

ABSTRACT

CHARLES VANCE BROOKS, IV. The Practical Use of Chlorine Dioxide for Trihalomethane Control in Drinking Water (Under the direction of DR. PHILIP C. SINGER).

Three Southeastern United States water treatment plants using chlorine dioxide, one of the methods available for controlling trihalomethanes, are studied in detail. Treatment records are reviewed, and tests of the water are made for THM, TOX, TOC, and residual disinfectants.

A treatment scheme using ClO_2 as a pre-oxidant/disinfectant and Cl_2 as a final disinfectant is found to give fairly equivalent water to that from the same treatment scheme using Cl_2 alone. Trihalomethane concentration is greatly reduced when using ClO_2/Cl_2 rather than Cl_2 alone. However, high chlorite concentration and microorganism regrowth in the distribution system can both be problems in poor quality waters.

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Charles Vance Brooks, IV
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I. INTRODUCTION

A. Trihalomethane Problem and Regulation.

Trihalomethanes were first reported to exist in drinking water as a result of chlorination by Rook in 1974.¹ In an effort to verify this as well as study the prevalence of the trihalomethane problem throughout the nation, the United States Environmental Protection Agency (EPA) initiated the National Organics Reconnaissance Survey (NORS)² in 1975. EPA confirmed that trihalomethanes were produced as a result of chlorination, found that chloroform appeared to be the dominant trihalomethane present, and demonstrated a correlation between the total organic carbon (TOC) content of the raw water and the amount of trihalomethane present in the finished water. Singer *et al.*³, in a study of North Carolina waters, found UV light absorbance as well as TOC to be good surrogate measurements for the trihalomethane precursor content of the raw water. (Trihalomethane precursor is a measure of the natural organic material in the water capable of reacting with free halogens to form trihalomethanes.) Conducting the National Organics Monitoring Survey (NOMS)⁴ in 1975 through 1977, EPA found that trihalomethanes increased over time in the water distribution system and that their concentration was much greater than that of any of the other synthetic organic contaminants found.

Epidemiological evidence was needed to show whether or not the small amount of trihalomethanes found in drinking water was harmful to humans. Due to the low concentrations involved,

full-scale epidemiological studies were not very fruitful, especially during short study periods. For this reason several short-term, high concentration animal studies were performed. Bull⁵ concluded from his studies that even though trihalomethanes produced toxicological effects in the liver and kidneys, the carcinogenicity of trihalomethanes was the most important issue at the concentrations typically found in drinking water.

Convinced that trihalomethanes in drinking water were a health hazard, EPA promulgated a trihalomethane regulation on November 29, 1979.⁶ It established a maximum contaminant level (MCL) for Total Trihalomethanes (TTHM) of 0.10 mg/l. This MCL was based upon statistical extrapolation from animal data. It was estimated that lifetime exposure (70 years) to 0.10 mg/l chloroform in drinking water would result in a cancer risk of 1 in 10,000 to 1 in 100,000.⁷

TTHM is defined as the arithmetic sum of chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), chlorodibromomethane (CHClBr_2), and bromoform (CHBr_3) in mg/l, with all numbers rounded to two significant figures. Determination of the TTHM concentration in the water system is determined by taking four samples from within the distribution system within a 24-hour period once per quarter for each treatment plant. Three of the samples must be representative of the system and one must be taken at a point representing the maximum detention time in the system. Compliance with the MCL is based on a running annual average of these quarterly samples. Reduced monitoring

requirements are possible for utilities consistently below the MCL.⁶

This regulation applies to all community water systems serving 10,000 or more people. For systems serving 75,000 people or more, monitoring for THM was required beginning in November 1980 with enforcement of the MCL beginning in November 1981. For systems serving 10,000 to 75,000 people, monitoring was required beginning in November 1982 with enforcement beginning in November 1983.⁶

B. Trihalomethane Control Methods.

There are three basic ways to reduce the trihalomethane content of the water reaching the consumer: the use of an alternative disinfectant that does not produce THM, the removal of THM precursors before chlorine addition, or the removal of THM after it is formed. EPA issued a Final Rule early in 1983 concerning the acceptable and expected alternative methods of treatment to reduce trihalomethanes in drinking water.⁸ The treatment techniques listed as generally available could be required to be installed by a utility in order to reduce the THM concentration below the MCL. These techniques are as follows:

- (1) Use of chloramines as an alternate or supplemental disinfectant or oxidant.
- (2) Use of chlorine dioxide as an alternate or supplemental disinfectant or oxidant.
- (3) Improved existing clarification for THM precursor reduction.
- (4) Moving the point of chlorination to reduce THM formation and, where necessary, substituting for the use of chlorine as a pre-oxidant chloramines, chlorine dioxide or potassium permanganate.

- (5) Use of powdered activated carbon for THM precursor or TTHM reduction seasonally or intermittently at dosages not to exceed 10 mg/L on an annual average basis.⁶

Any treatment change requires careful biological monitoring to insure that disinfection is not compromised.⁶

Should a utility not be able to meet the MCL with the above treatment methods, it could be required to use one or more of the following:

Introduction of off-line water storage for THM precursor reduction.

Aeration for TTHM reduction, where geographically and environmentally appropriate.

Introduction of clarification where not currently practiced.

Consideration of alternate sources of raw water.

Use of ozone as an alternate or supplemental disinfectant or oxidant.⁶

C. Cost of Trihalomethane Control.

Along with the Final Rule issued in November 1979, EPA published a summary of estimated costs for the regulation. These estimates included a total capital expenditure of 85 million dollars, a total operation and maintenance cost of 10 million dollars, and total revenue requirements of 19 million dollars. The estimated annual per capita cost of treatment for THM compliance was \$0.60 for systems serving 10,000 to 75,000 people and \$0.90 for systems serving more than 75,000 people. This amounted to \$0.70 per capita for populations served by both systems. The increase in the annual residential bill was estimated to be twice the annual per capita cost of treatment for THM compliance.⁶

D. Alternative Disinfectant Use for THM Control.

Examining all the techniques available for THM control, Symons *et al.*⁹ concluded that alternative disinfectant use appeared "to be the most effective and the least costly." Carswell *et al.*¹⁰ studied the use of alternative disinfectants in place of free chlorine. They stated that an alternative disinfectant must have the following characteristics to be acceptable: be easily generated and in widespread use, be a good biocide, result in fewer undesirable by-products than free chlorine, be cost effective, and result in a residual which can be easily measured. They also felt that a residual was needed in the distribution system to prevent regrowth of microorganisms and provide some cross-connection protection and indication. They concluded that two alternatives met these requirements (especially in waters with 1 mg/l or less disinfectant demand): chlorine dioxide as the primary disinfectant and chlorine dioxide used in combination with ozone as the primary disinfectant.

E. Objective of this Report.

The trihalomethane problem often dictates a more severe treatment strategy in the Southeastern United States as opposed to the rest of the nation, due in large part to higher temperature water (e.g., faster reaction kinetics) and higher natural organic content (e.g., more THM precursors). Thus many Southeastern water utilities cannot effectively control trihalomethanes by simply reducing chlorine dosage or moving the point of chlorine addition from the raw water to some point

later in the treatment process. Many of these utilities are forced to turn to alternative oxidants and disinfectants for trihalomethane control. Several have opted to use chlorine dioxide either on a temporary or permanent basis.

It is the objective of this report to investigate the use of the alternative disinfectant chlorine dioxide for trihalomethane control in waters typical of the Piedmont and Coastal areas of North and South Carolina. Chapter II of this report is a literature review of chlorine dioxide including chemistry, generation, biocidal efficiency, and toxicity. Chapters III through V discuss a field study of three Southeastern water treatment facilities using chlorine dioxide. Chapter III details the analytical procedures used in the study. Chapter IV reviews data from the three treatment facilities investigated. Conclusions of the study and recommendations for future research are given in Chapter V.

II. Chlorine Dioxide Literature Review

A. History of Use.

Chlorine dioxide (ClO_2) was discovered by Sir Humphrey Davy in 1811 by reacting KClO_3 with HCl . This reaction produced a gas which he called euchlorine, a mixture of Cl_2 and ClO_2 . Euchlorine was mentioned by Watt and Burgess in 1834 as being suitable as a bleaching agent for soda pulp.¹¹ Benarde, *et al.*¹² stated that ClO_2 was used after 1850 for water treatment in Europe. Thus the uses of chlorine dioxide were recognized early. However, the practical generation of ClO_2 was not developed until much later.

In the 1930's, the first commercial process for producing chlorine dioxide from NaClO_3 was developed by the Mathieson Alkali Works. Chlorine dioxide from NaClO_3 was used on a commercial basis by 1939 to make sodium chlorite (NaClO_2), a bleaching agent.¹¹

In 1943 the Niagara Falls Water Treatment Plant began using chlorine dioxide (from NaClO_2) as a disinfectant and for taste and odor control of phenol-contaminated water. Surveys by several researchers^{13,14} have indicated that chlorine dioxide is now used by several hundred water treatment plants in the United States, Canada, and Europe. Uses of ClO_2 at these facilities include taste and odor control, disinfection, algae control, and removal of iron, manganese, organics, and color.

B. Physical and Chemical Properties.

Some relevant physical and chemical properties of chlorine dioxide are shown in Table 2.1. Chlorine dioxide in the gas or liquid phase is very unstable and is sensitive to minute changes in pressure and temperature. Therefore, it cannot be shipped in bulk but must be generated on site.^{11,15} For the low concentrations needed in water treatment, aqueous solutions of ClO_2 are generated since they are safer and more convenient to handle than gaseous mixtures of ClO_2 .¹⁵ As can be seen in Table 2.1, ClO_2 is very soluble in water; at room temperature, chlorine dioxide is five times more soluble in water than chlorine.^{11,16} One drawback, however, is that ClO_2 is much more volatile in water than Cl_2 .^{11,16} This is due in part to the fact that chlorine dioxide does not hydrolyze in water as chlorine does but remains as a dissolved gas.^{11,12,15} It is stable in this manner unless the pH rises above nine, where disproportionation of ClO_2 occurs.^{17,18,19}

Chlorine dioxide is a powerful oxidant. It is often claimed to have an available Cl_2 content of 263% calculated as follows:

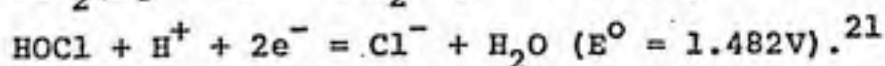
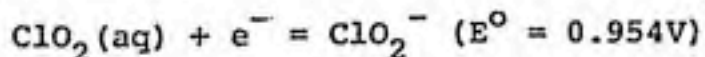
$$\% \text{ Available } \text{Cl}_2 = \frac{(\# \text{Electron changes})(35.5)(100)}{(\text{Molecular Weight})} \quad .15$$

This is based upon the reduction of ClO_2 all the way to Cl^- (a 5 electron transfer), which only occurs at very low pH.²⁰ At or near neutral pH, ClO_2 is normally reduced to ClO_2^- ^{19,20} (a one electron transfer), resulting in an available Cl_2 content of 52.6%. As a result, Cl_2 has more oxidant capacity for water treatment than ClO_2 and is more powerful, as further evidenced by the following half reactions:

Table 2.1 Chlorine Dioxide: Physical and Chemical Properties

<u>Property</u>	<u>Value or Description</u>	<u>Reference</u>
Color		
gas (as conc. increases)	yellow-green to orange-red	11, 15, 16, 17, 18
liquid	red or orange	15, 17
solid	red	17
Melting Point	-59 deg. C	11, 15, 16, 17, 18
Boiling Point	+11 deg. C	11, 15, 16, 17
Density		
liquid @ +11 deg. C	1.62 (water = 1)	11
liquid @ 0 deg. C	1.64 (water = 1)	17
vapor (gas)	2.4 (air = 1)	16, 17
Odor of gas		
description	resembles both Cl ₂ and O ₃	---
17 ppm in air	becomes evident	11, 15
45 ppm in air	becomes very irritating	11, 15, 16
Explosion Hazards of Gas		
≤4% in air	safe	18
>4% in air	detonated by sparks	11, 18
>10 or 11% in air	explode when exposed to light, heat, shock, or organics	11, 16, 18
magnitude	similar to H ₂ /O ₂ mixtures	16
Solubility in Water*		
room temp.	2.9 g/l	15, 16
chilled water	10.0 g/l	15

* At 30 mm Hg partial pressure = 4% in air, if total pressure is 760 mm Hg.



C. Generation.

Chlorine dioxide can be generated by the reduction of ClO_3^- in the presence of a strong acid (usually H_2SO_4) with a reducing agent such as NaCl , HCl , SO_2 , or methanol.¹¹ Large volumes and high concentrations can be generated in this manner, making this method ideal for the pulp and paper industry.¹⁵ However, the equipment necessary for the ClO_3^- generation method is fairly complicated and requires too large a capital expenditure to be economical for smaller applications of ClO_2 , such as water treatment.

The most economical method of generation for water treatment facilities is the oxidation of ClO_2^- . The generation equipment required is not very capital or maintenance intensive.¹¹ However, NaClO_2 is relatively expensive since it is made by the reaction of ClO_2 (produced using ClO_3^-) with H_2O_2 in a solution of NaOH . Thus, NaClO_2 is much more expensive than NaClO_3 and is not economical for large applications such as in the pulp and paper industry.^{11,17,18}

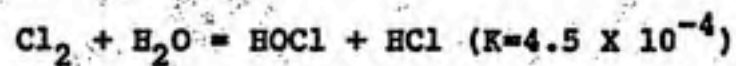
Several ClO_2^- oxidation methods are available, but two are most often used. The most popular of these is the generation of ClO_2 by the oxidation of ClO_2^- with chlorine. The various reactions involved and the kinetics of this method are detailed in Table 2.2. An inspection of the reaction mechanism shown in Table 2.2 reveals that Cl_2O_2 a metastable

Table 2.2 Chlorine Dioxide:
Generation from Chlorite and Chlorine

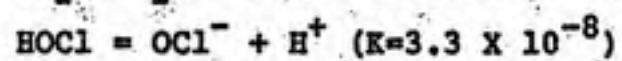
		Reference
Overall Reaction:	$\text{Cl}_2 + 2\text{ClO}_2^- = 2\text{ClO}_2 + 2\text{Cl}^-$ <p>(fast at low pH)</p>	11, 13, 15, 22, 24 16, 18, 22
Side Reaction:	$\text{Cl}_2 + \text{ClO}_2^- + \text{H}_2\text{O} = \text{ClO}_3^- + 2\text{Cl}^- + 2\text{H}^+$ <p>(very slow at high pH)</p>	13, 18, 22, 24
Suggested Mechanism:	$*\text{Cl}_2 + \text{ClO}_2^- = [* \text{Cl} - \text{Cl} \langle \text{O} \rangle] + *\text{Cl}^-$ $2[* \text{Cl} - \text{Cl} \langle \text{O} \rangle] = 2\text{ClO}_2 + *\text{Cl}_2$ <p>-or-</p> $[* \text{Cl} - \text{Cl} \langle \text{O} \rangle] + \text{H}_2\text{O} = \text{ClO}_3^- + *\text{Cl}^- + 2\text{H}^+$	18, 22
Kinetics:	$\frac{d\text{ClO}_2}{dt} = k_2[\text{Cl}_2][\text{ClO}_2^-] \text{ where } k_2 \approx 10^4 \text{M}^{-1} \cdot \text{s}^{-1} \pm 17\%$	22
Temperature Effect on k_2 :	$\ln(k_2) = 25.6 - 4766 (1/T)$ <p>where T is in deg. K</p>	
Ionic Strength Effect on k_2 :	$\ln(k_2/k_{2,0}) = (-0.085)I$ <p>where I is in moles/l and</p> $k_{2,0} = 1.62 \times 10^4 \text{M}^{-1} \cdot \text{s}^{-1} \text{ at } 20 \text{ deg. C}$	

Table 2.2 (continued)

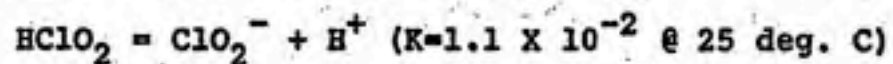
Pertinent
Equilibria:



13, 16



13, 16



13, 16, 18

intermediate, is the rate-limiting step and that ClO_2 production can be maximized (resulting in a minimum of ClO_2^- , ClO_3^- , and Cl_2 in the product) by using a high concentration of initial reactants and a low pH.^{18,22} Thus, contrary to the wide-spread belief that an excess of chlorine is needed for complete reaction of the ClO_2^- ,^{11,19,23} the stoichiometric amount of chlorine is sufficient providing that the reactant concentrations are high and the pH is low, as noted above.^{25,26} A $\text{ClO}_2^-/\text{Cl}_2$ generator, operated in this manner, can produce a yield greater than 95% with a 300 sec. reaction time and is capable of a feed range of 1:10 (e.g., maximum ClO_2 output capability ten times greater than minimum ClO_2 output capability).²⁶

The other commonly used method of generation of ClO_2 is the acidification of ClO_2^- . This method is detailed in Table 2.3. A review of the reactions in Table 2.3 shows that a pH less than 2 minimizes the side reactions and that the use of HCl rather than another acid favors Reaction A over Reaction B (due to the presence of Cl^-), producing a higher yield of ClO_2 .^{17,22,23} Masschelein¹⁷ reported that HCl should be applied in excess (equal weight proportions of NaClO_2 and HCl) to yield a reaction pH less than 0.5. Aieta and Roberts²⁵ reported that generation with H_2SO_4 resulted in a 50% molar yield while generation with HCl gave a 75-80% molar yield (stoichiometric yield = 80%). Masschelein²⁶ further stated that, in general, a $\text{ClO}_2^-/\text{HCl}$ reactor should provide greater than 76% molar yield with a reaction time of 360 to 600 sec. and should have a feed range of 1:7.

Table 2.3 Chlorine Dioxide: Generation from Chlorite and Acid

		<u>References</u>
Overall Reactions:	A. $5\text{HClO}_2 = 4\text{ClO}_2 + 2\text{H}_2\text{O} + \text{HCl} (\text{pH} \leq 2)$ -or- B. $4\text{HClO}_2 = 2\text{ClO}_2 + \text{HClO}_3 + \text{HCl} + \text{H}_2\text{O} (\text{pH} \leq 2)$	11, 17, 18, 22 13, 16, 17, 18, 22, 27
Side Reactions:	$5\text{ClO}_2^- + 5\text{H}^+ = 3\text{ClO}_3^- + \text{Cl}_2 + 3\text{H}^+ + \text{H}_2\text{O}$ $4\text{ClO}_2^- + 4\text{H}^+ = 2\text{Cl}_2 + 3\text{O}_2 + 2\text{H}_2\text{O}$	17
Suggested Mechanism for Reaction B:	$2\text{HClO}_2 = \text{HOCl} + \text{ClO}_3^- + \text{H}^+$ $\text{HOCl} + 2\text{HClO}_2 = 2\text{ClO}_2 + \text{HCl} + \text{H}_2\text{O}$	13
Pertinent Equilibria:	See Table 3.2	

D. Inorganic Reactions Related to Water Treatment

Inorganic reactions involving chlorine dioxide which are important to water treatment are listed in Table 2.4. Chlorine dioxide, as can be seen, is a good oxidant. Chlorine dioxide works very well in the oxidation of manganese, due in part to the fact that the $\text{ClO}_2/\text{Mn}^{+2}$ reaction is much faster than the chlorine/ Mn^{+2} reaction.²⁸ The fact that ClO_2 does not react with NH_3 as Cl_2 does is a definite advantage when treating waters high in NH_3 .

The most undesirable inorganic reaction of ClO_2 is the first disproportionation reaction listed in Table 2.4. This reaction is more prevalent than the other disproportionations listed. One suggested mechanism for this reaction results in a half-life of about three hours at pH 12 for an initial ClO_2 concentration of 5 to 10 mg/l.¹⁷ Photodecomposition is also undesirable. However, the loss of ClO_2 through UV decomposition is small compared to losses resulting from its volatility.¹⁶ Lastly, reactions of ClO_2 with Cl_2 are undesirable, resulting in a decomposition of the ClO_2 residual and a corresponding increase in ClO_3^- , an unwanted by-product.

E. Organic Reactions Related to Water Treatment.

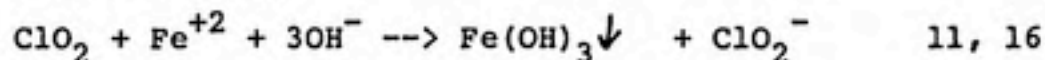
Chlorine dioxide is a very selective oxidant of organic compounds.¹⁸ It reacts very slowly, if at all, with primary and secondary aliphatic amines but reacts significantly with tertiary aliphatic amines.^{11,17,18,29} Iron and manganese, effectively oxidized in the free aqueous state, can also be

Table 2.4 Inorganic Reactions Related to Water Treatment

References

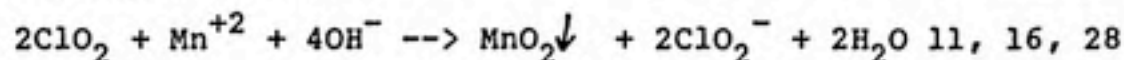
1. Desired Reactions

A. Iron oxidation



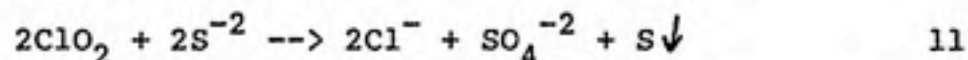
(Optimum pH > 7, best pH = 8 or 9)

B. Manganese oxidation

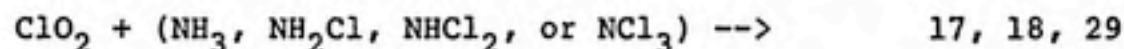


(Optimum pH > 7)

C. Sulfide oxidation

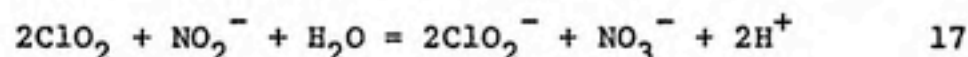


D. Reaction w/ Ammonia or Chloramines

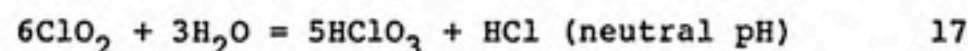
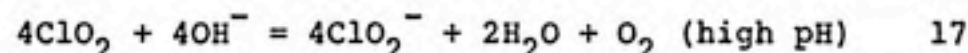
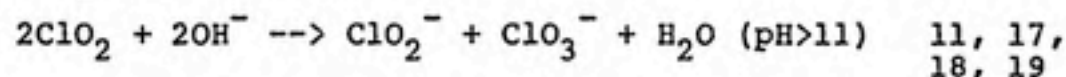


No Reaction

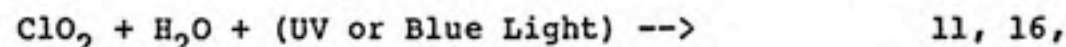
E. Nitrite oxidation



2. Undesired Reactions

A. ClO_2 Disproportionations

B. Photolysis



(reaction faster at high pH)

Table 2.4 (continued)

References

C. Reactions involving Chlorine

$3\text{OCl}^- = \text{ClO}_3^- + 2\text{Cl}^-$ (slow at room temp.)	22
$2\text{ClO}_2 + \text{OCl}^- + \text{H}_2\text{O} = 2\text{ClO}_3^- + \text{Cl}^- + 2\text{H}^+$ (appreciable rate at neutral pH)	17, 22 22, 30
$\text{ClO}_2 + \text{HOCl} = \text{ClO}_3^- + \text{H}^+ + 0.5\text{Cl}_2$ and $\text{ClO}_2 = 0.5\text{Cl}_2 + \text{O}_2$ with the following kinetics: $\frac{-d[\text{ClO}_2]}{dt} = K_2[\text{ClO}_2][\text{HOCl}] + K_3[\text{ClO}_2]$ where $K_2 = 1.28$ and $K_3 = 0.022$ at 25 deg. C	17
$\text{HOCl} + \text{ClO}_2^- + \text{OH}^- = \text{ClO}_3^- + \text{Cl}^- + \text{H}_2\text{O}$ (near neutral pH) (a fairly fast reaction)	13, 18 22, 24 31

oxidized from organic complexes such as humic acids. Some pesticides can also be oxidized by ClO_2 .¹⁷

Taste and odor can be removed with ClO_2 . Chlorine dioxide has been used for many years as a treatment alternative to Cl_2 in waters containing phenol.²⁹ Phenol is oxidized to quinone and chloroquinone using equal weight portions of ClO_2 and phenol.^{17,29} If the weight ratio of ClO_2 /phenol is increased to five, phenol is reported to be oxidized to maleic and oxalic acid within fifteen to thirty minutes.¹⁷

Nonhalogenated oxidation products of ClO_2 treatment are similar to those of Cl_2 treatment. A thorough discussion of this is found in the work by Miller, *et al.*¹⁴

Under most conditions prevalent in water treatment, ClO_2 does not produce a significant amount of chlorinated organics.^{11,14} It does not produce trihalomethanes and forms 10 to 100 times less chlorinated organics than does chlorine under similar conditions.^{22,32,33} Symons, *et al.*⁹ reported the following decreasing order of yield for organic halogen formation: $\text{Cl}_2 > \text{chloramines} > \text{ClO}_2 > \text{O}_3$. Lykins, *et al.*³⁴ reported that ClO_2 does not form any priority pollutant organic by-products other than those formed by Cl_2 . Colclough³⁵ reported that high concentrations of ClO_2 and fulvic acid at pH 7.8 result in the formation of dichloroacetic acid but, in general, result in less chlorinated products than the same reaction with Cl_2 .

Chlorine dioxide has been found to reduce the trihalomethane precursor content of water and to reduce THM formation when applied at the same time as Cl_2 .^{24,31,32,33,34}

It has also been found that secondary wastewater effluent treated with ClO_2/Cl_2 mixtures produced lower levels of total organic halogen (TOX) as well as trihalomethanes.³¹

Miltner³³ reported an increasing percent reduction in TTHM formation as the ratio of ClO_2/Cl_2 increased. He found an eighty percent reduction in TTHM formation with a ClO_2/Cl_2 weight ratio of 2.0, compared to Cl_2 alone. These results were for a fairly clean water having a TOC concentration of about 1.8 mg/l. Miltner also reported that a raw water containing about 2.5 mg/l TOC and dosed with 2.44 mg/l ClO_2 yielded a 19% reduction in the TOC concentration. Miltner summarized this by suggesting that his results were attributable to a reaction between ClO_2 and THM precursors rather than a reaction between ClO_2 and THMs or between ClO_2 and Cl_2 .

Work by Noack and Doerr²⁴ confirmed the findings of Miltner. They found that a 1:1 weight mixture of ClO_2 and Cl_2 yielded minimum concentrations of THM and ClO_2^- in the finished water. Rav-Acha, *et al.*³¹ agreed with this, providing the raw water does not contain appreciable amounts of bromide. They found under such circumstances that Cl_2 rapidly oxidizes Br^- to Br_2 which in turn reacts with precursors to form brominated THM before ClO_2 has time to oxidize the precursors. They recommended the addition of ClO_2 before Cl_2 if Br^- is present.

F. Disinfection Capabilities.

Benarde, *et al.*¹² concluded that chlorine dioxide is a better bactericide than chlorine. They showed that ClO_2

bacterial disinfection kinetics are proportional to concentration and temperature and are not first order, as opposed to Chick's Law.^{36,37} They found that disinfectant concentration and time of exposure have the following relationship:

$$C^n t = D$$

where $C = \text{ClO}_2$ concentration in mg/l, $n =$ dilution coefficient $= 1.08$ at 20 deg. C, $t =$ contact time in seconds, and $D =$ constant $= 10.0$ at 20 deg. C. As the temperature decreases, D increases while n remains practically constant.³⁶

Cronier, et al.³⁸ reported that ClO_2 kills bacteria and virus in the following order at pH 7.0 and 15 deg. C: E. coli, coxsackievirus A9, and poliovirus 1. They showed that the time required for inactivation of poliovirus 1 with ClO_2 decreases with increasing temperature and increasing pH.

In a study of nitrified and non-nitrified secondary wastewater effluents, Aieta and Roberts³⁹ found ClO_2 to be at least equal to Cl_2 in disinfection effectiveness. Their study was based on disinfection of total coliform.

Masschelein¹⁷ reported that ClO_2 is better than Cl_2 as a bactericide, sporicide, and viricide. He stated that in "a water with high chlorine demand, the ClO_2 is about ten times as effective as chlorine, while it is twice as efficient as hypochlorite in water free of chlorine demand." He also observed "that the simultaneous use of chlorine and chlorine dioxide has a superior bactericidal effect than if both agents are used separately at the same equivalent concentrations." He found that ClO_2 is better than copper sulfate as an algicide

but is about twice as expensive. Finally, Masschelein stated that ClO_2^- , a by-product of ClO_2 treatment, is only a minor disinfectant, being bacteriostatic and slightly bactericidal.

After reviewing the available ClO_2 disinfection studies, the writers of Drinking Water and Health²³ concluded that ClO_2 is effective as a bactericide and viricide under the conditions normally encountered in drinking water treatment. They stated that the relative activity of the various disinfectants is as follows: $\text{ClO}_2 > \text{HOCl} > \text{OCl}^- > \text{NHCl}_2 > \text{NH}_2\text{Cl}$.⁴⁰

G. Toxicity.

Recent studies of ClO_2 and its by-products ClO_2^- and ClO_3^- have been made to determine if the toxicity historically associated with this disinfectant is in fact true.

Masschelein¹⁷ reported that several decades of using chlorine dioxide in Europe and the United States have not resulted in any adverse effects on health. He has recommended a practical MCL for ClO_2^- of no more than 0.5 mg/l. This agrees with the accepted taste and odor threshold of 0.4 to 0.5 mg/l for ClO_2^- , above which a slight metallic taste occurs.^{17,19} Greenberg⁴¹ reported that ClO_2^- can cause hemolytic anemia, possibly at levels used in water disinfection, and that humans with a glucose-6-phosphate dehydrogenase deficiency are particularly susceptible. This deficiency is estimated to occur in 13% of black males in the U.S. Bull⁵ reported that ClO_2^- , as well as ClO_2 and ClO_3^- to a lesser extent, produces hemolytic anemia at doses less than those required to produce methemoglobinemia.

Reviewing various reports, Drinking Water and Health, Vol 3,⁴⁰ recommends the following Suggested No-Adverse-Response Levels (SNARL's): 0.38 mg/l for ClO_2 (chronic exposure) and 0.21 mg/l for ClO_2^- (seven day exposure). No SNARL was calculated for ClO_3^- . Vol. 4 of Drinking Water and Health⁴² revises these limits to the following: 24 hour exposure SNARL = 0.125 mg/l ClO_3^- , 0.125 mg/l ClO_2^- , and 1.2 mg/l ClO_2 ; seven day exposure SNARL = 0.125 mg/l for each of ClO_2^- , ClO_3^- , and ClO_2 .

Federal regulations have not kept pace with these data. However, based on a study of cats which showed deleterious effects on red blood cells for ClO_2 concentrations greater than 10 mg/l, EPA⁷ proposed with the THM regulation in 1978 that ClO_2 dose not exceed 1 mg/l. The final THM regulation in 1979⁶ deleted this proposed limit and left this area of regulation to the states, recommending that a combined residual of ClO_2^- , ClO_2 , and ClO_3^- not exceed 0.5 mg/l in the distribution system. As of November 1984, there have been no changes to this regulation.

III. Analytical Procedures and Data Collection

A. Introduction.

As part of a larger research project funded by the U.S. Environmental Protection Agency ("An Evaluation of Alternative Oxidant and Disinfectant Strategies for Controlling Trihalomethane Formation in Drinking Water," CR-811108), three Southeastern United States water treatment facilities using chlorine dioxide for trihalomethane control were located. These three utilities were Chester Metropolitan Water and Sewer District, Chester, South Carolina; Lancaster County Water and Sewer Authority, Lancaster, South Carolina; and City of Chesapeake, Virginia. Each of these facilities utilizes a surface water source with a high trihalomethane precursor content and treats the water using a conventional sedimentation/filtration process.

The purpose of the field study at each treatment plant was to determine the merits of chlorine dioxide treatment for trihalomethane control by evaluating both the quality and cost of drinking water before and after chlorine dioxide treatment was begun. This was first done by a review of plant records for items such as chemical dosages, microbiological quality, iron and manganese content, turbidity, and color. Second, the water was tested at three month intervals at various points in the treatment plant and distribution system in a more detailed effort to determine the effectiveness of each treatment process and to ascertain the quality of water in the distribution system. Tests were made for trihalomethanes (THM), total

organic halogens (TOX), total organic carbon (TOC), and residual oxidants (Cl_2 , ClO_2 , and ClO_2^-).

B. Sample Collection.

All samples for THM, TOX, and TOC analysis were collected in 40 ml Pierce glass vials with Teflon septa. These vials had been cleaned with acid dichromate for a minimum of fifteen minutes, rinsed thoroughly with distilled, deionized water, and oven-dried at 110 deg. C. The septa were washed with distilled, deionized water and air-dried. Vials were then capped and stored until used, usually not longer than one week.

THM and TOX samples were obtained in the field by slowly filling the vials head-space free such that loss of volatile THM was kept to a minimum. Instantaneous THM and TOX samples (i.e., concentration in water at time of sampling) were quenched with an excess of Na_2SO_3 to reduce any oxidants present. Terminal THM and TOX samples were buffered at pH 7 with about 1 ml of 1.5 M phosphate buffer and dosed with a predetermined excess of free chlorine which had been freshly prepared at approximately 1200 mg/l and standardized using DPD.

TOC samples were collected as above except that the head-space free criterion was not necessary. These samples were acidified with about 1 ml of 3M phosphoric acid for preservation until analyses were made.

Following collection, all samples were stored in the dark at ambient temperatures while in transport to the laboratory (usually one to two days). TOC and instantaneous THM and TOX samples were then stored in a refrigerator in the dark until

analyses could be performed. Terminal THM and TOX samples were stored in the dark at room temperature for a total of seven days from the time of collection. At the end of seven days the samples were unsealed, checked to assure that a free chlorine residual still remained and that the pH had remained constant, quenched with an excess of Na_2SO_3 , resealed head-space free, and stored with the instantaneous samples until analysis. The difference between terminal and instantaneous concentrations was a measure of the precursor content of the water.

C. Analytical Procedures.

1. THM.

The trihalomethane analytical procedure used was the liquid/liquid extraction technique from Supplement to Standard Methods, Fifteenth Ed.⁴³ as modified by Reckhow.⁴⁴ The analyzer used was a Perkin-Elmer Sigma 1 equipped with an electron capture detector and an "A" column operated at 65°C constant temperature. The solvent used was pesticide grade pentane.

For each sampling location, the contents of at least two sample vials were analyzed. One extraction and one injection were made for each vial. If these two injections did not agree with one another, a third sample vial was tested. In general, the results agreed within 2 ug/l. The average of these results, disregarding any obvious extraneous values, was reported.

2. TOX.

Total Organic Halogen concentration was measured using the technique developed by the Dohrmann Division of Xertex (Santa Clara, Cal.) and as modified by Reckhow.⁴⁴ The titration equipment used included a Dohrmann MCTS-20 microcoulometric titration system with pyrolysis furnace, Dohrmann T-620 Titration cell, and Dohrmann AD-2 adsorption module. The granular activated carbon used for adsorption was Filtrasorb-400 from Calgon Corp. (Pittsburgh, Pa.) ground to a uniform size between 100 and 200 mesh sieves.

For each sampling location, one volume of water (consisting of one or two vials) was tested. If the results appeared satisfactory, no more samples were run. If inconsistent with previous data collected, then one or two more volumes would be tested as needed. Duplicate samples generally agreed within 20 ug/l if undiluted. TOX results were reported in ug/l as Cl^- .

3. TOC.

Total Organic Carbon was analyzed according to Standard Methods⁴³ using a Beckman Model 915B Carbon Analyzer for the earlier samples and a Beckman Model 915B Tocamaster on the later samples. After purging all CO_2 from sample with nitrogen gas, microliter quantities of the sample were injected directly into the instrument for analysis. Concentrations reported (as mg/l C) were the average of several injections.

4. Residual Oxidants.

Earlier field measurements of free and combined chlorine were made using a Hach Model CN-70 chlorine test kit. In order to measure and distinguish among the various oxidant species, the procedure developed by Aieta, *et al.*²⁰ was used in later sampling.

This method involves the amperometric titration of I_2 liberated by the reaction of I^- and oxidant at various pH values. This enables the researcher to distinguish free Cl_2 , ClO_2 , ClO_2^- , and ClO_3^- . Most researchers have not found chlorate at significant concentrations in drinking water compared to chlorine, chlorine dioxide, and chlorite.^{9,20,37} This, combined with the cumbersomeness of the ClO_3^- test, led to the elimination of that part of the procedure for this study.

The amperometric titrator used was a Fisher CL Titrimeter Model 393 with a dual platinum electrode. The chemicals used were as follows:

Phenylarsine Oxide (0.00564N) - Fisher Certified

Potassium Iodide granules - Baker, 99.8%

Hydrochloric Acid - Mallinckrodt, 37.90%

Buffer (pH 7) - Fisher

Nitrogen gas - Linde prepurified (uncertified)

Dilution water for making 2.5 M HCl was distilled, deionized water which had been ozonated for twenty hours and then deozonated with oxygen for eight hours.

All samples were collected head-space in one liter borosilicate glass bottles which were covered with aluminum foil to protect the sample from light and had been cleaned as

prescribed by Aieta, *et al.*²⁰ The bottles were flushed several times before slowly being filled with a minimum of turbulence. Samples taken at the water treatment plant were analyzed immediately. Samples collected in the distribution system were stored on ice until they were returned to the water treatment plant laboratory for analysis (usually no more than thirty to ninety minutes). Each sample took about thirty to forty-five minutes to analyze. Due to the time required, only one sample (with only one titration sequence) was taken for each sampling point unless there was an obvious error, in which case another sample was collected if time permitted.

Upon returning to the water treatment plant laboratory, the sample was buffered at pH 7 and divided into two titration beakers. Potassium iodide (KI) was added to the first beaker, reducing free Cl_2 and one fifth of the ClO_2 , and the iodine liberated was titrated with phenylarsine oxide. The pH was lowered with HCl, resulting in the reduction of four fifth's of the ClO_2 and all of the ClO_2^- . The liberated iodine was again titrated to end point.

The chlorine dioxide was purged from the second beaker with nitrogen gas for fifteen minutes. Upon adding KI, the sample was titrated to end point to eliminate any Cl_2 remaining in the sample. The pH was lowered with HCl, resulting in the reduction of all ClO_2^- , and the sample was titrated to end point. The amount of titrant required for each of these titrations was then used to calculate the concentrations of free Cl_2 , ClO_2 , and ClO_2^- .

IV. CASE STUDIES OF SEVERAL SELECTED WATER TREATMENT PLANTS USING CHLORINE DIOXIDE FOR TRIHALOMETHANE CONTROL

A. Introduction.

As explained in the previous chapter, three water treatment plants using chlorine dioxide and located in the Southeastern United States were chosen to participate in a larger nationwide EPA project to evaluate the use of alternative oxidants and disinfectants for trihalomethane control. These three utilities were basically chosen for two reasons:

- high trihalomethane precursor content in the raw water, typical of the Piedmont and Coastal areas of North and South Carolina, and
- use of chlorine dioxide specifically for the control of trihalomethanes.

This chapter presents a detailed case study of each of these treatment plants, using both data normally collected and reported by each utility and data collected by this research group as part of the larger EPA parent project.

B. Chester Metropolitan Water and Sewer District, S.C.

1. General Description.

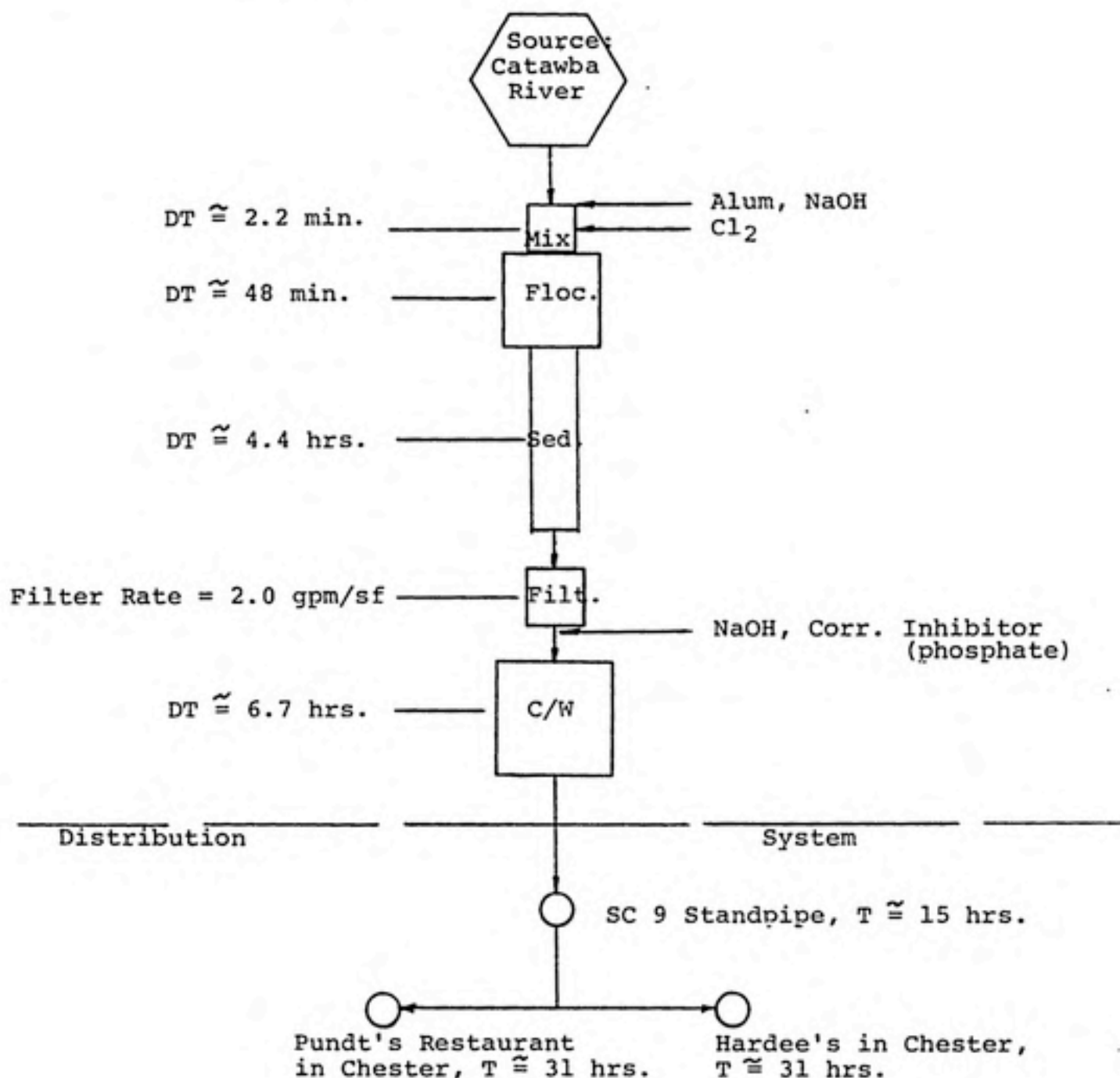
Chester Metropolitan Water and Sewer District serves approximately 19,000 people in Chester County, in the northern Piedmont area of South Carolina. It obtains its water from the Catawba River at Fort Lawn, which is downstream of Charlotte, N. C., Rock Hill, S.C., and several industrial point-source

discharges. After being treated, the water is piped to two separate metropolitan areas, Chester and Great Falls. The travel time for the water is about 31 hours from the water treatment plant to Chester (26 miles distant) and about fourteen hours from the water plant to Great Falls (13 miles distant).

The water treatment plant is located next to the river. All treatment, including all disinfection, is performed at this location. A schematic of the treatment process and distribution system sampling points is shown in Figure 4.1. There are one flash mixer, two horizontal reel-type flocculator units in parallel, two sedimentation basins in parallel, four filters in parallel (three sand and one dual-media), and one clearwell. The theoretical detention time shown is calculated by dividing the total volume of the particular unit process by the operating treatment rate of 7.2 MGD. The water plant operates at this rate for about ten hours/day. The chemical additions are shown as they were prior to modification for THM control. The distribution system locations shown are the distribution sampling points used for THM/TOX and residual oxidant analysis during this study.

Due to high THM concentrations in the finished water, chlorine addition was discontinued at the flash mixer and moved to the bottom of the filters in February 1983. This resulted in iron and manganese problems in the finished water and algal growth in the sedimentation basins. Addition of potassium permanganate to the raw water was then tried in an effort to alleviate this problem. Plant personnel indicated that this

Figure 4.1 Chester Metropolitan Water and Sewer District, S.C.
Water Treatment Plant



Notes: ← indicates chemicals normally added.
(before modification for THM Control).
DT = Theoretical Detention Time (based on 7.2 MGD)
T = Transmission Time from Clearwell

was not successful, and the utility began feeding chlorine dioxide at the flash mixer and moved the chlorine addition point from the bottom to the top of the filters in October 1983. This apparently solved the manganese and algal growth problems. A dose of 2 mg/l ClO_2 was initially used, but this was subsequently lowered to 0.7² mg/l and has remained at this level ever since.

Chester Metropolitan uses an acid/ ClO_2^- system for ClO_2 generation. The generator used is made by the Rio Linda Company of Sacramento, Cal., and is furnished by the Perolin Company of Chattanooga, Tenn., which also supplies the NaClO_2 used. The generator uses HCl and NaClO_2 and is claimed to have an efficiency of 96 to 98% by the manufacturer.⁴⁵ (This is assumed to be 96 to 98% of 80%, the theoretical maximum yield.) The sodium chlorite used is sold under the name Perosan 3990 and is a 16% by weight solution of NaClO_2 . The hydrochloric acid used is 20 deg. Baume' (about 31.5% HCl by weight) muriatic acid and is supplied by Burris Chemical Co. of Charlotte, N. C.

2. Water Plant Records -- Water Quality Characteristics vs. ClO_2 Use.

Water treatment records for Chester Metropolitan were reviewed to determine if any pertinent treatment or water quality parameters have changed as a result of ClO_2 treatment. Table 4.1 summarizes these records. Manganese and iron are generally not a problem at this water treatment plant. Manganese averages about 0.015 mg/l in the raw water

Table 4.1 Chester Metropolitan Water and Sewer District, S.C.
Water Quality Characteristics and Treatment
Parameters Before and After Change to Chlorine
Dioxide

<u>Item</u>	<u>Before</u> ^b	<u>After</u> ^b
Cl ₂ Dose (mg/l)	11.5 (2.69)	3.9 (1.82) ^g
Coagulated Cl ₂ Residual (mg/l) ⁱ	3.9 (0.36)	---
Finished Cl ₂ Residual (mg/l) ^{c,i}	1.6 (0.18)	1.3 (0.45) ^g
Dist. Cl ₂ Residual (mg/l) ^{d,i}	0.8 (0.35)	0.5 (0.32) ^g
ClO ₂ Dose (mg/l)	---	0.7 (0.00)
Coagulated ClO ₂ Residual (mg/l) ⁱ	---	0.2 (0.04)
Alum Dose (mg/l) ^e	9.7 (2.54)	11.3 (3.67)
Caustic Dose (mg/l) ^f	30.8 (5.91)	25.2 (13.10)
Raw pH	7.0 (0.10)	6.9 (0.08)
Coagulated pH	6.0 (0.03)	6.0 (0.30)
Finished pH	7.1 (0.04)	7.1 (0.07)
Temperature (deg. C)	15.6 (7.51)	14.8 (6.21)
Raw Alkalinity (mg/l as CaCO ₃)	20.3 (1.23)	19.5 (2.76)
Finished Alkalinity (mg/l as CaCO ₃)	19.5 (4.79)	20.6 (3.15)
Raw Color (C.L.L.)	48.1 (9.85)	38.5 (9.98)
Finished Color (C.U.)	0.09 (0.13)	0.35 (0.30)
Raw Turbidity (JTU)	31.7 (21.3)	31.9 (20.88)
Finished Turbidity (NTU)	0.19 (0.15)	0.41 (0.16)
Raw Coliform Count (#/100 ml)	441 (187)	683 (418) ^g
Finished Coliform Count (#/100 ml)	0 (0)	0 (0)
Dist. Coliform Count (#/100 ml)	0 (0)	0 (0) ^g
Dist. Standard Plate Count	---	13.3 (11.85) ^h

Table 4.1 (Continued)

- a. All results have been calculated from monthly averages reported by the utility to the State of South Carolina. The results shown for each item are the average value with the standard deviation in parentheses.
- b. Time period 'Before' is for the time that pre- Cl_2 was used and includes data from January 1982 to February 1983. Time period 'After' is for the period in which pre- ClO_2 and pre-filter Cl_2 was used and includes October 1983 to November 1984, approximately one complete year each period.
- c. 'Finished' refers to samples taken post-clearwell.
- d. 'Dist.' refers to an average of at least ten samples taken in the distribution system.
- e. Alum dose is shown as mg/l Al_2O_3 .
- f. Caustic is shown as mg/l NaOH .
- g. These values do not include the time during 2/84 - 3/84 when no Cl_2 was fed.

Table 4.1 (Continued)

- h. These values are for the period 4/84 - 11/84 only. The maximum SPC occurring in any of these months was 141 in April 1984 (other than one TNTC in May 1984).
- i. Chlorine residuals were measured using a DPD colorimetric test for total Cl_2 . Chlorine dioxide residuals were measured with the same test, after addition of glycine to reduce all Cl_2 .

and less than 0.01 mg/l in the distribution system. Iron averages about 0.17 mg/l in the raw water and about 0.02 mg/l in the finished water.

It can be seen from this summary that the raw water characteristics before and after the change to ClO_2 are essentially the same except for color, which has decreased somewhat. With regards to finished color and turbidity, however, the present treatment scheme using ClO_2 has not produced as good a finished water as the previous treatment scheme using Cl_2 .

Again examining Table 4.1, the oxidant demand of the distributed water appears to be adequately met both before and after ClO_2 use was begun. However, only 0.7 mg/l ClO_2 has replaced about 8 mg/l Cl_2 . This may be largely due to organic matter in the raw water being removed in the sedimentation basin before Cl_2 is added. This can be seen by examining the coagulated and finished Cl_2 residuals. The results here show that ClO_2 survives the flash mixer. However, the results to be shown in Section 3 below, using a better measurement technique, show only a trace of ClO_2 leaving the mixer. Therefore, ClO_2 serves only as a pre-oxidant and pre-disinfectant here, helping keep the treatment process in an oxidized condition and free of algae.

Based upon finished and distributed coliform counts, ClO_2/Cl_2 combination has provided as good a disinfection quality as Cl_2 alone even though raw coliform increased and temperature decreased slightly. However, the use of 0.7 mg/l ClO_2 alone during February and March 1984 resulted in poor

quality water. The distributed coliform count in March averaged 0.08/100 ml with a maximum of 3/100 ml out of 90 samples. The distributed standard plate count for the same period averaged more than 931 with a maximum of more than 6500. This was most likely due to there being no disinfectant other than ClO_2^- (a weak disinfectant at best) following the sedimentation basin. Note that the raw coliform count averaged 2500/100 ml in February and 4619/100 ml in March, possibly contributing to the resultant poor quality.

Lastly, the use of ClO_2 rather than HOCl has resulted in the use of less NaOH , even though the alum dose increased slightly. However, cause and effect cannot necessarily be associated here since the natural alkalinity decreased, the water temperature decreased, and the coagulated pH was very sporadic.

3. THM/TOX/ ClO_2 Results.

THM, TOX, TOC, and disinfectant doses and residuals are shown in Table 4.2. Except as noted otherwise, the results presented were measured by researchers at the University of North Carolina according to the procedures described in Chapter III. Several observations can be made from this data:

- ClO_2 is reduced within a matter of seconds, so that very little leaves the flash mixer.
- About 60% of the ClO_2 applied appears as ClO_2^- leaving the flash mixer.
- The ClO_2^- residual decreases but is persistent out to the far reaches of the distribution system (at least 43 hours).

Table 4.2

Chester Metropolitan District, South Carolina
Residual Oxidant and Halogenated Organics Results

Location	Free Chlorine ^a Dose/Residual (mg/l)	ClO ₂ ^a Dose/Residual (mg/l)	ClO ₂ ⁻¹ Residual (mg/l)	TOC (mg/l)	CHCl ₃ (ug/l)	TTHM (ug/l)	TOX (ug/l)	TERM THM (ug/l)	TERM TOX (ug/l)
Raw Water									
Dec. 15, 1983	0.0/-	0.0/-	-	7.6 ^b	0	0	424 ^c	402 ^d	2064 ^d
Mar 8, 1984	0.0/-	0.0/-	-	6.5 ^b	0	0	157	299 ^d	766 ^{d,e}
May 17, 1984	0.0/-	0.0/-	-	4.6 ^b	1	1	150	290 ^d	950 ^d
July 12, 1984	0.0/-	0.0/-	-	6.5 ^b	0	0	231	357 ^d	990 ^d
Oct 15, 1984	0.0/0 ⁱ	0.0/0 ⁱ	0.07 ^j	7.8	1	1	429	470 ^f	1644 ^f
Dec 4, 1984	0.0/0	0.0/0	0.10 ^j	8.9	-	-	-	-	-
Rapid Mix									
Dec. 15, 1983	0.0/-	0.7/-	-	-	-	-	-	-	-
Mar 8, 1984	0.0/-	0.7/-	-	-	-	-	-	-	-
May 17, 1984	0.0/-	0.7/0.2	-	-	-	-	-	-	-
July 12, 1984	0.0/-	0.7/0.25 ⁱ	-	-	-	-	-	-	-
Oct 15, 1984	0.0/0 ⁱ	0.7/0.03 ⁱ	0.56 - 20 ^{1/2}	-	-	-	-	-	-
Dec 4, 1984	0.0/0 ⁱ	0.7/0 ^j	0.5 - 71 ^{1/2}	-	-	-	-	-	-
Settled Water									
Dec 15, 1983	0.0/0.0	0.0/-	-	3.7 ^b	3	6 ^c	195 ^c	191 ^d	752 ^d
Mar 8, 1984	0.0/-	0.0/-	-	2.5 ^b	0	0	43	115 ^d	502 ^d
May 17, 1984	0.0/-	0.0/-	-	2.4 ^b	2	3	40	146 ^d	440 ^d
July 12, 1984	0.0/-	0.0/-	-	2.6 ^b	2	2	112	183 ^d	414 ^d
Oct 15, 1984	0.0/0 ⁱ	0.0/<0.04 ⁱ	0.26	2.7	1	4	180	202 ^f	788 ^f
Dec 4, 1984	0.0/0 ⁱ	0.0/0.04 ⁱ	0.41	-	-	-	-	-	-

Table 4.2 (continued)

Location	Free Chlorine ^a Dose/Residual (mg/l)	ClO ₂ ^a Dose/Residual (mg/l)	ClO ₂ ⁻¹ Residual (mg/l)	TOC (mg/l)	CHCl ₃ (ug/l)	THM (ug/l)	TOX (ug/l)	TERM THM (ug/l)	TERM TOX (ug/l)
Pre-Filter									
Dec 15, 1983	3.7 ^h /-	0.0/-	-	-	-	-	-	-	-
Mar 8, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
May 17, 1984	2.6 ^h /-	0.0/-	-	-	-	-	-	-	-
July 12, 1984	5.0/-	0.0/-	-	-	-	-	-	-	-
Oct 15, 1984	3.74/-	0.0/-	-	-	-	-	-	-	-
Dec 4, 1984	4.1/-	0.0/-	-	-	-	-	-	-	-
Filtered Water									
Dec 15, 1983	0.0/1.4	0.0/-	-	3.4 ^b	31	36	284	-	-
Mar 8, 1984	0.0/-	0.0/0.15	-	2.5 ^b	-	-	-	-	-
May 17, 1984	0.0/1.0	0.0/-	-	1.9 ^b	22	30	122	-	-
July 12, 1984	0.0/2.2 ^g	0.0/-	-	2.5 ^b	40	46	162	-	-
Oct 15, 1984	0.0/1.80 ⁱ	0.0/0.08 ⁱ	0.29	1.5	24	37	216	-	-
Dec 4, 1984	0.0/1.58 ⁱ	0.0/0.04 ⁱ	0.32	-	-	-	-	-	-
Finished (Tap) Water									
Dec 15, 1983	0.0/1.4	0.0/-	-	-	43	52 ^c	268	-	-
Mar 8, 1984	0.0/-	0.0/0.18	-	-	0	0	52	-	-
May 17, 1984	0.0/0.8	0.0/-	-	-	30	41	142	-	-
July 12, 1984	0.0/2.2 ^g	0.0/-	-	-	56	68	267 ^c	-	-
Oct 15, 1984	0.0/1.42 ⁱ	0.0/0.03 ⁱ	0.24	-	35	53	234	-	-
Dec 4, 1984	0.0/1.34 ⁱ	0.0/0.05 ⁱ	0.33	-	-	-	-	-	-
S.C. 9 Standpipe									
Dec 15, 1983	0.0/-	0.0/-	-	-	-	-	-	-	-
Mar 8, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
May 17, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
July 12, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
Oct 15, 1984	0.0/0.68 ⁱ	0.0/0.02 ⁱ	0.15	-	-	-	-	-	-
Dec 4, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-

Table 4.2 (continued)

Location	Free Chlorine ^a Dose/Residual (mg/l)	ClO ₂ ^a Dose/Residual (mg/l)	ClO ₂ ⁻¹ Residual (mg/l)	TOC (mg/l)	CHCl ₃ (ug/l)	TTHM (ug/l)	TOX (ug/l)	TERM THM (ug/l)	TERM TOX (ug/l)
Hardee's									
Dec 15, 1983	0.0/0.7	0.0/-	-	-	77	106	389	-	-
Mar 8, 1984	0.0/-	0.0/0.1	-	-	0	81	81	-	-
May 17, 1984	0.0/0.5	0.0/-	-	-	44	61	200	-	-
July 12, 1984	0.0/0.0 ^g _i	0.0/0.0 ^g _i	-	-	73	96	192	-	-
Oct 15, 1984	0.0/0.56 ⁱ	0.0/0 ⁱ	0.18	-	71	114	315	-	-
Dec 4, 1984	0.0/0.98 ⁱ	0.0/0 ⁱ	0.39	-	-	-	-	-	-
Pundt's									
Dec 15, 1983	0.0/0.4	0.0/-	-	-	81	116 ^c	353	-	-
Mar 8, 1984	0.0/-	0.0/-	-	-	0	2	76	-	-
May 17, 1984	0.0/0.0	0.0/-	-	-	52	72	195	-	-
July 12, 1984	0.0/0.0 ^g _i	0.0/0.0 ^g _i	-	-	61	81	159	-	-
Oct 15, 1984	0.0/0.07 ⁱ	0.0/0 ⁱ	0.13	-	73	119	285 ^c	-	-
Dec 4, 1984	0.0/0.18 ⁱ	0.0/0 ⁱ	0.24	-	-	-	-	-	-

a. Values obtained from water plant personnel unless otherwise noted.

b. Total organic carbon; best estimate.

c. Run in duplicate for confirmation; value reported is average of duplicate measurements.

d. Terminal organic halide samples; buffered at pH 7.0 with phosphate, chlorinated with 20mg/l HOCl (as Cl₂) stored at 20°C in absence of light for seven days. The terminal THM (or TOX) of the raw water is equivalent to its trihalomethane (or total organic halide) formation potential.

e. Value seems low.

f. Same as d except 30 mg/l Cl₂ applied.

g. Residual measured with Bach Model CN-70.

h. Dose is monthly average.

i. ClO₂ measurements (except as noted otherwise) made using Aieta method. Cl₂ and ClO₂ measurement made using Aieta method.

j. Interference.

- The Cl_2 dose of about 3 to 5 mg/l on top of the filter is quickly reduced by about 59% across the filter. The residual is fairly stable through the clearwell and slowly diminishes in the distribution system to a trace at the extremities of the system.
- ClO_2 produces essentially no THM.
- The raw water has a relatively high concentration of TOX, probably due to industrial discharges upstream of the water plant.
- Sedimentation, in combination with ClO_2 , reduces the TERM THM and TERM TOX by about 54% and 53% respectively. Sedimentation also reduces TOX already present in the raw water by about 62%. These all correspond very well with the 57% reduction in TOC.
- Upon addition of pre-filter Cl_2 , THM and TOX begin to form. In the distribution system, about 38 hours following pre-filter Cl_2 addition, THM and TOX levels have reached about 52% and 44% respectively of the settled water TERM THM and TERM TOX. The TTHM at this point is close to the MCL.
- On 3/8/84, when only ClO_2 was being added, ClO_2 and/or ClO_2^- reacted with precursor to form small amounts of TOX. The concentration of TOX at the extremity of the distribution system was twice that after sedimentation and made up only 16% of the settled water TERM TOX.

Trihalomethane concentrations are monitored for compliance with the MCL of 0.10 mg/l quarterly by the South

Carolina Division of Environmental Control. The compliance records show an average (maximum) of 0.16 mg/l (0.33 mg/l) before ClO_2 use began and 0.08 mg/l (~ 0.12 mg/l) after ClO_2 use was started. Thus, the use of ClO_2 has brought Chester Metropolitan into compliance with the trihalomethane regulation. Discussion of these observations and others is made in Section ^ED of this chapter.

4. Costs.

The cost of using ClO_2 rather than Cl_2 is presented below and is compared with the total cost of providing water to the public. The data used are from treatment records and conversations with utility personnel.

Data:

Average monthly consumption of NaClO_2 = 5,530 lb. of 16% solution.
 Average monthly consumption of HCl = 2,210 lb. of 31.5% solution.
 Average monthly consumption of Cl_2 before pre- Cl_2 stopped = 7,650 lb.
 Average monthly consumption of water before pre- Cl_2 stopped = 79.4 MG.
 Average monthly consumption of Cl_2 after ClO_2 started = 2,800 lb.
 Average monthly consumption of water after ClO_2 started = 81.3 MG.

Chemical Costs (as of 1/24/85):

NaClO_2 = \$0.65/lb. diluted (510 lb. drums)

HCL = \$0.089/lb. diluted (500 lb. drums)

Cl_2 \$0.185/lb (1 ton cylinders)

ClO_2 Chemical Cost =

$(5530 \text{ lb. NaClO}_2)(\$0.65/\text{lb.}) + (2210 \text{ lb. HCl})(\$0.089/\text{lb.})$

$(81.3 \text{ MG}) (10^3 \text{ 1000 gal./MG})$

= \$0.0466/1000 gal. treated

Cl_2 Chemical Savings =

$$\frac{7650 \text{ lb. Cl}_2 / 79.4 \text{ MG} - 2800 \text{ lb. Cl}_2 / 81.3 \text{ MG}}{10^3 \text{ 1000 gal/MG}} (\$0.185/\text{lb.})$$

$$= \$0.0115/1000 \text{ gal. treated}$$

$$\text{Net Change in Chemical Cost} = \frac{\$0.0466 - \$0.0115}{1000 \text{ gal.}}$$

$$= \$0.0352/1000 \text{ gal. treated}$$

The ClO_2 generator is provided and installed free of charge by the Perolin Co., which provides the NaClO_2 . Thus, the cost of the generator is included in the cost of the NaClO_2 . There are no significant increases in maintenance or labor costs which can be attributed to this operation. Therefore, the true total cost of ClO_2 treatment for Chester Metropolitan is simply the net change in chemical cost, or $\$0.0352/1000 \text{ gal. treated}$.

The average residential water bill per 1000 gal. is broken down in Table 4.3.

Table 4.3 Chester Metropolitan Water and Sewer District, S.C.
Cost of Water

<u>Item</u>	<u>Cost(\$/1000 gal. metered)</u>
Administrative Treatment	0.3905
Chemicals =	0.2684
Power =	0.2048
Labor =	0.2300
Misc. =	<u>0.2319</u>
Total	0.9351
Dist. System O & M	0.5748
Meters & Meter Reading	0.2228
Interest on Debt	0.2778
Debt Retirement (incl principal & depreciation)	<u>0.3493</u>
Grand Total	2.75

Neglecting the difference between quantity of water treated and

quantity of water metered, the percentage impact of ClO_2 treatment on the total water cost is $\frac{(\$0.0352)(100)}{\$2.75} = 1.28\%$.

Similarly on chemical costs alone, the impact is 13.11%. The average residence uses 4200 gal./month. Hence, the cost of ClO_2 use per residence per year is $(\$0.0352/1000 \text{ gal.})(4200 \text{ gal./mth})(12 \text{ mths./year}) = \1.77 . The additional cost of water attributed to ClO_2 is therefore negligible for this utility.

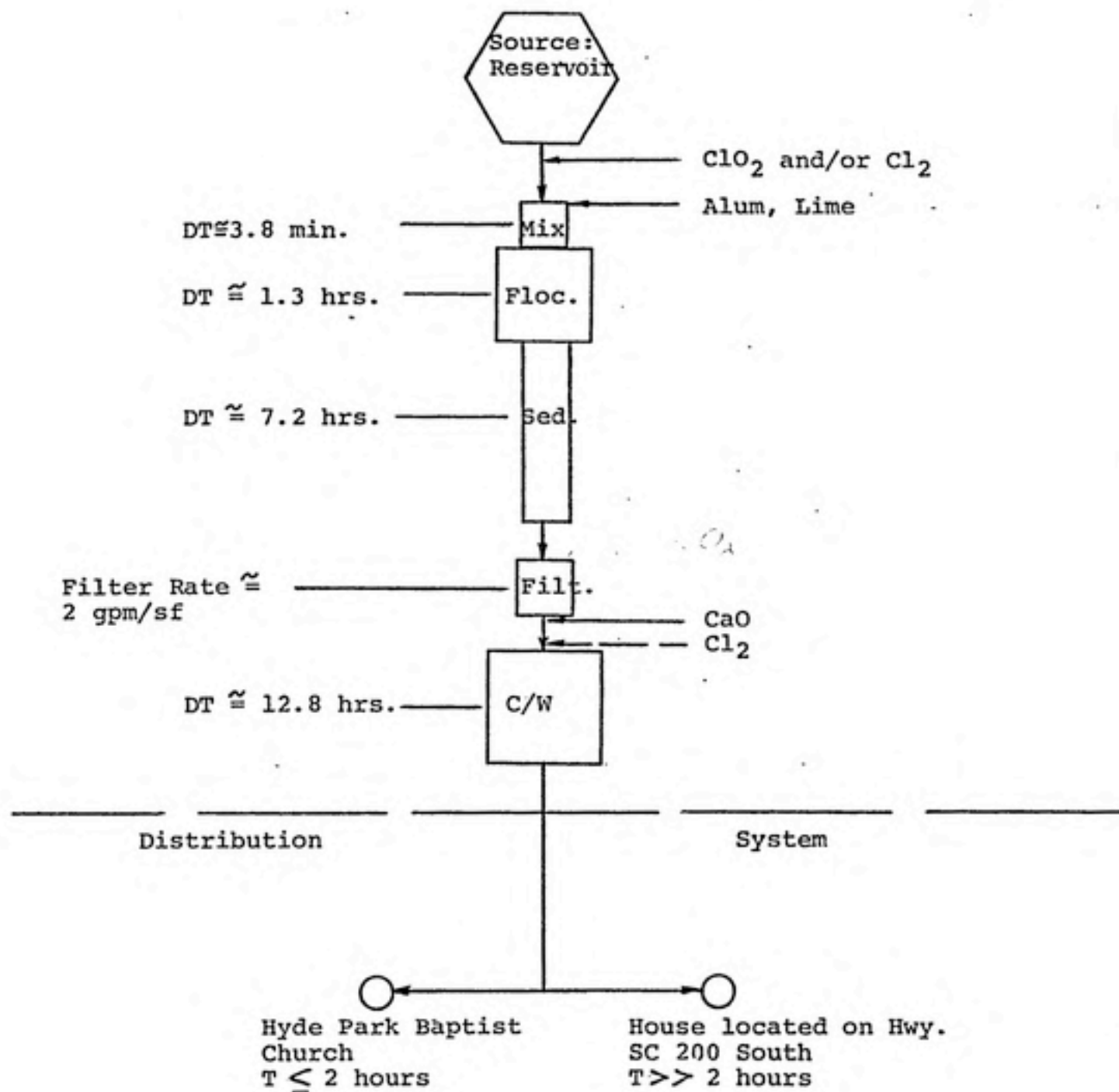
C. Lancaster County, S.C.

1. General Description

Lancaster County Water and Sewer Authority serves about 28,000 people in Lancaster County, S.C. (excluding the City of Lancaster). It is located in the northern Piedmont area of South Carolina, east of Chester County. The water treatment plant is in the City of Lancaster and draws its water from a series of impoundments which are fed by small creeks. After being treated, the water is piped into a sprawling distribution network which covers much of the county.

A schematic of the treatment process and distribution sampling points is shown in Figure 4.2. Included in the treatment process are one flash mixer, two horizontal reel-type flocculator units in parallel, two sedimentation basins in parallel, four dual-media filters in parallel, and three clearwells. The theoretical detention times shown are calculated as in Section A above except that the treatment rate is 1.5 MGD, and the water treatment plant operates 24 hours/day. The distribution system locations shown are the sampling points used for THM/TOX and residual oxidant analysis.

Figure 4.2 Lancaster County, S.C. Water Treatment Plant



Notes:

- indicates chemicals normally added
- - - indicates chemicals intermittently added
- DT = Theoretical Detention Time (based on 1.5 MGD)
- T = Transmission Time from Clearwell

Lancaster County began using its present water plant in April 1983. Due to high TTHM concentrations in the finished water as well as a persistent manganese problem in the impoundment water, the utility began to feed ClO_2 to the raw water in February 1984. At the same time, chlorine dosage was lowered and moved to post-filtration. TTHM concentrations were lowered as a result of this modification, and manganese oxidation occurred to a greater extent. However, the high cost of NaClO_2 along with the high ClO_2 doses required for satisfactory treatment prompted personnel to use KMnO_4 in the raw water in combination with a lower ClO_2 dose beginning in November 1984. This modification is still being evaluated by plant personnel at the time of this writing. The utility also plans to test the actual yield of the ClO_2 generator in the near future to determine the efficiency of NaClO_2 utilization.

Lancaster County originally used a ClO_2 generation system identical to that of Chester Metropolitan, described above. The high cost of NaClO_2 quickly prompted personnel to purchase technical grade solid NaClO_2 (Perolin 3970, 80% concentration by weight) and dilute this to the required 16% solution themselves. Complaints from workers regarding inhalation of NaClO_2 dust while dissolving the chemical in water and several minor fire or explosion accidents with the chemical alerted the utility to the hazards of using solid NaClO_2 . As a result, workers were carefully instructed in the safety precautions to be used and were provided with breathing filters. The utility manager has also been investigating the purchase of dilute liquid NaClO_2 again.

High cost also prompted the utility to change the ClO_2 generation process from an acid-type to a chlorine-type in an effort to further reduce costs. This change was made in September 1984.

The $\text{ClO}_2^-/\text{Cl}_2$ generator is made by Rio Linda Co. and is furnished by the Perolin Co., which still supplies the NaClO_2 . The generator uses a 25% solution of NaClO_2 and a concentrated Cl_2 solution from an existing chlorinator.

2. Water Plant Records -- Water Quality Characteristics vs. ClO_2 Use.

Water treatment records for Lancaster County have been reviewed to determine if any changes have occurred as a result of ClO_2 treatment. Table 4.4 summarizes these data. The Cl_2 poundage used in the calculations does not include the Cl_2 used for ClO_2 generation since September 1984. The measurement of Cl_2 and ClO_2 is the same as that described for Chester Metropolitan. Color and iron are not problems at this water plant and are therefore not measured routinely.

Raw water characteristics have remained practically the same before and after the change to ClO_2 , except alkalinity, which has decreased drastically. The reason for this is not known at present.

The present treatment scheme using pre- ClO_2 and post-filter Cl_2 has apparently produced water equivalent to the previous scheme using only Cl_2 , when looking at finished turbidity and manganese oxidation. However, neither ClO_2 nor

Table 4.4 Lancaster County S.C.
Water Quality Characteristics and Treatment
Parameters Before and After Change to Chlorine
Dioxide^a

Item	Before ^b	After ^b
Cl ₂ Dose (mg/l)	13.6 (4.02)	0 (0); 8.2 (3.60) ^c
Coagulated Cl ₂ Residual (mg/l)	4.7 (0.58)	0 (0); 5.3 (1.04) ^c
Finished Cl ₂ Residual (mg/l) ^d	2.2 (0.25)	1.2 (0.28)
Dist. Cl ₂ Residual (mg/l) ^e	0.9 (0.19)	0.4 (0.20)
ClO ₂ Dose (mg/l)	---	3.2 (1.26)
Coagulated ClO ₂ Residual (mg/l)	---	0.6 (0.66)
Alum Dose (mg/l) ^f	5.3 (1.09)	3.4 (0.58)
Lime Dose (mg/l) ^g	10.6 (4.46)	9.7 (1.14)
Raw pH	6.9 (0.23)	6.6 (0.08)
Coagulated pH	5.6 (0.37)	5.5 (0.20)
Finished pH	7.7 (0.35)	7.7 (0.30)
Temperature (deg.C) ^h	19.4 (10.28)	---
Raw Alkalinity (mg/l as CaCO ₃)	17.5 (9.10)	4.8 (1.55)
Finished Alkalinity (mg/l as CaCO ₃)	21.9 (12.63)	Not measured
Raw Turbidity (JTU)	33 (16.49)	30 (15.54)
Finished Turbidity (NTU)	0.2 (0.03)	0.2 (0.04)
Raw Manganese (mg/l)	0.77 (0.24)	0.66 (0.10) ^h
Finished Manganese (mg/l)	0.08 (0.02)	0.07 (0.02) ^h

Table 4.4 (continued)

Raw Coliform Count		
(#/100 ml)	820 (432)	690 (314)
Finished Coliform Count		
(#/100 ml)	0 (0)	0 (0)
Dist. Coliform Count		
(#/100 ml)	0 (0)	0 (0) ⁱ

- a. All results have been calculated from monthly averages reported by the utility to the State of South Carolina unless otherwise noted. The results shown for each item are the average value with the standard deviation in parentheses.
- b. Time period 'Before' is for the time in which pre-Cl₂ was used and includes data from April 1983 to February 1984.² Time period 'After' is for the time in which pre-ClO₂, post-filter Cl₂, and sometimes pre-Cl₂ were used and includes February 1984 to November 1984. Almost one year of records are included for each period.
- c. No pre-Cl₂ was fed and therefore coagulated Cl₂ residual is 0 mg/l except during the months of 6/84 to 9/84 when pre-Cl₂ was fed along with ClO₂. The average and standard deviation for these months is as shown.
- d. 'Finished' refers to samples taken post-clearwell.

Table 4.4 (continued)

- e. 'Dist.' refers to an average of at least 10 samples taken in the distribution system.
- f. Alum dose is shown as mg/l Al_2O_3 .
- g. Lime dose is shown as mg/l $\text{Ca}(\text{OH})_2$.
- h. Data for the 'After' period was available only for 2/84 - 6/84.
- i. In 8/84, several distribution system samples were reported positive. Average coliform count = 46/100 ml, and maximum coliform count = 800/100 ml. Some of these samples may have been contaminated; however, no confirmation tests were made. A small chlorine residual⁴⁵ was reported to exist in each sample.

Cl_2 has been able to reduce the manganese concentration below the MCL of 0.05 mg/l, even though the kinetics of manganese oxidation with ClO_2 are faster than with Cl_2 . As will be shown with the residual oxidant data below, this may be due in part to the coagulated pH of 5.6, well below that required for a fast and complete reaction, and to the ClO_2 residual being reduced to only a trace on top of the filters, possibly resulting in reducing conditions in the filters and subsequent manganese breakthrough. Post-filter Cl_2 addition at a pH of 7.7 would then oxidize the manganese in the clearwell and distribution system. This has been observed by plant personnel.

The use of ClO_2 at this utility does not replace as much Cl_2 as it does at Chester Metropolitan. This may be due to the predominance of compounds capable of being oxidized by Cl_2 but not ClO_2 and also not readily amenable to coagulation and sedimentation. Manganese can represent only part of this problem. Referring to Table 2.4, the average raw manganese concentration of 0.77 mg/l (if all Mn^{+2}) requires only 1.89 mg/l ClO_2 to oxidize it to MnO_2 , a little over half the average dose being used. Also, only 0.99 mg/l Cl_2 would be required for the same amount of Mn^{+2} oxidation, much less than the Cl_2 demand of the filtered water. Thus, other compounds must also be involved.

As can be seen in Table 4.4, a ClO_2/Cl_2 combination seems to provide good disinfection with the one exception noted for August 1984. ClO_2 and ClO_2^- have been effective algicides for the treatment process.

3. THM/TOX/ClO₂ Results

THM, TOX, TOC, and disinfectant doses and residuals are shown in Table 4.5. The results shown have been collected in the manner described in Section A above. Several observations are made from this data:

- ClO₂ doses as high as 4 and 6 mg/l are reduced to about 0.5 mg/l within a matter of seconds in the flash mixer and are further reduced to about 0.1 mg/l or less during sedimentation. (One exception to this is noted for the finished water on 12/5/84 where ClO₂ residual = 0.3 mg/l. This measurement is probably in error.)
- Almost 50% of the ClO₂ dose appears as ClO₂⁻ in the rapid mix.
- This concentration of ClO₂⁻ is stable and persistent throughout the treatment process and distribution system (at least 24 hours).
- The post-filter Cl₂ dose (with pre-ClO₂ being added) is reduced by about 80% through the clearwell (about 13 hours detention time), indicating that the filtered water is not chemically stable, possibly due to continued manganese oxidation, as discussed above, and to residual TOC.
- ClO₂ produces essentially no THM.
- Sedimentation and filtration, in combination with ClO₂, reduce the TERM THM, TERM TOX, and TOC by about 66%, 73%, and 69%, respectively. However, on 7/12/84, when pre-Cl₂ as well as pre-ClO₂ were being fed, the percent reductions were only 34%, 40%, and 57%, respectively.

Table 4.5

Lancaster County, S.C.
Residual Oxidant and Halogenated Organics Results

Location	Free Chlorine ^a Dose/Residual (mg/l)	ClO ₂ ^a Dose/Residual (mg/l)	ClO ₂ ⁻ⁱ Residual (mg/l)	TOC (mg/l)	CHCl ₃ (ug/l)	TTHM (ug/l)	TOX (ug/l)	TERM THM (ug/l)	TERM TOX (ug/l)
Raw Water									
Dec 15, 1983	0.0/-	0.0/-	-	>10 ^b	197 ^e	198 ^{c,e}	709 ^e	939 ^d	3740 ^d
Mar 8, 1984	0.0/-	0.0/-	-	16.4 ^b	0	0	115	856 ^f	3085 ^f
July 12, 1984	0.0/-	0.0/-	-	14.2 ^b	0	0	34	755 ^f	1824 ^f
Oct 16, 1984	0.0/0.03 ^{h,i}	0.0/0.04 ^{h,i}	0.31 ⁱ	17.0	1	1	36	956 ^f	3015 ^f
Dec 5, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
Pre-rapid Mix									
Dec 15, 1983	10.6 ^j /-	0.0/-	-	-	-	-	-	-	-
Mar 8, 1984	0.0/-	2.5/-	-	-	-	-	-	-	-
July 12, 1984	9.43/-	0.7/-	-	-	-	-	-	-	-
Oct 16, 1984	0.0/-	6.03/-	-	-	-	-	-	-	-
Dec 5, 1984	0.0/- ^k	3.99/-	-	-	-	-	-	-	-
Rapid Mix									
Dec 15, 1983	0.0/-	0.0/-	-	-	-	-	-	-	-
Mar 8, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
July 12, 1984	0.0/5.0	0.0/-	-	-	-	-	-	-	-
Oct 16, 1984	0.0/0.40 ^h	0.0/0.46 ^h	3.1858 ^{*/i}	-	-	-	-	-	-
Dec 5, 1984	0.0/-	0.0/1.2	-	-	-	-	-	-	-

Table 4.5 (continued)

Location	Free Chlorine ^a Dose/Residual (mg/l)	ClO ₂ ^a Dose/Residual (mg/l)	ClO ₂ ⁻¹ Residual (mg/l)	TOC (mg/l)	CHCl ₃ (ug/l)	TTHM (ug/l)	TOX (ug/l)	TERM THM (ug/l)	TERM TOX (ug/l)
Settled Water									
Dec 15, 1983	0.0/-	0.0/-	-	6.6 ^b	119	120 ^c	741	-	-
Mar 8, 1984	0.0/-	0.0/0.2	-	-	-	-	-	-	-
July 12, 1984	0.0/-	0.0/0.3	-	-	-	-	-	-	-
Oct 16, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
Dec 5, 1984	0.0/0.21 ^h	0.0/0.09 ^h	1.74	-	-	-	-	-	-
Filtered Water									
Dec 15, 1983	0.0/-	0.0/-	-	6.0 ^b	139	140 ^c	629	-	-
Mar 8, 1984	0.0/-	0.0/-	-	4.8 ^b	0	0	68	224 ^f	628 ^f
July 12, 1984	0.0/-	0.0/-	-	6.1 ^b	148	159	480	502 ^f	1090 ^f
Oct 16, 1984	0.0/0.17 ^h	0.0/0.03 ^h	2.99	5.5	4	6	103	398 ^f	1012 ^f
Dec 5, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
Pre-clearwell									
Dec 15, 1983	0.0/-	0.0/-	-	-	-	-	-	-	-
Mar 8, 1984	7.4/-	0.0/-	-	-	-	-	-	-	-
July 12, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
Oct 16, 1984	8.56/-	0.0/-	-	-	-	-	-	-	-
Dec 5, 1984	7.05/-	0.0/-	-	-	-	-	-	-	-
Finished (Tap) Water									
Dec 15, 1983	0.0/3.0	0.0/-	-	-	287	292 ^c	885	-	-
Mar 8, 1984	0.0/0.7 ^g	0.0/-	-	4.2 ^b	21	25	147	-	-
July 12, 1984	0.0/1.2 ^g	0.0/-	-	6.0 ^b	205	224	456 ^c	-	-
Oct 16, 1984	0.0/1.70 ^h	0.0/0.04 ^h	2.90	4.5	79	95	258 ^c	-	-
Dec 5, 1984	0.0/1.15 ^h	0.0/0.3 ^h	1.61	-	-	-	-	-	-
Hyde Park Baptist Church									
Dec 15, 1983	0.0/0.8	0.0/-	-	-	311	316 ^c	887	-	-
Mar 8, 1984	0.0/0.3 ^g	0.0/-	-	-	48	54	194	-	-
July 12, 1984	0.0/Tr. ^g	0.0/-	-	-	242	261	410	-	-
Oct 16, 1984	0.0/0.79 ^h	0.0/0.12 ^h	3.06	-	63	77 ^c	258 ^c	-	-
Dec 5, 1984	0.0/≤ 0.38 ^h	0.0/0.10 ^h	1.32	-	-	-	-	-	-

Table 4.5 (continued)

Location	Free Chlorine ^a Dose/Residual (mg/l)	ClO ₂ ^a Dose/Residual (mg/l)	ClO ₂ ⁻¹ Residual (mg/l)	TOC (mg/l)	CHCl ₃ (ug/l)	TTHM (ug/l)	TOX (ug/l)	TERM THM (ug/l)	TERM TOX (ug/l)
SC 200 South									
Dec 15, 1983	0.0/1.0	0.0/-	-	-	298	304 ^c	968 ^c	-	-
Mar 8, 1984	0.0/0.3 ^g	0.0/-	-	-	65	71	174	-	-
July 12, 1984	0.0/Tr. ^g	0.0/-	-	-	270	280	360	-	-
Oct 16, 1984	0.0/0.28 ^h	0.0/0.04 ^h	2.93	-	109	130	252	-	-
Dec 5, 1984	0.0/0.15 ^h	0.0/Tr. ^h	1.43	-	-	-	-	-	-

- a. Values obtained from water plant personnel unless otherwise noted.
- b. Total organic carbon; best estimate.
- c. Run in duplicate for confirmation; value reported is average of duplicate measurements.
- d. Terminal organic halide samples; buffered at pH 7.0 with phosphate, chlorinated with 20 mg/l HOCl (as Cl₂), stored at 20°C in absence of light for seven days. The terminal THM (or TOX) of the raw water is equivalent to its trihalomethane (or total organic halide) formation potential.
- e. Questionable value.
- f. Same as d except 30 mg/l Cl₂ applied.
- g. Residual measured with Hach Model CN-70.
- h. ClO₂⁻ measurements (except as noted otherwise) made using Aieta method. Cl₂ and ClO₂ measurement made using Aieta method.
- i. Interference.
- j. Dose is monthly average for entire WTP. Dose not necessarily added all in one location.
- k. KMnO₄ dose at raw water intake = 1.97 mg/l.

- Using pre- Cl_2 with pre- ClO_2 on 7/12/84, the TTHM concentration exceeded the MCL of 0.10 mg/l before the water reached the filters. In the distribution system, this water ultimately attained TTHM and TOX concentration approaching 54% and 35%, respectively, of the settled water TERM TTHM and TERM TOX.
- Using pre- ClO_2 and post-filter Cl_2 , the TTHM concentration approaches and sometimes exceeds the MCL in the distribution system. In this mode, the TTHM and TOX concentrations in the distribution system only approach 27% of the settled water TERM TTHM and TERM TOX. Thus, the importance of the sedimentation/filtration step to remove TTHM precursor before chlorine is added cannot be overemphasized.

Quarterly TTHM monitoring by the South Carolina Division of Environmental Control has not shown a significant decrease in trihalomethane concentration in the distribution system to a point below the MCL of 0.10 mg/l. Further discussion of these observations is made in Section ^ED below.

4. Costs.

The cost of using ClO_2 rather than Cl_2 is presented below and is compared with the total cost of providing water and sewer to the public. The data used are from utility records and conversations with utility personnel.

Data:

Average monthly consumption of $\text{ClO}_2 = 1290 \text{ lb.}$

Average monthly consumption of Cl_2 before $\text{ClO}_2 = 4973 \text{ lb.}$

Average monthly consumption of Cl_2 during $\text{ClO}_2 = 3409 \text{ lb.}$

Average monthly consumption of water before $\text{ClO}_2 = 44.1 \text{ MG}$

Average monthly consumption of water during $\text{ClO}_2 = 45.6 \text{ MG}$

For $\text{ClO}_2^-/\text{HCl}$ generation, 1290 lb. ClO_2 /month requires approximately 1544 gal. of 16% NaClO_2 and 418 gal. of 31.5% HCl . This is approximately 2,455 lb. of pure NaClO_2 (assuming the volume of NaClO_2 in sol'n. is negligible) and about 4,034 lb. of 31.5% HCl .

For $\text{ClO}_2^-/\text{Cl}_2$ generation, 1,290 lb. ClO_2 /month requires approximately 695 gal. of 25% NaClO_2 and 777 lb. Cl_2 . With the same assumption as above, the weight of NaClO_2 used is about 1727 lb. pure NaClO_2 .

Chemical Costs (as of 1/24/85):

16% $\text{NaClO}_2 = \$0.65/\text{lb.}$ (prices from Chester Metropolitan used for comparison purposes)

31.5% $\text{HCl} = \$0.089/\text{lb.}$ (prices from Chester Metropolitan used for comparison purposes)

$\text{Cl}_2 = \$0.185/\text{lb.}$ (1 ton cylinders)

80% $\text{NaClO}_2 = \$1.63/\text{lb.}$

Monthly labor required for preparation of 25% NaClO_2 solution from dry $\text{NaClO}_2 \approx 16$ hr. @ \$4.00/hr. = \$64.00/mth. for 1,727 lb. pure NaClO_2 . As for Chester Metropolitan, the generator is furnished and installed free by the Perolin Co. The cost of the generator is therefore included in the chemical cost.

$$\begin{aligned} \text{Net ClO}_2 \text{ Cost} &= \text{ClO}_2 \text{ Chemical Cost} + \text{Labor Cost} \\ &\quad - \text{Cl}_2 \text{ Chemical Savings} \end{aligned}$$

where chemical cost and savings are calculated similarly to that for Chester Metropolitan, and Labor Cost =

$$\frac{\text{Labor Cost/Month}}{\text{Water Pumped/Month}}$$

Results for the various combinations of NaClO_2 sources and generators is shown in Table 4.6. Thus, a $\text{Cl}_2/\text{dry ClO}_2^-$ generation scheme is the most economical in this case. This is the method currently being used.

The average cost of providing water and sewer services is broken down in Table 4.7. Utility personnel have not separated water costs from sewer costs. All are combined into the same budget. The utility has 6,801 water connections and 1,306 sewer connections. It sells about 37 MG of water each month and treats about 7 MG of sewage each month.

The utility produces about 1.2 times the amount of water that is metered. Neglecting this difference, the percentage impact of ClO_2 treatment on chemical costs is $(\$0.0747/\$0.3590)(100) = 20.81\%$ and on total water and sewer

Table 4.6 Lancaster County, S.C.
Cost of ClO_2 /1000 gal. water pumped

Type of Generation	80% NaClO_2 (dry)	16% NaClO_2
HCl	$\text{ClO}_2 = \$0.1176$ Labor = 0.0020 $\text{Cl}_2 = (0.0070)$ Total = \$0.1126	$\text{ClO}_2 = \$0.2266$ Labor = 0.00 $\text{Cl}_2 = (0.0070)$ Total = \$0.2196
Cl_2	$\text{ClO}_2 = \$0.0803$ Labor = 0.0014 $\text{Cl}_2 = (0.0070)$ Total = \$0.0747	Not applicable (liquid must be 25% sol'n.)

Table 4.7 Lancaster County, S.C.
Cost of Water and Sewer

<u>Item</u>	<u>Cost (\$/1000 gal. sold)</u>
Sewer Treatment	0.2391
Salaries and Benefits	0.4715
Office Expense	0.0556
Professional Fees	0.0078
Utilities	0.2651
Chemicals	0.3590
Insurance	0.0495
Plant and Motor Equipment	1.1694
Interest	0.8916
Depreciation	<u>0.6464</u>
Grand Total	4.1550

cost is only $(\$0.0747/\$4.1550)(100) = 1.80\%$. The average user consumes 5,440 gal./month. The cost of ClO_2 use per water connection per year is $(\$0.0747/1000 \text{ gal.})(5440 \text{ gal/mth.})(12 \text{ mths./year}) = \4.88 . Thus the economic impact of using ClO_2 here is over twice as much as that for Chester Metropolitan but is still a relatively low yearly incremental cost.

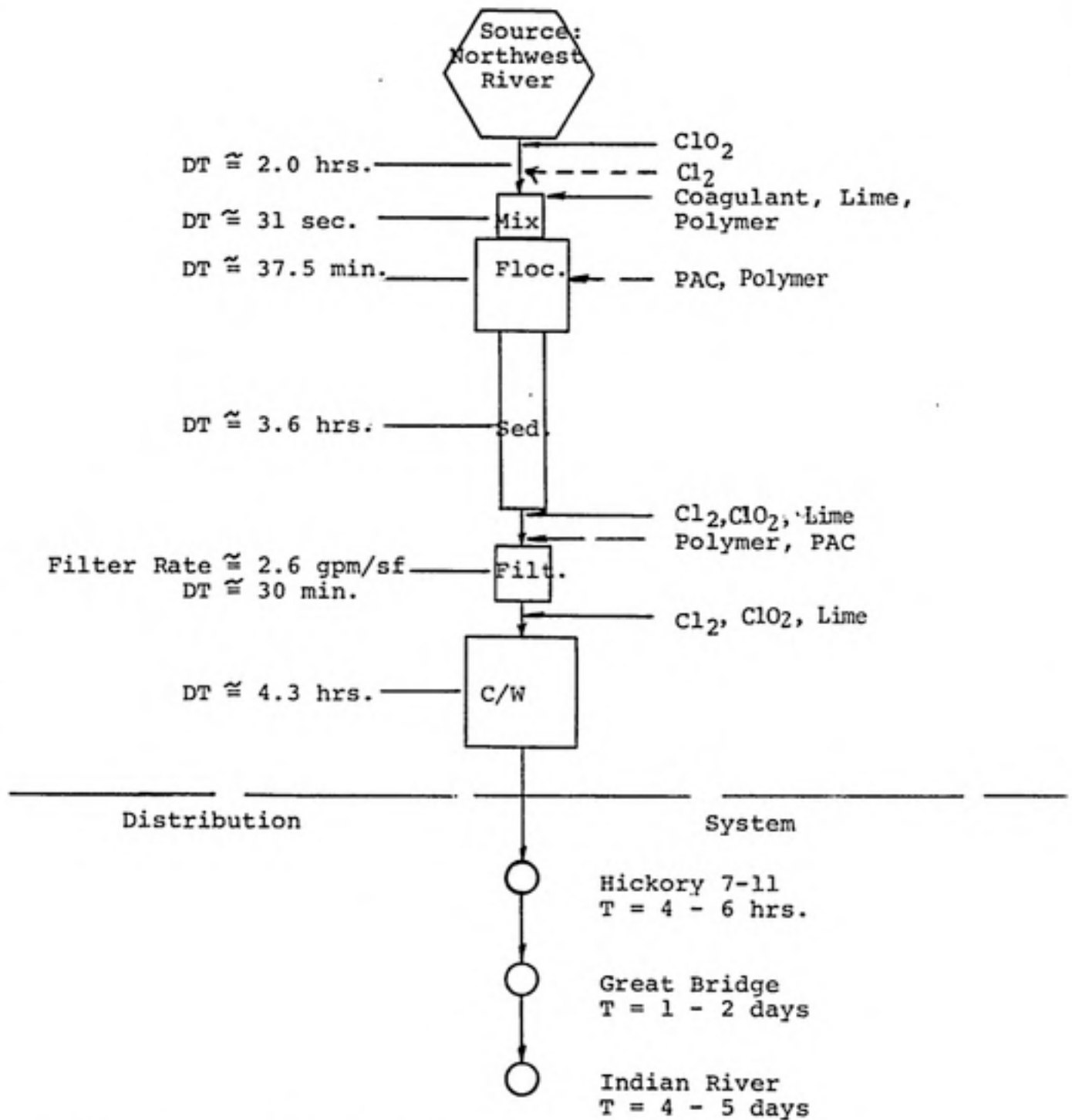
D. Chesapeake, Va.

1. General Description.

The water utility for the City of Chesapeake serves approximately 77,000 people in and around Chesapeake, located in the southeastern corner of Virginia. The water treatment plant is located south of Chesapeake within a few miles of the state border with North Carolina. Raw water is drawn from the Northwest River, whose waters originate in the Dismal Swamp and travel to Currituck Sound. The raw water intake is sometimes subject to salt water intrusion from the Sound. After being treated, the water is piped through a long distribution main to the city, with a travel time to the most remote point of four to five days.

A schematic of the treatment process and distribution sampling points is shown in Figure 4.3. Included in the treatment process are one flash mixer, three flocculation units in parallel, three sedimentation basins in parallel, six dual-media filters in parallel, and one clearwell. The water treatment plant operates at a rate of 8 to 10 MGD for 24 hours/day. The distribution system locations shown are the

Figure 4.3 Chesapeake, Va. Water Treatment Plant



Notes:

- indicates chemicals normally added
- - indicates chemicals intermittently added
- DT = Theoretical Detention Time (based on 10 MGD)
- T = Transmission Time from Clearwell

sampling points used for THM/TOX and residual oxidant analysis and are representative of the system configuration.

Chesapeake began using its present water plant in 1980. Due to the poor quality of the raw water (TOC of 25 to 35 mg/l), the treatment process has to be carefully monitored, and a variety of chemicals is required, as shown in Figure 4.3. Chlorine dioxide has been used practically from the beginning. It was originally used as a pre-oxidant and pre-disinfectant in the raw water transmission main. Its use was later extended to post-disinfection in conjunction with chlorine due to continually high THM levels in the distribution system. The high cost associated with ClO_2 , however, has prompted the utility to begin construction of an air-stripping tower for THM removal. When this construction is complete, the water treatment plant will operate using Cl_2 alone rather than a ClO_2/Cl_2 combination.

There are two ClO_2 generators at the Chesapeake water treatment plant. One is located at the raw water intake. This generator is a $\text{ClO}_2^-/\text{Cl}_2$ -type generator manufactured by the Olin Corp. of New York and modified by plant personnel to fit treatment conditions. It is controlled by operation at a pH of 3-3.5 (with Cl_2), producing a yield of 85 - 90% (according to utility personnel).

The other ClO_2 generator is located at the water treatment plant. It is also a $\text{ClO}_2^-/\text{Cl}_2$ -type generator and is made by Rio Linda Co. of Sacramento, Cal. It is operated in a similar manner to the generator above.

Both generators use a concentrated Cl_2 solution originating from gaseous Cl_2 (provided in ton cylinders) and a 25% NaClO_2 solution which is stored in bulk tanks. The NaClO_2 is delivered by tank truck as a 42% solution and is diluted 50/50 on a volume basis to yield an approximate 25% solution for storage.

2. Water Plant Records -- Water Quality Characteristics and ClO_2 Use

Water treatment records for Chesapeake have been studied to determine the effectiveness of ClO_2 use. Water quality data before the use of ClO_2 began represent a time period of less than one year and are therefore not entirely comparable with the quantity of data available for the time period after ClO_2 use began. Therefore, this study deals only with the time period after ClO_2 use was initiated. Table 4.8 presents a summary of water treatment data for this period. Iron and manganese data are not shown in the table, as they are generally not a problem and are not routinely measured.

The treatment plant is designed and operated mainly for color removal and disinfection. Note that the raw water color is reduced from 184 C.U. to about 3 C.U., the major reduction occurring during coagulation/sedimentation. Color increases slightly following addition of pre-filter chemicals, possibly due to the pH increase.

The coliform count shows that ClO_2 is a very effective pre-disinfectant in this process, reducing the count by more than one-half. Some coliform regrowth appears to be occurring

Table 4.8 Chesapeake, Va.
Water Quality Characteristics and Treatment
Parameters During Chlorine Dioxide Use^{a,b}

<u>Item</u>	<u>Quantity</u>
Water Treated (MGD)	8.43 (0.91)
Raw Chemical Doses (mg/l)	
PAC	3.5 (2.70)
Coagulant	126 (27.09)
CaO	23 (19.84)
Polymer	0.4 (0.10)
Cl ₂	0 (-)
ClO ₂	1.2 (0.72)
Pre- and Post-Filter Chemical Doses Combined (mg/l)	
CaO	31 (19.52)
Cl ₂	8.1 (3.32)
ClO ₂	1.5 (1.37)
Cl ₂ Residuals ^d (mg/l) ^c	
Influent ^e	0 (-)
Settled ^e	0 (-)
Pre-Filtered ^f	1.4 (2.49)
Filtered ^g	3.7 (1.26)
Finished ^h	2.9 (0.94)
pH	
Influent	6.4 (0.19)
Pre-Filtered	8.6 (1.11)
Finished	7.8 (0.51)
Temperature (deg. C)	18 (6.42)
Alkalinity (mg/l as CaCO ₃)	
Influent	17 (5.78)
Settled	5 (1.43)
Finished	22 (5.18)
Turbidity (NTU)	
Influent	9.0 (6.41)
Finished	0.6 (0.25)
Color (C.U.)	
Influent	184 (50.13)
Settled	10 (3.86)
Pre-Filtered	12 (5.53)
Filtered	4 (1.53)
Finished	3 (1.33)
Coliform Count (#/100ml)	
River ⁱ	>440 (244)
Influent	>191 (205)
Pre-Filtered	<1.3 (1.19)
Filtered	<1 (0)
Finished	<1 (0) ^j
Distribution ^k	<1.2 (0.35) ^l
Distribution Standard Plate Count ^k	>128 (145.87)

Table 4.8 (Continued)

- a. All results are calculated from monthly averages unless otherwise noted. The results shown for each item are the average value with the standard deviation in parentheses.
- b. Due in part to the poor quality of the raw water, various chemicals are changed from time to time, such as using ferric sulfate for a few days instead of alum or using Cl_2 rather than ClO_2 for one day, etc. These small modifications are neglected here for the sake of simplification.
- c. Cl_2 residuals listed are actually total oxidant (free and combined Cl_2 and $1/5 \text{ ClO}_2$), measured by plant personnel using a DPD² titrimetric method.
- d. 'Influent' refers to samples taken pre-flash mix.
- e. 'Settled' samples are taken from settled water before pre-filter chemical addition.
- f. 'Pre-Filtered' refers to samples taken on top of the filters (after pre-filter chemicals).
- g. 'Filtered' samples are taken after post-filter chemicals are added.
- h. 'Finished' samples are taken post-clearwell.
- i. 'River' samples are taken directly from the raw water source.
- j. Maximum count for any one month is $<1/100$ ml except 10/83, where the maximum count is $2/100$ ml.
- k. Data is available only for 9/83 through 6/84, excluding 1/84. Data is from samples taken at Hickory 7-11, Indian River, and Deep Creek (located about the same distance from the water plant as Indian River). Average number of samples taken per month is 67 for coliform count and 45 for standard plate count.
- l. Maximum coliform count for any one month is $<1/100$ ml with the following exceptions:

9/83	--	9
10/83	--	60
11/83	--	2
12/83	--	1
2/84	--	27
6/84	--	3

Though confirmation tests were not made, water treatment plant personnel believe these results to be correct.⁴⁶

in the distribution system, especially at the extreme ends. The water leaving the treatment plant does not seem to be stable enough to carry a free Cl_2 or ClO_2 residual to the end of the system, at the Cl_2 and ClO_2 dosages employed. A higher dose, however, would probably result in higher TTHM values, and as a result, the operators try to minimize the use of Cl_2 . Unfortunately, disinfection of the water may be suffering. The problem might be solved by adding chlorine and/or chlorine dioxide at some point in the distribution system, such as a booster pump station.

3. THM/TOX/ ClO_2 Results

THM, TOX, TOC, and disinfectant doses and residuals are shown in Table 4.9. The data were collected in the manner described for Chester Metropolitan above. Several observations are made from this data:

- The ClO_2 added at the raw water pump station is reduced to only a trace by the time the water reaches the treatment plant.
- About 50% of the raw water ClO_2 dose appears as ClO_2^- in the rapid mix.
- The water entering the filters still has a high oxidant demand, as evidenced by the sometimes large differences in oxidant dose and residual within the few minutes required for filtration.
- Cl_2 , ClO_2 , and ClO_2^- residuals seem to be fairly stable in the distribution system, decreasing slowly with time.
- ClO_2 does not produce TTHM.
- ClO_2 produces TOX.

Table 4.9

Chesapeake, Va.
Residual Oxidant and Halogenated Organics Results

Location	Free Chlorine ^a Dose/Residual (mg/l)	ClO ₂ ^a Dose/Residual (mg/l)	ClO ₂ ^{-e} Residual (mg/l)	TOC (mg/l)	CHCl ₃ (ug/l)	THM (ug/l)	TOX (ug/l)	TERM ^c THM (ug/l)	TERM ^c TOX (ug/l)
Raw Water									
Jan 18, 1984	0.0/-	0.0/-	-	26.6	1	1	280	-	-
Apr 9, 1984	0.0/-	0.0/-	-	26.9	0	0	50	2080	6250
July 25, 1984	0.0/-	0.0/-	-	24.1	0	0	55	1580	4850
Oct 10, 1984	0.0/0.0 ^e	0.0/0.0 ^e	0.14 ^f	33.7	0	0	103	1603 ^g	4670 ^g
Post Raw									
Jan 18, 1984	0.0/-	2.4 ^d	-	-	-	-	-	-	-
Apr 9, 1984	0.0/-	1.6 ^d	-	-	-	-	-	-	-
July 25, 1984	0.0/-	2.26/-	-	-	-	-	-	-	-
Oct 10, 1984	0.0/-	2.3/-	-	-	-	-	-	-	-
Rapid Mix Influent									
Jan 18, 1984	0.0/-	0.0/-	-	28.3	7	7	462	-	-
Apr 9, 1984	0.0/-	0.0/-	-	-	0	0	280	2180	6230
July 25, 1984	0.0/-	0.0/-	-	-	0	0	280	1790	5190
Oct 10, 1984	0.0/0.0 ^e	0.0/0.08 ^e	1.17-53 ^h	-	0	0	310	1721	4760
Settled Water									
Jan 18, 1984	0.0/0.18 ^b	0.0/-	-	10.6	0	0	186	-	-
Apr 9, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
July 25, 1984	0.0/-	0.0/-	-	6.4	3	3	210	730	1420
Oct 10, 1984	0.0/0.10 ^{b,e}	0.0/0 ^e	0.60	11.9	1	2	144	1082	2860

Table 4.9 (continued)

<u>Location</u>	<u>Free Chlorine^a Dose/Residual (mg/l)</u>	<u>ClO₂^a Dose/Residual (mg/l)</u>	<u>ClO₂^{-c} Residual (mg/l)</u>	<u>TOC (mg/l)</u>	<u>CHCl₃ (ug/l)</u>	<u>THM (ug/l)</u>	<u>TOX (ug/l)</u>	<u>TERM^c THM (ug/l)</u>	<u>TERM^c TOX (ug/l)</u>
Pre-Filter									
Jan 18, 1984	0.0/-	1.0/-	-	-	-	-	-	-	-
Apr 9, 1984	2.0/0.42	1.0/0.13 ^b	0.62 ^{a,b}	8.0	32	33	250	600	1780
July 25, 1984	0.0/0.07	2.0/0.06	0.68 ^a	-	-	-	-	-	-
Oct 10, 1984	0.0/-	1.2/-	-	-	-	-	-	-	-
Filtered Water									
Jan 18, 1984	4.0/1.14	2.0/1.9	-	11.5	5	5	213	-	-
Apr 9, 1984	0.0/0.14	3.0/2.74	-	7.8	-	-	-	-	-
July 25, 1984	6.0/2.02	2.0/1.22	0.0 ^a	5.6	-	-	-	-	-
Oct 10, 1984	6.0/3.07 ^e	2.4/0.32 ^e	2.25	11.6	43	54	272	-	-
Finished (Tap) Water									
Jan 18, 1984	0.0/0.1	0.0/2.28	-	-	66	69	358	-	-
Apr 9, 1984	0.0/0.12	0.0/3.04	-	-	52	55	220	-	-
July 25, 1984	0.0/2.20	0.0/1.41	0.0 ^a	-	74	85	418	-	-
Oct 10, 1984	0.0/2.41 ^e	0.0/0.33 ^e	1.99	-	92	115	468	-	-
Hickory 7-11									
Jan 18, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
Apr 9, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
July 25, 1984	0.0/-	0.0/-	-	-	-	-	-	-	-
Oct 10, 1984	0.0/1.94 ^e	0.0/0.25 ^e	1.94	-	-	-	-	-	-
Great Bridge									
Jan 18, 1984	0.0/0.6	0.0/0.04	-	-	79	85	453	-	-
Apr 9, 1984	0.0/-	0.0/-	-	-	48	51	320	-	-
July 25, 1984	0.0/-	0.0/-	-	-	77	89	443	-	-
Oct 10, 1984	0.0/2.25 ^e	0.0/0.23 ^e	1.42	-	95	120	540	-	-

Table 4.9 (Continued)

<u>Location</u>	<u>Free Chlorine^a Dose/Residual (mg/l)</u>	<u>ClO₂^a Dose/Residual (mg/l)</u>	<u>ClO₂^{-e} Residual (mg/l)</u>	<u>TOC (mg/l)</u>	<u>CHCl₃ (ug/l)</u>	<u>TTHM (ug/l)</u>	<u>TOX (ug/l)</u>	<u>TERM^c THM (ug/l)</u>	<u>TERM^c TOX (ug/l)</u>
Indian River									
Jan 18, 1984	0.0/0.4	0.0/0.10	-	-	119	129	440	-	-
Apr 9, 1984	0.0/0.0	0.0/0.4	-	-	43	46	260	-	-
July 25, 1984	0.0/0.4	0.0/0.2	-	-	102	120	467	-	-
Oct 10, 1984	0.0/1.35 ^e	0.0/0.09 ^e	1.40	-	129	167	574	-	-

a. Values obtained from water plant personnel unless otherwise noted.

b. Questionable value.

c. Terminal organic halide samples; buffered at pH 7.0 with phosphate, chlorinated with 60 mg/l HOCl (as Cl₂), stored at 20°C in absence of light for seven days. The terminal THM (or TOX) of the raw water is equivalent to its trihalomethane (or total organic halide) formation potential.

d. Dose is monthly average.

e. ClO₂⁻ measurements (except as noted otherwise) made using Aieta method. Cl₂ and ClO₂ measurement made using Aieta method.

f. Interference.

g. No free Cl₂ residual present after 7 days.

- ClO_2 does not reduce TERM THM or TERM TOX, at least at low ClO_2 dose/TOC ratios.
- Sedimentation reduces TERM THM, TERM TOX, TOX, and TOC by about 48%, 56%, 46%, and 66%, respectively. All of these reductions, however, are extremely variable with the exception of TOC.
- Using the present treatment scheme, the TTHM concentration approaches and sometimes exceeds the MCL in the distribution system. The TTHM and TOX concentrations in the far ends of the distribution system are about 14% and 26%, respectively, of the settled water terminal values.

Further discussion of these comments is made in ^E_D below.

4. Costs

The cost of using ClO_2 is presented below and is compared with the total cost of providing water to the public. The results shown cannot be compared directly with the other two water treatment plants since the savings resulting from using less Cl_2 cannot be accounted for due to insufficient information available for operation prior to the use of ClO_2 . The data used are from records and conversations with utility personnel unless otherwise noted.

Data: Average daily consumption of NaClO_2 = 300 lb. of
 25% solution
 Average daily consumption of Cl_2 for generation of ClO_2 =
 280 lb.
 Average daily consumption of water = 8.43 MG

Chemical Costs (as of 7/84):

NaClO_2 = \$1.60/lb. pure
 Cl_2 = \$0.185/lb. (in 1 ton cylinders -- price from
 data for Chester Metropolitan)

Other costs:

Labor = \$21,000/year (from study of Chesapeake water treatment plant by Malcolm Pirnie Engineers, April 1983)

Capital costs for generators:

Generator at Raw Water Pump Station = \$2,000

Generator at WTP = \$8,000

Capital cost for bulk storage of NaClO_2 = \$80,000 - 10,000 = \$70,000 (from study by Malcolm Pirnie referenced above).

An amortization period of 20 years at an interest rate of 10% compounded annually is assumed for these capital costs. Thus, the annual cost of the capital investment is as follows:

$$(\$2,000 + \$8,000 + \$70,000)(A/P, 10\%, 20) \\ = (\$80,000)(0.1175) = \$9,400.$$

$$\begin{aligned} \text{ClO}_2 \text{ Cost} &= (300 \text{ lb. NaClO}_2 @ 25\%)(0.25)(\$1.60/\text{lb.}) \\ &+ (280 \text{ lb. Cl}_2)(\$0.185/\text{lb.}) \\ &+ \frac{(\$21,000/\text{yr} + \$9,400/\text{yr.})(1 \text{ yr}/365 \text{ days})}{(8.43 \text{ MGD})(10^3 \text{ 1000 gal./MG})} \\ &= \frac{(\$120.00 + \$51.80 + 83.29)}{8430 \quad 1000 \text{ gal.}} \\ &= \$0.0303/1000 \text{ gal.} \end{aligned}$$

Thus, the largest incremental cost of ClO_2 is the purchase of NaClO_2 . The cost of ClO_2 shown above is lower than that for Chester Metropolitan or Lancaster County due in large part to the purchase of NaClO_2 in bulk.

The average cost of providing water in Chesapeake is shown in Table 4.10. Neglecting the difference between water sold and water treated, the economic impacts of ClO_2 on chemical cost, treatment cost, and total costs are 12.63%,

Table 4.10 Chesapeake, Va.
Cost of Water

<u>Item</u>	<u>Cost (\$/1000 gal. sold)</u>	
Treatment		
Wages	0.20	
Chemicals	0.24	
Electrical (incl. dist. system)	0.11	
Misc.	0.06	
Debt retirement	<u>0.59</u>	
Total	1.20	
Other costs (administration, meter reading, etc.)	<u>1.01</u>	
Grand Total	2.21	

2.53%, and 1.37%, respectively.

The average residential customer uses 6,700 gal./month. The cost of ClO_2 use per water connection per year is therefore $(0.0303/1000 \text{ gal.})(6,700 \text{ gal./month})(12 \text{ months/year}) = \2.44 . Again, the cost of ClO_2 treatment is negligible.

E. General Discussion and Comparison.

A summary comparison between the three water treatment plants studied is given in Table 4.11. The quality of the raw water with respect to precursor content varies greatly from plant to plant -- Chester having the best quality and Chesapeake having the worst.

All three treatment plants modified their treatment process in the same way to control trihalomethanes. The chlorine added to the raw water was replaced with chlorine dioxide, the chlorine addition point was moved downstream of the sedimentation process, and less chlorine was added. The sedimentation process was then able to remove much of the precursor material before it could react with chlorine (Table 4.11). The percent reduction in TERM THM was higher but on the same order of magnitude as that found by Singer, *et al.*³ They found a 42% reduction for sedimentation and a 54% reduction for sedimentation and filtration combined for water treatment plants in North Carolina. They also reported the following correlation between raw water TOC and TERM THM:

$$\text{Raw TERM THM} = (64.63)(\text{TOC Raw}) + 9.84 \text{ with} \\ r = 0.844 \text{ and } n = 53.$$

The data for these three raw waters agree with this producing

Table 4.11 Chlorine vs. Chlorine Dioxide^a

Item	Chester	Lancaster	Chesapeake
Raw Water ^b			
TOC (mg/l)	7	16	28
TERM THM (ug/l)	360	880	1800
TERM TOX (ug/l)	1300	2900	5300
Oxidant Dose (Before/After ClO ₂)			
ClO ₂ (mg/l)	0/0.7	0/3.2	---/2.7
Cl ₂ (mg/l)	11.5/3.9	13.6/8.2	---/8.1
% Reduction by Sedimentation ^h			
TOC (mg/l)	57	69	66
TERM THM (ug/l)	54	66	48
TERM TOX (ug/l)	53	73	56
Finished Water (Before/After ClO ₂)			
Color (C.U.)	0.09/0.35 ²	---	---/3
Turbidity (NTU)	0.19/0.41	0.2/0.2	---/0.6
Manganese (mg/l Mn ⁺²)	---	0.08/0.07	---
Coliform Count (#/100 ml)	0/0	0/0	---/0 ^d
TOC ^b (mg/l)	---/2.4 ^g	---/4.9	---/9.1 ^g
THM ^b (ug/l)	---/40	290/110	---/80
TOX ^b (ug/l)	---/190	890/290	---/370
Cl ₂ ^b (mg/l)	1.6 ^c /1.4	3.0/1.4	---/2.4
ClO ₂ ^b (mg/l)	---/0.0	---/0.2	---/0.3
ClO ₂ ^{-b} (mg/l)	---/0.3	---/2.3	---/2.0
Distribution System (Before/After ClO ₂)			
Coliform Count (#/100 ml)	0/0	0/0 ^e	---/<1.2 ^f
THM ^b (ug/l)	---/80	310/150	---/100
TOX ^b (ug/l)	---/220	930/270	---/440
Cl ₂ ^b (mg/l)	0.8 ^c /0.4	0.9/0.4	---/1.8
ClO ₂ ^b (mg/l)	---/0.0	---/0.1	---/0.2
ClO ₂ ^{-b} (mg/l)	---/0.2	---/2.2	---/1.6
ClO ₂ Cost (\$/1000 gal.)	0.0352	0.0747	0.0303

- a. All data taken from treatment plant records unless otherwise noted.
- b. Results taken only from data measured by UNC research team unless otherwise noted. This data is from intermittent monitoring only and may not represent the norm.
- c. Data taken from treatment plant records.

Table 4.11 (continued)

- d. Maximum count for any one month is <1/100 ml except 10/83, where the maximum count is 2/100 ml.
- e. In 8/84, several distribution system samples were positive. Average coliform count = 46/100 ml, and maximum coliform count = 800/100 ml.
- f. Maximum coliform count for any one month is <1/100 ml with the following exceptions:
- | | | |
|-------|----|----|
| 9/83 | -- | 9 |
| 10/83 | -- | 60 |
| 11/83 | -- | 2 |
| 12/83 | -- | 1 |
| 2/84 | -- | 27 |
| 6/84 | -- | 3 |
- g. This sample was taken at the bottom of the filter rather than post-clearwell (finished).
- h. Data shown for Lancaster includes sedimentation and filtration.

the following correlations by linear regression analysis:

$$\begin{aligned} \text{Raw TERM THM} &= (60)(\text{TOC Raw}) - 25 \\ &\text{with } r = 0.94 \text{ and } n = 12 \end{aligned}$$

and

$$\begin{aligned} \text{RAW TERM TOX} &= (172)(\text{TOC Raw}) + 150 \\ &\text{with } r = 0.91 \text{ and } n = 12 \end{aligned}$$

Thus, TOC appears to be a good surrogate measurement for TERM TOX as well as TERM THM.

Referring to the finished and distributed water characteristics listed in Table 4.11, the "chlorine treatment scheme" can be compared with the "chlorine/chlorine dioxide treatment scheme". Using chlorine dioxide and chlorine, turbidity and color removal at Chester are not as good as that with chlorine alone. Turbidity removal at Lancaster, however, is the same for both Cl_2 and ClO_2 , but manganese removal is not satisfactory under either method ($\text{Mn MCL} = 0.05 \text{ mg/l}$).

When compared with raw and finished water TOC, the coliform count under ClO_2/Cl_2 treatment improves as the TOC decreases. This could be due to less oxidant demand, leaving more oxidant available for disinfection, and to less biodegradable organics capable of supporting microorganism regrowth in the lower TOC water.¹⁴ Also, the poorer disinfection associated with the ClO_2/Cl_2 scheme (compared to Cl_2 alone) may be more a result of using less disinfectant (ClO_2 and Cl_2) than is needed, in an effort to control trihalomethanes, rather than a disinfection limitation of ClO_2 .

Referring again to Table 4.11, the TTHM and TOX concentrations in the finished and distributed water have been lowered dramatically by using a ClO_2/Cl_2 treatment strategy.

Referring to Tables 4.2, 4.5, and 4.9, it can be seen that ClO_2 produces some TOX but does not form TTHM. At the low oxidant to TOC and ClO_2 to Cl_2 ratios present in the treatment plants investigated, ClO_2 also does not reduce the TERM THM of the water. This contradicts the findings of Miltner, who worked with low TOC waters ($\text{TOC} \approx 1.8 \text{ mg/l}$).³³

About 50% of the raw water ClO_2 dose appears as ClO_2^- in the rapid mix. This agrees well with the findings of others.^{9,40} This ClO_2^- residual is fairly stable throughout the treatment process and distribution system. Table 4.11 reveals that the use of ClO_2 as a pre-oxidant and disinfectant at Lancaster and Chesapeake requires that a rather large amount of ClO_2 be added to the raw water to attain the desired level of treatment. This results in stable ClO_2^- concentrations in the distribution system which exceed the recommended MCL of 0.5 mg/l.⁶

Finally, the cost of ClO_2 treatment has not been found to be prohibitive (Table 4.11). The controlling factors for determining the cost of using ClO_2 are the amount of NaClO_2 used and the bulk quantity in which it is purchased. Since this varies with the dose required and the generation method used, the cost of ClO_2 /1000 gal. is extremely variable and not easily compared from plant to plant. When compared to the total cost of providing water to the consumer, however, the cost of chlorine dioxide treatment is generally not significant.

V. Conclusions and Recommendations

Chlorine dioxide is a good oxidant and disinfectant. It does not form trihalomethanes and can be used quite effectively and economically as an alternative to free chlorine to treat waters with a low to moderate TOC concentration.

In waters with a high oxidant demand and high THM precursor content, chlorine dioxide should be used with caution. High doses of chlorine dioxide may be required to stabilize and disinfect the raw water, resulting in high residual chlorite concentrations and high chemical costs. Lower ClO_2 doses may give inadequate disinfection. Also, if low chlorine doses are used in post-disinfection in an effort to further reduce trihalomethane formation, this may further compromise disinfection.

It is recommended that waters having a high concentration of TOC, manganese, and/or iron be treated first with an oxidant/algicide such as potassium permanganate. This oxidant will oxidize the iron and manganese and allow them, as well as a major portion of the TOC, to be removed in the coagulation and sedimentation processes. Chlorine dioxide can then be added on top of the filters to maintain strong oxidizing conditions and to begin disinfection of the water. Finally, free chlorine can be added for post-disinfection, if necessary, before the water enters the clearwell or distribution system. This scheme will reduce the amount of chlorine dioxide and chlorine required, thereby reducing chlorite residuals, THM formation, and overall chemical costs. Lastly, the quality of

the finished water will not be compromised, especially with regards to disinfection.

It is recommended that field research be continued on disinfection with chlorine dioxide alone and with chlorine dioxide combined with chlorine, especially in high TOC waters. This research should include an evaluation of the biocidal effects of these disinfectants against viruses, spores, and cysts as well as against bacteria.

It is also recommended that Miltner's research³³ on the removal of THM precursors by ClO_2 be continued under controlled conditions in the laboratory to include waters of varying TOC. The study of TTHM formation as a function of Cl_2 , ClO_2 , ClO_2^- , and TOC under controlled laboratory conditions may lead to a better understanding of the mechanism involved in THM precursor removal by ClO_2 .

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