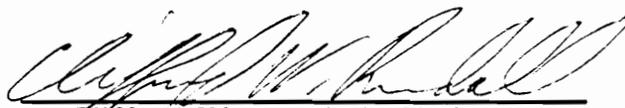**The Removal of Phenols From Oily Wastewater**

by Chlorine Dioxide
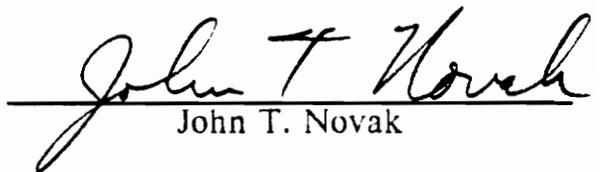
by

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in partial fulfillment of the requirements for the degree of

Master of Science

in

Environmental Engineering

APPROVED:

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Blacksburg, Virginia

The Removal of Phenols From Oily Wastewater
by Chlorine Dioxide

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Clifford W. Randall, Chairman

Environmental Engineering

(ABSTRACT)

Treatability studies were performed on oily wastewaters produced by petroleum and canning industries.

Chlorine dioxide was used for the removal of phenolic compounds from these oily wastewaters. Most of phenolic compounds can be destroyed by chlorine dioxide within 15 minutes if ClO_2-to-phenol ratios of higher than 5.0 are provided. Factors such as pH, temperature, and COD have little effect on phenol removal.

The effectiveness of chlorine dioxide treatment depends critically on the performance of the chlorine dioxide generator. High yields of chlorine dioxide generation can be achieved by maintaining the pH between 2.5 and 3.5, and by controlling the concentration of feed chemicals.

For small treatment plants, chlorine dioxide treatment may be an economical process because no expensive equipment is required.

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Chapter 1   Introduction

The priority pollutant list issued by the U.S. Environmental Protection Agency (EPA) includes 11 phenols [1]. This group of chemicals has very low taste and odor thresholds, and are highly toxic to both aquatic life and humans, even at very low levels. Many industries, such as oil refineries and canning industries, are characteristic sources of phenolic pollutants. These industries produce oily wastewaters containing high concentrations of phenolic compounds and other toxic pollutants.

Phenols can be removed from wastewaters by either biological or physiochemical treatment. Both treatment processes have been used successfully for fullscale industrial application, and high efficiencies of treatment have been reported [2]. However, the suitability of a specific treatment method for a particular industrial waste stream will depend on the composition of the wastewater. It has been reported that when phenol removal is the primary concern, chemical oxidation processes should be considered because of the ability of these processes to produce low effluent phenol concentrations on a consistent basis [3]. Among the oxidants employed for phenol removal, chlorine dioxide (ClO_2) may be the one of choice because of its high oxidation power (263% available chlorine). This chemical has been regarded as a "last resort" when other oxidants failed [4].

Although ClO_2 has been used for more than 40 years for phenolic taste and odor control, its chemical behavior in treating wastewater is still not well understood. The possible variables that may influence the reaction between phenols and ClO_2 are: ClO_2-to-phenol molar ratio, contact time, temperature, pH, COD values, and others [5,6,7].

Chlorine dioxide must be generated on site due to the instability of this chemical. In the wastewater industry chlorine dioxide is most frequently generated in aqueous solution by using sodium chlorite ($NaClO_2$) as the precursor chemical along with chlorine gas (Cl_2) and hydrochloric acid (HCl). If chlorine gas can not be used for any reason, a hypochlorite (OCl^-) solution can be substituted. It has been reported that the effectiveness of chlorine dioxide treatment is critically dependent on the performance of the generator [8]. Therefore, it is essential that the yield of chlorine dioxide be maximized. This can be achieved through control of pH and the concentrations of the feed chemicals [9].

This project was conducted at Environmental Technology Southeast, Inc. (ETS), at Jacksonville, Florida. This plant operates oily wastewater treatment processes and waste oil recycling processes. The oily wastewaters received during this project were mainly from petroleum and canning industries, and contained significant amounts of phenol. Before they could be discharged to the sewer under industrial pretreatment permits, the wastewaters were first treated by physiochemical processes followed by biological treatment. During the project period, ETS was constructing a new plant at Miami, Florida. That plant was designed to treat the same types of wastewaters by the same processes employed

at the Jacksonville plant. However, the effluent discharge limits in Miami are more stringent than those at Jacksonville especially for phenols. ETS realized that a polishing process after the biological process would have to be employed to remove the bio-resistant phenols to the desired level (less than 1.00 mg/l). Chlorine dioxide treatment was considered for this purpose.

The objectives of this project, therefore, were:

1. to determine the optimum operating conditions of the chlorine dioxide treatment for the removal of phenols from wastewaters to a residual level of less than 1.0 mg/l,
2. to evaluate the performance of a trial unit ClO_2 generator system.

In addition, a cost study for chlorine dioxide treatment was performed because such information would assist the plant manager in his consideration of ClO_2 treatment as an option.

Chapter 2   Literature Review

2.1 General Considerations for Phenol Removal

Phenols are defined as hydroxy derivatives of benzene and its condensed nuclei. This waste catogory consists of a variety of similar chemical compounds among which are various substituted polyphenols, chlorophenols, and phenoxyacids. The concentrations of phenolic materials measured by colorimetric analytical methods are often reported as phenol (C_6H_5OH) itself because these methods are not able to differentiate between different kinds of phenols. Complete determination of the individual phenolic compounds can be achieved by gas-liquid chromatographic technic.

Phenols are prevalent in wastewaters from oil refineries, chemical plants, explosive manufacturing, resin manufacturing, and coke ovens, with effluent concentrations as high as 500 mg/l [2]. Phenolic wastes often contain large quantities of other waste constituents such as oil and cyanides which require special treatment procedures. The commonly accepted processes for phenol removal include biological treatment, carbon adsorption, and chemical oxidation.

In the absence of high concentrations of other toxic materials, biological treatment is widely employed for treatment of phenol containing wastewaters.

The biological processes include activated sludge, trickling filters, oxidation ditches, and lagoons. Among those, activated sludge systems have been reported as preferable to other biological processes because of ease of control and high efficiency [10]. If phenol removal is the primary concern, the biological treatment processes would not normally be considered because of the questionable ability of these processes to produce low effluent phenol concentrations on a consistent basis [3].

The use of activated carbon has been found to be extremely efficient as a process for the removal of phenol from wastewaters. However, there have been reports of rapid phenol breakthrough in activated carbon columns [11]. Carbon adsorption was found to be the most expensive among the applicable treatment processes for phenol removal [3].

Chemical oxidation is effective for the removal of phenol constituents from wastewaters. Chlorine (Cl_2), Chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), potassium permaganate ($KMnO_4$), and ozone (O_3) have been employed as oxidants [12,13,14,15].

From an economic standpoint, chlorine has the advantage of lower cost per unit of oxidizing equivalence as compared to other oxidants. However, due to the possibility of forming offensive chlorophenols and toxic carcinogens, chlorination is not considered a favorable means of phenol removal.

The acceptance of chlorine dioxide as an alternative to chlorine gas for phenol removal has arisen largely from the fact that chlorine dioxide does not lead to the

formation of trihalomethanes (THMs). In addition, chlorine dioxide also possesses the following desirable characteristics over chlorine:

- It does not react with ammonia nitrogen and other organics which react with chlorine.
- It does not react with water, so its oxidation potential is not pH dependent.

In spite of the advantages, chlorine dioxide has remained a speciality chemical and seems to have been used only as a last resort when all else failed. This is mainly due to its relatively high cost and to insufficient knowledge of its chemical behavior and oxidation characteristics in treating wastewater [4].

Hydrogen peroxide is reported to readily oxidize phenol from 500 mg/l to 3 mg/l in the presence of ferrous salt catalyst [3]. However, the associated costs involved in this process would make hydrogen peroxide an undesirable choice, since this chemical has to be treated with a catalyst at a pH of 1.5 and then the pH raised to 11 to remove phenol.

Potassium permanganate has been used to destroy phenolic compounds. In one application of permanganate to a wastewater with initial phenol concentration of 125mg/l, phenol removal of 62% was achieved [12].

Ozone has long been recognized as one of the most powerful oxidizing agents available. In one application of ozonation to an industrial wastewater, phenol was reduced from 47 to 0.13 mg/l [16]. However, the operating and capital costs of ozonation may be very high, thus ozone would likely be considered only as a low level treatment.

2.2 Properties of Chlorine Dioxide

Chlorine dioxide is a yellow-green to orange gas, its color changing to red with increasing concentration. The most significant characteristic of the gas is its explosiveness. Generally, it can be safely handled only if its concentration in air does not exceed 10% [4]. This gas has a disagreeable, irritating odor similar to chlorine, and is detectable by humans at 17 mg/l [17]. Exposure to chlorine dioxide may cause violent headaches and general fatigue lasting for several days. When concentrated and compressed, chlorine dioxide becomes unstable. For this reason, it must be generated and used on site in its aqueous form.

Water solubility of chlorine dioxide depends upon temperature and pressure. At room temperature and atmospheric presure, it has a solubility of approximately 2,900 mg/l [20]. In chilled water, solution concentrations up to 10,000 mg/l have been reported [12]. Unlike chlorine, chlorine dioxide does not react with water but forms a true solution. ClO_2 is extremely volatile and can be easily stripped from acqeous solution by a minimum of aeration. Therefore, solution transfer systems should be designed to eliminate this potential loss. Chlorine dioxide should always be stored in the dark due to the fact that it may be readily decomposed on exposure to ultraviolet light [19]. The product of this photochemical decomposition are chlorine heptoxide, chlorine monoxide, chlorine, and possibly oxygen [20]. The rate of photodecomposition is a function of both time and intensity of the ultraviolet light source, and is low as compared to decomposition from its volatility.

The oxidation power of ClO_2 has been referred to as having an available chlorine content of 263% [13]. However, the potential of ClO_2 is not always fully utilized in water treatment practice. It depends in large measure on the pH of the system and the nature of the reacting substances in the water. In waterworks practice, chlorine dioxide seldom undergoes complete reduction. The common reaction in mildly acid, neutral, and alkaline solution is to form chlorite, ClO_2^-. In this situation, only 20% of its oxidizing capacity is utilized. Complete reduction to chloride, Cl^-, may occur at low pH [21]. It has long been recognized that chlorine is a better oxidant than chlorine dioxide except under special conditions. One of these special conditions is the reaction of chlorine dioxide with phenol where six valence changes take place. In this instance, ClO_2 utilizes its full oxidizing potential of 263% available chlorine and even more.

2.3 Reaction of Chlorine Dioxide with Phenols

The reactions of chlorine dioxide with phenol and phenolic compounds are important to the wastewater treatment field because they include the reactions involved in taste and odor control and help explain the ClO_2 demand of a particular wastewater.

The organic products identified from the reaction between chlorine dioxide and phenols include chlorophenols, benzoquinone, and maleic and oxalic acid [22]. The reaction products of phenols with chlorine dioxide can be summarized

in Figure 1 [5]. The product distribution is dependent on the chlorine-dioxide-to-phenol ratio. In solutions with phenol in excess, chlorophenols are an intermediate formed by the slow reaction between hypochlorous acid and the excess phenol [7]. When chlorine dioxide is in excess, the main products found are benzoquinone, maleic acid, and oxalic acid [6].

Detailed investigations of the reactions of chlorine dioxide with phenols have been carried out by Glabisz [23]. According to Glabisz, at phenol concentrations of 1 mg/l and above, the character of the reaction products of phenols fall into two groups. The first group is made up of hydroquinone and monohydric phenols that are not para-substituted. They retain their ring structure upon the reaction with ClO_2 and are oxidized mainly to chloroquinones as well as chlorophenols. The second group is characterized by those phenols which undergo ring cleavage upon their reactions with ClO_2 and are oxidized to carboxylic acids as end products. Examples include para-alkyl phenols and ortho or meta-dihydric phenols.

Stoichiometrically, each mole of phenol reacts rapidly with 2 moles of chlorine dioxide in a reaction which is first order with respect to each reactant [6].

$$phenol + 2\ ClO_2 \rightarrow products$$

$$-d[ClO_2]/dt = 2\ k\ [phenol][ClO_2], \quad where$$

[phenol] = total phenol concentration, and k = rate constant.
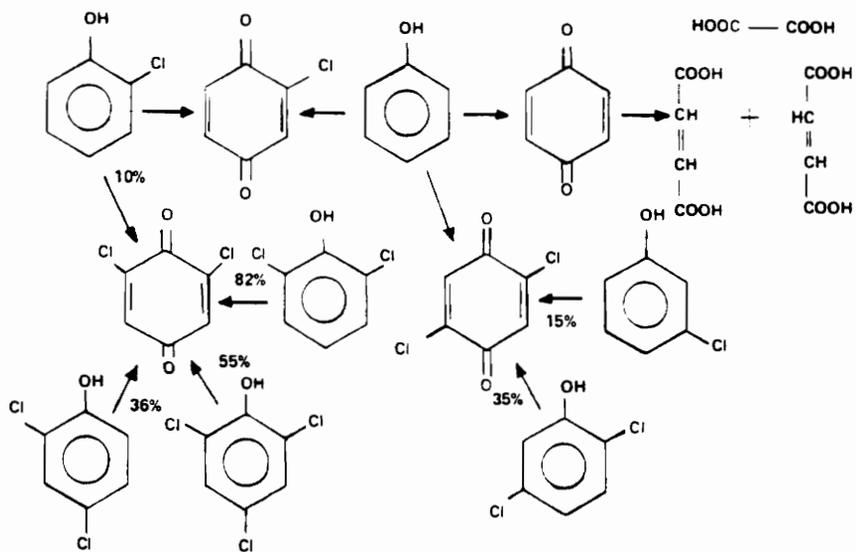
Figure 1.   A reaction scheme for phenols with chlorine dioxide. (after Masschelein, 1979)

The recent report by Wajon [7] has shown that the reaction between chlorine dioxide and phenol at pH 7 with chlorine dioxide in excess is complete within 2 seconds, and that phenol is completely consumed. In this instance, the rate constant, k, has been reported in the range of 2 to 4 x 10^4 M^- S^-, at 25° C and neutral pH. The second-order rate constants increase with increasing pH. A mechanistic scheme for the reaction of ClO_2 with phenol was shown in Figure 2 [6].

Investigation of the oxidation properties of chlorine dioxide against the most commonly found constituents of industrial wastewater indicated that at neutral pH values, 1.5 parts by weight ClO_2 will oxidize 1 part by weight of phenol to benzoquinone. At pH's greater than 10, an average of 3.3 parts by weight ClO_2 will oxidize 1 part by weight phenol to carboxylic acids [4].

In practice, it has been reported that 1.7 to 5.0 g of ClO_2 per g of phenol which is to be eliminated gives good results within a contact period of 15 to 30 minutes [5].

2.4 Synthesis of Chlorine Dioxide

Like ozone, chlorine dioxide must be generated *in situ* due to the instability of this chemical in its gaseous form. Chlorine dioxide may be generated from sidium chlorate ($NaClO_3$) or sodium chlorite ($NaClO_2$).
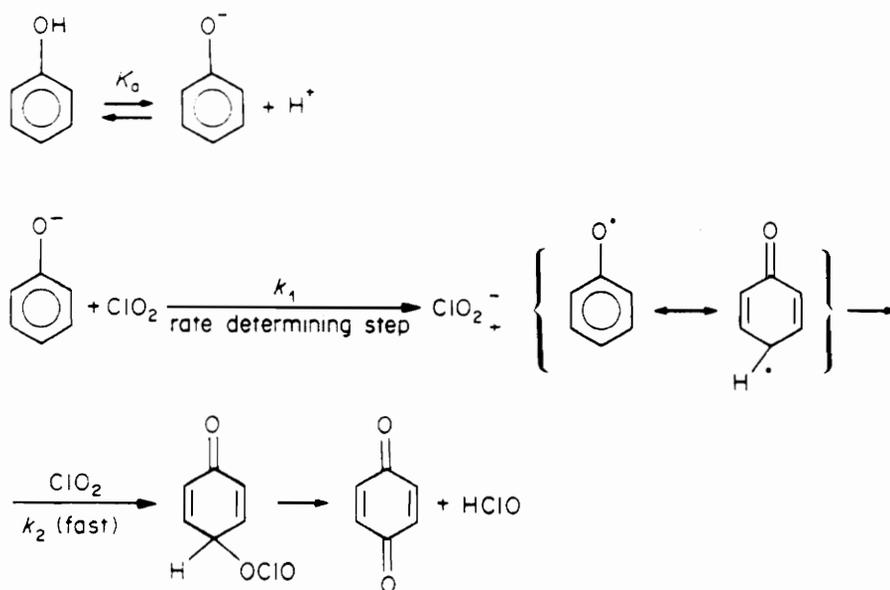
Figure 2.   A mechanistic scheme for the reaction of ClO$_2$ with phenol. (After Rav-Acha, 1984)

For large production units such as the bleaching of paper pulp and texiles, chlorine dioxide is generated by reduction of $NaClO_3$ from the following processes:

1. The Mathieson or SO_2 process [24]

$$2\ NaClO_3 + H_2SO_4 + SO_2 \rightarrow 2\ ClO_2 + 2\ NaHSO_4$$

2. The Solvay or Methanol process [25]

$$2\ NaClO_3 + CH_3OH + H_2SO_4 \rightarrow 2\ ClO_2 + HCHO + Na_2SO_4 + 2\ H_2O$$

3. The Hooker R-2 process [26]

$$NaClO_3 + NaCl + H_2SO_4 \rightarrow ClO_2 + 1/2\ Cl_2 + Na_2SO_4 + H_2O$$

For small production units such as potable water and wastewater process, ClO_2 is generated from sodium chlorite. Three processes for the synthesis of ClO_2 from sodium chlorite have been developed. These include the treatment with acid and the reaction with chlorine gas or hypochlorite [17].

1. from Cl_2

At treatment plants where gaseous chlorine is already in use or is preferred for economical reason, ClO_2 is produced by the following reactions :

The overall reaction is :

$$2 \ NaClO_2 \ + \ Cl_2 \ \rightarrow \ 2 \ ClO_2 \ + \ 2 \ NaCl$$

The stepwise reactions are :

$$ClO_2 \ + \ H_2O \ \rightarrow \ HOCl \ + \ HCl$$

$$HOCl \ + \ HCl \ + \ 2 \ NaClO_2 \ \rightarrow \ 2 \ ClO_2 \ + \ 2 \ NaCl \ + \ H_2O$$
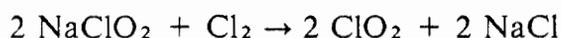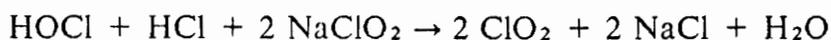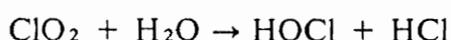
The stoichiometry of reactants is 1 mole ClO_2 to 2 moles $NaClO_2$. In practice, however, the chlorine to chlorite weight ratio 1:1 is recommended so that the excess of Cl_2 will increase the reaction rate and insure complete activation of the chlorite to give the best possible yield of ClO_2 [19]. Yields up to 98 % have been reported by Aieta and Roberts when using 4 % excess chlorine [9]. The excess amount of chlorine necessary for the complete conversion of chlorite becomes less important with gradual increase of Cl_2 concentration. Masschelein [5] has reported that an excess of 10 % chlorine is ample for the total oxidation of chlorite if the Cl_2 concentration is 2 g/l, and the reaction proceeds stoichiometrically when the Cl_2 concentration is 4 g/l. For efficient generation of ClO_2, the chlorine solution should contain at least 500 mg/l Cl_2 [13]. The required contact time to form ClO_2 is about one minute. pH is controlled between 2 to 4 [19].

2. from acidification

This process can use either hydrochloric acid or sulfuric acid as the acid reagent for ClO_2 generation. The basic reactions of this process are :

$$5 \, NaClO_2 + 4 \, HCl \rightarrow 4 \, ClO_2 + 5 \, NaCl + H_2O \quad , or$$

$$10 \, NaClO_2 + 5 \, H_2O \rightarrow 8 \, ClO_2 + 5 \, Na_2SO_4 + 4 \, H_2O$$

HCl is more commonly used in water and wastewater treatment operations because explosion can occur when sulfuric acid comes into contact with solid $NaClO_2$.

Catalysts used for the reaction include sodium peroxide, potassium perborate and cobalt sulfate [5]. Yield of 85 to 95 % has been obtained by using a 10 % solution of $NaClO_2$ and 12 % HCl in a 250-300 % excess [27]. Yield up to 100 % has also been reported when using equal weight proportions of $NaClO_2$/HCl and starting from a 7.5 % solution of sodium chlorite and 9 % hydrochloric acid. The practical excess of HCl is about three times the stoichiometric amount. The velocity of the reaction depends on the temperature and mixing of the reagents. A reaction time of 2 minutes is generally sufficient to achieve the reaction. At equal weight proportions of HCl and $NaClO_2$ the reaction usually is completed at pH less than 0.5 [5].

3. from sodium hypochlorite and sodium chlorite

Chlorine dioxide solution can be generated using a hypochlorite solution if chlorine gas cannot be used for any reason. The acid is required to reduce the pH to the level necessary for complete conversion of the chlorite to chlorine dioxide. the stepwise reaction of HCl and NaOCl forming ClO_2 are as follows :

$$NaOCl + HCl \rightarrow NaCl + HOCl$$

$$HCl + HOCl + 2\,NaClO_2 \rightarrow 2\,ClO_2 + 2\,NaCl + H_2O$$
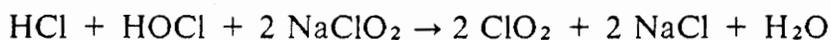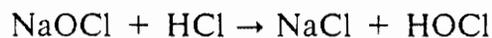
The overall reaction then can be summarized as :

$$2\,NaClO_2 + NaOCl + 2HCl \rightarrow 2\,ClO_2 + 3\,NaCl + H_2O$$

A typical installation using a 1% NaOCl solution requires a 2.42% $NaClO_2$ solution for mixing with a 2.0 % H_2SO_4 solution. The H_2SO_4 is used in about 50 % excess of stoichiometric in order to give the desired pH range, 3 to 4 [20].

Usually the three chemicals are stored and fed seperately, but hypochlorite feed systems may be adapted to Cl_2-chlorite generation process. In this approach, hypochlorite and chlorite solutions can be combined and fed through one pump to the generator. Diaphragm pumps are usually used to feed the chemical solutions into a packed column where rapid and thorough mixing of the reactants occurs. Columns are usually constructed of plastic, ceramic, or glass. If the column is not transparent, a transparent section of piping must be included. This

facilitates control by providing an inspection point where the yellow-green color of the ClO_2 solution may be rapidly seen, and the concentration of ClO_2 can be estimated by an experienced operator.

2.5 Determination of Chlorine Dioxide

One of the factors preventing the widespread use of chlorine dioxide is the difficulty in determining its concentration. This is because ClO_2 is generated by reactions involving sodium chlorite, chlorine gas or hypochlorite, and sulfuric acid or hypochloric acid, so Cl_2, ClO_2^-, and OCl^- will frequently be found occurring with it in solution as by-products or unreacted starting materials [28].

The sixteenth edition of Standard Methods lists three alternatives for testing chlorine dioxide [29].

1. The iodometric method is primarily used for standardizing chlorine dioxide solutions needed for the preparation of temporary standards. These standards are used for the construction of photometric calibration curves, for checking permanent color standards, or as a primary base for checking the accuracy of the amperometric methods. The principle of this method is that ClO_2 releases I^- from a KI solution, and I^- is then titrated with a standard sodium thiosulfate ($Na_2S_2O_3$) solution with starch as the indicator. Since this

method does not permit differentiation between ClO_2 and other chlorine compounds, it is inapplicable to industrial waters.

2. The amperometric method is first described by Haller and Listek [30] for the determination of free chlorine, chloramines, chlorine dioxide, and chlorite present in any combination and at any concentration of each component greater than 0.01 mg/l chlorine-equivalent. This method utilizes the conversion of chlorine dioxide to chlorite and chlorate to eliminate the interference of chlorine dioxide with the free residual titration. Phenylarseneoxide is used as titrant. The method is free from interference by ferric and chlorate ions, turbidity, and color. Though this is a reasonably accurate test, the accuracy is compromised because of the possibility of volatilization of ClO_2. It is also unpopular due to the requirement of specialized equipment and considerable analytical skill.

3. The N,N-diethyl-P-phenylene-diamine (DPD) method is able to distinguish between ClO_2 and various forms of chlorine. To suppress the free chlorine so that only ClO_2 reacts with the indicator, glycine is added to the water. The glycine converts the free chlorine to chloroaminoacetic acid, but has no effect on chlorine dioxide. Ferrous ammonium sulfate (FAS) is used as the titrant in this method. Though not as accurate as the amperometric method, the DPD method may yield results adequate for most applications.

Chlorine Dioxide possesses a greenish yellow color which makes it possible to determine it spectrophotometrically at 360 nm. The detection limit of this technique has been reported in the range of 1 to 2 mg/l ClO_2 [5]. The molar adsorptivity of ClO_2 at 360 nm is about 1,100 l/mole-cm. This value is reasonably independent of conditions such as temperature, salinity, ionic strength, and acidity [22]. The limit to direct determination of ClO_2 is set by the cell length of spectrophotometer. It has been reported that the linearity exists in the range of 6.0 - 60.0 mg/l, by using a 1-cm cell and working at a wavelength of 360 nm [28]. Other ranges are possible if shorter or longer cells are available. For high concentration, one may operate at wavelengths off the 360-nm peak.

Direct spectrophotometry can be reasonably accurate if signal is maintained within proper photometric limits. This technique may experience interference from other species which adsorb appreciably at 360 nm. This problem may be minimized by using another wavelength, but sensitivity will be sacrificed. Suspended solids must be removed from the solution by filtration, since they will cause great interference.

2.6 Uses of ClO_2 in Water and Wastewater Treatment

Chlorine dioxide has been used for more than forty years for the treatment of potable and non-potable waters for disinfection, taste and odor control, and iron and manganese removal.

2.6.1 Water and Wastewater Disinfection

Chlorine dioxide has been suggested and used as a water and wastewater disinfectant since early in this century [13]. Ridenour and Ingols reported that ClO_2 was superior to chlorine in the destruction of spores[31], and in contrast to chlorine the bactericidal efficiency of ClO_2 was relatively unaffected by pH values [32]. In 1953, Malpas [33] reported that the bactericidal efficiency of chlorine dioxide towards *E. coli, Salmonella typhosa,* and *Salmonella paratyphi* was greater than that of chlorine. Bernarde *et al.* [34] confirmed the findings of earlier workers, and established the mechanism of ClO_2 disinfection. More recent work by Roberts *et al.* [35] again desmonstrated that chlorine dioxide is a far superior viricide than is combined chlorine.

Despite its superiority to chlorine, ClO_2 has suffered a cost disadvantage when compared with chlorine as a disinfectant. Until recently, renewed interest in chlorine dioxide was stimulated by the US Environmental Protection Agency's amendment to the National Interim Primary Drinking Water Regulations that set a maximum contaminant level of 0.10 mg/l for total trihalomethanes (THMs) [36]. In 1983, chlorine dioxide was listed as one of the most suitable treatment technologies for control of THMs because chlorine dioxide reactions with humic substances do not result in the formation of THMs [37].

2.6.2 Control of Tastes and Odors

Chlorine dioxide was first used in the United States at the No. 2 Niagara Falls Water Treatment Plant in 1944 [38]. This plant experienced serious trouble from phenolic tastes and odors as a result of industrial waste pollution of the raw water. Since then, chlorine dioxide has been used successfully for the prevention or control of phenolic tastes and odors. As discussed in a previous section, the rapid reaction of ClO_2 and phenol yields a tasteless end product, as opposed to those compounds produced when phenols are chlorinated.

In addition to the control of phenolic tastes and odors, chlorine dioxide also has been found to be very effective in controlling a variety of tastes and odors occurring from both algae and vegetation decomposition. Algae contributing to this problem have been reported as *Antinomycetes, Anabena, Asterionella, Synura, Vorticella,* and others [39].

2.6.3 Manganese and Iron Removal

Manganese and iron can be oxidized by chlorine dioxide to form precipitates, and removed by sedimentation followed by filtration.

Manganese, even in minute quantities, can cause offensive black water in distribution systems. The problem arises when manganese is oxidized by chlorination to form a black precipitate (MnO_2). Since free chlorine oxidized

manganese very slowly, so that the precipitate forms after the treated water has entered the distribution system.

Chlorine dioxide, with its greater oxidation capacity, reacts much more rapidly with manganese than does chlorine, so it is often used in conjunction with manganese removal. The overall reaction is:

$$2\ ClO_2 + MnSO_4 + 4NaOH \rightarrow MnO_2 + 2\ NaClO_2 + Na_2SO_4 + 2\ H_2O$$

The process is generally preceded by chlorination to satisfy the chlorine demend and to start the oxidation process. Because of its high cost, chlorine dioxide is usually limited to applications where the total manganese content is less than 1.0 mg/l [20].

In the case of iron removal, the choice between ClO_2 and Cl_2 is based largely on economic considerations. If the water to be treated has a high ammonia content, chlorine dioxide may be the chemical of choice because it does not react with ammonia while chlorine does. The oxidation of iron by chlorine dioxide is shown by the following equation:

$$ClO_2 + FeO + NaOH + H_2O \rightarrow Fe(OH)_3 + NaClO_2$$

The optimum pH for this reaction is always higher than 7, preferably 8 or 9. Jar tests are required to determine the exact value.

CHAPTER 3   Materials and Methods

In this chapter, details will be given of the treatment plant, the ClO_2 generation methods, and the methods of sampling and analysis used during this evaluation of ClO_2 for the removal of phenolic compounds from oily wastewaters. Specific details of the quality control methods for analysis also will be presented.

3.1 Plant Description

The study of phenol removal by chlorine dioxide was held at the Environmental Technology Southeast, Inc. (ETS) plant and laboratories at Jacksonville, Florida. The plant includes oily wastewater treatment and waste oil recycling processes, and has a processing capacity of 40,000 gallons per day. Oily wastewaters are received into the plant via 5,000-gallon-tank trucks. These wastewaters are off-loaded into storage tanks to accomodate gravity separation of free oil and water. Water is then pumped from storage tanks through an oil/water separator to an equalization tank. The free floating oil is pumped to separate storage and is then processed for reuse as industrial burner fuel.

After the equalization tank has been filled and thoroughly mixed, jar tests are conducted to determine floculant chemical dose rates for floculation of the suspended solids and remaining emulsified oil. The correct flocculant chemicals are added to an inline mixer through which wastewater from the equalization tank is pumped. The wastewater passing through the mixer is fed into a clarifier where solids and emulsified oils are settled to the bottom. The sludge from the bottom of the clarifier is blended back into the oil phase prior to distillation.

Clarified water is subjected to chemical tests to prevent upsets in the subsequent biological process. These tests include pH, temperature, COD, phosphorous, nitrogen, oil and grease, phenols, and heavy metals.

Sequential biological reactors (SBRs) are used for biodegradation of the remaining contaminants in the wastewater. Microorganisms acclimated to petroleum and phenolic wastewater streams and approprate nutrients are added to the reactor, and the resulting mixed liquor is aerated. The aerators are shut off after an appropriate biodegradation time and the activated sludge is allowed to settle. The supernatant is then pumped to a storage tank where ClO_2 is fed from the bottom of the storage tank through a perforated feeder which provides complete mixing of ClO_2 in the water. After an appropriate reaction time, the treated wastewater is discharged to the local POTW under industrial pretreatment permits.

A schematic diagram of this plant is presented in Figure 3.
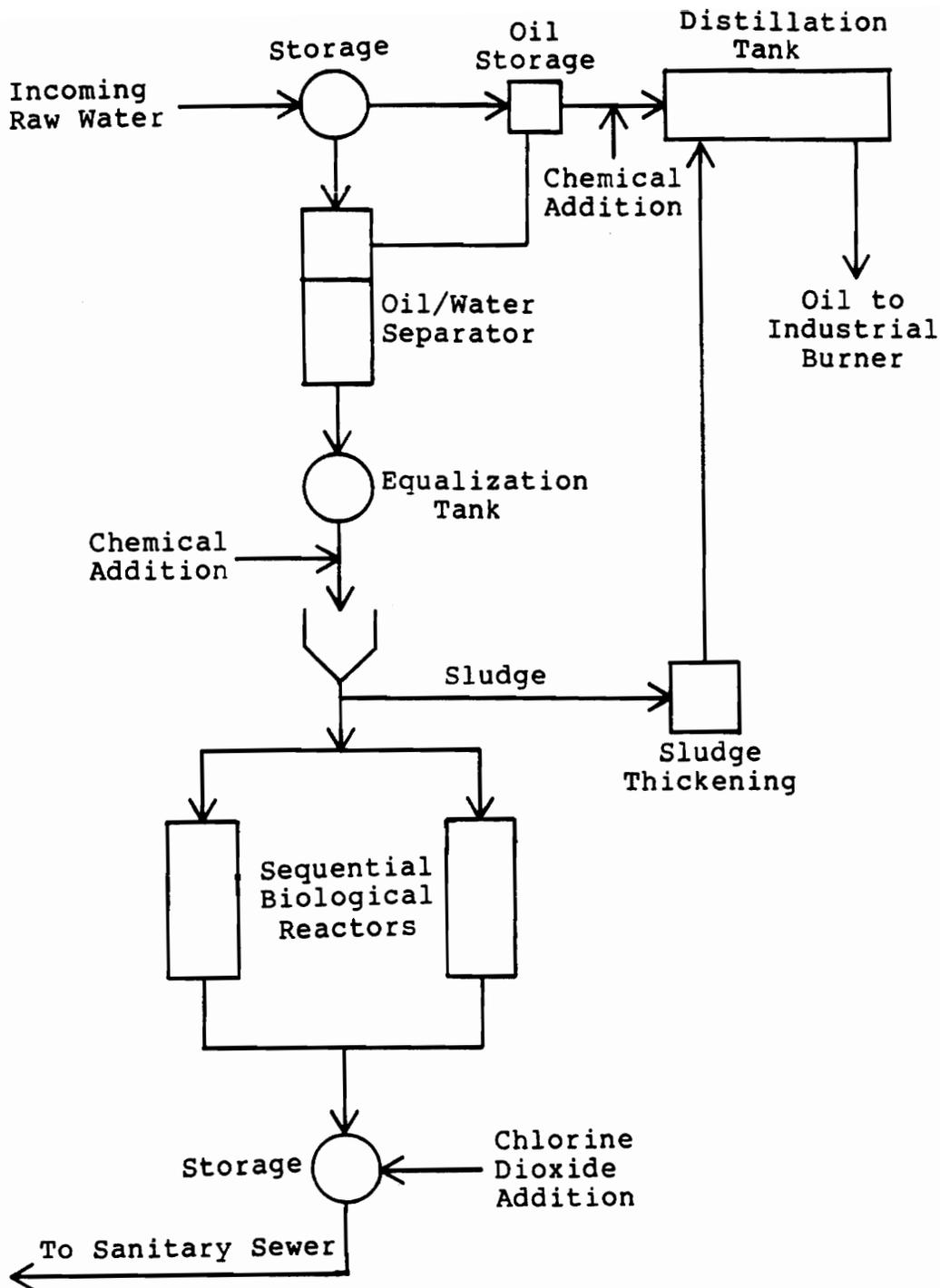
Figure 3.   A schematic diagram of the ETS treatment plant.

3.2 Characteristics of Wastewaters

Wastewaters to be treated in the ETS plant were mainly waste streams from petroleum and canning industries. These waste streams are characterized by high concentrations of chemical oxygen demand (COD), biological oxygen demand (BOD), oil and grease, and phenolic compounds. The average concentrations of these constituents during the study period, before and after biological treatment, were as follows:

before biological treatment

COD	12,600 mg/l
BOD$_5$	3,600 mg/l
Oil & grease	10.50 mg/l
Phenol	10.40 mg/l
pH	5.0 - 8.0

after biological treatment

COD	7,400 mg/l
BOD$_5$	1,200 mg/l
Oil & grease	5.20 mg/l
Phenol	2.50 mg/l
pH	5.5 - 7.8

The quantity of wastewater treated by this plant was in the range of 15,000 to 30,000 gallons per day.

3.3 Basic Laboratory Procedure

All reagents except those used for ClO_2 generation purposes were made from reagent-grade chemicals according to procedures outlined in Standard Methods [29]. Demand-free water was prepared by passing tap water through an ion exchange column. All glassware was washed with a phosphorus-free detergent and then rinsed three times in deionized water and allowed to air dry.

The concentrations of phenolic compounds were determined by the Direct Photometric Method as described in Section 510B of Standard Methods [29]. This method is unable to differentiate between different kinds of phenols, so phenol (C_6H_5OH) itself was used as a standard for photometric procedures, and any color produced by the reaction of other phenolic compounds was reported as phenol. All samples were either analyzed immediately after collection or preserved at 4°C by chemical addition and analyzed within 24 hours. Biological degradation was inhibited by the addition of 1 g/l of copper sulfate to the sample and acidification to a pH of less than 4 with phosphoric acid.

Spectrophotometric analyses were conducted using a Bausch & Lomb Spectronic 20 spectrophotometer, and pH was measured using a Corning 125 pH

meter. A Fisher Thermix Model 120M stirrer was used for general mixing purposes.

COD tests were conducted according to an EPA-approved method introduced by the Hach Company [40]. In this method, small volumes of the water samples were pipetted into vials containing the premeasured reagents, including catalysts and chloride compensator. The vials were digested at 150°C for two hours and cooled. The COD determination was then made with the spectrophotometer.

The generation and determination of chlorine dioxide is described in detail in the following sections.

3.4 Bench-scale Studies

The purpose of the bench-scale studies was to develop an understanding of the chemical reactions between chlorine dioxide and phenols at various conditions. Stoichiometric reactions between phenol and chlorine dioxide were investigated using pure phenol solution with predetermined concentrations. In addition, the effects of ClO_2-to-phenol ratio, reaction time, pH, temperature and COD on phenol residual were studied. The samples used in these experiments were from the effluent of the biological reactors.

3.4.1 Generation of Chlorine Dioxide

The chlorine dioxide used in these studies was prepared each day by use of the method recommended by the Drew Chemical Corporation. This method used Drewchlor and household bleach as precursors for the generation of chlorine dioxide. The typical properties of Drewchlor are given in Appendix A.

The procedures for producing a 750 to 1,000 mg/l solution of ClO_2 in aqueous solution were:

1. Prepare the following solutions with chilled (34°F) deionized water:

    a. 1.61 grams Drewchlor (25% $NaClO_2$) diluted to 100 ml.

    b. 1.05 grams household bleach (5.25% $NaOCl$) diluted to 100 ml.

    c. 1.0 grams reagent-grade concentrated hydrochloric acid diluted to 100 ml.

2. Mix 100 ml of hydrochloric acid solution with 100 ml of sodium hypochlorite solution and stir for 2 minutes.

3. Add 100 ml Drewchlor solution and continue to stir for 10 seconds.

The resulting ClO_2 solution was tranferred to a 250-ml, stoppered, brown glass bottle to minimized the free space above the liquid and to prevent decomposition of the ClO_2 by light. The stock solution was then stored in a refrigerator at 34°F.

3.4.2 Determination of Chlorine Dioxide

The concentration of the stock chlorine dioxide solution was determined before each experiment and was found to remain very consistent. Iodometric Method, described in Section 410A of Standard Methods [29], was used to measure the ClO_2 concentration.

3.5 Field Studies

The purposes of the field studies were to determine the optimum operation conditions for phenols removal, as well as to compare the yield of ClO_2 under various generating conditions. Wastewater samples used in these experiments were either from the effluent of the equalization tank or from the effluent of the biological reactors.

3.5.1 Chlorine Dioxide Generator

The chlorine dioxide used in the field studies was generated on site by a Drewchlor Chlorine Dioxide Generator System, as shown in Figure 4.

This system was equipped with three Neptune Series 500 dia-pumps, one for Drewchlor, one for NaOCl, and one for HCl to acidify the two reacting solutions
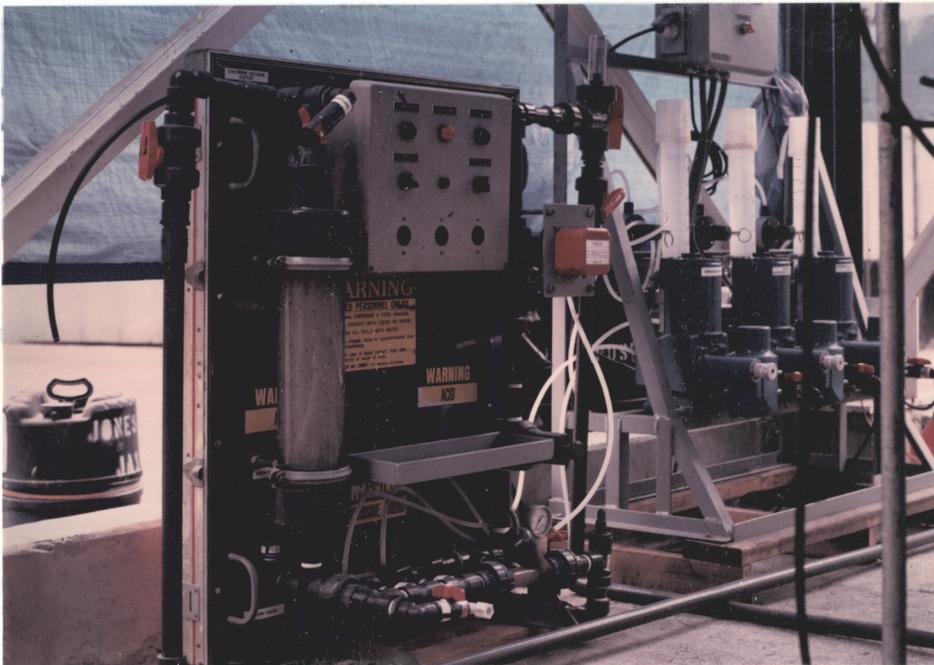
Figure 4.   A Drewchlor Chlorine Dioxide Generator System.

to the optimum pH. These pumps were hydraulically actuated diaphragm types, and their capacity could be adjusted by changing the settings marked on a control rod which controlled the volume of hydraulic fluid passing the diaphragm cavity. The flowrates of each were measured at various pump settings, and the calibration curves for each pump were then constructed. These calibration curves, as shown in Appendix B, were checked every week and were found to remain fairly accurate.

Chemicals used for the generation of ClO_2 were all commercially available. Drewchlor was delivered in a 55-gal drum from Drew Chemical Corporation. Sodium hypochlorite solution (9.2% by weight NaOCl), and technical grade muriatic acid (31.45% by weight HCl) were manufactured by Jones Chemical Inc., and were stored in a 55-gal drum and a 25-gal carboy, respectively. The storage drums and tubings used for transferring these chemicals were made of black PVC to eliminate the possibility of photodecomposition of these oxidants.

Tap water was used as dilution water, and was fed to the generator unit at a predetermined flowrate and pressure. The required chemicals were added to this line by the metering pumps. The aqueous solution moved upward through the mixing column where the reaction to form chlorine dioxide occurred. The column was made of a transparent plastic material which allowed the operator to visually inspect the color of the chlorine dioxide being produced. When it was being formed properly, the mixture in the reaction column turned a greenish yellow. Absence of color indicated that no chlorine dioxide was being produced. The mixing action inside the reaction column was caused by the solution flowing

around and through the porcelain Raschig rings. The ClO_2 solution exited the top of the reactor column and traveled through the discharge piping to a storage tank where phenol-containing water was to be treated.

A sampling valve was provided on the discharge line located outside the reaction column. Samples were drawn off periodically in order to monitor the operation of the system. The concentration of ClO_2 solution was found to be in the range of 1,000 to 3,000 mg/l. In this range ClO_2 was extremely volatile and vaporized easily from aqueous solution. Therefore, in sampling this solution for analysis, several volumes of the sample were allowed to overflow the container, and the container was capped immediately after sampling to minimize contact of the sample with the air. Layout of the 3-pump ClO_2 generator is given in Figure 5.

3.5.2 Determination of Chlorine Dioxide

The samples were analyzed immediately after each collection using a direct spectrophotometric method recommended by the Drew Chemical Corporation. A Bausch & Lomb Spectronic 20 spectrophotometer with a 1-inch viewing cell was used for the analysis. A calibration curve, shown in figure 6, was prepared using the following procedure:

1. standardize the ClO_2 solution by the iodometric method [29].

2. dilute the solution to desired concentrations.

3-PUMP CLO₂ GENERATOR

1" FNPT
Chlorine Dioxide
Outlet —

Electrical Inlet
1" FNPT Water Inlet
Pump Outlet Box

Hydrochloric Acid Inlet

Drewchlor Inlet

Sodium Hypochlorite Inlet

Steel Leg Stand
Epoxy Coated —

Drain Holes

A. Water Motorized Valve
B. Isolation Valve
C. Wye Strainer
D. Pressure Regulator
E. Flow Meter
F. Pressure Gauge (2)
G. Pressure Relief Valve Outlet
H. Pressure Relief Valve
I. Flow Throttle Valve
J. Flow Switch
K. Check Valve
L. Sodium Hypochlorite Inlet
M. Hydrochloric Acid Inlet
N. Drewchlor Inlet
O. Drain Outlet
P. Reaction Chamber Column
Q. Electrical Panel
R. Sample Outlet
S. Hinged Door With Plexiglas Window

Section "a-a"

Figure 5. Layout of the 3-pump ClO₂ generator (After Drew Chemical Company, 1986).

3. measure the absorbance of each concentration at 400 nm.

4. plot the calibration curve.

The concentrations of ClO_2 determined by this method were limited to the range of 0-60.0 mg/l, so a 1:50 dilution was necessary. The ClO_2 concentrations were determined by the following procedure:

1. Warm up the spectrophotometer for 10 minutes, and adjust the wavelength dial to 400 nm.

2. Place a sample cell containing deionized water in the cell holder, and adjust the meter reading to zero absorbance.

3. After uncapping the sample, quickly transfer 10 ml of sample to a 500 ml flask. Dilute to 500 ml with deionized water. Mix well.

4. Transfer 25 ml of the diluted sample to the same sample cell.

5. Place the sample cell containing the diluted ClO_2 solution in the cell holder and read the absorbance.

6. Convert absorbance to concentration using Figure 6.

3.5.3 Yields of Chlorine Dioxide Generations

Stochiometrically, 1 mole of $NaClO_2$ yields 1 mole of ClO_2. However, a 100% yield can never be achieved practically due to the insufficient reaction time provided, as well as due to competitive reactions of ClO_2 with other waste con-
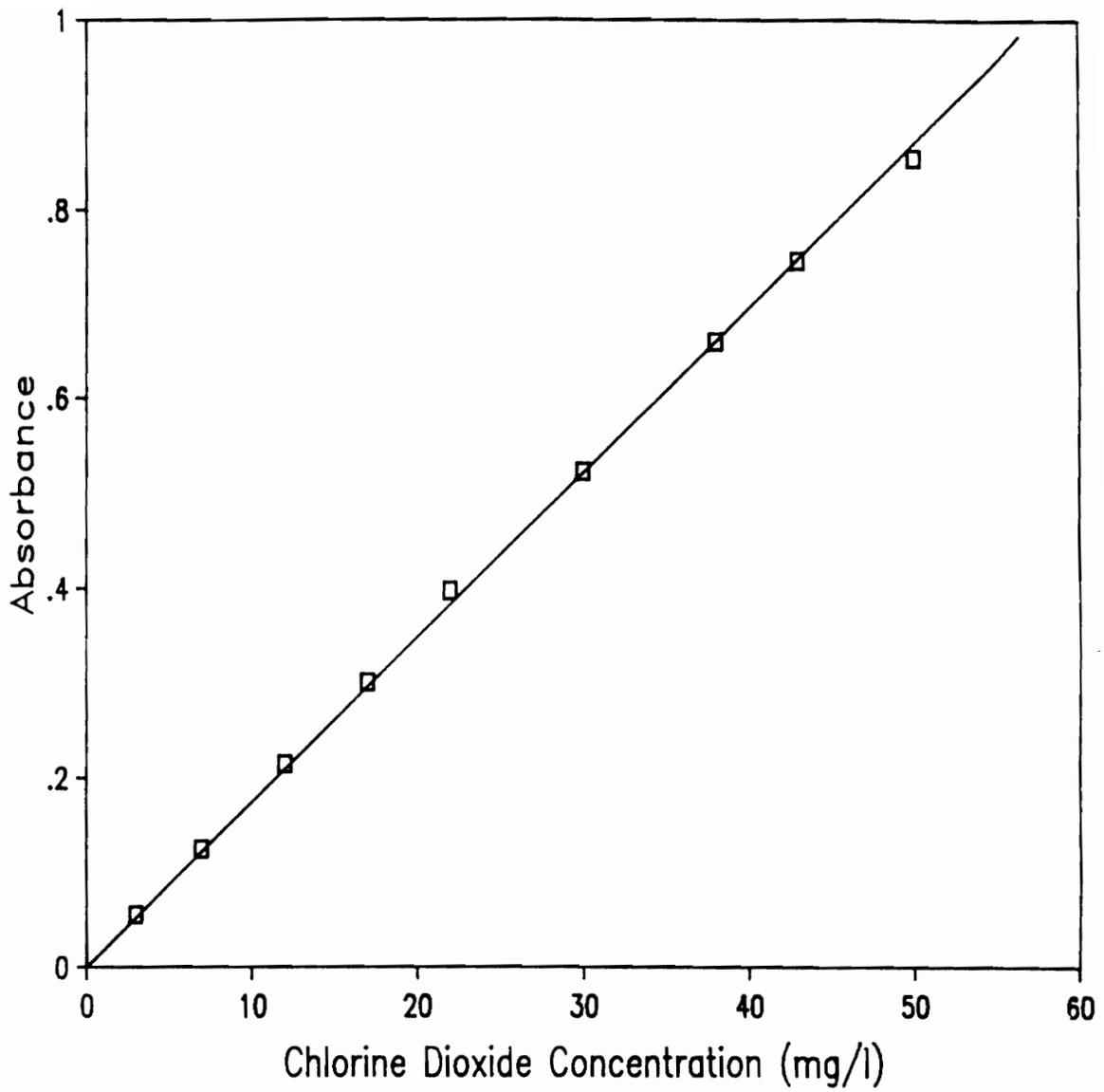
Figure 6. A calibration curve for ClO$_2$ determination.

stituents. Because of the high unit cost of the sodium chlorite reactant, it is important that the yield of ClO_2 based on feed chlorite be determined and maximized.

The yields of chlorine dioxide generation were determined by the procedure listed in Appendix C.

3.6 Quality Assurance Methods for Analysis

Quality assurance methods were used to ensure that the precision and accuracy of laboratory measurements were reliable. Techniques developed from control charts were used to evaluate the quality of data produced in the laboratory [41,42]. The construction of control charts were achieved by analyzing replicated samples. A minimum number of 15 replicate sets were recommended to determine the accuracy and precision criteria [41]. In these studies, the quality control charts were developed using 15 sets of duplicate samples. The control limits on these charts indicated whether the observed values were acceptable. Any value beyond the control limits indicated an out-of-control situation. When this situtation occurred, analyses were stopped until the problem had been identified and resolved.

3.6.1 Quality Control Chart for Accuracy

The accuracy of measured data was evaluated through the use of spiked samples. The percent recovery of the spiked samples was determined using the following formula:

$$P = 100 \times \frac{(O - B)}{A}$$

Where   P = % recovery

         O = observed value in spiked sample

         B = background value (unspiked sample)

         A = added value

The average percent recovery, $\overline{P}$, and the standard deviation, S, were calculated from the following equations:

$$\overline{P} = \sum_{i=1}^{n} \frac{P_i}{n}$$

$$S = \sqrt{\frac{\sum_{i=1}^{n} P_i^2 - (\sum_{i=1}^{n} P_i)^2 / n}{n - 1}}$$

where n = number of replicate sets of samples.

The accuracy control limits were calculated using the following formulas:

$$UCL = \overline{P} + 3S$$

$$LCL = \overline{P} - 3S$$

These control limits were then drawn on the control chart. A typical accuracy control chart is shown in Figure 7.

3.6.2 Quality Control Chart for Precision

Precison is the degree of agreement of repeated measurments. To determine the precision criterion, the range of duplicate sets, R, was first calculated using the formula:

$$R = |X_1 - X_2|$$

The average range, $\overline{R}$, was then calculated:

$$\overline{R} = \sum_{i=1}^{n} \frac{R_i}{n}$$

The precision upper control limit, UCL, was then calculated using the equation:

$$UCL = D_4 \overline{R}$$
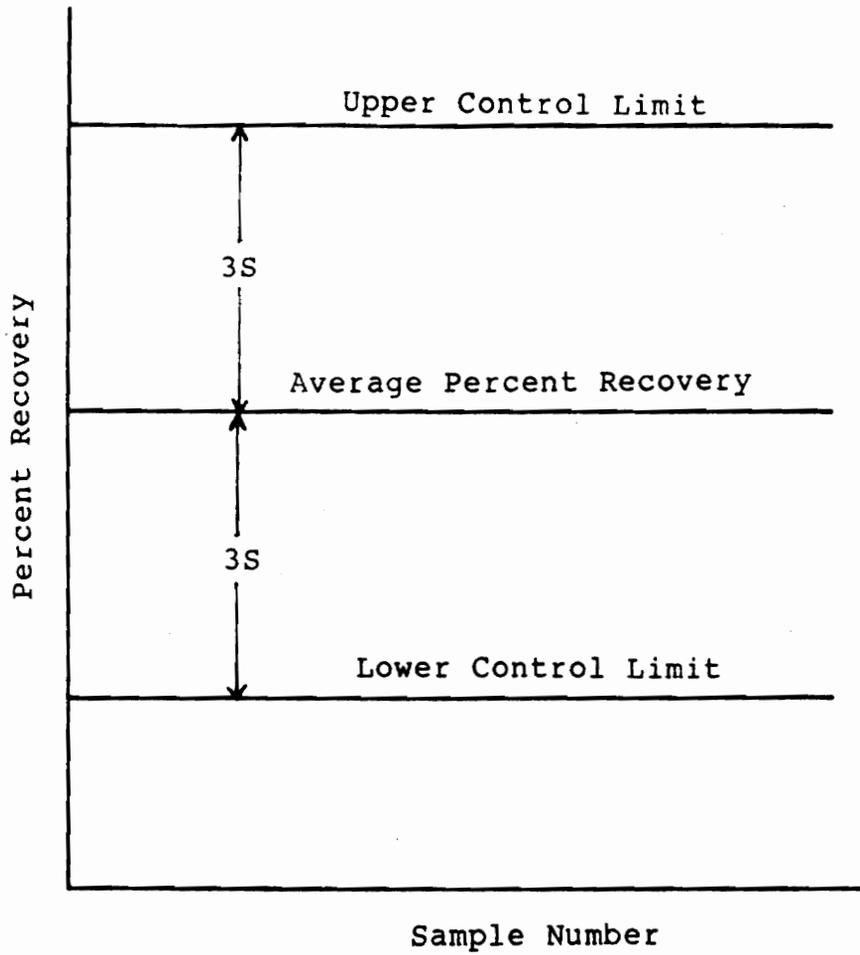
Figure 7. A typical accuracy control chart.

Where D_4 is the Shewhart factor[43]. For duplicate samples D_4 is 3.27 when three standard deviations are used to set the upper control limit.

The upper control limit was then drawn on the precision control chart, and was used as a guideline to check if a analytical process was out of control. A typical precision control chart is given in Figure 8.

3.6.3 Use of Quality Control Charts

Reliable experimental results were achieved through the continuous checking of data plotted on the quality control charts. If a control limit was exceeded on either an accuracy or precision control chart, the analytical process was considered out of control, and analyses were stopped until the problem had been identified and resolved.
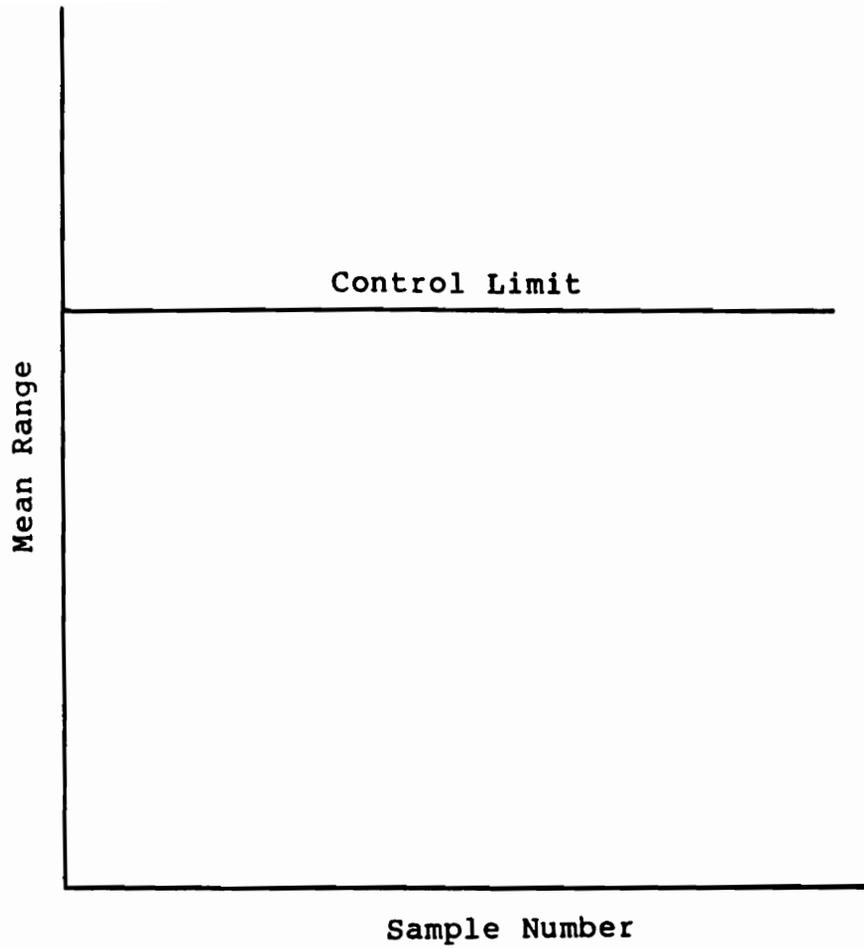
Figure 8.   A typical precision control chart.

CHAPTER 4   Results

This section presents the results of both bench-scale studies and field studies. The figures presented in this section were derived from the experimental data presented in Appendix D. They were arranged in the same sequence as the figures derived from them, and were labled to indicate the corresponding figures in this section.

4.1 Bench-scale Studies

Bench-scale studies consisted of six sets of experiments. One set of experiments was developed to investigate the stoichiometric reaction of phenol with ClO_2. The other five sets of experiments were designed to evaluate the effects of some variables on phenol removal. These variables included ClO_2-to-phenol molar ratio, reaction period, temperature, pH, and COD.

4.1.1 Stoichiometric Reaction of Phenol with ClO₂

It has been reported that each mole of phenol reacts rapidly with 2 moles of chlorine dioxide [6]. To verify this statement, a set of experiments was done under carefully controlled conditions. Pure phenol solutions were freshly prepared to eliminate the possibilities of competitive reactions of ClO_2 with other contaminants. The conditions set for these experiments were as follows:

Initial phenol concentrations:

    high   : 10.00 mg/l

    intermediate: 4.00 mg/l

    low   : 1.20 mg/l

ClO_2 concentration: 850 mg/l

Reaction time: 10 minutes

Temperature: 89°F

pH: 6.8

Results of the experiments are shown in Figure 9. Note that regardless of its initial concentrations the percent phenol removal increased sharply with increasing ClO_2-to-phenol molar ratio up to 2, then the removal became insignificant at higher ratios.
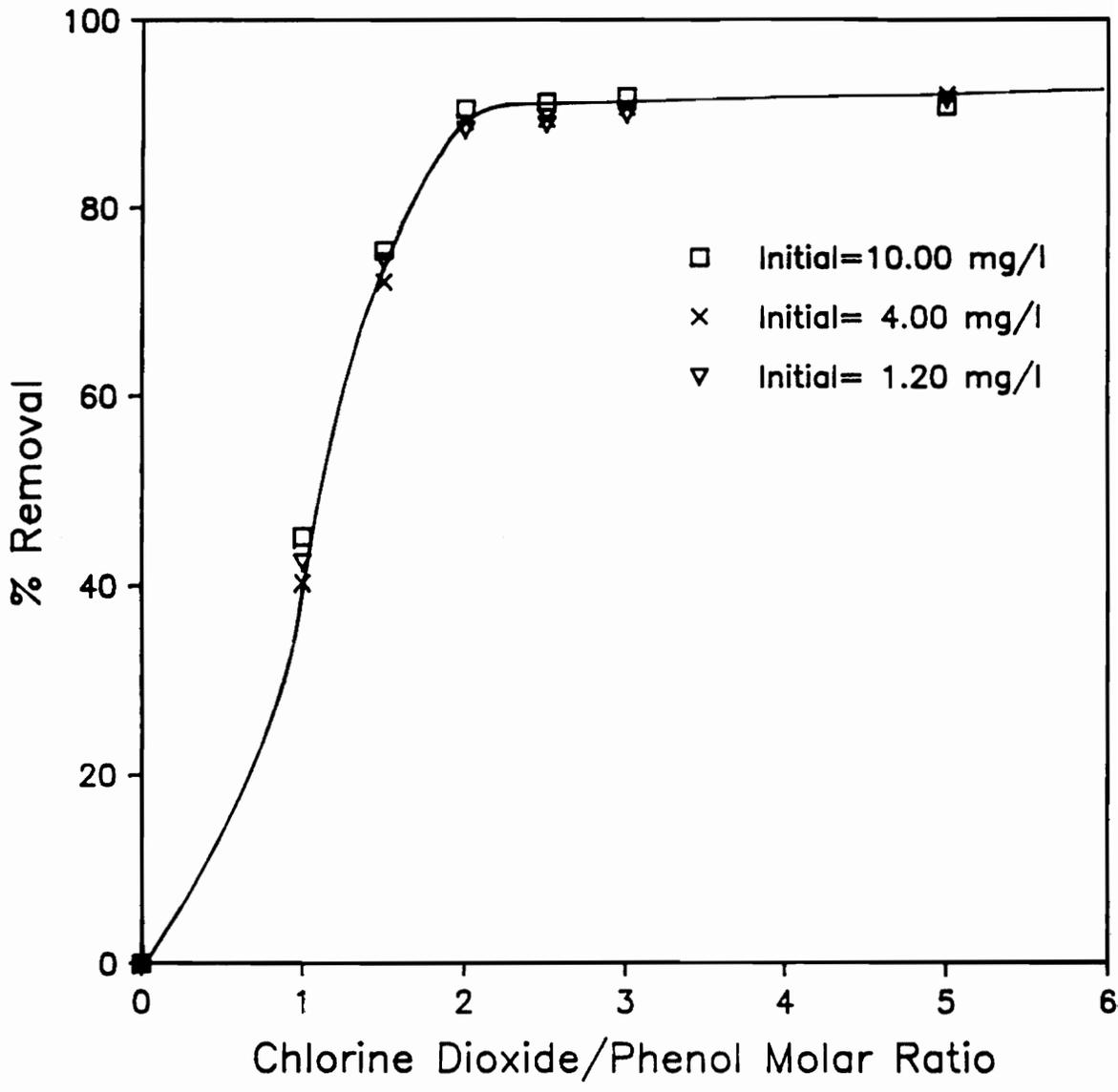
Figure 9. Percent phenol removals in clean water as a function of ClO_2-to-phenol molar ratios.

4.1.2 Effect of ClO_2-to-Phenol Molar Ratio

Results of previous experiments showed that to completely destroy pure phenol, a ClO_2-to-phenol molar ratio of higher than 2.0 must be provided However, higher ratios could be expected for the treatment of phenols in wastewaters due to the complexity of the wastewaters, as well as to the competitive reactions of ClO_2 with other constituents. A set of experiments was then performed to investigate the effect of the ClO_2-to-phenol ratio on phenol removal. The reaction provided in these tests was 30 minutes. Wastewater samples used in these tests had the following characteristics:

Sample 1:

Initial phenol concentration: 10.10 mg/l

Temperature: 88°F

pH: 6.5

Sample 2:

Initial phenol concentration: 14.50 mg/l

Temperature: 89°F

pH: 7.2

Sample 3:

Initial phenol concentration: 6.50 mg/l

Temperature: 88°F

pH: 7.5

The results are shown in Figure 10. Note that in order to reduce the phenol concentration to a level of less than 1.0 mg/l, a ClO_2-to-phenol molar ratio of higher than 5.0 must be provided.

4.1.3 Effect of Reaction Time

It has been reported that the reaction between chlorine dioxide and phenol can be completed within 2 seconds [7]. However, for removing phenols from wastewaters a contact period of 15 to 30 minutes is necessary [5]. A set of experiments was performed to investigate the effect of reaction time on phenol removal for the oily wastewaters. The characteristics of the wastewater samples were as follows:

Sample 1:

Initial phenol concentration: 10.40 mg/l

Temperature: 90°F

pH: 6.8

Sample 2:

Initial phenol concentration: 8.60 mg/l

Temperature: 88°F

pH: 7.5
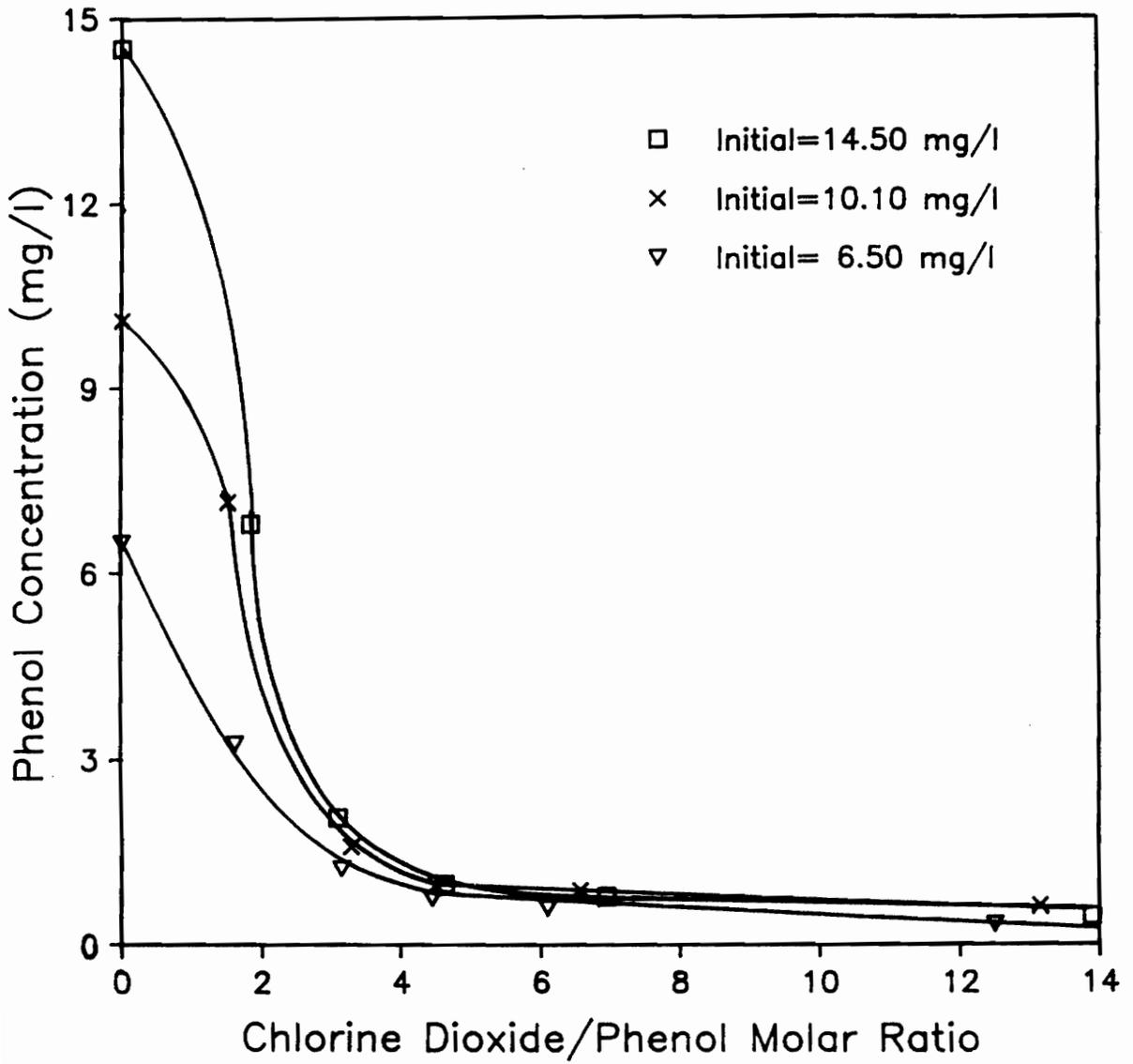
Figure 10. Phenol residuals in wastewaters as a function of ClO$_2$-to-phenol molar ratios.

Sample 3:

Initial phenol concentration: 3.50 mg/l

Temperature: 88°F

pH: 7.1

A ClO_2-to-phenol molar ratio of 5.0 was used in these experiments. The results are shown in Figure 11. Note that phenol concentrations decrease rapidly within a few minutes after contacting with ClO_2.

4.1.4 Effect of Temperature

Wastewater temperature at this plant ranges from 40°F in the winter to 100°F in the summer. As temperature may greatly influence the reaction rate and the consequential phenol residual, it is necessary to conduct a set of experiments to investigate the effect of temperature on phenol removal. The ClO_2-to-phenol molar ratio used in the experiments was 5.0, and the reaction time was 30 minutes. The wastewater samples had the following characteristics:

Sample 1:

Initial phenol concentration: 35.50 mg/l

Temperature: 80°F

pH: 7.2
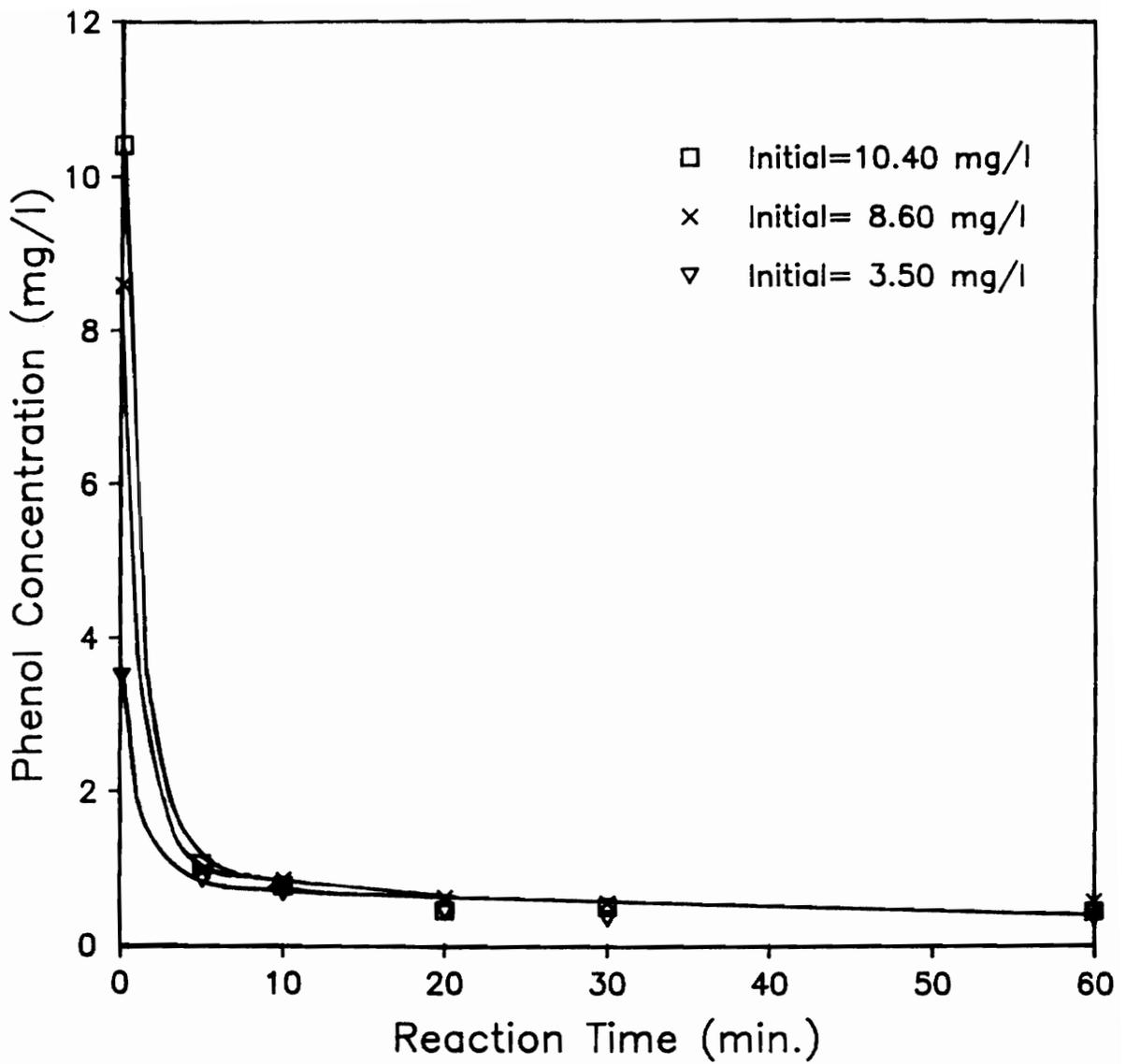
Figure 11. Phenol residuals as a function of reaction periods.

Sample 2:

Initial phenol concentration: 12.80 mg/l

Temperature: 82°F

pH: 6.8

The results of these experiments are shown in Figure 12. Note that phenol residuals decrease with increasing temperature.

4.1.5 Effect of pH

It has been reported that under different pH values the reaction between phenols and ClO_2, and the consequential end products differ from each other [4]. As the pH of the wastewaters treated in the ETS plant may range from 5.0 to 9.0, it was necessary to investigate the effect of pH on phenol removal. A set of experiments was conducted using the following conditions:

ClO_2-to-phenol molar ratio: 5.0

Reaction time: 30 minutes

Initial phenol concentration:

Sample 1: 17.20 mg/l

Sample 2: 8.15 mg/l
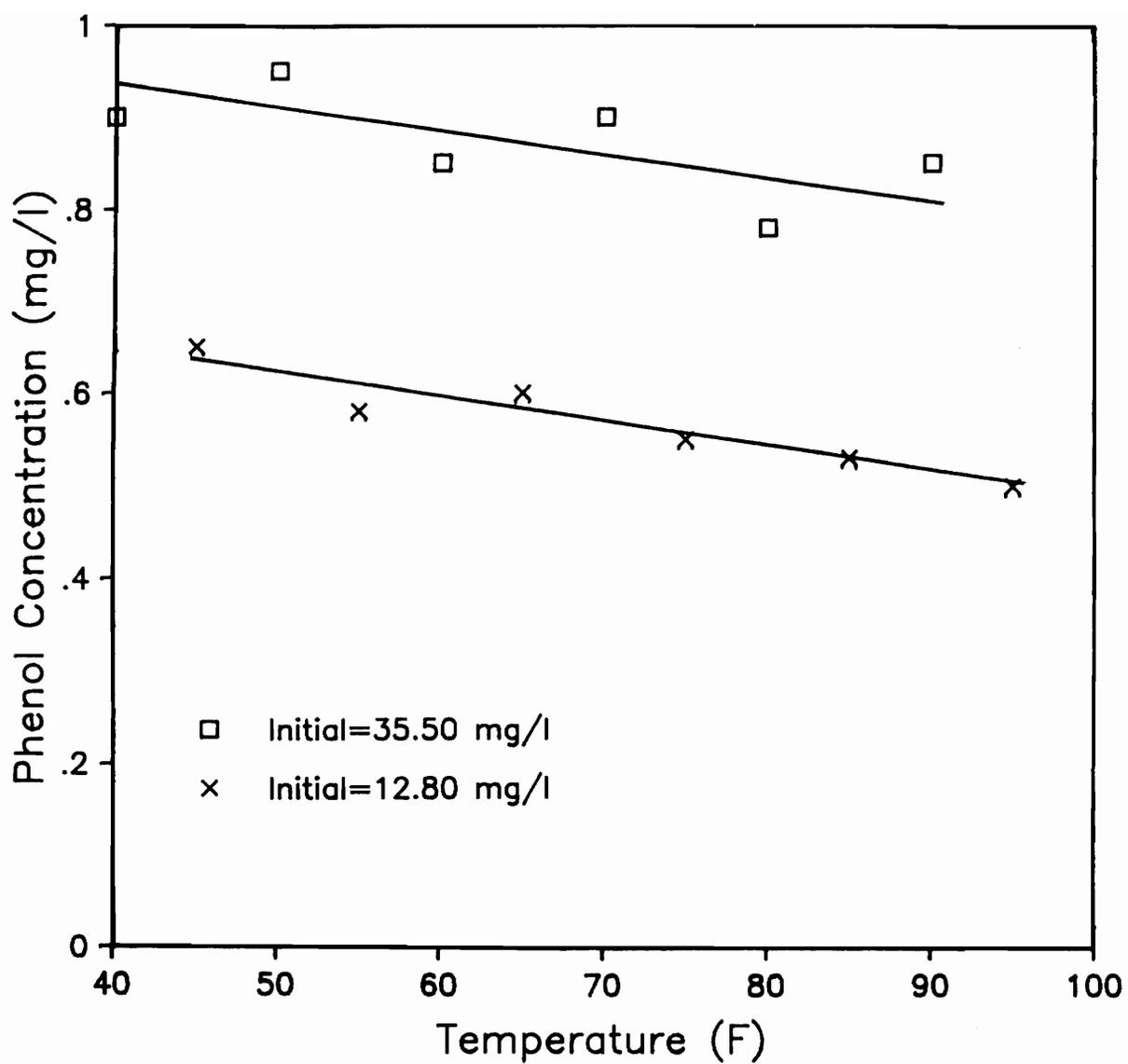
Figure 12.   Phenol residuals as a function of temperature.

Temperature:

Sample 1: 85°F

Sample 2: 86°F

The results are shown in Figure 13. Note the tendency of decreasing phenol residual with increasing pH.

4.1.6 Effect of COD

It has been reported that the quantity of ClO_2 required to eliminate phenols from wastewaters is influenced by the amount of COD present [44]. As wastewaters treated in this plant have high COD values, it was necessary to conduct a set of experiments to investigate the relationship between COD and phenol removal when ClO_2 was used as an oxidant. The experiments were performed using the following conditions:

ClO_2-to-phenol molar ratio: 5.0

Reaction time: 30 minutes

Temperature: 85°F

pH: 7.1

The results are presented in Figure 14 and Table 1. Note that phenol residuals decrease with decreasing COD values. However, it is concluded in the fol-
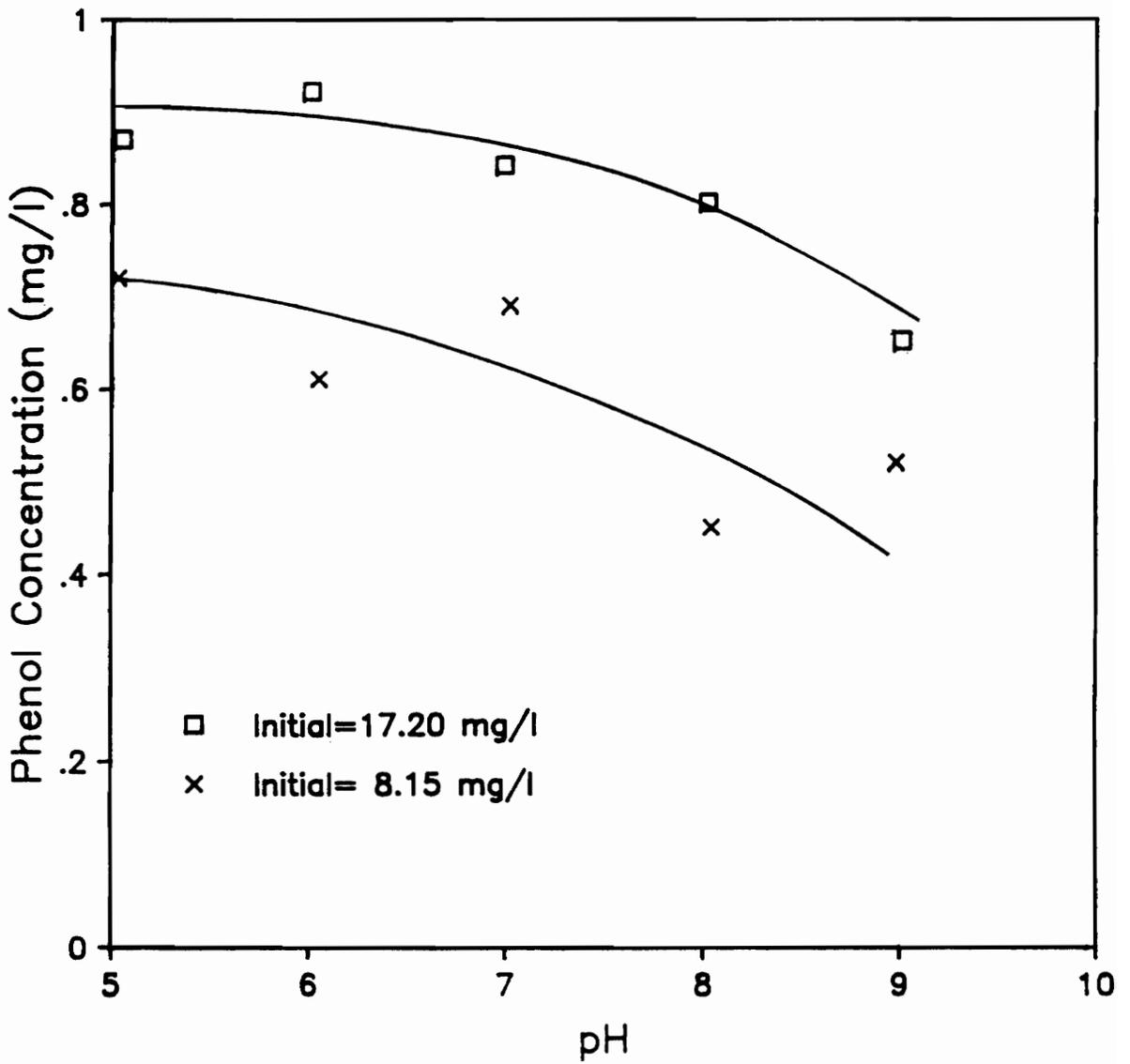
Figure 13.   Phenol residuals as a function of pH values.

lowing section that COD value does not have signifficant effect on phenol removal.

4.2. Field Studies

Field studies consisted of twenty experiments. Each experiment served two purposes:(1) to evaluate the yield of chlorine dioxide based on feed chlorite, and (2) to verify the optimum operating conditions found in bench-scale studies.

4.2.1. Yield of Chlorine Dioxide

To evaluate the performance of a ClO_2 generator system, it is necessary to determine the yield of ClO_2 generation. Table 2 shows that the yields of ClO_2 in the field experiments ranged from 75% to 95% depending on pH, chlorite concentration in feed stream, and chlorite-to-hypochlorite molar ratio.

Table 1.   Phenol residuals at various COD values.

Initial COD (mg/l)	COD residual (mg/l)	Initial phenol (mg/l)	Phenol residual (mg/l)
1800	1600	6.73	0.35
2800	2200	2.35	0.44
4600	3600	11.50	0.52
6500	5400	4.80	0.52
9600	8900	10.10	0.75

ClO_2/phenol molar ratio $= 5.0$
Reaction period $= 30$ minutes
Initial pH $= 7.1$
Temperature $= 85°F$
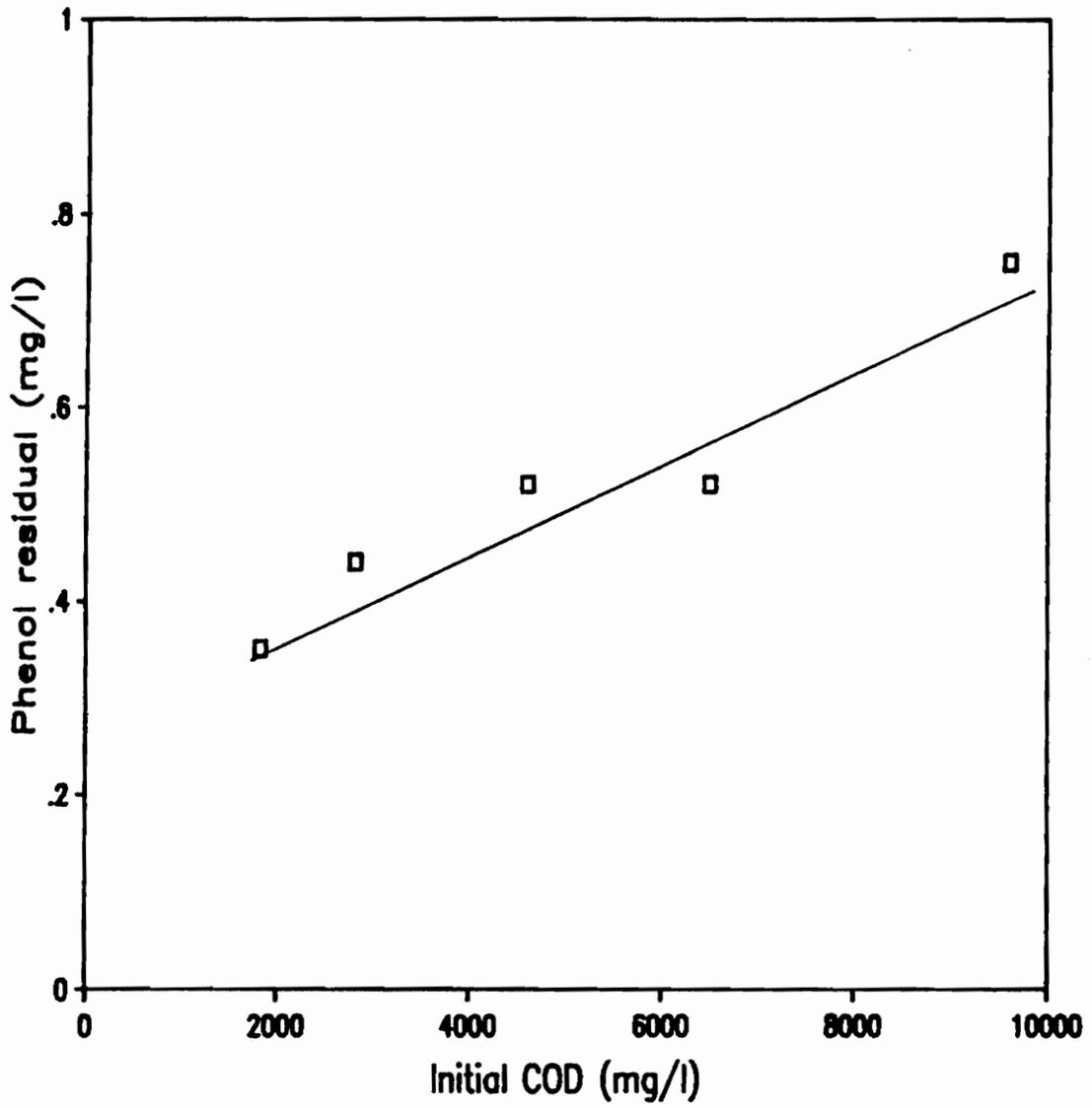
Figure 14. Phenol residuals as a function of COD values.

Table 2. Yields of ClO_2 in field experiments.

Experiment	Chlorite conc. (mole/l)	Hypochlorite conc. (mole/l)	HCl conc. (mole/l)	pH	ClO_2 conc. (mg/l)	ClO_2 yield (%)
1	0.043	0.028	0.128	1.70	2400	82.7
2	0.043	0.028	0.089	2.37	2350	81.0
3	0.043	0.057	0.165	1.80	2380	82.1
4	0.022	0.016	0.063	2.10	1325	89.3
5	0.022	0.024	0.070	2.57	1340	90.3
6	0.022	0.016	0.056	2.60	1420	95.7
7	0.022	0.016	0.053	2.70	1380	93.0
8	0.022	0.016	0.049	2.91	1400	94.3
9	0.022	0.016	0.046	3.12	1355	91.3
10	0.022	0.016	0.040	3.52	1300	87.6
11	0.022	0.015	0.050	2.77	1280	86.3
12	0.022	0.012	0.050	2.85	1250	84.2
13	0.037	0.031	0.093	2.21	2150	86.1
14	0.037	0.031	0.090	3.05	2200	88.2
15	0.037	0.031	0.087	6.00	1875	75.8
16	0.037	0.031	0.078	6.65	1850	75.1
17	0.050	0.036	0.110	2.60	2650	78.6
18	0.050	0.036	0.105	2.72	2600	77.1
19	0.050	0.036	0.102	2.90	2530	75.0
20	0.050	0.036	0.100	3.10	2720	80.7

4.2.2. Residual Phenol Concentrations

The phenol concentrations remaining after ClO_2 treatment are presented in Table 3. This table shows that the goal of phenol residual of less than 1.0 mg/l can be achieved for most cases, and the optimum conditions found in bench-scale studies can be applied to field operations. However, there were two instances when the phenol residuals were higher than 1.0 mg/l.

This table also shows that initial phenol concentrations in experiment 9 and 14 were lower than those in other experiments. These two wastewater samples were from the effluent of biological reactors while the other were from the effluent of the equalization tank.

4.2.3. Costs for ClO_2 Treatment of Phenolic Wastewaters

The capital cost for a ClO_2 generator system having the capacity for treating 30,000 gallons of phenolic wastewater was about $ 20,000 in 1987 [45]. The treatment costs depend on the concentration of phenolic compounds in the wastewaters. A sample calculation of treatment costs is presented in Appendix E. Table 4 shows the costs for ClO_2 treatment of phenolic wastewaters based on the cost data of 1987.

Table 3.   Results of field experiments.

Experiment	ClO$_2$/Phenol molar ratio	Contact period (min.)	Initial phenol (mg/l)	Phenol residual (mg/l)	Initial COD (mg/l)	COD residual (mg/l)
1	8.66	60	17.50	0.95	5800	3800
2	6.83	30	14.50	0.50		
3	5.56	15	12.50	0.65	6600	5900
4	4.00	20	12.20	0.29		
5	5.24	30	13.00	0.05		
6	5.61	25	11.60	1.35		
7	5.25	10	7.70	0.30	10400	7800
8	7.22	20	5.80	0.83		
9	5.92	10	1.52	0.25		
10	5.08	20	6.90	0.75		
11	4.10	30	7.00	0.45		
12	4.15	30	8.80	0.75	7450	6000
13	4.64	30	7.50	0.65		
14	4.85	30	2.10	0.31		
15	5.12	30	4.38	0.25		
16	4.65	30	10.68	1.50		
17	4.96	30	6.30	0.75	8200	6000
18	5.21	30	5.20	0.20		
19	6.02	30	4.85	0.15		
20	5.47	30	13.00	0.45		

Table 4.   Costs for ClO_2 treatment of phenolic wastewaters.

★Capital Cost : $ 20,000

Chemical Costs for treatment :

Phenol (mg/l)	Treatment Cost ($/1,000 gallon)
5	1.70
10	3.40
15	5.10
20	6.80
25	8.50

★Based on capacity for treatment of 40,000 - 400,000 gpd.

Chapter 5 Discussion

5.1. Reaction of Phenol with ClO₂

The results of phenol removal as a function of ClO_2-to-phenol molar ratio, presented in Figure 9, indicated that regardless of its initial concentration, phenol can be removed by ClO_2 at ClO_2-to-phenol molar ratios of higher than 2. The results agreed with the stoichiometric reaction between phenol and chlorine dioxide as described in Section 2.3.

It can be seen from Figure 9 that phenol cannot be completely removed within 10 minutes even at high ClO_2-to-phenol molar ratio, and the removal of phenol leveled off at the molar ratio of higher than 2. These can all be explained from the following equation:

$$-d[phenol]/dt = k\,[phenol][ClO_2]$$

As the reaction between phenol and ClO_2 proceeded toward completion, the concentration of phenol became less and less, so the rate of phenol removal became slower and slower. As a result, it took a long time to complete the reaction even though the rate constant, k, was relatively high.

The ClO$_2$-to-phenol molar ratio required for the removal of phenolic compounds from wastewaters can be estimated according to the result shown in Figure 9. However, higher ratios are expected for the treatment of wastewaters. The reason are explained in the following section.

5.2. Results of Bench-scale Studies

The results shown in Figure 10 indicated that regardless of its initial concentration, phenol residuals of less than 1.0 mg/l can be achieved if ClO$_2$-to-phenol molar ratios of 5 or higher were provided. ClO$_2$-to-phenol molar ratios of 5 convert to a weight ratio of 3.6. The results agreed with Masschelein's [5] claim that 1.7 to 5.0 g of ClO$_2$ is required to eliminate 1 g of phenol in wastewater. The ClO$_2$-to-phenol molar ratio required to treat phenolic wastewater was much higher than that found in the previous section where pure phenol was the only contaminant in the water. This is because wastewaters contain thousands of constituents other than phenols which also react with ClO$_2$, thus a higher ClO$_2$-to-phenol molar ratio was required to compensate for the competitive reactions. Another reason could be due to the decreased effective concentration, or activity, of ClO$_2$, as influenced by the presence of other species in the wastewaters.

It can be seen from Figure 10 that to destroy phenols to a concentration of minute level, the required ClO_2-to-phenol molar ratio must be very high. Thus, it is a trade-off between low phenol residual and high ClO_2 dose.

The results shown in Figure 11 indicated that the reaction period required to destroy phenols to a residual of less than 1.0 mg/l was about 15 minutes if sufficient ClO_2-to-phenol molar ratios were provided. The results again agreed with Masschelein's [5] findings that good results of phenol removal could occur within a contact period of 15 to 30 minutes.

The rate of phenol removal was very fast at the begining of the reaction of phenol with ClO_2 because of the high rate constant. The reaction time required to achieve a desired phenol residual was independent of the initial phenol concentrations as can be seen from Figure 11.

The results shown in Figure 12 indicated that phenol residual decreases as temperature increases. It is because the reaction rate constant increases with increasing temperature, thus, within the same period of time a more complete reaction occurs at higher temperature. The increased temperature also favored endothermal reaction, as occured in the reaction of phenols with ClO_2.

However, the effect of temperature on phenol removal was insignificant because most phenols had been destroyed by ClO_2 in a few minutes. So, if sufficient contact period was provided the temperature effect could be neglected.

The results presented in Figure 13 showed that phenol residual tends to decrease with increasing pH values. It agreed with Wajon's [7] claim that the rate constant of the reaction between ClO_2 and phenol increases with increasing pH.

The results shown in Figure 14 indicated that phenol residual increased with increasing initial COD values. This is because there were many organic and inorganic materials which contributed to the COD values could also be oxidized by ClO_2. Wastewaters having higher COD values consumed more ClO_2, so the avaliable ClO_2 for phenol removal became less. As a result, the phenol residual became higher.

5.3. Yields of ClO_2 Generations

The yields of ClO_2 based on feed chlorite ranged from 75% to 95.7% as presented in Table 1. The high yields obtained in the experiments indicated that the ClO_2 generator system functioned properly. The yields of ClO_2 depended on its concentration in the solution as can be seen from Table 1. At a ClO_2 concentration of approximately 2,600 mg/l, yields of less than 80% were obtained. It was found that the ClO_2 concentration was very close to its solubility in water. Water solubility of ClO_2 at room temperature (22°C) and atmosphere pressure is about 2,900 mg/l [20]. The highest yields of ClO_2 were obtained at ClO_2 concentrations of approximately 1,400 mg/l, which is about half of the water solubility of ClO_2. Since low ClO_2 concentrations were obtained by adding more dillution water to the generator, it was not practical to generate ClO_2 solutions with very low concentrations.

pH values has been reported as a critical factor for synthesizing ClO_2 [5]. The reason why the ClO_2 generator systems should always be operated at acidic solution could be explained by the following equation:

$$2\ NaClO_2 + NaOCl + 2HCl \rightarrow 2\ ClO_2 + 3\ NaCl + H_2O$$
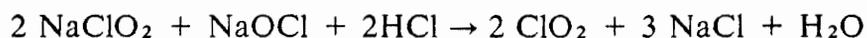
Yield of ClO_2 of near 100% has been reported by producing ClO_2 at pH's of lower than 0.5 [5]. However, this is not the condition desired for operation of the ClO_2 generator system because the extremely low pH may damage the whole system. Drew Chemical Company has recommended the ClO_2 generator system be operated at pH's between 2.5 to 3.5. The results of the field studies agreed with the suggestion. As pH is such a criticale parameter for generating ClO_2, it is recommended by the auther that an on-line pH meter be installed to monitor the generation of ClO_2. Good results of ClO_2 generation can be achieved by adding excess amounts of hypochlorite and acid. About 50% in excess of chlorite, and 100% in excess of HCl were sufficient to completely convert chlorite to chlorine dioxide.

5.4. Results of Field Experiments

The results of bench-scale studies (Figure 9 to Figure 14) showed that variables such as ClO_2-to-phenol molar ratio, reaction period, temperature, pH, and

COD value all had an effect on phenol residual. However, among these variables COD value was uncontrollable, and temperature could not be controlled economically. It had also been found from the previous experiments that both temperature and pH has only a small effect on phenol removal. Thus, the remaining two variables (ClO_2- to-phenol molar ratio, and contact period) were controlled in the field experiments according to the optimum conditions found in the bench-scale studies. It was shown from Table 2 that the goal of a phenol residual of less than 1.0 mg/l was achieved except for two instances. The failure in these two cases could be attributed to the characteristics of the wastewaters which were from the canning industry. These wastewaters contained high concentrations of emulsified oil, and have been regarded by the plant operator as "trouble waters". Studies of biological treatment conducted in this plant have also shown that this type of wastewater is resistant to biodegradation to some extent. To reduce the phenol residual to the desired level, higher ClO_2-to-phenol ratios and longer reaction periods may be required.

The ClO_2-to-phenol molar ratios used in these experiments varied from 4.0 to 8.7. It was found that there is no distinct relationship between phenol residual and ClO_2-to-phenol molar ratio. It was also true that longer contact periods did not necessarily produce lower phenol residuals. However, the optimum conditions found in the bench-scale studies could still be applied to field operation.

Comparing the results of experiment 9 and 14 to others, it was shown that ClO_2 treatment can be employed to treat the effluent wastewater from the equalization tank. No biological treatment prior to ClO_2 treatment was neces-

sary. However, in this instance, the COD values as well as other pollutants can still be so high that the treated wastewater can not be discharged to the sewer.

In addition to phenol removal, ClO_2 treatment also reduced the COD values by 11% to 34% depending on the type of the wastewater. The reductions of COD values were the results of competitive reactions between ClO_2 and other constituents of wastewaters.

Data shown in Table 3 indicated that ClO_2 treatment, with high treatment costs, may be not a cost effective process for the removal of phenols from wastewaters. In 1971, Hershaw [46] evaluated the costs of activated carbon treatment for the removal of phenol from a waste stream with a flow of 0.15 MGD, and an average phenol concentration of 6 mg/l. He claimed that the capital cost was $ 300,000, and the treatment cost was $ 0.18/1,000 gallon. The operating cost for treating the approximately equal amount of phenols by ClO_2 treatment was about 10 times higher than that of the activated carbon system. However, note must be taken that the capital cost of the former was only 1/15 of the latter. Thus, for a small treatment plant, ClO_2 treatment may be an economical choice because of its low equipment investment.

Chapter 6   Conclusions

The purpose of this project was to define the optimum operating conditions for the removal of phenols from oily wastewaters to a residual level of less than 1.0 mg/l. To do this, the reaction stoichiometry between phenol and ClO_2 was first studied. The relationships between phenol residuals and the ClO_2-to-phenol molar ratio, reaction period, temperature, pH, and COD value were then investigated using bench-scale study techniques.

Field experiments were conducted using the optimum conditions found from the bench-scale experiments. A 3-pump chlorine dioxide generator system was used to synthesize ClO_2 for the field experiments. Chemicals used for the generation of ClO_2 were: sodium chlorite, sodium hypochlorite, and hydrochloric acid. The yields of ClO_2 generation were evaluated through the control of pH and the concentration of the ClO_2 solutions. The costs for ClO_2 treatment of phenolic wastewaters were also estimated.

The significant conclusions that can be derived from this project are:

1. Chlorine dioxide treatment can be an effective process for the removal of phenols from oily wastewaters because ClO_2 has high selectivity for phenolic compounds present in the oily wastewater.

2. The reaction between phenols and ClO_2 can be influenced by parameters such as ClO_2-to-phenol molar ratio, reaction period, temperature, pH, and COD. However, only the first two parameters have significant effects on phenols removal.

3. The optimum operating conditions for the removal of phenols from oily wastewaters were:

    ClO_2-to-phenol ratio = 5.0

    Reaction period $\geq$ 15 minutes

4. The effectiveness of ClO_2 treatment does not depend on the initial phenol concentration.

5. Yields from ClO_2 generation depend on the pH, concentration of feed chlorite, and chlorite-to-hypochlorite ratio. Good yields can be achieved by maintaining the pH between 2.5 to 3.5, and controlling ClO_2 solution concentrations to about 1,500 mg/l.

6. For small plant applications, ClO_2 treatment may be a cost effective process for phenol removal.

After reviewing all of the work that has been done at the ETS wastewater treatment plant, the author recommends that more tests should be done on the wastewater from canning industry to improve effectiveness of the ClO_2 treatment. If good results still cannot be obtained, then carbon adsorption treatment should be tried.

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Appendix A. The Properties of Drewchlor

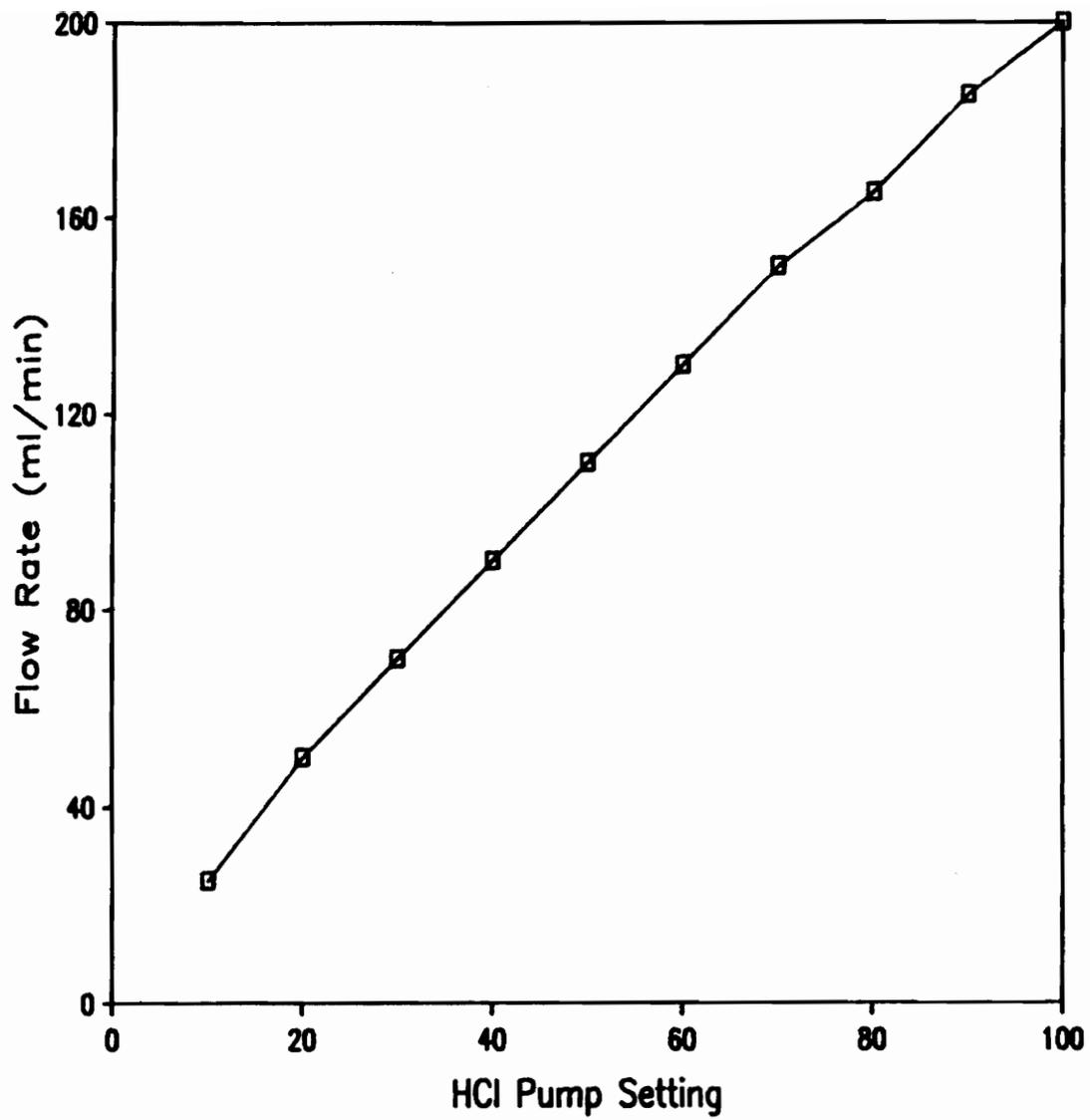|	
Composition :	25% sodium chlorite
Appearance :	Clear, slightly yellow liquid
Feeeze point :	-7°F
Specific gravity (25°F) :	1.25
pH :	12.0
Storage :	Avoid extreme heat and freezing
Packaging :	55 gallon, lined stell drums

Source: product Data, Drew Chemical Corporation, Boonton, NJ, 1987.

Appendix B. Calibration Curve for Feeding Pumps
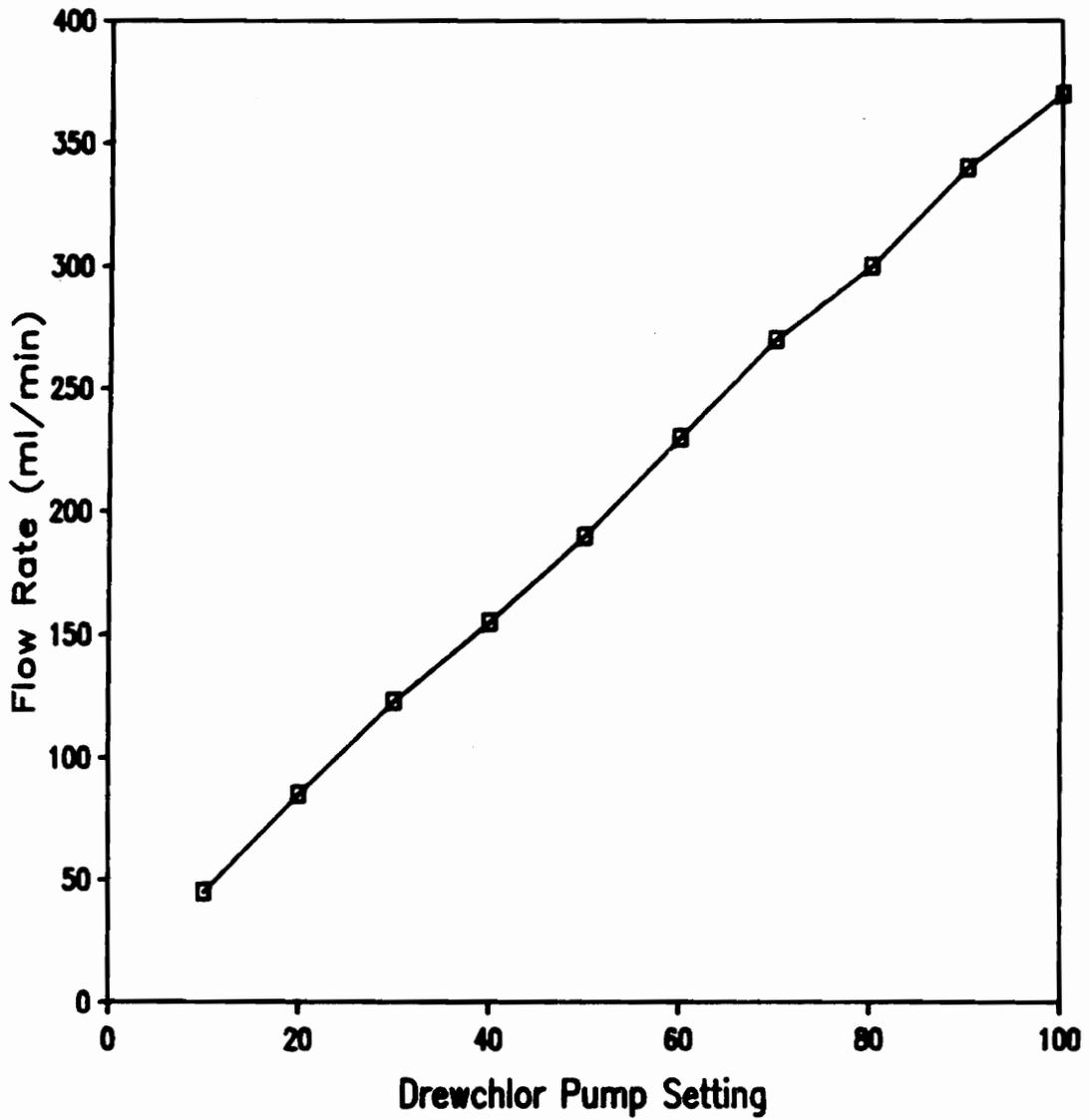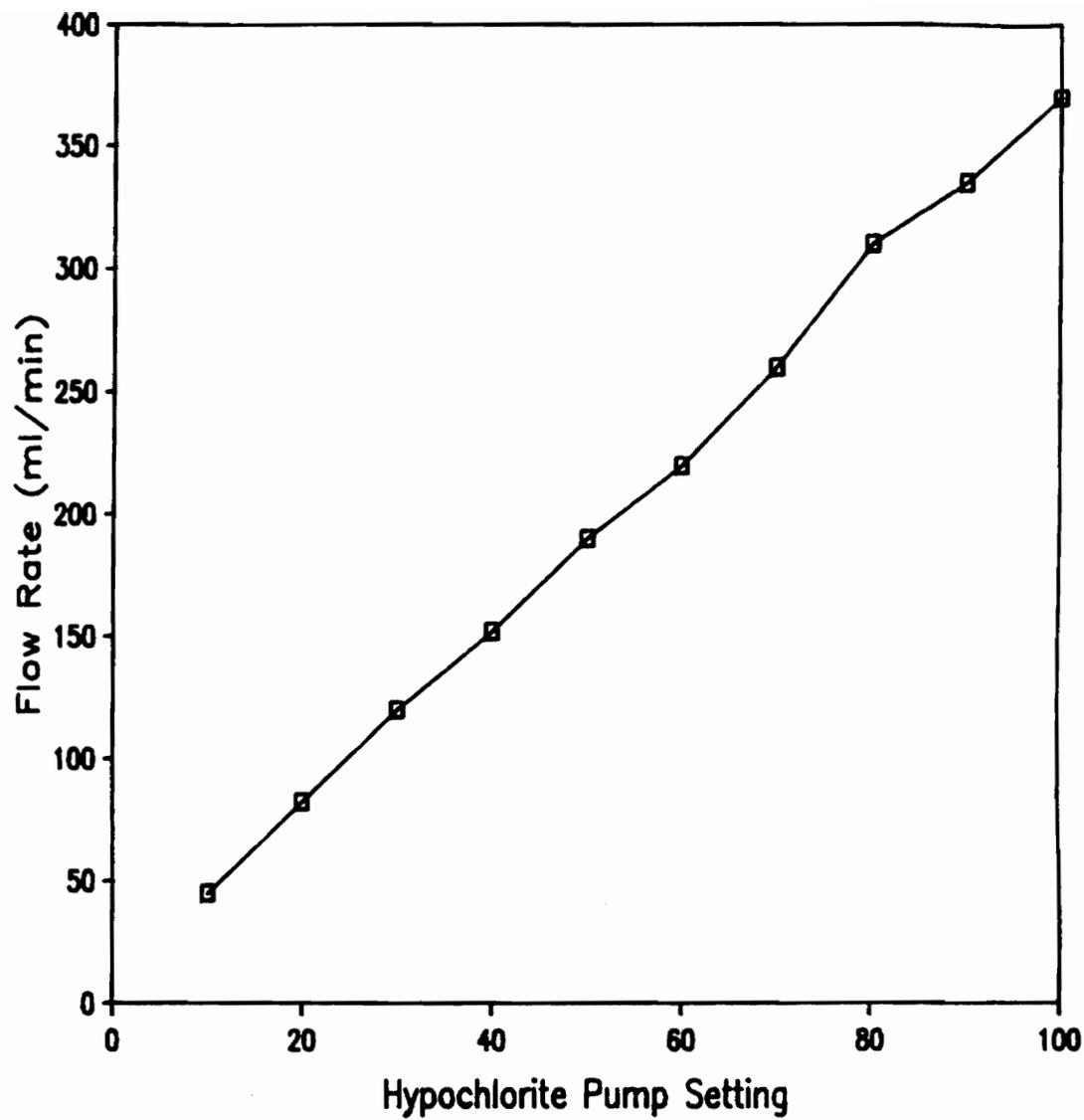
Appendix C. Procedures for the Determination of yield of ClO$_2$

1. Determine ClO$_2$ concentration, a mg/l.

2. Calculate ClO$_2$ molar concentration, b mole/l. (b = a/67,450)

3. Determine the Drewchlor flow rate, c ml/min, from calibration curve in Appendix B.

4. Calculate the amount of Na$_2$ClO$_2$ used per minute, d g/min, according to the properties of Drewchlor listed in Appendix A. (Specific gravity = 1.25 g/ml, purity = 25%) (d = cx1.25x25%)

5. Convert d g/min of Na$_2$ClO$_2$ to e mole/min. (e = d/90.5)

6. Determine the amount of ClO$_2$ generated, f l/min.

7. Calculate NaClO$_2$ molar concentration, g mole/l. (g = e/f)

8. Calculate yield of ClO$_2$ (yield = b/g)

Appendix D. Raw Data Tables

Table 5. Percent phenol removal at various ClO_2-to-phenol ratios (Figure 9).

ClO_2-to-phenol molar ratio	Phenol removal (%)	
1.0	45.1	
1.5	75.3	
2.0	90.4	Initial phenol = 10.00 mg/l
2.5	91.1	
3.0	91.7	
5.0	90.7	
1.0	40.3	
1.5	72.0	
2.0	89.0	Initial phenol = 4.00 mg/l
2.5	89.3	
3.0	90.5	
5.0	92.0	
1.0	42.5	
1.5	74.2	
2.0	88.2	Initial phenol = 1.20 mg/l
2.5	88.2	
3.0	89.8	
5.0	91.5	

Table 6.   Phenol residuals at various ClO_2-to-phenol ratios (Figure 10).

ClO_2-to-phenol molar ratio	Phenol concentration (mg/l)	
0	10.10	
1.52	7.15	Initial pH = 6.5
3.29	1.58	Reaction period = 30 min.
4.50	0.95	Temperature = 88°F
6.57	0.88	
13.15	0.63	
0	14.50	
1.85	6.80	Initial pH = 7.2
3.10	2.05	Reaction period = 30 min.
4.63	0.98	Temperature = 89°F
6.95	0.78	
13.90	0.46	
0	6.50	
1.62	3.25	Initial = 7.5
3.15	1.23	Reaction period = 30 min.
4.45	0.75	Temperature = 89°F
6.10	0.60	
12.50	0.33	

Table 7. Phenol residuals at various reaction periods (Figure 11).

Reaction period (minutes)	Phenol concentration (mg/l)	
0	10.40	
5	1.05	ClO_2/phenol molar ratio = 5.0
10	0.77	Temperature = 90°F
20	0.45	Initial pH = 6.8
30	0.50	
60	0.46	
0	8.60	
5	0.95	ClO_2/phenol molar ratio = 5.0
10	0.85	Temperature = 88°F
20	0.62	Initial pH = 7.5
30	0.55	
60	0.58	
0	3.50	
5	0.85	ClO_2/phenol molar ratio = 5.0
10	0.68	Temperature = 88°F
20	0.43	Initial pH = 7.2
30	0.35	
60	0.38	

Table 8. Phenol residuals at various temperatures (Figure 12).

Temperature (°F)	Phenol concentration (mg/l)	
40	0.90	
50	0.95	Initial phenol concentration = 35.50 mg/l
60	0.85	ClO_2/phenol molar ratio = 5.0
70	0.90	Reaction period = 30 minutes
80	0.78	Initial pH = 7.2
90	0.85	
45	0.65	
55	0.58	Initial phenol concentration = 12.80 mg/l
65	0.60	ClO_2/phenol molar ratio = 5.0
75	0.55	Reaction period = 30 minutes
85	0.53	Initial pH = 6.8
95	0.50	

Table 9.   Phenol residuals at various pH values (Figure 13).

pH	phenol concentration (mg/l)	
5.05	0.87	Initial phenol concentration = 17.20 mg/l
6.01	0.92	ClO_2/phenol molar ratio = 5.0
6.99	0.84	Reaction period = 30 minutes
8.02	0.80	Initial pH = 7.2
9.01	0.65	Temperature = 84°F
5.03	0.72	Initial phenol concentration = 8.15 mg/l
6.05	0.61	ClO_2/phenol molar ratio = 5.0
7.02	0.69	Reaction period = 30 minutes
8.04	0.45	Initial pH = 7.6
8.98	0.52	Temperature = 83°F

Appendix E. A Sample Calculation of Treatment Cost

Chemical costs :

    Drewchlor (25% $NaClO_2$)   : $ 2.5/kg

    Household bleach (9.2% $NaOCl$)   : $ 0.132/kg

    Hydrochloric acid (31.45% HCl)   : $ 0.172/kg

    assume phenol concentration $= 5$ mg/l, and the yield of ClO_2 generation based on feed chlorite $= 85\%$. For 1,000 gallons of wastewater treated at ClO_2-to-phenol molar ratio of 5, the amount of ClO_2 needed $=$

$$5 \text{ mg/l x } 1,000 \text{ gal. x } 3.8 \text{ l/gal. x } 5 = 95 \text{ g } = 1.41 \text{ mole}$$

the amount of $NaClO_2$ needed $= 1.41/0.85 = 1.66$ mole $= 150$ g

the amount of Drewchlor needed $= 150$ g$/0.25 = 600$ g

the amount of $NaOCl$ needed (100% in excess) $=$

$$1.41 \text{ mole x } 74.5 \text{ g/mole } = 105 \text{ g}$$

the amount of bleach needed $= 105$ g$/0.092 = 1,140$ g

the amount of HCl needed (100% in excess) $=$

$$1.41 \text{ mole}/0.3145 \text{ x } 2 \text{ x } 36.5 \text{ g/mole } = 330 \text{ g}$$

the cost of Drewchlor $= 0.6$ kg x $ 2.5/kg $= $ 1.5

the cost of bleach $= 1.14$ kg x $ 0.132/kg $= $ 0.15

the cost of HCl = 0.33 kg x $ 0.172/kg = $ 0.05

Total chemical cost = 1.5 + 0.15 + 0.05 = $ 1.7/1,000 gal.

Vita

Chung-Jung Hsu was born in Tainan, Taiwan, The Republic of China on May 9, 1956. He received the Bachelor of Science degree in Mineral and Petroleum Engineering from National Cheng Kung University in Taiwan, R.O.C. in 1980. He worked for Asian Mineral Development Corporation, Inc. for approximately one year prior to attending the University of Alaska-Fairbanks in 1983. He received the Master of Science degree in Mineral Preparation Engineering from University of Alaska-Fairbanks in September of 1985. In January 1986 he entered Virginia Polytechnic Institute and State University. He received the Master of Science degree in Environmental Engineering from VPI & SU in February of 1988, his second master's degree.

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