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BROMINE CHLORIDE TREATMENT OF AQUEOUS GASIFIER EFFLUENT

by
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Submitted to the Graduate Faculty

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for the degree of

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This Thesis submitted by Theodore T. Poppke in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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(Chairman)

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This Thesis meets the standards for appearance and conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

A. William Johnson
Dean of the Graduate School

Permission

Title Bromine Chloride Treatment of Aqueous Gasifier Effluent

Department Chemical Engineering

Degree Master of Science

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Date April 26, 1982

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ABSTRACT

The feasibility of treating slagging gasifier wastewater with bromine chloride was studied. The aqueous effluent was collected from the spray washer of the Grand Forks Energy Technology Center's slagging fixed-bed gasifier during run RA-94.

It was found that slagging gasifier wastewater is only partially treatable using bromine chloride as the principal treatment step. After a pretreatment scheme consisting of lime addition and ammonia stripping, bromine chloride was unable to reduce the total carbon concentration of the wastewater to acceptable discharge or reuse levels.

Bromine chloride addition as an aqueous solution, a liquid, and a vapor was investigated. Bromine chloride vapor gave the largest total carbon removal. Phenolic compounds were brominated and precipitated from the wastewater. Other organic compounds appear to be oxidized by bromine chloride.

An installed equipment cost of approximately \$3,120,000 can be expected for a facility employing BrCl oxidation followed by treatment with activated carbon. The facility would purify pretreated wastewater from a slagging gasification plant capable of producing 7.08 million standard cubic meters of methane daily. Bromine chloride can be expected to contribute \$14.30 to the total cost of each cubic meter of wastewater treated.

INTRODUCTION

The United States has become increasingly dependent on foreign sources of petroleum and other raw materials in recent years. This dependency has caused large amounts of capital to leave the country for these resources and has made the country vulnerable to the actions of other nations. In response, increased attention has been placed upon the development of native energy resources, both by increasing production of oil and natural gas to directly offset imports and by replacing these fuels where possible with coal and synthetic fuels.

Coal is an attractive alternative because of its abundance and ability to be used directly or converted to liquid and gaseous fuels. It is estimated that the United States contains 20 percent of the world's total coal resources (1).[1] In this country, the total remaining coal resources are 3.6×10^{12} metric tons (M.T.) of coal and 4.9×10^{11} M.T. of lignite (1, 2). The portion considered mineable at present is 4.0×10^{11} and 3.7×10^{10} M.T. of coal and lignite, respectively (3, 2). At current usage and growth projections the demonstrated reserve base will be depleted by approximately the year 2050, but increases in prices coupled with possible technical develop-

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[1] Numbers in parenthesis refer to references which are listed at the end of this report.

ments should extend the reserve base for at least 200 years (4, 5). The reserve base is that portion of the coal that is considered mineable under current conditions.

Coal is often an undesirable replacement for oil or natural gas because it is more difficult to handle and has problems with sulfur and particulate emissions. These problems associated with the handling, transportation, and burning of coal may be reduced by converting the coal to a liquid or gaseous fuel before transportation and use. Gasification is the process for converting coal into a gaseous fuel. Various processes are in commercial use around the world. One process that is still in the development stage is that of the slagging fixed-bed gasifier. A gasifier of this type using lignite is currently being tested on a pilot-plant scale at the Grand Forks Energy Technology Center (GFETC), U.S. Department of Energy (6). A description of the status and operation of the gasifier may be found in Appendix A.

With any coal conversion process, pollution is a major concern. In the slagging fixed-bed technology, an aqueous stream high in coal-derived organics is collected when the product gas is cleaned and cooled. Typically, the wastewater contains 15,000 mg/l of organic carbon and some 10,000 mg/l of ammonia. The concentration of organic compounds must be reduced before the water may be released into the environment.

OBJECTIVES

The primary objective of this research project was to determine if chemical oxidation with bromine chloride would be feasible as a major treatment step for the gasifier wastewater. The method of oxidant addition, possible design parameters for the oxidant reactor, a postulated reaction scheme, and the capital and operating costs for a gasification plant producing 7.08 million standard cubic meters (250 mscf) per day synthetic natural gas were to be determined also.

GENERAL TREATMENT METHODS FOR WASTEWATER

Treatment methods for industrial wastewater may be distinguished by function, which can be divided into broad categories of primary, secondary, and tertiary treatment. Primary treatment usually involves the separation of tars, oils, sediment, and easily coagulated or flocculated material that may interfere with subsequent treatment steps. Secondary treatment removes pollutants by biological treatment, adsorption, or a similar process. Tertiary treatment is considered to be a final polishing step, of which ion exchange serves as an example.

Treatment processes may also be divided into biological or physical-chemical treatment methods. Two general reviews of this subject are given by Degremont (7) and Mulligan and Fox (8).

Biological Treatment

Biological treatment uses microorganisms to break down the organic compounds into innocuous matter. These microorganisms may be broadly classified into three groups depending on their use of oxygen. Aerobic organisms require oxygen for metabolism while anaerobes derive energy from organics in the absence of oxygen. Facultative organisms can function in either environment.

Two methods are employed to contact the organisms with the wastewater. The activated sludge method mixes a suspension of microorganisms with the wastewater, and the fixed film method affixes the growth to an inert medium over which the wastewater passes.

Aerobic treatment takes place in an agitated and aerated environment to stimulate bacterial growth and enhance contact. The bacteria capture and digest the organics, incorporating them into the sludge or film which is easily removed by sedimentation. Anaerobic fermentation is a two step process where one group of bacteria first converts the waste into simpler organic acids which the second group of bacteria then attack to produce methane and carbon dioxide.

Microbial populations have the advantage of being adaptable to metabolize specific compounds. A disadvantage is that heavy metals and organics such as pesticides and PCBs may be toxic to the biological growth and can interfere with the treatment.

Physical-Chemical Treatment

Coagulation and Flocculation

Coagulation is the process of destabilizing a colloid to allow the particles to precipitate. The sulphates and chlorides of aluminum and iron are common coagulants. The cations neutralize negatively charged colloid particles which allows the particles to flocculate.

Flocculation is the aggregation of smaller particles and can be initiated by the addition of a coagulant, but the process is improved either by increasing the contact between neutralized colloid particles and an existing precipitate or by the addition of a flocculating agent. Contact between the colloid particles and the floc may be increased by sludge recirculation or with slow stirring to bring the particles together. Flocculating agents are added either to increase the flocculation rate or to produce a better floc. Activated silica is the most common flocculating agent used.

Precipitation

Precipitation is the process of removing a species from the wastewater by using a chemical reaction to produce a more insoluble material. The insoluble product may then be collected and removed from the water. For illustration, the removal of calcium and magnesium compounds by lime is shown. With the addition of lime the alkalinity is reduced to a value determined by the solubility of $CaCO_3$ and $Mg(OH)_2$:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow 2MgCO_3 \downarrow + 2H_2O$$

$$Ca(OH)_2 + MgCO_3 \rightarrow CaCO_3 \downarrow + Mg(OH)_2\downarrow$$

Sedimentation and Filtration

Sedimentation or filtration is used to remove solid particles formed by flocculation or by precipitation. Sedimentation uses the differences in density between the solids and water to separate the mixture into a relatively clear supernatant liquid and a sludge. The separation takes place in large settling ponds or in clarifiers that remove the sludge continuously from the tank. A porous medium is used in filtration to allow the water to pass through while solids are retained. The solids are removed as a wet filter cake.

Adsorption

Dissolved material may be removed by adsorption, solvent extraction, reverse osmosis, and ion exchange. Dissolved substances are removed by adsorption as a result of differences in physical, chemical, or electrical attraction for the solute between the wastewater solvent and the adsorbant. Activated carbon is finding increased use in wastewater treatment for the removal of organics because of the hydrophobic nature of dissolved organics. Ions and polar molecules are not removed as effectively by carbon because these solutes have a higher affinity for water.

Extraction

Solvent extraction is useful where the solute is soluble in a solvent which is immiscible in the wastewater. The solvent and the wastewater are brought into intimate contact in a column or mixer and separated. The solvent is cleaned for reuse either by steam stripping or distillation.

Reverse Osmosis

Reverse osmosis uses a membrane that is permeable to water and smaller solutes but is impermeable to particles and the larger dissolved species. The waste stream is separated into relatively pure water and a concentrated brine. The term reverse osmosis is used because the water flows from the wastestream to a stream of nearly pure water, which is against natural tendencies. The system is made to operate in this manner by applying up to 1500 psi external pressure in opposition to the osmotic pressure gradient.

Ion Exchange

An ion exchange resin consists of an insoluble substrate with one or more acid or basic functional groups per unit of substrate. Cation exchangers have sulphonic or carboxylic functional groups that can exchange their attached protons (or other positive ions) for metal cations in the wastewater. The resin is regenerated with a higher concentration of an acid or of another positive ion. Anion resins contain amines or quaternary ammonium functional groups which exchange hydroxide ions for sulphate, chloride, or silicate and are regenerated with a strong base. By using combinations of both types of resins, virtually all ions may be removed. An example of ion exchange is water softening, in which calcium and magnesium are replaced with sodium to remove temporary hardness.

Chemical Oxidation

Oxygen demand in wastewater is harmful when introduced into receiving waters because it can remove oxygen necessary for aquatic life. Biological oxidation is often used to reduce oxygen demand, but some wastewater may contain organics that are resistant to biological degradation or may be toxic to bacterial growth. Fluctuations in the wastewater loading can also harm the biomass used in biological treatment either by overloading the system with high concentrations of pollutants or by not supplying enough nutrients to the biomass.

There is also some question whether biological treatment can achieve some of the proposed 1983 EPA effluent regulations (8). For these situations, chemical oxidation should be considered for treatment.

Two major advantages of chemical oxidation over biological treatment are that less space is required for equipment and that chemical oxidation is easier to adjust to load or quality fluctuations. The major disadvantage is in higher operating and chemical costs.

Chemical oxidants may be divided into two major groups. The first group are the oxygen-based compound. oxygen, ozone, hydrogen peroxide, and potassium permanganate The second group are the halogen-based compounds: chlorine, bromine chloride, chlorine dioxide, and hypochlorite.

Ozone is a very powerful oxidizing agent but its generation is expensive and inefficient. Hydrogen peroxide is weaker than ozone and has been shown to be ineffective in removing organics from gasifier wastewater treated with activated carbon (9). The major advantage of ozone and hydrogen peroxide is that they add no new pollutants to the wastewater. Potassium permanganate is less expensive than ozone, but problems associated with disposal of the MnO_2 sludge produced must be considered.

Chlorine dioxide is also a powerful oxidizing agent, but it is expensive. Hypochlorite is a weaker oxidant than chlorine. Chlorine use for treatment of wastewater containing ammonia is now questioned because stable chloramines that may form are considered toxic. Bromine chloride forms bromamines, but these are unstable and have a short half-life.

Hird (9) indicated that bromine chloride removed more organic material than did more common oxidizing agents (O_3, H_2O_2, $KMnO_4$, Cl_2) in a tertiary treatment step. Because of this performance, the actions of BrCl on gasifier wastewater warranted further investigation.

BROMINE CHLORIDE

Aqueous Equilibria

The aqueous equilibria of BrCl control the concentration of the active oxidizing species. The relative strength of the oxidation potentials are:

$$HOBr > BrCl > OBr^-$$

The oxidation potentials are a measure of the strength of the oxidant. Hypobromous acid is a stronger oxidant than BrCl, but BrCl is more reactive (10).

The solubility of BrCl in water is 8.5 gm per 100 gm of water. The first reaction occurring when BrCl is in solution is hydrolysis to hypobromous *acid:*

$$BrCl_{(aq)} + H_2O \rightleftarrows HOBr_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)}$$

$$K_1 = \frac{[HOBr]\ [H+]\ [Cl-]}{[BrCl]} = 2.9 \times 10^{-5} \text{ g mole}^2/l^2 \qquad (11)$$

Hypobromous acid dissociates to hypohalite ion:

$$HOBr_{(aq)} \rightleftarrows H^+_{(aq)} + OBr^-_{(aq)}$$

$$K_2 = \frac{[H+]\ [OBr-]}{[HOBr]} = 2.0 \times 10^{-9} \text{ g mole/l} \qquad (12)$$

The magnitude of the constants indicates that a 25 gm/l BrCl solution initially at pH 12 would be 92% (mole) BrCl, 8% HOBr, and $<10^{-6}$ % OBr^-. This indicates that the most reactive oxidant, molecular BrCl, is the major species in solution. Other BrCl properties are summarized in Appendix B.

Wastewater Reactions

Halogenation of organic compounds is an electrophilic aromatic substitution in which hydrogen is replaced by a halogen. The first step of the reaction is the formation of a complex between the electrophile (i.e. - BrCl) and the organic molecule. The second is a deprotonation step to the halogenated organic product. The first step is generally rate-controlling except in high concentrations of halide ions when the second step becomes rate-controlling (13).

Bromination may occur with positive bromine electrophiles (X^+ = $BrOH_2^+$, Br^+; ArH = aromatic ring):

$$BrOH + H^+ \rightleftarrows BrOH_2^+ \tag{10}$$

$$BrOH_2^+ \rightleftarrows Br^+ + H_2O$$

$$ArH + X \xrightarrow{slow} ArHX^+$$

$$ArHX^+ \xrightarrow{fast} ARX + H^+$$

The electrophile may also be a neutral species:

$$ArH + BrCl \rightleftarrows ArHBrCl$$

$$ArHBrCl \rightarrow ArBr + H^{+} + Cl^{-}$$

The major impurities of interest in this study in the gasifier wastewater are organic, specifically phenol and substituted phenols. In acidic solutions, chlorination of phenol proceeds to 2,4,6-trichlorophenol. Additional chlorination is thought to form pentachlorophenol, various cyclic ketones, or an aliphatic product of benzene ring cleavage. Since BrCl should react in a manner similar to Cl_2, reactions between phenol and chlorine are shown in Figure 1 for illustrative purposes.

A reaction scheme (Figure 1a) was developed from observing the treatment of refinery effluent with hypochlorite (14). The effluent initially contained 78 mg/l phenol and 100 to 5000 mg/l available chlorine. Reactions were followed using UV spectroscopy. Initial formation of trichlorophenol was followed by ring-cleavage to form aliphatic acids (alkyl-substituted 2,4-dichloro-2,4-hexadiene-1,6-dicarboxylic or 2,4-dichloro-3,5-hexadione-1,6-dicarboxylic acids).

The second reaction scheme (Figure 1b) was determined by treating a 1 mg/l phenol solution with 1 to 8 mg/l chlorine (15). The main reaction is oxidation to a quinone with further oxidation to maleic anhydride. A possible side reaction is formation of trichlorophenol followed by oxidation to tetrachloroquinone.

In the first reaction scheme, the chlorine to phenol mole ratio was varied from 1.7 to 86. In the second scheme, the ratio was varied from 1.3 to 10. In the present investigation, the BrCl to

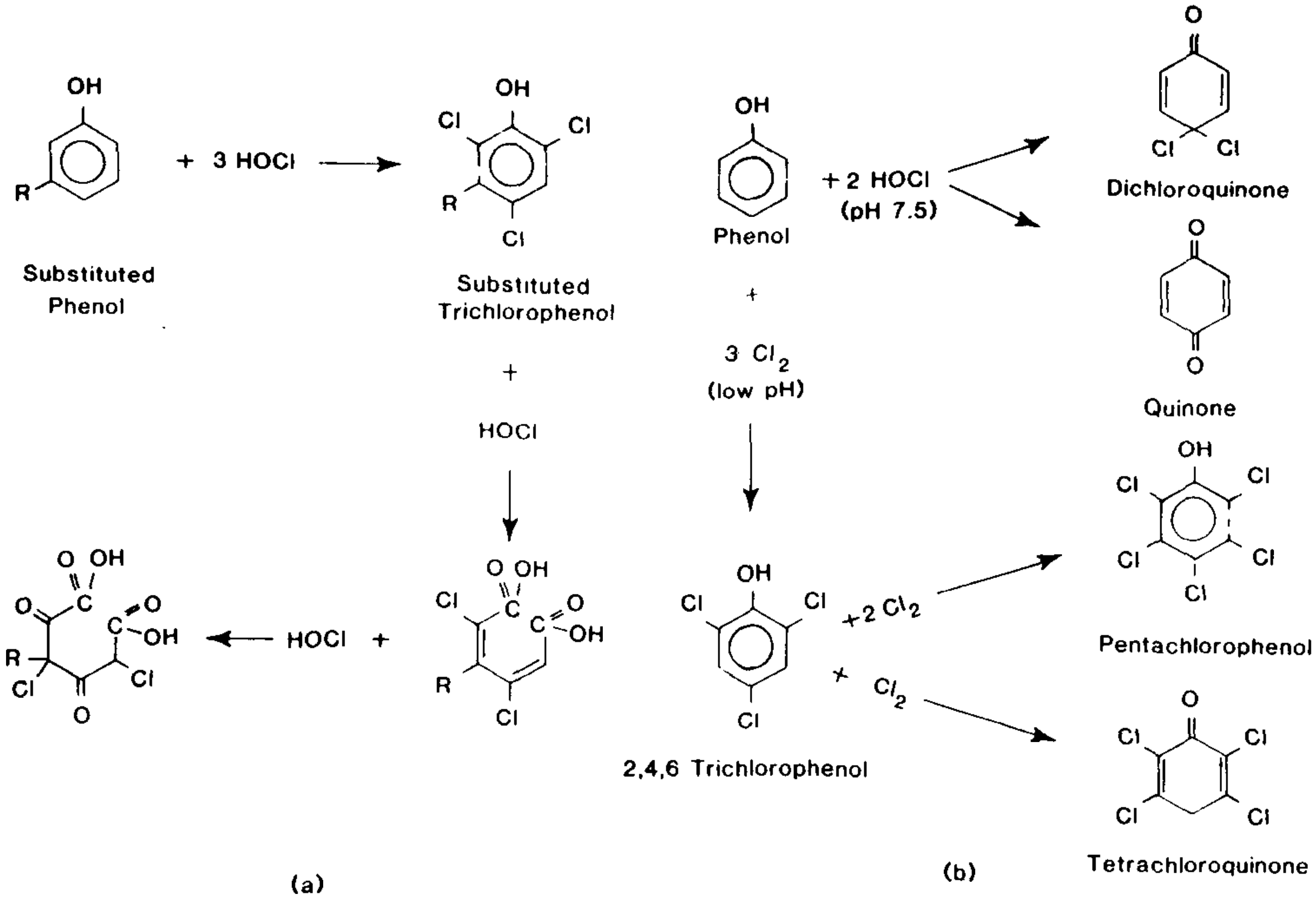


Figure 1. Suggested Phenol-Chlorine Reactions in Wastewater Treatment

phenolic mole ratio was varied from 0 to 14. This should provide sufficient oxidant to form products similar to those produced in the chlorination studies.

Chlorination of a 10 wt % phenol solution for 14 days indicated that 2,4,6-trichlorophenol was first formed with the final product being 2,2,4,5,6,6-hexachloro-3-cyclohexen-1-one (16).

When wastewater is treated with BrCl, molecular bromine chloride would be the major oxidizing species. A small amount of HOBr would also be present. Gasifier wastewater has a high concentration of phenolic compounds. If reactions analogous to those of chlorine occur, BrCl treated wastewater should contain lower concentrations of organic compounds than the pretreated wastewater.

EXPERIMENTAL PROCEDURE

Wastewater for testing was collected from the spray washer of the GFETC slagging fixed-bed gasifier during the operation of run RA-94. In this run, pre-dried Indian Head lignite was gasified at a pressure of 2.1 MPa (300 psig) and a steam/oxygen mole ratio of 0.9. Forty liters of aqueous effluent from the spray washer was collected and frozen in three twenty liter containers. Before pretreatment, the waste liquor was allowed to thaw at room temperature. After the pretreatment, the liquor was kept at ambient temperature until use. The average composition of the aqueous effluent during run RA-94 is given in Table 1.

Pretreatment Rationale

The purpose of the pretreatment scheme was to remove undissolved tars and oils, alkalinity, and ammonia. The tars and oils could possibly interfere with the subsequent treatment steps so their early removal is desirable. Ammonia is known to react with bromine chloride to form bromamines (17) so its removal was considered necessary prior to bromine chloride treatment to conserve the reagent. Alkalinity (measured as $CaCO_3$) was removed during the lime addition necessary to raise the pH for ammonia stripping.

A previously developed pretreatment scheme proved satisfactory to meet these objectives. The scheme adopted by Hird (9) may be summarized as follows:

TABLE 1

AQUEOUS EFFLUENT COMPOSITION OF WATER COLLECTED FROM SPRAY WASHER OF THE GFETC GASIFIER FROM RUN RA-94 AND THE AMOUNT PRODUCED PER TON MAF LIGNITE GASIFIED

Liquor-Effluent Data (18)	Concentration, mg/l	Quantity Formed (kg/metric ton maf lignite gasified)
pH	9.5	
Alkalinity	29,164	
Ammonia	10,457	4.72
Cyanide	69	0.03
Thiocyanate	221	0.10
Sulfide	744	0.34
Total Sulfur	788	0.36
Total Carbon	18,119	8.22
Inorganic Carbon	2,296	1.06
Organic Carbon	15,810	7.15
Phenol	6,133	2.73
o-Cresol	899	0.40
m-,p-Cresol	1,996	0.89
Tar		41.76
Water - Total		455.40

(raw liquor) → lime addition → ammonia stripping →
recarbonation → coagulation → pretreated liquor.

The recarbonation step was necessary when this scheme was originally developed because the pH had to be lowered to optimize the subsequent carbon adsorption treatment. Since carbon adsorption was not intended in the present investigation until after the pH-lowering bromine chloride addition, the pretreatment procedure was modified by eliminating recarbonation. Coagulation was also omitted from the present pretreatment scheme. The final treated liquor would probably require clarification prior to discharge. Therefore, coagulation was reserved for a final step in an overall treatment process. The pretreatment scheme employed in the present investigation was:

(raw liquor) → lime addition → ammonia stripping →
(pretreated liquor)

Treatment Rationale

Two treatment schemes were considered for testing:

1. (pretreated liquor) - bromine chloride oxidation - carbon adsorption - (treated liquor)
2. (pretreated liquor) - carbon adsorption - bromine chloride oxidation - (treated liquor)

The first scheme was adopted as bromine chloride addition would be followed by removal of residual free halogen in the treated liquor. Carbon treatment can remove free halogen (19). The first treatment scheme would allow the carbon treatment to remove remaining organic compounds and bromine in the same step.

Pretreatment Procedures

Pretreatment involved lime addition, settling, and ammonia stripping. Twenty-four liters of raw RA-94 wastewater was treated with 0.83 kg of lime to raise the pH from 8.5 to 12. The treatment was accomplished in two batches in a 20 l container. The slurry was first stirred for forty minutes using a Fisher "Jumbo Stirrer" with a 9 cm propeller, then allowed to settle for one hour before the liquid was decanted. The decanted liquor was then stripped of ammonia using several passes through a 0.1 m diameter acrylic column packed to a depth of 1.1 m with 9.5 mm unglazed porcelain Raschig rings. Liquor circulation was achieved by means of a peristalic pump. Stripping air was added by a compressor operating at 112 kPa. Dow 544 anti-foam solution was added as necessary to control foaming which otherwise might have flooded the tower. The stripping was done batchwise with twenty-four passes in eight hours.

Bromine Chloride Test Procedures

Liquid bromine chloride was obtained in a 4.5 kg cylinder equipped with a dip tube, valve, and a straight thread connection. The research quantities used were supplied by Dow Chemical Corp. A cylinder bracket was constructed to secure the cylinder safely in a hood.

Initial Screening

The first tests using bromine chloride involved a Latin square design in which the effects of phenol, ammonia, and bromine chloride dosages on the total carbon removed were studied. Appropriate quantities of a 51.3 mg/ml stock phenol solution, a 175.0 mg/ml stock ammonia solution, and water were pipetted into a beaker to a total volume of 25 ml. A saturated bromine chloride solution was then pipetted into the beaker to achieve a bromine chloride to phenol ratio near 2, 5, 8, or 11 mg/mg. The solutions were stirred rapidly for two minutes, allowed to settle for one hour, filtered, and a sample analyzed for total carbon. Table 2 indicates the Latin square design used in the experiment.

Following the initial screening of the Latin square experiments, the effects of three different methods of bromine chloride addition on the pretreated wastewater were investigated: as an aqueous solution, as a liquid, and as a vapor.

Aqueous Bromine Chloride

An 8.5 wt % saturated solution of bromine chloride was prepared by slowly releasing liquid from the cylinder into a gas washing bottle. The slow rate allowed the bromine chloride to vaporize before contacting the water. The solution was judged to be saturated after bromine chloride vapor was observed to exit from the solution for several minutes. Large quantities of this solution were measured in a graduated cylinder while smaller amounts were pipetted.

TABLE 2

LEVELS OF PHENOL, AMMONIA, AND BROMINE CHLORIDE IN LATIN SQUARE DESIGN

Rows: Milligrams of phenol added
Columns: Milligrams of bromine chloride added per mg. phenol
Treatments: Milligrams of ammonia added

		mg BrCl/mg Phenol			
		2	5	8	11
mg Phenol	26	0	525	175	350
	103	350	175	525	0
	205	175	350	0	525
	308	525	0	350	175

mg ammonia

The tests with aqueous bromine chloride involved the addition of 0.1 to 0.35 l of the saturated bromine chloride solution to 0.2 l of the pretreated liquor. Upon addition of the bromine chloride, the samples were stirred for one hour, decanted, and the solutions analyzed.

Liquid Bromine Chloride

To handle liquid bromine chloride safely, it must first be cooled below its normal boiling point of -5°C. Liquid was slowly removed from the cylinder into a flask or graduated cylinder surrounded with crushed dry ice. The volume and temperature of the liquid were recorded to determine precise dosages. Because of its high density, 2.4 g/ml, the liquid could not be accurately pipetted.

Three types of tests using liquid bromine chloride were performed. In the first, 0.2 l of pretreated liquor was adjusted to pH 2 or 12 using sulfuric acid or lime. The pH-adjusted liquor was then treated with 3, 4, or 5 ml of liquid bromine chloride, stirred for one hour, filtered, and analyzed. The second differed only in that larger bromine chloride dosages were used and the pretreated liquor was not pH-adjusted. The third studied the reaction as it progressed after 3 ml of liquid BrCl was added to 0.2 l of pretreated liquor. Samples were removed during the reaction and analyzed for total carbon and residual halogen concentrations.

Bromine Chloride Vapor

A schematic of the equipment used in vaporizing and delivering the bromine chloride is shown in Figure 2. The liquid is drawn from the dip tube in the tank and is metered across a valve into the vaporizer, which is a section of stainless steel pipe kept at approximately 90°C with heat tape. The vapor flow rate is measured with a Gilmont flowmeter which was jacketed with hot water to prevent condensation of the bromine chloride vapor in the rotometer tube. Heat taped Teflon tubing then delivered the vapor to the reaction vessel.

The Gilmont flowmeter was calibrated by timing the addition of bromine chloride into a measured quantity of water and then determining the resultant bromine chloride concentration with an iodometric titration.

The vapor-liquor reaction vessel originally consisted of an open beaker, but a closed vessel was substituted to contain the corrosive vapors. A 0.5 l three-necked round bottom flask with an overhead

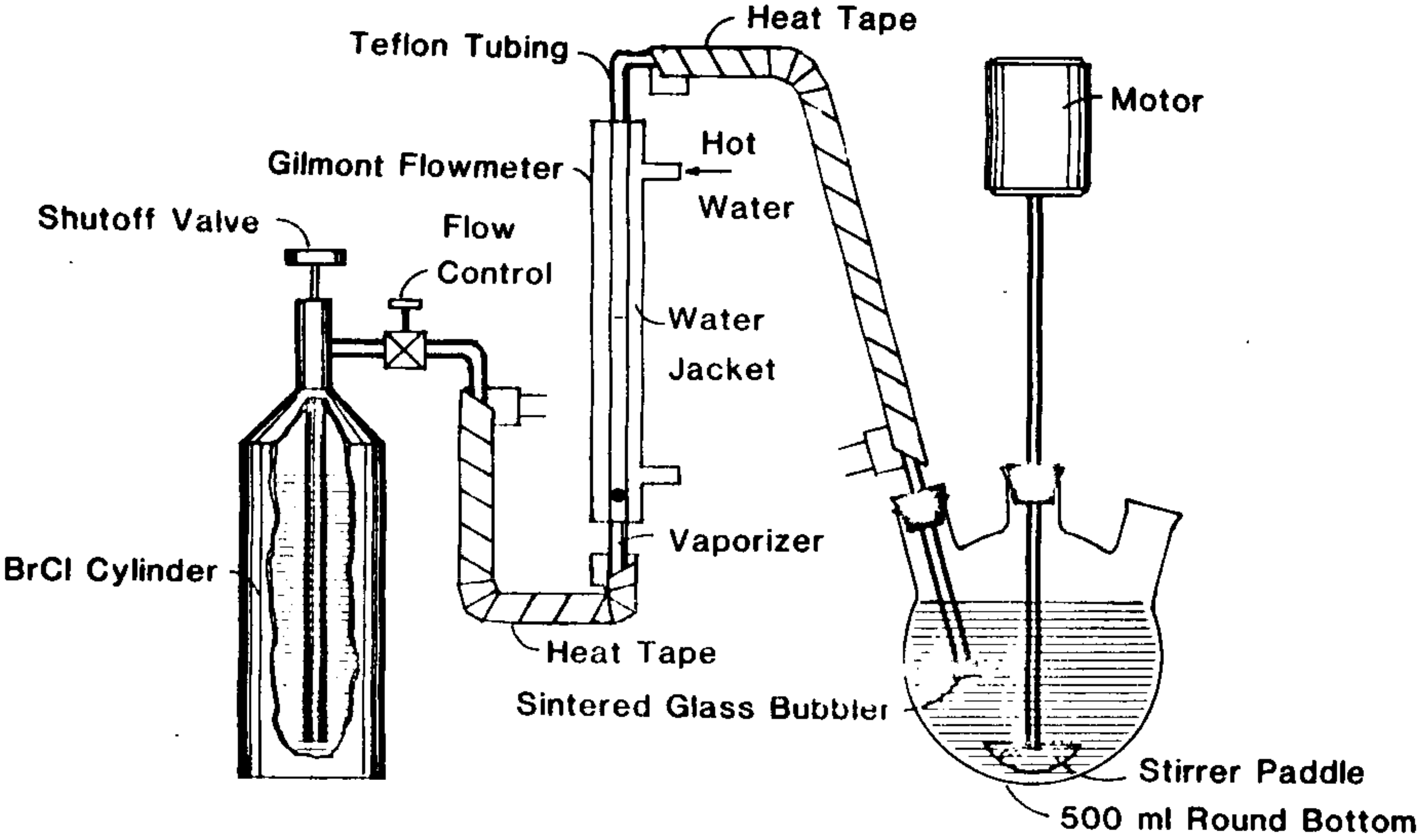


Figure 2. BrCl Vapor Treatment Schematic

stirrer was satisfactory. A sintered glass bubbler was fitted to the flask for bromine chloride delivery. The remaining opening was used for removal of the liquid samples.

During the first test with bromine chloride vapor, 1.7 gm of the BrCl was added to 0.1 l of pretreated liquor over a period of 11.5 minutes. Liquid samples were removed during BrCl addition and analyzed for total carbon and residual bromine chloride. The major purpose was to determine the amount of unreacted bromine chloride in the solution as the halogen was being added.

The next series of tests with the vapor added BrCl to pretreated liquor over periods of up to 3 hours to determine the effect of BrCl dosage on TC removal. Liquid samples were removed during BrCl addition, filtered, and analyzed for total carbon.

Liquor Analysis

The extent of lime and sulfuric acid addition was determined by glass electrode pH measurements. Ammonia was determined by the Kjedahl ammonia distillation (20). Phenol, o-cresol, and m-,p-cresols were determined using a Varian 1400 gas chromatograph and a Hewlett Packard 3380A Integrator (21). Residual BrCl was determined on a Bausch and Lomb Spectronic 20 at 400 nm for dilute solutions (11) or with an iodometric titration for solutions with large BrCl concentrations (20).

Total and inorganic carbon were determined using a Beckman Model 915A TOC Infrared Analyser. Total organic carbon is the difference between the total carbon content and the inorganic carbon content as determined in the analysis. Total organic carbon was initially used as the measure of organic compound removal by BrCl. Because residual BrCl interfered with the inorganic carbon determination, later samples were only analyzed for total carbon. Total carbon was a good indicator of the total organic carbon since the inorganic carbon levels never exceeded 95 mg/l or about four percent of the total carbon in the BrCl treated liquor.

Characterization by NMR of the oxidation products was performed on a Varian XL-200. For this analysis, the phenolics were extracted from the aqueous phase. Fifty ml of the BrCl treated liquor were adjusted to pH 13 with potassium hydroxide to convert the phenolics into phenoxides, and then extracted with 50 ml of dichloromethane to remove any organic bases which would interfere with the analysis. The aqueous phase was then adjusted to pH 1 by the addition of sulfuric acid to convert the phenoxides back to phenols. The aqueous phase was then extracted three times with 50 ml portions of dichloromethane. These portions containing the phenolics were then combined, concentrated by evaporation, dried over sodium sulfate, and filtered. Drying and filtration were necessary to remove water and suspended material that would interfere with the analysis.

With the exception of pH, residual BrCl, and NMR determinations, most analyses were performed by Stearns-Roger's chemists. A list of other analyses performed and the analysis method employed is given in Table 3.

TABLE 3

ANALYTICAL METHODS FOR WASTEWATER CHARACTERIZATION

Parameter	Method of Analysis
Alkalinity	Acid titration to pH 4.2 (20)
Sulfide	Silver-silver sulfide electrode (20)
Total Sulfur	Combustion iodimetric titration (22)
Total Dissolved Solids	Total suspended matter (20)

RESULTS AND DISCUSSION

Data and Calculations

The experimental data are presented in Tables 11 through 24, Appendix C. Experimental variables are bromine chloride concentration, pH, or reaction time. The dependent variables are final total carbon (TC) or bromine chloride concentration.

For presentation and discussion, the experimental data is converted either to mg of TC removed versus mg of bromine chloride added or to TC and BrCl concentrations versus reaction time. These conversions are presented in the same tables as original data.

Latin Square Screening Test

The placement of the four different levels of the phenol, ammonia, and bromine chloride dosages was described in Table 2 of the preceeding section. The calculations for the analysis of variance are in Appendix C. The dependent variable used in the analysis was the percent reduction in TC. The levels of the independent variables and the percent reduction in TC are presented in Table 4. The BrCl was added as an aqueous solution.

Milligrams of phenol added and the bromine chloride to phenol dosage ratio were found to be significant ($\alpha = 0.05$) while the milligrams of ammonia added was not. The ammonia content probably does not significantly influence BrCl treatment over the range of concentrations tested and removal before BrCl treatment is not necessary despite the possibility of bromamine formation.

TABLE 4

LATIN SQUARE DESIGN: TREATMENT LEVELS AND POSITIONS AND DEPENDENT VARIABLE RESULTS

Rows: Milligrams of phenol added
Columns: Milligrams of bromine chloride added per milligram of phenol
Treatments: Milligrams of ammonia added
Dependent Variable: Percent reduction in Total Carbon (TC)

		Bromine Chloride to Phenol Ratio, mg/mg			
		2:1	5:1	8:1	11:1
Phenol Dosage	26 mg	0 mg 5.17%	525 mg 0.78%	175 mg -0.59%*	350 mg of Ammonia -3.41% TC removed
	103 mg	350 mg 3.69%	175 mg 46.70%	525 mg 40.68%	0 mg of Ammonia 90.81% TC removed
	205 mg	175 mg 6.08%	350 mg 19.89%	0 mg 96.92%	525 mg of Ammonia 92.50% TC removed
	308 mg	525 mg -0.52%	0 mg 84.95%	350 mg 97.30%	175 mg of Ammonia 93.72% TC removed

* Negative TC removal may be the result of experimental error in either the phenol addition or sample analysis.

An additional calculation was then performed to determine which specific levels of the independent variables caused a significant change in the dependent variable ($\alpha = 0.05$). There was a significant difference only between the 26 and 308 mg phenol dosages and the 2:1 and 11:1 bromine chloride to phenol (mg/mg) ratios. This means that only large changes in the phenol or BrCl dosage levels will affect the percent removal of TC from the wastewater. Formation of soluble bromination products may offset the reduction in phenolic TC as these soluble products would be measured in the TC determination.

Wastewater Pretreatment

The analysis of the raw gasifier liquor is given in Table 1 and that of the pretreated liquor in Table 5. The lime addition step reduced the ammonia from 10,460 mg/l to 6090 mg/l and the total carbon from 18,120 to 9750 mg/l. The air stripping step further reduced the ammonia from 6090 to 2550 mg/l and the total carbon from 9750 to 9375 mg/l. The overall pretreatment resulted in a 76% reduction in ammonia and a 48% reduction in TC. The lime addition was very effective in the removal of both ammonia and TC.

Although the stripping time was insufficient to reduce the ammonia to acceptable discharge levels, the results of the Latin square screening test show that NH_3 would not affect the BrCl treatment step. Ammonia stripping was placed before BrCl treatment because NH_3 removal was necessary somewhere in the overall process and early removal would eliminate raising the pH to 12 again. Early NH_3 removal would also lessen the possibility of bromamine formation.

Bromine Chloride Treatment

Aqueous Bromine Chloride Addition

Six batch oxidation tests were completed with aqueous bromine chloride and the pretreated liquor. Although the bromine chloride dosages were varied from 42 to 149 gm/l, there was essentially no difference in the final TC concentration. Because final TC concentrations were constant and liquor volume increased due to aqueous BrCl addition, the actual amount of TC removed decreased at higher

TABLE 5

ANALYSIS OF PRETREATED AND BROMINE CHLORIDE VAPOR-TREATED LIQUOR

	Pretreated Liquor	BrCl Dosage, mg/l		
		25,000	54,000	74,000
pH	12.02	2.31	1.03	1.34
Alkalinity (as $CaCO_3$), mg/l	9200	nd[1]	nd[1]	nd[1]
Ammonia, mg/l	1970	2315	2145	2315
Total sulfur, mg/l	nd[2]	nd[2]	nd[2]	nd[2]
Sulfide, mg/l	400	tr	tr	285
Total carbon, mg/l	10,375	4375	3375	2125
Phenolic:				
Phenol, mg/l	4165	310	45	60
o-cresol, mg/l	570	20	nd[3]	nd[3]
p-,m-cresol, mg/l	1665	60	nd[3]	nd[3]
Cyanide, mg/l	na	nd[4]	nd[4]	nd[4]
Total dissolved solids, mg/l	1995	2515	3005	3080

nd not detected
na not available, insufficient sample
tr trace amounts

[1] Less than 100 mg/l (23)
[2] Less than 250 mg/l (23)
[3] No peak seen (23)
[4] Less than 5 mg/l (23)

BrCl dosages. This suggests that TC removal is limited by the solubility of a treatment product. Because of this effect liquid BrCl treatment was investigated.

Liquid BrCl Addition

Eleven separate batch oxidation tests were performed with liquid bromine chloride and pretreated liquor. Results of seven tests at pH 12 and three at pH 2.4 are presented in Figure 3. Bromine chloride removes TC below 50 gm/l BrCl, but at higher levels no additional TC was removed. There was no apparent difference between the two pH's tested. In the last test, the reaction was followed as a function of time. The relative rate of the oxidation reaction is indicated by the initial slope of the curve in Figure 4; fifteen minutes after bromine chloride addition, 99+% of the bromine chloride had reacted and 33% of the TC in the pretreated wastewater had been removed. The lower TC removal is a result of lower BrCl dosages than at the other ten liquid BrCl tests.

At 40 gm/l of BrCl, liquid BrCl addition removes the same quantity of TC as treatment with aqueous BrCl does. However, liquid BrCl was difficult to handle and deliver accurately. Consequently, a bromine chloride vapor delivery method was attempted.

BrCl Vapor Addition

A bromine chloride vapor semi-batch oxidation test was conducted to determine the residual bromine concentration during the reaction. During the addition of 24 mg/sec of bromine chloride vapor per

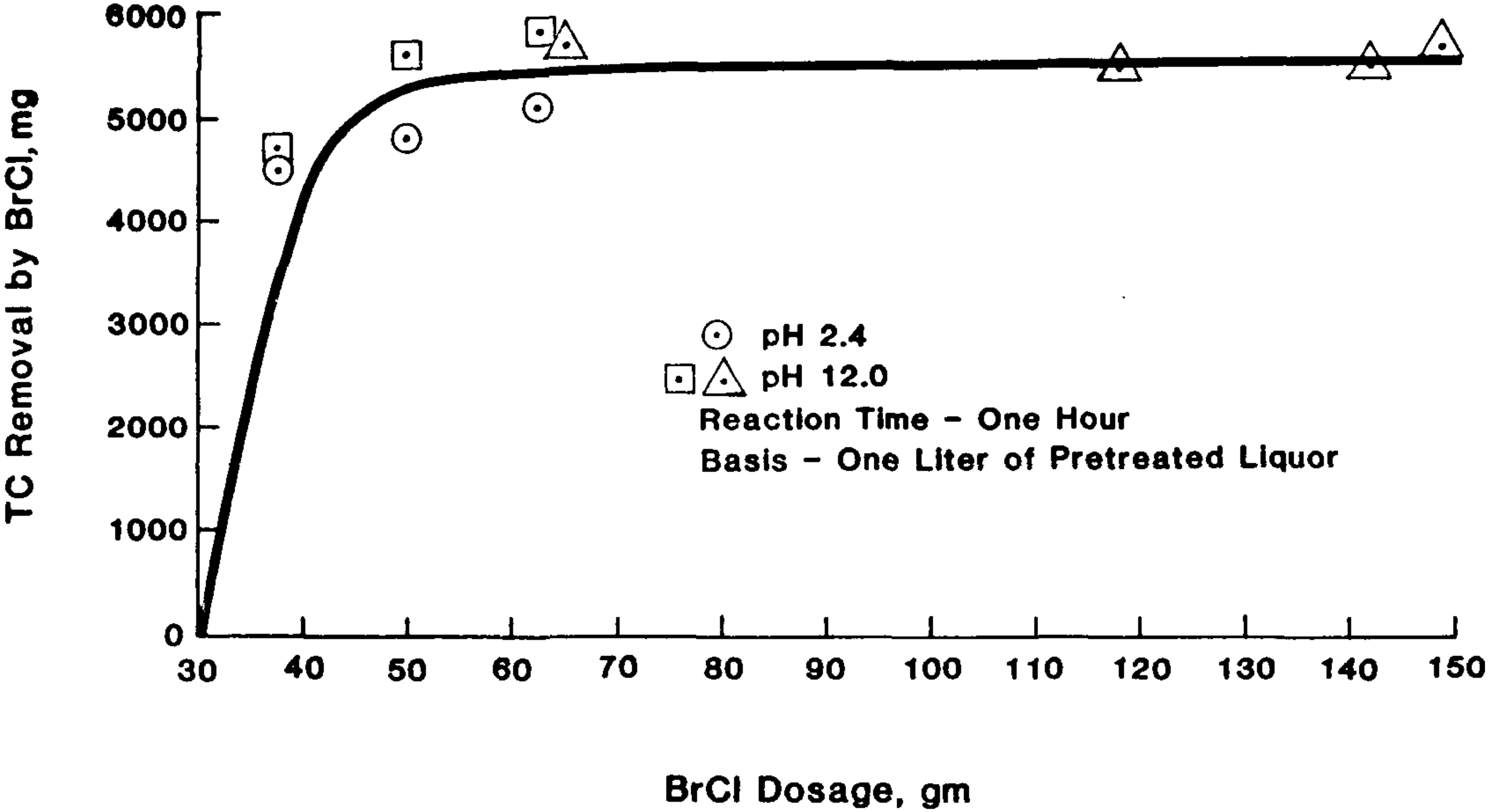


Figure 3. Dependence of TC Removal on BrCl Dosage (liquid BrCl).

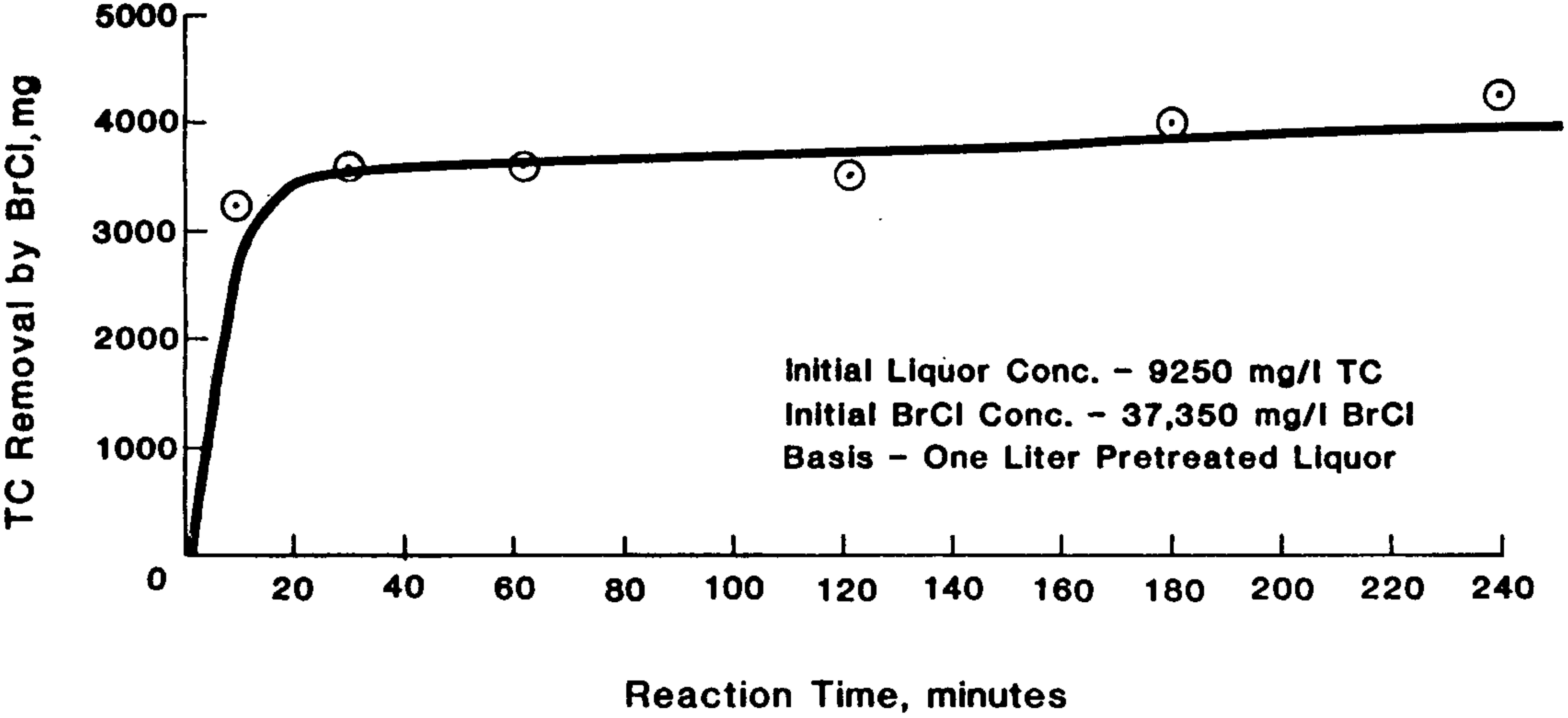


Figure 4. Dependence of TC Removal on Reaction Time (Liquid BrCl).

liter of wastewater over a 12 minute period, the residual BrCl concentration did not exceed 18 mg/l, or 0.4% of the total BrCl delivered. This indicates a rapid reaction because even during BrCl addition the concentration unreacted in solution remained low.

The results of two trials of a vapor-liquor semi-batch test to determine the effects of large bromine chloride dosages on TC removal are presented in Figure 5. No additional TC was removed above a dosage of approximately 25 mg/l of wastewater. At the same dosage unreacted bromine chloride vapor was beginning to exit from the solution. This observation together with the fact of no additional TC removal, indicated that the initially rapid reaction between BrCl and the wastewater had essentially ceased. This 25 mg/l BrCl was chosen as the dosage to be employed in design of a proposed wastewater treatment facility.

BrCl - Wastewater Reactions

BrCl Treatment Stoichiometry

Theoretical quantities of bromine chloride needed to halogenate phenol, cresol, and the phenolics in the pretreated wastewater are summarized in Table 6. The solubilities of phenol bromination products in weight percent and mg/l of TC are listed in Table 7. Pretreated wastewater treated with sufficient bromine chloride to completely form the dibromophenolic compounds would have at least 88% of the phenolic TC removed, assuming that the cresol bromination products are only as soluble as corresponding phenol products. If tribromophenolic compounds were completely formed, the removal would be in excess of 99%.

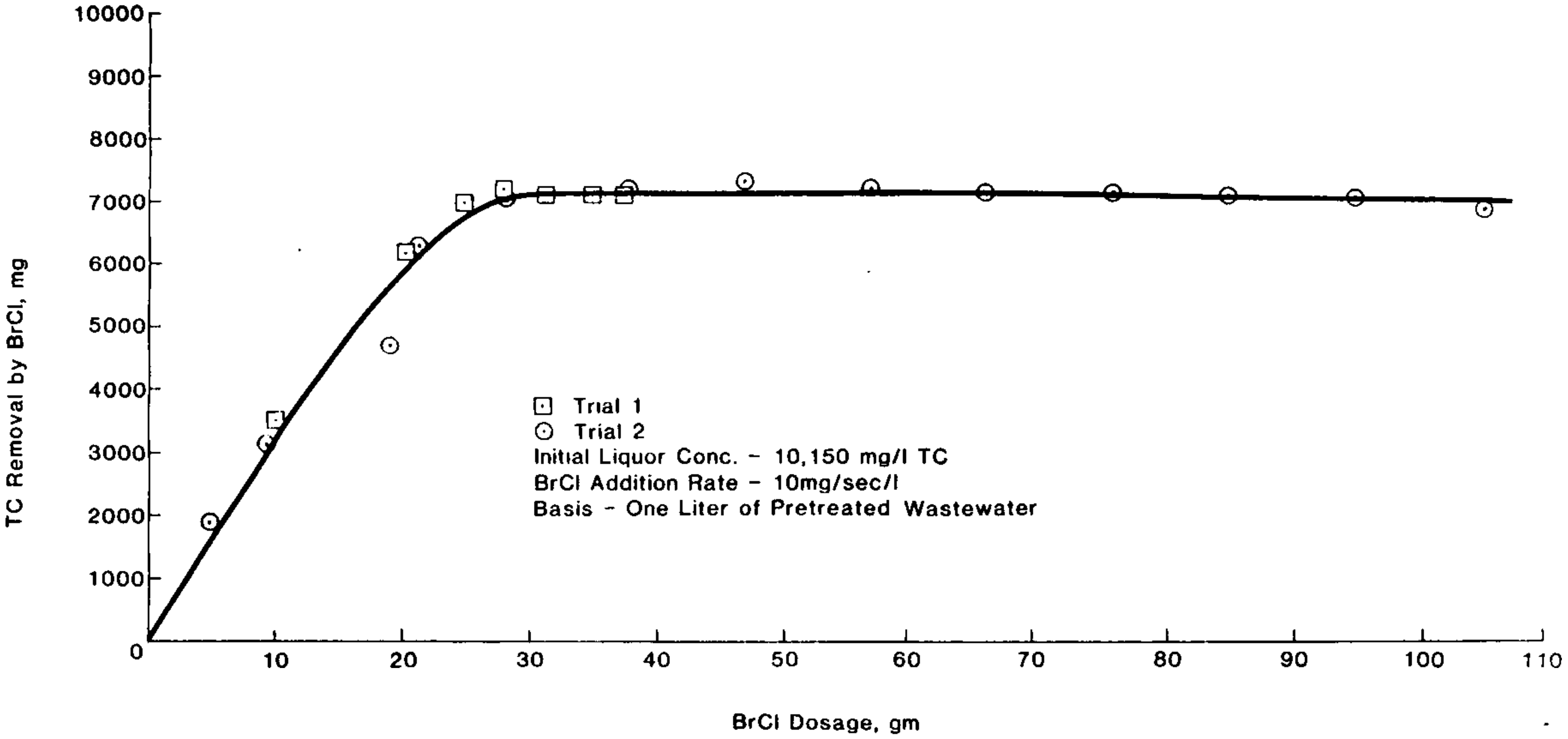


Figure 5. Dependence of TC Removal on BrCl Dosage (BrCl vapor).

TABLE 6

THEORETICAL BROMINE CHLORIDE TO ORGANIC CARBON RATIOS FOR BROMINATION

Phenolic Bromination Product	Stoichiometry			
	$\frac{\text{moles BrCl}}{\text{moles phenolic}}$	Phenol[1] $\frac{\text{mg BrCl}}{\text{mg TC}}$	Cresols[2] $\frac{\text{mg BrCl}}{\text{mg TC}}$	Wastewater[3] $\frac{\text{mg BrCl}}{\text{mg TC}}$
monobromo	1	1.6	1.4	1.5
dibromo	2	3.2	2.7	3.0
tribromo	3	4.8	4.1	4.6

[1] 72 grams (6 g moles) of carbon per g mole of phenol.

[2] 84 grams (7 g moles) of carbon per g mole of cresol.

[3] This sample of pretreated wastewater had a phenol to cresol ratio of 1.9.

TABLE 7

SOLUBILITIES OF PHENOL AND ITS BROMINATION PRODUCTS

Compound	Molecular Weight	Solubility (24)	
		$\frac{\text{gram}}{\text{100 gm } H_2O}$	mg/l TC
Phenol	94.11	8.2	62,700
p-bromophenol	173.02	1.4	5,800
2,4-dibromophenol	251.91	0.21	600
2,4,6-tribromophenol	330.83	0.01	20
pentabromophenol	448.63	insoluble	0

The ratio of BrCl added to TC removed would be useful as an aid to understanding the reactions taking place between the BrCl and organic compounds in the wastewater. For the purpose of this discussion, this ratio will be called the oxidant effectiveness, and is defined as the mg of bromine chloride added divided by the mg of TC removed. This ratio was determined from three vapor-liquor semi-batch trials below 28 gm/l BrCl dosage (Tables 20-22). For the three trials and a total of 17 separate data points, the 95% confidence interval for the ratio is 3.6 ± 0.4 mg/mg.

If it is assumed that all of the bromination products formed were removed from solution and the experimental oxidant effectiveness of 3.6 mg/mg is compared to the last column of Table 6, the reactions taking place in the wastewater could be considered to be forming the di- or tribromophenolic products. The solubilities of these bromination products indicate that this assumption is valid if the conversion to higher-order bromophenolics is complete.

BrCl Treatment Products

Further evidence of the formation of the halogenated phenolic products is found when the organics in the wastewater are analyzed by nuclear magnetic resonance (NMR) spectroscopy. The phenolics from three treated liquor samples and the pretreated wastewater were extracted and analyzed. For comparison, a phenol and a cresol solution were also treated with bromine chloride and the products extracted and analyzed. The results of the analysis appear in Table 8.

TABLE 8

RESULTS OF BROMINE CHLORIDE TREATED WASTEWATER NMR ANALYSIS

Sample*	BrCl dosage mg/l	NMR peaks
1) Phenol Solution:		
methylene chloride extract	14,940	mainly p-bromophenol some phenol some 2,4,6-tribomophenol
precipitate	14,940	2,4,6-tribromphenol
2) Cresol Solution:		
methylene chloride extract	14,990	cresols at least 2 products (unidentified)
precipitate	14,990	cresols one product (unidentified)
3) Pretreated Wastewater:		
methylene chloride extract	0	phenol, cresols
methylene chloride extract	3,830	mainly phenol, cresols some 2,4,6-tribromophenol
methylene chloride extract	15,310	mainly 2,4,6-tribromophenol some phenol, cresols
methylene chloride extract	28,710	mainly p-bromophenol some 2,4,6-tribromophenol some phenol, cresols

*Description of original samples given in Table 23.

The extract from the treated phenol solution indicated that the compounds present were chiefly p-bromophenol with some phenol and 2,4,6-tribromphenol. The precipitate formed upon treating the phenol solution with bromine chloride was essentially all 2,4,6-tribromophenol. The extract from the treated cresol solution showed the starting cresol material and at least two unidentified products. The precipitate formed during the treatment also contained some cresol and one of the unidentified products found in the extract. All treated wastewater extracts contained the phenol and cresol starting material and 2,4,6-tribromophenol. One of the three contained mainly p-bromophenol.

The presence of the starting material and two different bromination products together in the same sample indicates that the bromine chloride does not first react with all of the phenol to form p-bromophenol and then *all* of the p-bromophenol to form 2,4-dibromophenol, but rather that the bromination process is less selective and reacts with the organics on more of a random basis under the conditions used in these experiments.

Total carbon, phenol, and cresol concentrations for the pretreated and three BrCl treated wastewater samples are listed in Table 5. After 25 gm/l BrCl has been added, 93% of the phenol and 96% of the cresol have reacted. After 54 gm/l BrCl has been added, 94% of the phenol and essentially all of the cresol are gone.

Phenols constitute 47% of the TC in the pretreated liquor, indicating the presence of unidentified organics which may have a different reactivity with BrCl than phenol. With phenol the aromatic ring is activated for attack by BrCl due to the attached -OH group (25). If the unidentified organics were aromatics, they may contain weaker activating or even deactivating substituent groups which would render the compound less reactive than phenol toward BrCl. Any aliphatic compounds present would also be less reactive toward electrophilic substitution than phenols.

The quantity of unidentified organics can be estimated from the TC level (Appendix D). Assuming that phenol will be converted to 2,4,6-tribromophenol and that cresols will be dibrominated, the ratio of BrCl added to the amount of unidentified organic reacted may be calculated. At the 25 gm/l BrCl level, this ratio is 3.2 moles BrCl added per mole of unidentified organic removed. This ratio suggests a tri-substitution reaction with the unidentified organic compounds. From 25 to 54 gm/l BrCl, the ratio is 34, suggesting that BrCl is oxidizing the organics almost completedly (i.e. - to CO_2). An example of this would be the oxidation of toluene:

$$C_6H_5CH_3 + 14\ H_2O + 36\ BrCl \rightarrow 7\ CO_2 + 18\ Br_2 + 36\ HCl$$

Comparison of Addition Methods

A comparison of the three different methods of bromine chloride addition is given in Figure 6. Aqueous bromine chloride removes a maximum of 53% of the TC in the pretreated wastewater, liquid removes 64%, and bromine chloride vapor removes a maximum of 72%. Bromine chloride vapor addition appears to be the optimum treatment addition method.

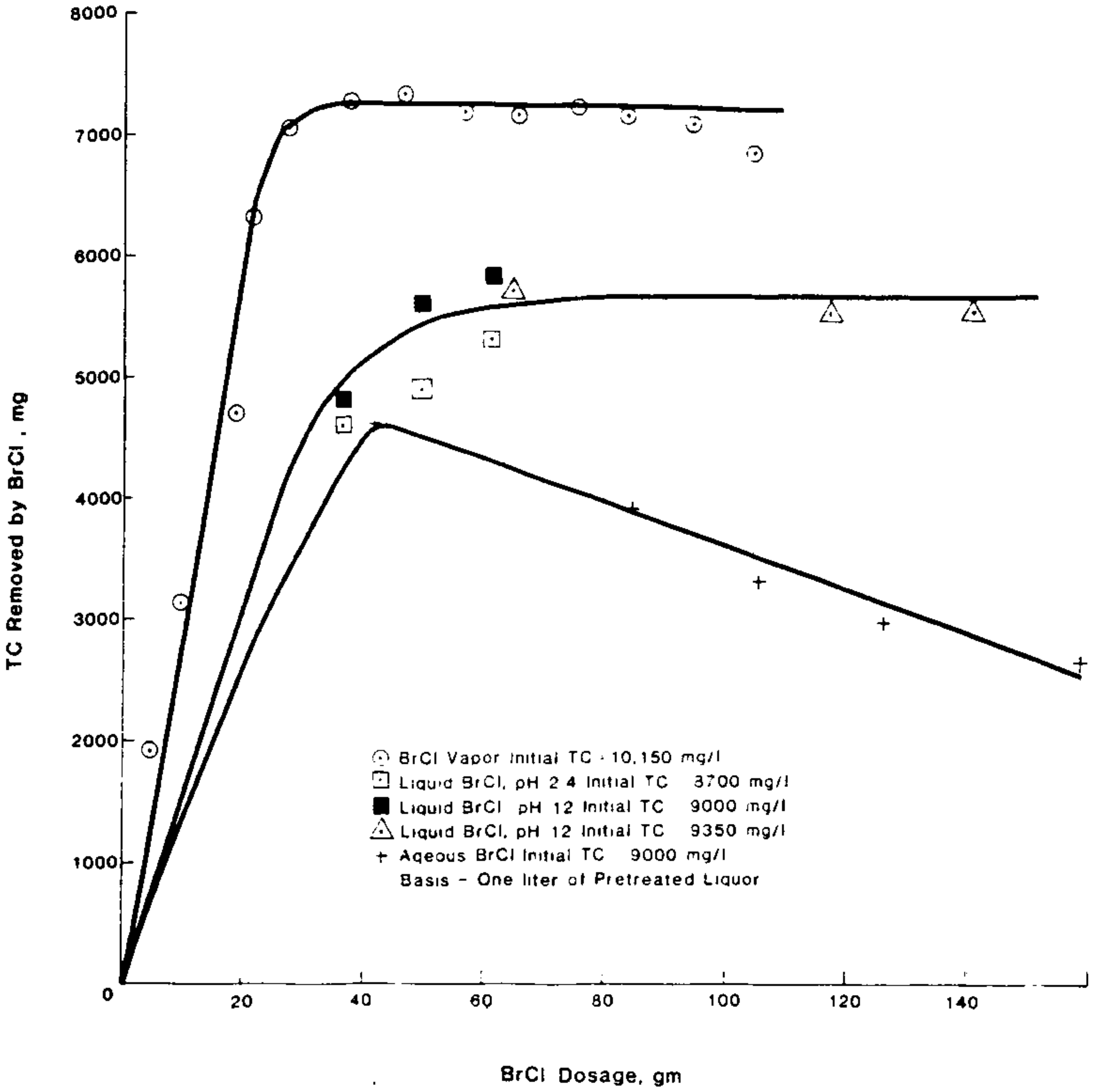


Figure 6. Comparison of BrCl Additions Methods on TC Removal.

The increase in TC removal using BrCl vapor addition rather than liquid BrCl is not clearly understood, but is believed to be primarily due to differences between the BrCl vapor-wastewater and the liquid BrCl-wastewater reactions.

Liquor Analysis

The effects of bromine chloride on wastewater are shown in Table 5. Increasing the halogen dosage lowers the alkalinity, sulfide, total carbon, and phenolic concentrations. Increasing the dosage raises the total dissolved solids in the wastewater, possibly due to the formation of inorganic salts. For example, the ammonia and HCl present could react to form ammonium chloride. This problem could be eliminated by complete removal of NH_3 in the stripping column. Neutralizing the BrCl-treated liquor with lime would leave calcium chloride which could be removed by electrodialysis, reverse osmosis or ion exchange.

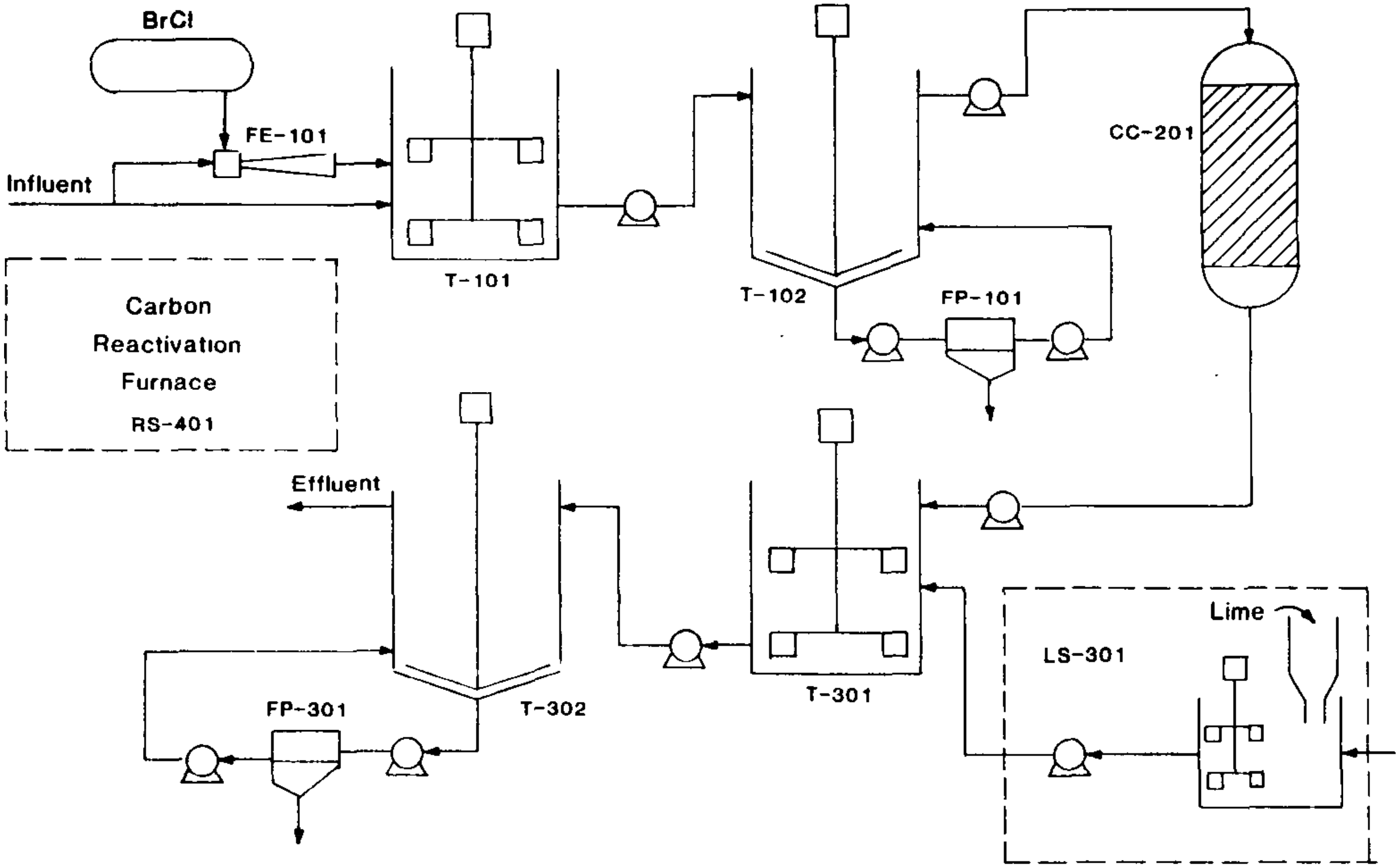
PLANT DESIGN

Process Description

A process flow diagram for treating aqueous gasifier effluent is presented in Figure 7. The facility was designed to treat 295 m^3/hr of aqueous effluents from a gasification plant producing 7.08 million standard cubic meters (250 mscf) of methane daily.

Initially, the wastewater is lime treated and ammonia stripped (9). The wastewater from pretreatment contains approximately 10,000 mg/l TC and 240 mg/l ammonia and is pumped into the BrCl-wastewater mixing tank T-101. A side stream of wastewater carries 7375 kg/hr of bromine chloride from the liquid BrCl feeder, FE-101, into the bulk of the wastewater. After 0.7 hours of contact the treated wastewater is pumped to T-102, a settling tank with a 0.5 hour holding time. Approximately 6790 kg/hr of oxidation sludge is removed and dewatered in filter press FP-101.

The bromine chloride treated wastewater now contains 3000 mg/l TC and is pumped to CC-210, a moving bed activated carbon contacting column. Spent carbon is reactivated in furnace RS-401 at a rate of 4100 kg/day. From the carbon contactor, the wastewater is pH-adjusted from 2.3 to 7.5 with 61 kg/hr of hydrated lime. The lime is slurried in a slaking unit, LS-301. After 0.25 hours in T-301 the wastewater and lime sludge are separated for 0.5 hours in T-302. Approximately 39 kg/hr of lime sludge is removed and dewatered in filter press FP-301.



Note: Letters refer to equipment descriptions in table 9.

Figure 7. Process Flowsheet for Proposed Gasifier Effluent Treatment Facility Employing Liquid BrCl.

The treated wastewater leaves the lime settling tank and should contain approximately 100 mg/l TC, 200 mg/l NH_3, 2500 mg/l dissolved solids, and have a pH of 7.5. The dissolved solids would limit the reuse of this water for steam production in boilers operating at less than 4.1 MPa (600 psi) (26). Phenols and polynuclear aromatics may be present as part of the 100 mg/l TC. These compounds are included in the Toxic Pollutant List (P.L. 92-500), so the treated wastewater may not be pure enough for discharge (27).

The equipment list for the proposed facility is presented in Table 9. Descriptions are given for all equipment larger than the pumps.

Cost Estimation

An initial cost estimate was made based on the cost of the bromine chloride usage only. The current cost for BrCl in bulk is 0.24 to 0.26 dollars per pound (28). At a dosage of 25 kg/m^3 and a wastewater production rate of 295 m^3/hr, the cost for the bromine chloride alone is:

$$(25\ \text{kg/m}^3)(2.20\ \text{lb/kg})(\$0.26/\text{lb}) = \$14.30\ \text{per m}^3$$

This is equivalent to $54.20 per 1000 gallons of wastewater treated. Previous estimates by Mann (29) and Hird (9) place the cost of treatment for solvent extraction and carbon adsorption at $12.89 and $13.12 per 1000 gallons, respectively. Their estimates are based on December 1980 dollars and include capital investment and operating costs.

TABLE 9

PROPOSED PLANT EQUIPMENT LIST

Item Number	No. Req'd.	Description
CC-201	1	Carbon Contacting Column, H = 7 m, D = 6.1 m, carbon steel, packed with 207 m^3 LCK activated carbon, 5% pulsed moving bed
FE-101	4	Liquid BrCl Feeder, 44,250 kg/day
FP-101	1	Filter Press, 10.5 m^2, PVC coated iron
FP-301	1	Filter Press, 7.9 m^2, aluminum
LS-301	1	Lime Slaker, 61 kg/hr lime, 7080 m^3/day water treated
RS-401	1	Reactivation System, 4540 kg/day activated carbon
T-101	4	BrCl-Liquor Mixing Tank, H = 5.7 m, D = 3.8 m, SS 304 clad steel
T-102	1	Oxidation Settling Tank, H = D = 6.2 m, carbon steel
T-301	1	Lime Addition Tank, 92 m^3, carbon steel
T-302	1	Lime Settling Tank, H = D = 6.2 m, carbon steel

Because the cost of BrCl alone is several times more than the total cost of other treatment facilities, no attempt was made to assign costs to the investment, or operation of the treatment facility. The installed cost of the equipment listed in Table 9 is estimated to be $3,120,000.

CONCLUSIONS

Slagging gasifier wastewater does not appear to be economically treatable using bromine chloride as the principal treatment step with the procedure investigated. Of the methods of addition tested, bromine chloride vapor gave the best TC removal.

Based upon test results and observations, other conclusions of this investigation are:

1. The presence of ammonia in aqueous solutions of phenol did not affect the percentage removal of organics by bromine chloride.
2. In the semi-batch reactor used, the amount of total carbon removed was directly proportional to the amount of bromine chloride added until approximately 25 kg/m^3 of the reagent was added.
3. At BrCl dosages below 25 kg/m^3, the organic compounds are di- and tribrominated. Phenols were almost totally removed while other organics were only partially removed.
4. At the 25 kg/m^3 bromine chloride dosage, a seventy percent removal of total carbon was seen for the wastewater, with no further removal at higher bromine chloride dosages.
5. At this bromine chloride dosage level, the current cost of the reagent alone is $54.20 per 1000 gallons of wastewater treated.

RECOMMENDATIONS

Because of unfavorable economics, BrCl is only recommended as a polishing treatment step for relatively dilute phenolic wastewaters. Many aspects of the bromine chloride reaction with aqueous gasifier effluent have not been investigated in this study. Recommendations for further study on dilute phenolic wastewaters are:

1. Because continuous treatment systems are prefered over batch systems, the effects of BrCl on TC removal using continuous flow reactors should be investigated (i.e., continuous stirred reactors and bubble columns).
2. To better understand the mechanisms involved:
   a) More samples should be taken as the reaction proceeds.
   b) Better characterization of all major starting and product compounds in the samples should be performed.

APPENDICES

APPENDIX A

THE GRAND FORKS SLAGGING FIXED-BED GASIFIER

THE GRAND FORKS SLAGGING FIXED-BED GASIFIER

The slagging fixed-bed gasifier located at GFETC is the only gasifier of its type in operation in the United States. The original purpose of the pilot plant was to develop data to support commercial and demonstration applications of fixed-bed gasification (6). The pilot plant gasifier is a modification of a commercial dry ash fixed-bed process in which the use of excess steam keeps the temperature low enough so that the ash can be removed as a solid. In the slagging gasifier only the steam required for gasification is added so the temperature above the hearth is higher than the dry ash gasifier and the ash can be removed as a molten slag. There are two distinct advantages to using the slagging technology. Compared with dry ash units of similar hearth area, the slagging gasifier uses only one-fourth of the steam and produces 3 or 4 times as much gas. A flowsheet of the pilot plant gasifier is shown in Figure 8.

During the operation of the gasifier, the coal is introduced at the top through one of two coal locks and descends countercurrently to the hot product gases. The descending coal is dried, devolatilized, and heated before reaching the combustion/gasification zone at the bottom of the gasifier. The reaction is maintained by the introduction of a steam-oxygen mixture just above the hearth. The molten ash formed then drains into a water quench bath where it is periodically discharged. The GFETC gasifier operates at pressures of up to 2.9 MPa and a gasification zone temperature of 2000 K.

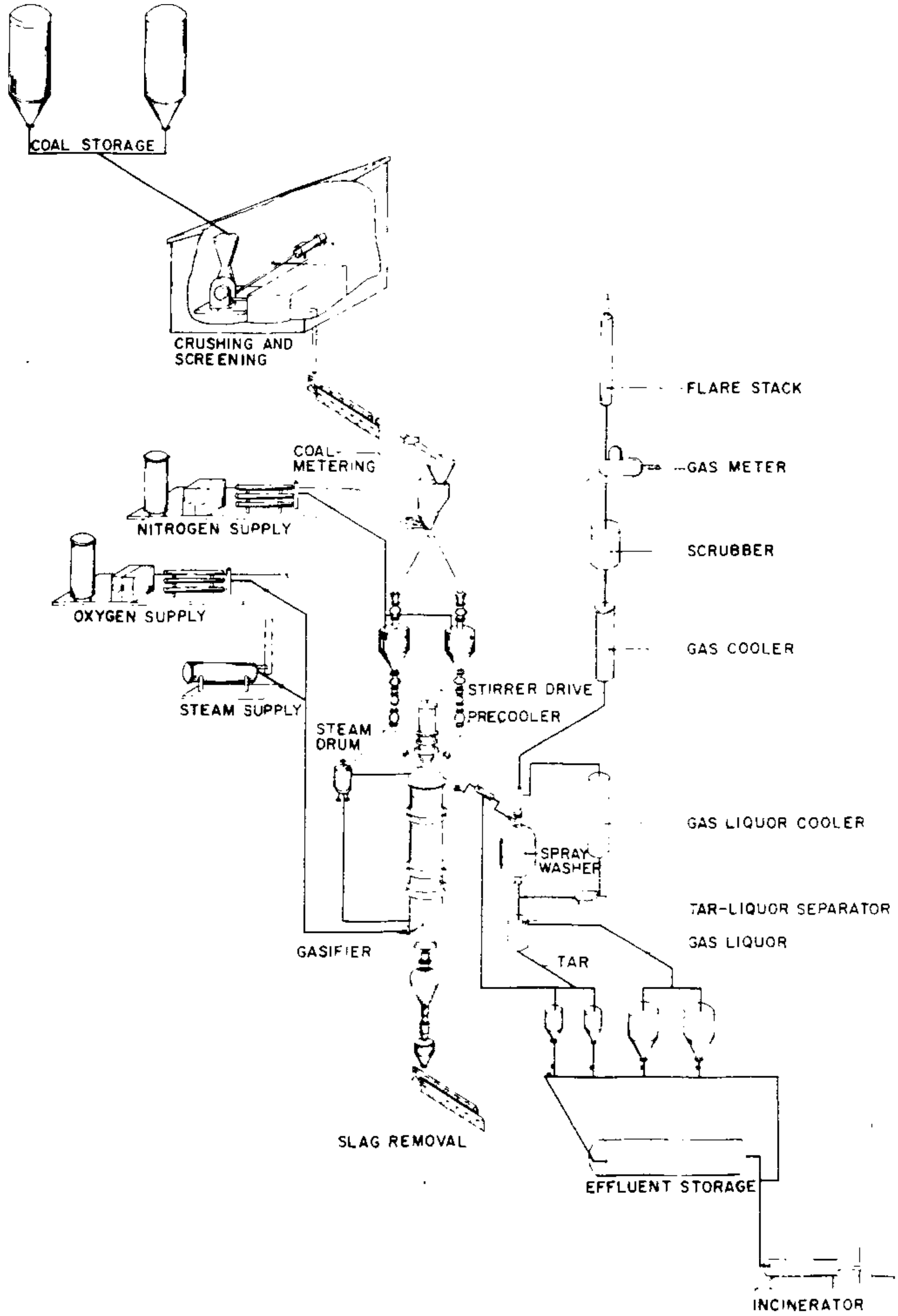


Figure 8. Process Flow Sheet of Modified Gasifier System

As the hot product gas rises through the bed it heats and dries the coal before leaving the top of the gasifier. The raw product gas then enters a spray washer where recycled condensate liquor cools the gas and removes water, tars, oils, and entrained dust. The gas then passes through an indirect gas cooler and a scrubber, and is metered before being flared. A portion of the gas liquor condensate is cooled and recycled to the spray washer and the rest is drained into an atmospheric tar-liquor separator. The tars are incinerated but the liquor cannot be discharged into the environment without treatment to remove the impurities.

APPENDIX B

PHYSICAL PROPERTIES OF BROMINE CHLORIDE

TABLE 10

BROMINE CHLORIDE PROPERTIES

Property	Value (11)
Molecular Weight	115.37
Freezing Point	-66° C
Normal Boiling Point	- 5° C
Vapor Density at 0° C and 1 atm	5.153 g/l
Density, -20° C	2.46 g/ml
-10° C	2.43 "
0° C	2.40 "
Latent Heat of Vaporization at 25° C	50.0 cal/gm
Solubility in Water, 5° C	3.3 gm/100 gm
10° C	5.5 "
15° C	8.9 "
20° C	8.5 "
Dry BrCl Corrosion Rates (30 day trials)	
Carbon Steel	23.62×10^{-6} m/yr
SS 304	1.88×10^{-6} "
SS 316	2.79×10^{-6} "
SS Type 20CB	1.83×10^{-6} "
Nickel 200	3.30×10^{-6} "
INCONEL 600	17.27×10^{-6} "

APPENDIX C

SUMMARY OF EXPERIMENTAL DATA

TABLE 11

GILMONT FLOWMETER CALIBRATION DATA

Volume of Water, ml	Gilmont BrCl Rate, mg/sec	Addition Time, sec	Calculated BrCl Concentration, gm/l	Sample Volume, ml	Titrant Volume, ml	Experimental BrCl Concentration, gm/l
419.62	1.30	350	1.08	3.0	20.51	3.94
				3.0	20.41	3.92
				3.0	21.26	4.09
						3.99
376.35	1.31	275	0.95	2.0	12.25	3.53
				2.0	12.61	3.64
				2.0	13.03	3.76
				2.0	13.23	3.82
						3.67

TABLE 12

DATA FROM BATCH OXIDATION TESTS WITH AQUEOUS BROMINE CHLORIDE, PHENOL, AND AMMONIA FOR LATIN SQUARE DESIGN

Phenol Solution:	51.3 mg/ml
Ammonia Solution:	175.0 mg/ml
Bromine Chloride Solution:	85.0 mg/ml

Phenol, ml	Ammonia, ml	Bromine Chloride, ml	Initial Volume, ml	BrCl/Phenol, mg/mg	Initial TC, mg/l	Final TC, mg/l	% TC Removed
0.5	0	0.5	25.5	1.66	770	730	5.17
0.5	3	1.5	26.5	4.97	741	735	0.78
0.5	1	2.5	27.5	8.28	714	718	-0.59
0.5	2	3.0	28.0	9.94	701	725	-3.41
2.0	2	2.5	27.5	2.07	2855	2750	3.69
2.0	1	6.0	31.0	4.97	2533	1350	46.70
2.0	3	9.5	34.5	7.87	2276	1350	40.68
2.0	0	13.0	38.0	10.77	2066	190	90.81
4.0	1	4.5	29.5	1.86	5323	5000	6.08
4.0	2	12.0	37.0	4.97	4244	3400	19.89
4.0	0	19.0	44.0	7.87	3569	110	96.92
4.0	3	26.0	51.0	10.77	3079	231	92.50
6.0	3	7.0	32.0	1.93	7361	7400	-0.52
6.0	0	17.5	42.5	4.83	5543	834	84.95
6.0	2	28.0	53.0	7.73	4445	120	97.30
6.0	1	39.0	64.0	10.77	3681	231	93.72

TABLE 13

BROMINE CHLORIDE BATCH OXIDATION TESTS WITH PRETREATED GASIFIER LIQUOR (TRIAL 1)

Pretreated Wastewater: 0.2 liters, 8700 mg/l TC
Bromine Chloride Addition: 8.5 wt. % aqueous solution

BrCl Dosage, liters	Total Volume, liters	Initial TC, mg/l	Final TC, mg/l	BrCl Dosage, mg*	TC Removed, mg*	Final BrCl, mg/l
0.10	0.30	5800	2700	42,500	4650	0
0.15[1]	0.35	4970	3700	64,000	2225	175
0.20	0.40	4350	2400	85,000	3900	311
0.25	0.45	3870	2400	106,500	3310	319
0.30	0.50	3480	2300	127,500	2950	434
0.35	0.55	3160	2200	149,000	2650	730

*Basis is one liter of pretreated liquor.

[1] Because of the high final TC value, this point is not plotted.

TABLE 14

BROMINE CHLORIDE BATCH OXIDATION TESTS WITH PRETREATED GASIFIER LIQUOR (TRIAL 2)

Pretreated Liquor:	0.2 liters
Bromine Chloride Addition:	Liquid
Reaction Time:	1 hour

	BrCl					
Initial pH	Dosage, ml	Temp., °C	Dosage, mg*	Initial TC, mg/l	Final TC, mg/l	TC Removed, mg*
2.4	3.0	-43	37,500	8700	4200	4500
2.4	4.0	-43	50,000	8700	3900	4800
2.4	5.0	-43	62,500	8700	3400	5300
12.0	3.0	-43	37,500	9000	4300	4700
12.0	4.0	-43	50,000	9000	3400	5600
12.0	5.0	-43	62,500	9000	3200	5800
12.0	5.3	-19	65,000	9350	3650	5700
12.0	9.6	-22	118,000	9350	3850	5500
12.0	11.6	-19	142,000	9350	3850	5500
12.0	12.0	-31	149,000	9350	3650	5700

* Basis is one liter of pretreated liquor.

TABLE 15

BROMINE CHLORIDE BATCH OXIDATION TESTS WITH PRETREATED GASIFIER LIQUOR (TRIAL 3)

Pretreated Lqiuor:	0.2 liters, 9250 mg/l TC
Bromine Chloride Addition:	3 ml of liquid, -43°C, 7470 mg (37,350 mg/l)

Time, min.	Final BrCl, mg/l	Final TC, mg/l	TC Removed, mg*
15	118	6000	3250
30	na	5625	3625
38	136	na	na
46	120	na	na
61	99	5625	3625
122	71	5750	3500
182	na	5000	4250
240	na	4875	4375

* Basis is one liter of pretreated liquor

na = not analyzed

TABLE 16

BROMINE CHLORIDE BATCH OXIDATION TESTS WITH PRETREATED GASIFIER LIQUOR (TRIAL 4)

Pretreated Liquor:	0.2 liters, 9000 mg/l TC
Bromine Chloride Addition:	Vapor, 75°C

BrCl Rate, ml/min air	Contact Time, min	BrCl Dosage, mg*	Final TC, mg/l	TC Removed mg*
100	1	3830	8000	1000
150	1	5740	7130	1870
200	1	7660	7120	1880
250	1	9570	6630	2370
400	1	15,310	6650	2350
500	1	19,140	6000	3000
1000	1	38,280	4130	4870
300	1.5	17,230	6630	2370
400	1.5	22,970	6130	2870
500	1.5	28,710	4150	4850
200	3	22,970	5130	3870

* Basis is one liter of pretreated wastewater.

TABLE 17

BROMINE CHLORIDE SEMI-BATCH OXIDATION TEST WITH PRETREATED GASIFIER LIQUOR (TRIAL 5)

Pretreated Liquor:	0.1 liter, 9000 mg/l TC
Bromine Chloride Addition:	Vapor, 90°C, 20 ml/min air 24 mg/l sec BrCl

Time, sec	BrCl Dosage, mg*	Final BrCl, mg/l	Final TC, mg/l	TC Removed, mg*
40	980	na	7000	2000
145	3550	na	7125	1875
220	5390	18	na	na
280	6860	na	6125	2875
350	8580	8	na	na
415	10,170	na	6250	2750
510	12,500	8	na	na
610	14,950	na	5625	3375
690	16,910	11	na	na

* Basis is one liter of pretreated wastewater.

na = not analyzed

TABLE 18

BROMINE CHLORIDE SEMI-BATCH OXIDATION TEST WITH PRETREATED GASIFIER LIQUOR (TRIAL 6)

Pretreated Liquor:	0.2 liters, 9000 mg/l TC
Bromine Chloride Addition:	Vapor, 80°C, 45 ml/min air 28 mg/l/sec BrCl

Time, sec	BrCl Dosage, mg*	Final TC, mg/l	TC Removed, mg*
100	2830	8380	620
220	6225	8380	620
300	8490	8000	1000
400	11,320	7500	1500
500	14,150	7000	2000
610	17,265	6500	2500

* Basis is one liter of pretreated wastewater.

TABLE 19

BROMINE CHLORIDE SEMI-BATCH OXIDATION TEST WITH PRETREATED GASIFIER LIQUOR (TRIAL 7)

Pretreated Liquor:	0.2 liters, 9000 mg/l TC
Bromine Chlordie Addition:	Vapor, 80°C, 45 ml/min air 28 mg/l/sec BrCl

Time, sec	BrCl Dosage, mg*	Final TC, mg/l	TC Removed, mg*
105	2970	8500	500
300	8490	7630	1370
600	16,980	6000	3000
900	25,470	4000	5000

* Basis is one liter of pretreated wastewater.

TABLE 20

BROMINE CHLORIDE SEMI-BATCH OXIDATION TEST WITH PRETREATED GASIFIER LIQUOR (TRIAL 8)

Pretreated Liquor:	0.5 liters, 10,150 mg/l TC
Bromine Chloride Addition:	Vapor, 95°C, 40 ml/min air 9.8 mg/l/sec BrCl

Time, sec	BrCl Dosage, mg*	Final TC, mg/l	TC Removed, mg*
400	3860	8500	1650
810	7820	7390	2760
1200	11,580	6870	3280
1600	15,440	6440	3710
2010	19,400	5760	4390
2410	23,260	4780	5370
2710	26,160	4210	5940
3000	28,960	3550	6600
3305	31,900	3500	6650
3600	34,750	3770	6380
3900	37,640	3680	6470
4200	40,540	4080	6070
4500	43,430	3880	6270
4800	46,330	3900	6250
4865	46,960	4330	5820
5100	49,230	3200	6950
5400	52,120	3150	7000
5580	53,860	2830	7320

* Basis is one liter of pretreated wastewater.

TABLE 21

BROMINE CHLORIDE SEMI-BATCH OXIDATION TEST WITH PRETREATED GASIFIER LIQUOR (TRIAL 9)

Pretreated Liquor:	0.48 liters, 10,150 mg/l TC
Bromine Chloride Addition:	Vapor, 80°C, 40 ml/min air 10.5 mg/l/sec BrCl

Time, sec	BrCl Dosage, mg*	Final TC, mg/l	TC Removed, mg*
1000	10,480	6630	3520
2000	20,960	3920	6230
2410	25,260	3150	7000
2750	28,830	2970	7180
3010	31,550	3050	7100
3340	35,010	3050	7100
3605	37,790	3050	7100

* Basis is one liter of pretreated liquor.

TABLE 22

BROMINE CHLORIDE SEMI-BATCH OXIDATION TEST WITH PRETREATED GASIFIER LIQUOR (TRIAL 10)

Pretreated Liquor:	0.5 liters, 10,150 mg/l TC
Bromine Chloride Addition:	Vapor, 100°C, 40 ml/min air 9.5 mg/l/sec BrCl

Time, sec	BrCl Dosage, mg*	Final TC, mg/l	TC Removed, mg*
520	4950	8230	1920
1000	9520	7000	3150
2020	19,240	5420	4730
2500	23,810	3810	6340
3000	28,570	3130	7020
4000	38,090	2880	7270
5000	47,610	2810	7340
6000	57,140	2940	7210
7000	66,660	3000	7150
8000	76,180	2940	7210
8900	84,750	3000	7150
10,000	95,230	3060	7090
11,030	105,040	3310	6840

* Basis is one liter of pretreated wastewater.

TABLE 23

DESCRIPTION OF BROMINE CHLORIDE TREATED SAMPLES EXTRACTED WITH METHYLENE CHLORIDE FOR ANALYSIS WITH NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Starting Material	Concentration, mg/l	BrCl Dosage, mg/l	Final TC, mg/l
Aqueous Phenol	4000 mg/l Phenol	14,940	na
Aqueous Cresol	2000 mg/l Cresol	14,990	na
Pretreated Wastewater	9000 mg/l TC	0	na
Pretreated Wastewater	9000 mg/l TC	3830	8000[a]
Pretreated Wastewater	9000 mg/l TC	15,310	6650[b]
Pretreated Wastewater	9000 mg/l TC	28,710	4150[c]

na = not analyzed.

[a] From Table 16, line 1.
[b] From Table 16, line 5.
[c] From Table 16, line 10.

TABLE 24

ORIGIN OF SAMPLES OF ANALYSIS APPEARING IN TABLE 5

Pretreated Liquor: 0.5 liters
Bromine Chloride Addition: Vapor, 90°C

Initial TC, mg/l	BrCl Rate, mg/l/sec	Addition Time, sec	BrCl Dosage, mg/l
9000	9.9	2520	24,860
10,150	9.7	5580	54,010
9000	61.2	1210	74,000

APPENDIX D

SAMPLE CALCULATIONS FOR COMPUTING RATE OF WASTEWATER PRODUCTION, LATIN SQUARE ANALYSIS OF VARIANCE, GILMONT FLOWMETER CALIBRATION, IODOMETRIC TITRATIONS, BrCl TO TC RATIO, AND EQUIPMENT SIZES AND PRICES

RATE OF WASTEWATER PRODUCTION

Sample calculations for computing rate of wastewater production for generation of 7.08 million standard cubic meters per day (250 million ft^3/day) synthetic natural gas.

Basis - 1 kg maf lignite gasified

For run RA-94, 0.455 kg of wastewater and 1.67 standard m^3 of gas were produced per kg of maf coal. With the gas composition given below, the amount of each type of gas produced may be calculated by multiplying the volume fraction times the total volume of gas produced.

After gasification the H_2/CO ratio is increased by means of the shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

A stripping step then removes the H_2S and approximately 95% of the CO_2 present. Approximately 75% of the CO_2 remaining is then reacted in a shift converter (9):

$$CO_2 + H_2 \rightarrow CO + H_2O$$

The remaining product gas should now have a H_2/CO ratio of 3/1 and is sent to the methanator for conversion into methane:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

An examination of these steps will show that for this 3/1 ratio to be achieved, 0.639 m^3 of CO must be converted into hydrogen in the hydrogen producing second step. The above steps and their products (on a 1 kg maf coal basis) are listed below:

Step	Product gas content per kg of maf lignite	
1) Gasification	0.416 scm H_2	(24.96 mole %)
	0.950 scm CO	(56.97 mole %)
	0.114 scm CH_4	(6.82 mole %)
	0.176 scm CO_2	(10.53 mole %)
2) $CO + H_2O \rightarrow CO_2 + H_2$	1.055 scm H_2	
	0.311 scm CO	
	0.114 scm CH_4	
	0.814 scm CO_2	
3) 95% of CO_2 stripped	1.055 scm H_2	
	0.311 scm CO	
	0.114 scm CH_4	
	0.041 scm CO_2	
4) $CO_2 + H_2 \rightarrow CO + H_2O$	1.024 scm H_2	
	0.342 scm CO	
	0.114 scm CH_4	
	0.010 scm CO_2	
5) $CO + 3H_2 \rightarrow CH_4 + H_2O$	0.455 scm CH_4	
	0.010 scm CO_2	

Converting to daily rates,

$$\text{Kgs maf coal gasified per day} = \frac{7.08 \times 10^6 \ \text{m}^3/\text{day}}{0.455 \ \text{m}^3/\text{kg maf coal}}$$

$$= 1.56 \times 10^7 \ \text{kg maf/day}$$

$$\text{cubic meters of wastewater produced per day} = (1.56 \times 10^7)\left(0.455 \ \frac{\text{kg } H_2O}{\text{kg}}\right)$$

$$= 7084 \ \text{m}^3/\text{day}$$

Converting to an hourly rate,

$$(7084 \ \text{m}^3/\text{day})\ (\text{day}/24 \ \text{hr}) = 295 \ \text{m}^3/\text{hr wastewater}$$

LATIN SQUARE ANALYSIS OF VARIANCE

Sample calculations for the Latin square test analysis of variance (30). The actual design used is presented in Table 2, the results are presented in Tables 4 and 12.

Actual Latin square positions and results:

Values in parenthesis are the percent reductions in TC.

Rows are mg of phenol added.

Columns are the BrCl to phenol ratio, mg/mg.

Treatments are the mg of ammonia added.

	2	5	8	11
26	0 (5.17)	525 (0.78)	175 (-0.59)	350 (-3.41)
103	350 (3.69)	175 (46.70)	525 (40.68)	0 (90.81)
205	175 (6.08)	350 (19.89)	0 (96.92)	525 (92.50)
308	525 (-0.52)	0 (84.95)	350 (97.30)	175 (93.72)

The sums of squares (SS) for the mean, rows, columns, treatments, and error are calculated:

$$SS_M = (\sum_{ij}\sum Y_{ij(k)})^2/m^2 \qquad \text{mean}$$

$SS_R = \sum_i R_i^2/m - SS_m$ phenol levels

$SS_C = \sum_i C_j^2/m - SS_m$ BrCl/phenol ratios

$SS_{Tr} = \sum_k T_k^2/m - SS_m$ NH_3 levels

$SS_T = \Sigma\Sigma\Sigma Y^2_{ijk}$ total

$SS_E = SS_T - SS_M - SS_R - SS_C - SS_{Tr}$ error

Where:

Y = individual value

$i=j-k=m$ = number of rows, columns, or treatments

R = ΣY in ith Rows

C = ΣY in jth column

T = ΣY in kth treatment

The mean square (MS) is calculated as the SS divided by the degrees of Freedom (df):

Variation	SS	df	MS	f	Significant?
Mean	28,448.73	1	-	-	-
Phenol	10,388.69	3	3462.90	6.44	yes
BrCl/Phenol	9,845.87	3	3281.96	6.10	yes
Ammonia	4,075.22	3	1358.41	2.53	no
Error	3,226.43	6	537.74	-	-
Total	55,984.94	16	-	-	-

$F_{3,6,0.95} = 4.76$ (effect is significant if f is greater than or equal to the critical F value)

Since the treatment effect is insignificant, we can pool the treatment sum of squares with the error:

Variation	SS	df	MS	f	Significant?
Mean	28,448.73	1	-	-	-
Phenol	10,388.69	3	3462.90	4.27	yes
BrCl/Phenol	9,845.87	3	3281.96	4.05	yes
Error	7,301.65	9	811.29	-	-
Total	55,984.94	16	-	-	-

$F_{3,9,0.95} = 3.86$

Sample calculations to determine which levels cause significant difference. Initial observation indicated that the only large differences occur between phenol level one and the other three phenol levels and between BrCl level one and the other BrCl levels.

Phenol Level	Average % Red.	BrCl Level	Average % Red.
1	0.49	1	3.61
2	45.47	2	38.08
3	53.85	3	58.58
4	68.86	4	68.41

Duncan's multiple range test was used to compare the means (31). There is a significant difference between two means if $\bar{X}_a - \bar{X}_b > R_p$.

$R_p = r_p S\bar{x}$

$S\bar{x} = (MSE/4)^{0.5} = (811.29/4)^{0.5} = 14.24$

$v = 12$

P	2	3	4
r_p	3.08	3.23	3.33
R_p	43.86	46.00	47.42

	Phenol levels	BrCl levels
$\bar{X}_4 - \bar{X}_3$	15.01	9.83
$\bar{X}_4 - \bar{X}_2$	23.29	30.33
$\bar{X}_4 - \bar{X}_1$	68.37	64.80
$\bar{X}_3 - \bar{X}_2$	8.38	20.50
$\bar{X}_3 - \bar{X}_1$	53.36	54.97
$\bar{X}_2 - \bar{X}_1$	44.98	34.44

Therefore:

For phenol levels, $\bar{X}_4$, $\bar{X}_3$, and $\bar{X}_2 > \bar{X}_1$

For BrCl levels, $\bar{X}_4$, $\bar{X}_3$, and $\bar{X}_2 > \bar{X}_1$

GILMONT FLOWMETER CALIBRATION

Sample calculations for the Gilmont flowmeter calibration:

Trial 1 BrCl Addition:

mass of water	419.62 grams
vaporizer temperature	87.5°C
flowmeter rate	40 ml/min air
time of addition	350 seconds

Applying a density correction factor from the flowmeter instructions:

$$40\ \frac{\text{ml air}}{\text{min}} \times \frac{(1.2928\ \text{gm/l air})^{1/2}}{(5.153\ \text{gm/l BrCl})^{1/2}} = 20.04\ \frac{\text{ml BrCl}}{\text{min}} \qquad (11,\ 32)$$

$$20.04\ \frac{\text{ml BrCl}}{\text{min}} \times \frac{5.153\ \text{gm BrCl}}{1000\ \text{ml}} \times \frac{\text{min}}{60\ \text{sec.}} \times \frac{273.15\text{K}}{360.65\text{K}} \times \frac{1000\ \text{mg}}{\text{gm}} = 1.30\ \frac{\text{mg BrCl}}{\text{sec}}$$

$$1.30\ \frac{\text{mg BrCl}}{\text{sec}} \times \frac{350\ \text{sec}}{0.41962\ \text{liters}} \times \frac{\text{gm}}{1000\ \text{mg}} = 1.08\ \frac{\text{gm BrCl}}{\text{liter}}$$

BrCl concentrations from iodometric titration:

total sample volume	3.0 ml (average of 3 trials)
total titrant	20.73 ml (average of 3 trials)
titrant	0.005 N (0.01 N for chlorine titration)

$$\frac{0.005\ \text{N} \times 62.18\ \text{ml}}{9.0\ \text{ml}} \times \frac{115.37\ \text{gm BrCl}}{\text{mole BrCl}} = 3.\text{[illegible]}\ \frac{\text{mg BrCl}}{\text{[illegible]}}$$

Therefore, the actual BrCl rate is equal to 3.09/1.08 times the rate as determined by the Gilmont flowmeter's scale. The actual BrCl rate is:

$$\text{mg/sec} = (Z)\ \frac{\text{ml air}}{\text{min}} \times \frac{43.41}{(Y)\ K} \qquad [1]$$

For Trial 2 the factor for the above equation was found to be 45.39.

Average:

$$\frac{\text{mg BrCl}}{\text{sec}} = (Z)\ \frac{\text{ml air}}{\text{min}} \times \frac{44.4}{(Y)\ K}$$

This correction was then used to calculate BrCl flow rates.

IODOMETRIC TITRATION

Sample calculations for determining bromine chloride concentration in the Gilmont flowmeter calibration. The calculations are similar to those used in determining residual oxidant concentrations.

In a trial, 3.0 ml of a BrCl unknown was added to a solution of 100.0 ml of 1.9 wt % potassium iodide solution and 5.0 ml glacial acetic acid. The unknown was titrated with 20.51 ml of 0.01 molar sodium thiosulfate. Starch solution is added when the endpoint is near, changing the solution from light yellow to blue. The solution is then titrated until clear.

The bromine chloride initially reacted with water to form hypobromous acid:

$$\mathrm{BrCl + H_2O \rightleftarrows HOBr + HCl}$$

Upon addition to the potassium iodide solution, free iodine was formed:

$$\mathrm{HOBr + 2I^- + 2H^+ \rightleftarrows I_2 + HBr + H_2O}$$

It is this free iodine which was then titrated:

$$\mathrm{I_2 + 2S_2O_3{}^{2-} \rightarrow S_4O_6{}^{2-} + 2I^-}$$

Overall, the stoichiometry is:

$$\mathrm{BrCl + 2H^+ + 2S_2O_3 \rightarrow HBr + HCl + S_4O_6{}^{2-}}$$

For this titration, the titrant is:

$$0.01\ \frac{\text{moles}}{\text{liter}} \times \frac{\text{equivalent}}{2\text{ moles}} = 0.005\ \frac{\text{equivalents}}{\text{liter}} = 0.005\ \mathrm{N}$$

Therefore:

$$\frac{(20.51\text{ ml}) \times (0.005\text{ N}) \times (115.37\text{ gm/mole})}{3\text{ ml}} = 3.94\ \frac{\text{gm BrCl}}{\text{liter}}$$

BrCl TO TC RATIOS

Sample calculations to calculate BrCl to TC ratio. Data points used are from the initial sections of mg TC removed versus mg of bromine chloride added curves for vapor bromine chloride addition.

BrCl Dosage, mg	TC Removed, mg	BrCl/TC, mg/mg	
2,480	960	2.60	(Table 22)
4,760	1,580	3.02	
9,620	2,370	4.06	
11,900	3,170	3.76	
14,280	3,580	4.00	
5,030	1,690	2.98	(Table 21)
10,060	2,990	3.37	
12,130	3,360	3.61	
13,840	3,450	4.02	
1,930	830	2.34	(Table 20)
3,910	1,380	2.83	
5,790	1,640	3.53	
7,720	1,890	4.16	
9,700	2,200	4.42	
11,630	2,690	4.33	
13,080	2,970	4.40	
14,480	3,300	4.39	
		61.88	

$\bar{x} = 3.64$

$n = 17$

$Sx = 0.68$

$t_{0.975,16} = 2.120$

$$x = 3.64 \pm \frac{(0.68) \times (2.120)/(17)^{1/2}}{} = 3.64 \pm 0.35 \ \frac{\text{mg BrCl added}}{\text{mg TC removed}}$$

Sample calculations for determining the moles of BrCl added per moles of unidentified organic reacting:

Assumptions:

1. The inorganic carbon is 4% of the TC in the pretreated wastewater and remains constant.
2. Phenol reacts to form 2,4,6-tribromophenol.
3. Cresol reacts to form dibromocresols which are half as soluble as 2,4-dibromophenol.
4. Bromination products precipitate to their Handbook solubilities.
5. Unidentified organic compounds contain an average of 100 gm TC/ g mole (i.e. - 8.3 carbons per molecule).

Solubility of 2,4,6-tribromophenol:

$$\frac{(0.01)\ (1000)\ (72)\ (1000)}{(100)\ (330.83)} = 22 \text{ mg/l TC}$$

Solubility of dibromocresol:

$$\frac{(0.5)\ (0.21)\ (1000)\ (84)\ (1000)}{(100)\ (265.91)} = 332 \text{ mg/l TC}$$

BrCl dosage, gm/l	0	25	54
TC, mg/l	10,375	4375	3375
IC, mg/l	415	415	415
Phenol TC, mg/l	3186	237	34
Cresol TC, mg/l	1736	62	0
Tribromophenol TC, mg/l	0	22	22
Dibromocresol TC, mg/l	0	332	332
Unidentified TC, mg/l	5038	3307	2572
Additional BrCl, mmoles		217	251
Phenol reacted, mmoles		41	3
BrCl used by phenol, mmoles		123	9
Cresol reacted, mmoles		20	1
BrCl used by cresol, mmoles		40	2

Remaining BrCl, mmoles	54	240
Unidentified organics, mmoles	17	7
BrCl added/unidentified organics, mmole/mmole	3.2	34

EQUIPMENT SIZES AND PRICES

Sample calculations to size and price equipment. The equipment was sized based on wastewater flow rates, BrCl dosage, and contact time. The references used indicated which parameters to be calculated for pricing. All costs were updated to fourth quarter 1981 dollars by means of the Marshall and Swift (M+S) all-industry pricing index. The M+S value for this period is 736.4 (33).

CC-201

To design the carbon contacting column from experimental data for gasifier liquor, the bed-depth/service-time (BDST) equation will be used (34). The initial volume versus bed-depth information was for pretreated wastewater, but halogenated phenols are more easily removed by activated carbon than are phenols, so the data should be sufficient to design for a BrCl treated liquor (19).

Pretreated wastewater data (9):

C_o = 5740 mg/l TOC
C_b = 100 mg/l TOC
V = 4.89 $m^3/hr\ m^2$ liquor flow rate
4 columns, 3 ft high, 1.25 in ID

From this reference, the liters of wastewater treated versus the bed depth is converted to a bed service time:

Liters Treated	Bed Depth ft	Bed Depth, m (x)	Bed Service Time, hours (t)
5	3	0.91	1.29
17	6	1.83	4.39
30	9	2.74	7.75
41	12	3.66	10.59

A least-squares regression was performed on the third and fourth column values to fit the form of $t = ax + b$ (34).

a = 3.41 hr/m

b = -1.79 hr

correlation = 1.00

Where $a = K1/C_oVf$ and

$b = K2(\ln(C_o/C_b - 1))/C_o$

For the design we will assume:

C_o = 3000 mg/l TOC

C_b = 100 mg/l TOC

V = 10.0 m^3/hr m^2

1 column, 7 m high, 0.02 m thick carbon steel

5% pulsed moving bed contactor ($f = 0.054$)

The factors a and b must then be corrected for the new V, C_o, and f:

$$a = \frac{(3.41\ \text{hr/m})(5740\ \text{mg/l})(4.89\ \text{m}^3/\text{hr m}^2)}{(0.054)(3000\ \text{mg/l})(10.0\ \text{m}^3/\text{hr m}^2)} = 59.1\ \text{hr/m}$$

$$b = \frac{(-1.79\ \text{hr})(5740\ \text{mg/l})\ln(3000/100\ -1)}{(3000\ \text{mg/l})\ln(5740/100\ -1)} = -2.86\ \text{hr}$$

Calculate the cross-sectional area and diameter:

$(295\ \text{m}^3/\text{hr})/10.0\ \text{m}^3/\text{hr m}^2) = 29.5\ \text{m}^2 = 3.14D^2/4$

$D = 6.1$ m

Calculate the contactor volume and carbon dosage:

$(29.5\ \text{m}^2)(7\ \text{m}) = 207\ \text{m}^3$ volume

$(207\ \text{m}^3)(340\ \text{kg/m}^3) = 70{,}380$ kg of carbon

Applying the BDST equation:

$t = ax + b$

$(59.1\ \text{hr/m})(7\ \text{m}) -2.86\ \text{hr} = 411$ hours of service time

Calculate the carbon usage rate:

$(70.380\ \text{kg})/(411\ \text{hours}) = 171\ \text{kg/hr} = 4104\ \text{kg/day}$

Weight of column ((35), p. 773):

$$Wt = \frac{(6.1\ \text{m})(0.02\ \text{m})(3.14)(7\ \text{m})(490\ \text{lb/ft}^3)(1.12)}{(0.3048\ \text{m}^3/\text{ft}^3)} = 52{,}000\ \text{lb}$$

Cost ((35), p 768, M+S = 561):

Cost of column is \$68,000

Cost of auxiliaries (p 771) is (0.43)((30)(7)+(6000)) = \$29000

Total cost is \$70,900

Updated cost is (736.4)(70,900)/(561) = \$93,070

FE-101

The total BrCl flow rate is:

$(295\ m^3/hr)(25\ kg/m^3) = 7375\ kg/hr$ BrCl

(7375 kg/hr)(24 hr/day)(2.20 lb/kg) = 389,900 lb/day

The current cost for a 20,000 lb/day liquid feeder is \$30,000 (36). Since four mixing tanks are being used, four feeders will be used. Assuming a cost scaling power of 0.6 (35):

$$\text{Cost} = ((389{,}900)/(4)(20{,}000))^{0.6}(30{,}000) = \$77{,}490 \text{ each}$$

FP-101

From three experimental trials, the average oxidation sludge collected was 23 kg/m^3 treated. The sludge rate is:

$(23\ kg/m^3)(295\ m^3/hr) = 6785\ kg/hr$

Assume: Sludge density is 1.588 (p-bromophenol, (32))

10 gallon filtered/ft^2/hr (32)

The filter area is then:

$$\frac{(6785\ \text{kg/hr})}{(1588\ \text{kg/m}^3)(3.79 \times 10^{-3}\text{m}^3/\text{gal})(10\ \text{gal/ft}^2\ \text{hr})} = 113\ \text{ft}^2$$

For corrosion resistance, use PVC coated iron.

Cost ((35), p589) = \$7300 (M+S = 561)

Updating:

(736.4)(7300)/(561) = \$9580

FP-301

Assume: 39 kg/hr (85 lb/hr) sludge (9)

0.1 lb/gal filter cake (9)

10 gal/ft^2 hr loading (9)

aluminum

Filter area:

(58 lb/hr)/0.1 lb/gal)(10 gal/hr ft^2) = 85 ft^2

Cost: ((35), p 589) = \$4000 (M+S = 561)

Updating:

(4000)(736.4)/(561) = \$5250

LS-301

Assume: Effluent from CC-201 is pH 2.3 (Table 5)

Desired pH is 7.5

1 mole of lime ($Ca(OH)_2$) neutralized 2 moles of acid

lime is 90% $Ca(OH)_2$ (37)

pH 2.3 = 5.01×10^{-3} M H^+, pH 7.5 = 3.16×10^{-8} M H^+

Calculate lime addition rate:

$(5.01 \times 10^{-3} - 3.16 \times 10^{-8}$ gmol/l)(1000/l/m^3)(295 m^3/hr)

= 1478 gmol/hr H^+

(1478 gmol/hr)/(2) = 739 gmol/hr $Ca(OH)_2$

(739 gmol/hr)(74.08 gm/gmol)/(0.9)(1000 gm/kg)

= 61 kg/hr lime

Lime dosage:

(61 kg/hr)(1000 mg m^3/kg l)/(295 m^3/hr) = 207 mg/l

Capacity is 295 m^3/hr or 1.9 mgd. An equivalent capacity base on a lime dosage of 300 mg/l is calculated to find the cost (37):

(1.9)(207)/(300) = 1.3 mgd

Cost: $26,300 ((37), M+S = 335.9)

Updating: (736.4)(26,300)/(335.9) = $57,660

RS-401

The carbon regeneration rate is 4104 kg/day or 9040 lb/day. The cost for a complete regeneration system with 10,000 lb/day capacity is $360,000 ((38), M+S = 545)

Updating: (736.4)(360,000)/(545) = \$486,400

The reference also provides the fuel, power, steam, and makeup carbon (7%) rates.

T-101

Assume: 4 in parallel for better mixing

SS 304 steel clad steel for corrosion resistance

80% of capacity

$H = 3D/2$

Contact time:

$(25\ \mathrm{kg/m^3})/(36\ \mathrm{kg/m^3\ hr}) = 0.7$ hours

(*BrCl dosage/BrCl rate*)

Tank dimensions:

$(295\ \mathrm{kg/m^3})(0.7\ \mathrm{hr})/(0.8)(4) = 65\ \mathrm{m^3} = 17{,}200$ gal

$(3)(3.24)(D^3)/(8) = 65\ \mathrm{m^3}$ $D = 3.8$ m
$H = 5.7$ m

Agitator hp ((35), p 791): 85 hp

Cost ((35), p 572, carbon steel): \$32,000

Correcting for material of construction:

(5)(32,000) = \$160,000 (M+S = 561)

Updating: (736.4)(160,000)/(561) = \$210,020

T-102, 302

Assume: 30 minute contact time

$H = D$

80% of capacity

Tank dimensions:

$(295\ m^3/hr)(0.5\ hr)/(0.8) = 184\ m^3$

$(3.14)(D^3)/(4) = 184\ m^3 \qquad D = H = 6.2\ m$

Surface area:

$(3.24)(D^2)/(4) + (3.14)(D)(H) = 151\ m^2 = 1625\ ft^2$

Cost based on surface area (37):

$62,000 (M+S = 335.9)

Updating:

(736.5)(62,000)/(335.9) = $135,920

T-301

Assume: 15 minute contact time

80% of capacity

carbon steel

Tank capacity:

$(295\ m^3/hr)(0.25\ hr)/(0.8)(3.79 \times 10^{-3}\ m^3/gal) = 24,330\ gal$

Mixer hp ((35), p 791) = 110 hp

Cost base on capacity (35) = $37,000 (M+S = 561)

Updating costs:

(736.4)(37,000)/(561) = $48,570

The purchased equipment cost (PEC) is the sum of the costs of all equipment appearing in Table 9. The installed new cost is 1.47 times the PEC (35).

PEC:

CC-201	93,070
FE-101	(4)(77,490)
FP-101	9,500
FP-301	5,280
LS-301	57,660
RS-401	486,430
T-101	(4)(210,020)
T-102	135,920
T-301	48,570
T-302	135,920
TOTAL	$2,122,440

Installed cost = (1.47) (2,122,440) = $3,120,000.

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