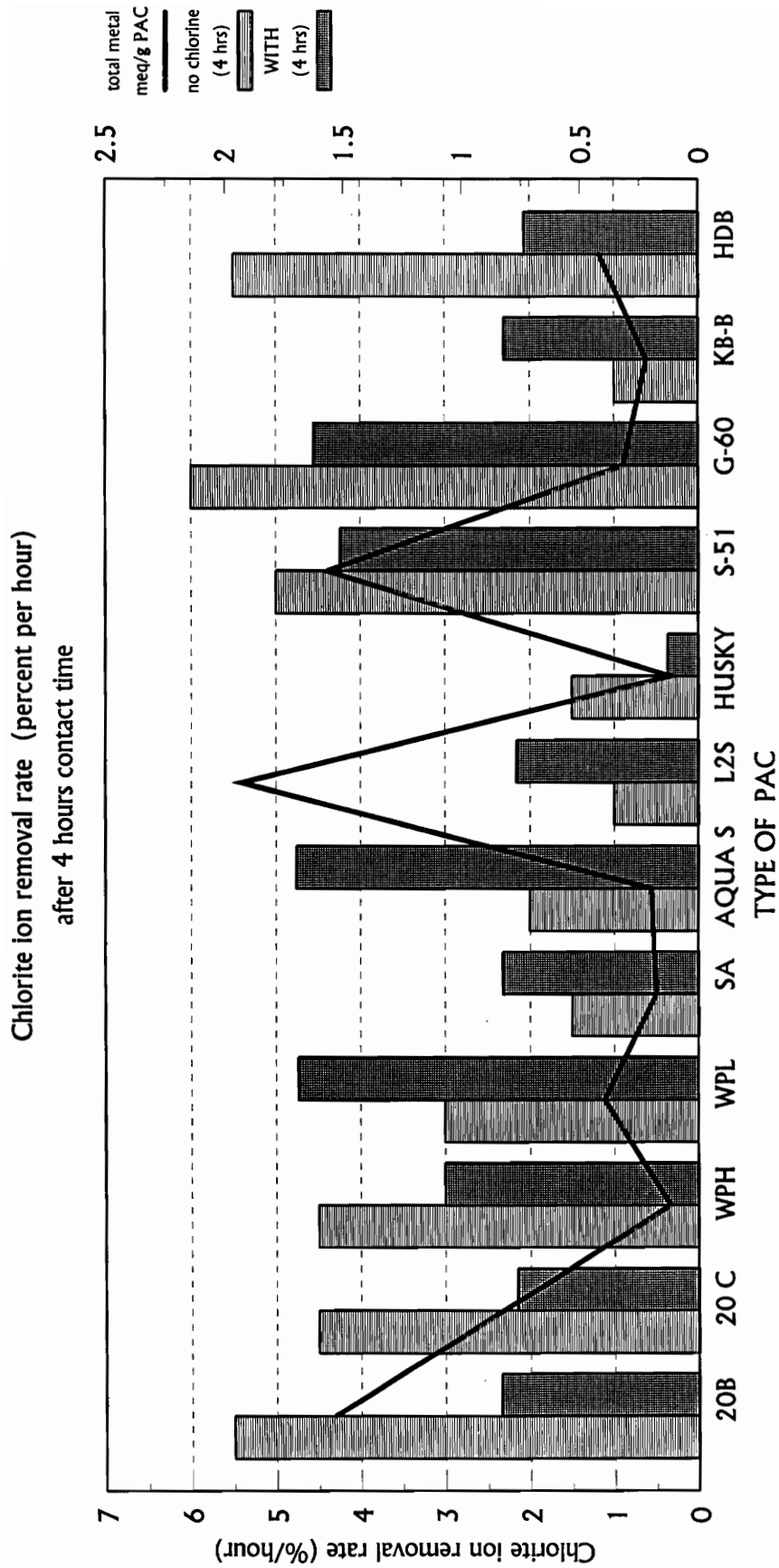


Figure C16. Rate of removal of ClO_2^- by each of the tested PACs after 4 hours contact time.

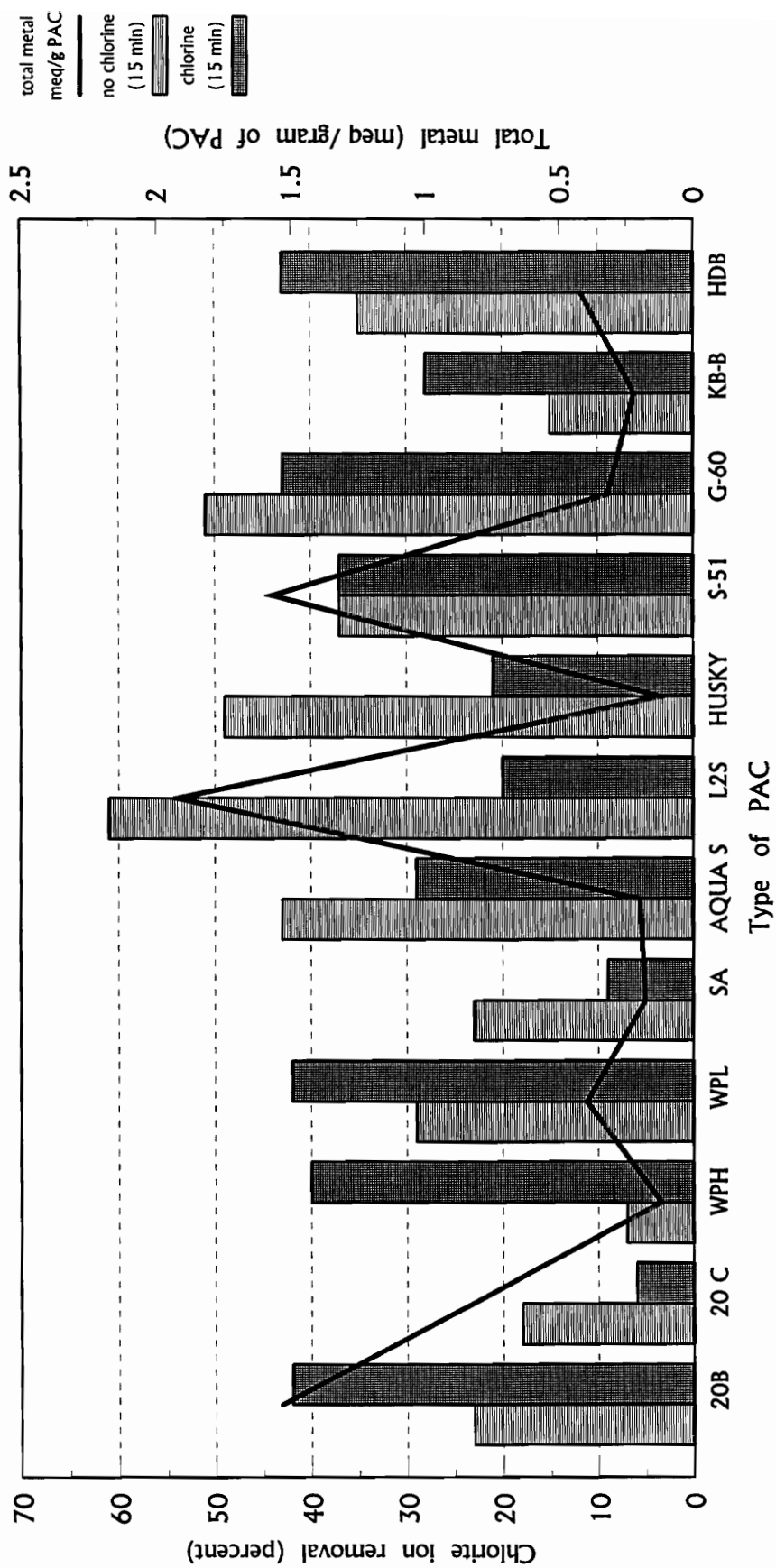


Figure C17. Percent removal of ClO_2^- by each of the tested PACs after 15 minutes contact time.

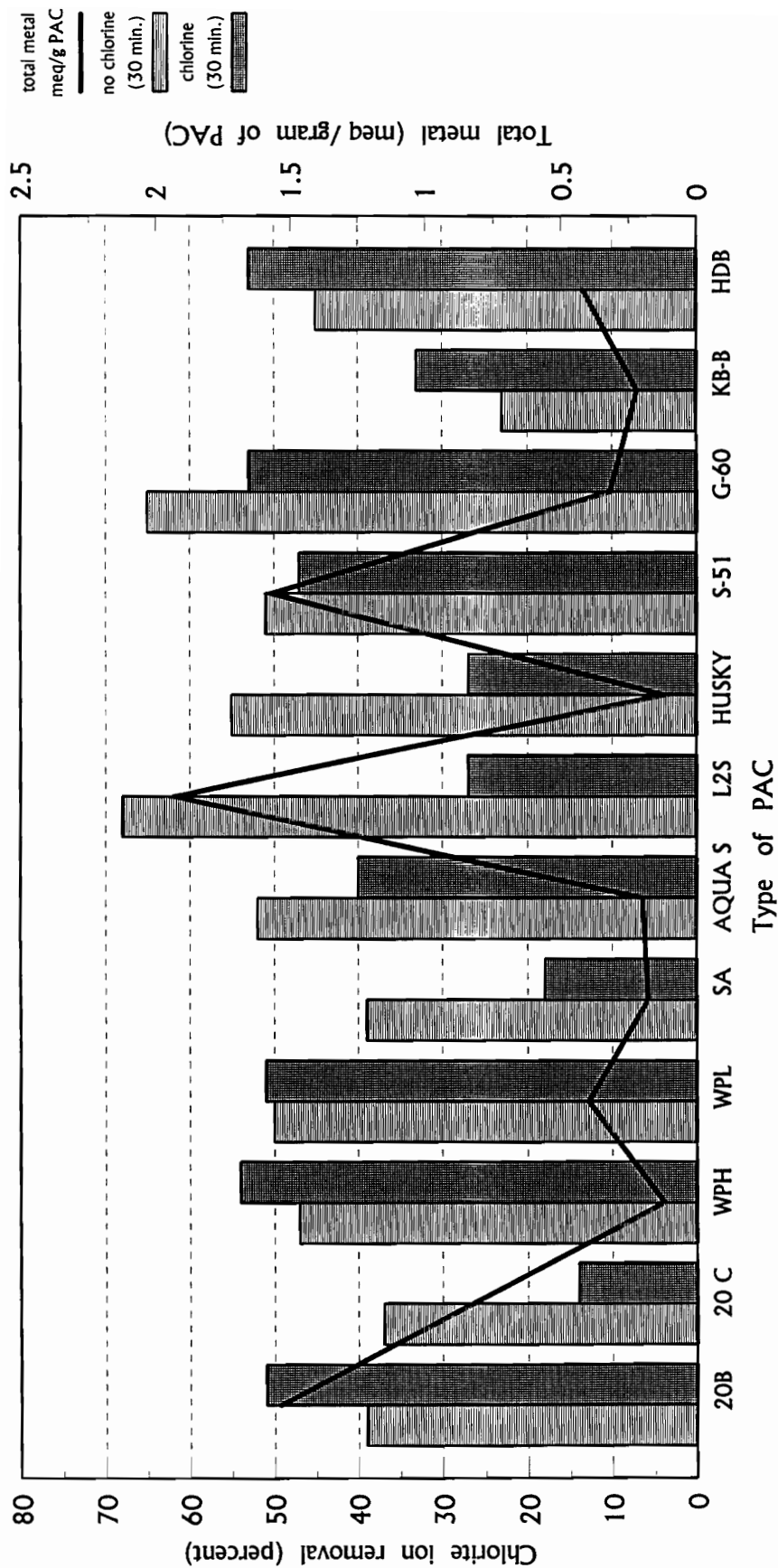


Figure C18. Percent removal of ClO_2^- by each of the tested PACs after 30 minutes contact time.

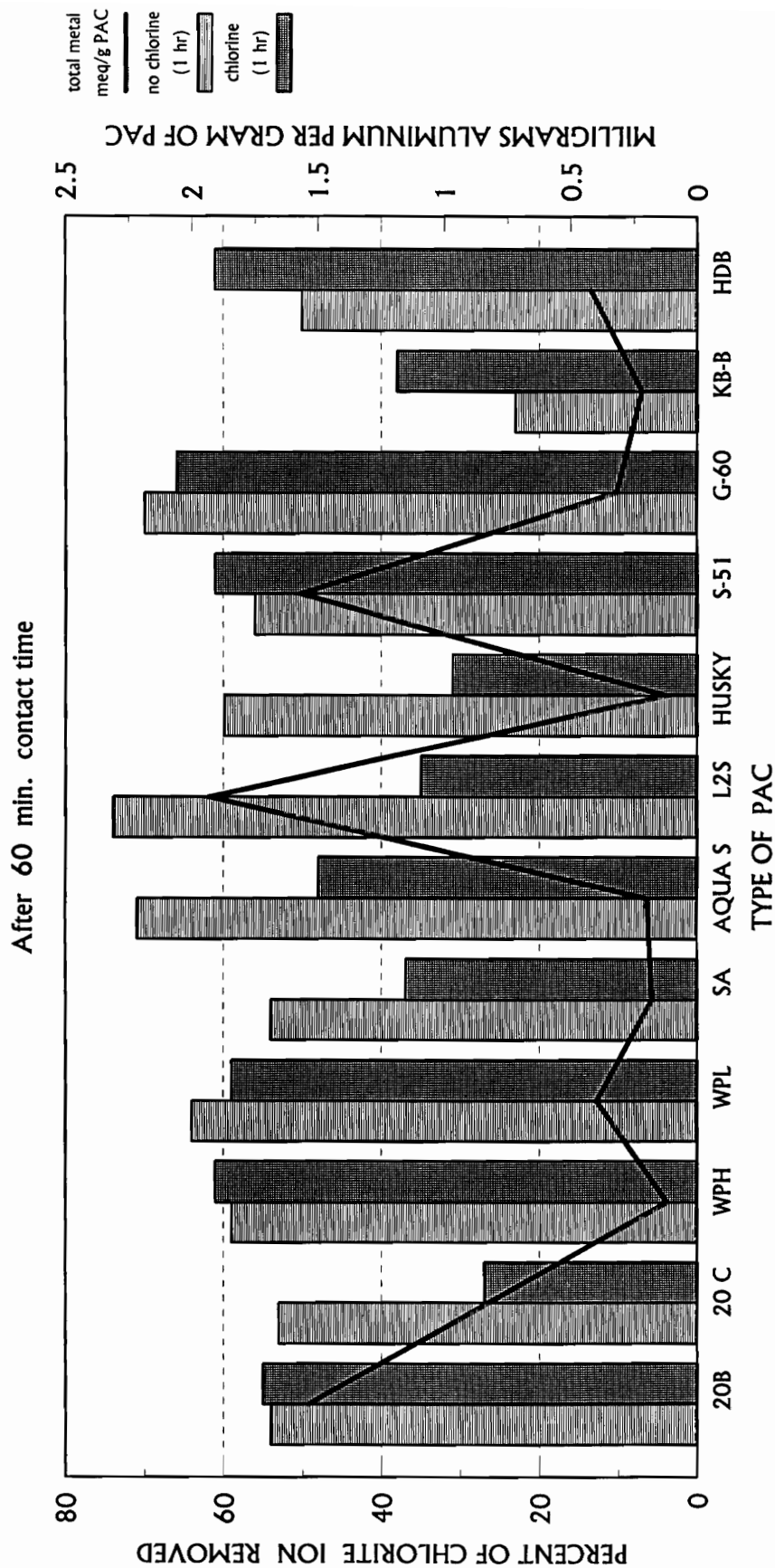


Figure C19. Percent removal of ClO_2^- by each of the tested PACs after 1 hour contact time.

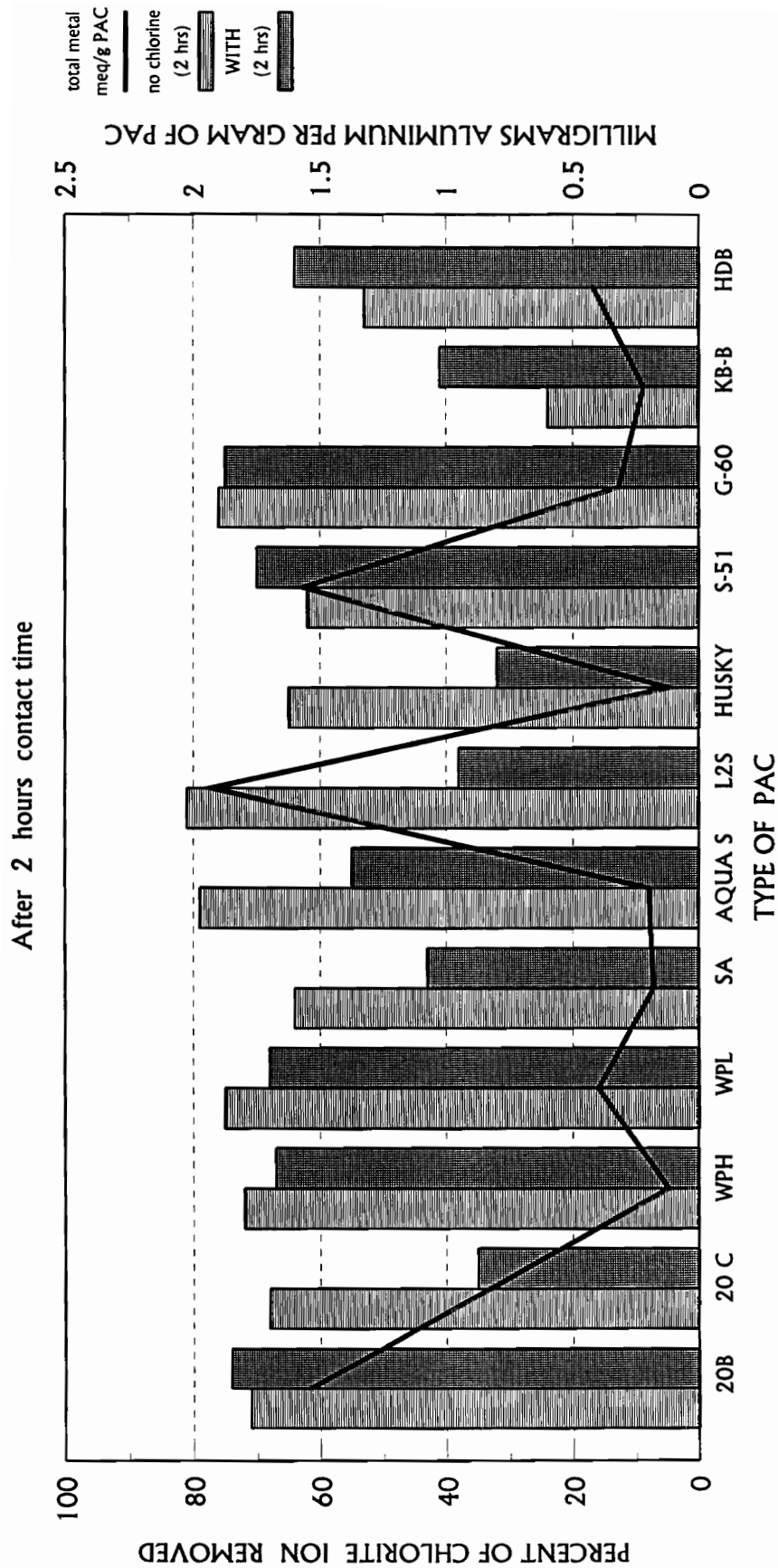


Figure C20. Percent removal of ClO_2^- by each of the tested PACs after 2 hours contact time.

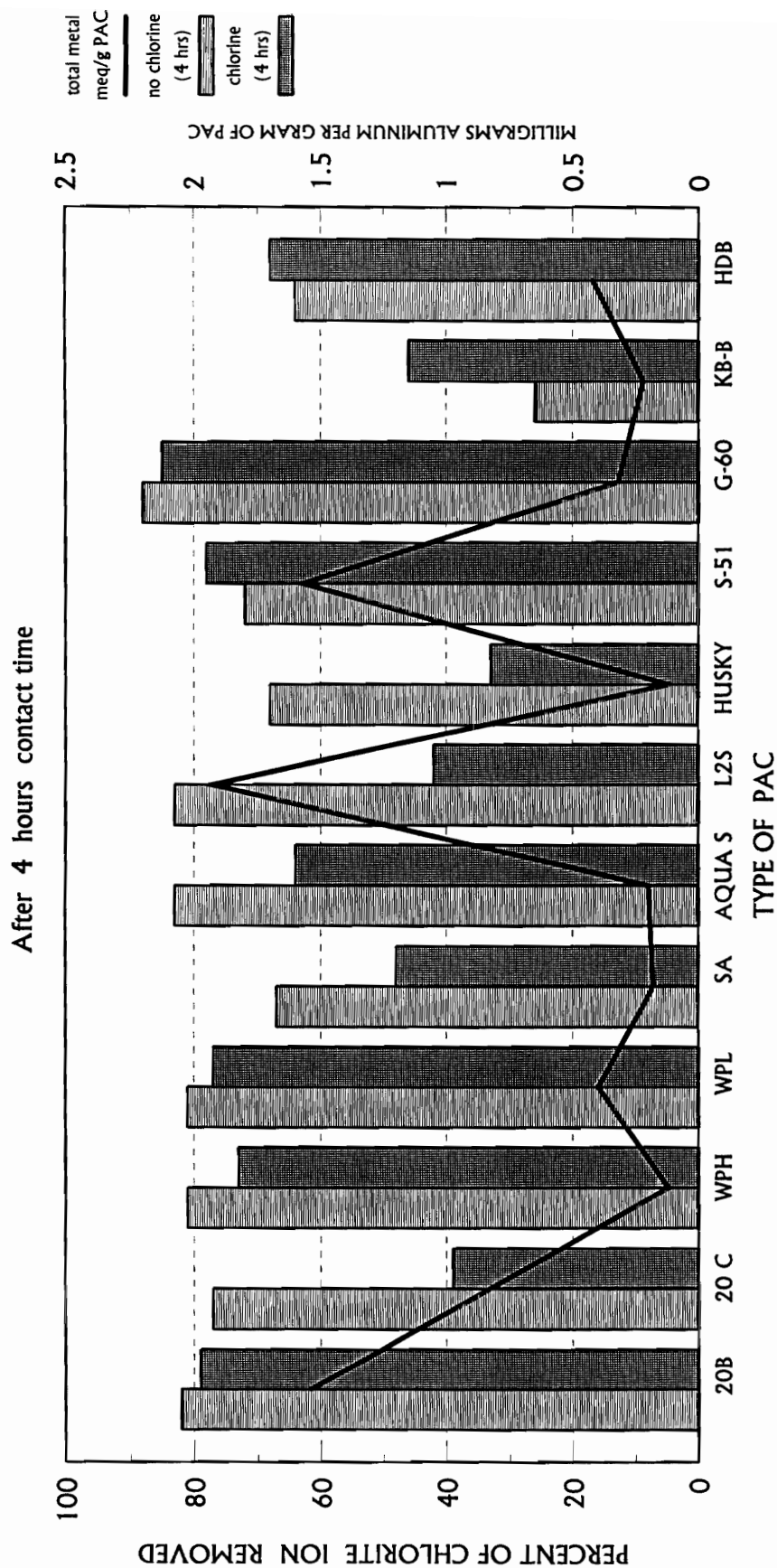


Figure C21. Percent removal of ClO_2^- by each of the tested PACs after 4 hours contact time.

Table C1. Results of measurements of metal content for each PAC.

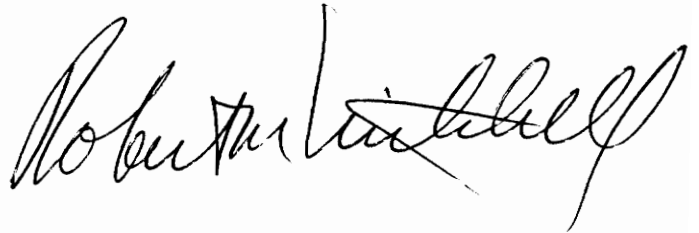
METALS CONTENT OF PACS AND MEQ OF METALS

PAC	BORON		IRON		ALUM.		MAG.		MAG.		MANG		MANG		TOTAL	
	mg per g PAC	meq per g PAC	mg per g PAC	meq per g PAC	mg per g PAC	meq per g PAC	mg per g PAC	meq per g PAC	mg per g PAC	meq per g PAC	mg per g PAC	meq per g PAC	mg per g PAC	meq per g PAC	mg per g PAC	meq per g PAC
20 B	0.177	0.03	1.78	0.10	9.67	1.07	4.07	0.33	0.059	0.00	0.00	0.00	0.00	0.00	1.54	0.83
20 C	0.174	0.03	3.18	0.17	3.91	0.43	2.33	0.19	0.095	0.00	0.00	0.00	0.00	0.00	0.83	0.12
SA	0.002	0.00	0.016	0.00	1.01	0.11	0.058	0.00	0.015	0.00	0.00	0.00	0.00	0.00	0.12	0.40
AQUA S	0.026	0.00	3.56	0.19	1.72	0.19	0.182	0.01	0.024	0.00	0.00	0.00	0.00	0.00	0.40	0.18
WPL	0.009	0.00	1.91	0.10	0.663	0.07	0.065	0.01	0.034	0.00	0.00	0.00	0.00	0.00	0.18	0.20
WPH	0.018	0.00	2.04	0.11	0.708	0.08	0.068	0.01	0.006	0.00	0.00	0.00	0.00	0.00	0.20	1.93
HDB	0.402	0.07	4.71	0.25	9.06	1.01	7.14	0.59	0.214	0.01	0.00	0.00	0.00	0.00	1.93	0.12
KB-B	0.002	0.00	0.069	0.00	1.05	0.12	0.013	0.00	0.002	0.00	0.00	0.00	0.00	0.00	0.12	1.57
S-51	0.013	0.00	1.53	0.08	12.9	1.43	0.659	0.05	0.024	0.00	0.00	0.00	0.00	0.00	1.57	0.32
G-60	0.003	0.00	0.152	0.01	2.43	0.27	0.528	0.04	0.005	0.00	0.00	0.00	0.00	0.00	0.32	0.22
L 2 S	0.008	0.00	3.32	0.18	0.198	0.02	0.204	0.02	0.016	0.00	0.00	0.00	0.00	0.00	0.22	0.42
HUSKY	0.025	0.00	1.59	0.09	1.92	0.21	1.29	0.11	0.327	0.01	0.00	0.00	0.00	0.00	0.42	

(NOTE: ZINC IS 0.00 meq per gram of PAC TO THE TWO SIGNIFICANT DIGITS USED HERE)

Vita

Robert Mitchell was born on January 27, 1939 in Fort Morgan, Colorado. He graduated from the University of Colorado in Boulder, Colorado with a B. S. degree in Electrical Engineering. He worked for the United States Navy as a submarine officer and nuclear engineer for 28 years before returning to school at Virginia Tech where he received a Master of Science in Environmental Engineering, Spring, 1993.

A handwritten signature in black ink, reading "Robert Mitchell". The signature is written in a cursive style with a large, stylized initial 'R' and a long, sweeping underline.