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A Preliminary Investigation of Physical-Chemical Treatment of Slagging Gasifier Aqueous Effluent

Kirk B. Hird

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A PRELIMINARY INVESTIGATION OF PHYSICAL-CHEMICAL TREATMENT OF SLAGGING GASIFIER AQUEOUS EFFLUENT

by
Kirk B. Hird

Bachelor of Science, Chemical Engineering

University of North Dakota, 1978

A Thesis

Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

Grand Forks, North Dakota

August
1979

This thesis submitted by Kirk B. Hird 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.

Wayne R Kube
(Chairman)

Harold H. Schobert

Michael B. Gregory

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

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Department Chemical Engineering

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ABSTRACT

The feasibility of treating slagging gasifier wastewater by physical-chemical means was studied. Pretreatment and treatment flow schemes were developed by using batch and continuous tests. Results were based mainly on wastewater residual total organic carbon (TOC). A treatment facility was designed and economically evaluated.

It was found that slagging gasifier wastewater is treatable by physical-chemical means using activated carbon and chemical oxidation as the two principal treatment steps. A pretreatment scheme consisting of lime addition, ammonia stripping, and recarbonation-coagulation was found to sufficiently purify the raw gasifier liquor so that activated carbon adsorption and chemical oxidation could be applied as secondary and tertiary treatment.

Oxidants found to be ineffective were: chlorine, sodium hypochlorite, hydrogen peroxide, and potassium permanganate. Ozone and bromine chloride were determined to be capable of oxidizing gasifier wastewater although bromine chloride oxidation seems to be more economical.

LCK activated carbon, manufactured by Union Carbide, proved to be the preferred granular carbon for slagging gasifier liquor treatment.

A total capital investment of approximately $14,748,000 can be expected for a facility capable of purifying pretreated wastewater

produced from a slagging gasification plant having a large enough gas output to produce 250 million standard ft^3/day of methane. Annual operating costs are estimated to be \$7,413,000, i.e., \$10.75 per 1000 gallons of pretreated liquor.

CHAPTER I

INTRODUCTION

The United States, along with the rest of the world, is in the midst of a very serious energy shortage. From all indications, this crisis will become only worse in the near future. The energy shortage has been caused by several factors: 1) total energy consumption has increased annually due to the increase in both worldwide population and living standards; 2) not only is our domestic supply of oil and natural gas decreasing, but international supplies are becoming increasingly difficult to obtain; 3) more stringent pollution control regulations limit use of some potential and actual energy resources; and 4) newly developed energy sources can not keep pace with the increasing demand (1).

One of the most promising energy resource alternatives is increased use of coal. Past use of coal had been severely restricted due to the more competitive and convenient conventional fuels. However, recent developments have altered this situation with coal utilization for conversion to other energy forms becoming more and more favorable.

Coal and lignite resources are distributed so that about 95 percent are found in the Northern Hemisphere and the larger part of this is found in North America. Total reserves amount to about 5×10^{12} tons of coal and 1×10^{12} tons of lignite. Of this, about

2×10^{12} and 8×10^{10} tons of coal and lignite, respectively, are mineable (2). These reserves are sufficient to meet our energy demands for at least the next 200 years (3). Hence, any hope of meeting our energy demand must include utilization of coal.

Coal is used as both a fuel source and as a source of synthetic liquid and gaseous fuels. Coal-fired power plants constitute the major use of coal in the United States. Fluidized-bed combustion and low- or intermediate-Btu gasification processes may be important energy sources for both utility and industrial applications. Promising coal conversion products include synthetic natural gas and solvent-refined coal. Therefore, it can be seen that numerous coal conversion possibilities exist and advanced coal utilization technology is likely.

The Grand Forks Energy Technology Center at Grand Forks, North Dakota, has been doing pilot plant studies of a slagging fixed-bed gasification unit. This pilot plant unit is a modified version of a conventional dry-ash fixed-bed gasifier. In the dry-ash model, the operating temperature is maintained low by use of excess steam to permit removal of the ash in the dry state. Most proposed synthetic natural gas plants are based on the fixed-bed dry-ash process. The slagging gasifier differs from the dry-ash unit by maintaining operating temperatures sufficiently high by reduction in the steam-oxygen ratio so that the ash can be removed in the form of slag. Two important advantages are obtained by slagging gasifier operation: 1) only about one-fourth the quantity of steam is consumed; and 2) the gas production capacity per square foot of hearth is three to four times that of a dry-ash gasifier (4). Hence, slagging fixed-bed gasification may well be utilized as a second generation gasifier. Non-agglomerating coals, such as lignite, are good feedstocks for a fixed-bed unit since no pretreatment is required to eliminate coke formation and subsequent plugging of the reactor.

The flow diagram for the slagging gasifier pilot plant at Grand Forks Energy Technology Center is given in Figure 1. Coal, 3/4 x 1/4 inch size, is introduced into an isolated coal lock. The coal lock is subsequently closed, purged, and repressurized with inert and/or product gas before the coal is released into the gasifier by means of a cone valve. As the coal descends, it is dried and devolatilized before combustion/gasification occurs. The gasification reaction is sustained by introducing a steam-oxygen mixture into the hearth through four water-cooled tuyeres. The molten ash formed drains continuously into a water quench bath where it is periodically discharged.

The raw product gas enters a spray washer where it is scrubbed with recycled condensate liquor to remove water, tars, oils, other organics, and dust. The gas exits the spray washer at approximately 150^{o}F and is then further cooled by means of an indirect gas cooler to approximately 60^{o}F. Both the spray washer and gas cooler are periodically drained into a settling vessel to be weighed and sampled. Lastly, the product gas is sampled, depressurized, demisted, metered, and flared (4).

Waste liquids from a gasification unit cannot be discharged directly into the surrounding land or streams because of environmental contamination.

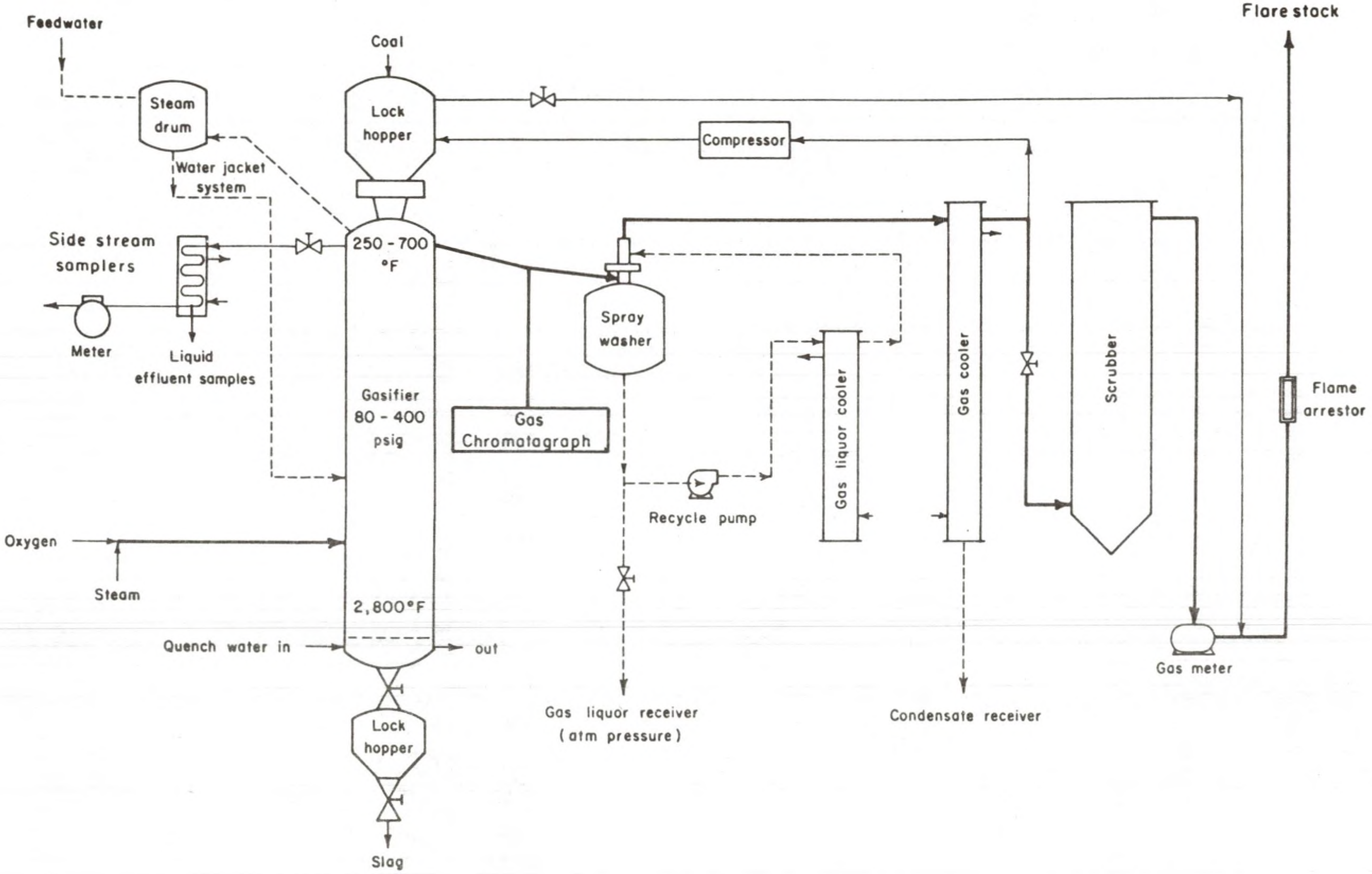

Figure I. Flowsheet of slagging gasifier pilot plant.

CHAPTER II

OBJECTIVES

The wastewater collected from the spray washer of the slagging gasifier is highly concentrated in pollutants. Before the slagging gasifier can be brought on stream an economical method of cleaning the wastewater must be developed.

The primary objective of this research project was to determine the treatability of slagging gasifier wastewater by use of activated carbon and/or chemical oxidation as the principal treatment step or steps to reduce environmental impact. Other objectives were to determine a possible pretreatment scheme; relative effectiveness of chlorine, sodium hypochlorite, bromine chloride, ozone, hydrogen peroxide, and potassium permanganate in treating the gasifier liquor; the best commercially available activated carbon for adsorbing gasifier liquor pollutants; and capital and operating costs of a treatment facility for purifying pretreated wastewater from a slagging gasifier with large enough capacity for a subsequent gas plant to produce 250 million standard ft^3/day synthetic coal-substitute natural gas.

CHAPTER III

INDUSTRIAL WASTEWATER TREATMENT TECHNIQUES

Introduction

There are three basic types of industrial wastewater treatment systems in use today: biological, physical-chemical, and a combination of the two. Biological treatment involves the use of a heterogeneous bacterial culture to break down pollutants. Physical-chemical treatment (PCT) refers to any system that does not contain a biological treatment process.

Biological Treatment

By far the most widely used treatment is biological. Two main types of biological treatment are used: film flow and suspended-culture process (5).

Film Flow Processes

The trickling filter and the rotating biological contactor (RBC) are two types of film flow processes. The trickling filter is a packed bed of support media covered with slime over which wastewater is sprayed. Bacterial cultures exist in the slime film and extract organic material and inorganic nutrients from the liquid film. The RBC process operates in much the same way as the trickling filter except the cylindrical contactor is rotated through the wastewater and the slime film is formed on the surface of the cylinder.

Suspended-Culture Processes

The most commonly used suspended-culture processes are activated sludge, aerated lagoons, and anaerobic treatment processes.

Activated sludge processes are continuous systems which require stimulation of bacterial growth by aeration and agitation. Bacterial cultures develop on the suspended organic material and agglomerate until the floc can be settled and removed.

Aerated lagoons are essentially activated sludge processes. These large shallow stabilization ponds increase the rate of algae photosynthesis by using mechanical aerators.

Activated sludge and aerated lagoons are "aerobic" systems in which the bacteria require oxygen for metabolism. "Anaerobic" digesters are used to stabilize concentrated organic solids removed from aerobic systems. The waste is mixed with bacterial cultures in an oxygen-free environment where they convert the organic solids to carbon dioxide and methane (6).

Physical-Chemical Treatment

The main physical-chemical treatment processes in use are coagulation, filtration, sedimentation, and flotation. The major purpose of these processes is to remove suspended solids.

Coagulation

Certain suspended impurities in wastewater may be removed by gravity settling. Others must be aggregated into larger particles before gravity settling is possible. The process of converting a finely divided or colloidally dispersed suspension of a solid into large-size particles to cause rapid settling is called coagulation.

Coagulation occurs in two steps: 1) particle transport to increase particle-to-particle contact, i.e., flocculation; and 2) particle destabilization to permit aggregation when particle-to-particle contact is attained (7). Since stability of a colloid is primarily due to electrostatic forces, destabilization is usually obtained by neutralization. Finely dispersed wastewater solids usually have a negative charge. By adding metal salt or polymer coagulants to the dispersion, their cations can be adsorbed to neutralize the charge.

Other destabilizing actions of coagulants may occur by interparticle bridging or colloidal enmeshment in precipitates (8). Interparticle bridging occurs when the coagulant and the suspended particle have the same electric charge. Interaction between the colloid and the coagulant occurs only when the coagulant contains chemical groups which can interact with sites on the surface of the colloid. When colloids interact at multiple sites bridging occurs.

Hydroxides of iron, aluminum, and magnesium form hydrolysis precipitates which, if formed rapidly enough, can enmesh colloidal particles.

Filtration

The two main uses of filtration are removal of settled bacteria floc from secondary settling basins and sludge removal after chemical coagulation or precipitation.

Sedimentation

After eliminating easily removable solids by screening, the remaining settleable solids are usually removed by sedimentation in clarifiers. Settled solids are removed by continuously scraping the bottom of the clarifier to a discharge point.

Flotation

Removal of solids by flotation is possible when the specific gravity of the suspended solids is about the same or less than that of water. By forcing air to dissolve in the wastewater by pressurization, suspended solids can be removed when abrupt depressurization releases air bubbles causing flotation of the suspended solids to the surface.

Miscellaneous

Other frequently used physical-chemical processes are solvent extraction, steam stripping, ion-exchange, reverse osmosis, molecular sieving, neutralization, adsorption, and chemical oxidation. The latter two processes will be discussed throughout the remainder of this report.

Physical-Chemical vs. Biological Processes

The Federal Water Pollution Control Act, passed in 1972, stipulates that the best practiceable treatment technology and the zero pollution discharge requirements for wastewater treatment must be met by 1983 and 1985, respectively (9).

Since the passage of the Act, many studies on the potential of activated carbon treatment and comparisons between it and conventional treatment methods have been made. For instance, one study reports that "Various studies as well as field operations in foreign countries have shown that activated carbon is the best available broad spectrum control technology currently known" (10). Another study (11) showed that: 1) most of the EPA proposed dissolved organic toxic chemicals can be removed from water by activated carbon; and 2) other chemically similar contaminants, such as OSHA defined carcinogens and the chemicals under examination by the EPA for inclusion on the toxic chemical list, are also predicted to be adsorbable from water by activated carbon.

Biological treatment facilities looking for better means of treatment have found the advantages of purification by activated carbon. One chemical process treatment plant (12) reported that cost and performance of an adsorption/filtration system outperformed several process alternatives including biological systems. A refinery (13) discovered that activated carbon treatment had a capital cost of $500,000 less than biological treatment and an annual operating cost of $31,500 less. A 10 million gal/day treatment plant (14) determined that physical-chemical treatment using activated carbon has a capital cost of $200,000 less than an activated sludge process.

Below are listed advantages that studies have found physical-chemical treatment has over biological systems:

1. no additional disposal or pollutional problems are created (15)
2. 75 percent less land area required (16)
3. increased ease of operation (17)
4. more flexible so water quality can be easier selected (17)
5. removes suspected carcinogens such as carbon tetrachloride,

chloroform, and trihalomethanes (10)

6. upsets or spills do not disturb effluent quality as readily (12).

Not all wastewaters are treatable by physical-chemical means. Some disadvantages of PCT using activated carbon include:

1. relatively high capital and operating costs, especially when thermal reactivation is required (18)

2. low tolerance of suspended solids (19)

3. inability to remove low molecular weight and/or highly soluble organic chemicals (e.g. methanol, ethanol, glycol, soaps) (19)

4. operational problems reported with thermal reactivation system (19).

CHAPTER IV

TREATMENT BY ACTIVATED CARBON

Introduction

The most popular adsorbent used today in wastewater treatment is activated carbon. An adsorbent must have an extremely large surface area, be selective in its adsorption, have available several types for various applications, and obviously must not adsorb water. Usually activated carbon is the only adsorbent that can economically meet these requirements.

This chapter incorporates theory, design, and history pertaining to the use of activated carbon.

Historical Background

The first recorded use of activated carbon dates back to 1550 B.C. when wood chars were used in medicine. Not until 1773 did carbon's adsorptive powers become known when Scheele discovered its gas phase application (20). Later in 1785, Lowitz reported carbon's liquid phase decolorizing ability (20). Throughout the 1800's various activated carbons were developed from sources such as paper mill waste, cocoanut char, and a mixture of potash and blood (21). These carbons created a market in the beet sugar and sugar refinery industries. Modern carbonization techniques were developed in 1900 by Ostrijko (21).

Chemical warfare during World War I caused increased interest in the adsorptive ability of activated carbon. Because powdered carbons were not suitable for use in gas masks, granular forms were developed. After the war gas phase applications continued growing. Applications developed included extracting organic vapors from manufactured gas and recovery by desorption, purification of industrial gases (such as sulfur dioxide removal from stack gases), and use in recirculation systems for improving air freshness (20).

Present industrial applications include use in reclamation of white sidewall rubber tires, crystallization and filtration aids, and use as a defoaming agent (20).

Municipal wastewater purification with activated carbon became popular starting early in this century to correct odor and taste problems in municipal water supplies. More recently, industrial wastewater treatment with activated carbon has increased in use because of the development of a more efficient regeneration system.

Theoretical Considerations

In wastewater treatment, the adsorption process occurs at a liquid-solid interface. Adsorption is therefore dependent on the surface area of the solid. It should be emphasized that the solid surface is separated from the liquid surface and both masses affect the adsorption process at the interface.

Two primary driving forces cause the adsorption of a liquid onto a solid. The solute may have a high affinity for the solid and/or the solute may have only a small affinity for the solvent (5). The former driving force results from one or a combination of three main types of adsorption: electrical, chemical, and physical (7).

Electrical, or exchange, adsorption occurs when solute ions are attracted to the solid surface due to oppositely charged sites at the surface. Hence, the larger the charge and smaller the size of an ion, the greater potential it has for being adsorbed on an oppositely charged surface site.

Physical adsorption results from van der Waals forces which are made possible because of an unbalanced inward attraction of surface molecules. This type of adsorption does not bind a molecule to a specific surface site but allows movement within the interface.

The third type of adsorption, chemisorption, involves much stronger forces than physical or electrical adsorption. Chemisorption occurs when some type of chemical interaction between the solute and surface molecules is present. This process is usually irreversible in which case any molecules that were originally adsorbed can only be recovered in the form of compounds containing atoms of the adsorbent.

Primary factors that influence adsorption and will assist in the choice of operating conditions if properly weighted in terms of importance include (7,21):

1. attraction of carbon for solute
2. attraction of carbon for solvent
3. solubilizing power of solvent for solute
4. ionization
5. interactions of multiple solutes
6. coadsorption
7. molecular size of molecules in the system
8. pore size distribution in carbon
9. surface area of carbon

10. temperature.

Solute-Solvent-Carbon Interactions

Intuitively, an increase in solute solubility should decrease the solute's ability to be adsorbed. Hence, because of solubilities polar molecules are usually less adsorbable and nonpolar molecules are usually more adsorbable from aqueous solutions. Adsorption in aqueous solutions generally increases as the chain length in a homologous series of adsorbates increases. This is because the solubility of a nonpolar compound in water decreases with increasing chain length.

Ionization

Ionized molecules are generally not adsorbable. This holds true for both organic and inorganic compounds. Hydrogen ions are exceptions as these ions are adsorbable quite strongly. Since the pH influences the ionization of compounds, an increased effect occurs from hydrogen ion concentration in water. Also, the carbon surface contains negatively charged sites with the number varying with the specific carbon used (7). Lowering the pH neutralizes these negative charges causing an increase in organic diffusion and more available surface area.

Multiple Solutes and Coadsorption

In wastewater purification, aqueous solutions usually contain numerous pollutants that must be removed. Multiple solutes generally decrease the adsorbability of each solute. When the solutes tend to compete for the same active sites, less surface area is available for each solute thereby decreasing its ability to be adsorbed (22). Other factors decreasing the adsorption of multiple solutes include lack of interaction between solutes, similar relative solute adsorption affinities, and adsorption occurring only within a few molecular layers (7).

If a solute increases or decreases the solubility of a second solute the degree of adsorption of the latter solute generally decreases or increases, respectively. When adsorption of a species is enhanced by the addition of another species, it is referred to as coadsorption (21).

Temperature

An increase in solution temperature increases the molecular activity thereby decreasing adsorption. Also, adsorption reactions are exothermic causing less adsorption at higher temperatures. Because adsorption is dependent on both the properties of the carbon and the solute temperature, effects will vary with carbon types. Generally temperature effects on adsorption are relatively unimportant in wastewater treatment.

Available Surface Area

Since activated carbons have surface areas in the range of 500-1400 square meters per gram, it is apparent that most of its surface area exists in micropores. Because many of these micropores may have diameters too small for solute molecules to enter, adsorbability is directly related to solute molecular size and pore size distribution.

The concept of molecular screening is depicted in Figure 2 (23).

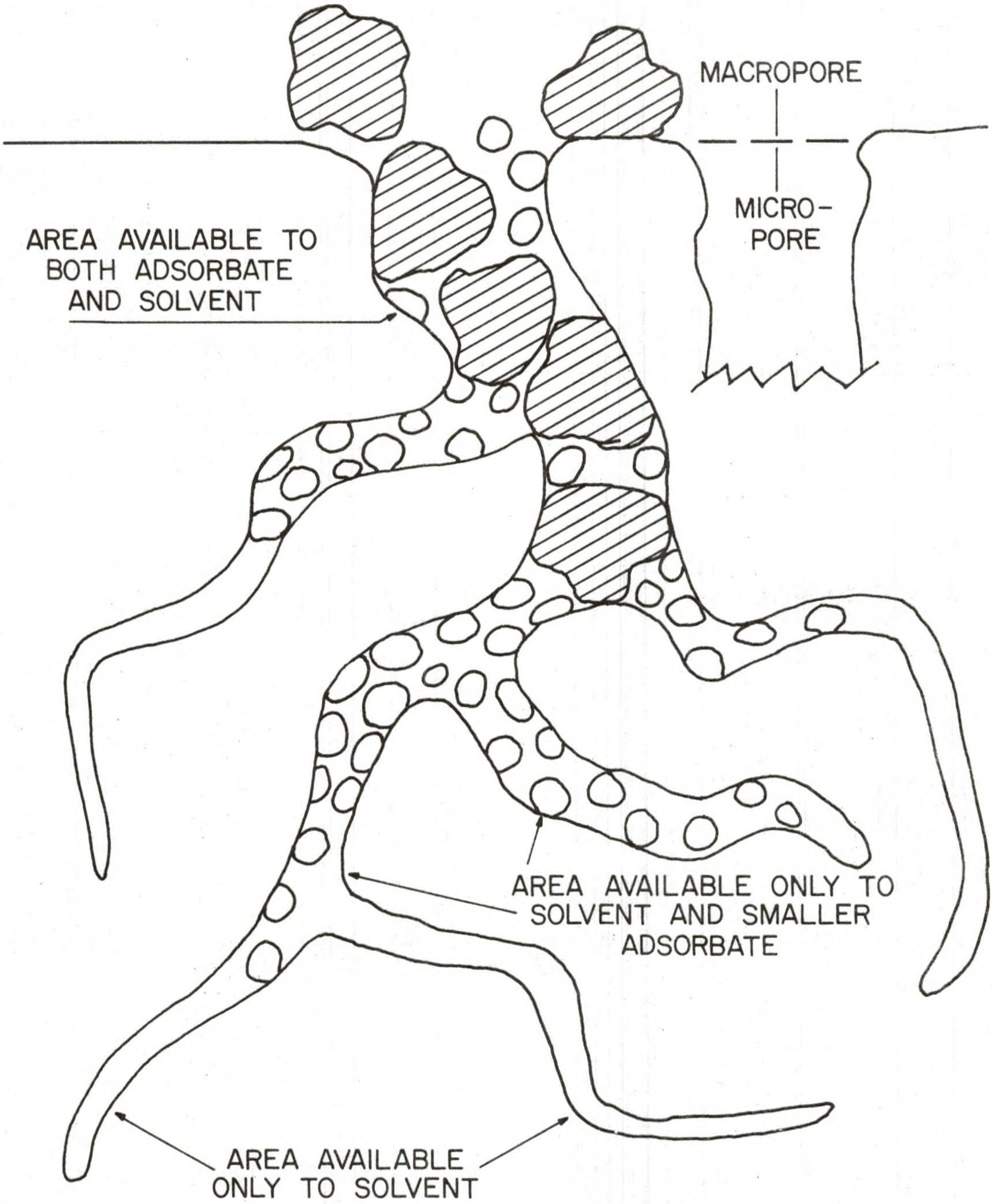

Figure 2. Concept of molecular screening in micropores.

Two types of adsorbate molecules are shown competing for adsorbent surface. The fine pores are still available to the small adsorbate molecules even when blocked by large molecules because of constant molecular motion. The surface area accessible to any adsorbate molecule is called the available surface area. If the chemical nature of the surface is unimportant, the adsorptive properties of activated carbon can be attributed to the available surface area (23).

Adsorption Isotherms

Two equations, Langmuir's and Freundlich's, are commonly used to compare carbons at several conditions for wastewater treatment. The Langmuir equation is based mostly on theoretical considerations whereas the Freundlich equation is largely empirical.

Langmuir Equation

This equation was developed by Langmuir in 1918 using both kinetic and thermodynamic adsorption considerations. The assumptions made to formulate the Langmuir equation were: maximum adsorption corresponds to a saturated single layer of solute molecules on the adsorbent surface, the energy of adsorption is constant, and no migration of the adsorbate occurs in the mono-layer (7).

The Langmuir isotherm can be written as:

$$x/m = \frac{(x/m)^{o} bC}{1 + bC} \tag{1}$$

where x/m = number of moles adsorbed per weight adsorbent at concentration C

$(x/m)^{o}$ = number of moles adsorbed per weight adsorbent in forming a complete monolayer on the surface

C = concentration of solute at equilibrium

b = constant related to the energy of adsorption

Equation 1 is usually transformed into linear form:

$$\frac{1}{(x/m)} = \frac{1}{(x/m)^{o}} + \left(\frac{1}{b(x/m)^{o}}\right)\left(\frac{1}{C}\right) \qquad (2)$$

The limiting values of equation 2 are very useful. For small amounts of adsorption (i.e., $bC<<1$):

$$x/m = (x/m)^{o}bC \qquad (3)$$

For large amounts of adsorption (i.e., $bC>>1$),

$$x/m = (x/m)^{o} \qquad (4)$$

Hence, as the equilibrium concentration approaches the saturation concentration, x/m approaches $(x/m)^{o}$. By assuming the adsorbent surface area covered per molecule, σ^{o}, the specific area (surface covered per mole), Σ_s, can be determined:

$$\Sigma_s = (x/m)^{o}N_{Av}\ \sigma^{o} \qquad (5)$$

where N_{Av} = Avogadro's number.

Freundlich Equation

The Freundlich equation is the most popular equation used in wastewater treatment and is based on the Langmuir equation in which the energy term, b, varies as a function of surface covered by molecules, x/m, strictly due to variations in the heat of adsorption. The equation is of the form

$$x/m = KC^{1/n} \qquad (6)$$

where K and n are constants. The limiting value of x/m as the equilibrium concentration approaches the initial concentration represents the ultimate adsorptive capacity. The value of 1/n is an indicator of adsorption intensity.

The Freundlich equation generally does not agree with the Langmuir equation at very high or low solute concentrations.

Breakthrough Curves

Batch adsorption isotherm tests reveal if a reasonable carbon dosage can be used to purify the wastewater. Many mathematical models have been developed to predict carbon performance from equilibrium data for dynamic situations (24, 25, 26, 27); however, they are all too complex and limited for practical use. The only informative method developed as of yet to determine dynamic parameters is actual laboratory or pilot plant column tests.

In a fixed-bed steady state adsorber, the carbon at the inlet section will initially adsorb the solute. As time increases, this section will become saturated with adsorbate and lower sections of the column will gradually adsorb more and more solute until also becoming saturated. The extent of saturation will be dependent on the system design and parameters. The zone between carbon saturation and negligible adsorbate loading is called the mass transfer zone.

Figure 3 is an example of a four column system in which, for each column, the percent adsorbate remaining in the wastewater is plotted versus liquid throughput. Each of these curves is referred to as a breakthrough curve. The point at which the effluent has an adsorbate concentration equal to the desired treated value is called breakthrough. Two empirical methods for interpreting breakthrough curves for design purposes are discussed in literature by Hutchins (28) and by Erskine and Schuliger (29). The latter method has been chosen for design purposes in this report. From the breakthrough curves the carbon dosage as a function of carbon bed depth or contact time can be plotted as shown in Figure 4. Note that the curve presents the data in terms of a single fixed-bed system. From this data a reasonable system can be selected.

Physical-Chemical Treatment Plants

It is estimated that approximately 100 industrial/municipal plants use some type of large-scale activated carbon system (20). Most of these systems are for tertiary treatment or treatment of some specific industrial waste stream. A few systems are full physical-chemical treatment plants. A PCT plant as a rule employs activated carbon adsorption as the principal treatment step. Use of PCT plants is very recent with the first full-scale plant going on line in 1973 (30). Table 1 lists PCT plants that are currently in operation.

All but four of the plants treat municipal wastewater. Typical carbon loadings for the municipal plants are in the range of 0.4-0.6 lb COD/lb carbon and 0.15-0.30 lb TOC/lb carbon (20).

The four full-scale PCT plants in operation or under construction are in Tuscaloosa, Alabama (Reichhold Chemicals), Marcus Hooke, Pennsylvania (BP Oil Corporation), Fieldsboro, New Jersey (Stepan Chemical Company), and Portland, Oregon (Rhodia, Inc.).

The Tuscaloosa plant makes sulfuric acid, formaldehyde, phenylphenol, and a number of synthetic resins and plastics in its production units (31). Therefore, its waste effluent represents very complex and diverse pollutants. In 1966, the state of Alabama requested Reichhold

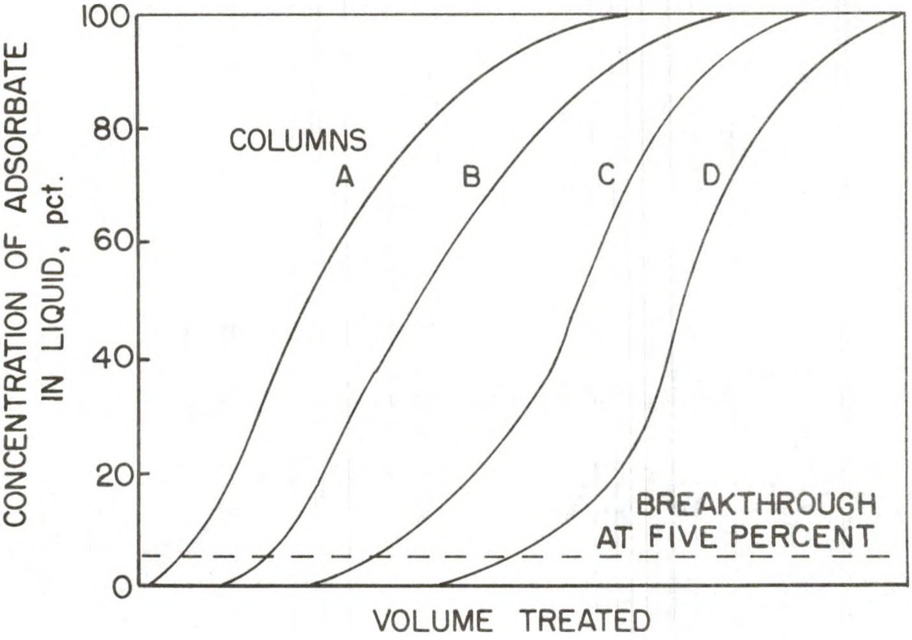

Figure 3. Example of breakthrough curves for four column system.

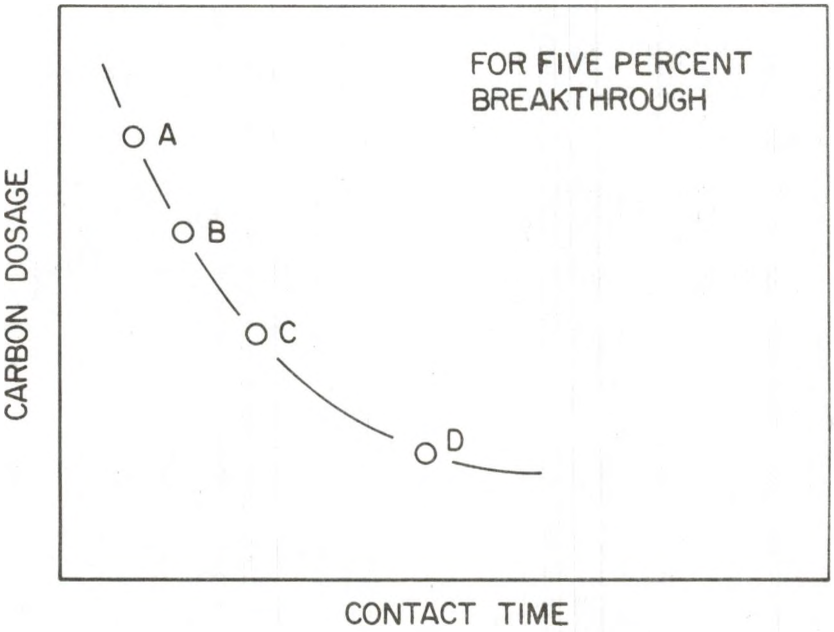

Figure 4. Example of dosage curve for single fixed-bed.

TABLE 1

PHYSICAL-CHEMICAL TREATMENT PLANTS

Site	Average Plant Capacity, million gal/day	Total Carbon Depth, ft	Treated Effluent Quality, mg/l
Cortland, Tx. (30)	10	17	35 TOD[a]
Cleveland, Oh. (30)	50	17	15 BOD[b]
Fitchburg, Mass. (30)	15	15.5	10 BOD
Garland, Tx. (30)	30	10	10 BOD
Leroy, N.Y. (30)	1	26.8	10 BOD
Niagra Falls, N.Y. (30)	48	9	112 COD[c]
Owosso, Michigan (30)	6	30	7 BOD
Rosemount, Minn. (30)	0.6	36	10 BOD
Rocky River, Oh. (30)	10	15	15 BOD
Vallejo, Cal. (30)	13	16	45 BOD
Markus Hooke, Penn. (13)	2.2	45	60 TOC[d]
Tuscaloosa, Ala. (31)	0.5	60	640 COD
Fieldsboro, N.J. (33)	0.015	25	289 TOC
Washington, D.C. (34)	0.1	20	6 TOC
Portland, Ore. (12)	0.15	50	1 phenol
Del City, Okla. (35)	5.25	24	10 BOD

[a] TOD- Total oxygen demand

[b] BOD- Biochemical oxygen demand

[c] COD- Chemical oxygen demand

[d] TOC- Total organic carbon

to reduce volumetric output while increasing quality of the effluent.

After considering several alternatives Reichhold decided on a PCT plant. The influent wastewater has a flow rate of 500,000 gal/day and a concentration of 6400 mg/l COD. The carbon system has a total bed depth of 60 feet, superficial contact time of 173 minutes, and a carbon dosage of 84 lb/1000 gals. The effluent is discharged with 640 mg/l COD.

The plant in Marcus Hooke, Pennsylvania, treats wastewater from B.P. Oil Corporation's 105,000 bbl/day refinery (13, 32). The refinery treats 2,200,000 gal/day of wastewater containing 400 mg/l TOC. The carbon system requires a bed depth of 45 feet, superficial contact time of 40 minutes, and a carbon dosage of one lb/1000 gal to reach the desired effluent quality of 60 mg/l TOC.

Another PCT plant in operation treats effluent from the Stepan Chemical Company plant in Fieldsboro, New Jersey (33). This chemical plant produces a variety of liquid detergent intermediates from raw materials including xylene, ethyl alcohol, other linear alcohols, and sulfuric acid. The PCT plant treats 15,000 gal/day of waste effluent with 6400 mg/l TOC. The carbon system employed requires a bed depth of 25 feet, 540 minute superficial contact time, and a carbon dosage of 437 lb/1000 gal to reduce TOC levels to 289 mg/l. The fourth PCT plant treats wastewater from a herbicide manufacturing facility in Portland, Oregon (12). The original treatment facility for the 150,000 gal/day of wastewater consisted of a lagoon and chlorination facilities. When the Oregon State Sanitary Authority set the maximum phenol discharge level at one mg/l, Rhodia, Inc. had to look for another processing method.

The PCT plant chosen outperformed in both cost and performance alternative processes such as conventional biological systems, ion-exchange, and oxidation using ozone, peroxide, or permanganate. The plant uses 18,000 pounds of activated carbon in each of two contactors having a bed depth of 25 feet.

Three demonstration PCT plants have also been constructed recently because of favorable activated carbon treatment data and the waste streams are also closely related to slagging gasifier wastewater. Two of these demonstration plants are in Germany and treat effluent from a coking plant and from a Lurgi pressure gasification plant (15). Wastewater from the coking plant (8000 gal/hr) is reduced in TOC concentration from 2000 to 100 mg/l. Because of the excess steam used in the Lurgi gasifier, waste effluent has a TOC content range of 700 to 1000 mg/l--lower than slagging gasifier systems. The activated carbon system for the Lurgi gasifier achieves a higher adsorbate loading than that of the coking plant.

In this same study, wastewater from a commercial Lurgi gasification plant in Great Britain was tested for possible activated carbon treatment. Results showed that the application of activated carbon is one of the most promising processes for cleaning such types of industrial wastes.

The third of the previously mentioned demonstration plants treats coking plant effluent and is located in Pennsylvania (36). Total organic concentrations are reduced from 2100 to 156 mg/l. Phenol levels are cut from 2235 mg/l to less than 0.1 mg/l.

CHAPTER V

TREATMENT BY CHEMICAL OXIDATION

Introduction

As federal and state regulatory agencies progressively require cleaner wastewater effluent, a greater need for non-conventional treatment arises. Chemical oxidation is one such method that is capable of treating materials that are resistant to conventional treatment processes.

Effective use of chemical oxidation does not require complete oxidation of the objectionable materials. Intermediate products of much less toxicity are either easily removed by tertiary processes or do not need to be eliminated, although, ideally, the oxidation products should be completely removed.

For rough design purposes, reducing agents may be categorized according to their relative reactivity (7):

1. high reactivity: phenols, aldehydes, aromatic amines, and certain organic sulfur compounds such as thioalcohols and thioethers

2. medium reactivity: alcohols, alkyl-substituted aromatics, nitro-substituted aromatics, unsaturated alkyl groups, carbohydrates, ketones , acids, esters, and amines

3. low reactivity: halogenated hydrocarbons, saturated aliphatic compounds, and benzene.

Common oxidants in use today are: chlorine, hypochlorites, chlorine dioxide, potassium permanganate, hydrogen peroxide, and ozone. An oxidant currently in the development stage is bromine chloride. The present experimental work involved all of the above oxidants except chlorine dioxide because of its explosive tendencies.

Chlorine

Chlorine is most widely used in water treatment as a disinfectant. Chlorine's use as an oxidant is usually limited to treatment of cyanide, ammonia, and hydrogen peroxide, and color removal (37). Chlorine is mostly used in the forms of chlorine dioxide, hypochlorites, and chlorine gas.

Chlorine hydrolyzes almost immediately in water according to the reaction:

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl$$

In aqueous solutions with pH values greater than 3.0, the equilibrium is such that no measurable amount of Cl_2 is in solution.

Hypochlorous acid ionizes in water as shown below:

$$HOCl \rightleftarrows H^+ + OCl^-$$

Nearly all of the chlorine exists as HOCl below a pH value of 5.0 and as OCl^- above pH 10.0 (38). Since hypochlorous acid is an extremely more powerful oxidant than hypochlorite ion (oxidation potentials are 1.50 and 0.90 volts, respectively (39)), the pH of the water should be controlled closely.

Hypochlorites will ionize when placed in an aqueous solution as indicated below:

$$MOCl \rightarrow M^+ + OCl^-$$

where M represents sodium or calcium. As with the application of Cl_2, hypochlorite ion will reach equilibrium with hypochlorous acid:

$$H^+ + OCl^- \rightleftarrows HOCl$$

Chlorine also reacts with ammonia to form chloroamines according to the following reaction:

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$$

Reactions of these chloroamines depend on pH, temperature, oxidant concentration, contact time, and nature of the pollutants. As successive amounts of chlorine are added to wastewater containing ammonia, the monochloroamine is converted to dichloroamine, and, if at least 10 mg chlorine per mg ammonia is applied, free residual chlorine appears as HOCl. The point when free residual chlorine is formed is called the breakpoint (7). All ammonia will be oxidized before other pollutants (40).

For phenol oxidation by chlorine the final pH after chlorination should be greater than 7.0 (40). The chlorine:phenol ratio must be greater than 6:1 or else chlorophenolics will be formed. Because of chlorine's many adverse side reactions its use as an oxidant remains minimal (5).

Potassium Permanganate

Potassium permanganate has been used extensively in municipal water plants for taste and odor control and for removal of iron and manganese since 1960 (7). The oxidations of iron(II) and manganese (II) occur as follows:

$$MnO_4^- + 3Fe^{2+} + 2H_2O + 5OH^- \rightarrow MnO_2 + 3Fe(OH)_3$$

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

The products are formed rapidly and have secondary oxidation qualities to further enhance the removal process.

Industrial waste treatment plants sometimes use potassium permanganate for hydrogen sulfide and cyanide removal. These oxidations proceed as follows:

$$4KMnO_4 + 3H_2S \rightarrow 2K_2SO_4 + S + 3MnO + MnO_2 + 3H_2O$$

$$2MnO_4^- + CN^- + 2OH^- \rightarrow 2MnO_4^{2-} + CNO^- + H_2O$$

The above mentioned oxidations proceed most quickly in alkaline solutions (41).

Studies have shown that oxidation of organic refractories result in minimal removal (38) although better results have occurred when manganese(II) was present within organic complexes (7).

Because insoluble manganese compounds are formed with permanganate addition, filters and coagulants are necessary for treatment. Chlorine addition has been found to be necessary before permanganate is added in order to satisfy the chlorine demand and reduce permanganate requirements (42).

Hydrogen Peroxide

Use of hydrogen peroxide as an oxidant has been found to be effective when ferrous iron is added as a catalyst (40). Ferrous iron is oxidized by hydrogen peroxide as follows:

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$$

The ferric iron formed then hydrolyzes:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

Iron-catalyzed hydrogen peroxide oxidation has been found to occur best in alkaline solutions with pH adjustment made by addition of calcium hydroxide (40).

Ozone

Ozone is a very powerful oxidizing agent that reacts quickly with many compounds such as iron, manganese, phenol, and cyanide. Other applications include color, taste, and odor removal. Because ozone is unstable it must be generated on site.

Several considerations must be taken into account when ozonation is used, such as (37):

1. Effectiveness of ozonation is influenced by the nature and concentration of pollutants.

2. The wastewater pH and temperature control the ozone reactivity efficiency. Ozone is more stable in alkaline solutions because of the catalytic decomposition of ozone by hydroxide ions. The reactivity of oxidizable material may also be influenced by the wastewater pH. High temperatures cause ozone instability.

3. The most efficient ozone loading and contact time are dependent on the nature of the wastewater, the degree of oxidation needed, and the efficiency of the ozone-wastewater contactor.

4. The extent and efficiency of ozonation is determined by the economics of the contactor system.

Literature contains several successful ozonation results. Coking plant effluent, with phenol concentration of 2000 mg/l, has been oxidized with 1.7 gm ozone per gm phenol causing a phenol content reduction to less than one mg/l (43). Because of high ozone generation costs, it has been suggested that sulfides, cyanides, and thiocyanates should be removed before applying ozone treatment (44).

Refinery effluent has been successfully treated with ozone with phenol concentrations being reduced from 11,600 to 2.5 mg/l by applying one mg ozone per mg phenol (40). Refinery wastes have also been treated with ozone after biological oxidation with satisfactory results (45). Best results were at pH 6 to 7 at which the effluent TOC concentration was reduced from 25 to six mg/l. Similar decreases were noted at other pH values but COD values remained the same.

Ozone/ultrasonic treatment has been used for phosphorus, manganate, and cyanide removal--with best results when used as a tertiary process (46, 47). Trace metal removal has also been successful by ozonation (48).

In other work, ozonation of Synthane gasifier waste effluent reduced TOC concentrations from 5800 to 3600 mg/l by applying 0.51 mg ozone per mg TOC (49).

Although ozone is capable of oxidizing many substances, high costs limit possible applications mostly to tertiary processes (43) or individual waste streams (50). The relative cost of chlorine: hypochlorite:ozone treatments is found roughly to be 1:2:3 (51).

Bromine Chloride

Chlorine oxidation requires strict pH and chlorine dosage control in order to discourage the formation of chloroamines and optimize the production of free residual chlorine. Even with proper control there is still uncertainty as to what products are formed from chlorine oxidation, and more importantly, what their harmful effects are.

In 1976, an EPA-funded study on disinfectants at the Wyoming, Michigan, wastewater treatment plant showed that bromine chloride was an acceptable substitute for chlorine (5). Also, in 1978, it was reported that two current field trials have shown that bromine chloride is a more effective disinfectant than chlorine with less toxic effects (52). Because the main reaction in disinfecting wastewater using bromine chloride is oxidation, its use as an oxidant has been explored in the present work.

Oxidation reactions of bromine chloride and chlorine are very similar but the differences that do exist are very important in wastewater treatment. In water, bromine chloride hydrolyzes completely to hypobromous acid as shown below:

$$BrCl + H_2O \rightarrow HOBr + HCl$$

The rate of bromine chloride hydrolysis is more rapid than that of chlorine. This can be attributed to the polarization of bromine chloride (53):

$$\overset{\delta+}{Br} - \overset{\delta-}{Cl}$$

Hypobromous acid is a weak acid and consequently ionizes in water as shown below:

$$HOBr \rightleftarrows H^+ + OBr^-$$

This reaction is not nearly as pH dependent as the hypochlorous acid-hypochlorite ion equilibrium, with over 90 percent of bromine appearing as hypobromous acid at pH 8 (54). Conversely, only 20 percent of chlorine appears as hypochlorous acid at pH 8. Since the hypohalous acids are much stronger oxidants than their respective hypohalite ions, bromine chloride retains most of its oxidative properties at high pH values, unlike chlorine.

Chlorination results in the formation of halogenated organic compounds that are suspected carcinogens. Halogenation by bromine chloride is rare, with these products being relatively unstable (39).

Bromine chloride also has advantages over chlorine when treating wastewater containing ammonia. In this case, monobromoamine and dibromoamine are the products:

$$NH_3 + HOBr \rightarrow NH_2Br + H_2O$$

$$NH_2Br + HOBr \rightarrow NHBr_2 + H_2O$$

The bromoamines have higher activity than the chloroamines and are much less stable, quickly breaking down into harmless species. Also, bromoamines produce much less toxic residuals than chloroamines (39).

Chlorobromination generally costs more than chlorination but less than ozonation. Because of bromine chloride's many advantages as an oxidant, its use in wastewater treatment should become significant in the future.

CHAPTER VI

MATERIALS AND EQUIPMENT

Introduction

Table 2 contains a list of the materials and equipment used in this experimental work, and is divided into two sections, process development and process, for discussion purposes.

The composition of the raw liquor used is given in Table 3. The wastewater is effluent from run RA-65 in which 32 percent moisture Baukol-Noonan lignite was gasified at 400 psig during a 5.25 hour test. Eighty gallons of liquor was collected. Approximately 40 gallons was preserved by freezing in five-gallon plastic containers and the remaining liquor was stored in a 55-gallon drum at ambient conditions.

Process Development

Four coagulants were tested: ferric chloride, ferric sulfate, ferrous sulfate, and alum. All coagulants were applied in the form of aqueous solutions. Coagulation tests (jar tests) were performed with a Bird and Phipps' six-paddle variable speed stirring apparatus and 400 ml beakers.

Four of the oxidants used (sodium hypochlorite, potassium permanganate, hydrogen peroxide, and bromine chloride) were applied as aqueous solutions. Batch oxidation tests accomplished with these oxidants were performed with the six-paddle stirrer and 400 ml beakers.

TABLE 2

EXPERIMENTAL MATERIALS AND EQUIPMENT

PROCESS DEVELOPMENT			
Chemical Processes		Physical Processes	
equipment	material	equipment	material
6-paddle stirrer	$FeCl_3$	ball mill	LCK carbon
400 ml beakers	$Fe_2(SO_4)_3 \cdot 9H_2O$	tray sieves	9LXC carbon
O_3 generator	$Al_2(SO_4)_3 \cdot 14H_2O$	6-paddle stirrer	CAL carbon
O_2 cylinder	$Fe_2SO_4 \cdot 7H_2O$	400 ml beakers	DARCO carbon
gas contactors	5% NaOCl		WV-G carbon
Cl_2 cylinder	2% KM_nO_4		WV-L carbon
BrCl cylinder	50% H_2O_2		WITCARB carbon
wet test meter	BrCl		ROW carbon
	Cl_2		
	O_3		
	O_2		

PROCESS			
Chemical Processes		Physical Processes	
equipment	material	equipment	material
55-gal drum	$Ca(OH)_2$	NH_3 strippers	Pall rings
1/2 hp stirrer	CO_2	carbon contactors	LCK carbon
20-gal container	$FeCl_3$	peristaltic pump	anti-foam sol'n.
var. speed stirrers	H_2SO	gear pump	3-way valves
	BrCl		

TABLE 3

RA-65 RAW LIQUOR COMPOSITION

pH	8.35
Alkalinity (as $CaCO_3$), mg/l	22,575
Ammonia, mg/l	10,115
Cyanide, mg/l	530
Total Sulfur, mg/l	2,265
Sulfide, mg/l	635
TOC: total carbon, mg/l	11,750
inorganic carbon, mg/l	2,500
organic carbon, mg/l	9,250
Phenolic: phenol, mg/l	5,070
o-cresol, mg/l	930
m,p-cresol, mg/l	2,045
Total Dissolved Solids, mg/l	1,275

Bromine chloride and chlorine had a Swagelok fitting and Teflon tubing attached to the Hoke valve outlet on each storage cylinder for ease of application. Ozone is unstable and had to be produced on site using a Welsbach T-23 ozone generator and oxygen (Figure 5). Ozonation and chlorine oxidation tests were performed with 500 ml gas washing bottles with glass fritted spargers and Teflon tubing. A wet test meter was also used to measure oxygen flow in the ozonation tests.

The eight granular activated carbons tested and their respective

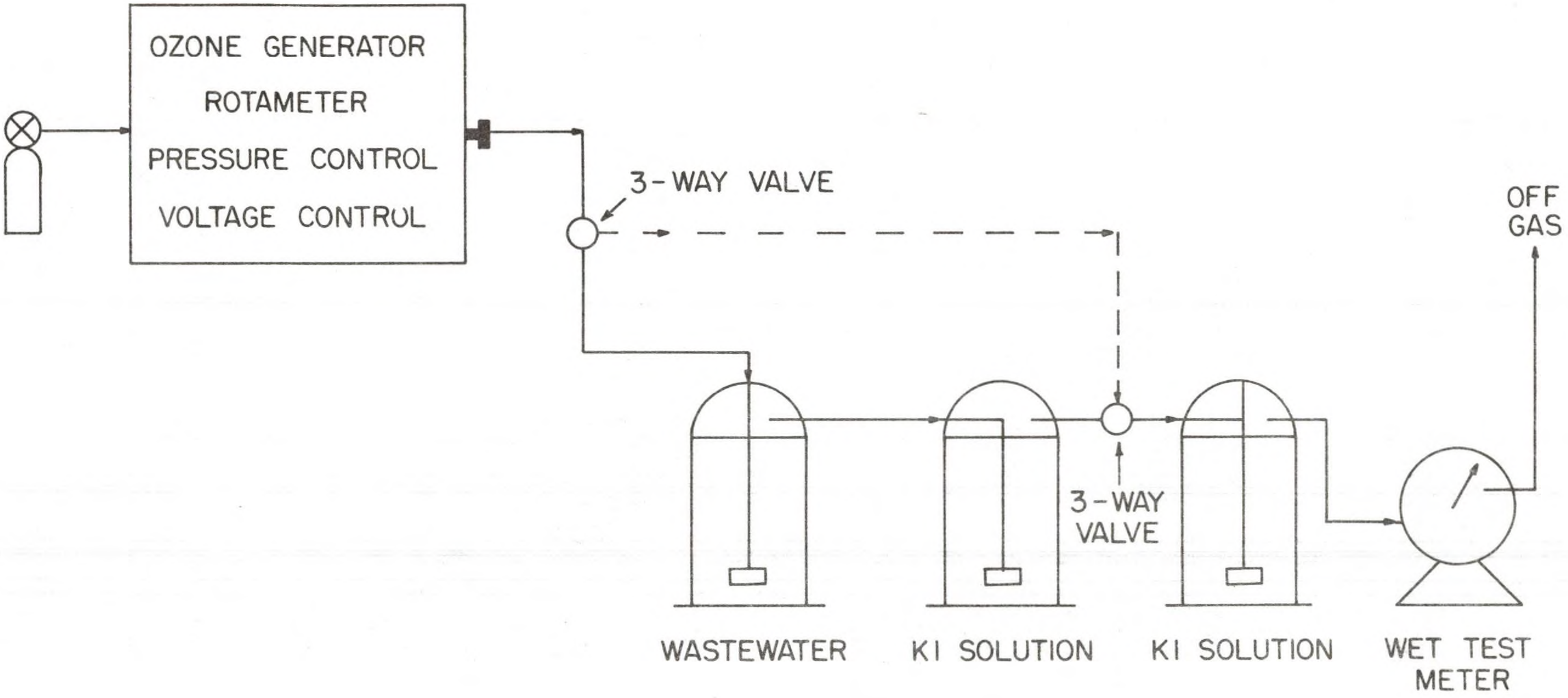

Figure 5. Ozonation schematic diagram.

United States producers are: LCK and 9LXC (Union Carbide), CAL (Calgon), ROW (Norit), HYDRODARCO 4000 (ICI United States), WV-G and WV-L (Westvaco), and WITCARB (Witco). Some specifications and physical properties of these carbons are listed in Table 4. The equipment used in batch adsorption isotherm tests included a 10-inch ceramic ball mill, ceramic pellets, six-paddle stirrer, and 400 ml beakers.

TABLE 4

SPECIFICATIONS AND PHYSICAL PROPERTIES OF GRANULAR ACTIVATED CARBONS[a]

Carbon	Bulk Cost $/lb	Mesh Size	Surface Area, m^2/g	Bulk Density, lb/ft^3	% Ash	% Moisture
LCK	0.54	12x28	1,000	25.5	2	2
9LXC	1.52	12x28	1,300	24	3	2
WV-G	0.65	12x40	1,100	28	1	2
WV-L	0.60	8x30	1,000	30	1	2
CAL	0.65	12x40	1,000	27.5	10	2
WITCARB	0.55	12x30	1,000	31	1	1
DARCO	0.445	12x40	600	23.5	18	9
ROW	0.85	0.8mm pellet	1,000	22.5	6	2

[a] SOURCES: Manufacturers' literature.

Process

Three variable speed stirrers and a 20-gallon plastic container were used for recarbonation, coagulation, bromine chloride oxidation, and pH adjustment. Lime pretreatment was accomplished with a 1/2 horsepower twin-bladed stirrer and a 55-gallon drum.

Two acrylic columns were used for stripping ammonia from the liquor (Figure 6). These columns were four feet high and had inside diameters of six and 6-1/2 inches. A porous acrylic plate was inserted two inches from the bottom of each column. The stripping columns were completely open at their tops and were packed with Norit 3/8 inch plastic Pall rings. Other material and equipment used for air stripping ammonia included a peristaltic pump, gear pump, "Rug Doctor" anti-foam solution, and tubing.

Four acrylic columns, each 38 inches high with inside diameters of 1-1/4 inches, were used as granular carbon contactors (Figure 7). A porous acrylic plate was inserted one inch from each end of the four columns. Each column also contained one side and two end 1/8 inch diameter outlets. Other equipment and materials used in the carbon contactor system included LCK carbon, three-way glass valves, persistaltic pump, five-gallon plastic containers, and tubing.

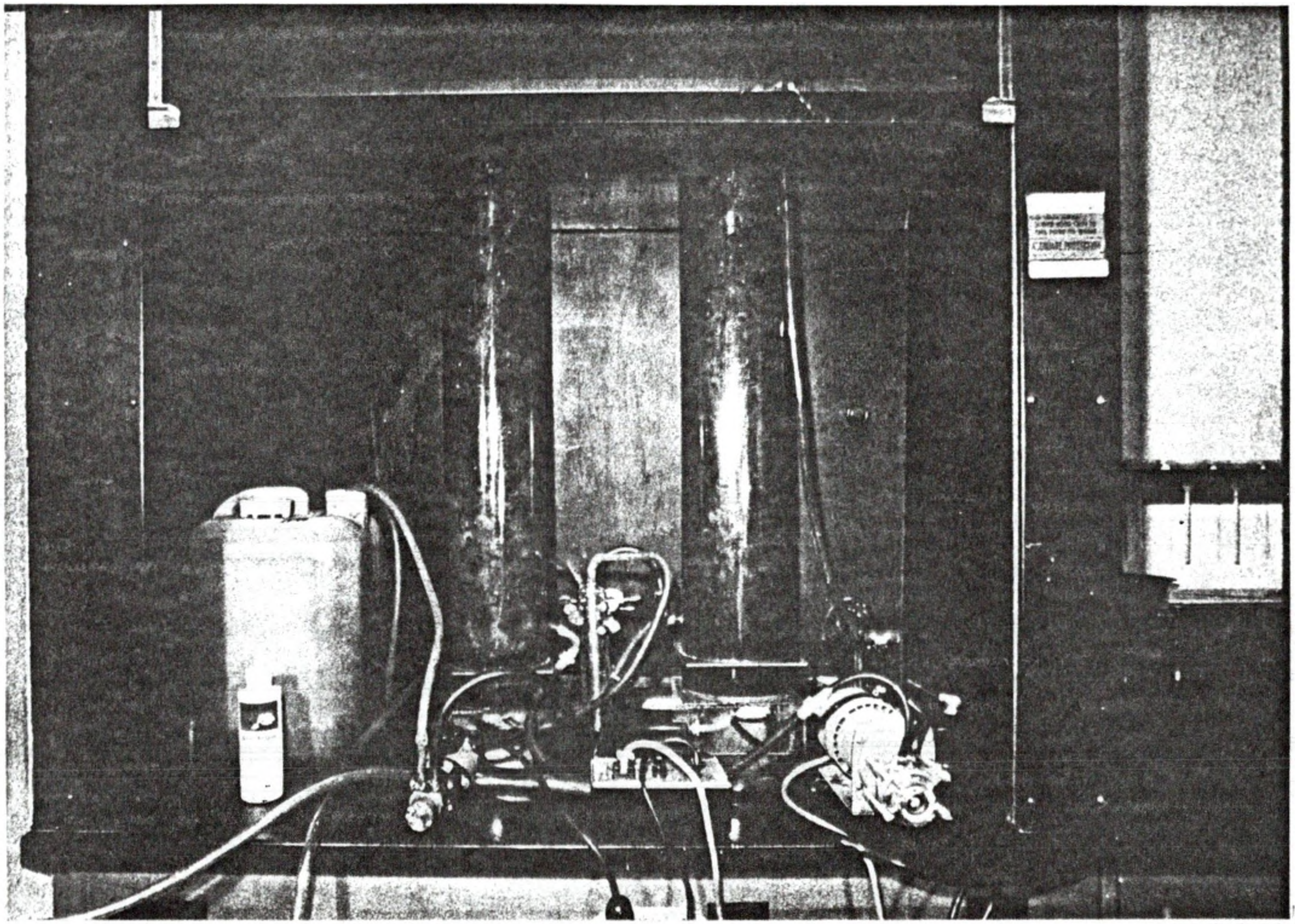

Figure 6. Experimental ammonia stripping system.

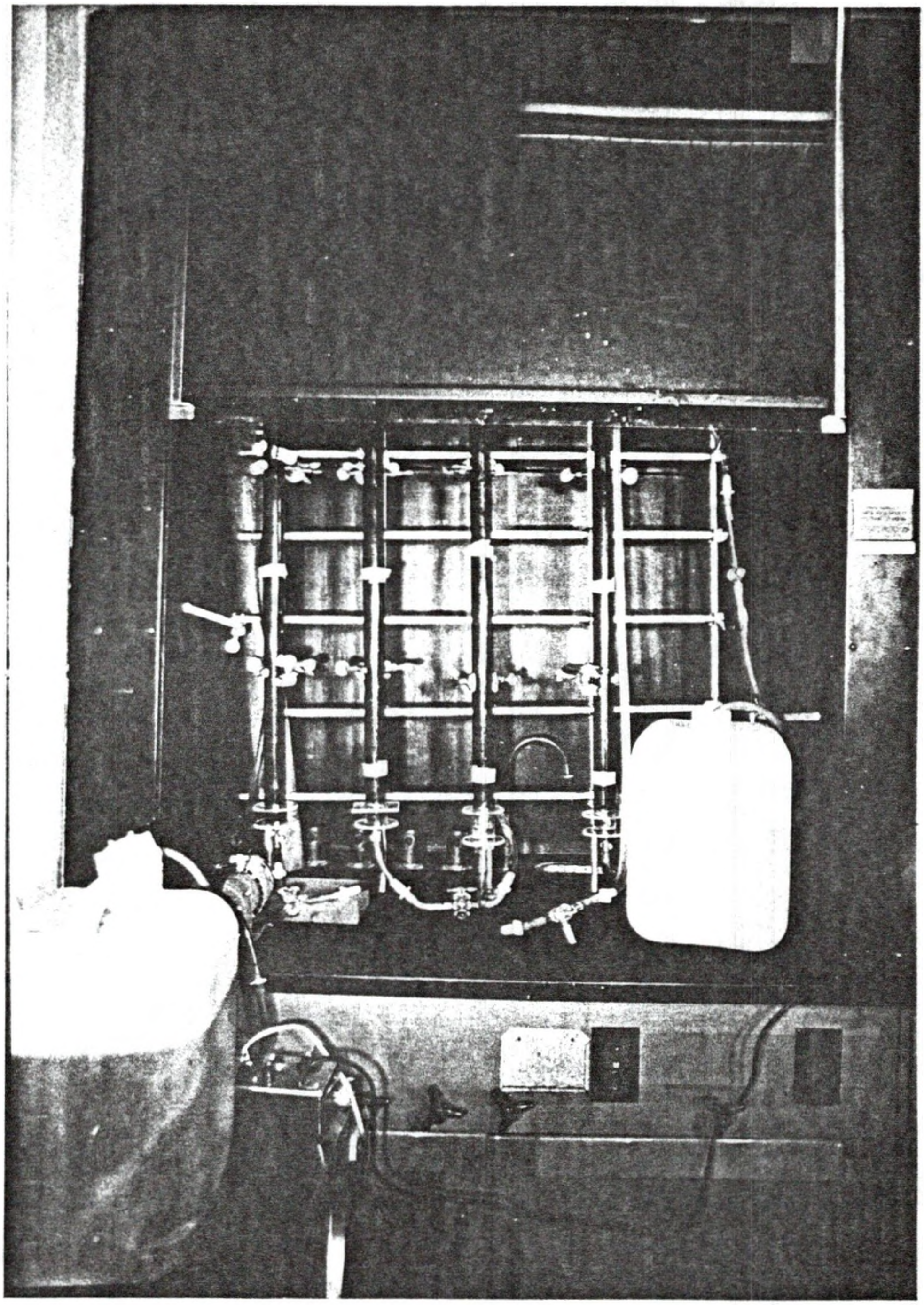

Figure 7. Experimental carbon contacting system.

CHAPTER VII

EXPERIMENTAL PROCEDURE

Introduction

The 40 gallons of raw liquor that was immediately frozen upon receiving was also preserved by freezing between treatment steps. It had been discovered that noticeable oxidation and polymerization occurs if the wastewater is allowed to be in contact with the atmosphere at ambient conditions. In a study done with Hygas coal gasification wastewater, no significant changes in composition were observed through as many as four freeze-thaw cycles (55). Only cyanide underwent any change because it degrades quickly. Consequently, cyanide should not appear in the treated effluent anyway.

The unpreserved liquor was generally used for process development. Because of the limited amount of available liquor, and of the need for large quantities for continuous carbon contactor tests, only experiments that were felt to be essential were performed with the RA-65 liquor.

Rationale for Pretreatment Scheme Selection

As noted in Table 3, the raw liquor has high alkalinity and TOC content. It was decided that dissolved tars and oils should be removed first before any carbon adsorption and/or oxidation could be applied. These easily removable organics would cause unnecessary high carbon and/or oxidant requirements. Lime treatment has proved to be successful in other slagging gasifier wastewater studies for removal of dissolved tars, dissolved oils, and alkalinity removal (56). Lime addition was therefore selected as the first pretreatment step.

Ammonia reacts with certain oxidants to form unwanted amines. In order to strip ammonia from an aqueous solution the pH must be high enough to free the ammonia. Hence, enough lime was added in the pretreatment to raise the pH above 11.5 so ammonia could be air stripped.

Raising the wastewater pH above 11.5 also precipitates bicarbonate, phosphate, and magnesium ions from the water:

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H_2O$$

$$5Ca^{2+} + 3H_2PO_4^- + 7OH^- \rightarrow Ca_5OH(PO_4)_3 + 6H_2O$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$

After lime addition and ammonia stripping, pH adjustment was accomplished by recarbonation because this process causes precipitation of excess calcium ions to lower liquor alkalinity:

$$Ca^{2+} + CO_2 + 2OH^- \rightarrow CaCO_3 + H_2O$$

Coagulation was chosen for liquor clarification because it is a simple, economical process.

The pretreatment scheme chosen can be shown as follows:

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

The pretreated liquor was used for all subsequent tests.

Rationale for Treatment Scheme Selection

Five potential treatment schemes were considered:

1. (pretreated liquor) → chemical oxidation → coagulation → (treated liquor)
2. (pretreated liquor) → carbon adsorption → (treated liquor)
3. (pretreated liquor) → chemical oxidation → coagulation → carbon adsorption → (treated liquor)
4. (pretreated liquor) → carbon adsorption → chemical oxidation → coagulation → (treated liquor)
5. (pretreated liquor) → carbon adsorption → chemical oxidation → carbon adsorption → (treated liquor).

Batch tests showed that the fourth scheme gave the best result in terms of final TOC content. Therefore, this particular flow scheme was chosen for all future experimental work.

Experimental Pretreatment Procedure

A total of 11.7 pounds of lime was added to 40 gallons of raw RA-65 liquor to raise the liquor pH from 8.5 to 12.0. The slurry was agitated for 40 minutes and settled for one hour before decanting the treated liquor.

Five gallons of lime-treated liquor was stripped of ammonia at one time. As seen in Figure 6, the two stripping columns were attached in series. The liquor was circulated through the system by means of a peristaltic pump and a gear pump. The liquor flow rate to the stripping columns was maintained at about 60 ml/min. Approximately 1-1/2 fluid ounces of anti-foam solution was added to the columns per five-gallon batch. As ammonia was being stripped, small dosages of lime were repeatedly added to sustain a pH level above 11.5. Periodically, liquor samples were taken to determine ammonia concentrations. Stripping was continued until the ammonia concentration was reduced to about 200 mg/1.

Recarbonation was accomplished by bubbling carbon dioxide through wastewater in a 20-gallon container until a pH of 7.5 was attained.

Coagulation jar tests were performed with coagulant dosages ranging from five to 10,000 mg/1 and pH values of 7.5, 8.0, 9.0, and 11.5. The chemicals were added rapidly and the liquor was stirred at 100 rpm for three minutes, 20 rpm for 15 minutes, and then allowed to settle for one hour. Coagulation results were judged on the appearance of the supernatant liquor and the settleability of the floc. The clarified liquor was decanted for future treatment.

Coagulation of the preserved recarbonated liquor was performed by adding 25 mg/1 ferric chloride to two batches of liquor in the 30-gallon container. Stirring rates and times were the same as in the jar tests.

Experimental Treatment Procedure

Batch Activated Carbon Contact Time Tests

Granular carbon was pulverized to minus 325 mesh and oven dried for three hours at 150°C for contact time tests. Ten grams of the powdered carbon was added to 250 ml of pretreated liquor and agitated at 100 rpm. Two ml samples were taken at time intervals of 2-1/2, 5, 7, 10, 15, 20, 25, 30, and 120 minutes and immediately filtered through 0.45 micron pore size filter pads to remove all of the activated carbon. TOC analysis was then performed on all samples.

Adsorption Isotherm Tests

These tests were performed at pH levels of 2.2 and 7.5 to determine the potential adsorptive capacity of the various activated carbons. The pulverized and dried activated carbon was divided into samples weighing 1/2, 1, 2, and 4 grams. These weighed samples were transferred to four beakers, each containing 100 ml of pretreated liquor. The liquor samples were then agitated for 30 minutes before samples were taken and filtered through 0.45 micron filter pads. TOC analysis was performed on all samples. Isotherm tests were repeated for all eight commercial carbons.

Continuous Carbon Contacting Tests

For the carbon contacting tests, approximately 1400 grams of granular LCK carbon was boiled in water for at least two hours. The degassed carbon was cooled and charged to the columns as a slurry, making sure a layer of water was always above the carbon during charging. After completely filling each column, all connecting tubing was filled with water to avoid formation of air pockets. Any air buildup during the run was released through the vents located near the top of each column.

After connecting the four columns in series (Figure 7) the test was begun by adjusting the liquor flowrate to 64.5 ml/min (2 gal/(min)(ft^2)) by means of the peristaltic pump. Hourly samples were taken from the three-way glass valves located after each column. The run was terminated when the effluent from the first column approached the same TOC content as the pretreated liquor, or until all liquor had been treated.

Oxidation Tests

The oxidation tests using oxidants applied as aqueous solutions (bromine chloride, sodium hypochlorite, potassium permanganate, and hydrogen peroxide) were all done similarly. Aqueous oxidant solutions were added to 200 ml samples of activated carbon-treated liquor. The samples, with initial oxidant concentrations ranging from 100 to 8,000 mg/l oxidant, were agitated at 100 rpm for two minutes and 20 rpm for the rest of the test. Tests were performed at final liquor pH values of 2.2, 4.0, and 8.0. Two ml samples were taken and filtered at 1/4, 1/2, 1, 2, and 4 hour intervals to determine residual oxidant and TOC concentrations.

Chlorine oxidation trials were performed by bubbling chlorine gas through 200 ml of activated carbon-treated liquor in a 500-ml gas washing bottle at six mg chlorine per second and a final pH value of 4.0. The unreacted chlorine was trapped in a 500 ml gas washing bottle containing 200 ml of two weight percent potassium iodide solution. Chlorine dosages applied were approximately 10,000 and 25,000 mg/l chlorine. The potassium iodide solutions were analyzed to determine the amount of chlorine not absorbed by the liquor.

The ozonation tests were performed similarly to the chlorine oxidation trials. The ozone generator was operated at 3.5 psig, 80 volts, and a rotameter-determined flowrate of two standard ft^3/hr for each test. The total volume of oxygen applied per test was determined by a wet test meter connected in series with three 500 ml gas washing bottles (Figure 5) containing 200 ml liquor, 200 ml two weight percent potassium iodide solution, and 150 ml two weight percent potassium idoide solution, respectively. The ozone was contacted with the liquor samples for one and two hours. Initial liquor pH values were 12, 10, and 7.

For each oxidation test, 100 ml of the longest reacting solution (1, 2, or 4 hours) was agitated with 10 grams of powdered LCK carbon at a liquor pH of 7.5. After 30 minutes of agitation at 100 rpm a sample was filtered through a 0.45 micron filter pad and analyzed for TOC content.

Blank Carbon Tests

Ten grams of powdered LCK carbon was also added to 100 ml of liquor that had not been subjected to chemical oxidation. A liquor sample (pH=7.5) was filtered and analyzed for TOC content after 30 minutes of agitation at 100 rpm. This sample is referred to as the blank sample.

Large Batch Process Tests

The pH adjustment of the pretreated liquor from 7.5 to 2.2 was accomplished by adding concentrated sulfuric acid slowly to two 15-gallon batches of liquor in the 20-gallon container. Three variable speed stirrers were used to agitate the liquor.

The large batch bromine chloride oxidations were performed by adding 500 mg/l bromine chloride to two 15-gallon quantities of liquor. The solution was agitated fast for five minutes, slow for 85 minutes, and settled for 15 minutes before decanting the supernatant liquor. The sludge was dried and weighed.

Before the final continuous carbon contacting run, the liquor pH was adjusted from 2.2 to 7.5 by adding 200 mg/l lime for two 15-gallon batches. The liquor was agitated fast for five minutes, slow for 25 minutes, and settled for 15 minutes before decanting the supernatant liquor and weighing the dried sludge.

Liquor Analysis

The extent of lime addition, sulfuric acid addition, and recarbonation was determined by pH measurements. During the ammonia stripping process periodic analyses were made to determine the residual ammonia concentration in the wastewater. Ammonia analysis was done using the ammonia nitrogen/acidimetric method in Standard Methods (57). Coagulation effectiveness was judged purely by floc appearance and settleability.

For all activated carbon treatments, i.e., contact time, adsorption isotherm, and continuous column tests, the wastewater was analyzed only for TOC content. This analysis was performed using a Beckman Model 915A Total Organic Carbon Infrared Analyzer. TOC content was calculated as the difference between the total carbon and inorganic carbon contents determined by the analyzer.

All residual oxidant concentrations, except permanganate, were determined by the iodimetric method as described in Standard Methods (57). Permanganate residuals were determined by spectrophotometric absorption at a wavelength of 526 nm on a Bausch and Lomb Spectrophotometer 21.

The more extensive liquor analyses after each process step were performed by Stearns and Roger's chemists. These parameters, excluding the above mentioned ones, are listed below along with methods of analysis in Table 5.

TABLE 5

ANALYTICAL METHODS FOR WASTEWATER CHARACTERIZATION

Parameter	Method of Analysis
Alkalinity	Acid titration to pH 4.2 (57)
Sulfide	Silver sulfide-silver electrode test (57)
Total sulfur	Combustion iodimetric titration (58)
Phenol	Gas chromatography (57)
m, p-cresol	Gas chromatography (57)
o-cresol	Gas chromatography (57)
Total Dissolved Solids	Total suspended matter (57)

CHAPTER VIII

EXPERIMENTAL RESULTS AND DISCUSSION

Pretreatment

Table 6 includes the liquor analyses after three pretreatment steps: lime treatment, ammonia stripping, and recarbonation-coagulation. The raw liquor analysis was presented in Table 3.

The pretreatment scheme seemed to show the best results in alkalinity removal, with 59 percent removal achieved by the lime addition step and an overall pretreatment alkalinity removal of over 96 percent.

Cyanide and sulfide concentrations were reduced to zero because of a combined effect of lime addition and liquor degradation. Phenolic, ammonia, and TOC concentrations were reduced by 53, 98, and 38 percent, respectively, by the pretreatment scheme.

The recarbonation-coagulation step was not very effective in organic removal as the TOC content was decreased by only five percent.

Overall, pretreatment sufficiently purified the raw liquor so that oxidation and activated carbon adsorption could be applied as secondary and tertiary treatment.

Treatment

Batch Activated Carbon Contact Time Tests

A typical batch contact time curve is represented in Figure 8.

TABLE 6

PRETREATMENT ANALYSES

	Lime Treated	Ammonia Stripped	Recarbonated-Coagulated
pH	12.2	11.6	7.5
Alkalinity (as $CaCO_3$), mg/l	9,250	4,025	875
Ammonia, mg/l	5,235	240	180
Cyanide, mg/l	5	0	0
Total Sulfur, mg/l	1,750	1,415	1,300
Sulfide, mg/l	0	0	0
TOC: total carbon, mg/l	6,450	6,230	5,920
inorganic carbon, mg/l	250	215	180
organic carbon, mg/l	6,200	6,015	5,740
Phenolic: phenol, mg/l	3,025	2,870	2,475
o-cresol, mg/l	475	420	390
m,p-cresol, mg/l	1,035	970	885
Total Dissolved Solids, mg/l	9,610	7,315	2,700

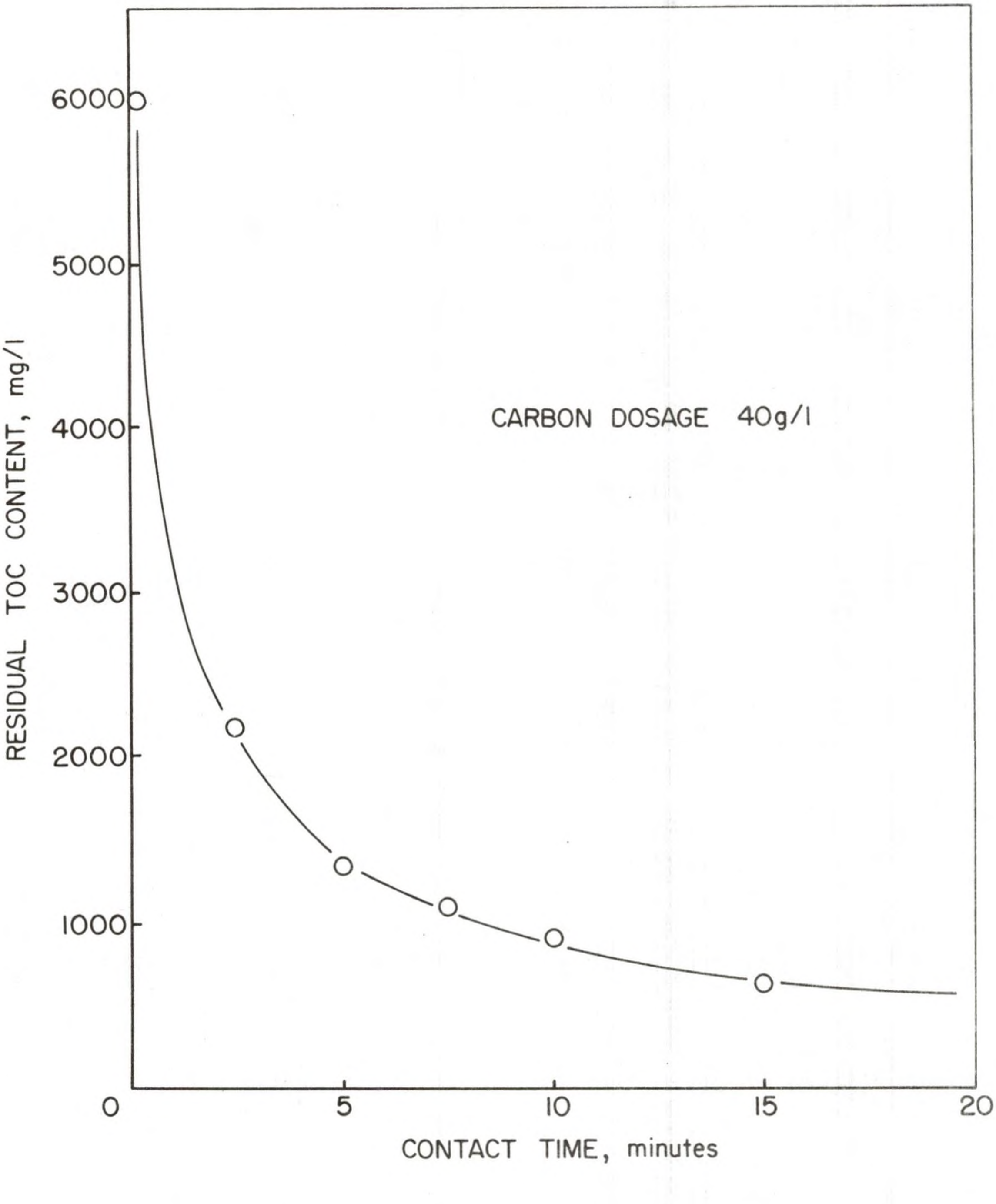

Figure 8. Batch contact time test.

The TOC content of pretreated liquor is decreased from 6015 mg/l to a near steady state value of 620 mg/l in 20 minutes by the addition of 40 gm/l powdered LCK carbon. To ensure that steady state conditions were achieved in all subsequent batch adsorption tests, a 30 minute contact time was used.

Adsorption Isotherm Tests

Figures 9 through 16 depict adsorption isotherm tests for all eight activated carbons at two pH levels, 2.2 and 7.5. The isotherm results are seen to fit the straight line Freundlich plots. A higher adsorption capacity is found to occur at pH 2.2 for all eight carbons.

Tables 7 and 8 are developed from the isotherm data. Carbon bulk costs were obtained from each producer and represent January, 1979, prices. The theoretical usage rates are related to the isotherms' TOC adsorbed per unit weight carbon values at an equilibrium TOC concentration of 6015 mg/l, i.e., the initial liquor concentration (sample calculation in Appendix A). Annual carbon costs were determined by allowing a three percent loss during regeneration. Costs were based on a production rate of 250 million ft^3/day methane. The carbon found most economical for treating the wastewater was LCK from Union Carbide.

By comparing LCK's annual cost at the two pH levels, the cost at pH 2.2 is seen to be $860,000 per year less than that at pH 7.5. The extra cost of sulfuric acid and lime additions for pH adjustments would be $303,000 per year. Hence, a net savings of approximately $557,000 per year would be realized by lowering the pretreated liquor pH to 2.2 before carbon adsorption. The additional capital costs be-

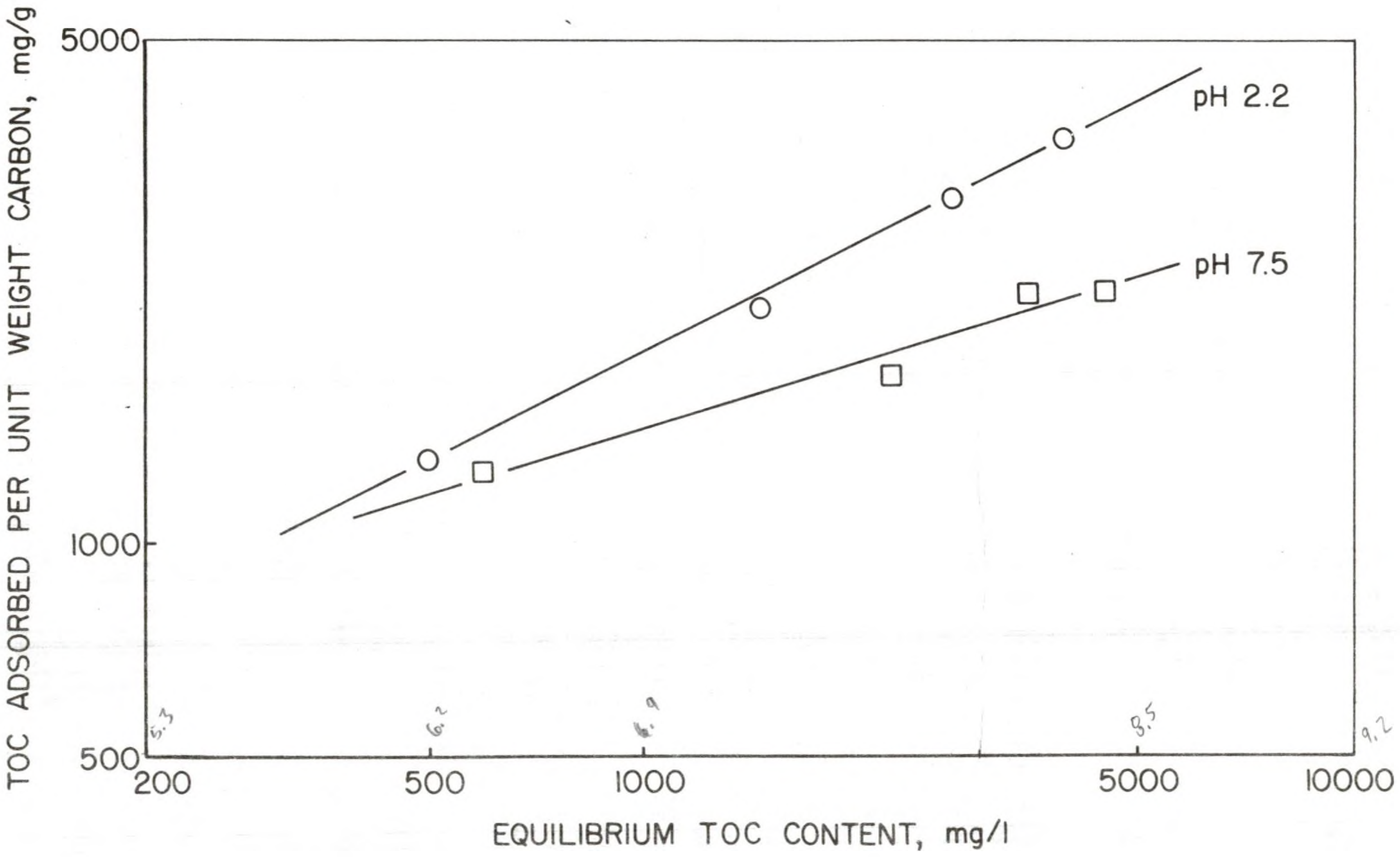

Figure 9. Adsorption isotherm using LCK activated carbon.

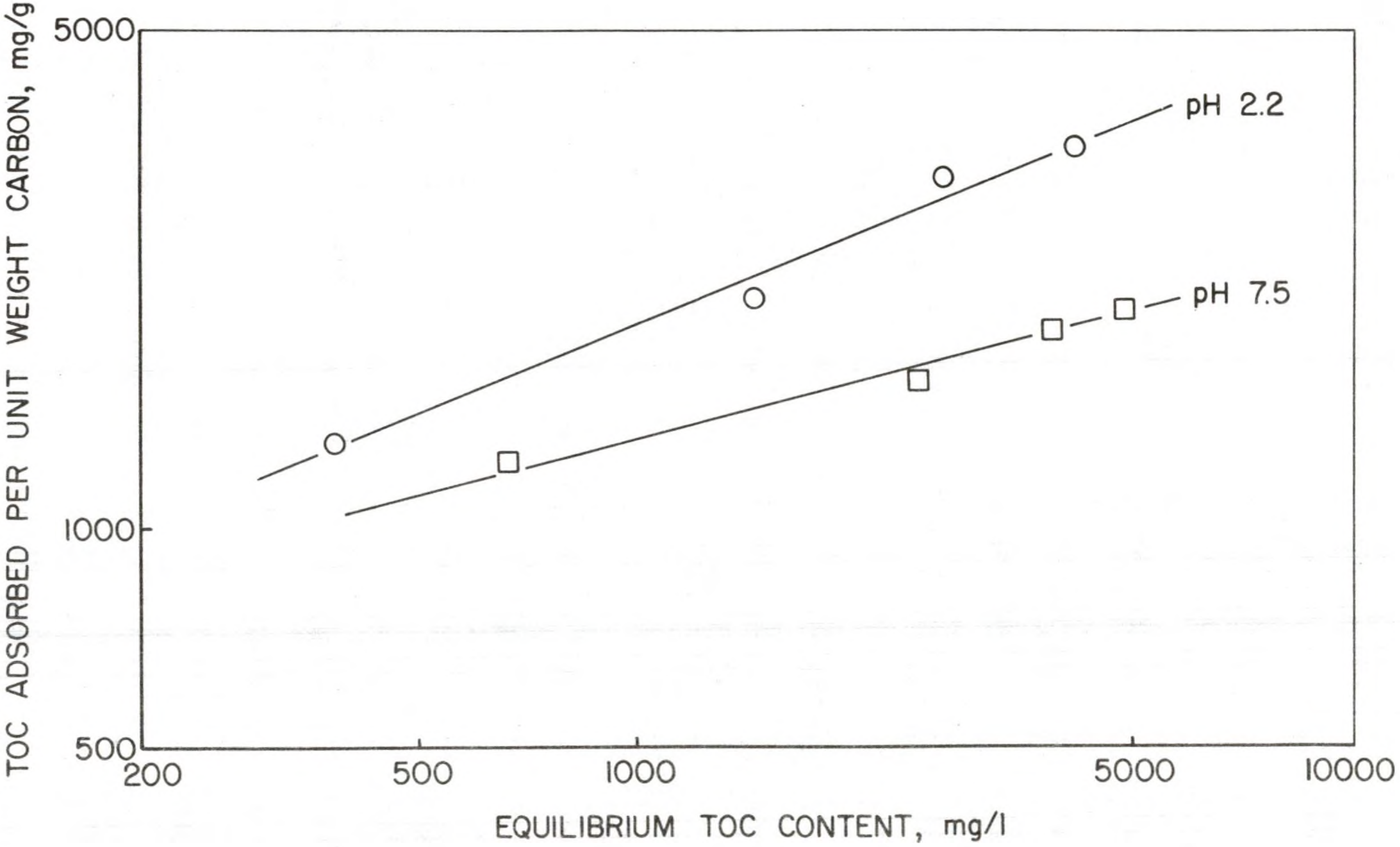

Figure 10. Adsorption isotherm using 9LXC activated carbon.

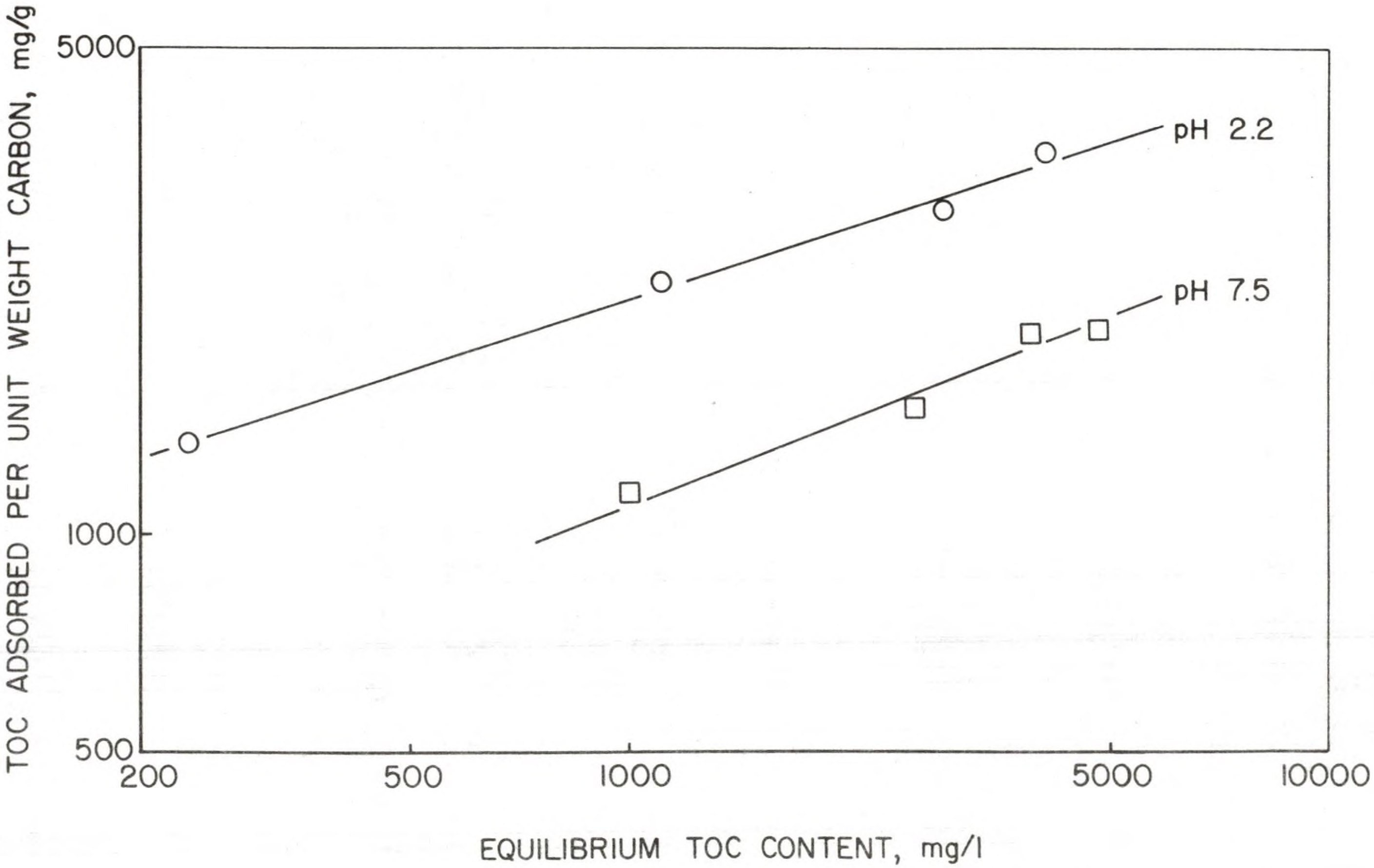

Figure 11. Adsorption isotherm using WV-G activated carbon.

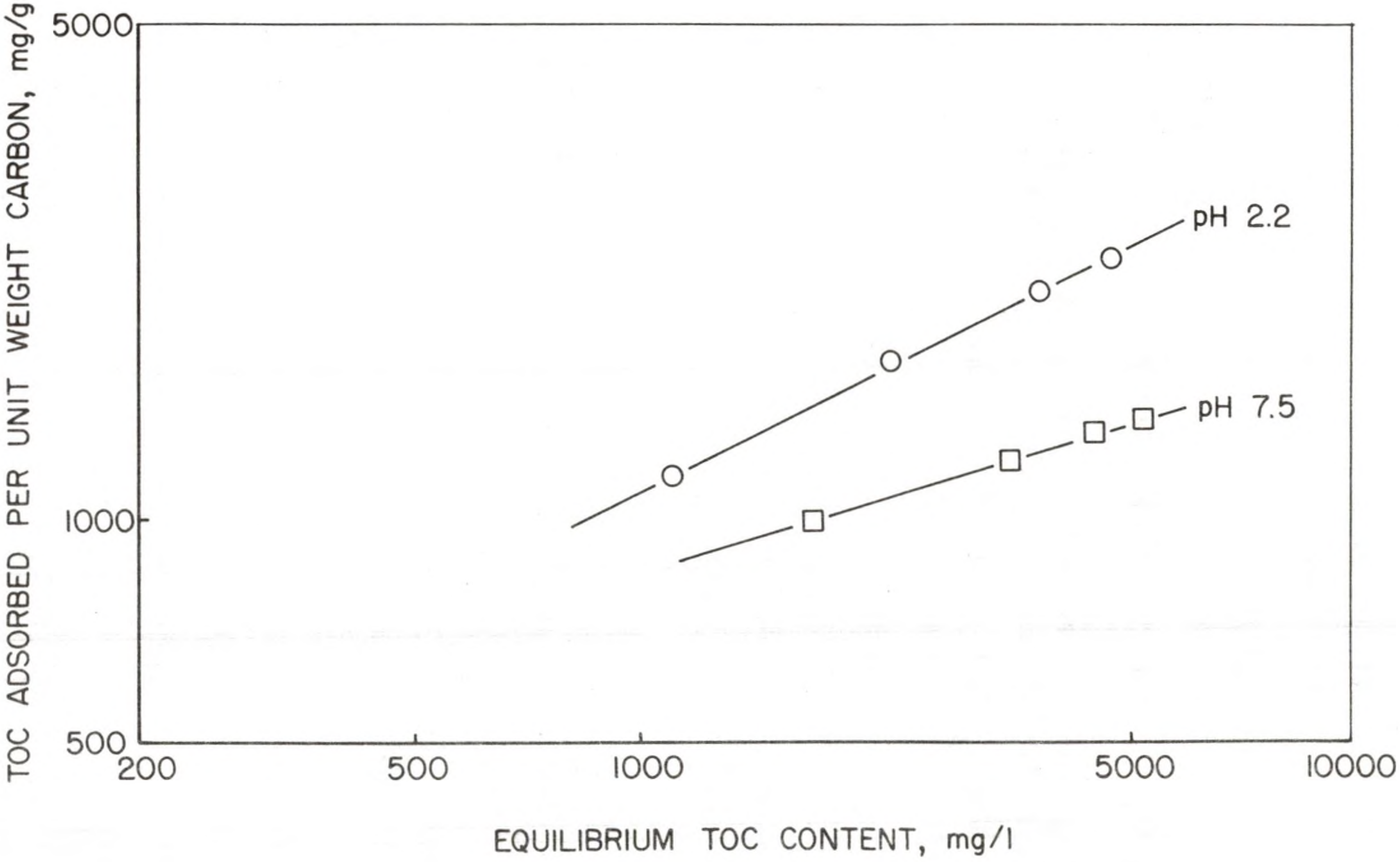

Figure 12. Adsorption isotherm using WV-L activated carbon.

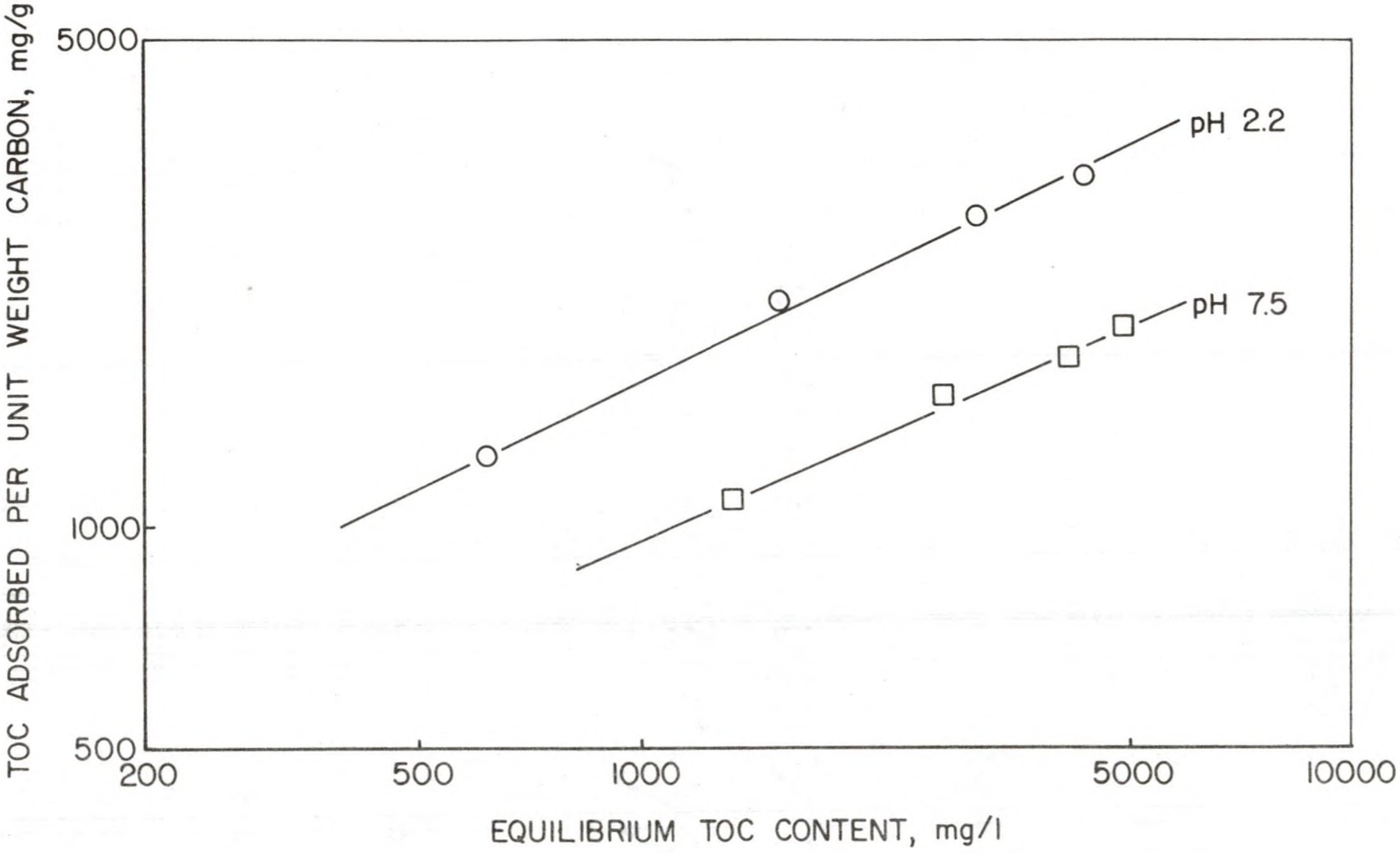

Figure 13. Adsorption isotherm using CAL activated carbon.

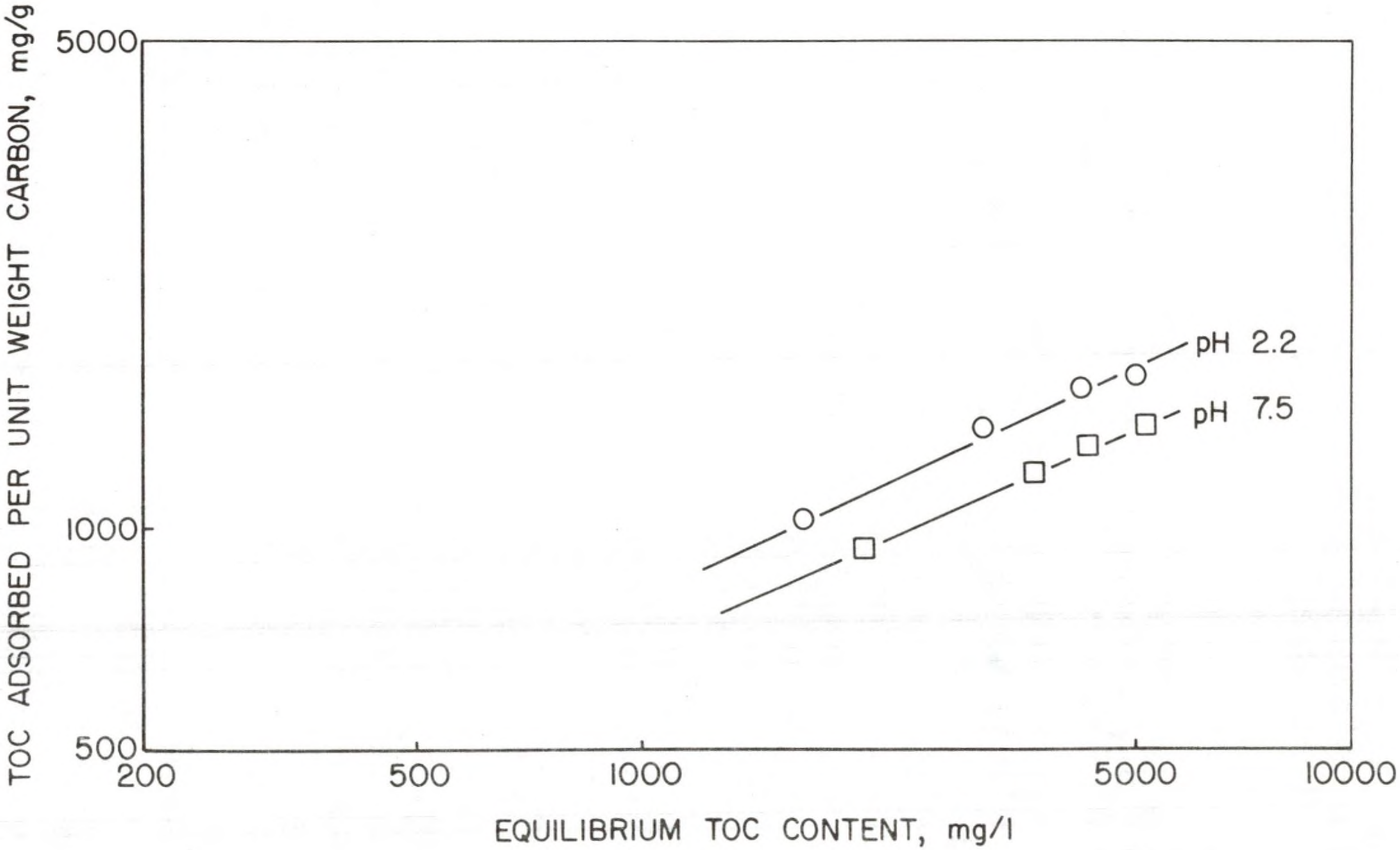

Figure 14. Adsorption isotherm using WITCARB activated carbon.

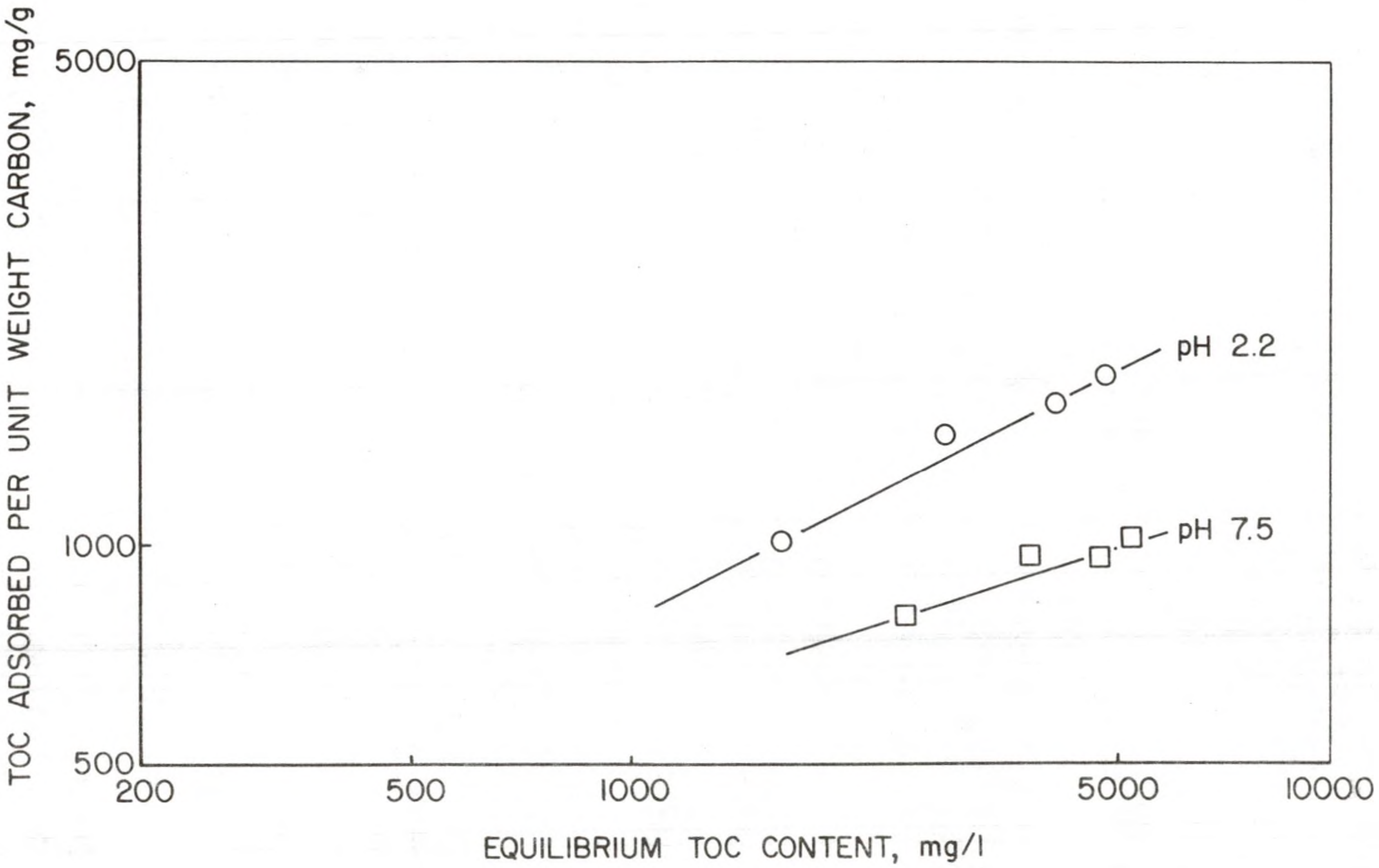

Figure 15. Adsorption isotherm using HYDRODARCO 4000 activated carbon.

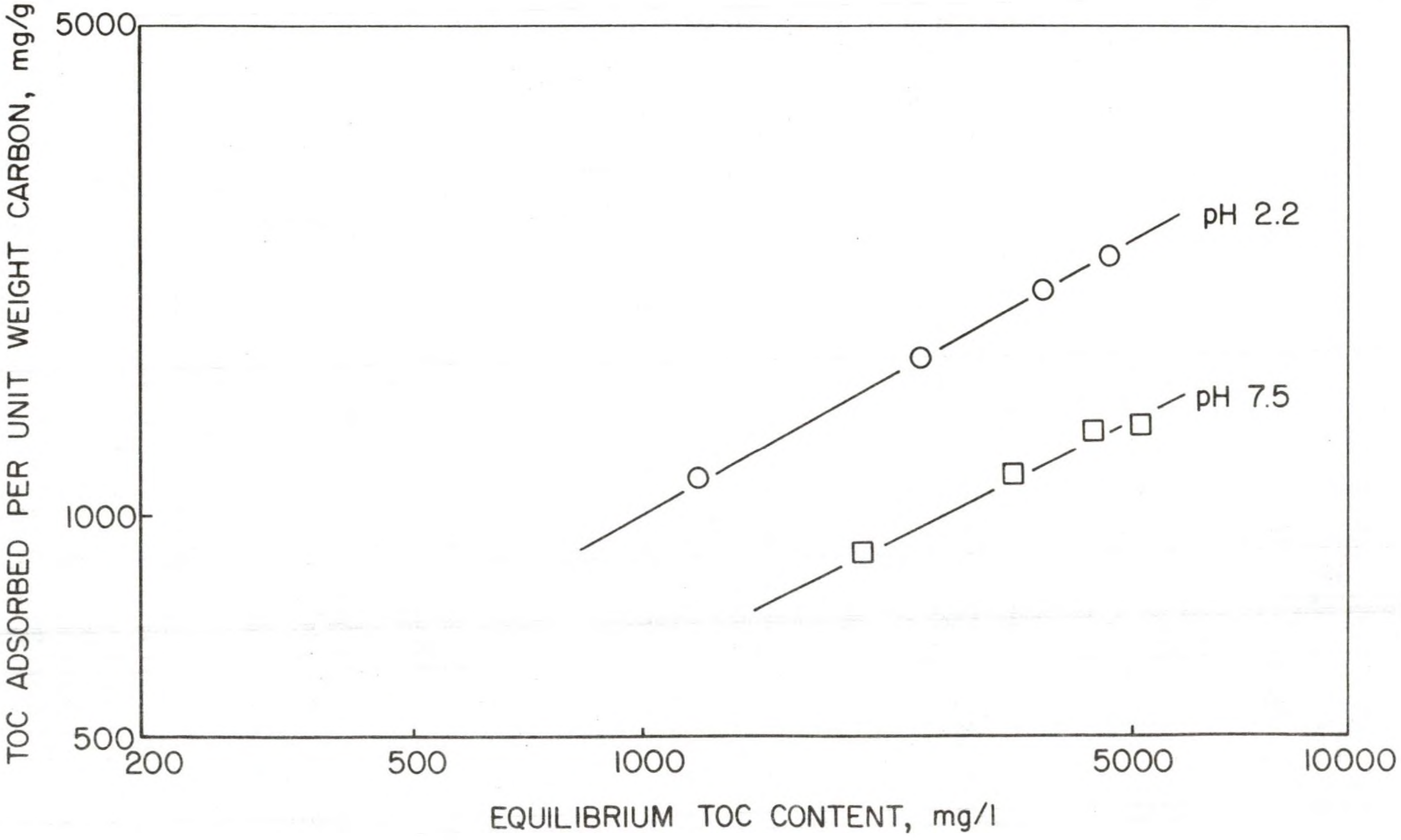

Figure 16. Adsorption isotherm using ROW activated carbon.

TABLE 7

COMPARISON OF ANNUAL CARBON COSTS (pH 7.5)[a]

Carbon	Bulk Cost, $/lb	Theoretical Usage Rate, lb/1000 gal	Annual Carbon Cost, million $
LCK	0.54	185.9	2.07
9LXC	1.52	222.6	6.99
WV-G	0.65	212.6	2.85
WV-L	0.60	334.3	4.14
CAL	0.65	236.8	3.18
WITCARB	0.55	339.3	3.85
DARCO	0.445	456.0	4.19
ROW	0.85	327.6	5.75

[a] Annual carbon costs based on a production rate of 250 million standard ft^3/day methane.

TABLE 8

COMPARISON OF ANNUAL CARBON COSTS (pH 2.2)[a]

Carbon	Bulk Cost, $/lb	Theoretical Usage Rate, lb/1000 gal	Annual Carbon Cost, million $
LCK	0.54	108.4	1.21
9LXC	1.52	120.0	3.77
WV-G	0.65	121.7	1.63
WV-L	0.60	180.9	2.24
CAL	0.65	128.4	1.72
WITCARB	0.55	267.6	3.04
DARCO	0.445	246.8	2.27
ROW	0.85	179.2	3.15

[a] Annual carbon costs based on a production rate of 250 million standard ft^3/day methane.

cause of pH adjustment equipment and increasing reactivation furnace capacity are assumed to be nearly the same.

pH Adjustment

RA-65 liquor pH adjustment was accomplished by adding one ml concentrated sulfuric acid per liter of wastewater. This reduced the liquor pH to 2.2.

Continuous Carbon Contacting Tests

Figure 17 shows the breakthrough curves developed from the

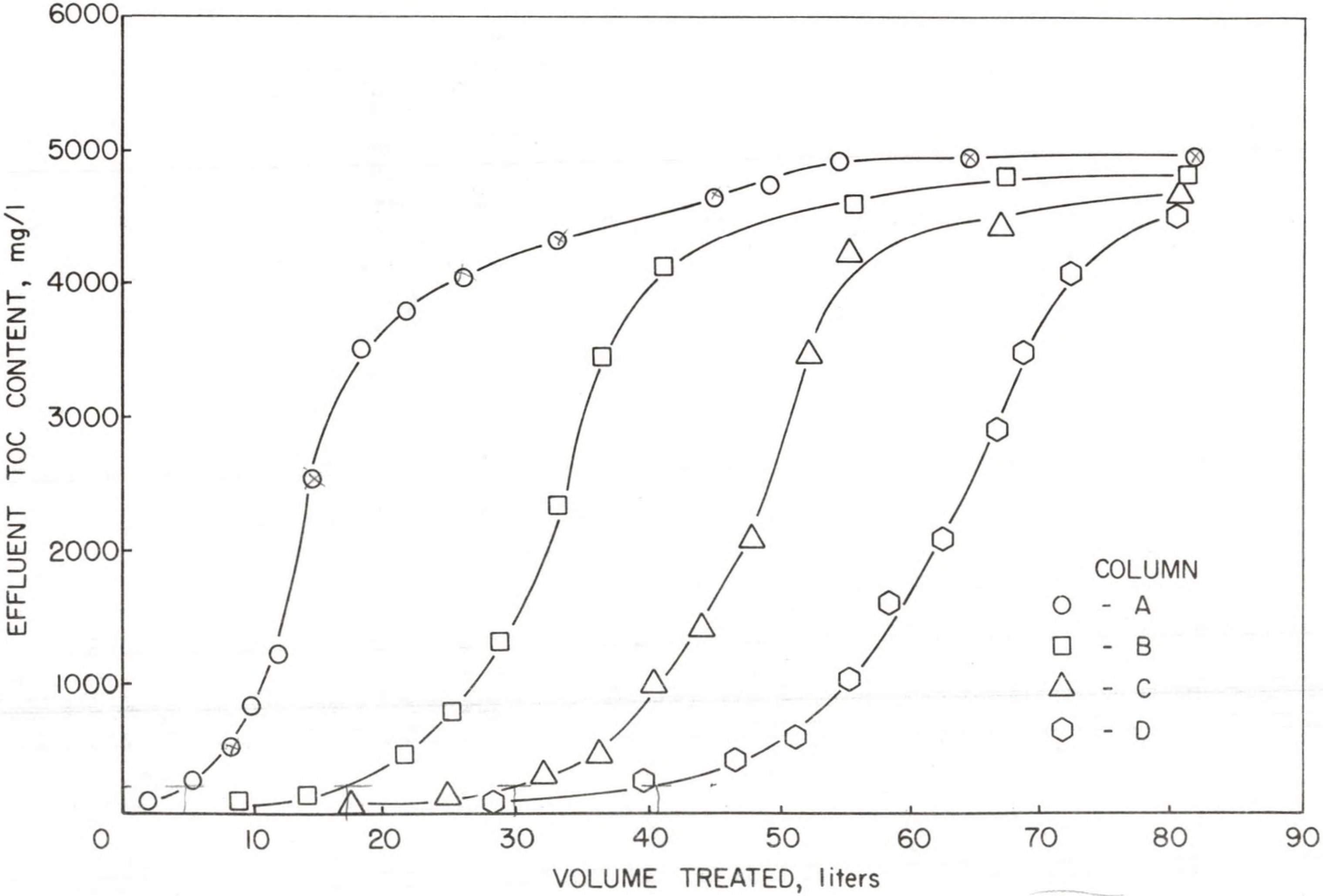

Figure 17. Breakthrough curves for four column system (pH 2.2).

granular carbon continuous test on the acidified pretreated liquor. The velocity of the mass transfer zone was fairly constant throughout the test as shown by the nearly parallel rising slopes after breakthrough. The abrupt change in slope directly after breakthrough (at approximately 500 mg/l residual TOC) indicates efficient carbon usage. A slower rising breakthrough curve would mean that the carbon would still have a large amount of adsorptive capacity remaining which would not be utilized after breakthrough.

The results from Figure 17 were used to develop the dosage curves shown in Figure 18. Dosage curves for liquor carbon-treated to TOC values of 100, 200, 400, and 1000 mg/l are shown. It can be seen that as the effluent TOC content approaches the influent concentration, the carbon dosage curves approach the isotherm value of 13 gms/liter.

From Figure 18, an effluent containing 200 mg/l TOC and a superficial contact time of 34 minutes was chosen as the design point for the first activated carbon treatment. A carbon dosage of 32 gm/l is seen to be required at these conditions. These dosage curves represent a one column system. For a multiple column system reactivation would not be required as frequently, therefore, a carbon dosage of 30 gm/l was predicted for design purposes.

Oxidation Tests

The results of batch oxidation tests using potassium permanganate, sodium hypochlorite, hydrogen peroxide, and chlorine are summarized in Table 9. The liquor used in these tests was unpreserved pretreated wastewater that had been carbon-treated to a TOC concentration of 700 mg/l.

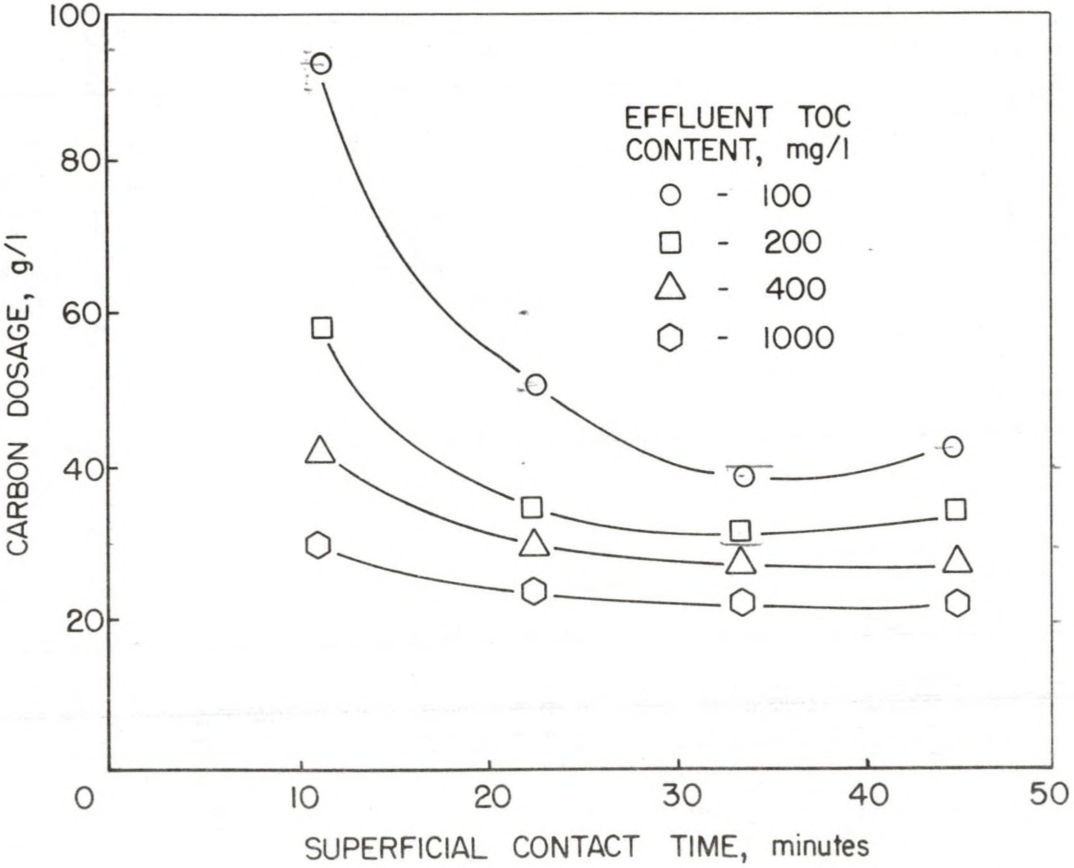

Figure 18. Dosage curves for single fixed-bed (pH 2.2).

TABLE 9

RESULTS OF BATCH OXIDATION TESTS

Initial Liquor Concentration: 700 mg/l TOC
Range of Contact Time: 1/4 - 4 hours
TOC Content After 100 gm/l Carbon: 185 gm/l

Oxidant	Range of Oxidant Concentrations, mg/l	Liquor pH	Avg. % TOC Removal	Avg. % After 100 g/l Carbon
$KMnO_4$	200 - 8,000	4,8.5	0.5	-5
NaOCl	1,000 - 8,000	4	4	+5
H_2O_2	4,000 - 8,000	4,8.5	0.7	0
Cl_2	9,000 - 22,400	4	2	+8

For all four oxidants no appreciable increase in TOC removal, before or after carbon adsorption, occurred. No change in residual oxidant concentration took place after a reaction time of four hours.

The same liquor was ozonated for one and two hour intervals as shown in Table 10. Three initial pH levels were tested--12, 10, and 7. Absorption efficiency, determined as the amount of ozone reacted divided by the amount applied, was found to decrease with decreasing initial liquor pH although the TOC removal maximized around an initial pH of 10. TOC levels were reduced to 145 mg/l after batch ozonation and carbon adsorption for both tests with initial liquor pH levels of 10 and 7. This is an overall TOC removal of 79.3 percent. The blank carbon adsorption test reduced the TOC level to 185 mg/l. Not a

TABLE 10

OZONE BATCH OXIDATION TESTS

Initial Liquor Concentration: 700 mg/l TOC

	Liquor pH Before Ozonation			
	12	10	7	10
Reaction Time, hr	1	1	1	2
Final Liquor pH	8.3	8.0	6.8	7.5
Oxygen Applied, l	75.61	71.85	80.60	165.25
Ozone Applied, mg	2,005	2,005	1,985	3,970
Ozone Reacted, mg	1,540	1,500	1,420	2,920
Ozone Conc., mg O_3/l liquor	7,710	7,485	7,100	14,600
Percent Ozone Efficiency	76.9	74.7	71.5	73.6
Final Liquor Conc., mg/l TOC	560	475	485	440
Blank Test Final TOC Conc., mg/l	150	145	145	140
Percent TOC Removal by Ozonation	20.0	32.1	30.7	37.1
Percent TOC Removal by Ozonation and 100 g/l Carbon	78.6	79.3	79.3	80.0

significant increase in TOC removal is indicated by increasing the ozone dosage above 7500 mg/l.

Figures 19 and 20 depict the results of bromine chloride oxidation tests using the same feed liquor (unpreserved) as the previous oxidation tests. As seen in Figure 19, although TOC removal increased with increasing bromine chloride concentration, a residual TOC con-

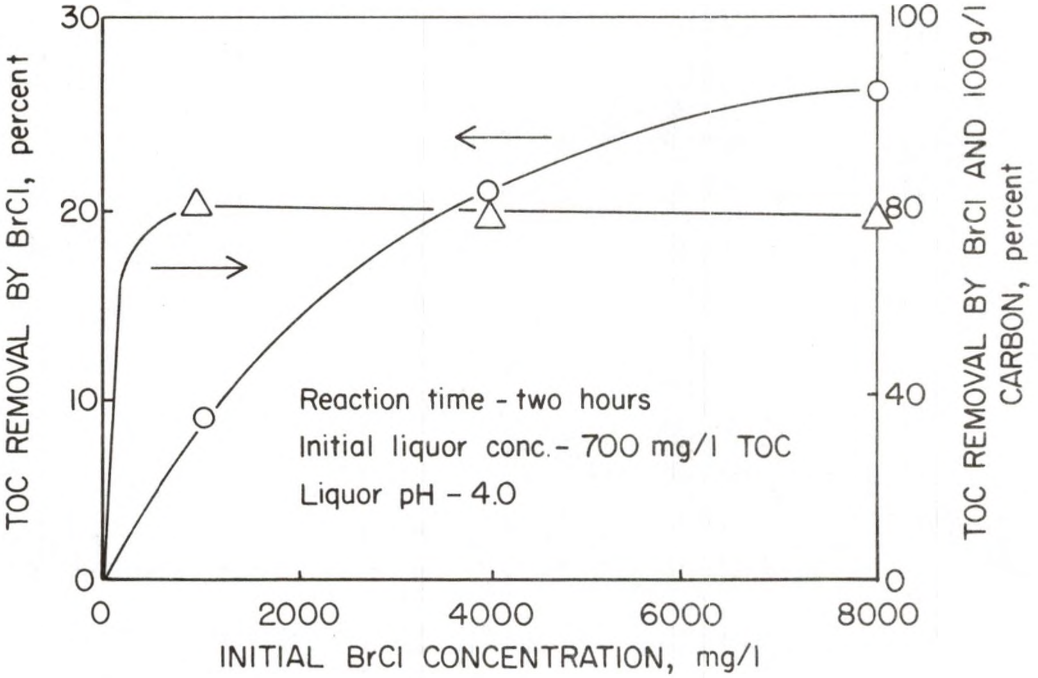

Figure 19. Dependence of TOC removal on BrCl dosage (unpreserved liquor).

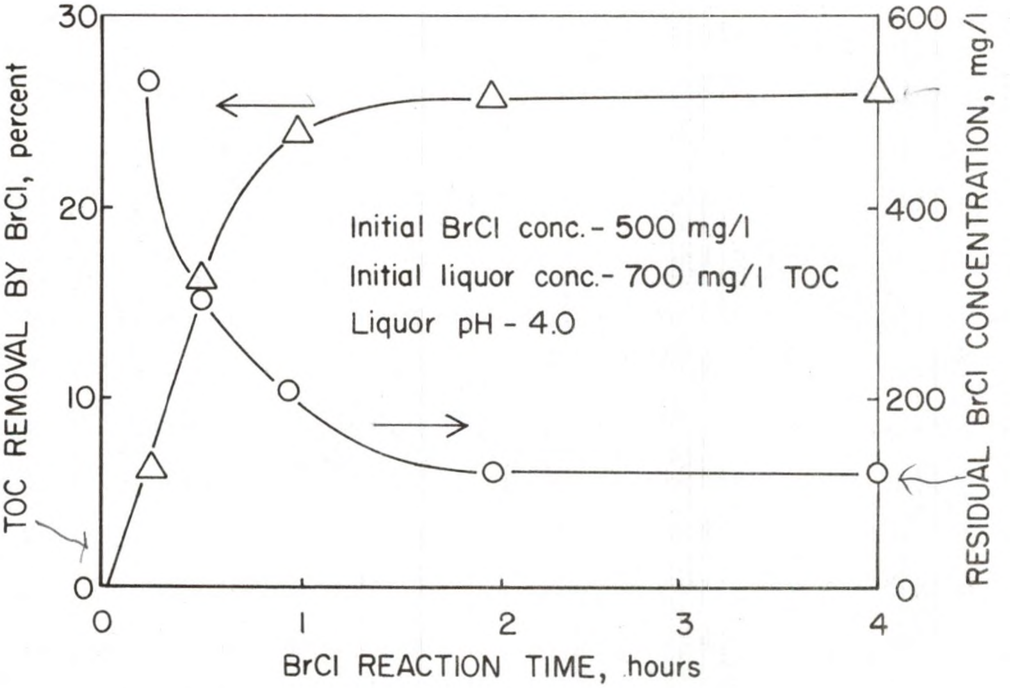

Figure 20. Dependence of TOC removal and residual BrCl on reaction time (unpreserved liquor).

centration of approximately 20 percent was not removable by either bromine chloride concentrations higher than 1000 mg/l or subsequent 100 mg/l activated carbon addition. Both residual bromine chloride concentration and TOC removal by bromine chloride reach steady state values after two hours of reaction (Figure 20). The initial bromine chloride concentration was 8000 mg/l for the data plotted in Figure 20.

Bromine chloride and ozone oxidation tests were comparable in results, although bromine chloride required smaller dosages for effective treatment. Because ozonation is a more expensive treatment, bromine chloride was chosen as the oxidant to be used in the treatment scheme.

Figures 21 and 22 show the results of tests done on the preserved RA-65 liquor that had been carbon-treated to a TOC concentration of 200 mg/l. Bromine chloride oxidation levels of 100, 200, 500, 1000, and 2000 mg/l were tested to determine which initial bromine chloride concentration not only gave the best TOC removal after oxidation and carbon adsorption, but also produced a low residual bromine chloride concentration after less than four hours of reaction time.

Figure 21 shows the results for a reaction time of two hours. Essentially no additional TOC removal was obtained at bromine chloride concentrations above 500 mg/l. TOC removal by bromine chloride is seen to stabilize after one hour of reaction time for an initial bromine chloride concentration of 500 mg/l (Figure 22). A reaction time of 90 minutes was chosen for the treatment scheme to allow residual bromine chloride concentrations to be less than 100 mg/l. Approximately the same results were achieved at the two pH levels tested--

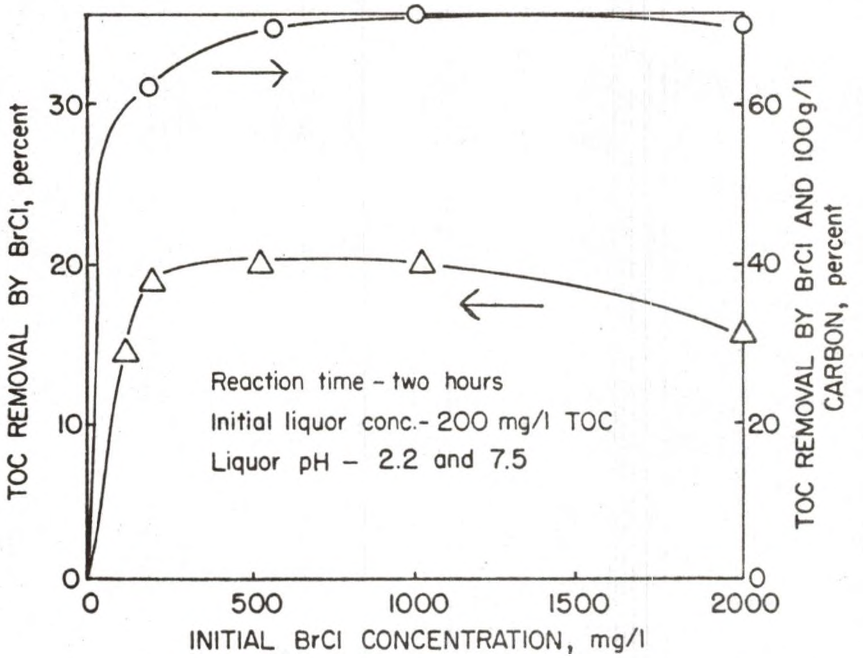

Figure 21. Dependence of TOC removal on BrCl dosage (preserved liquor).

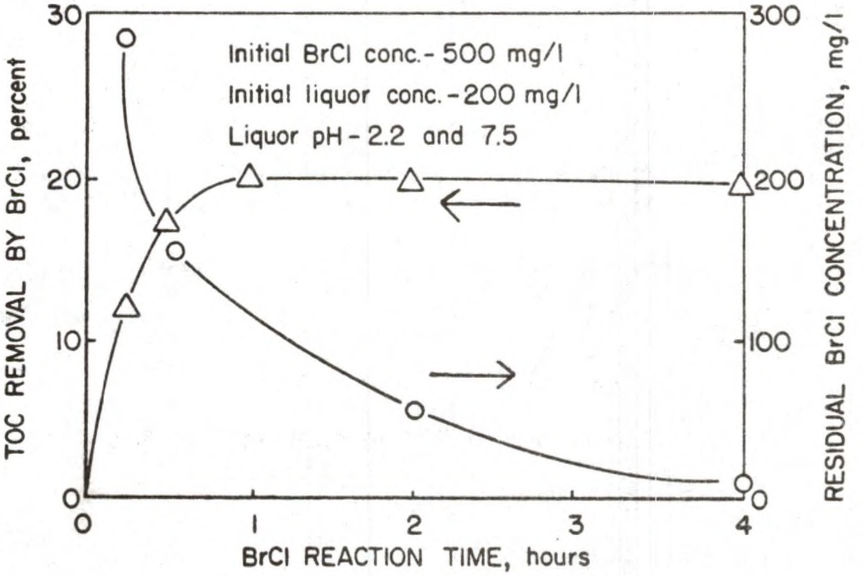

Figure 22. Dependence of TOC removal and residual BrCl on reaction time (preserved liquor).

2.2 and 7.5.

When the preserved carbon-treated liquor (TOC content of 200 mg/l) was oxidized with 500 mg/l bromine chloride for 90 minutes in two 15-gallon batches, 53 mg/l of precipitate was recovered. After oxidation the liquor pH was adjusted to 7.5 by adding 200 mg/l lime in two 15-gallon batches. The amount of precipitate recovered was 130 mg/l.

The final carbon treatment breakthrough curves are depicted in Figure 23. A premature breakthrough occurred because the carbon bed depth (12 feet) was not long enough for the required contact time. No useful information could be extracted from this test.

Treatment Analyses

Liquor analyses for the treatment steps are listed in Table 11. The final carbon-treated effluent analysis is based on samples taken during the continuous test. No total carbon or TOC values are listed for this liquor because they will be dependent on the contact time of the designed system. Because no more liquor was available, additional carbon tests could not be performed.

A high total dissolved solids concentration (2000 mg/l) was found in the treated liquor. X-ray fluorescence analysis showed that approximately 80 percent of the dissolved solids was calcium sulfate. Removal of calcium sulfate is usually accomplished by the addition of soda ash during coagulation.

Mass spectrometer (MS) analysis was done on the bromine chloride oxidized liquor and final carbon-treated liquor. The detectable

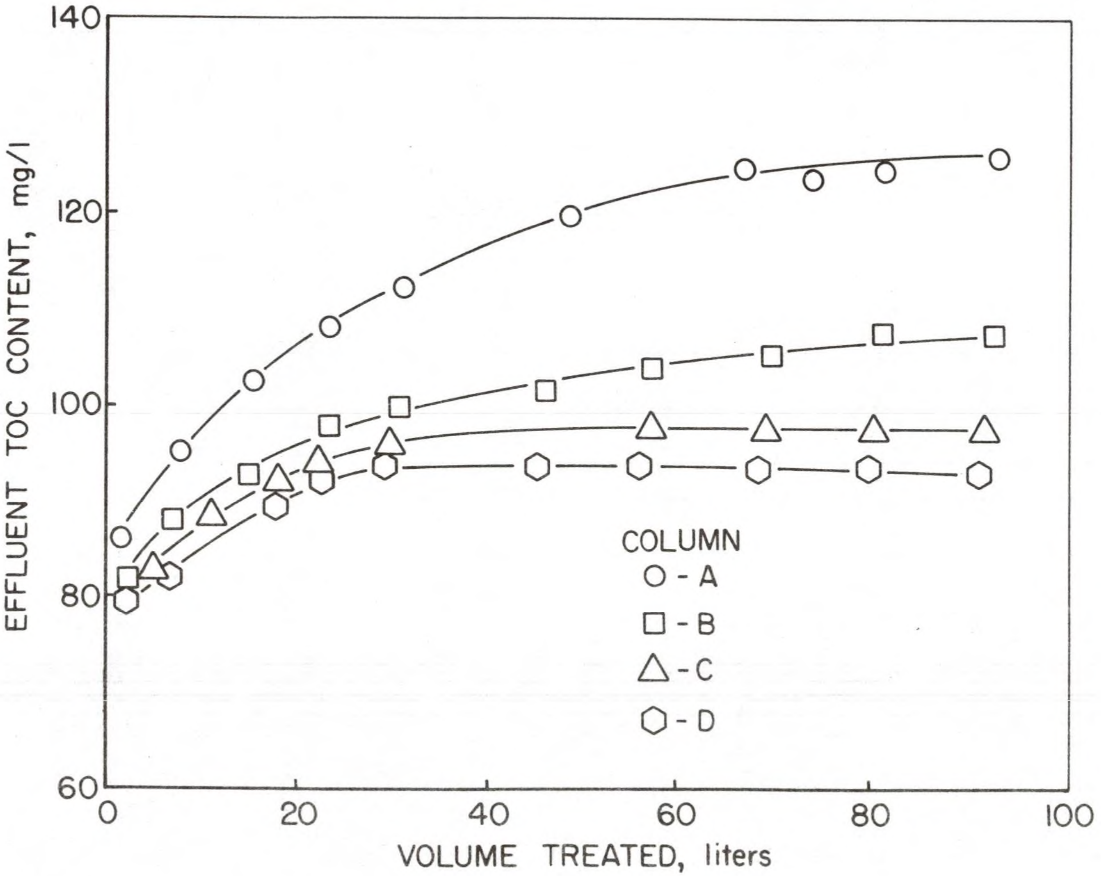

Figure 23. Breakthrough curves for four column system (pH 7.5).

TABLE 11

TREATMENT ANALYSES

	Carbon Treated	BrCl Oxidized	Lime Treated	Carbon Treated
pH	2.2	2.2	7.5	7.4
Alkalinity (as $CaCO_3$), mg/l	0	0	350	350
Ammonia, mg/l	180	120	120	120
Cyanide, mg/l	0	0	0	0
Total Sulfur, mg/l	1,210	1,190	910	895
Sulfide, mg/l	0	0	0	0
TOC: total carbon, mg/l	220	160	160	-
inorganic carbon, mg/l	20	20	20	20
organic carbon, mg/l	200	140	140	-
Phenolic: phenol, mg/l	15	0	0	0
o-cresol, mg/l	0	0	0	0
m,p-cresol, mg/l	0	0	0	0
Total Dissolved Solids, mg/l	2,600	3,350	3,090	2,000

organic compounds in the oxidized liquor were: chrysene (13 mg/l), pyrene (63 mg/l), dibenzothiophene (3 mg/l), phenanthrene (16 mg/l), and carbazole (44 mg/l). The final carbon-treated liquor (TOC concentration of approximately 50 mg/l) had no organics detected by MS analysis, most likely because of sample degradation.

Process Flow Scheme Summary

Most pretreatment and treatment results were satisfactory. Alkalinity and ammonia concentrations were reduced from 22,575 to 350 mg/l and 10,115 to 120 mg/l, respectively. Cyanide, sulfide, phenol, and cresol concentrations were all reduced to zero when initial concentrations had been 530, 635, 5070, and 2975 mg/l, respectively. Wastewater TOC content was decreased from 9250 mg/l to less than 50 mg/l.

Only dissolved solids (mostly calcium sulfate) remained unsatisfactory after treatment. With soda ash addition during coagulation, the dissolved solids concentration should be reduced considerably below the final treatment value of 2000 mg/l. A pretreatment and treatment flow scheme summary is given in Figure 24.

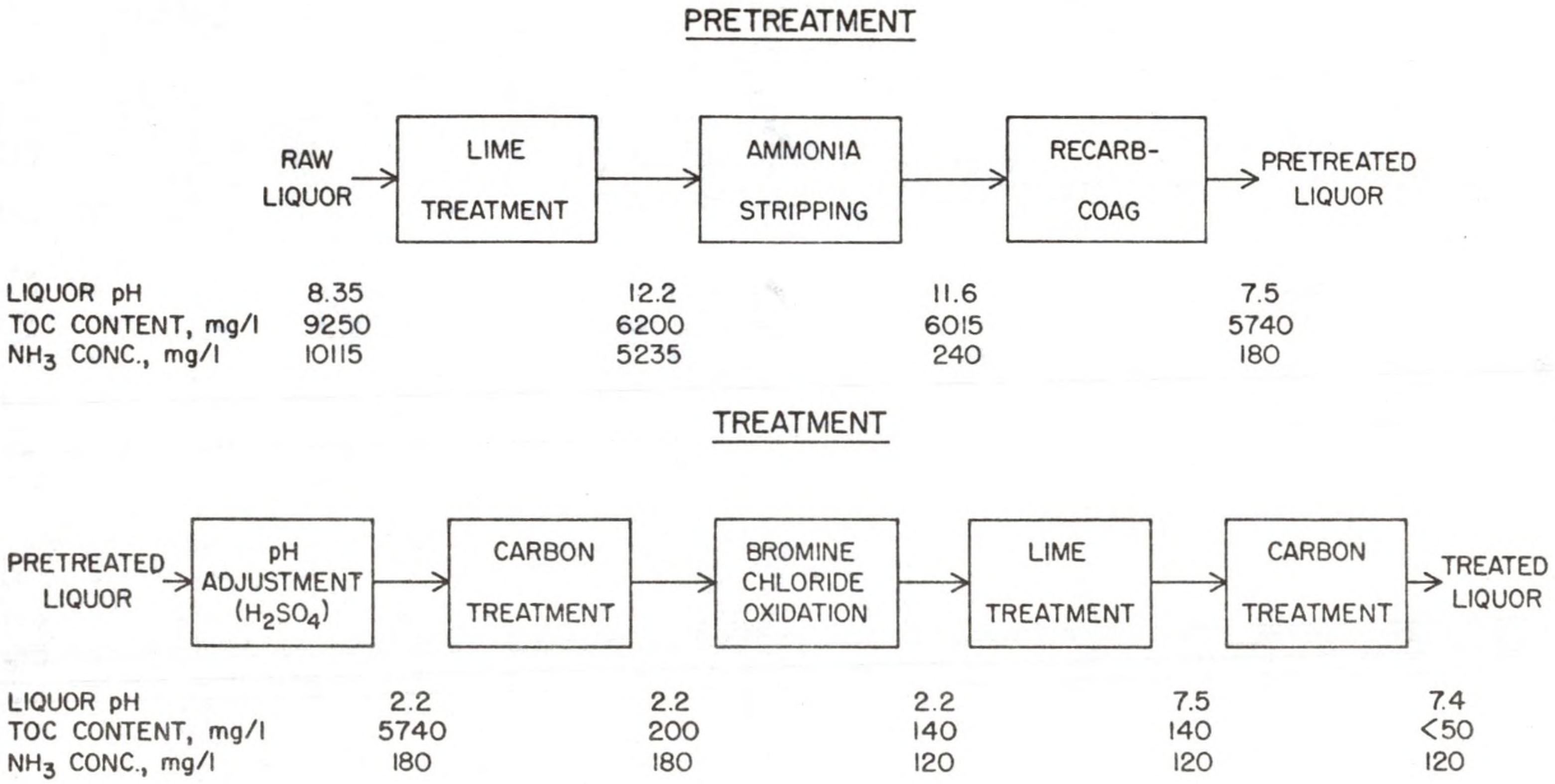

Figure 24. Process flow scheme summary.

CHAPTER IX

PLANT DESIGN

Process Description and Material Balances

The proposed slagging gasifier wastewater treatment plant flowsheet is shown in Figure 25. The treatment plant was sized for a gasifier capable of supplying enough gas to produce 250 million standard ft^3/day of methane. At this rate of synthetic natural gas production, approximately 16,300 tons/day of maf (moisture and ash-free) coal would have to be gasified and 78,600 gal/hr of wastewater would have to be treated.

For pH adjustment, 78,600 gal/hr of wastewater (pH=7.5) is mixed with 78.6 gal/hr of concentrated sulfuric acid in vessel T-102. The acidified wastewater (pH=2.2) is pumped through three pressure downflow granular carbon contactors (C-201, 202, 203) in series. These columns contain a total of 152,250 pounds of 12x28 mesh LCK granular carbon. Superficial contact time for the contactor system is 34 minutes.

The effluent from the carbon contacting system is mixed rapidly with 16.8 gal/hr bromine chloride for five minutes in the first section of oxidation tank T-301. The overflow is slowly agitated for 55 minutes in the second compartment of T-301. The oxidated liquor is then settled for 30 minutes in T-302.

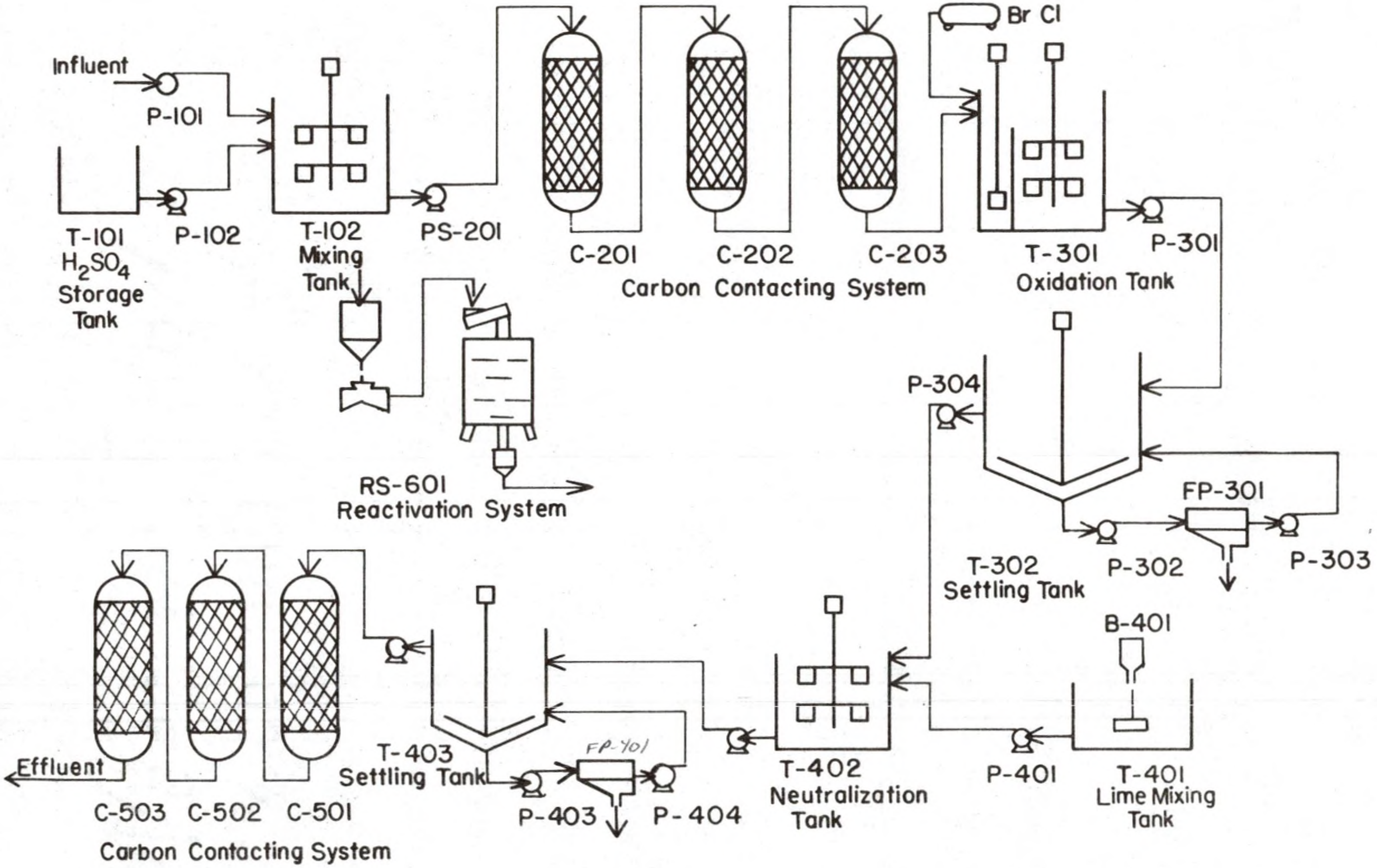

Figure 25. Slagging gasifier wastewater treatment plant flowsheet.

The settled sludge is removed from the bottom of T-302 and further concentrated by filter press FP-301 with the clarified water recycled. Approximately 34.7 lb/hr of dried sludge is removed by FP-301.

The oxidized liquor is then neutralized from pH 2.2 to 7.5 with 131 lb/hr lime in tank T-402. After 30 minutes of agitation the neutralized liquor is settled in tank T-403 for 30 minutes with approximately 85 lb/hr of dried sludge being removed by filter press FP-401.

The limed water, after sedimentation, is pumped through the final three downflow pressure carbon contactors before being discharged. These contactors contain a total of 448,000 pounds of 12x28 mesh LCK carbon and have a superficial contact time of 100 minutes.

The exhausted carbon from both contacting systems is reactivated in two multiple hearth furnaces at an approximate rate of 471,800 lb/day. A three percent loss of carbon due to combustion can be expected (15, 31, 33). An alternating fourth carbon contactor is to be filled with reactivated carbon while the other contactors are on line for both carbon contacting systems.

The purified water can be expected to have an alkalinity of approximately 350 mg/l, ammonia concentration of about 100 mg/l, and, if soda ash is added during pretreatment, total dissolved solids less than 500 mg/l. The organic carbon content should be less than 50 mg/l.

Equipment Design

Table 12 is the equipment list for the proposed physical-chemical treatment plant. All process, handling, and storage equip-

TABLE 12

EQUIPMENT LIST

Item No.	No. Req'd.	Description
B-401	1	Lime Storage Bin, 2360 ft^3, carbon steel
C-201, 202, 203	4	Down-Flow Pressurized Contactor, 1985 ft^3, H=15 ft, D=13 ft, carbon steel, acid brick-lined
C-501, 502, 503	4	Down-Flow Pressurized Contactor, 2925 ft^3, H=25 ft, D=17 ft, carbon steel
F-601	2	Multiple Hearth Reactivation Furnace, 5500 ft^2 hearth area
FP-301	1	Filter Press, 35 ft^2, aluminum
FP-401	1	Filter Press, 85 ft^2, aluminum
P-101	1, 1 spare	Centrifugal Pump, 15 hp, carbon steel
P-102	1, 1 spare	Centrifugal Pump, 1/4 hp, Hastelloy C
P-301, 402	2, 2 spare	Centrifugal Pump, 7 1/2 hp, s. steel fittings
P-302, 303, 401, 403, 404	5, 5 spare	Centrifugal Pump, open impeller, 1/2 hp, stainless steel
P-304	1, 1 spare	Centrifugal Pump, 10 hp, s. steel fittings
PS-201, 501	2	Contactor System Pump Station
T-101	1	Sulfuric Acid Storage Tank, 33000 gal, H=17.8 ft, D=17.8 ft, carbon steel, glass-lined
T-102	1	Mixing Tank, 8200 gal, H=14.7 ft, D=9.8 ft, stainless steel

TABLE 12--Continued

Item No.	No. Req'd.	Description
T-301	1	Oxidation Tank, 98,000 gal., H=33.4 ft, D=22.3 ft, carbon steel, glass-lined
T-302	1	Oxidation Settling Tank, 49,000 gal., H=20.3 ft, D=20.3 ft
T-401		
T-402	1	Lime Mixing Tank, 15 ft^3, s. steel
T-403	1	Lime Settling Tank, 49,000 gal., H=26.6 ft, D=17.8 ft

ment the size of a pump or larger have their equipment numbers, items required, and descriptions listed in this table.

Lime storage bin B-401 is for dry storage and is capable of storing a three weeks' supply of lime.

Carbon contactors C-201, 202, and 203 each have a diameter of 13 feet and a hydraulic loading of 9.9 gal/min/ft^2. These contactors are lined with acid brick because of the low wastewater pH. Carbon contactors C-501, 502, and 503 each have a diameter of 17 feet and a hydraulic loading of 5.8 gal/min/ft^2.

Reactivation furnace F-601 is a multiple hearth furnace in which the carbon is heated to approximately 1600°F. The off-gas is scrubbed and passed through an after-burner.

The seven tanks listed are used for either mixing, settling, or storage. These tanks have an average size of 34,000 gallons and are constructed of carbon steel or stainless steel. Tanks T-101 and T-301 are glass-lined.

Other equipment listed include 10 pumps, two pump stations, and two filter presses.

Cost Estimation

The estimated costs of all process, storage, and handling equipment are presented in Table 13. These costs are purchased equipment costs including delivery and sales tax, and are based on January, 1979, prices. All costs were updated by means of the Marshall and Stevens' chemical process industry equipment cost index.

The purchase costs for the carbon contacting systems, reactivation system, and pump stations were estimated from nomographs (30) and were determined as a function of effective volume, hearth area, and influent flow rate, respectively. The purchased costs of the carbon contactors include the cost of the carbon for the initial charge. Prices had to be updated from January, 1973, to January, 1979.

Settling tanks T-302 and T-403 were cost-estimated from nomographs based on tank surface area (59). These costs also had to be updated from January, 1973, to January, 1979.

The remaining purchased equipment costs were estimated from nomographs that required updating from January, 1967, to January, 1979.

All nomograph prices were adjusted if they included anything more than purchased equipment costs (e.g., installation and instrumentation costs). Adjustments were made according to literature values (60).

Table 13 lists the estimated capital costs of the treatment plant. These values were estimated either directly or indirectly from the purchased equipment cost of $3,629,000 as described in literature (60). As seen in Table 14, the fixed capital investment and the total capital

TABLE 13

ESTIMATED PURCHASED EQUIPMENT COSTS

Item No.	Description	No. Req'd.	Cost/Item	(Jan. 1979) Total Cost
B-401	Lime Storage Bin	1	$8,000	$8,000
C-201, 202, 203	Carbon Contactors	4	31,250	125,000
C-501, 502, 503	Carbon Contactors	4	58,500	234,000
F-601	Reactivation Furnace	2	1,430,000	2,860,000
FP-301	Filter Press	1	1,500	1,500
FP-401	Filter Press	1	2,800	2,800
P-101	Influent Pump	1, 1 Spare	2,250	4,500
P-102	H_2SO_4 Pump	1, 1 Spare	600	1,200
P-301	Settler Influent Pump	1, 1 Spare	1,750	3,500
P-302	Sludge Pump	1, 1 Spare	500	1,000
P-303	Recycle Pump	1, 1 Spare	500	1,000
P-304	Settler Effluent Pump	1, 1 Spare	1,500	3,000
P-401	Lime Slurry Pump	1, 1 Spare	600	1,200
P-402	Settler Influent Pump	1, 1 Spare	1,900	3,800
P-403	Sludge Pump	1, 1 Spare	500	1,000
P-404	Recycle Pump	1, 1 Spare	500	1,000
PS-201	Pump Station	1	23,500	23,500
PS-501	Pump Station	1	23,500	23,500
T-101	H_2SO_4 Storage Tank	1	17,000	17,000
T-102	Mixing Tank	1	17,000	17,000
T-301	Oxidation Tank	1	84,500	84,500
T-302	Settling Tank	1	79,000	79,000
T-401	Lime Mixing Tank	1	3,000	3,000
T-402	Neutralization Tank	1	50,000	50,000
T-403	Settling Tank	1	79,000	79,000

TABLE 14

FIXED CAPITAL INVESTMENT ESTIMATE

Items	Cost (Jan. 1979)
Direct Costs	
Purchased Equipment	$3,629,000
Purchased Equipment Installation	1,431,000
Insulation	326,000
Instrumentation and Controls	472,000
Piping	1,125,000
Electrical	877,000
Buildings (Including Services)	1,706,000
Yard Improvements	65,000
Service Facilities	88,000
Purchased Land	36,000
Total Direct Plant Cost	$9,755,000
Indirect Costs	
Engineering and Supervision	$ 488,000
Construction Expenses	488,000
Total Indirect and Direct Plant Costs	$10,731,000
Contactor's Fee	$ 195,000
Contingency	858,000
Start Up	752,000
Fixed Capital Investment	$12,536,000
Working Capital	2,212,000
Total Capital Investment	$14,748,000

investment were estimated to be $12,536,000 and $14,748,000, respectively.

The annual operating costs are estimated in Table 15. Operating costs are divided into treatment costs and general expenses.

The annual cost for raw materials ($4,063,000) includes

TABLE 15

ANNUAL TOTAL OPERATING COST ESTIMATE

Items	(Jan. 1979) Cost
Treatment Costs	
Direct Treatment Costs	
Raw Materials (Including Transportation)	$4,063,000
Operating Labor	158,000
Direct Supervisory and Clerical Labor	24,000
Utilities	74,000
Maintenance and Repairs	70,000
Operating Supplies	10,000
Laboratory Charges	8,000
Fixed Charges	
Depreciation	1,130,000
Local Taxes	125,000
Insurance	125,000
Plant Overhead Costs	88,000
General Expenses	
Administrative Expenses	63,000
Financing	1,475,000
Annual Total Operating Cost	$7,413,000
Operating Cost Per 1,000 Gallons	$10.75

transportation costs. The annual costs for sulfuric acid ($282,000) and lime ($19,000) were estimated from their January, 1979, listed prices ($53.40/ton and $33.00/ton, respectively) in the "Chemical Marketing Reporter" (61). A three percent carbon loss due to reactivation was used to estimate annual carbon costs. This percent loss is commonly used for very large reactivation systems (15, 31, 33). At a cost of $0.54 per pound, the annual carbon cost was estimated to be \$2,790,000. Bromine chloride costs were estimated as \$718,000 per year based on a cost of \$0.25 per pound (62). Annual incomes of \$7,000 and \$30,000 were estimated for selling the lime and oxidation sludges, respectively. Transportation costs of \$291,000 per year were determined using a bulk rail shipment estimate of \$25.60/ton (63).

The annual cost for operating labor (\$158,000) was determined using an average operator salary of \$4.50 per hour and a total of 12 operators.

The annual depreciation cost (\$1,130,000) is the sum of the depreciation costs due to fixed capital (\$1,079,000) and buildings (\$51,000) estimated as 10 percent of the depreciable fixed capital investment and three percent of the initial building cost, respectively.

The remaining annual costs listed in Table 15 are based on values given in literature (60). An approximate annual total operating cost of \$7,413,000 was determined to be required to treat the wastewater. This is equivalent to a cost of \$10.75 per 1000 gallons.

CHAPTER X

CONCLUSIONS

Slagging gasifier wastewater appears to be treatable by physical-chemical means using activated carbon adsorption and chemical oxidation as the two main treatment steps. The most economical results were achieved by acidifying the pretreated liquor before carbon adsorption.

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

1. A pretreatment scheme consisting of lime addition, ammonia stripping, and recarbonation-coagulation was found to sufficiently purify the raw gasifier liquor so that activated carbon adsorption and chemical oxidation could be applied as secondary and tertiary treatment.

2. Chlorine, sodium hypochlorite, hydrogen peroxide, and potassium permanganate were determined to be ineffective oxidants when applied to slagging gasifier liquor. Ozone and bromine chloride were found to be capable of oxidizing gasifier wastewater although bromine chloride oxidation seems to be more economical.

3. LCK activated carbon, produced by Union Carbide, proved to be the preferred granular carbon for slagging gasifier liquor treatment.

4. A total capital investment of approximately $14,748,000 can be expected for a facility capable of purifying pretreated wastewater

produced from a slagging gasification plant having a large enough gas output to produce 250 million standard ft^3/day of methane. Annual operating costs are estimated to be $7,413,000, i.e., $10.75 per 1000 gallons of pretreated liquor.

CHAPTER XI

RECOMMENDATIONS

Many aspects of physical-chemical treatment of slagging gasifier wastewater have not been investigated in this study. The following recommendations are suggested for future work:

1. Pretreatment parameters should be more precisely developed, including soda ash addition during coagulation.

2. Phenol recovery by liquid-liquid extraction should be investigated as a possible pretreatment step.

3. Continuous carbon contacting tests should be done at various liquor flow rates and contactor diameters. Tertiary carbon treatment tests should be conducted with a longer carbon bed depth.

4. Granular carbon reactivation parameters should be developed, such as spent carbon reactivation losses.

5. A more in-depth investigation of bromine chloride and ozone oxidations should be done, including pH effects.

6. The effect of gasification conditions on treated wastewater quality should be noted.

APPENDIX A

SAMPLE CALCULATIONS FOR COMPUTING RATE OF WASTEWATER PRODUCTION, THEORETICAL CARBON USAGE RATE, BEST FITTING STRAIGHT LINE, RESIDUAL OXIDANT CONCENTRATION, AND PURCHASED EQUIPMENT COST

Sample caluclation for computing rate of wastewater production for generation of 250 million standard ft^3/day synthetic natural gas.

Basis - 1 ton maf lignite gasified

For run RA-65, 966 pounds of wastewater and 59,500 standard ft^3 of gas were produced per ton of maf coal. The gas composition included the following percentages: 27.5% H_2, 53.3% CO, 5.6% CH_4, and 8.8% CO_2. Hence, the amount of these gases produced per ton of maf coal was:

$$(59{,}500 \text{ ft}^3 \text{ gas})\ (0.275) = 16{,}360 \text{ ft}^3 H_2$$

$$(59{,}500 \text{ ft}^3 \text{ gas})\ (0.533) = 31{,}710 \text{ ft}^3 CO$$

$$(59{,}500 \text{ ft}^3 \text{ gas})\ (0.056) = 3{,}330 \text{ ft}^3 CH_4$$

$$(59{,}500 \text{ ft}^3 \text{ gas})\ (0.088) = 5{,}240 \text{ ft}^3 CO_2$$

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

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

Approximately 75% of the CO_2 is then stripped along with H_2S before the shift conversion:

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

Approximately 75 percent of the CO_2 reacts in the shift converter (64). The remaining gas products are sent to the methanator for conversion:

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

Product gas should contain just methane and a small fraction of carbon dioxide. In order for this to occur the H_2 and CO must be sent to the methanator with a ratio of 3/1.

Trial and error calculations determined that for the H_2/CO ratio to equal 3/1, the H_2/CO ratio must equal 3.35/1 after H_2 production.

The above mentioned steps and their products are listed below (based on 1 ton maf coal):

step	product gas contents
gasification	16,360 scf H_2 31,710 scf CO 3,330 scf CH_4 5,240 scf CO_2
$CO + H_2O \rightarrow CO_2 + H_2$	37,020 scf H_2 11,050 scf CO 3,330 scf CH_4 25,900 scf CO_2
95% CO_2 stripped	37,020 scf H_2 11,050 scf CO 3,330 scf CH_4 1,300 scf CO_2
$CO_2 + H_2 \rightarrow CO + H_2O$ (75% CO_2 reacts)	36,060 scf H_2 12,020 scf CO 3,330 scf CH_4 324 scf CO_2
$CO + 3H_2 \rightarrow CH_4 + H_2O$	15,350 scf CH_4 325 scf CO_2 15,675

Converting to daily rates,

$$\text{Tons maf coal gasified/day} = \frac{250 \times 10^6 \text{ scf/day}}{153350 \text{ scf/ton maf coal}}$$

15,350

$$= 16280 \text{ tons/day}$$

$$\text{gallons wastewater produced/day} = (16280 \text{ ton/day}) \left(966 \frac{\text{lb}H_2O}{\text{ton}}\right)$$

$$= 1.89 \times 10^6 \text{ gal/day}$$

Converting to hourly rate,

$$(1.89 \times 10^{6} \ \frac{\text{gal}}{\text{day}}) \ (\frac{\text{day}}{24 \text{ hr}}) = 78{,}600 \text{ gal/hr}$$

Sample calculation for computing theoretical carbon usage rate.

The empirical Freundlich equation can be expressed as:

$$x/m = KC^{1/n}$$

where x = amount of adsorbate adsorbed

m = weight of carbon

K = equilibrium concentration of adsorbate K and n are constants.

Linearizing the equation by means of logarithms obtains the expression:

$$\log x/m = \log K + 1/n \log C$$

In Figure 9 the best straight line through the isotherm data (pH = 2.2) intersects the initial liquor concentration where the x/m value equals 4400 mg/l TOC. This value represents the ultimate capacity of the carbon at these conditions.

The theoretical usage rate can then be calculated from the equation:

$$R = \frac{Co}{(x/m)_o \, V}$$

where R = theoretical usage rate

Co = initial TOC concentration of liquor

$(x/m)_o$ = ultimate carbon capacity

V = volume of liquor

100 ml of liquor was used with an initial TOC concentration of 5740 mg/l

$$R = \frac{5740 \text{ mg/l}}{(0.10 \text{ l}) \left(\frac{4400 \text{ mg TOC adsorbed}}{1\text{-gm carbon}}\right)}$$

R = 13.0 gms LCK carbon per liter liquor

Sample caluclations for computing best fitting straight line through isotherm data.

Isotherm data: LCK carbon, liquor pH = 2.2

equilibrium concentration (C)	mg TOC adsorbed / weight carbon (x/m)
3900	3680
2720	3020
1470	2135
500	1310

equation of line: $Y = b_o + b_1X$

let $X = \log C$

$Y = \log x/m$

$\bar{X}$ = average X value

$\bar{Y}$ = average Y value

b_o = Y-intercept through best fitting line

b_1 = slope of best fitting line

C	X	x/m	Y	$X-\bar{X}$	$(X-\bar{X})^2$	$(X-\bar{X})\ Y$
3900	3.591	3680	3.566	0.368	0.1354	1.3123
2720	3.435	3020	3.480	0.212	0.0449	0.7378
1470	3.167	2135	3.329	-0.056	0.003136	-0.1864
500	2.699	1310	3.117	-0.524	0.2746	-1.633
	$\Sigma X=12.892$		$\Sigma Y=13.492$		0.458	0.2307
	$\bar{X} = 3.223$		$\bar{Y} = 3.373$			

$$b_1 = \frac{(X-\bar{X})Y}{(X-\bar{X})^2} = 0.5037$$

$$b_o = \bar{Y}-b_1\bar{X} = 1.7496$$

equation of line: $Y = 1.750 + (0.5037)X$

converting by antilogarithms: $x/m = (56.23)C^{0.5037}$

Sample calculation for computing residual oxidant concentration.

Iodimetric Titration: 431.69 ml of 0.1013 N $Na_2S_2O_3$ solution was titrated with 200 ml of acidified KI solution that had ozone applied to it.

The ozone reacts with acidified iodide to form free iodine:

$$O_3 + 2H^+ + 2I^- \rightarrow O_2 + I_2 + H_2O$$

When the iodine is titrated with sodium thiosulfate solution using starch as an indicator, the following reaction occurs:

$$I_2 + 2S_2O_3^= \rightarrow S_4O_6^= + 2I^-$$

Starch is added to the yellow solution when the free iodine is almost completely used up, changing the solution to a blue color. The blue color disappears when thiosulfate reduces all free iodine to iodide. Hence, two moles of sodium thiosulfate will react for every mole of ozone present.

$$\text{concentration ozone} = \frac{(431.69\text{ml})\ (0.1013\text{N})\ (48\ \frac{\text{gm}O_3}{\text{mole}})}{(2\ \text{equiv./mole})\ (200\ \text{ml})}$$

$$= \frac{5.248\ \text{gm}\ O_3}{1\ \text{KI soln.}}$$

Sample calculations for computing purchased equipment costs.

Sulfuric Acid Storage Tank (T-101)

Assume: 2 weeks storage

glass-lined carbon steel

$H = D$

80% of capacity

$$\text{Volume} = \frac{(78.6 \text{ gal/hr})\ (24 \text{ hr/day})\ (14 \text{ day})}{0.80} = 33{,}000 \text{ gallons}$$

$$= 4400 \text{ ft}^3$$

$$4400 \text{ ft}^3 = (\pi D^2/4)\ (D)$$

$$H = D = 17.8 \text{ feet}$$

from nomograph (60),

installed cost - \$10,000 Jan. 1967

Marshall and Stevens index - Jan. 1967: 261.2 (65)

Jan. 1979: 567.9 (66)

$$(\$10{,}000)\ \frac{(576.9)}{261.2} = \underline{\underline{\$22{,}000}} \text{ installed cost}$$

Mixing Tank (T-102)

Assume: five minute contact time

stainless steel

$H = 3/2\ D$

80% of capacity

$$\text{Volume} = \frac{(78{,}600 \text{ gal/hr})\ (5/60 \text{ hr})}{0.80} = 8{,}200 \text{ gallons}$$

$$= 1100 \text{ ft}^3$$

$$1100 \text{ ft}^3 = (\pi D^2/4)\ (3/2D)$$

$$D = 9.8 \text{ feet},\ H = 14.7 \text{ feet}$$

from nomograph (60),

installed cost - \$10,500 Jan. 1967

$$(\$10,500)\ \frac{(576.9)}{261.2} = \underline{\underline{\$23,000}} \text{ installed cost}$$

Carbon Contacting System (C-201, C-202, C-203)

Assume: 34 minute superficial contact time

4 contactors, 3 on line

H = 15 feet per column

50% void

$$\text{Contactor cross-sectional area} = \frac{(34\ \text{min})\ (78,600\ \text{gal/hr})\ (1\ \text{hr}/60\ \text{min})}{(3)\ (15\ \text{feet})\ (7.48\ \text{gal/ft}^3)}$$

$$= 132\ \text{ft}^2$$

$$132\ \text{ft}^2 = \pi D^2/4$$

$$D = 13\ \text{feet}$$

$$\text{effective volume} = (0.5)\ (132\ \text{ft}^2)\ (15\ \text{feet})\ (4)$$

$$= 3970\ \text{ft}^3 \text{ per four-column system}$$

from nomograph (30),

complete capital cost for system - \$130,000 Jan. 1973

Marshall and Stevens index - Jan. 1973: 335.9 (67)

$$(\$130,000)\ \frac{(576.9)}{335.9} = \underline{\$223,000}$$

$$\text{Cost of carbon inventory} = (\$0.54/\text{lb})\ (21.22\ \text{lb/ft}^3)\ (7940\ \text{ft}^3)$$

$$= \underline{\$91,000}$$

$$\text{Capital cost including carbon} = \underline{\underline{\$314,000}}$$

Settling Tank (T-302)

Assume: 30 minute contact time

carbon steel

H = D

80% of capacity

$$\text{Volume} = \frac{(78{,}700 \text{ gal/hr})\ (1/2 \text{ hr})}{0.80} = 49{,}000 \text{ gallons}$$

$$= 6600 \text{ ft}^3$$

$$6600 \text{ ft}^3 = (\pi D^2/4)D$$

$$H = D = 20.3 \text{ feet}$$

$$\text{Surface area} \cong (\pi/4)\ (20.3 \text{ ft})^2 + (\pi)\ (20.3 \text{ ft})^2$$

$$= 1600 \text{ ft}^2$$

from nomograph (66),

installed cost \$60,000   Jan. 1973

$$(\$60{,}000)\ \frac{(576.4)}{335.9} = \underline{\underline{\$103{,}000}} \text{ installed cost}$$

<u>Filter Press (FP-301)</u>

Assume: 34.7 lb dry solids per hour

10 gal filtered/ft^2/hr (68)

aluminum

$$\text{Surface area} = \frac{34.7 \text{ lb/hr}}{(0.1 \text{ lb/gal})\ (10 \text{ gal/ft}^2\text{/hr})}$$

$$= 35 \text{ ft}^2$$

from nomograph (60),

installed cost - \$1,000   Jan. 1967

$$(\$1{,}000)\ \frac{(576.4)}{261.2} = \underline{\underline{\$2{,}200}} \text{ installed cost}$$

<u>Granular Carbon Reactivation System (F-601)</u>

Assume: hearth loading of 45 lb/ft^2/day (30)

2 furnaces

471,800 lb/day reactivated

$$\text{Hearth area} = \frac{471{,}800\ \text{lb/day}}{45\ \text{lb/ft}^2\text{/day}}$$

$$= 10{,}500\ \text{ft}^2$$

add on 500 ft^2 hearth area for tertiary step

Hearth area = 11,000 ft^2

from nomograph (30),

Capital cost for complete system - \$3,500,000 Jan. 1973 (M+S = 335.9)

$$(\$3{,}500{,}000)\ \left(\frac{576.9}{\underset{\nwarrow(\text{Jan } 1967)}{261.2}}\right) = \underline{\underline{\$7{,}730{,}000}}$$

The reactivation system will be used as an example for determining purchased equipment costs (PEC) from nomograph costs. The calculated cost of \$7,730,000 includes installation, insulation, instrumentation, controls, piping, electrical, and buildings. To determine the PEC, these costs are approximated as a percent of PEC (60):

installation - 40% of PEC

insulation - 9% of PEC

instrumentation and controls - 13% of PEC

piping - 31% of PEC

electrical - 10% of PEC

buildings - 67% of PEC

Total - 170% of PEC

\$7,730,000 = PEC + (1.7) PEC

PEC = $\underline{\underline{\$2{,}860{,}000}}$ for reactivation system

APPENDIX B

EXPERIMENTAL DATA

TABLE 16

ADSORPTION ISOTHERM TESTS

Initial Concentration: 5740 mg/l TOC Liquor Volume: 100 ml

Carbon	Carbon Dosage, gms.	pH=7.5 Equilibrium Conc., mg/l TOC	pH=2.2 Equilibrium Conc., mg/l TOC
LCK	0.5	4600	3900
LCK	1	3510	2720
LCK	2	2285	1470
LCK	4	600	500
9LXC	0.5	4710	4000
9LXC	1	3800	2600
9LXC	2	2435	1430
9LXC	4	655	370
DARCO	0.5	5215	4840
DARCO	1	4760	4095
DARCO	2	3785	2850
DARCO	4	2500	1645
WV-L	0.5	5040	4550
WV-L	1	4375	3620
WV-L	2	3295	2290
WV-L	4	1725	1100
WV-G	0.5	4730	3940
WV-G	1	3740	2750
WV-G	2	2585	1100
WV-G	4	1005	230
ROW	0.5	5065	4555
ROW	1	4395	3630
ROW	2	3395	2410
ROW	4	2105	1200
CAL	0.5	4765	4155
CAL	1	3985	2940
CAL	2	2645	1530
CAL	4	1350	605
WITCARB	0.5	5055	4920
WITCARB	1	4450	4175
WITCARB	2	3515	3005
WITCARB	4	2045	1675

TABLE 17

BREAKTHROUGH CURVE DATA

Liquor pH: 2.2
Weight of Carbon: 1310 gms
Initial Liquor Concentration: 5740 mg/l
Flow Rate: 64.5 ml/min.
Superficial Contact Time: 45 Minutes
Number of Columns: four, labeled A-D
Column Diameter: 1-1/4 inch
Column Packing Height: 3 feet
Time Start: 7:00 P.M. 3/27/79
Stop: 4:15 P.M. 3/28/79

Time of Sample	Column Sampled	Total Time Column Displaced, min	Corrected Volume Throughput, liters	Sample TOC Content, mg/l
8:52 P.M.	D	80	5.16	80
9:00	B	106	6.84	85
9:02	C	100	6.45	75
9:06	A	119	7.68	475
10:44	D	192	12.38	95
10:45	B	211	13.61	130
10:45	C	203	13.09	85
10:46	A	219	14.13	2510
1:42 A.M.	D	372	23.99	110
1:42	B	388	25.03	785
1:42	C	380	24.51	110
1:42	A	395	25.48	4000
3:40	D	490	31.61	120
3:40	B	506	32.64	2330
3:40	C	498	32.12	305
3:40	A	513	33.09	4275
5:45	D	615	39.67	250
5:45	B	631	40.70	4125
5:45	C	623	40.18	960
6:40	A	693	44.70	4625
7:32	D	722	46.57	410
7:32	C	730	47.09	2050
8:47	D	797	51.41	565
8:47	C	805	51.92	3470
9:40	D	851	54.89	970
9:40	B	867	55.92	4630
9:40	C	859	55.41	4225
10:40	D	910	58.70	1555
11:40	D	970	62.57	2000
11:40	A	993	64.05	4950

TABLE 17--Continued

Time of Sample	Column Sampled	Total Time Column Displaced, min	Corrected Volume Throughput, liters	Sample TOC Content, mg/l
12:40 P.M.	D	1030	66.44	2895
12:40	B	1046	67.47	4810
12:40	C	1038	66.95	4420
2:10	D	1120	72.24	4075
3:17	D	1187	76.56	4245
4:15	D	1245	80.30	4480
4:15	B	1261	81.33	4810
4:15	C	1253	80.82	4720
4:15	A	1268	81.79	4950

TABLE 18

BROMINE CHLORIDE BATCH OXIDATION TESTS (pH 7.5)

Initial BrCl Conc., mg/l	Initial Liquor TOC Conc., mg/l	Contact Time, hr	Res. BrCl Conc., mg/l	Res. TOC Conc., mg/l	TOC After 100 gm/l Carbon
1000	684	0.25	20	630	-
1000	684	0.5	10	630	-
1000	684	1	0	625	-
1000	684	2	0	625	-
1000	684	4	0	625	145
4000	642	0.25	315	600	-
4000	642	0.5	110	560	-
4000	642	1	25	510	-
4000	642	2	0	510	-
4000	642	4	0	510	140
8000	592	0.25	540	550	-
8000	592	0.5	310	495	-
8000	592	1	210	450	-
8000	592	2	130	440	-
8000	592	4	125	440	140

TABLE 19

BROMINE CHLORIDE BATCH OXIDATION TESTS (pH 2.2)

Initial BrCl Conc., mg/l	Initial Liquor TOC Conc., mg/l	Contact Time, hr	Res. BrCl Conc., mg/l	Res. TOC Conc., mg/l	TOC After 100 gm/l Carbon
100	198	0.25	60	180	-
100	198	0.5	30	180	-
100	198	1	0	175	-
100	198	2	0	170	-
100	198	4	0	165	80
200	197	0.25	110	170	-
200	197	0.5	85	170	-
200	197	1	20	160	-
200	197	2	10	160	-
200	197	4	10	160	75
500	193	0.25	285	170	-
500	193	0.5	160	160	-
500	193	1	60	155	-
500	193	2	15	155	-
500	193	4	10	155	60
1000	186	0.25	510	165	-
1000	186	0.5	260	160	-
1000	186	1	160	150	-
1000	186	2	120	150	-
1000	186	4	120	150	55
2000	177	0.25	625	160	-
2000	177	0.5	390	160	-
2000	177	1	375	150	-
2000	177	2	240	150	-
2000	177	4	210	150	55

TABLE 20

BROMINE CHLORIDE BATCH OXIDATION TESTS WITH PRESERVED GASIFIER LIQUOR

Liquor pH: 7.5

Initial Liquor Concentration: 193 mg/l TOC

Initial BrCl Concentration: 500 mg/l

Contact Time, hr	Residual BrCl Conc., mg/l	Residual TOC Conc., mg/l	TOC After 100 gm/l Carbon
0.25	300	170	-
0.5	205	160	-
1	150	155	-
2	130	155	-
4	125	155	60

TABLE 21

BREAKTHROUGH CURVE DATA

Liquor pH: 7.5
Weight of Carbon: 1080 gms
Initial Liquor Concentration: 140 mg/l TOC
Flow Rate: 64.5 ml/min (2 gal/min/ft^2)
Superficial Contact Time: 45 minutes
Number of Columns: four, labeled A-D
Column Diameter: 1-1/4 inch
Column Packing Height: 3 feet
Time Start: 9:30 P.M. 4/6/79
Stop: 9:30 P.M. 4/7/79

Time of Sample	Column Sampled	Total Time Column Displaced, min	Corrected Volume Throughput, liters	Sample TOC Content, mg/l
10:30 P.M.	A	53	3.42	91
10:30	B	47	3.03	84
10:30	C	38	2.45	82
10:30	D	30	1.94	80
12:30 A.M.	A	173	11.16	100
12:30	B	167	10.77	89
12:30	C	158	10.19	84
12:30	D	150	9.68	82
2:30	A	293	18.90	106
2:30	B	287	18.51	96
2:30	C	278	17.93	92
2:30	D	270	17.42	90
4:30	A	413	26.64	110
4:30	B	407	26.25	98
4:30	C	398	35.67	96
4:30	D	390	25.16	94
8:30	A	653	42.12	114
9:30	B	707	45.60	102
9:30	C	698	45.02	96
9:30	D	690	44.51	94
10:30	A	773	49.86	120
12:30 P.M.	A	893	57.60	120
12:30	B	887	57.21	104
12:30	C	878	56.63	98
12:30	D	870	56.12	94
2:30	A	1013	65.34	124
3:30	B	1067	68.82	106
3:30	C	1058	68.24	98
3:30	D	1050	67.73	94
4:30	A	1133	73.08	124

TABLE 21--Continued

Time of Sampe	Column Sampled	Total Time Column Dis- placed, min	Corrected Volume Throughput, liters	Sample TOC Content, mg/l
6:30	A	1253	80.82	125
6:30	B	1247	80.43	108
6:30	C	1238	79.85	98
6:30	D	1230	79.34	94
8:30	A	1373	88.56	124
9:30	A	1433	92.43	126
9:30	B	1427	92.04	108
9:30	C	1418	91.46	98
9:30	D	1410	90.95	94

APPENDIX C

ANALYSES

TABLE 22

X-RAY FLUORESCENCE ANALYSIS FOR DISSOLVED SOLIDS IN TREATED WASTEWATER

Sample No. GF 79-1951

	Percent Composition
Silica, SiO_2	1.6
Aluminum Oxide, Al_2O_3	1.8
Ferric Oxide, Fe_2O_3	0.0
Titanium Oxide, TiO_2	0.0
Phosphorous Pentoxide, P_2O_5	0.4
Calcium Oxide, CaO	33.4
Magnesium Oxide, MgO	1.7
Sodium Oxide, Na_2O	2.2
Potassium Oxide, K_2O	0.2
Sulfur Trioxide, SO_3	46.2
Unaccounted	12.5
Total	100.0

TABLE 23

MASS SPECTROMETER ANALYSIS OF BrCl-TREATED LIQUOR

Nominal Mass	Compound	Percent Total Ion	Conc. in Liquor, mg/l
228	Chrysene	9.3	13.0
202	Pyrene	45.3	63.4
184	Dibenzothiophene	2.2	3.1
178	Phenanthrene	11.1	15.5
167	Carbazole	31.2	43.7
	Unknown	0.9	1.3
	Total	100.0	140

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