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TREATMENT OF PHENOLIC AIRCRAFT PAINT STRIPPING WASTEWATER

Ronald H. Kroop

Air Force Weapons Laboratory
Kirtland Air Force Base, New Mexico

January 1973

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AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base
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13. ABSTRACT

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A laboratory investigation was conducted to determine the optimum economic and technological treatment process to employ for treating large volumes of phenolic aircraft, and ground equipment, paint stripping wastewater. Three candidate unit processes were selected and tested to determine their effectiveness for the removal of the major contaminants in the wastewater. These processes were oxidation with ozone, oxidation with potassium permanganate, and adsorption with granular activated carbon. Granular activated carbon adsorption provided the best removal of the organic contaminants and was also the least expensive. Phenol concentration was reduced from 3000 mg/l to less than 2 mg/l in 60 minutes of contact time. The adsorptive capacity for phenols was 0.404 gm phenols/gm of activated carbon and for chemical oxygen demand, 1.79 gm of COD/gm of activated carbon.

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FOREWORD

This research was performed under Program Element 63723F, Project 683M3W15

Inclusive dates of research were 17 May 1972 through 17 September 1972. The report was submitted 1 November 1972 by the Air Force Weapon Laboratory Project Officer, Lt. Ronald H. Kroop (DEE).

This technical report has been reviewed and is approved.

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SECTION I

INTRODUCTION

1. PURPOSE

The purpose of this research was to find the optimum economical and technological treatment process that could be employed for treating large volumes of phenolic aircraft, and ground equipment, paint stripping wastewater. This treatment process would be geared toward "on-site" treatment of just the paint stripping wastewater or for treating the entire industrial wastewater flow where phenols represented the major portion of the organic contaminants. To determine what treatment process to employ, laboratory investigations were conducted using three unit processes with known capabilities for the removal of phenols and other organic contaminants. These processes were oxidation with ozone, oxidation with potassium permanganate, and adsorption with granular activated carbon.

2. BACKGROUND

Paint stripping (depaint) of aircraft and ground equipment is done by Air Force maintenance personnel periodically for the prevention of corrosion of the metallic surfaces. The frequency of depainting varies. For example, a B-52 is depainted every $3\frac{1}{2}$ years. Paint stripping is accomplished by brushing or spraying on a viscous paint remover/stripper. The paint remover is allowed to dwell on the paint for a period of time while it swells, wrinkles, and softens the paint, thus lifting the paint from the metallic surface. The paint remover and paint particles are then rinsed from the aircraft (ground equipment) with a high-pressure water stream. This constitutes the source of the wastewater.

The type of paint system (topcoat and primer) on an aircraft dictates the type of paint remover required. In the past, most aircraft in the Air Force inventory have had an acrylic lacquer topcoat with a zinc chromate primer. The depainting of these paint systems involved the use of paint removers containing primarily methylene chloride (dichloromethane, CH_2Cl_2) and hexavalent chromium with additional amounts of surfactants, thickners, and wetting agents. Applicable MIL specs are TT-T-248 and MIL-R-25134B. Treatment of the wastewater evolving from the use of these paint removers have not been a significant problem, or at least not documented to be, in that methylene chloride is significantly volatile, and much of it evaporates before being carried off in the wastewater in which it has only limited solubility anyway. At bases having industrial wastewater treatment facilities the hexavalent chromium in the paint stripping wastewater would be reduced to trivalent and precipitated as chromium hydroxide $Cr(OH)_3$.

In recent years the Air Force has started using paint systems having polyurethane topcoats with epoxy primers. Depainting of these paint systems is said to necessitate the use of paint removers containing, in addition to the above mentioned, significant concentrations of phenols (12 to 22 percent). The applicable MIL spec is MIL-R-81294 with a new MIL spec "Remover, Activated Solvent Type, For Difficult to Remove Finishes" being proposed for use. This new MIL spec will limit phenol concentration to 10 percent.

Phenol is an aromatic hydrocarbon that is highly soluble in water and is toxic to most forms of aquatic life. It is the standard upon which disinfectants are based, yet under controlled conditions it can be biologically degraded in a wastewater treatment plant (see literature review and discussion). Of most significance is that phenols present in water treated for domestic consumption and disinfected with chlorine yields chlorophenols, which is a malodorous and bad tasting compound detectable at very low concentrations. For this reason, the U.S. PHS Drinking Water Standards has a recommended maximum concentration of 0.001 mg/l phenol. Most states limit the concentration of phenols in receiving water to between 0.001 and 0.2 mg/l.

Depainting of aircraft is done when an aircraft is undergoing major maintenance and is, therefore, primarily accomplished at Air Force Air Materiel Areas (AMAs). Tinker AFB (OCAMA), Oklahoma, had been and was expected to depaint approximately 60 B-52s each fiscal year. Each B-52 requires approximately 3350 gallons of paint stripper of which 715 gallons is the phenolic paint stripper. This figures out to be 0.194 gallon of paint stripper used per square feet of aircraft surface. McClellan AFB (SMAMA) California, is expected to depaint 175 aircraft of the F-100, 105, 106 type during FY73. Approximately 300 gallons of paint stripper per aircraft is required.

Using the characteristics of the wastewater (phenol concentration) and knowing the concentration of phenols in the paint stripper, it was estimated that each gallon of paint stripper is rinsed with between 45 to 75 gallons of water (45 gal/gal for wastewater samples received from Vance AFB, Oklahoma, and 75 for wastewater samples from Tinker, AFB, Oklahoma).

3. CHARACTERISTICS OF PHENOLIC AIRCRAFT PAINT STRIPPING WASTEWATER

Paint stripping wastewater generated from use of phenolic paint strippers should be of the same characteristics for various bases. The concentration of the contaminants will vary depending on the phenolic paint stripper used and the amount of rinse water used. Table I lists the contaminants and concentrations expected for phenolic aircraft paint stripping wastewater. This is based on analysis of samples from Vance and Tinker AFB.

Table 1

CHARACTERISTICS OF PHENOLIC AIRCRAFT PAINT STRIPPING WASTEWATER

Contaminant	Concentration (mg/l except pH)
Phenols	1000 to 3000
Methylene Chloride	1000 to 3000
COD	5000 to 30000
Chromium	50 to 200
Suspended Solids	100 to 1000
Oils	100 to 2000
pH	8.0 to 8.5

SECTION II

LITERATURE REVIEW

1. OZONE

a. General

Ozone, a molecule of three oxygen atoms, O_3, exists as a gas. Ozone's principal value is that it is the second most powerful oxidizing agent readily available to man. Only fluorine and its oxides exhibit greater oxidizing power (ref. 1). Ozone's primary application to date has been in disinfecting and purifying potable water. The first installation for such a purpose was in Nice, France, in 1906 and is still operating today. The largest water treatment plant today using ozone is Choisy-le-Roi, near Paris, which is treating 238 million gallons per day (mgd) (ref 2). In the United States ozone has not gained the popularity of chlorine for water treatment even though it is a more powerful oxidizing agent with fewer associated side effects (ref. 1). The reasons for this lack of popularity are beyond the scope of this report.

b. Production of Ozone

Ozone is a relatively unstable gas produced by the reaction of oxygen in an electric discharge called a corona. This instability necessitates "on-site" production. The corona is created by imposing high voltage, 10 to 20 kV, alternating current across a discharge gap (capacitor). This basic method is inherently inefficient with only about 10 percent of the energy supplied being used to produce ozone. The remainder is lost as light, sound, and primarily heat. The decomposition of ozone back to oxygen is greatly accelerated by increasing temperatures. Therefore, all commercial scale ozone generators contain a method of heat removal (ref. 3).

Ozone production from corona using clean dry oxygen can be represented by the following relationship:

$$Y/A \propto \frac{f\varepsilon V^2}{d} \tag{1}$$

where

Y/A = ozone yield per unit area of electrode surface.

V = voltage across the discharge gap (peak volts). This is effected by the gas pressure and the width of the discharge gap.

f = frequency of applied voltage.
ε = dielectric constant of the dielectric.
d = thickness of the dielectric.

Commercial ozone generators fall into one of three basic types: the Otto plate, the tube type, and the Lowther plate. The principle of each, as described earlier, is the same. The main differences are the materials used for dielectrics, electrodes, etc., and the Lowther plate type is air cooled instead of water cooled (ref. 3).

The composition of the feed gas largely affects the ozone yield. Assuming that air is essentially nitrogen and oxygen, two and one half times as much ozone will be produced from a 100-percent oxygen stream as that from an air stream (assuming all other conditions are equal). Economically any large application of ozone necessitates a feed stream of oxygen or oxygen-enriched air to the ozonator. Systems are available for large-scale, on-site generation of oxygen. Whether feeding oxygen, oxygen-enriched air, or air, the gas stream must be dry to decrease ozone decomposition and to prevent damage to the dielectrics (ref. 3). Carbon dioxide present in the gas also decreases ozone yield (ref. 4).

The main requirements for the generation of ozone, using air-cooled generators, is that of power. For the production of 1 percent ozone by weight in the gas stream, 6.3 to 8.8 kwh/lb of ozone using an air stream and 2.5 to 3.5 kwh/lb using an oxygen stream is required. This is for a Lowther plate type generator. The Otto plate and the tube type require greater amounts. From the aspect of minimizing power requirements and obtaining highest wastewater treatment efficiency, 2 percent ozone by weight is the best concentration to use. This gives significantly higher oxidation rates than 1 percent but yet does not require much more power (ref. 4).

c. Ozone Treatment Systems

Economical use of ozone for large-scale operations necessitates the optimization of gas-liquid transfer. Discussion of gas-liquid transfer theory is beyond the scope of this report. There are two basic techniques by which ozone is applied to water or wastewater. One technique uses ozone under pressure and disperses it through porous diffusers in the bottom of a tank, typically 10 to 20 feet deep (figure 1). The other technique uses an injector (venturi) principle to draw oxygen (air) through the ozonator and intimately mix the ozone with the wastewater. The discharge from the venturi passes through a column of contact

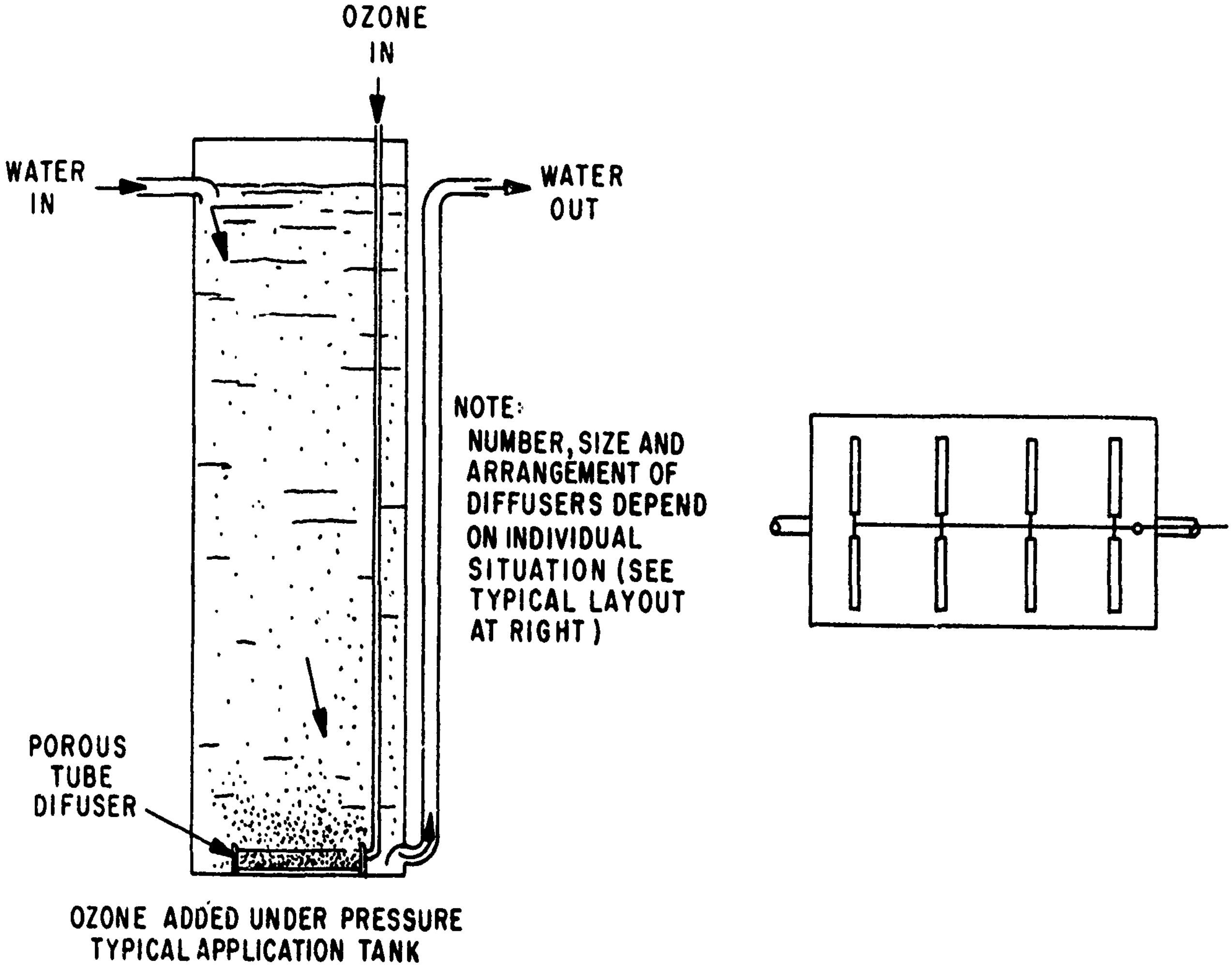


Figure 1. Porous Diffuser Reactor

into a retention chamber (figure 2). Of the two techniques, the first is said to be more flexible, permit better control, require less power, and provide better gas liquid transfer (ref. 5).

A complete treatment system using ozone is shown in figure 3. Since the decomposition product of ozone is oxygen, this oxygen is recycled to produce more ozone. If sufficient quantities of carbon dioxide (CO_2) are generated by oxidation of the organic contaminants in the wastewater, a CO_2 adsorber may be required for the recycled gas. This could be a hydroxide trap. This oxygen generator works on the principle of molecular sieve adsorption of the nitrogen. There are two adsorption columns illustrated, one would be in operation while the other is being "purged" of the nitrogen. The oxygen generator is reported to be capable of producing 95 percent pure oxygen (ref. 3).

d. Ozonation of Phenolic Wastewaters

Ozone has been studied by many for its possible application to the treatment of phenolic wastewaters such as from coke oven operations, oil refineries, wood distillation, etc. (ref. 6). Eisenhauer has done the most recent and complete studies on the use of ozone for oxidation of phenols (refs. 7 and 8). Eisenhauer determined that phenol degradation could be described by the following rate expression:

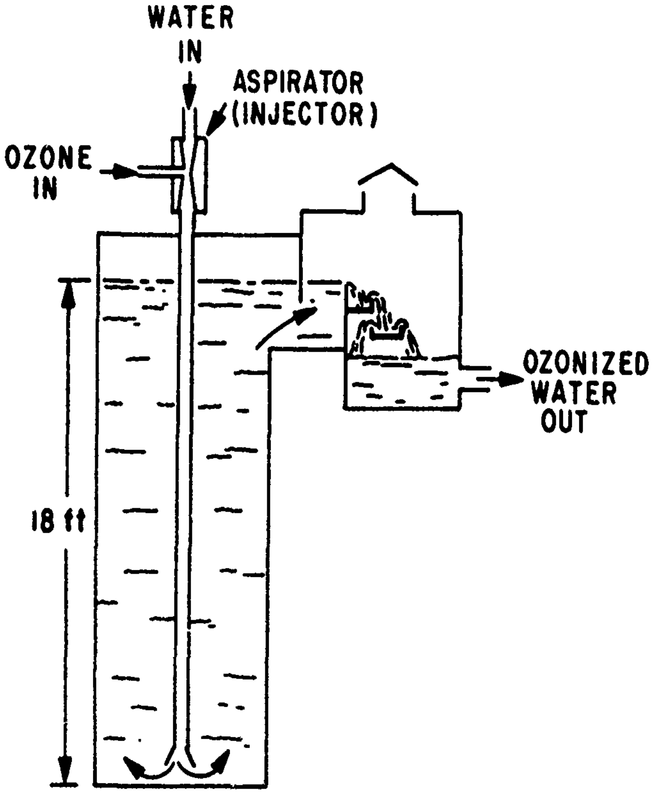
$$\ln \frac{Po}{Pt} = \frac{k_1 Rt}{F^{1/3}} \qquad (2)$$

where

Po = initial phenol concentration.

Pt = phenol concentration @ time t.

R = ozone dose rate (mole O_3/mole phenol/min).



INJECTOR METHOD
TYPICAL APPLICATION TANK
FOR
LARGE SYSTEM, E.G. MUNICIPAL

Figure 2. Injector Reactors

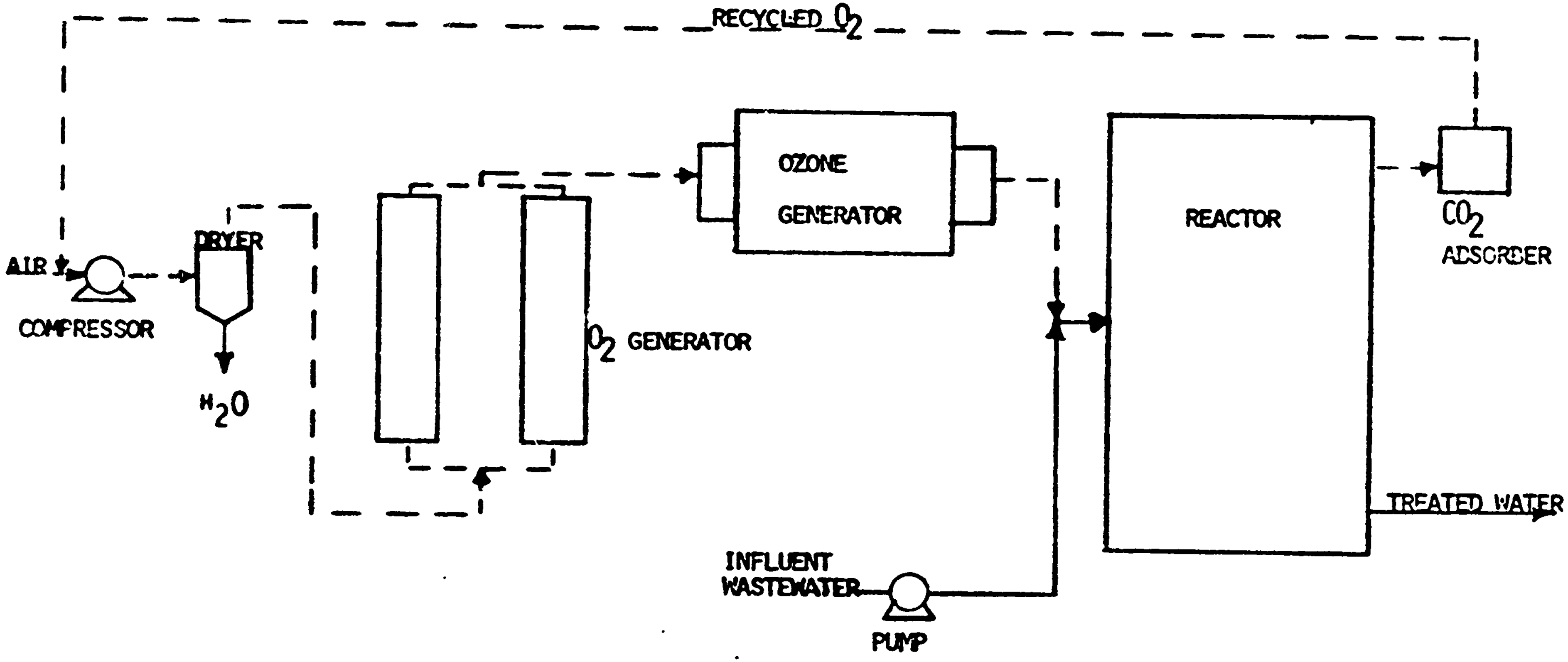


Figure 3. Closed Loop Ozone Treatment System for Wastewater

F = ozone flow l/min.

k_1 = phenol degradation rate constant (mole/phenol/mole O_3/dia) where the dia is the diameter of the ozone gas bubble. The ozone gas bubble diameter has been shown to be numerically equal to the 1/3 power of the gas flow ($F^{1/3}$).

t = time.

Significant factors evident from the rate expression equation are: the oxidation of phenols follows an exponential function and the gas bubble diameter's affect is only to the 1/3 power.

Various factors have been studied as to their effect on phenol ozonation. The effect of pH on the phenol degradation rate constant is as follows:

Initial pH	Final pH	k_1
3.00	2.93	0.229
5.01	3.44	0.247
5.57	3.30	0.256
9.14	3.60	0.307
11.06	9.90	0.658

Below a pH of 9.0 there is no significant increase in the degradation rate. However, above a pH of 11.0 this rate more than doubles. Niegowski has shown than the rate continues to increase up to a pH of approximately 11.8 (ref. 9). Further, the pH of unbuffered neutral or slightly alkaline solutions rapidly decreases to a pH of 3.0 to 3.5 when ozone contacts the wastewater. Raising the pH to an initial value of 11.0 permits only a slight decrease in pH, thus the wastewater remains alkaline (refs. 7 and 8). Further, it has been indicated that at elevated pHs, ozone becomes more selective for phenols than other organics or oxidizable materials present in the wastewater (ref. 9).

Temperature of the wastewater has been studied for its effect on phenol oxidation with Eisenhauer concluding that there was no significant effect on k_1 within the temperature range of 20 to 50° C. However, at elevated temperatures oxidation of phenols was more complete with increased amounts of CO_2 being produced (refs. 8 and 9).

In an attempt to catalyze the reaction between phenol and ozone, Eisenhauer tried adding ferrous salts such as ferrous sulfate, ferrous ammonium sulfate, etc., to the wastewater. Ferrous salts are known to catalyze the oxidation of phenols when added along with hydrogen peroxide (H_2O_2), thereby forming hydroxyl free radicals.

This combination of ferrous salts and H_2O_2 is known as Fenton's Reagent. However, instead of catalyzing the oxidation with ozone, the ferrous salts demonstrated an inhibitory effect (refs. 7 and 8).

The complete oxidation of phenols by ozone is given by the chemical equation:

$$C_6H_6O + 14O_3 \rightarrow 6CO_2 + 3H_2O + 14O_2 \qquad (3)$$

Therefore, stoichiometrically 14 moles of ozone are required for each mole of phenol. This is equivalent to 7.14 gm of ozone for each gm of phenol. This would require 100 percent transfer efficiency. Ozone demand has arbitrarily been taken to be the amount required for 99 percent reduction of phenols (ref 9). This ozone demand can be satisfied with about 5 moles ozone/mole of phenol in pure solutions of phenol at an elevated pH (refs. 7 and 8). The reason why the ozone demand is less than the stoichimetric requirement is that complete oxidation of phenols to CO_2 and H_2O does not occur.

The formation of intermediate products from phenol oxidation have been documented. The first intermediate product is catechol ($C_6H_5(OH_2)$ and should be completely formed after about 1.7 moles of O_3 per mole of phenol are applied. Orthoquinone ($C_6H_4O_2$) has been proposed as the next intermediate product. No evidence has been obtained to elucidate the details of the subsequent oxidation of orthoquinone to CO_2 and water (refs. 7 and 8). Niegowski showed that a 99-percent reduction of phenols produced only a 50-percent reduction in chemical oxygen demand (COD) (ref. 9). The toxicity of these intermediate products to aquatic life is said to be much less (i.e., less toxic) than for phenol (ref. 9). However, McKinney in a very detailed study on the metabolism of aromatic compounds by activated sludge micro-organisms concluded that micro-organisms acclimated to phenols had significant difficulty in degrading catechol and hydroquinone (ref. 10).

The mechanism for the oxidation of phenols by ozone has been thought to involve the formation of hydrogen peroxide as an intermediate product with subsequent use of its oxidizing power to assist the ozone. However, Eisenhauser demonstrated that H_2O_2 was not formed in significant concentrations based on the fact that ferrous salts inhibited rather than catalyzed the oxidation reaction. This, coupled with the fact that the oxidation of phenols was shown to be definitely pH dependent, fostered Eisenhauer to propose the oxidation mechanism as being ionic (ref. 7). A complete discussion of oxidation mechanisms is beyond the scope of this report.

The other significant factor involving ozonation of phenols is the color development. The color of the wastewater rapidly darkens to a dark brown or near black, and then gradually lightens to colorless (refs. 8 and 9).

2. POTASSIUM PERMANGANATE

a. General

Potassium permanganate ($KMnO_4$) is probably the strongest oxidizer that can be added dry to water or wastewater. Most applications have been in treating of potable water for taste and odor control (ref. 11). Potassium permanganate imparts a dark purple color when added to water, which will turn pink when all the organics have been oxidized.

Factors affecting the oxidation of organics by potassium permanganate are: pH, temperature, concentration of organic, concentration of potassium permanganate, type of organic compound, and reaction time. Oxidation for most organics by potassium permanganate appears to be favored in the alkaline range (refs. 11 and 12). Increased temperatures increases the reaction rate by providing increased molecular activity (refs. 11 and 12).

The initial concentration of the organic compounds being oxidized and of the potassium permanganate added affect the rate of oxidation. Spicher and Skrinde have shown that the oxidation, and rate of most organics, followed first order kinetics for residual organic concentration and residual potassium permanganate concentration (refs. 11 and 12).

Not all organics can be readily oxidized by potassium permanganate. Spicher and Skrinde found that the functional group was of primary importance in the oxidation and not the length of the chain. The carboxyl group (-COOH) of acids generally resisted oxidation, as did carbonyl groups (-C=O) of ketones and hydroxyl groups (-OH) of alcohols. On the other hand, the carbonyl group of aldehydes were readily oxidized. Amino groups ($-NH_3$) of amines and the C=C double bond groups of unsaturated compounds were readily oxidized. Aromatic compounds appeared to readily react with potassium permanganate (ref. 12).

The reaction between organics and potassium permanganate is not instantaneous and, therefore, require time to be in contact with each other. Most testing and applications involve a few minutes (1 to 5) of quick mixing, and then slow mixing for the required reaction time. The reaction time required will depend on the above mentioned factors and can vary from 20 minutes to 6 hours (ref. 12).

One of the reaction products is insoluble manganese dioxide (MnO_2). This product occurs as a relatively stable hydrous colloid with an indefinite number of water molecules attached to each MnO_2 group. The precipitate has a large surface area per unit weight and has been shown to act as a good adsorbent, particularly for metal ions (ref. 13).

b. Potassium Permanganate for Oxidation of Phenols

Stoichiometrically potassium permanganate oxidation of phenols is as shown in equation 4 (ref. 13).

$$3C_6H_6O + 28KMnO_4 + 5H_2O \rightarrow 18CO \;\; + 28KOH + 28MnO_2 \qquad (4)$$

This represents a mole ratio of 9.34 moles $KMnO_4$ required per mole of phenol or on a weight ratio 15.7. It has been found that phenols can be oxidized at a weight ratio of between 6.0 and 7.0. Dosing potassium permanganate at this weight ratio is said to be sufficient to break the benzene ring and form simpler compounds (ref. 13).

Spicher and Skrinde have postulated the intermediate oxidation products of phenol to be: first, dihydroxybenzene (hydroquinone) $C_6H_6O_2$, second, quinone $C_6H_4O_2$, third, maleic acid $C_4H_4O_4$, and fourth, mesotartaric acid $C_4H_6O_6$. The breaking of the ring coming between the quinone and maleic acid (ref. 12).

The rate use of potassium permanganate when reacted with phenols has been demonstrated to be relatively rapid with complete use of potassium permanganate, when dosed at 10 gr $KMnO_4$ per gram of phenol, occurring in approximately 1 hour (ref. 12). Although phenol oxidation is favored in the alkaline range (ref. 13), it was not demonstrated to affect the potassium permanganate use when tests were conducted at a neutral pH and a pH of 10.0.

3. ACTIVATED CARBON

a. General

Activated carbon, also referred to as activated charcoal, is produced in either a granular or a powered form. At present most wastewater treatment processes use granular activated carbon and, therefore, the discussion will be limited to this type. Activated carbon can be produced from a variety of high-carbon content materials; a good quality of coal being the most common.

Activated carbon is used primarily for the removal of soluble organics from wastewater. The mechanism for removal is adsorption, i.e., the organic molecule adheres to the surface of the activated carbon. There are many factors that affect this adsorption mechanism. Some of these factors are: Surface area, particle size, the compound being adsorbed, solubility of the organic compound, pH, temperature, concentration of the organic compound, contact time, and hydraulic loading.

Activated carbon is an extremely efficient adsorber because of its high surface area to weight ratio. This will vary with the activated carbon used, but this is generally on the order of 1000 m^2/gr (ref. 14).

The particle size on most activated carbons are in the range of being smaller than a No. 8 U.S. standard sieve size and larger than a No. 40 U.S. standard sieve. The particle size affects the rate of adsorption but not the total adsorptive capacity. Adsorptive capacity is the weight of organic compound or oxygen equivalent (COD) that can be adsorbed per unit weight of activated carbon, i.e., gr of COD/gr of activated carbon. The smaller the particle size the faster the rate of adsorption because the less distance the organic molecule has to travel (ref. 15).

The compound being adsorbed greatly affects the effectiveness of the adsorption process. In general, high molecular weight compounds are more readily adsorbed than low molecular weight ones. Nonpolar compounds are adsorbed better than polar ones. The more ionic the compound the less it is adsorbed. Compounds with molecule sizes close to that of the pore size of the activated carbon are more easily adsorbed (refs. 14 and 16).

The solubility of the organic compound in the wastewater (solvent) largely affects the adsorption efficiency. Sigworth has stated that adsorption is a "fight" against solubility (ref. 17). Although there are a few exceptions, highly soluble compounds are less readily adsorbed than slightly soluble. In fact, altering the solubility of the compound by changing the solvent or the pH permits the extraction from the activated carbon of an adsorbed compound. This will be discussed further under "regeneration of activated carbon."

The pH of the solution thus affects adsorption by primarily affecting the solubility of the organic compounds. Raising the pH of the solution in the case of phenols or organic acids tends to form phenolate salts and salts of the organic acid, both of which are not appreciably adsorbed. However, organic bases such as amines are adsorbed best at high pHs (ref. 17).

Temperature affects the adsorption process by affecting the molecular motion (activity) of the compound. In general, elevated temperatures result in increased adsorption because of increased opportunity for contact between the compound and the active surfaces. However, volatile compounds are more readily removed at lower temperatures (ref. 17).

The initial concentration of the compound to be adsorbed affects the required amount of activated carbon. The last traces of the compound are the most difficult to remove and, therefore, require more activated carbon. This will become more evident in the discussion of contact time. For batch adsorption it has been found that the Freundlich equation describes the adsorption mechanism. This equation is:

$$\frac{X}{M} = KC^{1/n} \tag{5}$$

where

X = weight of organic compound (or COD) adsorbed. (Initial minus final concentration times the volume).

M = weight of activated carbon used.

K, N = are constants.

C = concentration of compound still in solution.

This equation is a straight line on log-log paper in the range that it is applicable. Determining X/M at the initial concentration of the organic compound gives an estimate of the adsorptive capacity of the activated carbon. Since X, and therefore X/M, is affected by the initial concentration of the compound, then the required amount of activated carbon will be dependent on the initial concentration and the final concentration required. Theoretically, a final concentration of zero cannot be obtained. Sigworth has provided a good review of this concept (refs. 14 and 17).

From an engineering aspect, for a given wastewater and activated carbon, the main operating parameter is the contact time of the wastewater with the activated carbon. The contact time has been defined as the time required to fill the empty contact column at the given flow rate. Therefore, it is only a superficial contact time because of the volume of activated carbon in the column.

As expected, removal of a large percentage of the organic compound occurs in the first few minutes of contact, and then the removal rate slows considerably. Treating of secondary effluents from domestic sewage treatment plants require contact times of 40 to 50 miunutes to reduce COD concentrations from 60 mg/l to less than 3 mg/l (refs. 14, 16, and 18).

Another engineering factor that affects column design, and somewhat affects performance, is the hydraulic loading. The hydraulic loading is the gallons of wastewater applied per minute per square feet of surface area (gpm/ft^2) and is, therefore, a velocity of flow. It has been found that hydraulic loadings in the range of 4 to 10 gpm/ft^2 do not affect the removal efficiency to any significant degree (ref. 14). However, the hydraulic loading is important in sizing of the column and in head loss considerations (ref. 18).

Another application for activated carbon that is receiving attention is for the removal of heavy metals and some inorganic compounds. For years water has been dechlorinated by contacting it with activated carbon. Heavy metals have been demonstrated to "plate out" on activated carbon. In addition to the factors listed for adsorption of organics, Sigworth and Smith (ref. 19) have proposed two additional mechanisms for adsorption of the metals. One is that activated carbon has a limited cation exchange capability and the heavy higher valence metals are exchanged for H+, Na++ and other such ions. The second mechanism is that commercial grades of activated carbon contain reduced forms of iron and other metals, which can react with metallic ions lower in the electromotive series causing the metal ion to change state and be deposited on the surface.

Sigworth has classified the heavy metals as to their potential for being adsorbed on activated carbon. Metals with high potential are: antimony, arsenic, bismuth, chromium, and tin. Good potential are: silver, mercury, cobalt, and zirconium. Fair to good potential are: lead, nickel, titanium, vanadium, and iron. Low or unknown potential are: copper, cadmium, zinc, etc.

Extraction processes for the removal of heavy metals from the activated carbon has to date had limited success for most metals. Solubility again is the key factor. Chromium has been successfully extracted using a caustic solution (ref. 20).

b. Regeneration

One of the main process advantages of granular activated carbon is that it can be regenerated and reused again. For treating of large volumes of wastewater, "on-site" regeneration is the only feasible method of operation. For small wastewater flows, the capital cost for a regeneration system may be more than using the activated carbon on a "throw away" basis or transporting it to a central regeneration facility (refs. 14 and 18).

There are four general methods for regenerating activated carbon: solvent wash, acid or caustic wash, steam regeneration, and thermal regeneration. The two wash methods are based on solubility for extracting the compound from the activated carbon surface back into solution. These two methods are usually limited to the recovery of a valuable product. Steam regeneration is primarily applied in the case where the adsorbed compounds are volatile in nature. Thermal regeneration is the most popular process used to date (ref. 14).

Thermal regeneration consists of three steps: drying, baking, and oxidation. Drying is accomplished at temperatures of 212°F, baking between 212 and 1500°F, and oxidation above 1500°F (usually between 1650 to 1700°F) (ref. 14). At present direct-fired, multiple-hearth furnaces are used for regeneration. However, rotary kilns are being investigated and proposed for application because of some of the disadvantages of multiple hearths (refs. 14 and 20). There are physical losses of activated carbon on the order of 5 percent for each regeneration because of the transport of the activated carbon into, through, and out of the multiple-hearth furnace. In addition there is a slight decrease in adsorptive capacity, considered to be caused by quenching of the "red hot" activated carbon after regeneration. Figure 4 shows the various units required along with the multiple-hearth furnace to transport the "exhausted" activated carbon as a slurry for regeneration and placement back into the contact column (ref. 18).

c. Activated Carbon Systems

Granular activated carbon is maintained in a column, and the wastewater passes through the column to provide the necessary contact. There are many design options available, and the decision of which type to employ depends largely on the wastewater volumes and characteristics. The contact columns can be operated in series, in parallel, upflow, downflow, co-current, or countercurrent. The choice between series or parallel operation is largely influenced by the wastewater volumes and the required contact time. Many times activated carbon depths in excess of 20 feet are required to provide sufficient contact time and it may be more practical to have two or three columns in series instead of one. Parallel or parallel-series operation usually becomes necessary when the wastewater flow becomes large.

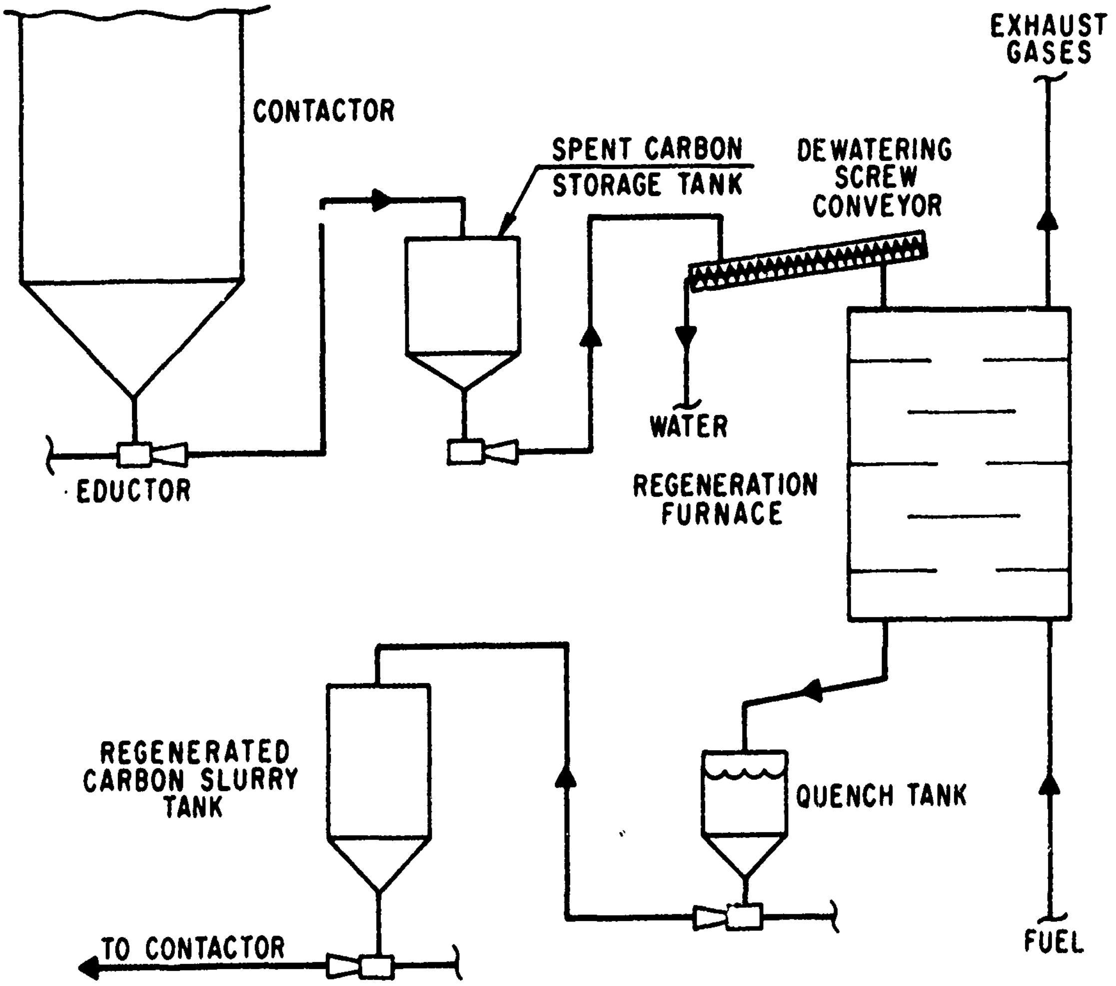


Figure 4. Regeneration System

Upflow or downflow operation along with co-current or countercurrent flow is usually dictated by the wastewater characteristics. Activated carbon is added at the top of a column and extracted at the bottom. Therefore, if a column is operated in a downflow, i.e., if wastewater enters at the top, it would be considered co-current, and if the wastewater enters from the bottom, it would be considered countercurrent operation. This is not strictly true in that the activated carbon is not withdrawn or moving continuously. The only reason for using a downflow operation is to use the activated carbon for filtration of the wastewater also. Countercurrent operation with the wastewater entering at the bottom is favored for most applications because it makes maximum use of the activated carbon and obtains the best removal efficiency. This is accomplished by having the freshest activated carbon at the top of the column permitting "polishing" of the wastewater and allowing the activated carbon to become completely "saturated" with organics before it is taken from the column at the bottom (ref. 14).

Upflow columns can be operated as either a packed bed or an expanded bed. Packed beds should be limited to wastewaters low in suspended solids to prevent plugging of the bottom of the column. Expanded beds, usually about 10 percent expansion, should be used when there is in excess of 20 mg/l suspended solids in the wastewater (ref. 20). This allows passing of the suspended solids without affecting soluble organic removal. For 8 x 30-activated carbon, a 10-percent expansion is obtained at a hydraulic loading of about 10 gpm/ft^2. Using 12 x 40-activated carbons requires about 5 gpm/ft^2 (ref. 14).

Figure 4 shows the transport system for the activated carbon once it was extracted from the column. Extracting the activated carbon from the bottom of the column is accomplished by increasing the flow to slightly "fluidize" the bed or by pressurizing the column. Activated carbon will easily move down a 60-degree slope and will move down a 45-degree slope. Columns greater than 9 feet in diameter usually use a conical bottom of 45 degrees to minimize overall height (ref. 14). Figure 5 is a section through an activated carbon column used at South Lake Tahoe's Advanced Waste Treatment Plant (ref. 14).

d. Activated Carbon Applied to Adsorption of Phenols

Review of the literature will reveal the wide application being afforded to activated carbon for treating of industrial wastewaters containing various organic and inorganic contaminants. Use of granular activated carbon for phenol bearing wastewaters has been applied to the wood preserving, coke oven, petroleum, and other industries (refs. 6 and 20). Some of these treatment operations have used chemical regeneration (solvent or caustic) for recovery and reuse of the phenols while others have applied thermal regeneration.

The pH of the incoming wastewater significantly affects the adsorption efficiency and capacity. Sigworth has stated that adsorption diminishes appreciably above a pH of 8.6 (ref. 17). Rizzo has stated that best adsorption occurs at a slightly acid pH, 6.5 to 7.0 (ref. 20). Adsorptive capacities from 0.15 to 0.45 grams phenol removed per gram of carbon have been reported (refs. 6, 17, and 20). Rizzo has stated that for wastewaters containing phenol concentrations in the range of 2500 to 3000 mg/l a contact time of approximately 50 minutes would be required to reduce phenol concentrations to below 2 mg/l (ref. 20).

Extraction of phenols from activated carbon using a hot 50-percent caustic soda solution (heating of the regenerant solution known to be required) resulted in extracting 89 percent of the adsorbed phenols with 2.5 bed volumes of

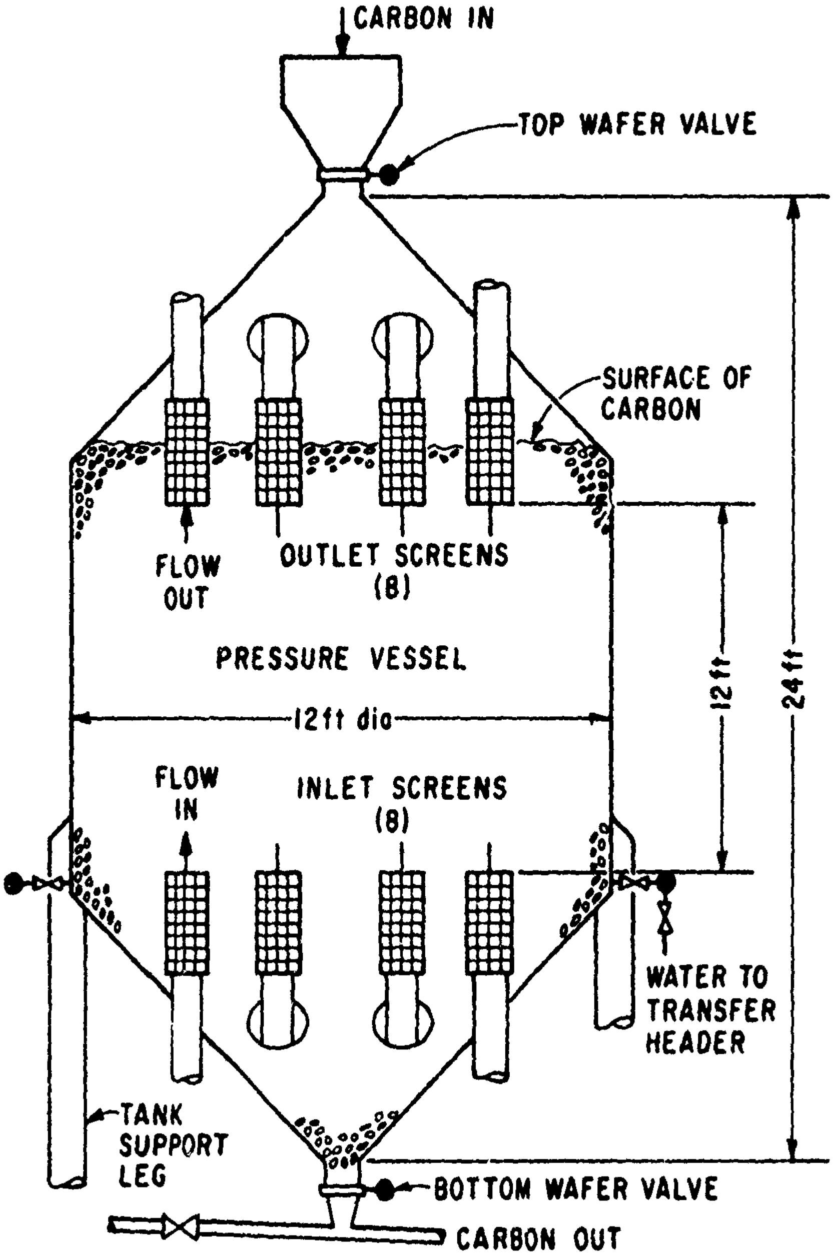


Figure 5. Section Through Activated Carbon Column

regenerant. Extraction was virtually complete at 89-percent removal, and additional throughput of regenerant would not increase removal (ref. 22).

4. OTHER POSSIBLE TREATMENT PROCESSES FOR PHENOLIC AIRCRAFT PAINT STRIPPING WASTEWATER

Various other methods exist for treating phenolic wastewaters, which will be covered briefly. These methods include recovery of the phenols, oxidation with chlorine, oxidation with chlorine dioxide, oxidation with hydrogen peroxide, electrolytic decomposition, and biological degradation.

a. Phenol Recovery

Recovery of phenols has been practiced for at least 40 years, primarily in the coke oven and petrochemical industries (ref. 23). There are two different processes available for recovery of phenols: one is steam stripping, and the other is solvent extraction (ref. 24).

The steam stripping process employs a tower containing some sort of packing (wood, slats, raschig rings, etc.) or trays. The steam contacts the trickling wastewater and removes the phenols. Steam is recycled after contact with caustic soda where the phenols are extracted from the steam as sodium phenolate. Operating efficiencies as high as 99 percent recovery have been reported with most processes obtaining 70 to 95 percent recovery (ref. 24).

The solvent extraction process is based on phenols dissolving more easily in the solvent than in water. Solvent and wastewater are contacted countercurrently, using either a tower (packed or spray type) or a mixer settling tank. However, recently centrifugal contactors have been applied that contain multistages and operate countercurrently. The solvent is regenerated and recycled by either contacting with caustic soda or by distillation (refs. 23 and 24).

Of upmost importance is the selection of a solvent that has the highest extraction capabilities, is insoluble in water, low volatility, significantly different specific gravity from that of the wastewater, and relatively cheap. Wurm has classified various solvents by their distribution coefficient that is a measure of the solvent's extraction capability. The higher the distribution coefficient the lower the residual phenol concentration and the smaller the quantity of solvent required. Table II lists the distribution coefficients for various solvents (ref. 23).

There does not appear to be a simple way of determining when to employ recovery as opposed to disposal of phenolic wastewaters. Factors having influence on the choice of going to a recovery process or not include: phenol concentration and variation, quantity of wastewater, purity of wastewater, and use or market for the recovered phenols.

b. Oxidation with Chlorine

Chlorine is widely used in water treatment for disinfection purposes. It is added either as a gas (Cl_2) or as a hypochlorite salt (NaOCl). When chlorine

Table II

DISTRIBUTION COEFFICIENTS OF DIFFERENT SOLVENTS IN 2 PERCENT (20,000 ppm) PHENOL SOLUTION

Solvents	Distribution Coefficients
Light Oil	0.2
Benzene	2.2
Alkanol	12
Diethyl Ether	17
Dipropyl Ether, normal	17
Butyl Alcohol	19
Phenosolvan (Isopropyl Ether)	20
Tricresyl Phosphate	28
Ethyl Acetate	36
Isopropyl Ester	45
Phenosolvan (Butyl Acetate)	49
Xylenyl Diphenyl Phosphate	60

gas is added to water the following reactions occur (ref. 26).

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (5)$$

$$HOCl \rightarrow OCl^- + H^+ \quad (6)$$

The relative amounts of HOCl and OCl^- in solution is largely pH dependent and somewhat temperature dependent. At a neutral pH and water temperature of 20°C there would be 72 percent HOCl and 28 percent OCl^- (ref. 26).

Ammonia (NH_3) present in the wastewater will exert a chlorine demand that must be satisfied before any significant oxidation occurs. Between 8 to 12 mg/l of Cl_2 gas is required for each 1 mg/l of ammonia.

When phenols are contacted with chlorine unless oxidation of the phenols (not necessarily complete oxidation) occurs chlorophenols are formed which are more toxic to aquatic life and present worse tastes and odors in potable water than the phenols themselves. However, excessive chlorination (superchlorination) will result in oxidation of the chlorophenols and of the phenols to simpler products such as maleic acid $C_4H_4O_4$, methylmaleic acid $C_5H_6O_4$, or CO_2(ref. 25).

Oxdiation of phenols with chlorine is favored in the alkaline pH range, at least above pH 7.7, and stoichiometrically complete oxidation is given by equation 7.

$$C_6H_6O + 14OCl \rightarrow 6CO_2 + 3H_2O + 14Cl \qquad (7)$$

This gives a requirement of 14 moles of chlorine for each mole of phenol or on a weight ratio 10.4 mg Cl_2/mg phenol. This is based on equations 5 and 6 where one more of Cl_2 forms one more of OCl^-.

Contact times of 1 to 3.5 hours have been reported as being required for oxidation (ref. 25).

At Boeing Aircraft's Wichita Kansas Plant, all their industrial wastewater is treated with chlorine. Part of this wastewater is phenolic aircraft paint stripping wastewater and part is cyanides from plating operations. The influent industrial wastewater is pretreated for chromium reduction, and the wastewater which has been elevated to a pH of 9 to 10 is batch treated with 7 to 10 pounds of Cl_2 per pound of phenol. Influent phenols are in the range of 200 to 1500 mg/l, and it is attempted to reduce this to 0.05 mg/l with the chlorine. After chlorination the wastewater is polished with ozone and then released (ref. 27).

c. Oxidation with Chlorine Dioxide

Chlorine dioxide ClO_2, reacts much the same way with phenols as does chlorine. Chlorine dioxide is more versatile than chlorine in that it is not pH dependent, and the required reaction time is only 2 to 15 minutes during which no chlorophenols are formed. Further, ammonia does not interfere with the oxidation. Coke wastewaters containing 6000 to 16,000 mg/l of phenols have been successfully treated with 1.0 to 1.7 gr of ClO_2 per gram of phenol even though the wastewater contained up to 4700 mg/l of ammonia (ref. 25).

Stoichiometrically the reaction for complete oxidation is given by equation 8.

$$C_6H_6O + 7ClO_2 \rightarrow 6CO_2 + 3H_2O + 7Cl \qquad (8)$$

This yields a mole requirement of 7 moles ClO_2 per mole of phenol or a weight ratio of 5.0 gr ClO_2 per gram of phenol. Chlorine dioxide can be produced on site by reacting chlorine gas with a chlorite salt such as sodium chlorite.

d. Oxidation with Hydrogen Peroxide

Hydrogen Peroxide H_2O_2, in the presence of ferrous salts as a catalyst (Fenton's Reagent) have been shown to be effective in oxidizing phenols.

The catalytic activity is further increased by the presence of aluminum, cupric, or chromic salts. The reaction proceeds best at a pH of 3 to 4. Complete oxidation is given by equation 9.

$$C_6H_6O + 7H_2O_2 \rightarrow 6CO_2 + 3H_2O + 14H^+ \qquad (9)$$

This yields a weight ratio requirement of 2.53 gr H_2O_2 per gram of phenol. With solutions of pure phenol, complete oxidation can be achieved using about 1.1 gram of H_2O_2 per gram of phenol. The oxidation is believed to proceed via quinones and muconic acid $C_6H_6O_4$(ref. 25).

e. Electrolytic Decompositon of Phenols

Electrolytic decomposition (oxidation) of phenols has been reviewed by Kuhn and Eisenhauer (refs. 25 and 28). Complete discussion of electrolytic technology is beyond the scope of this report; however, basically an electrolytic cell is used in which the wastewater passes through contacting an anode of platinum, lead oxide, or carbon and a cathode of iron or mild steel. A potential of 3 to 4 volts is applied at current densities of 0.5 to 0.8 amps/sq in. Power consumptions are 0.4 to 0.5 kwh/gr of phenol oxidized.

There are two basic techniques used. One depends on the liberation of oxygen at the anode to oxidize the phenols. The second technique is based on "in-situ" liberation of chlorine at the anode when a brine solution is added. The chlorine then reacts with the phenols in much the same manner as previously discussed. Using oxygen, the oxidation products are said to be polyhydroxybenzenes, quinones, and by ring cleavage to oxalic and formic acids. Only 6 to 17 percent of the phenols are oxidized to carbon dioxide (refs. 25 and 28).

f. Biological Degradation of Phenols

Biological treatment of organics in wastewater is by far the most widely practiced method of treatment. Basically the microorganisms use the organic compounds as a source of carbon in the synthesis of new cells (microorganisms). Biological treatment of phenolic wastewaters is practiced by many industries. However, there exists a rather significant controversy as to the limitations of a biological treatment process for phenols.

The two most common bilogical treatment processes are the fixed film reactor (trickling filter) and the fluidized reactor (activated sludge). Both have been and are presently used to treat wastewaters where phenols represent the sole carbon source. Applications of the activated sludge process for phenol removal reveal treatment processes treating wastewaters with up to 1200 mg/l of phenols. One pilot plant activated sludge units reduced phenol concentrations from 3900 mg/l to less than 1 mg/l (refs. 6 and 25). Trickling filters when receiving less than 50 mg/l of phenols would generally produce effluents of less than 1 mg/l. When loaded at between 200 to 500 mg/l, effluents were generally less than 75 mg/l (refs. 6, 25, and 29).

McKinney (ref. 10) presented a good review of metabolism of aromatic compounds by activated sludge microorganisms, and he concluded that the limiting factor was not the phenol concentration but rather was the rate of oxygen transfer. Further, he proposed that metabolism of aromatic compounds was by the beta-oxidation pathway not involving the intermediates formed by chemical oxidation.

The effectiveness of biological treatment for phenolic wastewaters is largely influenced by the presence of other organic and inorganic compounds. In the presence of other easily biodegradable organics, the microorganisms will not use the phenols as a carbon source until the other organics have been used. Inorganic compounds, primarily heavy metals, can be toxic to microorganisms as can certain organic compounds.

In the case of hexavalent chromium, which is present in the phenolic paint strippers used, there is somewhat conflicting results as to the toxicity. Reid reported that a rotating drum (bio-disc) receiving phenol concentrations of 50 to 400 mg/l and chromium concentrations of 1 to 10 mg/l deteriorated to negilible phenol removals after 2 months of operation. This deterioration was thought to be caused by accumulation of the chromium by the microorganisms (ref. 29). A very comprehensive study by the U.S. Public Health Service (ref. 30) revealed that activated sludge units receiving domestic sewage and up to 50 mg/l of hexavalent chromium showed no significant decrease in performance after 6 weeks of operation. At the 50 mg/l loading of hexavalent chromium an average of 40 mg/l "leaked" through in the effluent.

SECTION III

MATERIALS AND METHODS

1. GENERAL

Laboratory-scale investigations of the three unit processes described in the introduction were conducted to determine the effectiveness of each unit process for the removal of the contaminants of concern. This involved determination of the operating parameters that had a known effect on unit process performance. In all cases analyses were conducted for the determination of phenols, methylene chloride, COD, total chromium, and pH. Suspended solids were determined on the received wastewater. All experiments were conducted using 200 gallons of phenolic aircraft paint stripping wastewater from Vance AFB. The characteristics of the wastewater are listed in table III.

It should be noticed that the concentrations listed are averages of many determinations, and the values did vary within the accuracy of the analytical procedure used.

Table III

CHARACTERISTICS OF SETTLED PHENOLIC AIRCRAFT PAINT STRIPPING WASTEWATER USED DURING INVESTIGATION

Contaminant	Concentration (mg/l except pH)
Phenols	3000
Methylene Chloride	1600
COD	10100
Total Chromium	100
Filterable Solids	75
pH	8.3

2. OZONATION EXPERIMENTS

All ozone experiments were conducted using an Ozone Research and Equipment Corporation Model 03C12 ozone generator. This was a water-cooled, tube-type generator with a maximum output of 70 gr/hr of ozone using 20 kV of power at 60 Hertz. Since the generator had its own air purification system, it was used instead of bottled oxygen. Output of ozone could be varied by changing either the current applied to the dielectric, the gas flow rate, or the gas pressure. Appendix A shows the ozone output for varying current and air flow rate.

Batch and continuous flow studies were conducted varying the operating parameters to determine required conditions. Parameters that were varied included ozone concentration and dose rate, initial pH of the wastewater, and contact time.

For the batch experiments, 400 ml of sample was placed in a fritted glass bubbler, and the ozone was applied under a given set of controlled parameters. After the desired contact time was reached, the ozone flow was stopped, and the sample was analyzed for the residual contaminants concentration. In addition, the exhaust gas was passed through two additional bubblers. The first one was for adsorbing CO_2 liberated to quantify the amount produced. The second bubbler was to determine the amount of ozone not consumed. Further description of these procedures are in the analytical procedures later in this section. Figure 6 diagrams the batch experiment apparatus.

Continuous flow experiments were undertaken following the batch experiments. These experiments consisted of a two stage reactor, each stage maintained at 900 ml of liquid volume. Each stage was a glass cylinder $2\frac{1}{2}$ inches in diameter with $13\frac{1}{2}$ inches of liquid depth. The wastewater was pumped at varying flow rates to the first stage that was maintained under positive pressure, thus, forcing the liquid and gas into the second stage. The ozone stream was split between each reactor stage by teeing the main ozone line and using restricting clamps to

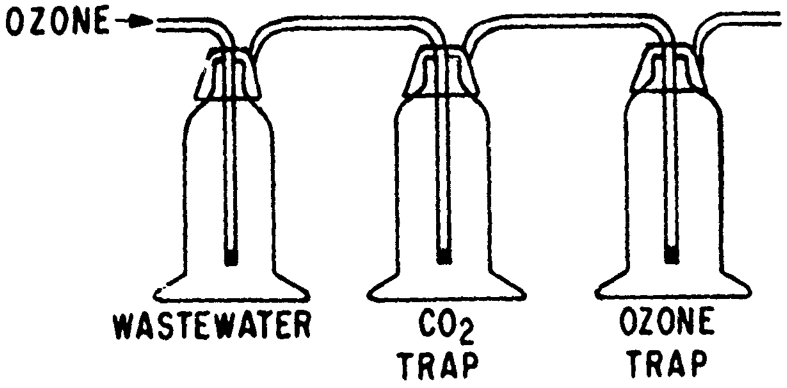


Figure 6. Apparatus for Batch Ozonation Experiments

control the distribution of ozone to each stage. This was accomplished by completely clamping shut the ozone line to the second stage and setting the desired total ozone flow rate through the rotameter and into the first stage. Then the clamp on the second stage line was slowly opened until the ozone flow rate through the rotameter and the first stage was as desired. Examination of figure 7 will make this procedure readily understood. It should be noted that since stage one was closed, i.e., not vented to the atmosphere, the gas flow to stage one was carried over into stage two. For example, if 2 l/min of total ozone flow was split equally, stage one would received 1 l/min and stage two would received 2 l/min, which is 1 l/min of virgin ozone and 1 l/min of exhausted or partially exhausted ozone. Operating in this manner would permit maximum use of the ozone.

Initial experiments were conducted to determine what would be the optimum ratio of ozone flow between stages. This was done by using only the first stage under a given set of conditions and increasing the ozone flow until significant carryover of ozone occurred. Then the first stage ozonated wastewater was collected and pumped into what would have been the second stage, and the ozone flow was increased until significant ozone carryover occurred. These ozone flows were taken to be the optimum.

The wastewater was delivered to the bottom of each stage and extracted from the top. Ozone was delivered at the bottom through porous stone diffusers.

It was necessary to separate the exhausted gas from the ozonated wastewater leaving the reactor such that ozone carryover could be determined. This was accomplished by using a separatory funnel to trap the liquid (figure 7).

Based on the results of the ozonation experiments where it was verified that intermediate oxidation products were formed, it was decided to conduct limited biodegradation studies on diluted quantities of untreated and ozonated wastewater. The objective being to determine the biodegradability of the ozonated wastewater relative to the untreated. Shaker flasks were set up containing 500 ml of liquid and 1 ml of settled sewage. A synthetic sewage was made up, and varying amounts of untreated and ozonated wastewater were mixed with the synthetic sewage to yield the 500 ml total quantity. Description of the contents of each shaker flask can be found in the results section. The flasks were agitated for a period of 9 days with a small amount (5 ml) being taken every other day for soluble COD analysis.

3. POTASSIUM PERMANGANATE EXPERIMENTS

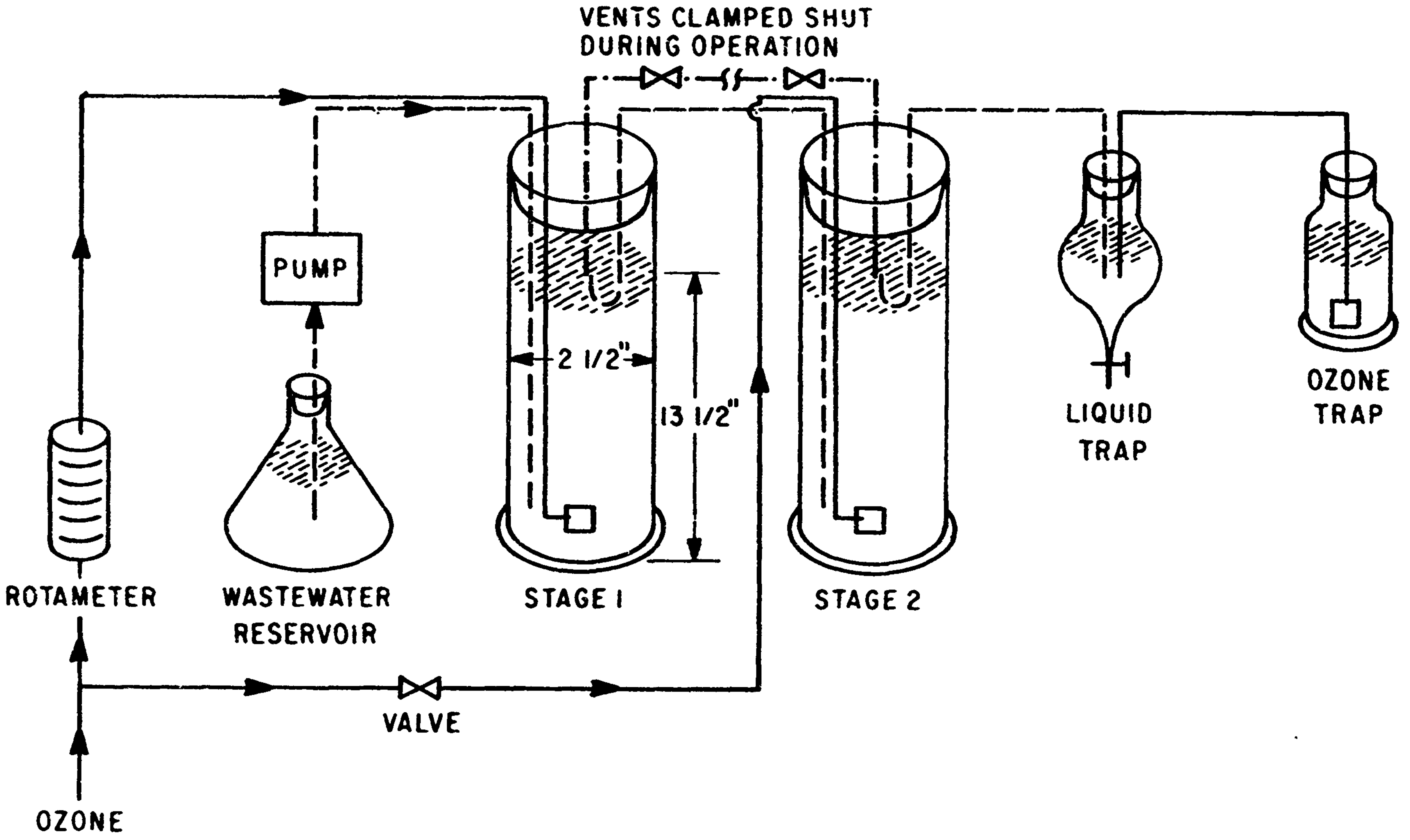


Figure 7. Continuous Flow Apparatus for Ozonation Experiments

Jar testing experiments were conducted using reagent grade potassium permanganate at varying concentrations for a fixed time, and then at fixed concentrations for varying time. Initial experiments consisted of three sets of jar tests using six breakers in a six paddle stirrer for each set. One set was used with the wastewater adjusted to a pH of 6.0; a second set was unadjusted and had a pH of 8.5; the third set was adjusted to a pH of 10.5. The potassium permanganate was added dry to each breaker containing 500 ml of wastewater. Potassium permanganate was added to each breaker to obtain the following concentrations: 4000 mg/l, 10,000, 20,000, 32,000, 48,000, and 70,000 mg/l. The breakers in the paddle stirrer were given a quick mix of 2 min at 100 rpm followed by 58 min of slow mix at 25 to 30 rpm. At the end of the 1 hour, residual potassium permanganate was measured (see Analytical Procedure). In addition to the standard tests performed total dissolved solids concentration and sludge concentration were determined. A modified procedure for COD had to be employed (see Analytical Procedure).

4. ACTIVATED CARBON EXPERIMENTS

Granular activated carbon was used in batch and continuous flow experiments. The batch experiments were limited to screening of four different activated carbons to determine which would provide the greatest adsorptive capacity in terms of phenols and COD. This was accomplished by conducting batch adsorption isotherms (refer to appendix C for isotherm procedure). The four activated carbons tested were: Calgon Filtersorb 400, 12 x 40; Westvaco Nuchar, 12 x 40; Witco, 12 x 30; and Darco, 8 x 35. The numbers 12 x 40 etc., refer to the size of the activated carbon. The numbers are U.S. Standard sieve size at which approximately 95 percent will be passed or retained. Since pH is a known factor affecting adsorption of organics, two adsorption isotherms were developed for each activated carbon. The first followed the established procedure of acidifying the sample to a pH of 4.5. The second was conducted without changing the initial pH.

On the basis of the batch experiments the best activated carbon was selected and the continuous flow columns were filled with this activated carbon. The activated carbon columns consisted of three 7-foot, 3.125-inch inside diameter clear acrylic plastic tubes connected in series. An average of 6 feet of activated carbon was maintained in each column giving a total activated carbon depth of 18 feet, which yielded 1.04 ft^3 of activated carbon (figure 8). The columns were operated in a pressure downflow condition, and the discharge was regulated to maintain a liquid depth of 6 inches at the top of each column. Sampling ports

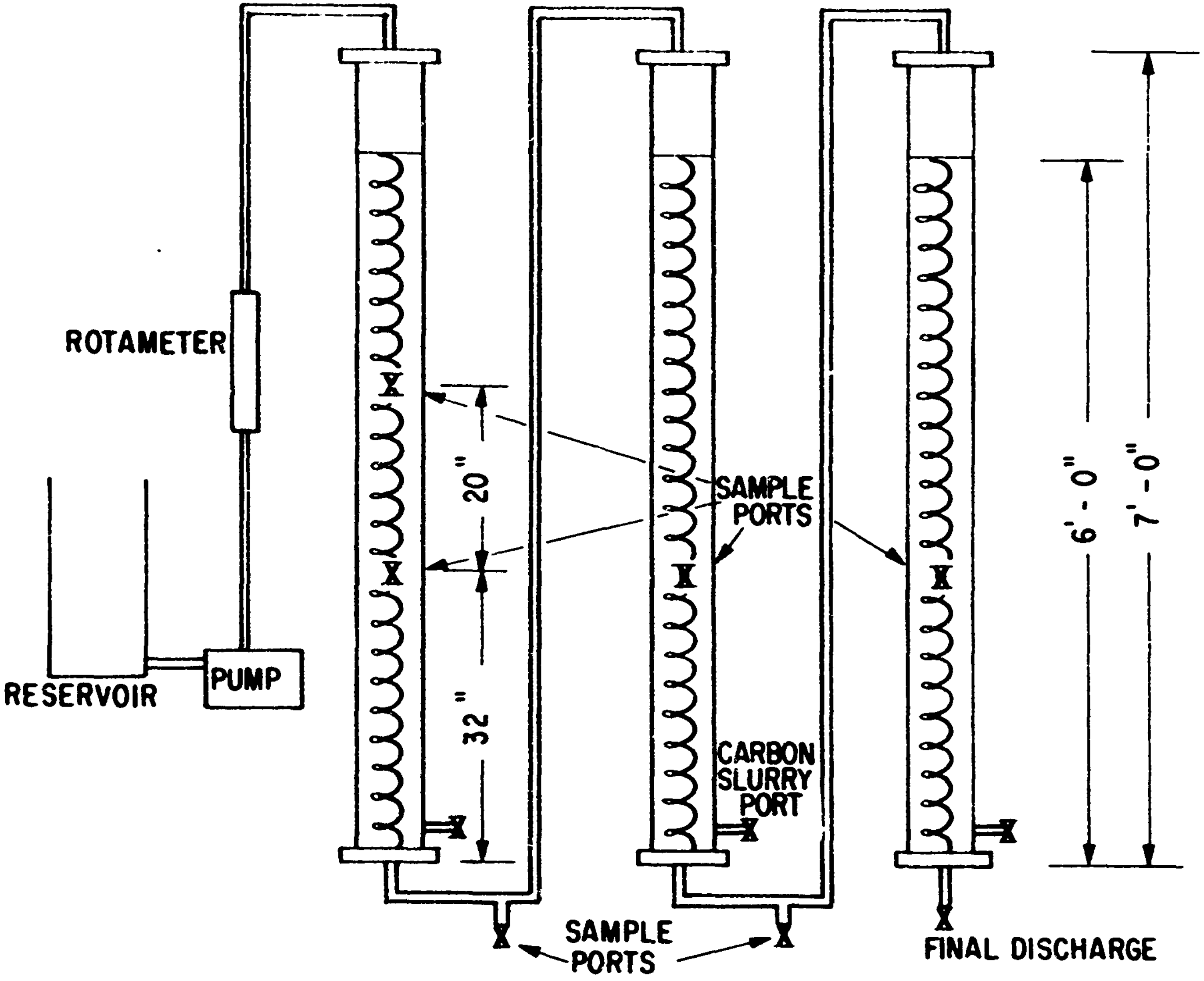


Figure 8. Granular Activated Carbon Columns

were installed at various depths to permit determination of contaminant removal versus contact time and to monitor "breakthrough" (exhaustion) of the activated carbon. The columns were "charged" by pumping the activated carbon in as a slurry with tap water.

In that contact time is the prime operating parameter for activated carbon systems, an overall contact time of 60 minutes was selected, i.e., at the discharge from the third column. The standard way of expressing contact time is the time required to fill the empty bed (column) with water. Therefore, this is only a superficial contact time. Deciding on the 60-minute contact time and having an activated carbon volume of 1.04 ft^3, dictated a flow rate of 0.13 gpm. This yielded a hydraulic loading of 2.28 gal/min/ft , which was in the range of normal operation for full scale units.

The first continuous flow experiment was conducted using the wastewater without pH adjustment. This experiment lasted for 6 hours with the primary objective being to obtain periodic samples for determination of contaminant removal versus contact time and breakthrough of the activated carbon. The second continuous flow experiment was conducted using the wastewater that had been acidified to a pH of 6.5. Refer to appendix A for the acid titration curve. The objectives of this experiment were to determine the effect of pH on contaminant removal versus contact time and to monitor breakthrough. This experiment lasted 9 hours. Between the experiments, virgin activated carbon was charged into the columns replacing the once used activated carbon, thereby maintaining equal conditions.

5. ANALYTICAL PROCEDURE

Chemical analyses were conducted on collected samples for determination of the desired compound (contaminant) and its concentration. Discussion of these procedures follows.

Phenol analysis was conducted by the "Direct Photometric Method" of Standard Methods (ref. 31) using 4-aminoantipyrine as the reactant. The distillation procedure was slightly modified to accomplish the methylene chloride procedure at the same time. That is only 50 ml of sample were distilled, and the condensor bottom was submerged in distilled water in a 100-ml beaker. After distillation all samples were diluted to 100 ml total volume.

Methylene chloride analysis was conducted by a procedure similar to that given in reference 32. As stated in the phenol analyses, 50 ml of sample were distilled, condensed into distilled water, and diluted to 100 ml. The distillate was analyzed on a gas chromatograph using known concentrations of methylene chloride for quantifying the area under the triangles. The gas chromatograph was operated at an injection head temperature of 175°C, column temperature of 150°C, and detector temperature of 180°C. The column was stainless steel packed with a divinyl benzene polymer. The carrier gas was nitrogen and the detector was flame ionization. An attenuation factor of 20 was used.

Realizing that distillation of chlorinated solvents did not yield 100 percent recovery in the distillate, determination of the percent recovery was attempted by distilling known concentrations of methylene chloride. The results of this showed recovery to be somewhat concentration dependent but not enough samples were distilled to obtain a statistically valid conclusion. In the concentration range that was expected and determined for the unknown samples analyzed, a recovery of 50 percent appeared to be valid, and all methylene chloride concentrations were corrected using 50 percent recovery. Therefore, methylene chloride concentrations can only be taken as an approximation.

Chemical oxygen demand, suspended solids, total dissolved solids, and pH were all analyzed according to standard methods (ref. 31). Total chromium was analyzed by the "Atomic Absorption Spectrophotometric Method" of standard methods (ref. 31).

Ozone concentrations and carryovers were determined using the iodometric method. This is ozone was bubbled through a fritted glass bubbler containing potassium iodide (KI) in distilled water for a known period of time. The KI solution was then acidified with IN glacial acetic acid, approximately 5 ml per 100 ml of KI solution and the liberated iodine was titrated with 0.1 N sodium thiosulfate using starch as an indicator. The amount of ozone was calculated based on equations 10 and 11.

$$O_3 + KI + H_2O \rightarrow O_2 + I_2 + 2KOH \qquad (10)$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI \qquad (11)$$

Carbon dioxide production was measured during the batch ozonation experiments by passing the exhaust ozone gas through 400 ml of 2N NaOH (actually 1.966 N when standardized with a standard HCl acid of 0.581 N). Twenty-five ml of the NaOH solution was titrated with the 0.581 N HCl to the phenolphthalein endpoint. This permitted determination of the amount of NaOH exhausted based on the principle of volumes times normality equals volume times normality. The amount of CO_2 produced was then calculated based on equation 12.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (12)$$

The amount of CO_2 in the ozonated gas before reacting with the wastewater was determined and subtracted from all values.

In the potassium permanganate experiments residual potassium permanganate was determined on a visible scanning spectrophotometer using the procedure outlined in reference 11. Absorbance was measured at 526 mμ and subtracted from the baseline absorbance occurring near this wavelength. The absorbance of known concentrations were determined and used to quantitify the residual potassium permanganate concentration.

To perform COD analysis on samples containing residual potassium permanganate, a special procedure of preparing the samples was adopted. It was known that residual potassium permanganate in an acid solution would compete with the dichromate for organic compounds and for the ferrous ammonium sulfate, thereby not permitting accurate determination of the COD. Residual potassium permanganate was determined by the above procedure and the normality calculated. Then 0.1 N ferrous ammonium sulfate was used to reduce the residual potassium permanganate in a sample of known volume by estimating the required amount and titrating the sample with slightly less than this amount, and then redetermining the residual potassium permanganate concentration. Small amounts of ferrous ammonium sulfate were then added until there was no residual potassium permanganate and no excess ferrous ammonium sulfate. Then the sample was diluted to a known volume and used for COD determination. An endpoint going from purple-pink to yellow was helpful in determining the quantity of ferrous ammonium sulfate required.

SECTION IV

RESULTS

1. OXIDATION WITH OZONE

a. Batch Experiments

Batch experiments were conducted to determine the optimum pH and to estimate the required contact time. Also varied was the ozone flow rate and concentration. The results of these experiments are presented in table IV and figures 9 through 14.

Reviewing the data listed in table IV reveals certain key factors. Phenol reductions of 99.7 percent (2700 mg/l-9 mg/l)÷(2700 mg/l) yielded COD reductions of only 57 percent, suggesting the formation of intermediate oxidation products. Adjusting the pH greatly increased the phenol reduction rate but did not appreciably affect the COD reduction. The formation of CO_2 was not substantial. If only the phenols were oxidized and the other organics were not, complete oxidation of the phenols at 60 minutes of contact time should have yielded 2.62 grams of CO_2, based on equation 3 in the literature review, as compared to 0.276 grams of CO_2 produced. Further, if methylene chloride was the only organic compound oxidized to CO_2, 0.33 grams of CO_2 should have been formed at the 60-minute contact time sample. This is based on equation 13.

$$CH_2Cl_2 + 2O_3 \rightarrow CO_3 + H_2O + 3/2O_2 + 2Cl^- \qquad (13)$$

Assuming that ozonation of methylene chloride cannot produce intermediate products, this indicates that methylene chloride was "stripped" by the ozone gas flow and not oxidized. Figure 13 substantiates this assumption. Based on these observations, CO_2 formation analysis was discontinued.

Table IV also indicates that samples without pH adjustment rapidly decreases into a very acidic range, whereas samples raised to a pH of at 11.5 remained neutral or slightly basic. It is hypothesized that in the formation of the intermediate catechol, the ozone ionizes the water and the hydroxide ion attaches to the phenol molecule leaving free hydrogen ions causing the pH depression.

Table IV

BATCH OZONATION EXPERIMENTS

Influent Wastewater Characteristics
Phenol-2700 mg/l COD-9643 mg/l
Methylene Chloride-1600 mg/l pH 8.1

Gas Flow (sec/min)	Ozone Flow (mg/min)	Contact Time (min)	Phenol Conc. (mg/l)	COD Conc. (mg/l)	CH_2Cl_2 Conc. (mg/l)	pH initial/ final	CO_2 Produced (gr)
	(2.5 wt)						
1000	22	15	1600	7944	408	8.1/4.0	0.505
1000	22	30	960	6837	368	8.1/2.9	0.145
1000	22	60	468	5849	244	8.1/2.5	0.276
1000	22	120	185	5059	150	8.1/2.1	---
1000	22	180	31	4550	39	8.1/1.9	---
1000	22	240	9.0	4160	90	8.1/1.9	---
	(1.3 wt)						
1000	14	30	1348	7825	285	8.1/3.7	---
1000	14	60	835	7035	228	8.1/2.8	0.025
1000	14	120	442	5849	160	8.1/2.4	0.075
	(3.75 wt)						
1000	45	45	1000	6200	266	8.1/2.6	---
1000	45	90	265	5580	290	8.1/2.1	---
1000	22	60	40.8	4980	218	10.2/3.2	---
1000	22	60	5.3	4980	189	12.5/7.3	---
1000	22	30	260	6260	230	11.2/6.7	
1000	22	60	20	4800	200	11.2/5.0	---
1000	22	120	2.4	---	135	11.2/3.9	---
1000	22	60	3.0	---	---	11.5/6.8	---
1000	22	60	1.0	---	---	11.8/9.8	---
1000	22	120	4.0	---	---	11.8/8.7	---
500	12	30	1540	7018	---	8.1/---	---
500	12	60	890	5794	---	8.1/---	---
500	12	120	493	4937	---	8.1/---	---

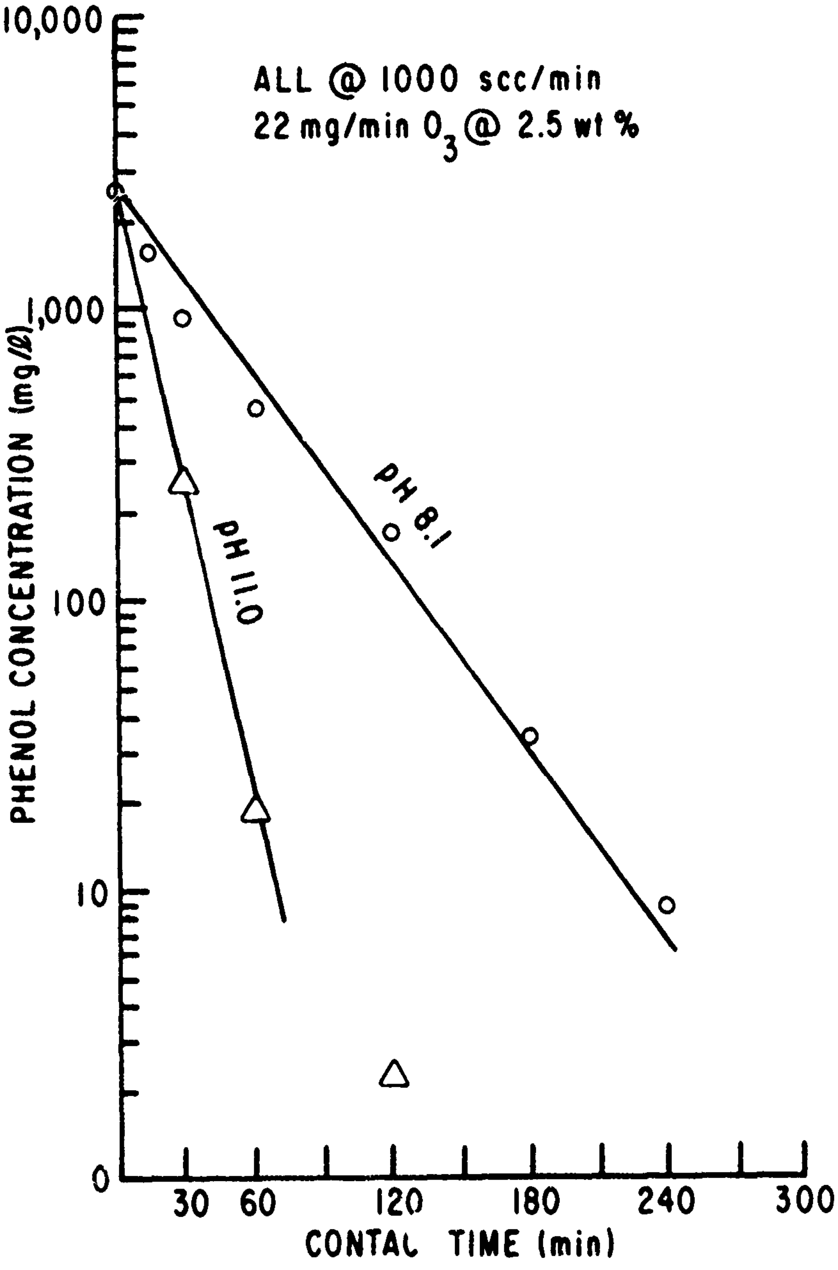


Figure 9. Phenol Concentration Versus Batch Contact Time for Varying pH

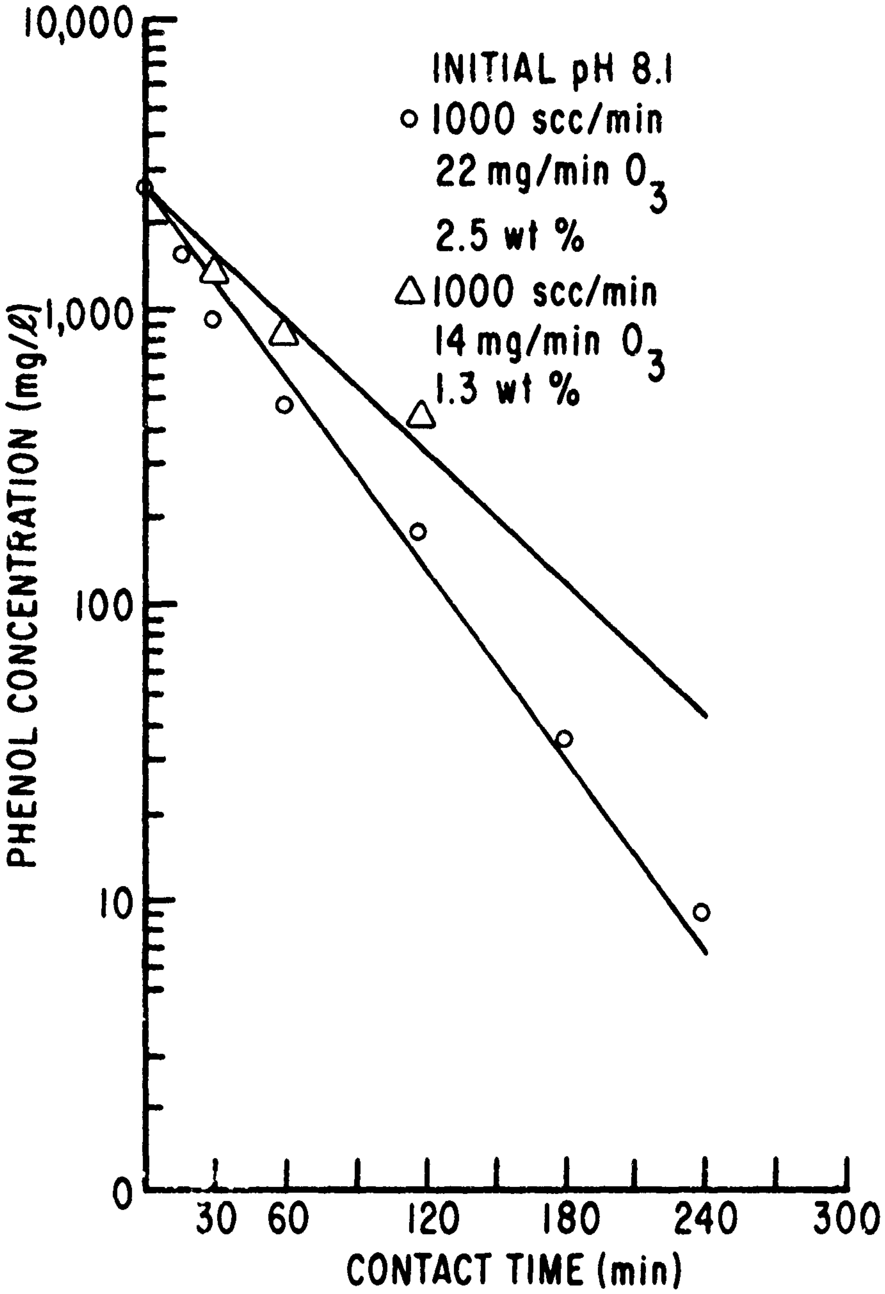


Figure 10. Phenol Concentration Versus Batch Contact Time for Varying Ozone Flow

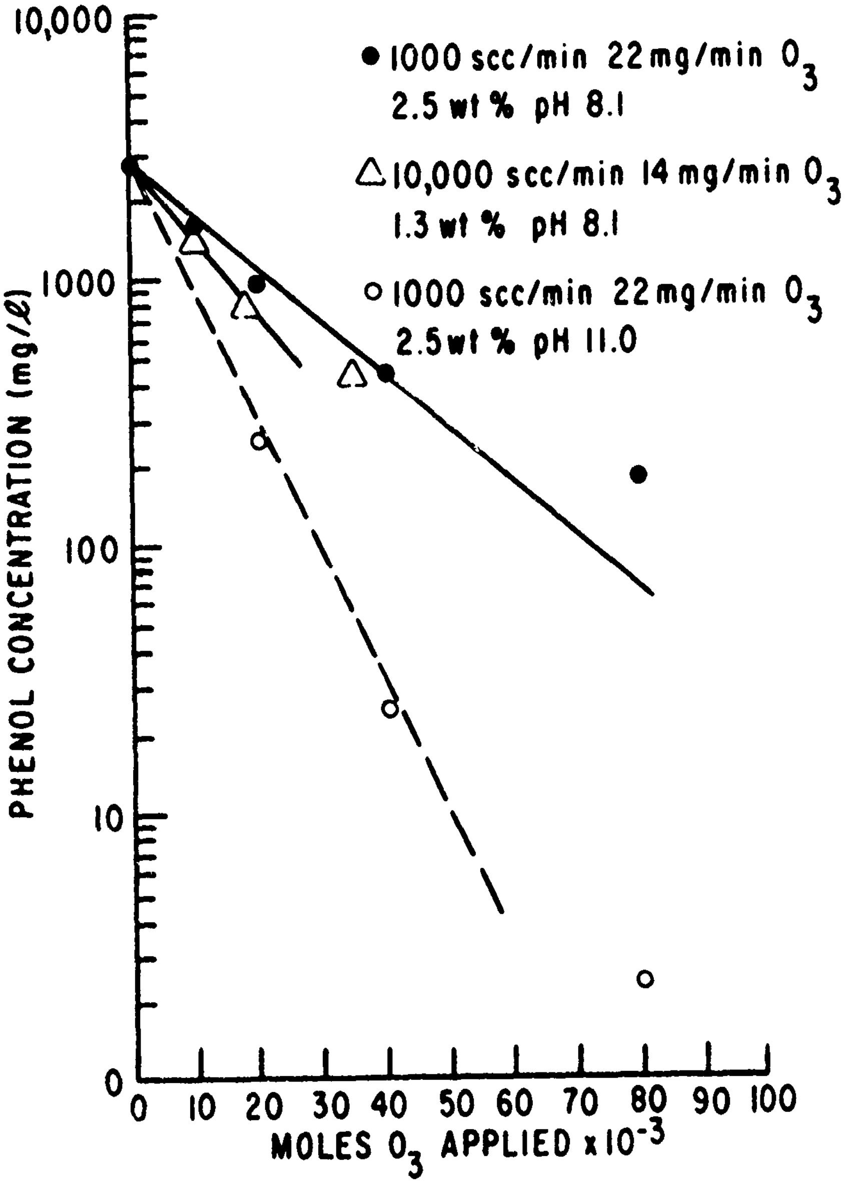


Figure 11. Phenol Concentration Versus Moles Ozone Applied (Batch)

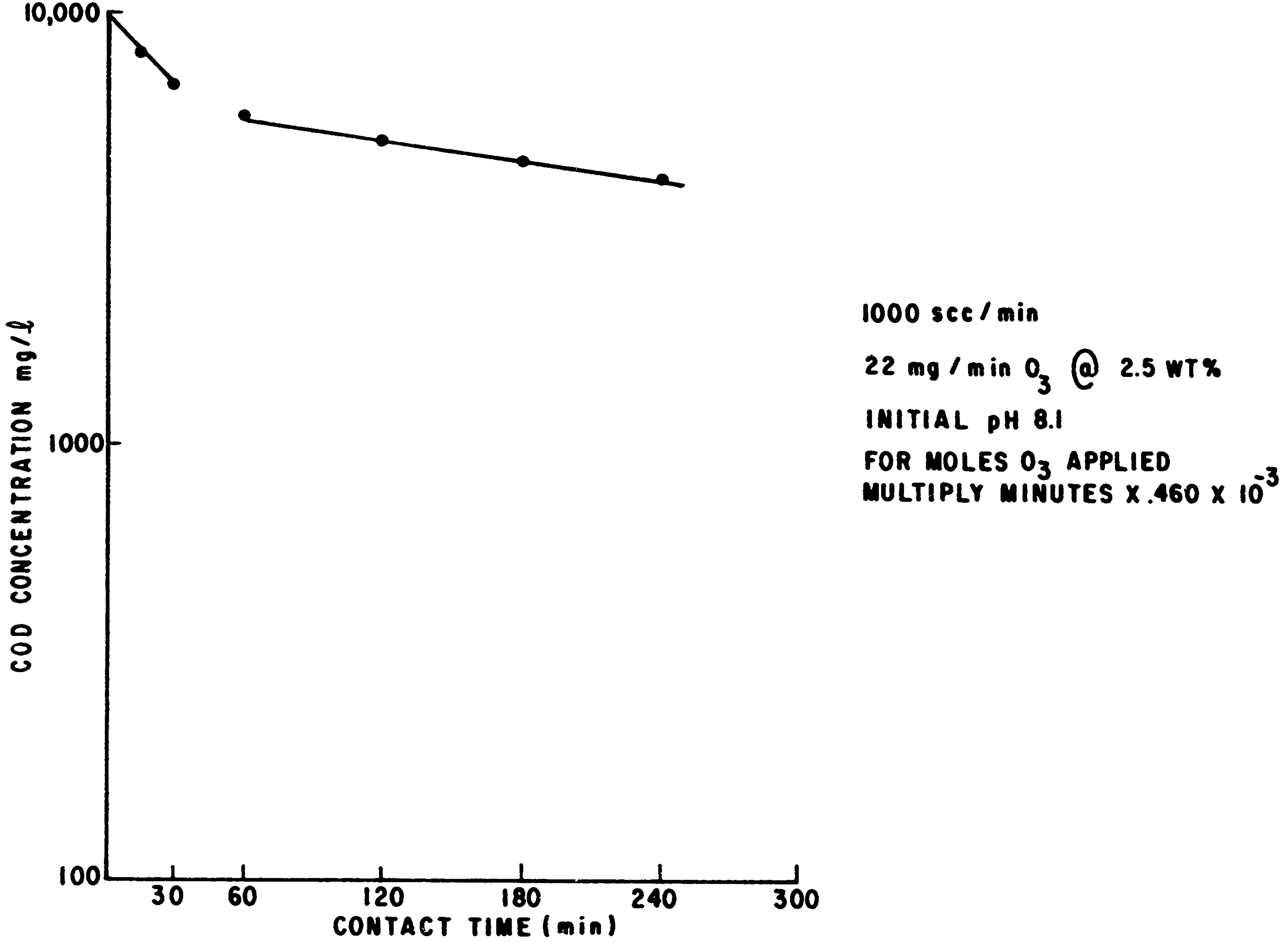


Figure 12. COD Concentration Versus Batch Contact Time

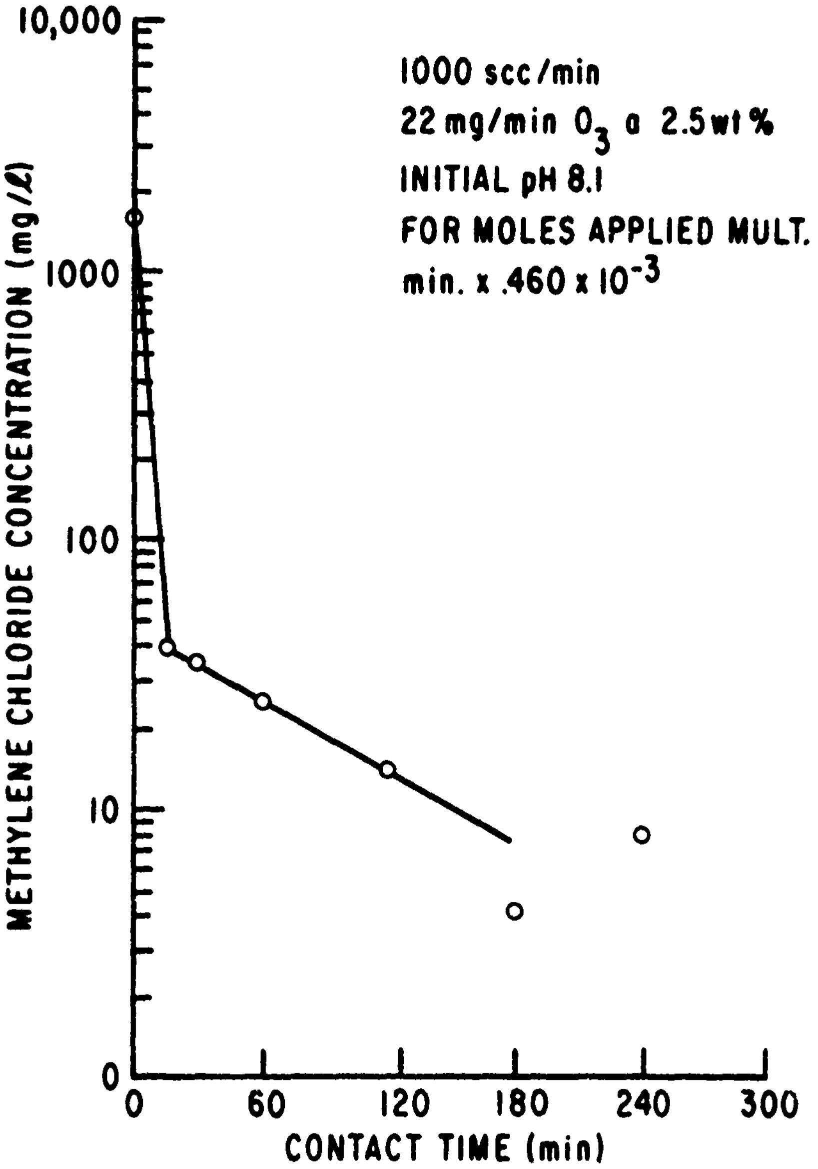


Figure 13. Methylene Chloride Concentration Versus Batch Contact Time

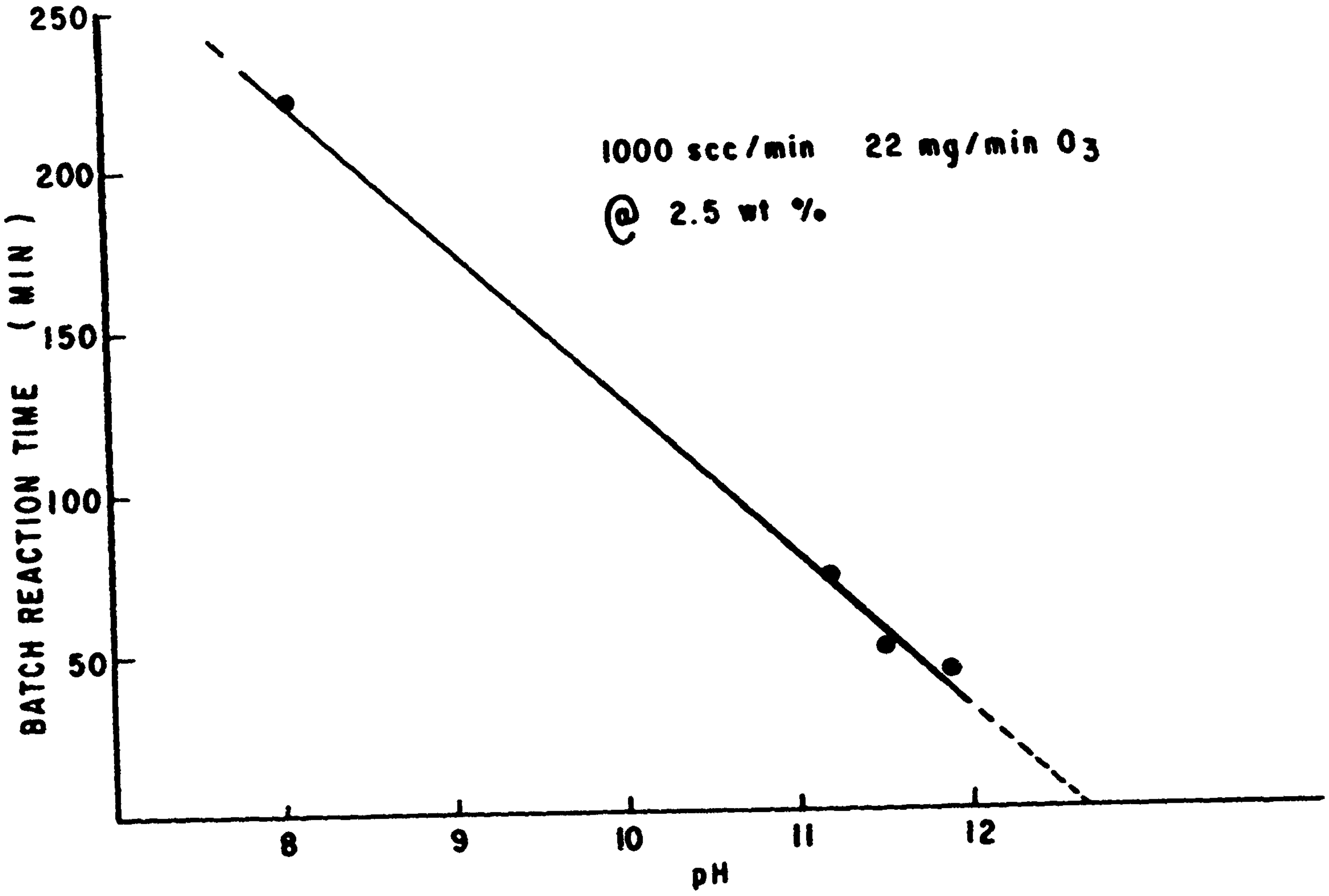


Figure 14. Batch Reaction Time to Reach 10 mg/l Phenols for Varying pH

Figure 9 reveals the effect of pH on phenol reduction for various contact times. Two things are evident. One, the increasing pH sharply decreases the required contact time. This is further demonstrated in figure 14 where required reaction time to reach 10 mg/l phenols is plotted against initial pH. The other evident fact is that phenol reduction is a first order decreasing rate function with respect to contact time or more precisely with respect to the moles of ozone applied as shown in figure 11.

Figures 10 and 11 show that better ozone use per mole of ozone is obtained at 14 mg/min than at 22 mg/min, but the phenol reduction is slower for the 14 mg/min ozone flow.

From figure 11 the ozone demand for a 99-percent phenol reduction can be calculated. For no pH adjustment, the batch ozone demand is 10.4 moles O_3/mole phenol or 5.30 lb/lb. For a pH of 11.0, this is reduced to 3.46 moles O_3/mole phenol or 1.77 lb/lb.

Figure 12 reveals that COD reduction did not follow first order reaction rate kinetics, but rather it is seen that there is a relatively rapid decrease in COD initially followed by a much slower decrease. This reduction of COD in the first 30 minutes can possibly be correlated to the rapid methylene chloride reduction occurring in the first 15 minutes as shown in figure 13. Based on the previous discussion of CO_2 production, it is postulated that the rapid COD and methylene chloride reduction initially is because of stripping of the methylene chloride.

Other data not presented were that of total chromium removal, ozone carryover, and color change. Total chromium concentration, as expected, was not affected by ozonation. Ozone carryover was observed visually by the yellow color development when the ozone reacted with the KI solution in the ozone trap. In most cases ozone carryover started after about 20 to 25 minutes of contact time. Initially, the ozone carryover was insignificant, but towards the 120 to 240 minutes of contact time carryover appeared to be as much as 25 percent. The color of the wastewater changed from its characteristic yellow to a brown within the first minute of contact, and then proceeded to turn a darker brown after which it started back towards a lighter shade of brown. In some cases the shift towards turning lighter shades of brown coincided with the onset of ozone carryover.

b. Continuous Flow Experiments

Using the results of the batch experiments as an indication of what would happen, continuous flow experiments were undertaken. All the continuous flow experiments were conducted using the apparatus shown in figure 7. The first undertaking was to determine how much time would be required to reach a steady state. Table V lists the results of these experiments. These three experiments were conducted at a gas flow of 1000 standard cubic centimeters (scc)/min to each stage of the reactor and an ozone flow of 22 mg/min to each stage. All the samples were collected from the separatory funnel. The pump output was set at 18 ml/min to provide 100 min total retention time (50 min each stage) and then checked for actual flow rate several times.

The results of table V reveal that a near steady state was reached at about the time required for one complete "turnover" of the wastewater in the reactor, i.e., 100 min. Further, for the ozone flows listed above, it can be seen that without pH adjustment an effluent containing 1000 mg/l of phenols could be expected. Raising the pH to 11.8 decreased the effluent phenol concentration to approximately 110 mg/l. It should be noted that at these ozone flow rates and detention time no ozone carryover occurred.

Since ozonation without pH adjustment was not as effective as required, the rest of the continuous flow experiments were conducted at a pH of 11.5. This pH was chosen because it could be obtained with relatively moderate dosages of NaOH, and to obtain a pH of 11.8 or 12.0 would have required excessive dosages of NaOH (see alkaline titration curve in appendix A).

Using a two-stage reactor necessitated determination of the optimum ozone flow rate to each stage. This was accomplished by using only stage one of the reactor and increasing the ozone and gas flow rate in steps and determining the phenol concentration in the discharge from this stage and any ozone carryover. A wastewater flow rate of 15 ml/min was used that provided 60 min retention time in stage one. A minimum of 90 min between changing of the ozone and gas flow rate and taking of a sample for analysis was used to allow a steady state to be reached. Figure 15 shows the results of this experiment. Based on these results, it was tentatively decided to use a gas flow of 2000 scc/min, which gave an ozone flow of approximately 40 mg/min. At this ozone loading there was only slight carryover. The discharge from stage one was collected for use in stage two.

To determine the optimum ozone flow to stage two, the previously collected ozonated wastewater from stage one was pumped into stage two directly, and ozone and gas flow rates were chosen to stimulate 2000 scc/min at near zero ozone

Table V

RUN TIME TO REACH STEADY STATE FOR CONTINUOUS FLOW

Wastewater Flow Rate (ml/min)	Initial pH	Run Time (min)	Phenol Conc mg/l	COD Conc mg/l
18.5	8.3	60	1260	6406
18.5	8.3	120	1008	5304
18.5	8.3	150	946	---
18.5	8.3	180	---	6202
18.5	8.3	240	1390	6500
17.4	11.8	30	768	---
17.4	11.8	60	160	5900
17.4	11.8	90	115	---
17.4	11.8	120	125	4480
17.4	11.8	150	114	---
17.4	11.8	180	110	5590
17.4	11.8	210	108	---
18.0	11.0	60	430	8020
18.0	---	120	250	5800
18.0	---	180	180	5550
18.0	---	240	160	5960

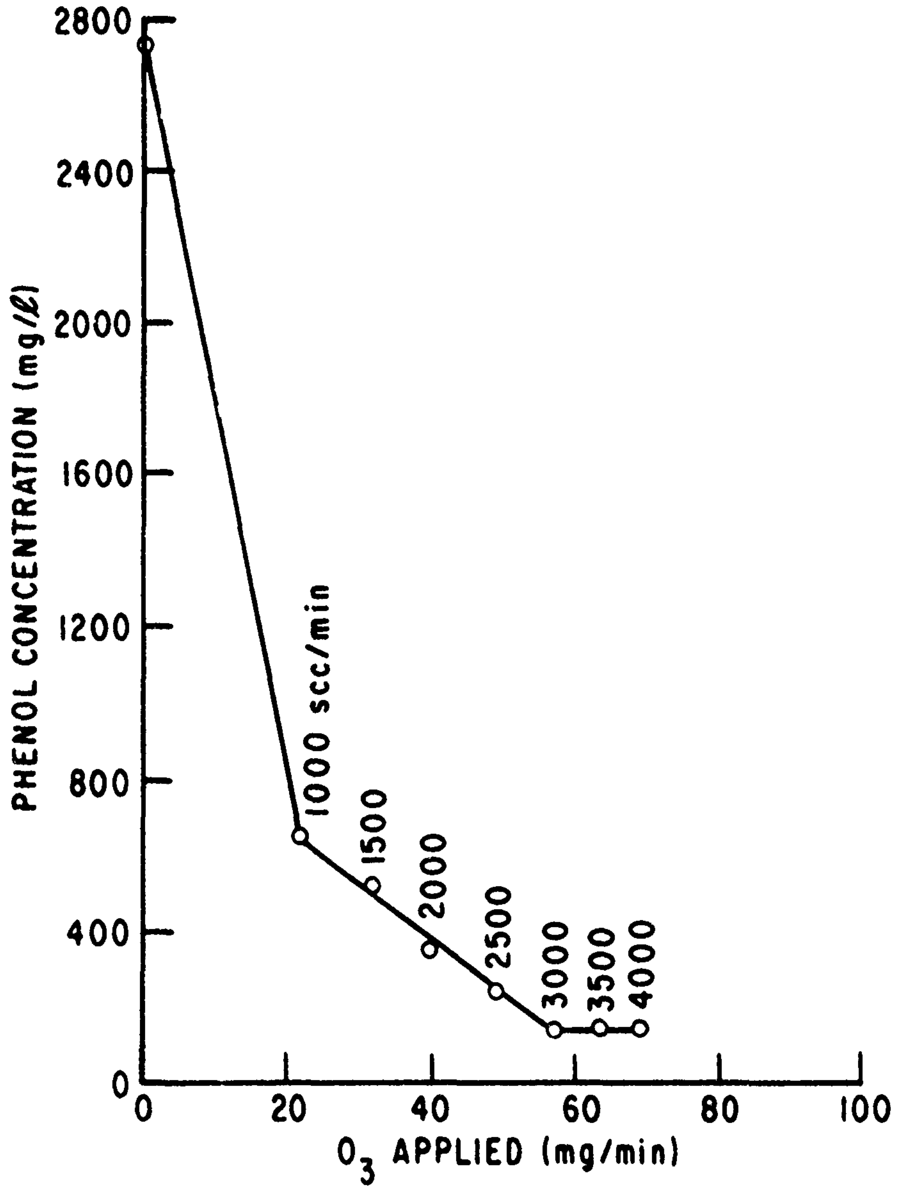


Figure 15. Phenol Reduction in Stage One Versus Ozone Applied

concentrations influent from stage one plus that desired for stage two. From this experiment, it was concluded that 1000 scc/min of gas flow was the optimum to use directly into stage two since this resulted in a total gas flow of 3000 scc/min. This includes 2000 scc/min to stage one at 40 mg/min ozone plus 1000 scc/min at 17 mg/min ozone to stage two. This total gives stage two 3000 scc/min at 17 mg/min ozone.

Experiments were then undertaken to determine the ozone demand and the required retention time. All these experiments were at an initial pH of 11.5 and 3000 scc/min total gas flow.

Figures 16 and 17 reveal the phenol reduction and COD reduction, respectively, for varying retention times. The reaction for phenols appears to be first order kinetics; however, these data are not sufficient to permit definite determination of this. It appears that a retention time of between 300 to 360 minutes will be required to reach a phenol concentration of 5 mg/l. The highest obtainable COD reduction was 65 percent, leaving 3500 mg/l of COD in the wastewater.

Ozone demand for varying phenol concentration reductions is plotted in figure 18. Again the function appears to be first order. It is expected that the ozone demand is a function of the initial phenol concentration. That is the ozone is more effective at higher phenol concentration. To satisfy the arbitrary ozone demand of 99 percent phenol reduction, 5.2 moles ozone/mole phenol is required, or on a weight ratio 2.66 lb/lb.

Other data determined but not illustrated were that of the pH and color development. For the 120-min retention time, the final pH was 6.9, for the 180-min retention time the pH was 6.9, and for the 240-min retention time the pH was 5.6. At the 120- and 180-min retention time experiments there was a significant color difference between stages, with stage one being a very dark brown and stage two a pale light yellowish brown. For the 240-min experiment, both stages were of a light yellowish brown color. Methylene chloride analyses had to be discontinued because of failure of the gas chromatograph.

c. Shaker Flask Experiments

To determine the biodegradability of the ozonated wastewater as compared to the untreated wastewater, shaker flasks were set up containing different concentrations, based on COD, of the various wastewaters, synthetic sewage, and seed of unacclimated microorganisms. Table VI lists the composition of each shaker flask.

The synthetic sewage that was used contained glucose as the carbon source. The shaker flasks were continuously agitated for 9 days at a temperature of 20°C. Visible growth of microorganisms could be detected in each flask by the start of the third day. However, soluble COD reduction for each flask was so variable that the only conclusions from the results are that no flask contained

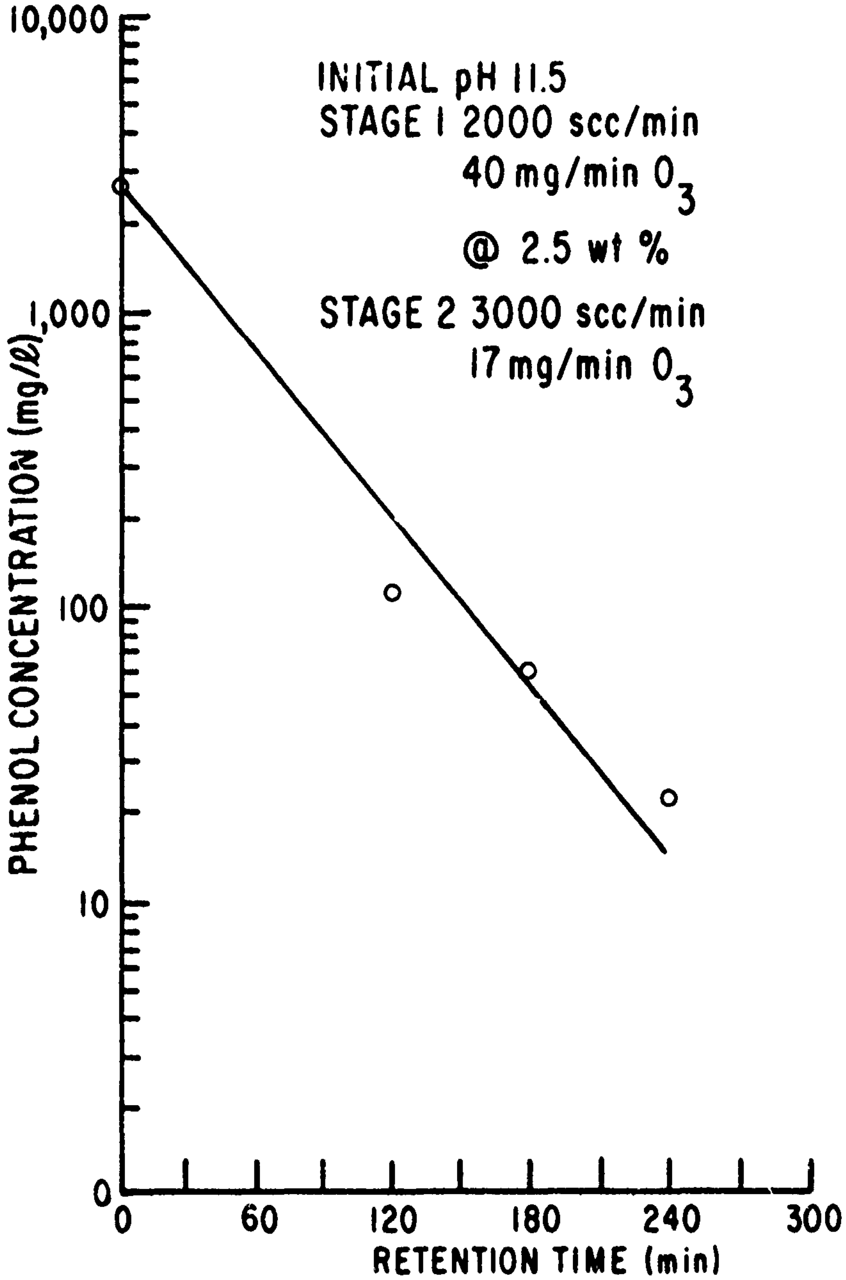


Figure 16. Phenol Concentration Versus Continuous Flow Retention Time

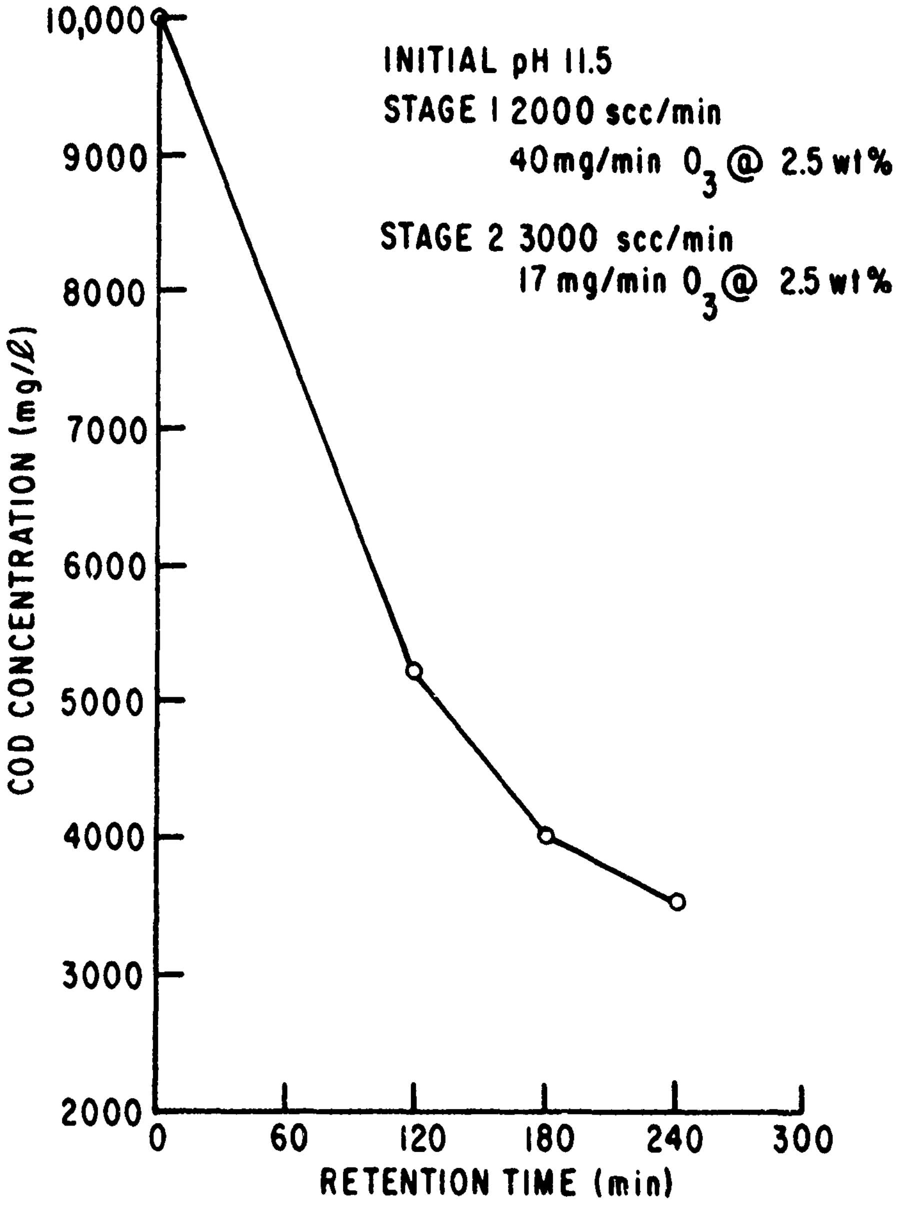


Figure 17. COD Concentration Versus Continuous Flow Retention Time

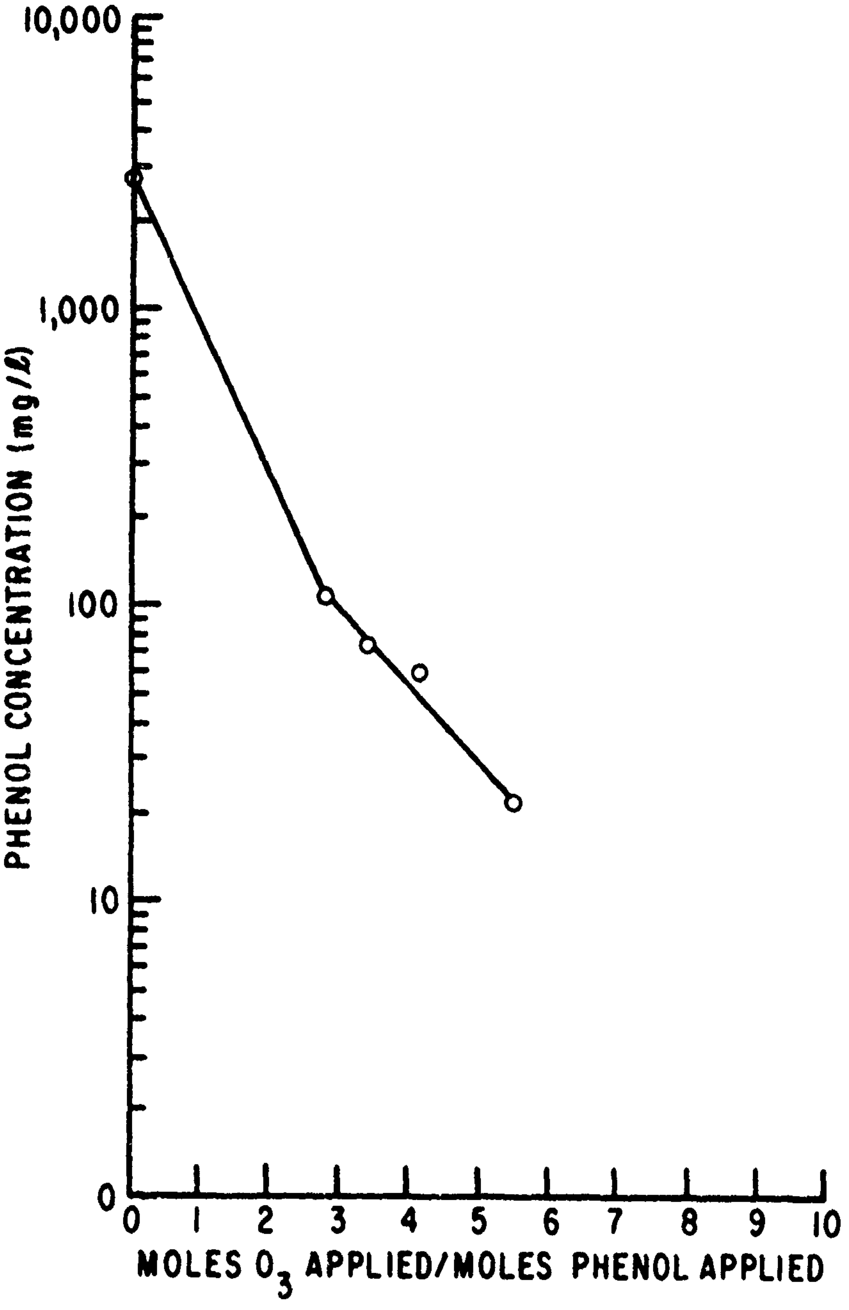


Figure 18. Phenol Concentration Versus Moles O_3 Applied/Moles Phenol Applied

Table VI

COMPOSITION OF SHAKER FLASKS

Shaker Flask	Synthetic Sewage	Ozonated Wastewater	Untreated Wastewater
	COD (mg/l)		
1	434	---	---
2	434	---	19.0
3	434	---	57.6
4	434	---	105
5	---	---	38.4
6	---	---	76.8
7	434	17.5	---
8	434	57.0	---
9	434	105	---
10	---	35	---
11	---	70	---

any detectable soluble COD at the end of 9 days and growth of microorganisms occurred in each flask.

2. OXIDATION WITH POTASSIUM PERMANGANATE

The results of jar test experiments using potassium permanganate are shown in table VII and in figures 19 and 20. All the values listed are for filtered samples using glass fiber filter paper. Set 1 was run with an initial pH of 8.4, set 2 was a pH of 6.0, and set 3 was a pH of 10.5. The influent wastewater had 2770 mg/l phenols, 9600 mg/l COD, 1500 mg/l TDS, <50 mg/l filterable solids, and 110 mg/l total chromium.

Figure 19 demonstrates the effect of the weight ratio loading of potassium permanganate to phenol on the residual phenol concentration. Figure 20 shows the effect of the potassium permanganate concentration on the residual COD concentration.

The experiments reveal several significant facts. Adjusting the initial pH did not significantly affect the results with set 2 yielding the best phenol removals. This is contrary to the literature reviewed (see literature review) where oxidation of phenols was favored under alkaline conditions. However, those

Table VII

RESULTS OF POTASSIUM PERMANGANATE EXPERIMENTS

Jar	$KMNO_4$ mg/l	$KMNO_4$ mg Phenol	Phenol mg/l	COD mg/l	TDS mg/l	pH	Sludge mg/l	Total Grams mg/l
				Set 1				
1	4000	1.44	2400	7540	1710	8.5	1126	52
2	10000	3.61	1840	6500	2800	8.7	2560	---
3	20000	7.22	1190	4860	4350	8.9	6620	46
4	32000	11.55	1050	2440	4150	8.8	3680	---
5	48000	17.30	250	2660	6160	8.9	9000	---
6	70000	25.20	710	3780	5460	8.9	5940	44
				Set 2				
1	4000	1.44	2320	7200	1970	7.7	452	44
2	10000	3.61	1880	6750	2490	8.0	1830	---
3	20000	7.22	1142	4640	4420	8.5	5580	43
4	32000	11.55	568	3280	5570	8.6	7820	---
5	48000	17.30	444	3240	5960	8.6	8300	---
6	70000	25.20	97.5	2550	7790	8.3	10550	36
				Set 3				
1	4000	1.44	2470	7700	4220	10.5	1090	52
2	10000	3.61	1880	6750	4700	10.7	2490	---
3	20000	7.22	1200	5900	5350	10.8	3570	52
4	32000	11.55	1080	5300	6100	10.9	5420	---
5	48000	17.30	1410	5700	5580	10.8	---	---
6	70000	25.20	520	3630	8420	10.2	23500	49

Table VII

RESULTS OF POTASSIUM PERMANGANATE EXPERIMENTS

Jar	$KMNO_4$ mg/l	$KMNO_4$ mg Phenol	Phenol mg/l	COD mg/l	TDS mg/l	pH	Sludge mg/l	Total Grams mg/l
				Set 1				
1	4000	1.44	2400	7540	1710	8.5	1126	52
2	10000	3.61	1840	6500	2800	8.7	2560	---
3	20000	7.22	1190	4860	4350	8.9	6620	46
4	32000	11.55	1050	2440	4150	8.8	3680	---
5	48000	17.30	250	2660	6160	8.9	9000	---
6	70000	25.20	710	3780	5460	8.9	5940	44
				Set 2				
1	4000	1.44	2320	7200	1970	7.7	452	44
2	10000	3.61	1880	6750	2490	8.0	1830	---
3	20000	7.22	1142	4640	4420	8.5	5580	43
4	32000	11.55	568	3280	5570	8.6	7820	---
5	48000	17.30	444	3240	5960	8.6	8300	---
6	70000	25.20	97.5	2550	7790	8.3	10550	36
				Set 3				
1	4000	1.44	2470	7700	4220	10.5	1090	52
2	10000	3.61	1880	6750	4700	10.7	2490	---
3	20000	7.22	1200	5900	5350	10.8	3570	52
4	32000	11.55	1080	5300	6100	10.9	5420	---
5	48000	17.30	1410	5700	5580	10.8	---	---
6	70000	25.20	520	3630	8420	10.2	23500	49

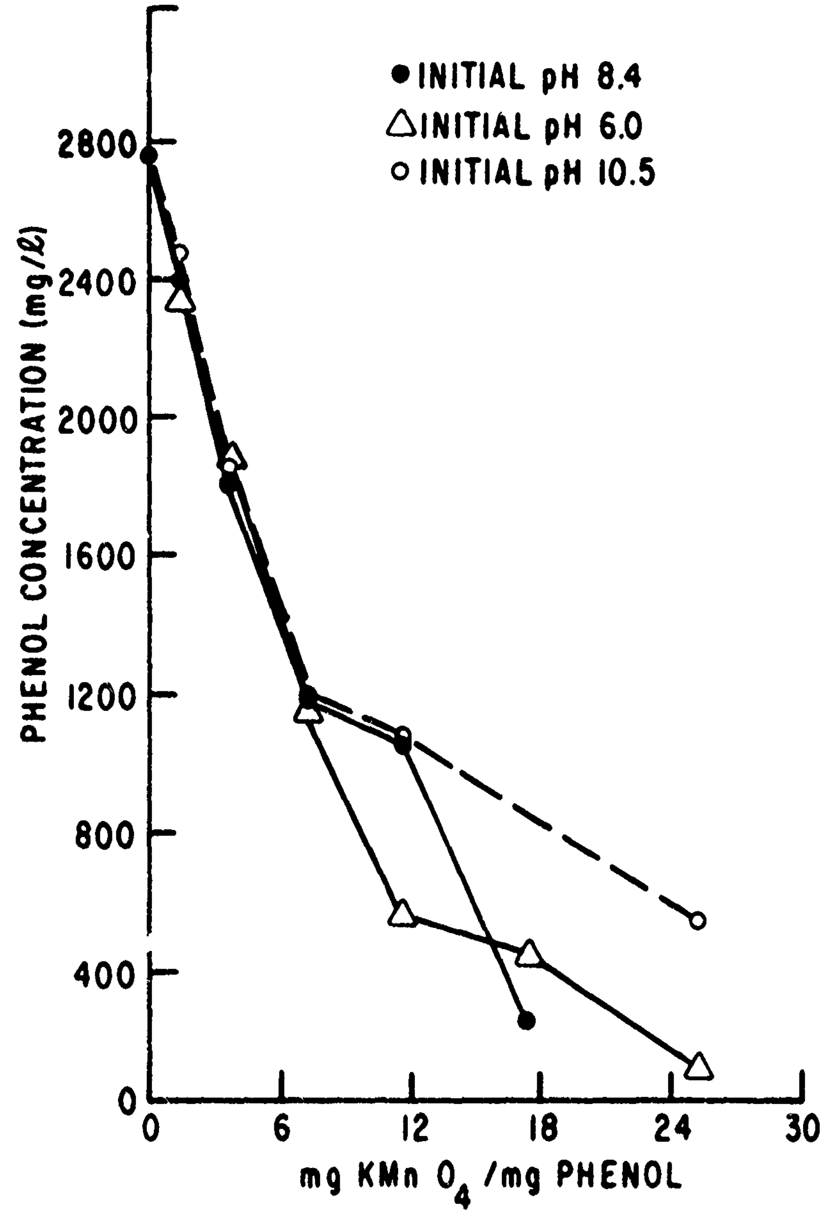


Figure 19. Phenol Concentration Versus mg $KMnO_4$ Applied/mg Phenol

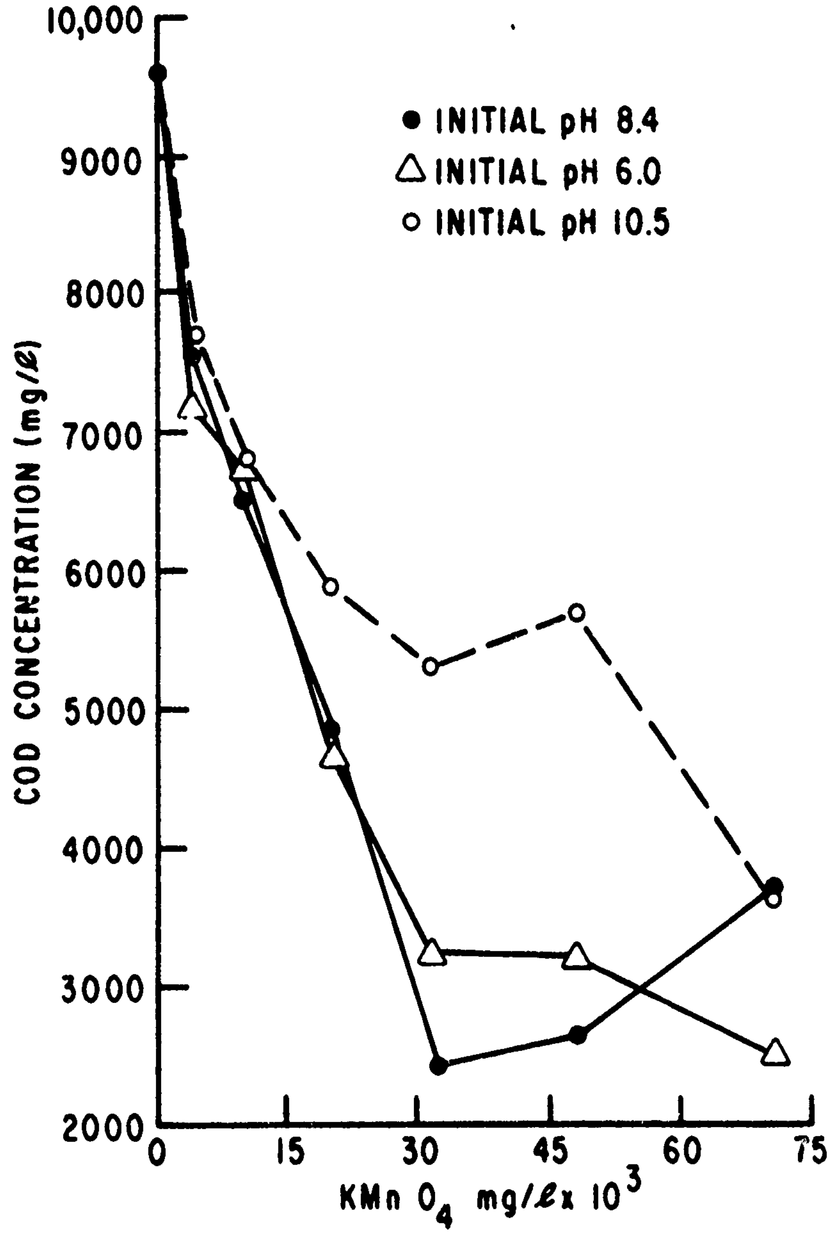


Figure 20. COD Concentration Versus mg/l $KMnO_4$ Applied

experiments were for pure solutions of phenols at dilute concentrations and may cause this difference. The lowest phenol concentration obtained was 97.5 mg/l. This was at a loading of 25.20 mg $KMnO_4$/mg phenol, which is much more than the stoichiometric amount of 15.7 mg/mg as given by equation 4 for complete oxidation. Phenol reduction did not follow any detectable pattern, such as a first order function, when plotted against the potassium permanganate loading.

Chemical oxygen demand reduction relative to phenol reduction was more effective than oxidation by ozone in that a phenol reduction of say 90 percent yielded a COD reduction of 73 percent. This may be slightly erroneous in that the modified COD procedure was not employed because there was no detectable residual potassium permanganate in the filtered samples. However, if in fact there was residual potassium permanganate in the sample it would result in lower COD values.

Total dissolved solids increased appreciably but were significantly lower than anticipated, based on the potassium permanganate dosages. The pH of the samples did not show any significant trends. Total chromium concentration was reduced by about 58 percent. This is attributed to being absorbed by the manganous dioxide sludge.

Significant quantities of insoluble matter (sludge) was formed. On a dry weight basis up to approximately 23000 mg/l of sludge was formed. This sludge was very hydrous and regardless of the dosage, represented over 50 percent of the volume in the jar test beakers even after 24 hours of settling. It was noticed that at the higher potassium permanganate loadings two distinctively different sludges were formed. When the sludges were washed with tap water, significant "leaching" of the purple color characteristic of potassium permanganate occurred; this occurred much more so for the second sludge that formed at the higher loadings. This indicates that there were significant quantities of unreacted potassium permanganate "tied up" in the sludge. This explains the relative ineffectiveness of reducing the phenol concentration.

Since the three sets of jar test experiments at 1 hour of mixing were not effective, the fourth set at a fixed concentration (loading) of potassium permanganate for varying contact time was not conducted.

3. ADSORPTION WITH GRANULAR ACTIVATED CARBON

a. Batch Adsorption Experiments

Batch experiments were conducted to select the best one of four different granular activated carbons and to determine the activated carbon loading that could be applied during continuous flow experiments. The four different activated carbons are listed in materials and methods and on figures 21 to 24. The activated carbons were pulverized and tested as indicated in the appendix. Two separate adsorption experiments were conducted: first, the pH of the wastewater was lowered to 4.5 as in the standard procedure, and second, there was no pH adjustment. Figures 21 to 24 give the results of these batch adsorption isotherm experiments. Figures 21 and 23 pertain to phenol adsorption. Figures 22 and 24 pertain to COD adsorption.

The results show the Witco activated carbon to be slightly better than Westvaco or Calgon and significantly better than the Darco. Further, the batch adsorption isotherms reveal that the pH did not significantly affect the removal of either phenols or COD. In terms of phenols, a loading of about 0.36 gr phenol per gr of carbon could be applied during the continuous flow experiments without experiencing complete exhaustion of the activated carbon. In terms of COD this loading approaches 1.0 gr COD per gr of carbon. These values are significantly higher than reported for phenols or COD in most wastewaters, indicating a high degree of affinity of the organic compounds for being adsorbed. At the high activated carbon dosages (4.0 and 6.0 gm) the resulting water was as clear as tap water, indicating complete disappearance of hexavalent chromium.

b. Continuous Flow Experiments

Continuous flow experiments were undertaken using the Witco activated carbon. The first experiment was for 6 hours at 0.13 gpm wihtout pH adjustment . Samples were taken periodically from the 7 sampling ports. The second experiment was for 9 hours at 0.13 gpm with prior adjusting of the pH to 6.5.

Figures 25 and 26 are, respectively, the phenol reduction obtained as a function of contact time (depth of activated carbon) and COD reduction as a function of contact time. The values are averages of the concentrations (phenol, COD) from the collected samples before breakthrough. It can be seen that lowering the pH to 6.5 did aid in obtaining higher removals of both phenols and COD, but more important, extremely effective removals of both phenols and COD was obtained. Residual phenol concentration was down to approximately 1.7 mg/l after only 5 minutes of contact time (19 inches of activated carbon depth). Removal of phenols below the 1.7 mg/l proceeded very slowly after the initial rapid reduction with 1.2 mg/l phenols left after 60 minutes contact time. This may in part be because

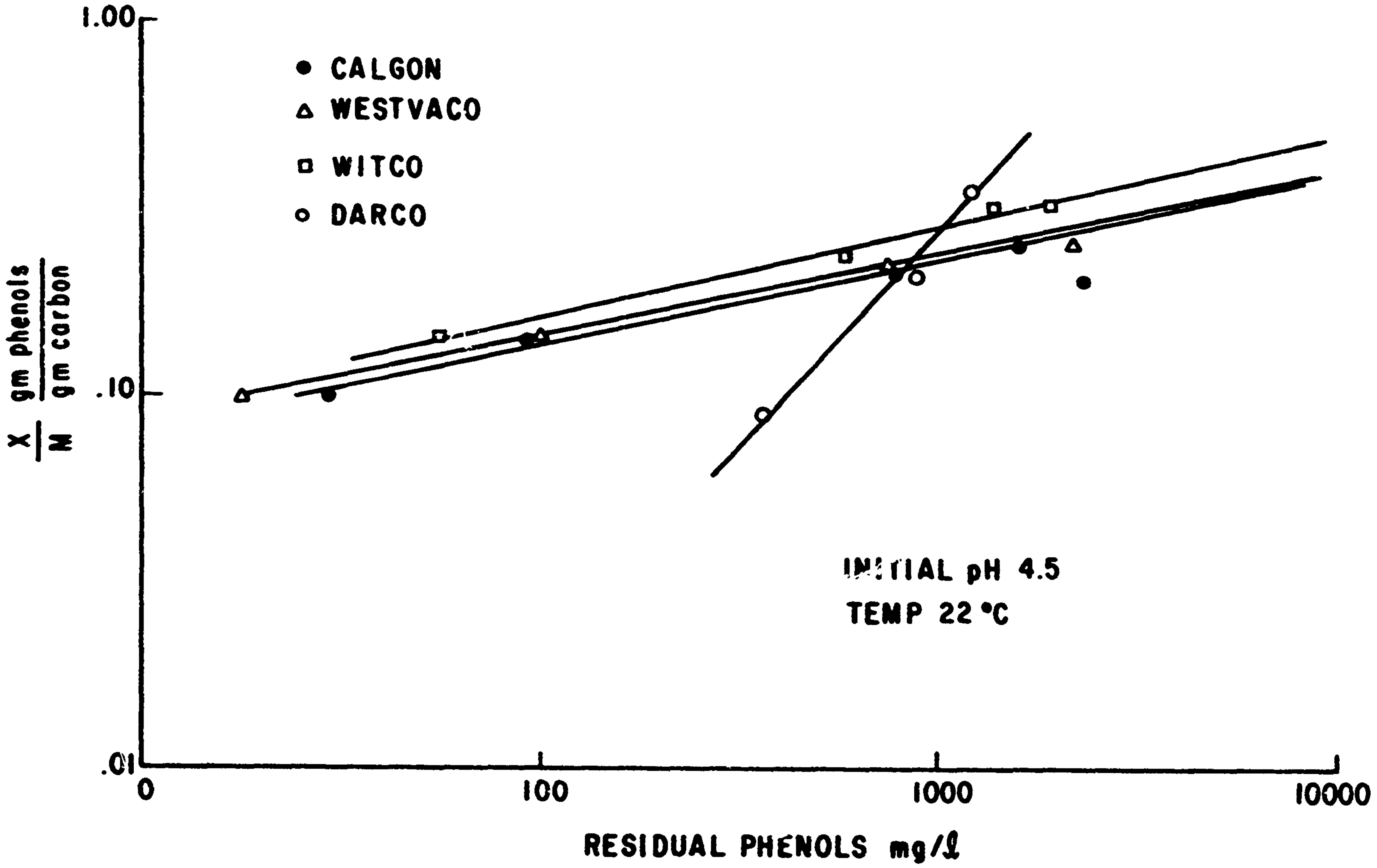


Figure 21. Batch Adsorption Isotherms for Phenols

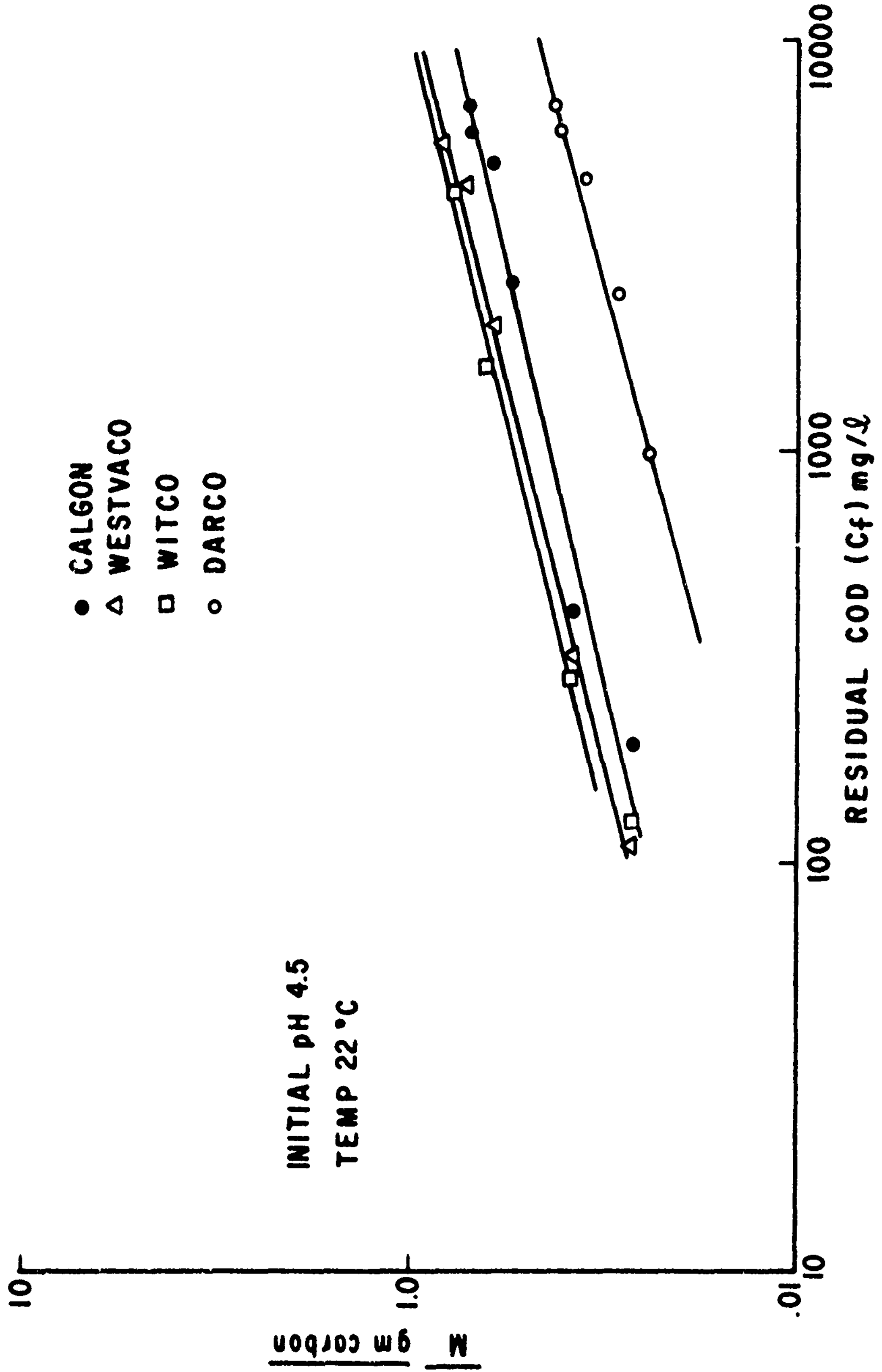


Figure 22. Batch Adsorption Isotherms for COD

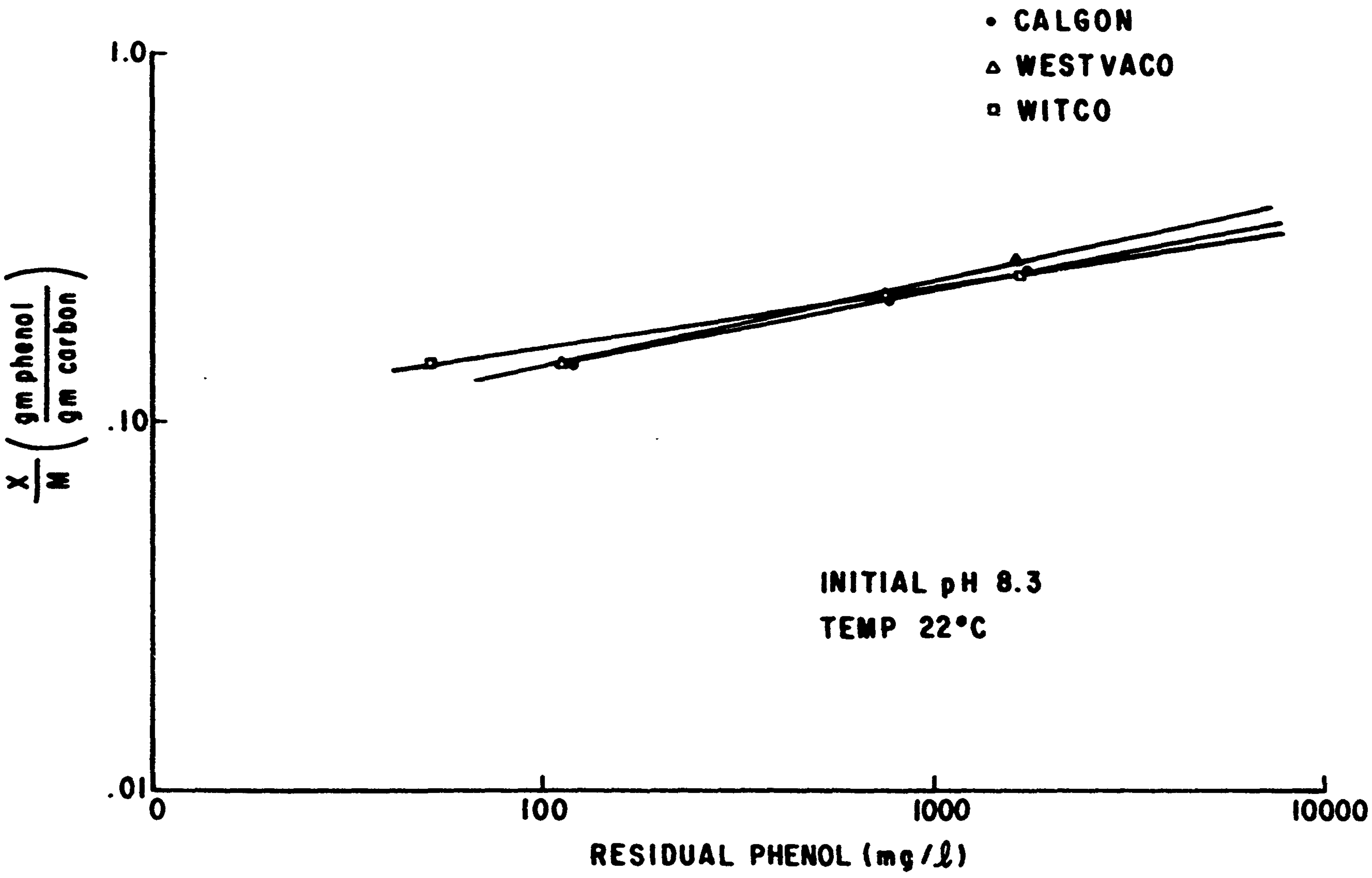


Figure 23. Batch Adsorption Isotherms for Phenols

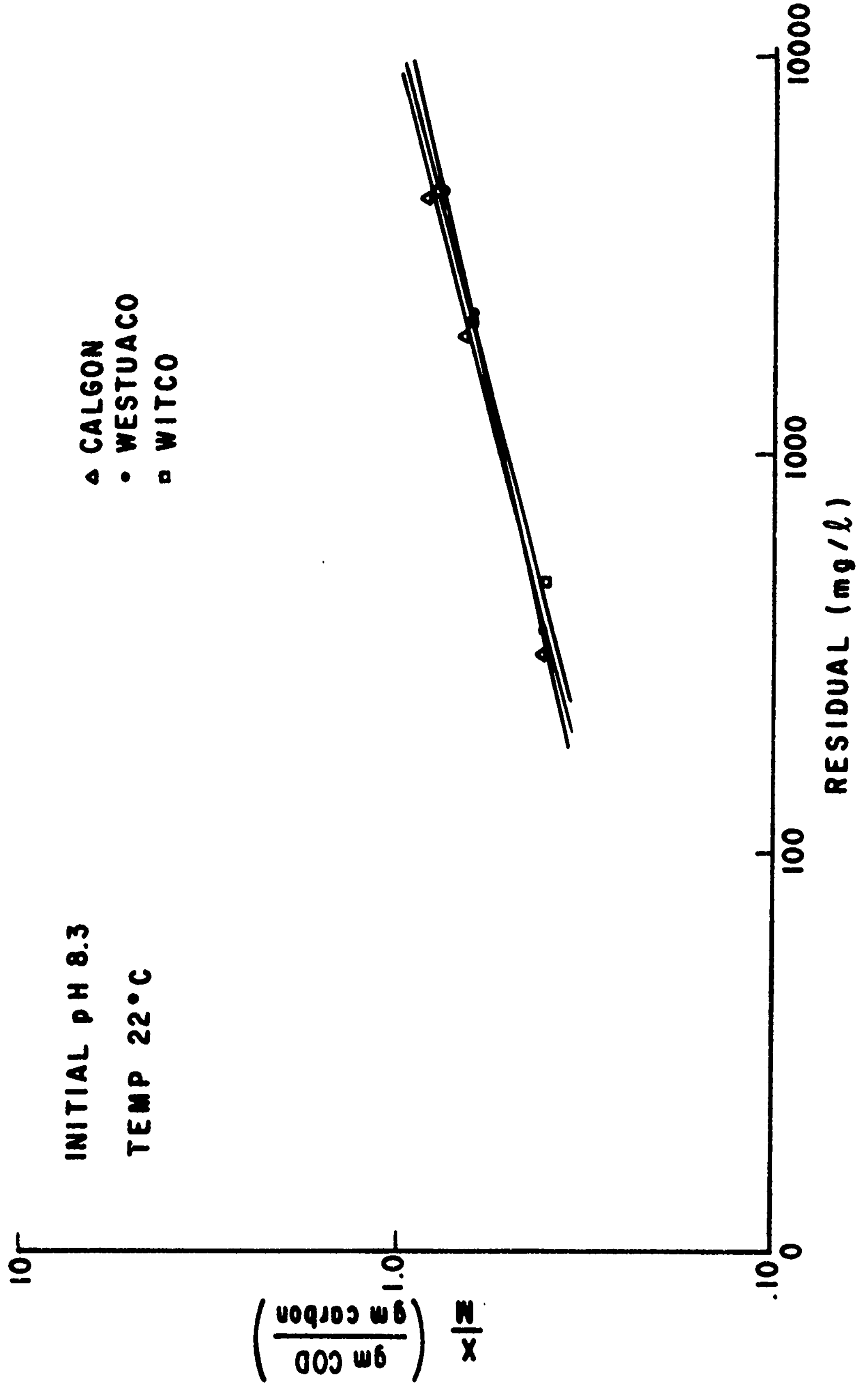


Figure 24. Batch Adsorption Isotherms for COD

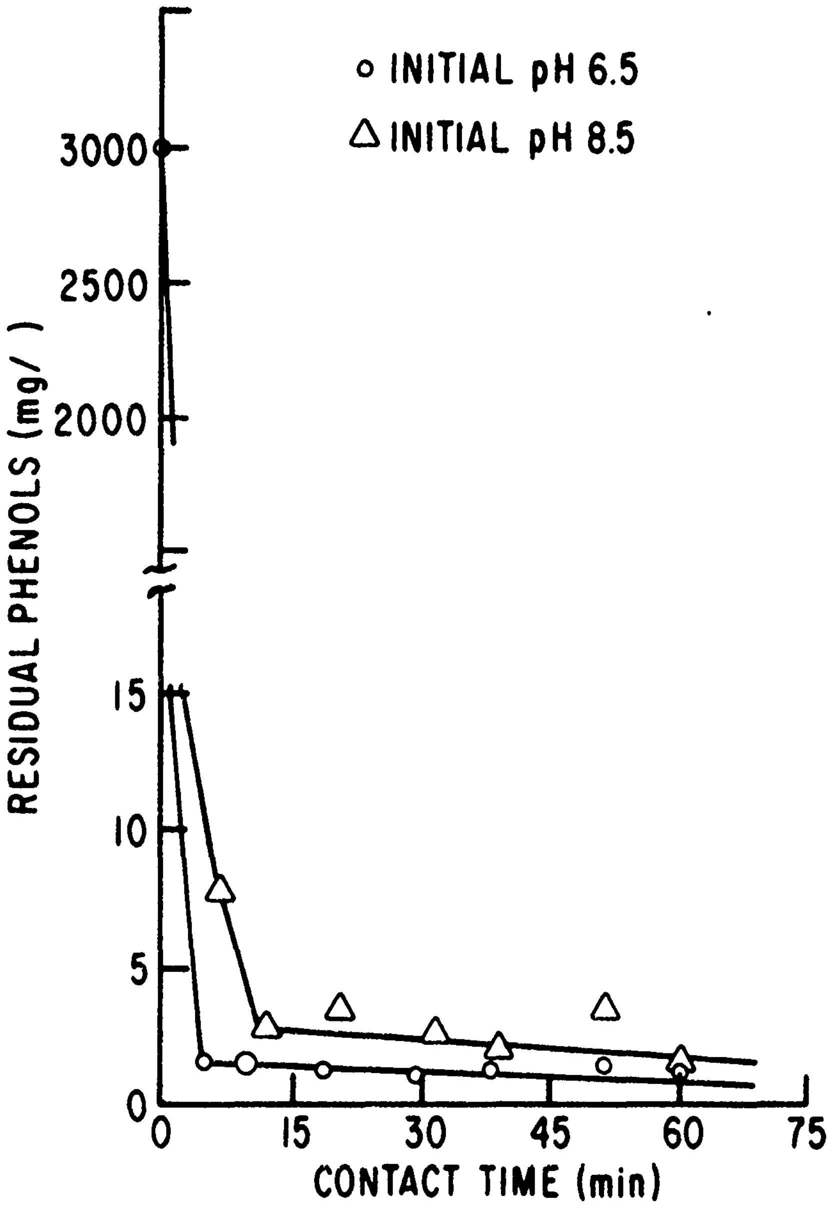


Figure 25. Phenol Concentration Versus Contact Time

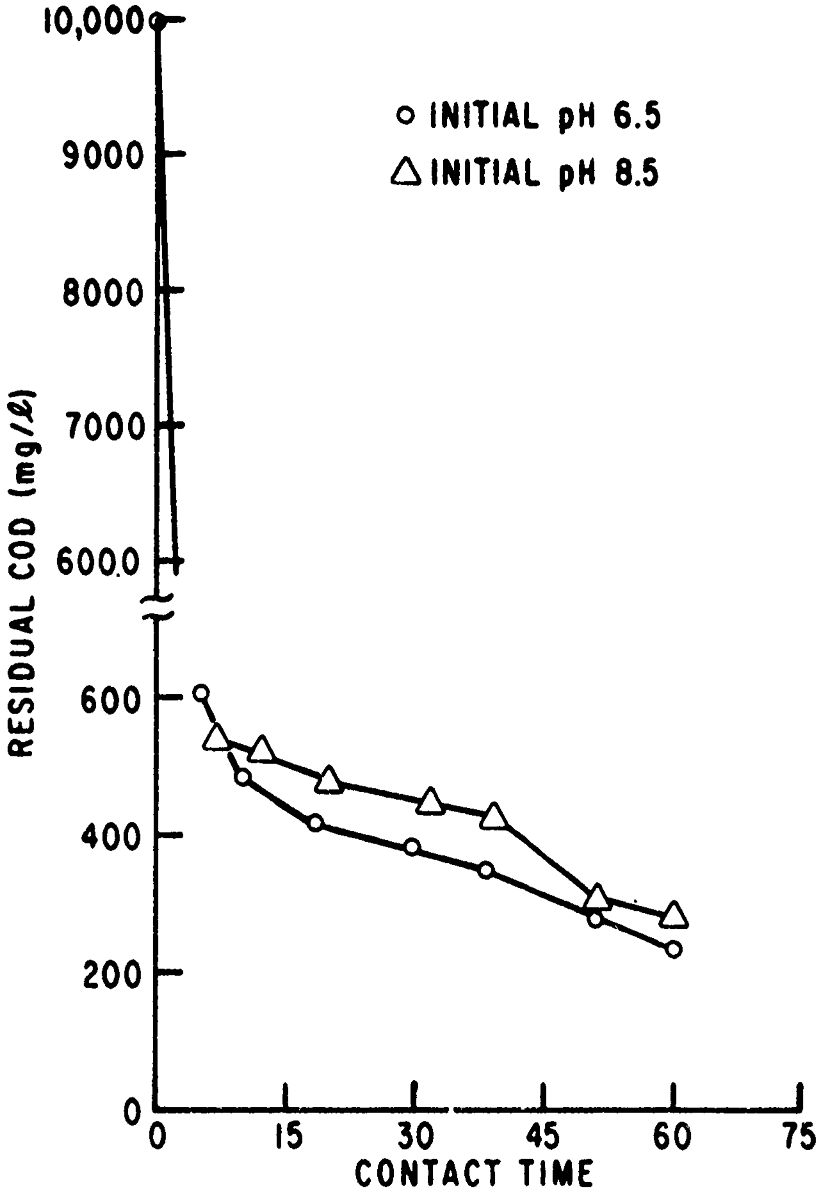


Figure 26. COD Concentration Versus Contact Time

of "sidewall effect" of the wastewater "slipping" along the column wall and not contacting the activated carbon.

Chemical oxygen demand reduction was also very rapid although slightly less effective than the phenol reduction. In that the COD concentration decreased from 610 mg/l at 5 minutes of contact (experiment No. 2) to 230 mg/l after 60 minutes of contact time indicates that organics other than phenols were being adsorbed since practically all the phenols were removed before 5 minutes of contact time. Unfortunately, as explained earlier, the capabilities to analyze for methylene chloride was lost, and therefore, methylene chloride reduction as a function of contact time could not be determined. However, it is fairly certain that methylene chloride was absorbed or at least removed in that an influent concentration of 1600 mg/l would represent a theoretical COD of 915 mg/l based on equation 14.

$$CH_2Cl_2 + 3/2O_2 \rightarrow CO_2 + H_2O + 2Cl \qquad (14)$$

Therefore, since only 230 mg/l of COD remained, a significant portion of the methylene chloride had to have been removed. This is, of course, not saying that the residual COD was because of methylene chloride.

Other data determined, but not plotted, that was a function of contact time was that of total chromium concentration and pH. For experiment 1 without pH adjustment, the total chromium was reduced from the influent concentration of 100 mg/l to 80 mg/l at sample port No. 1 (5 minutes of contact time) down to 6 mg/l after 60 minutes contact time. After 6 hours of run time, the concentration was still 80 mg/l at sample port No. 1, but the final discharge also contained 80 mg/l. There was no detectable trend in the pH at the various sampling ports (contact times) other than a general increase in pH of 0.4 to 1.0 units. For experiment 2 at a pH of 6.5, total chromium was 58 mg/l at sample port No. 1 and 15 mg/l at the final discharge for samples collected after 60 minutes of run time. After 5 hours of run time, total chromium was 67 mg/l at sample port No. 1 and 35 mg/l in the final discharge. Again the pH increased from 1.0 to 2.3 units.

Figure 27 and 28 are, respectively, phenol breakthrough and COD breakthrough at 5.2 minutes of contact time (19 inches of activated carbon depth) and 10.7 minutes contact time (39 inches of activated carbon depth). This was for experiment 2 with the initial pH of 6.5. The slopes of all the breakthrough curves were moderate for phenols and COD. For phenols, the time between the onset of breakthrough to complete breakthrough was approximately 200 minutes.

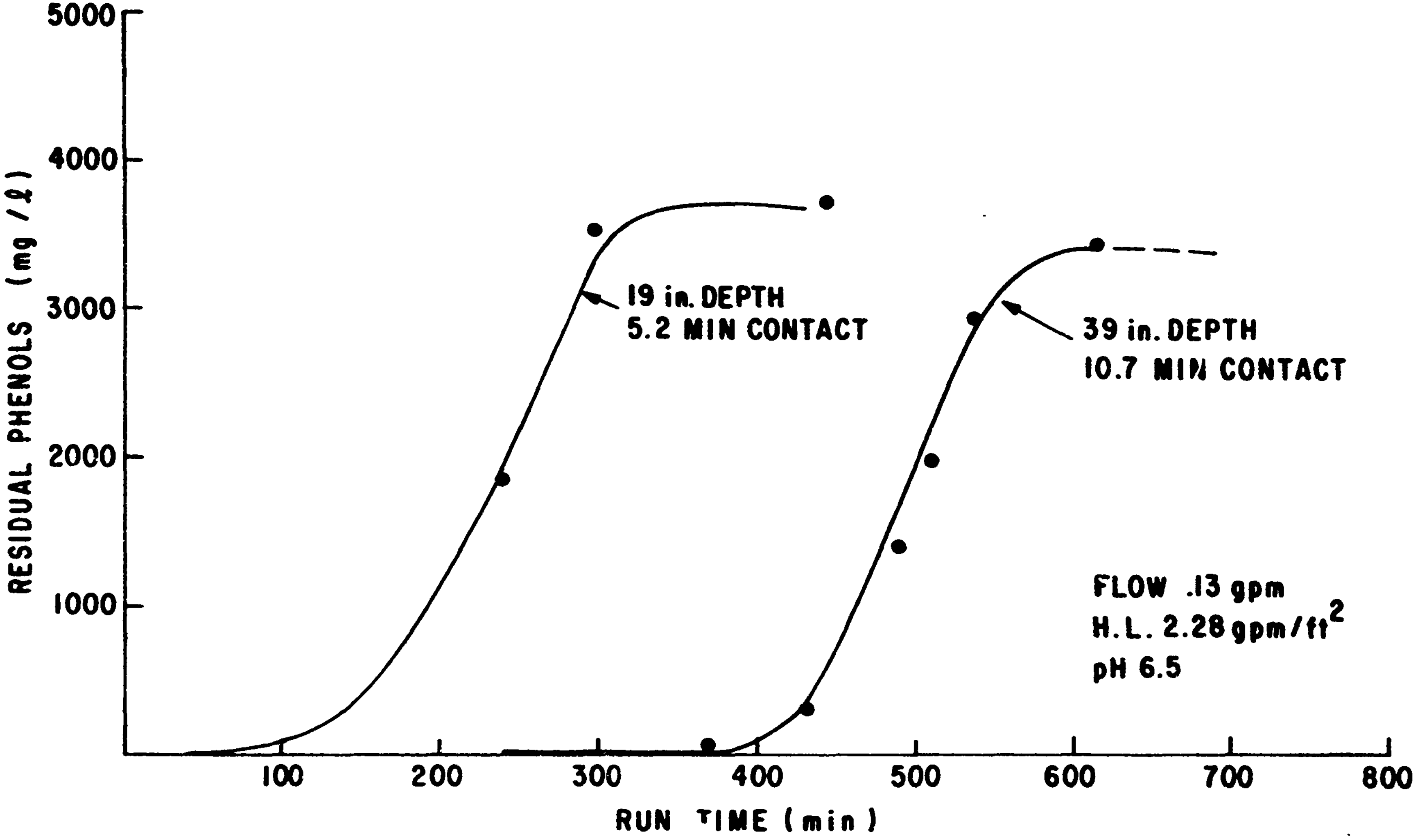


Figure 27. Phenol Breakthrough Curves

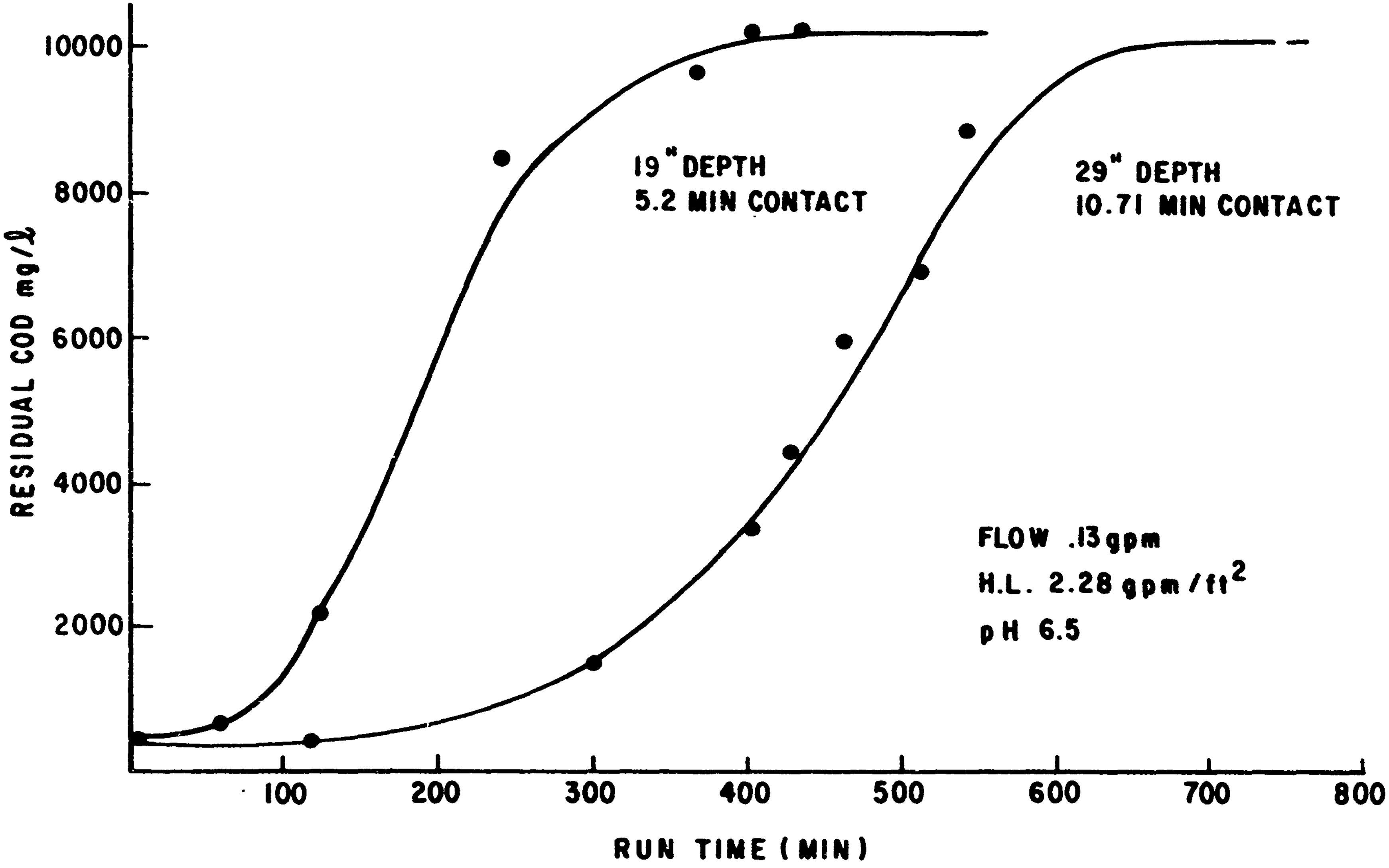


Figure 28. COD Breakthrough Curves

For COD this time was approximately 400 minutes. These breakthrough curves are typical and compare well with those found in the literature for activated carbon adsorption of various wastewaters.

It was noticed that after complete breakthrough occurred, the phenol concentration from sampling port No. 1 was higher than the influent indicating extraction of the phenols. Explanation of this fact is not readily known or understood.

Assuming complete breakthrough of phenols at sampling port No. 1, which occurs at 300 minutes of run time, yields an adsorptive capacity for the activated carbon of 0.404 gm phenol per gm of activated carbon. This is somewhat higher than the batch loading of 0.36. Chemical oxygen demand, assuming complete breaktrhough of sample port No. 1 at 400 minutes run time, yields an adsorptive capacity of 1.79 gm COD per gm of activated carbon. This is extremely high, which is very encouraging.

SECTION V

TREATMENT PROCESSES AND COSTS

1. GENERAL

The cost information presented for each treatment process, to be employed on site, are approximations based on personal communications with technical personnel of various manufacturers and from information available in the literature (refs. 4, 5, 14, 20, 25, and 33). Both capital and operating costs are given. Two flow rates have been selected as being typical for that expected from paint stripping facilities at AMA's. These flow rates are 42 gpm and 140 gpm for a 16-hour day, 5-day week. This would result in a daily flow of 40,500 gallons per day and 135,000 gallons per day for the 5-day week. If averaged over a 7-day week, with treatment of the wastewater 24 hours per day, the resulting flows would be 29,000 gallons per day and 96,000 gallons per day.

The cost analysis is based on the demands placed on the treatment process by the wastewater used during this investigation, i.e., phenol concentration approximately 3,000 mg/l, methylene chloride 1600 mg/l, and COD 10,000 mg/l. This is assuming that at least the major portion of the wastewater is the result of using phenolic paint strippers. The flow rates and concentrations further assumes that the paint stripping facility has not carelessly wasted large volumes of water nor have they reached the point where insufficient quantities of rinse water was used hampering the operation. One thing that should be kept in mind is that virtually always it is easier and cheaper to treat small volumes of concentrated wastewater than large volumes of dilute wastewater, the total pounds of contaminant being the same.

All the treatment processes are assumed to operate 24 hours per day, 7 days per week thereby requiring flow equalization. This is necessary anyway for effective and economical operation of the three treatment processes, especially ozonation and activated carbon.

2. OZONE SYSTEM AND COSTS

a. Ozone Treatment Process

This treatment process is one using an ozone oxidation system similar to that shown in figure 3. In addition there would be an equalization basin (not shown). This system can be completely automated requiring only a qualified technician to periodically check that everything is functioning correctly.

The equalization basin should be concrete and be sufficient to provide complete equalization of the flow and, therefore, the concentration of contaminants. It is assumed that most of the paint skins will have been screened out before entering the equalization basin. The wastewater is pumped out of the equalization basin at a constant flow.

The oxygen generator is similar to the one described in the literature review, i.e., molecular sieve for removal of nitrogen. The ozone generators are a "bank" of commercial size generators. A typical ozone generator has about 300 lb O_3/day capacity. These generators are air cooled, thus eliminating need for cooling water. The ozone generators are tied together by manifolds. Both the oxygen and ozone generators are protected from the weather, but also require good air circulation. This could be accomplished by using a roofed structure with exhaust fans and no walls. Each ozone generator requires about 64 square feet of floor space.

The reactor, of course, is the key to the whole treatment process. Optimizing gas liquid transfer is a necessity. Unfortunately there is not a general consensus as to which is the best reactor design. Both porous diffuser and venture injector reactors are used for full-scale treatment processes. However, packed spray towers are being successfully used also. A packed spray tower (using wooden slats, raschig, rings, etc.) operates on a counter current principle where wastewater is sprayed in the top of the tower and allowed to "trickle" down the sides. Ozone enters at the bottom of the tower. For cost analysis purposes, a three-stage, stainless steel, porous diffuser reactor is used. This reactor contains separate ozone feed rate control to optimize ozone use. The exhausted gas (oxygen) is collected from each stage and recycled.

It is not anticipated that a CO_2 scrubber (adsorber) would be required for the recycled oxygen because CO_2 production will likely be small.

b. The capital cost for generating ozone is commonly taken to be \$80/lb O_3/day. The major operating cost is for the electricity at 3 to 3.5 kwh/lb O_3 at 2 percent by weight. This costs the Air Force approximately \$.04/kwh. Assuming a pH adjustment is necessary; a 70-percent pure commerical grade NaOH (caustic soda) costs approximately \$52/500 lb drum. The wastewater requires 0.027 lb NaOH/gal to raise the pH to 11.5, which gives a cost of \$.00236/gal. For on-site generation of oxygen, operating costs including maintenance are estimated at \$.0075/lb $O_2(O_3)$. Maintenance of the ozone generators is estimated at 2 percent of the capital cost per year.

c. Costs for 29,000 Gallons Per Day Ozone Treatment Process

The capital and operating costs in tables VIII and IX are for two conditions: (1) reduction of phenols to 20 mg/l and (2) reduction of phenols to 2 mg/l. For a reduction of phenols to 20 mg/l, an ozone demand of 2.66 lb O_3/lb of phenol is used. For a reduction of phenols to 2 mg/l, an ozone demand of 4.0 lb O_3/lb of phenol is used. The cost for protection of the generators is not included. Adjustment of the pH would be accomplished in the equalization basin using pH controlled caustic feeders. Further, amortization of the equipment is not included.

Table VIII

CAPITAL COSTS FOR 29,000 GALLONS PER DAY (OZONE TREATMENT PROCESS)

Unit	Residual Phenols	
	20 mg/l	2 mg/l
	(\$ K)	(\$ K)
Equalization Basin 100,000 gal capacity 10 ft water depth x 37 x 37 ft	20	20
Oxygen Generator 20 mg/l - 2000 lb O_2/day 2 mg/l - 3000 lb O_2/day	75	100
Ozone Generator 20 mg/l - 1920 lb O_3/day need 7-300 lb O_3/day generators 2 mg/l - 2880 lb O_3/day need 10-300 lb O_3/day generators	154	230
Reactor 20 mg/l - 4 hrs retention (td) 15 ft water depth 3 stages each 3 x 5 ft 2 mg/l - 6 hrs td 15 ft depth 3 stages each 4.5 x 5 ft^2	25	30
Plumbing, Pumps, Electrical Hookup, and Instrumentation	115	125
Total Capital Cost	389	505

Table IX

OPERATING COSTS FOR 29,000 GALLONS PER DAY (OZONE TREATMENT PROCESS)

Item	Residual Phenols	
	2 mg/l	2 mg/l
	($)	($)
Electricity 20 mg/l - 6700 kwh/day 2 mg/l - 10,000 kwh/day	269	404
NaOH	69	69
Oxygen Generators	15	22
Ozone Generators	8	13
Manpower	40	40
Total Operating Costs Per Day	401	548

d. Costs for 96,000 Gallons Per Day Ozone Treatment Process

The treatment process for 96,000 gallons per day is the same as for the 29,000 gallons per day. The capital and operating costs for the 29,000 gallons per day are given in tables X and XI.

3. POTASSIUM PERMANGANATE SYSTEM AND COSTS

a. Potassium Permanganate Treatment Process

The potassium permanganate process is very similar to any coagulation-floculation-sedimentation process for treating water or wastewater. That is, the potassium permanganate is added dry to the wastewater (a quick mix of 30 seconds to 3 minutes is used to dissolve the potassium permanganate), a slow-mix cycle to provide contact between the potassium permanganate and the oxidizable organics, and a sedimentation period where the manganous dioxide sludge would settle out. The slow-mix cycle depends on the reaction rate but would likely be about 1 hour. Sedimentation also requires about 1 hour. Quick mix, slow mix, and sedimentation can be accomplished in one basin if correctly baffled. The manganous dioxide sludge is to be drawn out of the basin, dewatered and disposed of. Disposing of this very hydrous sludge presents a significant problem, possibly more so than treatment of the wastewater.

Since there were problems with getting the potassium permanganate to react with the organics at the higher loadings (see results), it may be necessary

Table X

CAPITAL COST FOR 96.00 GALLONS PER DAY (OZONE TREATMENT PROCESS)

Unit	Residual Phenols 2 mg/l	 2 mg/l
	($ K)	($ K)
Equalization Basin 200,000 gal capacity 10 ft water depth 51 x 51 ft	35	35
Oxygen Generator 20 mg/l - 6500 lb O_2/day 2 mg/l - 10,000 lb O_2/day	164	210
Ozone Generator 20 mg/l - 6360 lb O_3/day need 22-300 lb O_3/day generators 2 mg/l - 9550 lb O_3/day need 32-3000 lb O_3/day generators	510	760
Reactor 20 mg/l - 4 hrs td 15 ft water depth 3 stages each 7 x 7 ft 2 mg/l - 6 hr td 15 ft water depth 3 stages each 8.5 x 8.5 ft	35	40
Plumbing, Pumps, Electrical Hookup, and Instrumentation	300	375
Total Capital Costs	1044	1420

Table XI

OPERATING COSTS FOR 96,000 GALLONS PER DAY (OZONE TREATMENT PROCESS)

Item	Residual Phenols 20 mg/l	 2 mg/l
	($)	($)
Electricity 20 mg/l - 22,200 kwh/day 2 mg/l - 33,400 kwh/day	890	1340
NaOH	226	226
Oxygen Generators	48	72
Ozone Generators	28	42
Manpower	40	40
Total Operating Costs Per Day	1232	1720

to employ a two-stage process, that is quick mix, slow mix, settle, and then repeat again.

b. Costs

Since the results of the potassium permanganate experiments were not effective, the required operating parameters could not be determined so treatment process costs could not be estimated. Decreasing the phenol concentration down to 568 mg/l could be accomplished by adding 12 mg $KMnO_4$/mb phenol. Even if this was acceptable (obviously not) this would require 8640 lb $KMnO_4$/day for the 29,000 gallons per day flow and 28,600 lb $KMnO_4$/day for the 96,000 gallons per day flow. Commercial grade potassium permanganate, 97 to 99 percent pure, costs approximately $0.53/lb. This would result in a chemical operating cost of $4580 a day and $15,200 a day, respectively. This chemical cost makes the potassium permanganate treatment process prohibitive.

4. GRANULAR ACTIVATED CARBON SYSTEM AND COSTS

a. Granular Activated Carbon Treatment Process

Treatment of the wastewater, including thermal regeneration of the activated carbon, is accomplished by using a treatment process similar to the one shown in figure 29. The activated carbon column is an upflow countercurrent

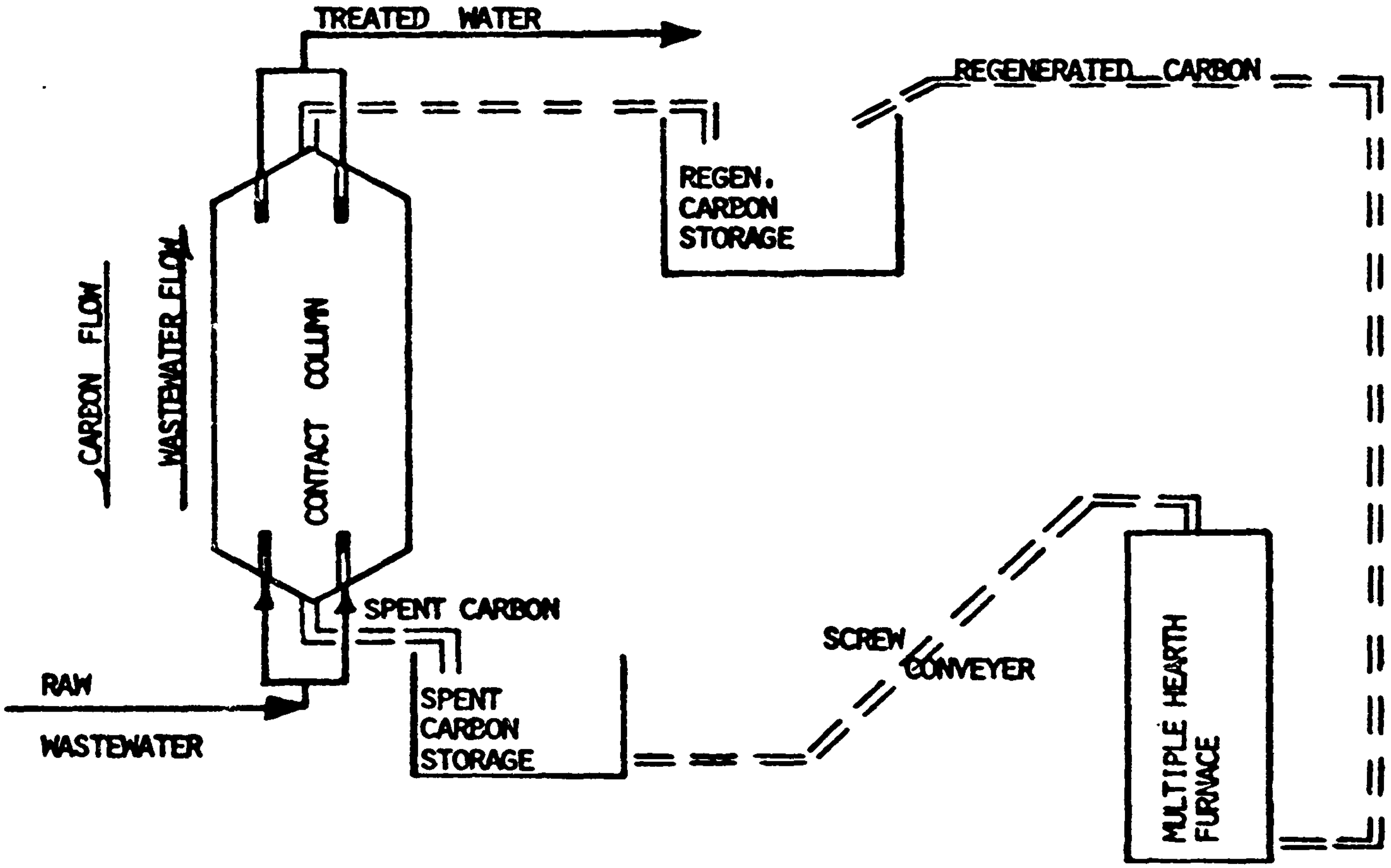


Figure 29. Activated Carbon Treatment System for Aircraft Paint Stripping Wastewater

contact column. Assuming the suspended matter will be less than about 50 mg/l, the hydraulic loading is such that the activated carbon bed remains packed.

The contact column is stainless steel that uses well screens to distribute the flow as shown in figure 5. The column is cylindrical with a 45-degree conical top and bottom for movement of the activated carbon.

For both flow rates only one column is required. A contact time of 100 min is provided to reduce the phenol concentration to less than 1 mg/l. An adsorptive capacity of 0.35 is taken as applicable. Based on the laboratory results, these are somewhat conservative. For 29,000 gallons a day, a hydraulic loading of 1.0 gpm/ft^2 is used, and for 96,000 gallons a day, a hydraulic loading of 1.5 gpm/ft^2 is used.

The contact column for 29,000 gallons a day would be sized as follows.

$$\text{Activated Carbon Volume} = 29{,}000\ \frac{\text{gal}}{\text{day}} \times 100\ \text{min}$$
$$= 2020\ \text{gals} = 270\ \text{ft}^3$$

$$A_H = \frac{20.2\ \text{gpm}}{1.0\ \text{gpm/ft}^3} = 20.2\ \text{ft}$$

Diameter = 5.1 ft

Activated Carbon Depth = 13.4 ft

$$\text{Total Depth} = 13.4\ \text{ft} + (2.55\ \text{ft})2 + 3.0\ \text{ft freeboard}$$
$$= 2.15\ \text{ft}$$

$$\text{Wt of Activated Carbon in Column} = \frac{25\ \text{lbs}}{\text{ft}^3} \times 270\ \text{ft}^3$$
$$= 6750\ \text{lbs}$$

$$\text{Lb of Activated Carbon Exhausted a Day} = \frac{720\ \text{lbs phenol}}{0.35\ \text{lb phenol/lb activated carbon}}$$
$$= 2060\ \text{lbs of activated carbon}$$

Exhausted activated carbon should be extracted twice a day, i.e., 1030 pounds extracted every 12 hours. At the time of this research, the smallest commercially available multiple-hearth furnace for regeneration of activated carbon is rated at 6000-pound activated carbon per day. This is a 54-inch diameter, six-hearth, gas-fired furnace with steam injection. Therefore, the furnace would be used only every third day.

For the 96,000 gallons per day flow, the contact column would be sized as follows.

$$\text{Activated Carbon Volume} = 96{,}000\ \frac{\text{gal}}{\text{day}} \times 100\ \text{min}$$

$$= 6660\ \text{gals} = 890\ \text{ft}^3$$

$$A_H = \frac{66.6\ \text{gpm}}{1.5\ \text{gpm/ft}^3} = 44.5\ \text{ft}^2$$

Diameter = 7.54 ft

Activated Carbon Depth = 20.0 ft

$$\text{Total Depth} = 20.0\ \text{ft} + (3.77\ \text{ft})2 + 4\ \text{ft freeboard}$$

$$= 31.54\ \text{ft}$$

$$\text{Wt of Activated Carbon in Column} = \frac{25\ \text{lbs}}{\text{ft}^3} \times 890\ \text{ft}^3 = 22{,}200\ \text{lbs}$$

$$\begin{array}{l}\text{Lb of Activated Carbon}\\ \text{Exhausted Per Day}\end{array} = \frac{2380\ \text{lbs phenol}}{0.35} = 6800\ \text{lbs}$$

Exhausted activated carbon should be extracted twice a day, i.e., 3400 pounds every 12 hours. A 64-inch diameter, six-hearth furnace is rated at about 8 to 10,000 pounds activated carbon per day. This furnace should be operated continuously for better use of fuel.

The transport and storage system for the activated carbon is similar to that in figure 4.

The costs given below assume pH adjustment is not necessary. However, if pH adjustment to 6.5 was necessary, it would only add an operation cost of $2.70 a day for the 29,000 gallons per day flow and $9.00 a day for 96,000 gallons per day.

For a more detailed review of activated carbon regeneration refer to reference 14.

b. Costs for 29,000 Gallons Per Day Activated Carbon Treatment Process

The capital and operating costs are presented in tables XII and XIII.

c. Costs for 96,000 Gallons Per Day Activated Carbon Treatment Process

The capital and operating costs are presented in tables XIV and XV.

Table XII

CAPITAL COSTS FOR 29,000 GALLONS PER DAY (ACTIVATED CARBON TREATMENT)

Item	Cost
	($ K)
Contact Column	15
Regeneration Furnace and Activated Carbon Transport and Storage Units	193
Plumbing 25 Percent of $208K	52
Wiring and Instrumentation 12 Percent of $208K	25
Initial Activated Carbon Inventory 1.5 x 6750 lb x $0.35/lb	3.5
Total Capital Cost	288.5

Table XIII

OPERATING COSTS FOR 29,000 GALLONS PER DAY (ACTIVATED CARBON TREATMENT)

Item	Cost
	($)
Regeneration fuel, power, steam, etc. $0.0323/lb exhausted Activated Carbon	67
Make Up Activated Carbon 5 Percent Loss on Regeneration	36
Total Operating Costs Per Day	103

Table XIV

CAPITAL COSTS FOR 96,000 GALLONS PER DAY (ACTIVATED CARBON TREATMENT)

Item	Cost
	($ K)
Contact Column	22
Regeneration Furnace and Activated Carbon Transport and Storage Units	230
Plumbing 25 Percent of $252K	63
Wiring and Instrumentation 12 Percent	30.2
Initial Activated Carbon Inventory 1.5 x 22,200 lb x 0.35/lb	11.7
Total Capital Costs	356.9

Table XV

OPERATING COSTS FOR 96,000 GALLONS PER DAY (ACTIVATED CARBON TREATMENT)

Item	Cost
	($)
Regeneration fuel, power, steam, etc. $0.0323/lb exhausted Activated Carbon	220
Make Up Activated Carbon 5 Percent Loss on Regeneration	119
Total Operating Costs Per Day	339

SECTION VI

DISCUSSION

1. GENERAL

The purpose of this research was to find the optimum economical and technological treatment process to employ for treating of large volumes of phenolic aircraft (and ground equipment) paint stripping wastewater. The findings of this research is also applicable to treatment of other wastewaters where phenols represented the major organic contaminant.

Analysis of the phenolic paint stripping wastewater yielded phenol concentrations of 2700 to 3000 mg/l, methylene chloride approximately 1600 mg/l, COD 9600 to 10,000 mg/l, and total chromium 100 mg/l. Therefore, phenols represented 71.5 percent of the COD and methylene chloride 9.1 percent. The wastewater was a yellowish brown color that is caused largely by the hexavalent chromium.

Since the phenol concentration of the wastewater was relatively high, it was at first considered that phenol recovery would be the best approach because it would reclaim a valuable product. However, after reviewing what would be involved as far as a process and what could be done with the recovered phenols, it was decided that this would not be the best approach because of complexity. While the other methods discussed in the literature review (chlorination, biological treatment, etc.) have been and are successfully treating phenolic wastewaters, it was considered at the start of this research, and is still considered, that these methods would not prove effective. The reasoning being that if ozone, the strongest gas oxidizer, or potassium permanganate, the strongest solid chemical oxidizer, would not be effective neither would any other method. While biological treatment has been demonstrated to be capable of treating phenols (concentrations in the 2000 to 3000 mg/l range (no toxic compounds such as chromium present) and at a much cheaper cost than any physical-chemical process), these processes were operated under extremely controlled condition, i.e., constant hydraulic loading and constant phenol concentration day in and day out.

2. OXIDATION WITH OZONE

The results of the ozonation experiments show that adjustment of the pH is necessary from reduction of contact time required and, more important, for reducing the ozone demand. Reducing the phenol concentration by 99.5 percent (residual phenol concentration less than 20 mg/l) only reduced the COD by 65 percent leaving a residual COD of 3500 mg/l. This substantiates the formation of intermediate oxidation products, which would require further treatment.

Optimizing ozone-liquid transfer is necessary to minimize ozone demand and maximize treatment efficiency. There is no consensus of optimum as to what is the best reactor to accomplish this. However, it appears that any reactor should be in separate stages where each stage has separate control as to the amount of ozone applied. This is an area of needed research. Pilot-plant scale investigation should definitely be researched before design or construction of a full-scale ozone treatment process.

The major capital and operating costs for the ozone system are in the oxygen and ozone generators and the electrical requirements. There is no way of minimizing these costs.

3. OXIDATION WITH POTASSIUM PERMANGANATE

Oxidation with potassium permanganate proved very ineffective. Even at very high loadings (Mg $KMnO_4$/mg phenol), phenol reduction was not near that required. There were significant quantities of unreacted potassium permanganate left. Even if a longer mixing time was used and the unreacted potassium permanganate did react, this method would still be unfeasible because of the large quantities of manganous dioxide sludge produced, which also requires treatment, and the high cost of the potassium permanganate.

4. ADSORPTION WITH GRANULAR ACTIVATED CARBON

Activated carbon adsorption proved very effective in reducing the phenol and COD concentration. This is so because the removal of phenols and other organics is a physical mechanism and involves no oxidation to intermediate products. Removal of phenols was slightly favored at the lower pH of 6.5; however, the wastewater could be treated without pH adjustment as long as it would not get much above 8.5. The adsorptive capacity in terms of phenols and COD was very high, indicating a strong affinity of the activated carbon for the removal of the organics present in the wastewater of concern.

Besides effective removal of the organics, chromium was substantially removed also. This is a positive factor in that it is necessary to remove the chromium from the wastewater anyway, and therefore it could eliminate or greatly reduce the necessity and cost of separate chromium reduction treatment processes. However, removal of the chromium by "plating out" on the activated carbon is not so desirable in that thermal regeneration would not extract it from the activated carbon, and therefore possibly might reduce the useful life of the activated carbon. This has not been documented one way or the other.

The major capital cost, and almost the entire operating cost for the activated carbon treatment process, is for the thermal regeneration. Unless the volumes or concentrations of the wastewater were very much reduced from say the 29,000-gallons per day flow (40,500 gal/day actual per day of operation), regeneration of the activated carbon is the only economical method of operation. All things being equal, activated carbon could be thermally regenerated 10 times for what it costs to buy new activated carbon. To escape the major capital investment for a multiple-hearth furnace and associated units, it may be possible to chemically regenerate the activated carbon by extracting the phenols with a regenerate of either a solvent or caustic soda. This would involve pumping the regenerant through the contact column under predetermined conditions and collecting it upon discharge. This is being effectively done today for recovery of the phenols and the regenerant. As seen below this is not considered applicable for replacing thermal regeneration. The problem now created, expecially at an Air Force Base, is what to do with the regenerant solution. Assuming the regenerant was effective there now exists a concentrated phenolic solution. Recovery of the phenols and the regenerant by separating the two (and reusing the regenerant) would be required for economical use of the regenerant, especially if it were a solvent. Separating the phenols and regenerant is a complex process in itself. This still leaves a phenol solution for reuse. Even though Air Force Bases and especially AMA's use large quantities of phenolic solutions for carbon removing, the recovered phenol is not in the same form as that phenol in the carbon removing solutions.

Further complicating the matter is what would be done with the adsorbed organics that were not extracted. Reuse of the activated carbon without complete removal of all organics will consequently decrease the adsorptive capacity each time until it is either "thrown away" or thermally regenerated anyway. Therefore, although chemical regeneration could at first thought eliminate the need for thermal regeneration, it also would create more problems than it would solve.

An alternative to on-site thermal regeneration would be to contract with the activated carbon manufacturer to have them regenerate the activated carbon at one of their sites. This would eliminate much of the capital cost but would greatly increase the operating cost.

Two costs would be incurred: The manufacturers charge and the transportation cost. Unfortunately, at this time, there is not any of the big activated carbon manufacturers on the West Coast with thermal regeneration systems available for contract. These systems are mainly in Pennsylvania and West Virginia. The cost that an activated carbon manufacturer would charge is in the range of $0.15 to $0.20 per pound of activated carbon. Concerning McClellan AFB, the cheapest way to ship the activated carbon would be by rail. The rate from Sacramento, California, to Pittsburgh, Pennsylvania, and return would be approximately $0.08 per pound (for 80,000 lb minimum). This would be by boxcar. This gives a regeneration cost of $0.23 to $0.28 per pound, neglecting the cost of transferring the activated carbon from the contact columns into containers and to the rail line. As stated before, virgin activated carbon can be purchased for about $0.35 per pound and regenerated on site for about $0.03 per pound.

Over a 1-year period, the contract regeneration cost for the 29,000 gallons per day wastewater flow (2060 lb activated carbon exhausted per day) would be between $173,000 to $210,000. This is as much or slightly more than the capital cost for an on-site thermal regeneration system. Therefore, on-site regeneration is the only feasible method.

5. LOCATION OF THE TREATMENT FACILITY

As described in the introduction, the research conducted was geared toward on-site treatment of just the phenolic aircraft paint stripping wastewater. However, since phenolic solutions are widely used at AMAs and phenols are present in industrial wastewaters at AMAs from sources other than the paint stripping facility(s), it may be better to treat the entire industrial wastewater flow by the same process as that which would be employed for on-site treatment. There are of course many factors that need be considered before any decision could be reached as to which way to go. These factors will be discussed below.

The first factor is: Can the existing wastewater treatment facility satisfactorily handle an increased phenolic load that would be imposed by using phenolic paint strippers? If it can, the solution is simple.

The second factor is: How much of the paint stripping operation involves the use of phenolic paint strippers? If the paint stripping operation consists of the use of both phenolic and nonphenolic paint strippers, of roughly equal quantities, it may be desirable to segregate the operation and treat on-site just the phenolic paint stripping wastewater. This of course would have to be considered relative to the cost of segregating the operation and wastewater flow as compared to the increased cost, if any, of treating both phenolic and nonphenolic paint stripping wastewaters on site. This, of course, would not be applicable to aircrafts having two paint systems necessitating the use of phenolic and nonphenolic paint strippers.

The third factor is: What percentage of the entire industrial wastewater flow is represented by the paint stripping wastewater? If this is a significant percentage of the entire industrial wastewater flow, on-site treatment of just the paint stripping wastewater may cost as much as treating the entire industrial wastewater by the same unit process. This is especially true for the cost of an activated carbon treatment process which is relatively insensitive to increases in flow.

The fourth factor and maybe the most important is: Has the existing industrial wastewater treatment facility been satisfactory only because maintenance operations were forced to be curtailed or modified to make the industrial wastewater treatment facility operate satisfactorily?

6. ELIMINATION OF THE WASTEWATER TREATMENT PROBLEM

At the outset of this research project some basic questions had to be asked and these questions warrant a discussion. This discussion is not intended to provide answers to these questions but merely to bring attention to them.

Why depaint aircraft and ground equipment in the first place? This is done to prevent intergranular corrosion of the metallic surfaces.

What is the effect of depainting say every 5 years instead of every 3 years?

Are phenolic paint strippers necessary to depaint polyurethane epoxy paint systems? The answer directly from manufacturers of paint strippers is that phenolic paint strippers are definitely superior to the nonphenolic types for removing polyurethane epoxy paints; however, some nonphenolic paint strippers are effective in removing <u>certain</u> polyurethane epoxy paints (refs 34 and 35). Therefore, it appears that the use of phenolic paint strippers is necessary, at least until a nonphenolic paint stripper is found that works satisfactorily.

Do the phenolic paint strippers need to be rinsed from the aircraft or could they along with the paint skins be brushed and "squeegeed" off collected and say incinerated? At the time of this report, United Airlines was using a hot water rinse, but extremely minimized to about 4 gallons of rinse water per gallon of stripper, and collecting all the water in a trough and "rebarreling" the water, paint stripper, and paint skins. Their disposal technique was contractor hauling to an evaporation pit (ref. 36). Delta Airlines does squeegee off the paint stripper and paint skins onto plastic sheets. These plastic sheets are then disposed of in a sanitary landfill. It is not the intent to endorse either of these methods but both of them does warrant further consideration (ref 37).

SECTION VII

CONCLUSIONS

1. Granular activated carbon adsorption with thermal regeneration is the best treatment process to use for treating phenolic aircraft paint stripping wastewaters. It provides better reduction of phenols and COD than does either ozonation or potassium permanganate, and it is less expensive to construct or operate.

2. Phenol concentration was reduced to less than 10 mg/l in the first 5 minutes of contact time after which removal proceeded at a much slower rate. A contact time of 75 to 100 minutes would be required to reduce the phenol concentration to 0.1 to 0.3 mg/l. Reducing the phenol concentration to this value would leave a residual COD concentration of less than 200 mg/l.

3. Total chromium concentration is substantially reduced by "plating out" on the activated carbon.

4. The adsorptive capacity of the activated carbon used was, respectively, for phenols and COD: 0.404 gm phenol/gm activated carbon and 1.79 gm COD/gm activated carbon.

5. Adjusting the pH to 6.5 did improve removal efficiency but removal efficiency was very high even without pH adjustment.

6. Thermal regeneration of the activated carbon using a multiple-hearth furnace is the major capital and operating cost of the treatment process, but unfortunately is the only feasible way to regenerate the activated carbon.

7. Ozonation is an effective oxidizer for phenols at elevated pHs, but oxidation of the phenols is incomplete and the ozone demand is high, expecially to reduce the phenol concentration below 20 mg/l.

8. Potassium permanganate was not an effective oxidizer for the phenols and created a sludge problem.

SECTION VIII

RECOMMENDATIONS

1. A pilot-plant scale activated carbon treatment process should be installed at McClellan AFB at the aircraft paint stripping facility to test the effectiveness of treating only phenolic paint stripping wastewater and combinations of phenolic and nonphenolic paint stripping wastewater. This will necessitate the use of phenolic paint strippers, but this should be segregated and the wastewater collected by some means. Thermal regeneration need not be attempted at the pilot-plant treatment facility, but this should be accomplished by contracting to have the activated carbon regenerated and then use the regenerated activated carbon to determine the effective of thermal regeneration. At least four cycles of exhaustion and regeneration should be accomplished.

2. Consideration should be given to subsections 5 and 6 of section VI, Discussion.

3. RESEARCH RECOMMENDATIONS

   a. Determine what organics in the phenolic paint stripping wastewater are not adsorbed by the activated carbon.

   b. Determine the effect of chromium and other heavy metals plating out on the life of the activated carbon.

APPENDIX A

OZONE PRODUCTION AND TITRATION CURVES

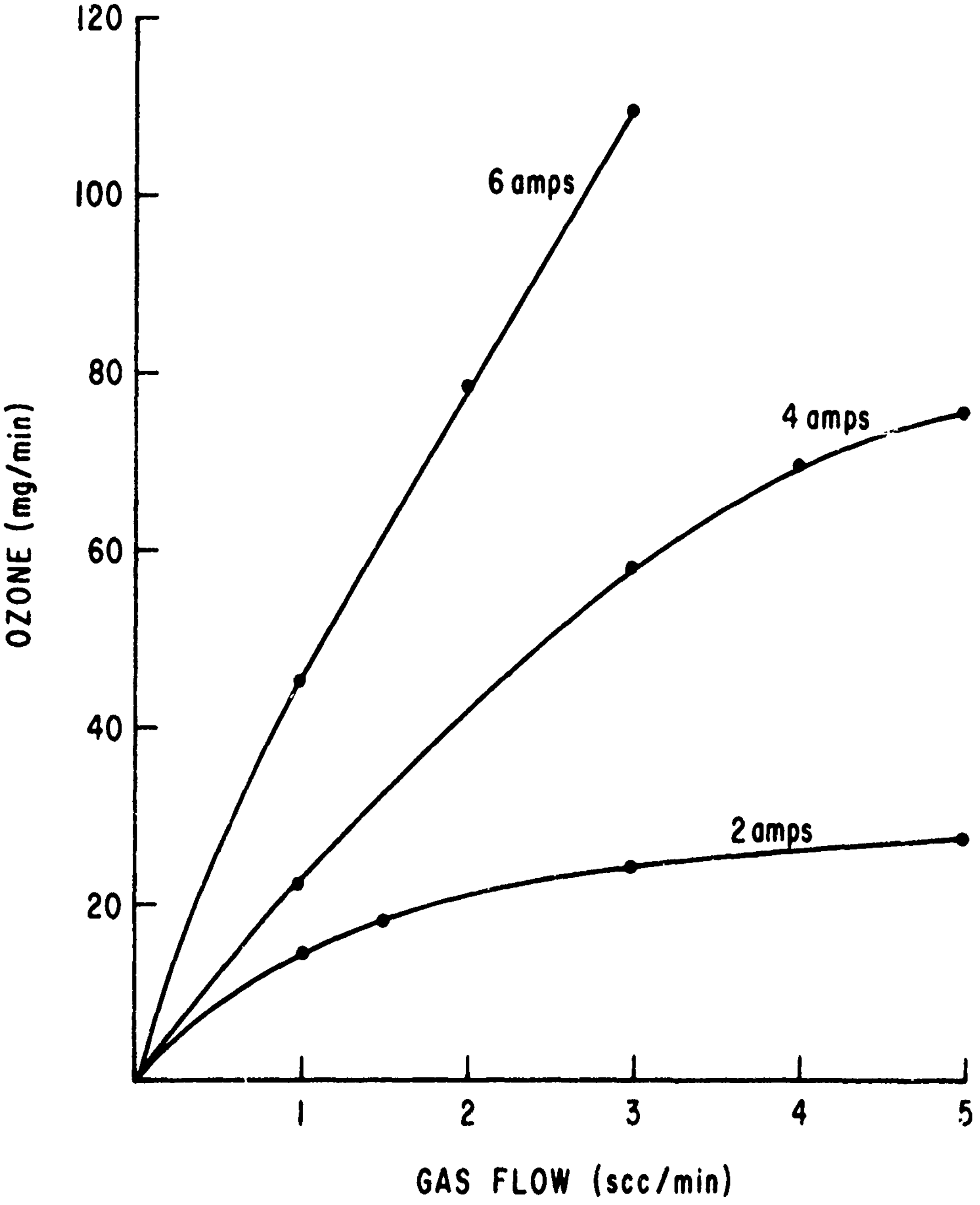


Figure 30. Ozone Production Versus Gas Flow for Varying Applied Current

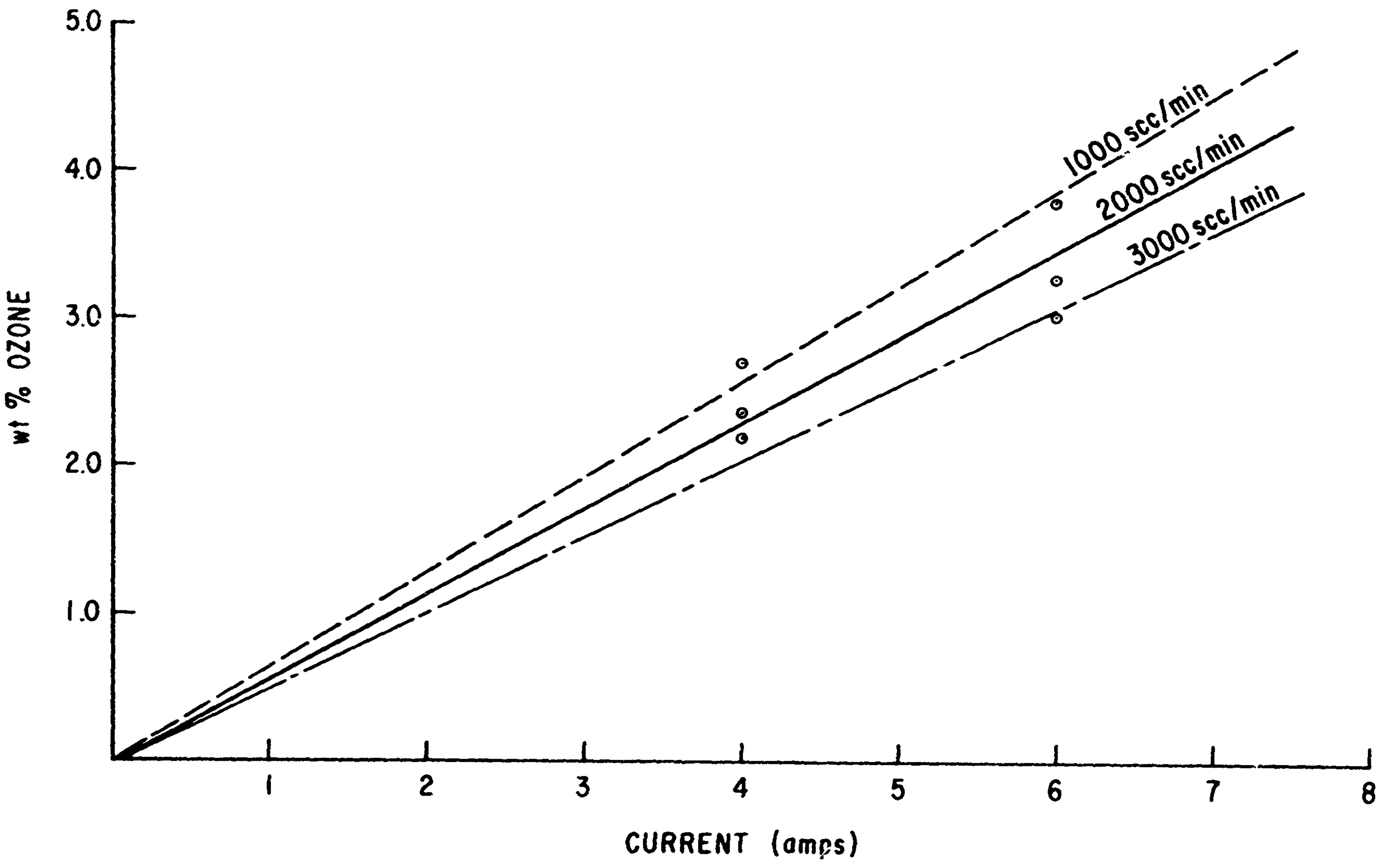


Figure 31. Ozone Production Versus Current

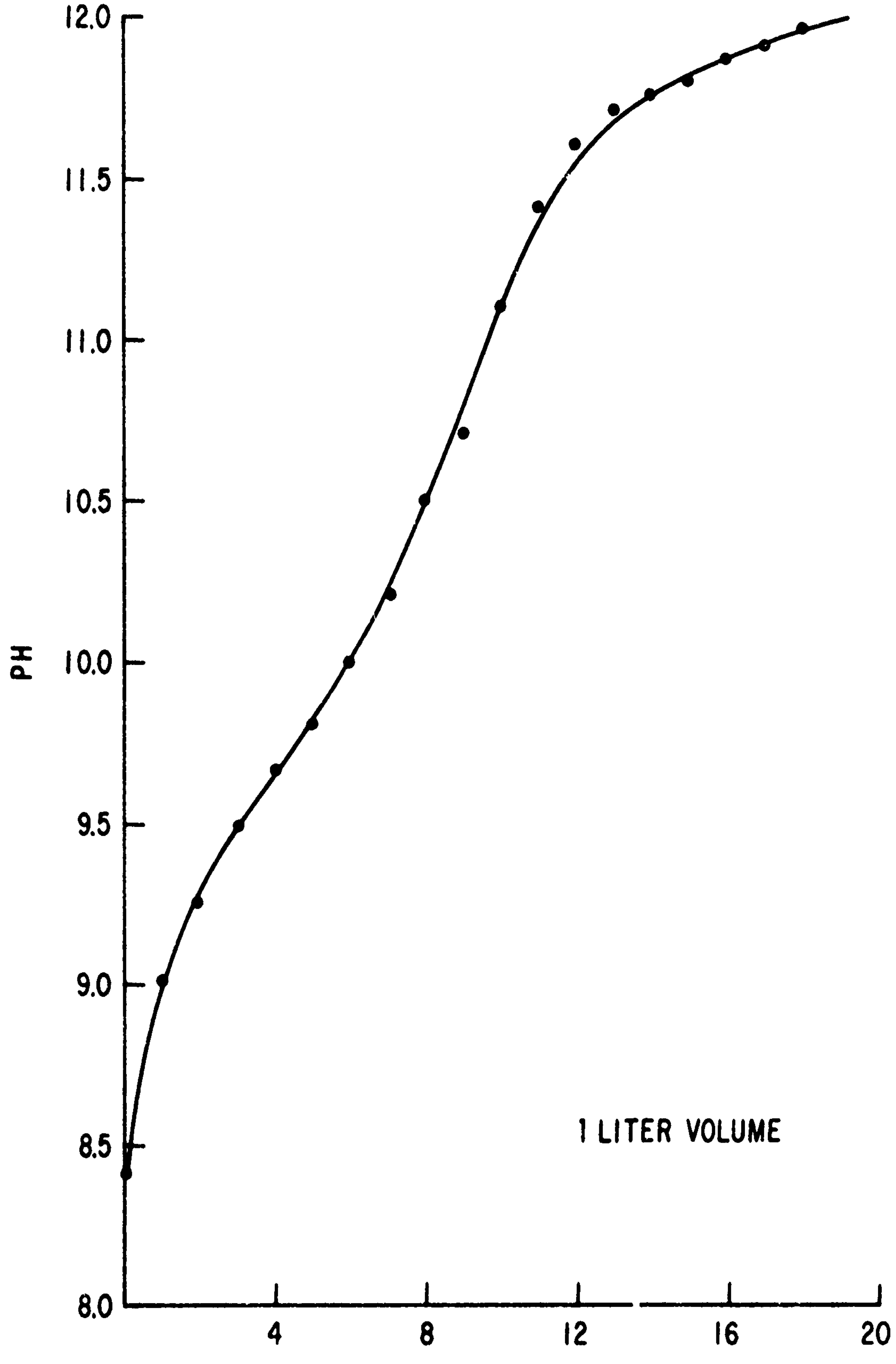


Figure 32. Alkaline Titration Curve

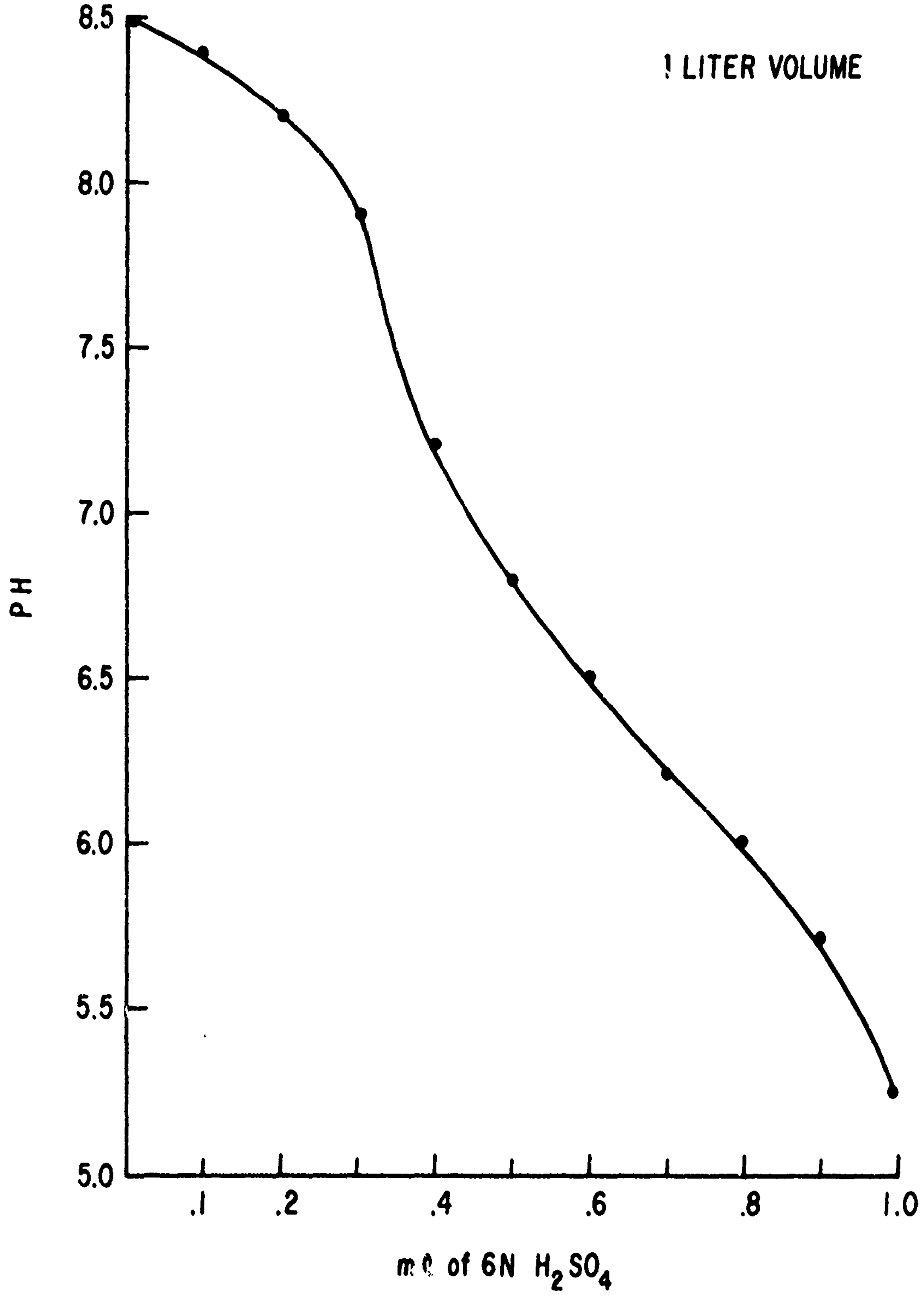


Figure 33. Acid Titration Curve

APPENDIX B

LETTERS REQUESTING RESEARCH

DEPARTMENT OF THE AIR FORCE
HEADQUARTERS 2852D AIR BASE GROUP (AFLC)
McCLELLAN AIR FORCE BASE CALIFORNIA 95652

REPLY TO ATTN OF: DE 29 MAR 1972

SUBJECT: Request for Phenolic Depaint (Stripper) Treatment Analysis and Recommendations

TO: AFWL/DEEW
ATTN: Capt Dean Nelson/Lt Kroop
Kirtland AFB NM 87117

1. This letter will formalize the initial telecon request for the subject information. It was initially agreed that McClellan would synthesize a 200 gallon waste sample and send it to the Weapons Lab for the treatment analysis. Because the paint system, stripper, and their interaction are unknown, such a sample has been difficult to produce. We are attempting to obtain the sample from Vance AFB, Oklahoma, inasmuch as they have a stripper operation of the type in question.

2. The stripper wastes generated by depaint (stripping) operations of the new aircraft polyurethane and epoxy paint systems will impose phenolic concentrations far in excess of our existing treatment capabilities. Our new industrial waste treatment facility is designed for treatment of 5 ppm maximum. Request the treatment analysis provide recommendations in regard to the following:

a. Waste treatment site - Shall we consider increasing the treatment capacity of our existing industrial waste treatment facility or shall we construct the required facility at the stripper site? The two facilities are located on opposite sides of the base approximately 1.1 miles distant.

b. Treatment method - In view of the stringent limitations imposed by the State of California on phenolic pollutants (0.005 ppm), the method utilized must effectively neutralize the stripper. Consideration should be given to possible air pollution implications of the treatment method in view of probable future restrictions on emissions.

c. Treatment costs - Any related cost, i.e., manpower, construction, chemicals, equipment, etc., is needed for comparative studies and programming purposes.

3. Although no firm deadline has been established, the first aircraft requiring this stripper are expected in June 1972. Considering the lead time required for construction of new facilities, the expeditious development of the subject information is requested. The McClellan coordinator will be G. Reitz, DEEE, Ext. 33046/7.

FOR THE COMMANDER

E. F. MYERS, JR., Deputy
Base Civil Engineer

DEE (Capt Nelson) 20 April 1972

Consultation Service for McClellan AFB

AFLC (SGPE)

1. Attached is a copy of a letter from the Civil Engineer at McClellan AFB requesting our assistance in solving a problem associated with phenolic paint strippers. We feel that finding an answer to paragraph 2b falls within the scope of our present efforts. Based on estimates of hydraulic loads of 140 gallons per minute for 16 hours per day, 5 days per week, and phenolic concentrations of 650 mg/l average and 3000 mg/l maximum, we feel that this problem does not fall within the scope of the bio-degradability studies accomplished by the EHL at Kelly AFB.

2. The soon to be constructed addition to the industrial waste treatment facility will be biological treatment in the form of a trickling filter. The 5 mg/l maximum allowable phenolic load may be conservative but could easily be valid when non-steady loading conditions are considered. It would appear that some form of pre-treatment of the stripping waste alone would be the best solution. Our intentions, as of this date, are to look at ozoneation and activated carbon.

3. Considering that some of the other requests from McClellan are of a nature normally accomplished by the EHL's, we would like your permission to work on McClellan's problem in order to lend more practicability to our R&D efforts and at the same time help solve a base problem.

FOR THE COMMANDER

DEAN D. NELSON, Capt, USAF, BSC
Chief, Water Resources Section
Environics Branch

1 Atch
Ltr, DE, McClellan AFB,
29 Mar 72

Copy to: DEE (Mr. Reitz)
McClellan AFB, CA

2793 USAF Disp
(AMM/Lt Col Channel),
McClellan AFB, CA

DEPARTMENT OF THE AIR FORCE
HEADQUARTERS AIR FORCE LOGISTICS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

REPLY TO ATTN OF: SGP 17 May 1972

SUBJECT: Consultation Service for McClellan AFB (your ltr 20 Apr 72)

TO: AFWL/DEE
Kirtland AFB NM 87117

1. This headquarters concurs with the Civil Engineers', McClellan AFB CA, request for your assistance in solving the phenolic paint stripper disposal problem.

2. Phenolic paint strippers are common to each Air Force facility removing urethane paints from aircraft. Aircraft such as C-141, C-5, and KC-135 are starting to use the urethane paints.

3. Recommend that your study include Tinker AFB where phenolic type paint strippers are being used to remove urethane paint from the B-52. Phenolic paint strippers are presently restricted in quantity per aircraft as the industrial waste treatment facilities are not adequate to support complete stripping of a B-52 with phenolic type paint strippers.

FOR THE COMMANDER

HAROLD W. DIETZ, Colonel, USAF, MC
Director of Professional Services
Office of the Surgeon

Cy to: 2854 ABGp/DE
Tinker AFB OK 73145

OCAMA/MA

APPENDIX C

BATCH ADSORPTION ISOTHERM PROCEDURE

1. Grind a representative sample of granular activated carbon with a mortar and pestle or mechanical grinder taking only what passes a #100 U.S. Standard Sieve.

2. Weigh out 0.3, 0.5, 1.0, 2.0, and 3.0 grams of ground activated carbon correct to 4 decimal places. Place each weighing in a separate 250 ml Erlenmeyer flask.

3. Adjust the pH of the wastewater to 4.5 with H_2SO_4.

4. Place 100 ml of the wastewater in each of the 250 ml Erlenmeyer flasks and agitate for 1 hour at constant temperature. If activated carbon was not ground agitate for 24 hours.

5. At the end of 1 hour, filter the sample to remove all the activated carbon.

6. Perform the desired analyses on the filtered sample to determine the residual concentrations.

7. On log-log paper, plot the residual (final) concentration (C_f) on the abscissa and the loading (X/M) on the ordinate.

$$X/M = \frac{(Co - Cf)\ V}{M}$$

Where

Co = initial concentration of the compound
Cf = final concentration of the compound
M = grams of activated carbon used'
V = volume of sample in liters

A straight line should result from the plot.

8. To determine the activated carbon loading, find the X/M value corresponding to Co.

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