Removal of Phenolic Compounds from Wood Preserving Wastewaters

Edward C. Jordan Co., Inc.
Portland, ME

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REMOVAL OF PHENOLIC COMPOUNDS
FROM WOOD PRESERVING WASTEWATERS

by

Bruce K. Wallin
Arthur J. Condren
Roy L. Walden

Edward C. Jordan Co., Inc.
Portland, Maine   04112

Project Officers

Donald L. Wilson and
Brian Westfall
Food and Wood Products Branch
Industrial Environmental Research Laboratory
Cincinnati, Ohio   45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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Laboratory and pilot-scale studies were undertaken to develop economically feasible technologies for the treatment of wastewaters from wood preserving operations. Of prime concern was the removal of phenol and its chlorinated derivatives, in particular, pentachlorophenol. Screening analysis of the wastewater indicated that pentachlorophenol was the only chlorinated derivative consistently present in concentrations of approximately 100 mg/l.

Treatment technologies investigated for the treatment of these wastewaters included: 1. adsorption; 2. biological oxidation; 3. chemical oxidation; 4. coagulation; 5. extraction; and 6. pH adjustment.

Each of the above, along or in combination, was capable of yielding a measurable reduction in the concentration of total phenols and pentachlorophenol in the untreated wastewater.

Two technologies yielded consistently high levels of treatment:
1. pH adjustment of the wastewater, followed by adsorption with bentonite clay and final polishing by the polymeric adsorbant, XAD-4; and
2. pH adjustment of the wastewater, followed by extraction with a mixture of #2 fuel oil and a co-solvent such as still bottoms from amyl alcohol production.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

Identification and evaluation of treatment techniques for removal or reduction of pollutant discharges in an industry (in this instance the wood preserving industry) provides useful information relative to the treatability of the pollutants of interest. Regulatory agencies can use such information to assess the applicability of the technology in controlling the pollutants of interest. The Food and Wood Products Branch, IERL-Ci, can be contacted for further information on the subject.

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David G. Stephan, Director
Industrial Environmental Research Laboratory
Cincinnati, OH

ABSTRACT

Laboratory and pilot-scale studies were undertaken to develop economically feasible technologies for the treatment of wastewaters from wood preserving operations. Of prime concern was the removal of phenol and its chlorinated derivatives, in particular, pentachlorophenol. Screening analysis of the wastewater indicated that pentachlorophenol was the only chlorinated derivative consistently present in concentrations of approximately 100 mg/l.

Treatment technologies investigated for the treatment of these wastewaters included:

1. adsorption;
2. biological oxidation;
3. chemical oxidation;
4. coagulation;
5. extraction; and
6. pH adjustment.

Each of the above, alone or in combination, was capable of yielding a measurable reduction in the concentration of total phenols and pentachlorophenol in the untreated wastewater.

Two technologies yielded consistently high levels of treatment:

1. pH adjustment of the wastewater, followed by adsorption with bentonite clay and final polishing by the polymeric adsorbant, XAD-4; and

2. pH adjustment of the wastewater, followed by extraction with a mixture of #2 fuel oil and a co-solvent such as still bottoms from amyl alcohol production.

Total annual operating costs for systems treating a typical 10,000 gpd of wastewater were calculated to be $40,000 and $23,600, respectively, for the two aforementioned technologies.

This report was submitted in fulfillment of Contract No. 68-03-2605, Work Directives Nos. 2, Part I, and 5, by the Edward C. Jordan Co., Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 20, 1978 to May 20, 1980, and work was completed as of May 20, 1980.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

BOD	--biochemical oxygen demand
BOD5	--5-day biochemical oxygen demand
COD	--chemical oxygen demand
DI	--de-ionized
ECD	--electron capture detection
EPA	--U.S. Environmental Protection Agency
ft	--feet (foot)
ft2	--square feet
ft3	--cubic feet
FID	--flame ionization detection
g	--gram
gal	--gallon
GC	--gas chromatography
GC/MS	--gas chromatography/mass spectroscopy
g/l	--grams/liter
gpd	--gallons per day
gpm	--gallons per minute
hp	--horsepower
in.	--inches
kg	--kilogram
kW	--kilowatt
kWh	--kilowatt-hour
l	--liter
lb	--pound
bl/day	--pound/day
min	--minute
ml	--milliliter
mg	--milligram
mg/l	--milligram/liter
ml/l	--milliliter/liter
mug/l	--millimicrograms/liter
MLSS	--mixed liquor suspended solids
MLVSS	--mixed liquor volatile suspended solids
N	--normality
nm	--logmeters
O&M	--operation and maintenance
POTW	--publicly owned treatment works
ppm	--parts per million
sec	--seconds
SVI	--sludge volume index
ug/l	--micrograms/liter
w	--watt(s)
wt	--weight

SYMBOLS

°C	degrees Centigrade
CH2C12	dichloromethane
°F	degrees Fahrenheit
HC1	hydrochloric acid
H2SO4	sulfuric acid
H20	water
NaOH	sodium hydroxide
±	plus or minus

ACKNOWLEDGMENTS

SECTION 1

INTRODUCTION

The U.S. Environmental Protection Agency has been involved in extensive investigations of toxic compounds being discharged from industrial facilities. Primary emphasis has been on the 65 "priority" pollutants, which are contained in the Settlement Agreement of 1976 and in the Clean Water Act of 1977 (PL 95-217). Phenolics and their chlorinated derivatives are a part of this group and are commonly found in the wood products industry's wastewater streams.

The initial objective of this study was to evaluate the treatability of 2,4,6-trichlorophenol, parachlorometacresol, 2-chlorophenol, 2,4-dichlorophenol, and pentachlorophenol in the wood products industry's wastewater. The wood preserving industry was selected for this program because wastewater from wood preserving facilities is usually low in volume but high in concentrations of chlorinated phenolics. A chemical screening of the wastewater revealed that it had a high organic content, but more significantly, it contained pentachlorophenol in concentrations exceeding 100 mg/l. The program's focus then shifted primarily to pentachlorophenol to the virtual exclusion of all else, since only trace levels of other chlorinated phenolics were found.

In conjunction with the treatability aspect, the program was intended also to explore atypical pretreatment schemes that would reduce chlorinated phenolics, namely pentachlorophenol, in typical wood preserving wastewater to levels at which the wastewater could be discharged to a POTW without causing an upset. Owing to constraints imposed by time and financial resources, it was not the objective of this program to investigate all aspects of each treatment scheme (e.g., residual catalyst after PCP removal, toxicity of the removal concentration, adsorptive capacity of the regenerated resin). The objective here was also not to improve the phenol-contaminated wastewater to drinking water quality, nor was it within the bounds of the study to make any conclusions concerning the toxicity of the residual pentachlorophenol concentration in the wastewater that would be discharged to the POTW.

The physical/chemical properties of pentachlorophenol, as distinguished from those of phenol, were important in considering the pretreatment systems which would be capable of reducing concentrations to an acceptable level. Pentachlorophenol consists of a benzene ring (C_6H_6) with all six hydrogen

sites substituted by one hydroxyl group (OH) and five chlorine atoms (Cl_5). The resulting compounds, C_6Cl_5OH, is mildly acidic, boils at 309°C, and is soluble in 50°C water at 30 mg/l. Oils or emulsions in wastewater can provide a "carrier" effect, allowing pentachlorophenol to far exceed its normal solubility in water. Table 1 summarizes the physical properties of several phenolic compounds. Figure 1 presents phenolic structures for several compounds.

TABLE 1

PHYSICAL PROPERTIES OF SEVERAL PHENOLIC COMPOUNDS

Compound	Boiling Point, °C	Solubility in H_2O mg/l @ 25°C	$Ka \times 10^{10}$
Phenol	182	93,000	1.1
o-Chlorophenol	173	28,000	77
m-Chlorophenol	214	26,000	16
p-Chlorophenol	220	27,000	6.3
2,4-Dichlorophenol	210	4,500	Large
2,4,6-Trichlorophenol	246	900	Very Large
Pentachlorophenol	309	30(50°C)	Very Large
o-Cresol	191	25,000	0.63
m-Cresol	201	26,000	0.98
p-Cresol	202	23,000	0.67
p-Chloro-m-Cresol	196	insol.	Unknown
2,4,6-Trichloro-m-Cresol	265	sl. sol.	Unknown

Ka = thermodynamic acid dissociation constant

A review of available literature assisted the investigators in identifying treatment techiques for investigation. Investigations were divided into two phases: preliminary bench-scale treatability studies and an evaluation of batch treatment techniques.

Unlike phenol, which is quite unstable and easily oxidized either chemically or biologically, pentachlorophenol is stable and resistant to oxidation. In some instances, though, when wastewater containing pentachlorophenol in concentrations which a biomass can tolerate is run through a biological treatment system, pentachlorophenol is adsorped onto the biofloc. Disposal of the sludge, now laden with pentachlorophenol, then presents a hazardous waste problem. Alkylinization of the sludge, a relatively common practice, would more than likely release the pentachlorophenol into the environment. If the sludge were incinerated, 2,3,7,8-tetrachlorodibenzo-p-dioxin, a thermal degradation product of pentachlorophenol, could be released into the atmosphere.

PHENOLIC RESISTANCE
TO BIODEGRADATION (2)

PHENOL

O – CHLOROPHENOL

2,4 DICHLOROPHENOL

2,4,6 TRICHLOROPHENOL

PENTACHLOROPHENOL

INCREASED RESISTANCE TO BIODEGRADATION

FIGURE I

3
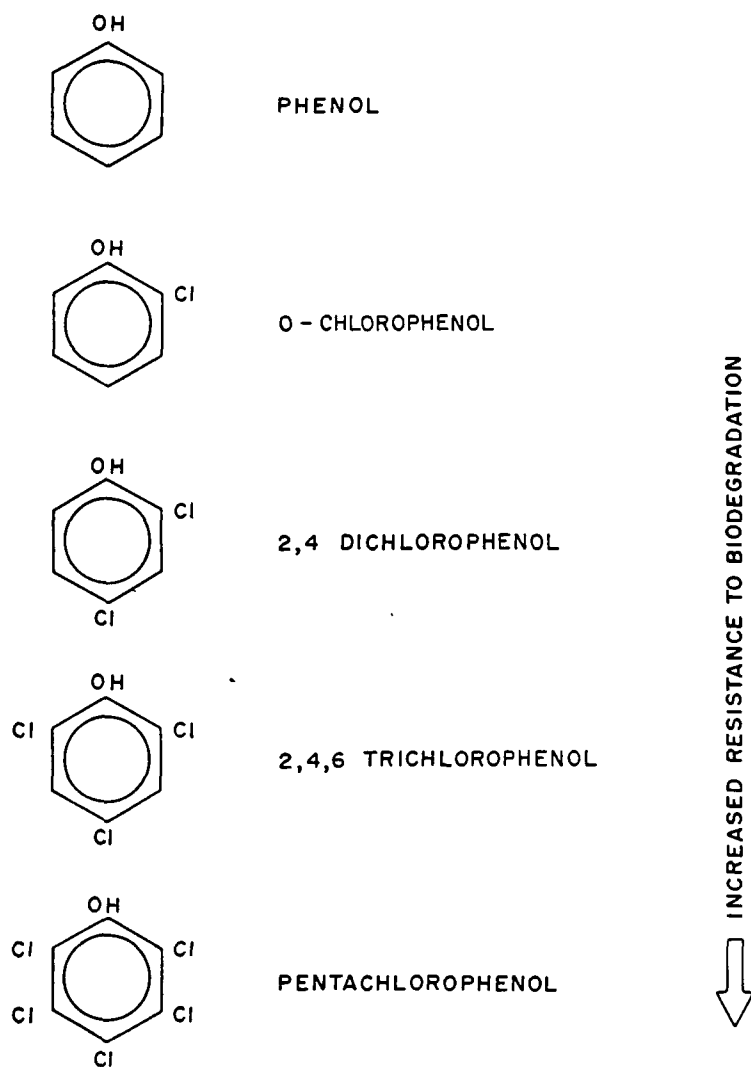
These rather ominous prospects make such treatment techniques as solvent extraction and batch polymeric resin adsorption, two schemes investigated during this study, more appealing from the standpoint of avoiding the creation of a hazardous waste problem while improving water quality.

In the preliminary bench scale studies the investigators traveled to a wood preserving facility on the west coast to evaluate treatment technologies, described in the literature, designed to lower pentachlorophenol concentrations. Treatment schemes tested included pH reduction, acid cracking, chemical coagulation, chemical oxidation, ultrafiltration, resin adsorption, and solvent extraction.

After conducting the preliminary bench scale studies, the investigators reported to representatives of the EPA. At this time, mid-course corrections were suggested. It was suggested that the program emphasis be shifted to focus on only those pretreatment systems that would both lower pentachlorophenol concentrations to levels acceptable for discharge to a POTW and be economically feasible for wood preservers.

To meet the revised criteria, pretreatment schemes had to be both efficient and economically feasible, which essentially eliminated from consideration the more elaborate treatment technologies (e.g., reductive degradation, electrochemical oxidation, ion exchange, rotary vacuum filtration with activated carbon). The effectiveness of these cannot be denied, but the cost of installing and operating any one of them makes it economically impractical for wood preservers.

Batch treatment systems were set up at the southern facility to provide some indication of which methods were cost effective. Technologies tested at the southern facility included batch biological treatment, chemical and polymeric coagulation, resin adsorption, acid cracking, bentonite clay, solvent extraction, and filtration. As at the west coast facility, a combination of these were tested. The size of the batch treatment reactors ranged from several liters to 50 gallons, depending on the pretreatment system being tested.

SECTION 2

SUMMARY AND CONCLUSIONS

Processes for the treatment of wastewaters from two wood preserving facilities were investigated at the laboratory and pilot scale levels. Included were various chemical, physical, and biological operations selected specifically for the removal of phenol and its chlorinated derivatives. Of the treatment technologies investigated, two systems consistently lowered the concentrations of pentachlorophenol in the wastewater from 100 mg/l to less than 1 mg/l.

In the first system, the wastewater was first acidified to a pH of 4.0 ± 0.1, then bentonite clay was added. A polymeric adsorbant, amberlite XAD-4 was used in the final polishing process. In the second system a mixture of No. 2 fuel oil and a cosolvent (amyl alcohol still bottoms) was used to extract pentachlorophenol from the waste stream. Reductions were consistently in excess of 99 percent. Since No. 2 fuel oil is used often in the preserving process, as it was at this facility, it is conceivable that a facility could operate this extraction process without incurring any additional chemical expense, except possibly for the cosolvent. Trials with No. 2 fuel oil alone yielded removal efficiencies in the vicinity of 97 percent, which may be high enough to allow the wastewater to be discharged to a POTW. For both systems to function consistently, the wastewater first had to be subjected to free oil separation and flow equalization. The following summarizes the findings of other investigations, based on reductions in total phenol and/or pentachlorophenol concentrations.

pH Adjustment

Lowering the pH of the wastewater with sulfuric acid was found to induce the formation of colloidal material. Subsequent removal of this colloidal material resulted in slight reductions· in total phenol concentrations as measured by the modified lowry procedure described in Appendix B-1. Pentachlorophenol concentrations, however, were consistently reduced from approximately 100 mg/l to less than 20 mg/l.

Biological Oxidation

Biological oxidation was not found to be an effective treatment technique because bioadsorption rather than biotransformation was found to be the pri-

-5-

mary removal mechanism. Removal rates continued to diminish as the adsorptive capacity of the biomass was approached.

Chemical Oxidation

At high doses, chlorine yielded substantial reductions in the compounds of concern. Hydrogen peroxide, on the other hand, had little effect. The high chemical demand observed precludes the use of chemical oxidation as a viable treatment alternative.

Coagulation

Coagulation with alum, ferric chloride, and/or polymers resulted in modest pollutant reductions. These reductions were not deemed sufficient to justify coagulation as a sole treatment technology.

Applicability of Technologies

In turning now to the applicability of the programs' findings to the wood preserving industry as a whole, it should be understood that the utility of any single pretreatment option is contingent upon both the volume and chemical make-up of the waste stream. Simply put, because wood preserving processes are so variant, each facility must be evaluated in terms of its preserving process, its waste stream, and the capital available for investing in a pretreatment system. The systems devised for wood preservers in connection with this study would probably not be transferable to the leather tanning industry or to the paper industry, not because a No. 2 fuel oil - cosolvent mixture would not remove pentachlorophenol from leather tanning or paper industry effluent just as effectively as it would from wood preserving wastewater, but because neither of these industries uses No. 2 fuel oil in its production process (non-combustion) as do some members of the wood preserving industry. The advantage of the fuel oil extraction process is that the pentachlorophenol can be removed from the wastewater without creating an additional waste and without bringing large capital and operating expense to bear on the wood preserver.

SECTION 3

RECOMMENDATIONS

If results obtained during these investigations are to be verified, a continuously flowing pilot-scale system must be established. Because this study was done on a quick response basis with limited financial resources, researchers could not investigate all aspects of each pretreatment scheme (e.g., residual catalyst after pentachlorophenol removal, toxicity of removal concentrations, utility or necessity of catalysts other than amyl alcohol still bottoms). Instead, the project provided an overview of the many economically achievable approaches to removing pentachlorophenol from wastewater and identified two systems especially successful in lowering pentachlorophenol concentrations in wood preservers' wastewater to levels that would allow it to be discharged to the POTW without causing an upset.

SECTION 4

LITERATURE REVIEW

The treatment of toxic compounds is a new and rapidly developing field. A detailed literature review was prepared on the removal of phenolics from wastewaters to assess the state-of-the-art.

Applicable treatment processes identified in the literature were as follows:

1.   biological oxidation;

2.   foam fractionation;

3.   solvent extraction;

4.   chemical oxidation;

5.   carbon adsorption;

6.   gas stripping;

7.   resin adsorption/ion exchange;

8.   coagulation/precipitation;

9.   electrochemical oxidation;

10. ionizing radiation; and

11. elimination of discharge.

None of the above exhibited universal applicability, although each was useful in specific instances. A detailed review of each process can be found in Appendix A, and a number of these are summarized below.

1.   Biological oxidation has been shown capable of 99-percent phenol removal under proper conditions (pH, detention time, nutrient supplements, etc.). Although phenol bio-oxidation is a generally recognized phenomenon, the abil-

ity of micro-organisms to chemically modify certain substituted phenols is controversial.

2. Foam fractionation has considerable value as a pretreatment technology, although it is not promising as an independent treatment system due to its low efficiency for phenol removals. Its ability to limit the effects of shock loadings and remove a portion of the wastewater's toxicity allows for more stable, and efficient use of existing biological treatment systems.

3. Solvent extraction is extremely effective because the solvent used can be tailored to the removal of specific compounds. Again, greater than 99 percent phenol removal has been reported. Recovery of chemicals can offset a portion of the operating costs. Capital costs, however, can prove excessive since considerable equipment and instrumentation is required for efficient process control. Additional downstream effluent polishing may be required prior to final discharge.

4. Chemical oxidation can completely remove phenolics from wastewater. However, the required doses of oxidizing agents are generally so high that the processes cannot economically compete with other processes, except in special applications. Similarly, high capital costs for the wet air oxidation process make this process uneconomical.

5. Carbon adsorption has been demonstrated commercially to achieve greater than 99-percent phenol removal. Reasonable service life, however, requires some form of wastewater pretreatment. System operation is also complex. The economical use of carbon necessitates regeneration of spent material, accomplished either onsite or through a contract regeneration service. A second use of carbon is the direct addition of this material to an activated sludge system. Removals of BOD_5, COD and TOC improve, and the biological system's ability to react to and recover from shock loadings is increased. Carbon adsorption alone is too expensive for the treatment of pulp, paper and wood products industry wastewaters. When combined with the proper pretreatment and other processes, however, it can provide effective and economical treatment.

6. Gas stripping failed to remove phenolics in all studies reported in the literature. On the other hand, steam stripping is viable. Steam stripping is frequently used as an odor removal/chemical recovery system. When this is the case, phenol removals can occur but probably not to acceptable levels since the operating parameters would be tailored to the unit's primary function.

7. Resin adsorption can also provide greater than 99 percent phenol removal. Under certain conditions, recovery of various marketable chemicals, such as phenol, is also possible. Several full scale systems have been constructed for chemical processing plants. Again, for the treatment of wood products industry effluents, some wastewater pretreatment is necessary to protect the resin (i.e., methanol). Operation of the system may be complex and expensive, if conventional regenerating substances are used.

8. Coagulation/precipitation processes for phenolic removals were reported by the SUNY College of Environmental Science and Forestry in a report entitled "Toxicity Reduction Through Chemical and Biological Modification of Spent Pulp Bleaching Liquors" (EPA-600/2-80-039). It was reported that coagulation/precipitation processes remove the higher molecular weight phenolics efficiently. The majority of toxicity, however, was attributable to the lower molecular weight species. Appendix A contains a review of the completed phases of this study through February 1978.

The remaining technologies investigated, electro-chemical oxidation, ionizing radiation, and elimination of discharge, are all reported to be highly efficient in terms of phenol removal, provided the proper operating conditions are maintained. In most cases, however, the achievement of high removals was economically infeasible.

SECTION 5

TREATABILITY STUDIES

INTRODUCTION

The objective of the program was to determine the treatability of pheno-
lic compounds and its chlorinated derivatives in the wood products industry.
Of particular interest was pentachlorophenol. The wood preserving industry
was selected for this program because wastewater from wood preserving facili-
ties are typically low in volume but high in concentrations of chlorinated
phenolics, particularly pentachlorophenol.

Wastewater treatment studies were conducted at two wood preserving facil-
ities. Preliminary studies were undertaken at a west coast facility while
more in-depth efforts were completed at a facility located in the south.
Table 2 presents the individual treatment techniques investigated at each.

TABLE 2. INDIVIDUAL TREATMENT TECHNIQUES

Type of treatment	Facility location	
	West coast	South
A. Acid addition	X	X
B. Biological oxidation		X
C. Chemical oxidation		
1. Chlorine	X	
D. Coagulation		
1. Alum	X	X
2. Ferric chloride	X	
3. Polymer		X
E. Extraction	X	X
F. Resin adsorption		
1. Amberlite XAD-2	X	
2. Amberlite XAD-4		X
3. Bentonite clay		X

Combinations of the above individual treatment techniques were also investigated and Table 3 presents those undertaken.

TABLE 3. COMBINED TREATMENT TECHNOLOGIES

| Type of treatment | | | Facility location | |
Preliminary	Intermediate	Final	West Coast	South
Acid addition	-	Chlorine oxidation	X	
Acid addition	-	Hydrogen peroxide oxidation	X	
Acid addition	-	Alum coagulation	X	
Acid addition	-	Ferric chloride coagulation	X	
Acid addition	-	Polymer coagulation		X
Acid addition	-	Extraction	X	X
Acid addition	-	XAD-2 resin adsorption	X	
Acid addition	-	XAD-4 resin adsorption		X
Acid addition	-	Bentonite clay adsorption		X
Alum coagulation	-	Polymer coagulation		X
Alum coagulation	-	XAD-2 resin adsorption	X	
Ferric chloride coagulation		XAD-2 resin adsorption	X	
Alum coagulation	Polymer coagulation	XAD-4 resin adsorption		X
Acid addition	Polymer coagulation	XAD-4 resin adsorption		X
Acid addition	Bentonite clay adsorption	XAD-4 resin adsorption		X

Due to differing wood preserving processes and chemicals at these two facilities, wastewater characteristics varied substantially. As a result, treatment techniques applicable to the wastewaters from one facility were not necessarily transferable to the other. Therefore, results of the treatability studies for each facility are presented in the order of type of treatment investigated, as in Tables 2 and 3.

The primary pollutants of concern in these studies were phenol and the chlorinated derivatives thereof. Total phenols were measured by a modification of the Lowry procedure, and chlorinated phenols were measured by gas chromatography. Appendix B gives specific analytical procedures.

INVESTIGATIONS AT A WEST COAST FACILITY

The wood preserving facility located on the west coast uses the boultonizing process of wood preparation and both organic and inorganic chemicals to impart preserving and fire retardency properties to the wood products processed. The resultant wastewater volumes approximating 10,000 gpd, are subjected to treatment using the following processes:

o   wastewater storage/flow equalization;

o   phase (free oil) separation employing a Lamella separator;

o   chemical coagulation;

o   filtration employing paper cartridge filters;

o   ultrafiltration; and

o   hyperfiltration (reverse osmosis).

The above treatment procedure was intended to remove all organic and inorganic pollutants from the wastewater, so that the resultant water could be used as boiler feed water. The pollutants separated from the wastewater were to be burned in the facility's boiler, thereby recovering potential energy. Due to problems with membrane fouling, the latter two unit operations were not continuously operative throughout the treatability studies at this facility.

The following subsections describe the studies undertaken at this facility.

Acid Addition

Preliminary investigations indicated that alteration of the wastewater's pH through the addition of concentrated sulfuric acid directly to the wastewater with constant mixing resulted in the formation of particulate matter that could be readily removed by filtration through Whatman No. 41 paper (mean pore diameter = 0.25 microns). Table 4 presents typical results of pH adjustment to a value of 2 and subsequent filtration on both total phenol (as 2,4-dichlorophenol) and pentachlorophenol concentrations.

TABLE 4. ACID ADDITION AND FILTRATION

Sample description	Total phenol,* mg/l			Pentachlorophenol, mg/l		
	Raw	Treated	% Removal	Raw	Treated	% Removal
Raw waste	9,800	8,400	14	14	12	14
Lamella effluent	1,300	1,300	0	6	4	33
UF filtrate	2,500	2,300	8	40	16	60

*as 2,4-dichlorophenol

There was indication that pH adjustment to 2 may be excessive; additional laboratory studies have shown that the solubility of pentachlorophenol at a pH of 3.7 and at 22°C approximates 15 mg/l. With raw wastewater pentachloro-

phenol concentrations of 80 to 100 mg/l, reductions in excess of 80 percent were realized after mild acidification to pH 2 to 4, and filtration. This was presumably a solubility phenomona.

Chemical Coagulation

Coagulation studies using a Phipps and Bird jar test apparatus were conducted using a rapid mix time of one minute, a flocculation time of 10 minutes, and a settling time of one hour. The resultant supernatant samples were then filtered through Whatman No. 41 paper prior to analysis. Optimum conditions using alum as the coagulant were a pH of 6.0 and a concentration of 150 mg/l; the optimum conditions for ferric chloride were a pH of 8.0 and a concentration of 300 mg/l. Typical results on the coagulation of the Lamella separator effluent, as shown in Table 5, indicate the effectiveness of both alum and ferric chloride for the reduction of both total phenol and pentachlorophenol. Based on the limited testing it was noted that as the pentachlorophenol concentration decreased, the removal efficiency increased.

TABLE 5. TYPICAL COAGULATION STUDY RESULTS

Coagulant	Total phenol,* mg/l			Pentachlorophenol, mg/l		
	Raw	Treated	% Removal	Raw	Treated	% Removal
Alum	4,600	4,200	9	12.5	5.0	60
Alum	300	N.A.	-	20.0	10.0	50
Ferric chloride	4,600	4,250	8	12.5	3.0	76
Ferric chloride	430	N.A.	-	90.0	70.0	.22

*as 2,4-dichlorophenol
N.A. - not analyzed

Chemical Oxidation

Oxidation of the organics in the wastewater was investigated using sodium hypochlorite as the oxidant. To achieve a slight chlorine residual after 30 minutes of reaction, the applied dose, as chlorine, approximated 3,000 mg/l. Such a dose usually reduced the total phenol concentration in Lamella separator effluent samples by approximately 70 percent (from 10,700 to 3,000 mg/l), and the pentachlorophenol concentration by 99 percent (from 6.0 to less than 0.05 mg/l). The high oxidant demand of the wastewater was felt to be of sufficient magnitude to terminate further chemical oxidation studies.

Extraction

Solvent extraction experiments were undertaken using a 4:1 sample:solvent (v/v) ratio. Lamella separator effluent samples were extracted with various organic solvents by rapid shaking in a separatory funnel for 30 seconds, followed by quiescent phase separation. Table 6 presents results of these studies.

TABLE 6. EXTRACTION STUDY RESULTS

Extractant	Total phenol,* mg/l			Pentachlorophenol, mg/l		
	Raw	Treated	% Removal	Raw	Treated	% Removal
1,1,1-Trichloro-ethane	1,300	500	62	6.0	2.0	67
Isobutyl alcohol	1,300	80	94	6.0	N.A.	-
Carbon tetrachloride	1,300	800	38	6.0	N.A.	-
Kerosene	1,600	1,450	9	16.0	15.0	6
Freon 113	1,600	1,350	16	16.0	20.0	-
Ethyl acetate	1,600	250	84	16.0	6.0	63

*as 2,4-dichlorophenol
N.A. - not analyzed

Although substantial reductions in both total phenol and pentachlorophenol were realized with certain extractants, additional studies were not undertaken because of the high solubility of these solvents in water.

Resin Adsorption

Adsorption studies using Rohm and Haas Company's XAD-2 polymeric resin were undertaken on Lamella separator effluent. Resin columns with a height to diameter ratio of four were used in these studies and the wastewater was passed through the columns at a rate of 0.1 bed volumes per minute. Five bed volumes of wastewater were applied during each trial. Results were usually a reduction in total phenol concentration of 98 percent (from 4,600 to 100 mg/l), and a pentachlorophenol reduction in excess of 99 percent (from 12.5 to less than 0.05 mg/l).

The resin was reused after regeneration with isopropyl alcohol. Regeneration was at a rate of 0.3 bed volumes per minute, and a total volume of three bed volumes of isopropyl alcohol was used per regeneration.

Acid Addition/Chemical Oxidation

Chemical oxidation of the organics in Lamella separator effluent which had been subjected to pretreatment by the acid addition process was also investigated. Both sodium hypochlorite and hydrogen peroxide were investigated as oxidizing agents. Chlorine demand of the wastewater, after 30 minutes of reaction, approximated 3,000 mg/l, and hydrogen peroxide, 5,000 mg/l. Table 7 presents typical results of pH adjustment to a value of 2 and subsequent chemical oxidation.

TABLE 7. COMBINED ACID ADDITION PRETREATMENT/CHEMICAL OXIDATION RESULTS

Chemical oxidant	Total phenol,* mg/l			Pentachlorophenol, mg/l		
	Raw**	Treated	% Removal	Raw	Treated	% Removal
Sodium hypochlorite	10,700	3,000	72	6.0	6.0	0
Hydrogen peroxide	10,700	11,600	-	6.0	4.5	25

*as 2,4-dichlorophenol
**before pH adjustment

Comparison of the results presented in Table 7 with those presented for individual treatment by either acid addition or chemical oxidation indicates no benefit to combining these two methods of wastewater treatment.

Acid Addition/Coagulation

Coagulation of Lamella separator effluent that had been subjected to pretreatment by the acid addition process previously described was also investigated. Both alum and ferric chloride were employed as coagulants. Optimum alum dose approximated 150 mg/l at a pH of 6.0. For ferric chloride, the optimum dose was 300 mg/l at a pH of 8.0. Table 8 presents results of these studies.

TABLE 8. COMBINED ACID ADDITION PRETREATMENT/COAGULATION RESULTS

Coagulant	Total phenols,* mg/l			Pentachlorophenol, mg/l		
	Untreated	Treated	% Removal	Untreated	Treated	% Removal
Alum	4,700	5,400	-	12.0	3.0	75
Ferric chloride	4,700	4,300	6	12.0	5.0	58

*as 2,4-dichlorophenol

Comparison of the results presented in Table 8 with those presented in Tables 4 and 5 indicates an increase in pentachlorophenol removal when the two processes are combined.

Acid Addition/Extraction

Extraction of Lamella separator effluent which had been subjected to pretreatment by the acid addition process was also investigated. The extraction technique employed was as previously described, and results of these studies are as follows:

TABLE 9. COMBINED ACID ADDITION PRETREATMENT/EXTRACTION RESULTS

Extractant	Total phenol,* mg/l			Pentachlorophenol, mg/l		
	Untreated	Treated	% Removal	Untreated	Treated	% Removal
1,1,1-Trichloro-ethane	1,300	550	58	6.0	2.0	67
Isobutyl alcohol	1,300	100	92	6.0	N.A.	-
Carbon tetra-chloride	1,300	800	38	6.0	N.A.	-
Kerosene	1,600	1,400	13	20.0	10.0	50
Freon 113	1,600	1,400	13	20.0	12.0	40
Ethyl acetate	1,600	N.D.	>99	20.0	<1	>95

*as 2,4-dichlorophenol

Comparison of the results presented in Table 9 with those presented in Table 6 indicates supplemental removal can be realized for certain extractants if the wastewater is first subjected to acid addition treatment.

Acid Addition/Adsorption

Pretreatment of Lamella separator effluent with the acid addition process followed by treatment with XAD-2 resin was also investigated. Greater than 99 percent removal of total phenols and pentachlorophenol was realized with this combined process. Wastewater subjected to this treatment contained 4,700 mg/l total phenols and 12.0 mg/l pentachlorophenol.

Coagulation/Adsorption

XAD-2 adsorption of Lamella separator effluent pretreated by alum and ferric chloride coagulation was also investigated. Coagulation conditions were as previously reported, and Table 10 presents results of these efforts.

TABLE 10. COMBINED COAGULATION/ADSORPTION RESULTS

Coagulant	Total phenol,* mg/l			Pentachlorophenol, mg/l		
	Untreated	Treated	% Removal	Untreated	Treated	% Removal
Alum	4,200	N.D.	>99	5.0	N.D.	>99
Alum	5,400	300	94	3.0	N.D.	>99
Ferric chloride	4,300	300	93	3.0	N.D.	>99

*as 2,4-dichlorophenol
N.D. - none detected

Comparison of these results with those presented for adsorption alone or acid addition/adsorption combined treatment where removals were already greater than 99 percent indicates no supplemental removal of either total phenol or pentachlorophenol.

INVESTIGATIONS AT A SOUTHERN FACILITY

Wood preserving at the southern facility was undertaken with organic compounds, primarily pentachlorophenol. The wood is preconditioned using the steaming process whereby the wood is steamed to prepare it for preservative impregnation. Production of the preserved product results in the generation of approximately 10,000 gpd of wastewater. The wastewater is subjected to free oil removal before it is conveyed to a storage/evaporation pond. Sometimes discharge from this pond enters the POTW system.

The following subsections describe the studies undertaken at this facility.

Acid Addition

Acid addition studies similar to those conducted at the west coast facility were conducted on the wastewaters from this facility. Upon decreasing the pH of the wastewater by sulfuric acid addition, the formation of colloidal matter was noted. Filtration through Whatman No. 41 paper would not remove this material; however, the material could be removed by filtration of the acidified sample through Gelman Type AE paper. The Gelman type AE paper has a mean pore diameter of 0.45 microns, whereas the Whatman type 41 has a mean pore diameter of 0.25 microns. Results of these acid addition/ Gelman paper filtration studies are presented in Table 11.

TABLE 11. ACID ADDITION STUDY RESULTS

	pH		Pentachlorophenol, mg/l		
Trial	Initial	Final	Untreated	Treated	% Removal
1	6.0	2.0	50	4.5	91
2	6.0	2.0	128	10.0	92
3	6.0	4.0	128	7.0	95

The above data indicate a substantial reduction in pentachlorophenol through pH adjustment.

Biological Treatment

Biological treatment (batch type) studies used three 50-gal aerobic reactors which were operated on a 24-hr fill and draw basis. Wastewater containing approximately 35 mg/l pentachlorophenol was added to the bioreactors according to the following schedule:

	Volume added daily, gal		
Reactor	Wastewater	Tap water	Total
A	25	0	25
B	20	5	25
C	15	10	25

Supplemental nutrients were added, as required, to insure a trace concentration in the supernatant withdrawn from the three bioreactors each day. MLVSS in the bioreactors increased during the study from an average of 610 to 1,735 mg/l.

After a suitable period of bioacclimation, more in-depth sample analyses were performed, and Table 12 presents certain results thereof.

All bioreactors were degrading certain constituents in the wastewater, as evidenced by both COD removal and oxygen uptake rate measurements. On the other hand, the pentachlorophenol data indicate a lesser amount of removal. The predominant removal mechanism seems to be adsorption on the biofloc and not biodegradation since total pentachlorophenol levels prior to settling remained constant. This phenomenon is evidenced by the increasing effluent concentrations with respect to time; decreasing the mass of pentachlorophenol in the bioreactor feed tended only to postpone the time for saturation of the biomass, and not prevention of its occurrence.

Chemical Coagulation

A number of jar tests were undertaken using alum, ferric chloride, cationic polymers, and anionic polymers. Following settling the supernatant was filtered through Whatman No. 41 paper. These chemical coagulation studies did not lead to any measurable reduction in the pentachlorophenol content of this wastewater.

Extraction

At this facility, pentachlorophenol is dissolved in an 85:10 mixture of No. 2 fuel oil and still bottoms from the production of amyl alcohol. Batch solvent extraction studies using No. 2 fuel oil alone, and the 85:10 mixture were undertaken. Waste:extractant volumes were constant at 4:1, and the results for two sets of tests are presented in Table 13.

TABLE 12. BIOLOGICAL TREATMENT RESULTS

Reactor/ date	O$_2$Uptake (mg/l/hr)	O$_2$(mg) hr/gr/MLVSS	MLVSS* (mg/l)	COD, (mg/l) Raw	Final	Pentachlorophenol (mg/l) Raw	Final
Reactor A							
5/28	11.0	12.6	870	3,920	755	37	0.27
5/29	6.0	5.5	1,100	3,475	1,080	30	0.15
5/31	20.0	13.6	1,470	3,275	1,325	N.A.	0.71
6/2	48.0	33.6	1,430	4,055	N.A.	N.A.	18.0
6/4	33.6	18.8	1,790	N.A.	1,970	30	26.0
6/5	22.0	14.9	1,480	3,815	N.A.	35	25.0
Reactor B							
5/28	10.8	39.3	275	1,080	1,030	24	0.58
5/29	6.0	5.7	1,060	2,780	1,080	24	0.95
5/31	31.5	22.5	1,400	2,620	1,365	N.A.	0.83
6/2	27.0	18.8	1,440	3,245	N.A.	N.A.	0.46
6/4	30.0	17.2	1,740	N.A.	950	24	6.60
6/5	32.0	17.3	1,850	3,050	N.A.	28	13.0
Reactor C							
5/28	16.0	23.5	680	1,405	975	35	0.19
5/29	9.6	9.1	1,050	2,085	920	30	0.25
5/31	20.0	12.0	1,660	1,965	1,000	N.A.	0.26
6/2	22.0	13.3	1,660	2,435	N.A.	N.A.	0.60
6/4	23.0	12.0	1,910	N.A.	1,075	18	4.50
6/5	23.0	12.2	1,880	2,290	N.A.	21	8.90

N.A. - not analyzed
*Mixed liquor volatile suspended solids.

TABLE 13.   SOLVENT EXTRACTION RESULTS

Extractant	Pentachlorophenol, mg/l		
	Untreated	Treated	% Removal
No. 2 Fuel oil	45	1.2	97
85:10 mixture	45	0.3	99

The 85:10 mixture of No. 2 fuel oil and amyl alcohol still bottoms yielded a higher level of treatment than No. 2 fuel oil alone.

Adsorption

Resin adsorption studies were also undertaken using Rohm and Haas Company's XAD-4 nonionic resin, using a Phipps and Bird jar test apparatus. The XAD-4 resin was chosen for the southern facility as compared to the XAD-2 used at the west coast facility. The XAD-4 has comparable porosity and capacity, but the pore diameter is smaller. The investigators thought that there would be some selectivity towards pentachlorophenol with the XAD-4 and thus increase the capacity. Initial investigations studied the addition of the resin directly to the wastewater. No apparent reduction in pentachlorophenol concentration occurred after 1 hour of reaction time in the presence of 15 grams of resin per liter of wastewater. Subsequent studies were conducted in which the resin was added at 10 g/l and the reaction time was varied. The results of this study are presented in Table 14.

TABLE 14. XAD-4 RESIN ADSORPTION RESULTS

Run no.	Contact time (hrs)	Pentachlorophenol (mg/l)		
		Untreated	Treated	% Removal
1	24	70	1.4	98
2	24	35	1.9	95
3	23	58	2.0	97
4	96	58	9.0	84
5	20	17	12.0	29
6	44	17	5.2	69

In all cases except Run No. 5, removal of pentachlorophenol was 69 percent or greater. Regression analysis showed no significant relationship between either contact time and percent removal or input concentration and percent removal.

Adsorption of pentachlorophenol in the wastewater onto bentonite clay was also investigated. Before the pH of the wastewater was adjusted, the bentonite stayed in suspension, and therefore this method of individual treatment was not pursued.

Alum/Polymer Coagulation

Limited coagulation trials were conducted using combinations of alum and polymers, followed by solids separation. These tests were conducted at the investigators' suggestion, following discussions with chemical suppliers after the studies at a west coast mill. This type of treatment provided less removal than other techniques and, therefore subsequent investigations were discontinued.

Acid Addition/Polymer Coagulation

As was noted, the addition of acid to the raw wastewater induced the formation of colloidal material which had an associated pentachlorophenol content. Attempts to coagulate this colloidal material with an anionic polymer had limited success. A 46-percent pentachlorophenol reduction was realized, from 70 to 38 mg/l, when 4 mg/l of polymer was added to a wastewater

sample at a pH of 4.0. Only a pin floc could be developed, and the floc had a tendency to float rather than settle.

Acid Addition/Extraction

Extraction of samples subjected to acid addition pretreatment was also investigated. The methodologies and extractant materials for these studies were as previously described. Table 15 presents typical results of this combined treatment technique.

TABLE 15. ACID ADDITION/EXTRACTION RESULTS

| Extractant | pH | Pentachlorophenol, mg/l | | |
		Untreated	Treated	% Removal
No. 2 Fuel oil	4	45	0.5	99
85:10 mixture No. 2 fuel oil cosolvent	4	45	0.2	>99

Comparison of these data with those presented in Table 13 indicate only a slight increase in pentachlorophenol removal over that achieved by extraction alone.

Acid Addition/Adsorption

A limited number of trials were conducted in which acid pretreated wastewater was also subjected to XAD-4 adsorption. A pH of 4 in the pretreatment step led to a final effluent pentachlorophenol concentration ranging from 0.4 to 1.1 mg/l, independent of the concentration present in the raw wastewater.

A combination of acid pretreatment/bentonite clay adsorption also yielded positive results since the lower pH of the waste not only allowed for adsorption of the pentachlorophenol onto the clay, but also the subsequent gravity phase separation of the clay from the wastewater. Results typical of this type of treatment are presented in Table 16.

TABLE 16. ACID ADDITION/BENTONITE CLAY ADSORPTION

| Trial no. | Pentachlorophenol, mg/l | | |
	Untreated	Treated	% Removal
1	26	2.6	90
2	33	4.1	88
3	35	3.4	90
4	50	7.0	86
5	50	5.0	90
6	50	6.3	87
7	58	5.0	91

The above results were achieved at optimum conditions of a pH of 4.0 and a bentonite clay concentration of 2 g/l. At these conditions, rapid settling occurred. Reductions in pentachlorophenol concentration following solids removal averaged 85 to 90 percent in 7 trials. Acidification, bentonite clay adsorption, solids removal and subsequent adsorption on XAD-4 resin reduced pentachlorophenol levels to less than 1 mg/l in 13 trials, as reported subsequently.

Coagulation/Adsorption

XAD-4 resin adsorption was also tried in conjunction with alum and polymer coagulation, with limited success. The minimum pentachlorophenol concentration obtained with this combination of treatment techniques was 1.7 mg/l. This was deemed inadequate and further investigations in this area were discontinued.

Acid Addition/Coagulation/Adsorption

One study was completed which involved acid addition to a pH of 4.0, coagulation with 4 mg/l of an anionic polymer, and XAD-4 adsorption of the supernatant. Raw waste pentachlorophenol concentration was 70 mg/l and the final treated effluent, 1.7 mg/l. Resin dose approximated 10 g/l and reaction time, 24 hours.

Acid Addition/Bentonite Adsorption/XAD-4 Adsorption

To insure a high level of treatment, studies involving acid addition, bentonite clay adsorption, and finally XAD-4 adsorption were undertaken. The optimum conditions established were:

1. pH adjustment to 4.0 with sulfuric acid.

2. Bentonite addition at 2 g/l;

    a. 30 seconds rapid mix;

    b. 30 minutes flocculation;

    c. 60 minutes settling; and

    d. decant supernatant.

3. XAD-4 addition at 10 g/l;

    a. 24 hour mixing;

    b. 5 minutes settling; and

    c. decant supernatant.

Table 17 gives results of this three-phased treatment approach. The average effluent concentration from this process was 0.21 mg/l pentachlorophenol.

Further work on this process indicated that the XAD-4 resin dose could be reduced to about 3 g/l without substantially altering the effluent quality reported above.

XAD-4 Resin Regeneration

Spent XAD-4 resin was found to be effectively regenerated using the 85:10 mixture of No. 2 fuel oil and amyl alcohol still bottoms used at this facility for dissolving pentachlorophenol prior to its use in the wood preserving process. Regeneration was accomplished using a 1:4 regenerant to resin volumetric ratio and a reaction time of one hour. Table 18 indicates the levels of regeneration achieved.

TABLE 17. ACID ADDITION/BENTONITE ADSORPTION/XAD-4 ADSORPTION

Trial no.	Pentachlorophenol, mg/l		
	Untreated	Treated	% Removal
1	33	0.20	>99.
2	50	0.08	>99.
3	50	0.05	>99.
4	50	0.22	>99.
5	58	0.06	>99.
6	58	0.36	>99.
7	58	0.75	>98.
8	58	0.06	>99.
9	58	0.05	>99.
10	10	0.10	>99.
11	58	0.06	>99.
12	35	0.55	>98.
13	26	0.17	>99.

TABLE 18. XAD-4 RESIN REGENERATION

Trial No.	Pentachlorophenol		Regeneration Efficiency (%)
	Adsorbed, g/g	Recovered, g/g	
1	2.2	1.6	73
2	2.2	1.5	68
3	2.2	1.5	68
4	2.2	1.3	59
5	2.2	1.6	73
6	2.2	1.3	59

Of the 2.2 grams of pentachlorophenol adsorbed per gram of resin, an average of 62 percent could be recovered and reused, if desired, in the wood preserving process.

SECTION 6

SELECTION OF TREATMENT ALTERNATIVES

It must be emphasized that the characteristics of wood preserving waste-waters are extremely variable. With such variance, it is difficult to identify one specific treatment process which can be applied uniformly across the industry. Two batch treatment processes, however, evolved from this study which were capable of consistently yielding a highly treated wastewater.

To allow for optimum removal of pollutants, the wastewaters from the wood preserving processes must first be subjected to: 1) free oil separation in a Lamella-type separator; and 2) wastewater flow equalization. For the purposes of estimating capital and operating costs, wastewaters from a typical wood preserving facility were approximated and are presented in Table 19.

TABLE 19. TYPICAL WOOD PRESERVING FACILITY WASTEWATER CHARACTERISTICS

Volume	10,000 gpd
Temperature	20 to 25°C
pH	5.0 to 5.5
Pentachlorophenol	
Average	3.6 lb/day (43 mg/l)
Peak	10.7 lb/day (129 mg/l)

The following subsections describe the two recommended batch treatment processes and the associated capital and operating costs.

Proposed Process No. 1: Acid Addition/Bentonite Adsorption/XAD-4 Adsorption

Proposed batch treatment process no. 1 involves the following operations following free oil separation and wastewater flow equalization:

1. Wastewater pH adjustment to 4.0+ using sulfuric acid. The requirement approximates 0.4 gal of 66° Baume sulfuric acid per 1,000 gal of wastewater.

2. The addition of 15 to 20 lb of bentonite clay per 1,000 gal of wastewater. Maintain suspension of the clay in the wastewater for 30 minutes with mixing; then allow gravity separation to occur for 1 hour. Remove clay sludge from bottom of reactor by pumping.

3. The addition of 25 lb of XAD-4 resin to the acidic bentonite treated wastewater. Maintain resin in suspension for 12 hr with mixing; then pass wastewater-resin mixture over a sidehill screen for resin separation.

4. Neutralize the wastewater to a neutral pH value prior to discharge to a POTW for further treatment.

The resin, after sidehill separation, is approximately 50-percent water (w/w) and will require drying before regeneration. This can be accomplished by using a vibratory fluid bed-type dryer. After drying, the resin is to be regenerated using a 1:4 resin-to-regenerant ratio (v/v), the regenerant being a mixture of No. 2 fuel oil and a co-solvent such as amyl alcohol still bottoms After one hour of mixing the resin/regenerant mixture should be conveyed to the sidehill screen for resin separation. The resin is to be stored until required for reuse while the spent regenerant will be returned to the wood preserving process for either reuse or disposal. This system is graphically depicted in Figure 2.

Table 20 presents estimated construction and operating costs (September 1979) for the 10,000 gpd treatment system utilizing acid addition, bentonite adsorption, and XAD-4 resin adsorption processes. Based on an equipment life of 20 years and an interest rate of 10 percent, the equivalent uniform annual cost was calculated to be approximately $20,000.[1]

Proposed Process No. 2: Acid Addition/Extraction

Proposed batch treatment process No. 2 involves the following operations following free oil separation and wastewater flow equalization.

1. Wastewater pH adjustment to 4.0 $\pm$ 0.1 with sulfuric acid, requirements approximating 0.4 gal of 66° Baume sulfuric acid per 1,000 gal of wastewater.

COAGULATION/ADSORPTION PROCESS FLOW DIAGRAM
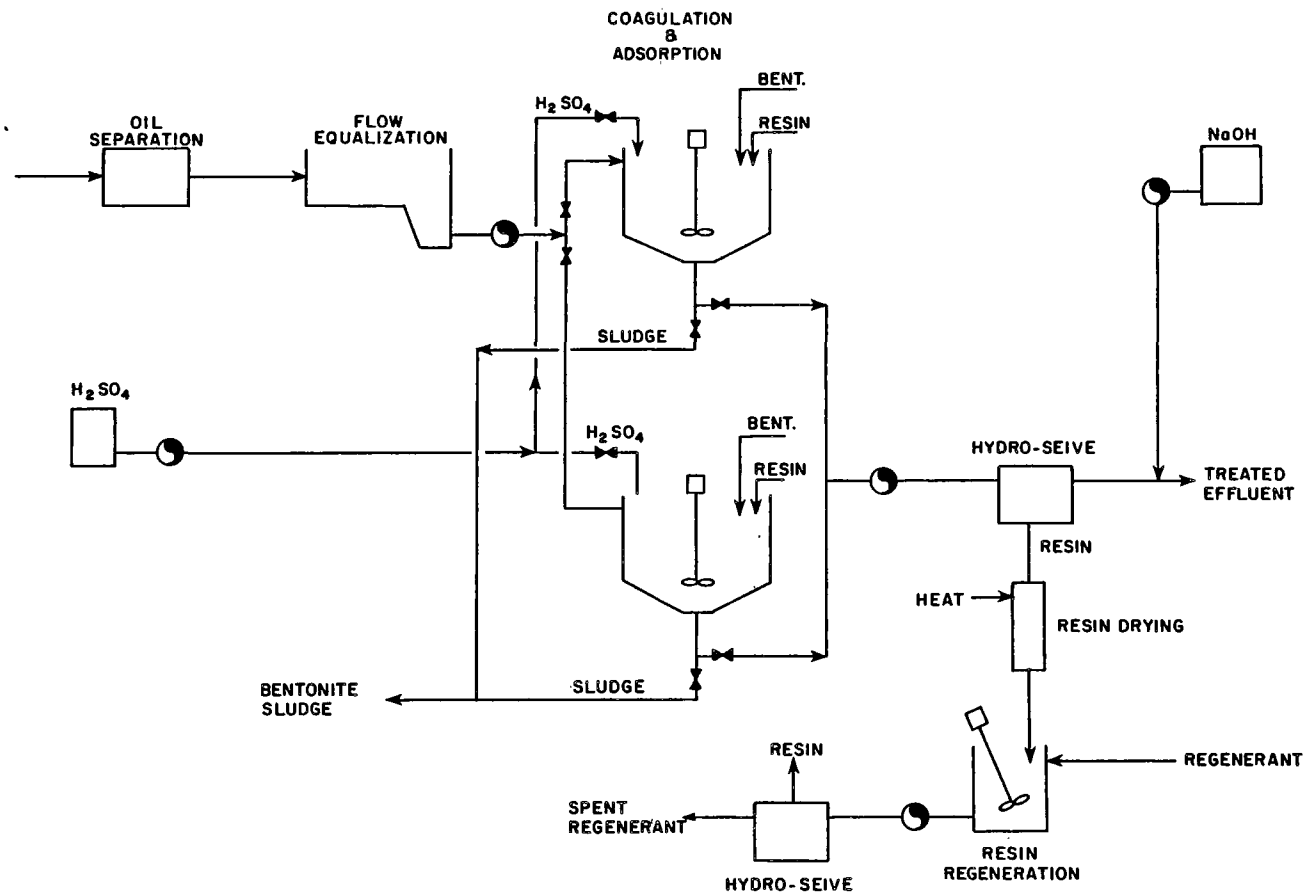
FIGURE 2

TABLE 20. PROPOSED PROCESS NO. 1 ESTIMATED COSTS

Construction costs

Site work		$ 2,000
Mechanical		81,100
Structural		43,200
Electrical		8,100
Engineering, administration, contingencies		33,600
	Total	$168,000

Annual operating expenses

Amortization		$ 20,000
Labor		14,000
Power*		800
Chemicals		5,200
	Total	$ 40,000/yr

*Power - $0.05/kWh

2. The addition of 250 gal of extractant per 1,000 gal of wastewater, a typical extractant being No. 2 fuel oil and a co-solvent such as amyl alcohol still bottoms. Mix the wastewater and the extractant for one hour; then allow phase separation to occur for about two hours.

3. Decant the spent extractant and return to the wood preserving process for either reuse or disposal.

4. Neutralize the treated wastewater to a neutral pH prior to discharge to a POTW for further treatment.

Table 21 presents estimated construction and operating costs (September 1979) for a 10,000 gpd treatment system utilizing acid addition and extraction processes. Based on an equipment life of 20 years and an interest rate of 10 percent, the equivalent uniform annual cost of this system was calculated to be approximately $24,000.[1]

TABLE 21. PROPOSED PROCESS NO. 2 ESTIMATED COSTS

Construction costs

Site work		$ 1,600
Mechanical		57,300
Structural		34,200
Electrical		8,500
Engineering, administration, & contingencies		25,400
	Total	$127,000

Annual operating expenses

Amortization		$ 15,000
Labor		5,300
Power*		300
Chemicals		3,000
	Total	$ 23,600

*Power - $0.05/kWh
**Chemical cost for fuel oil required above current use only.

SOLVENT EXTRACTION WITH OIL SEPARATION
PROCESS FLOW DIAGRAM

FIGURE 3

REFERENCES

1. National Resources Defense Council et al. versus Russell Train, United States District Court for the District of Columbia, (8 ERC 2120), June 7, 1976.

2. Ingols, R.S., et al. "Biological activity of Halophenols." Journal of Water Pollution Control Federation, 45(2):359-364, 1973.

3. Development Document for Effluent Limitations Guidelines and Standards for the Timber Products Processing Point Source Category. EPA 440/1-79/0230, U.S. Environmental Protection Agency, Washington, D.C., 1979. 427 pp.

APPENDIX A
REVIEW OF LITERATURE ON PHENOLIC TREATMENT TECHNOLOGIES

1.0 BIOLOGICAL OXIDATION

Numerous investigators have demonstrated the feasibility of biologically oxidizing phenols (1, 2, 3, 4, 5). In the laboratory, Radhakrishnan and Sinha Ray (3) found that the bacteria B. Cereus is capable of completely metabolizing phenol at a calculated detention time of 26 hours. The system parameters developed for continuous flow cultures were:

Heterogeneous metabolism rate   0.0022 mg phenol/hr/mg bacteria

True yield coefficient   81.8%

Maximum growth rate @40°C   0.628/hr

Minimum N to phenol ratio   1:10

Kirsch and Etzel (1) had similar success when biodegrading pentachlorophenate. They found that up to 68 percent of the radioactive pentachlorophenate added to an acclimated culture was recovered as radioactive carbon dioxide in 24 hours.

Kostenbader and Flecksteiner (2) have reported on the Bethlehem Steel Corporation's experience with biological oxidation of coke plant wastewaters at their Bethlehem, Pennsylvania facility. Their treatment process is shown schematically on Figure 4. The system was first put on line in September 1962, and it was learned that existing aeration capabilities limited the plant's capacity to 2,700 lb of phenol/day. As a result, they increased the aeration capacity in 1964, which in turn increased the plant's treatment capacity to greater than 4,000 lb of phenol/day. For the next 2-1/2 years, the plant

processed an average daily flow of 112,000 gallons at a phenol concentration of 1,390 mg/l (1,300 lb phenol/day). The system consistently removed 99.9 percent of the influent phenol which resulted in less than 0.1 mg/l in the effluent. It should be noted, however, that the plant was operating at approximately 35 percent of its design phenol removal capacity.

Miller (4) reported similar results when treating wastes from a cross-tie creosoting operation. The treatment scheme for this facility, as shown on Figure 5, consisted of nutrient addition, aeration, clarification, and land application. Actual plant operating data are shown in Table 22. Evaluation of this data clearly shows that 99 percent phenol reductions consistently achieved by biological treatment.

There was also one report of a system treating a combination of municipal sewage and a herbicide waste high in BOD and chlorophenols.(6) This system was unique in that a completely mixed aerated lagoon was installed between an existing conventional activated sludge treatment facility and existing stabilization ponds. The purpose of the aerated lagoon was to avoid hydraulic overloading of the conventional plant by accepting all raw wastewaters in excess of the conventional plant's design capacity and reduce the BOD to the stabilization ponds. The conclusions of this study were essentially that the organisms present in domestic sewage will remove complex phenolic compounds when sufficient biomass and nutrients are available. The phenolic removals actually achieved are shown graphically on Figures 6 through 10. It is interesting to note that the joint treatment of chlorophenolic waste and domestic sewage was reported to produce essentially the same biological data as a system treating only domestic sewage.

The chemical industry has also had experience with biological oxidation of phenols as evidenced by the work of Capestany et al(7) Wastewater from this facility was found to contain 1,000 mg/l of phenol. After reviewing past work concerning phenol removal, Capestany concluded that such wastes can be treated biologically with an acclimated, nutrient-supplemented, activated sludge system. The same conclusion was reached by Keith, (8) based on his work with two Georgia Kraft container board mills.

Capestany's initial pilot plant work found that adequate removals were obtained only when phenol feed concentrations were less than 250 mg/l. Subsequent investigations, however, revealed that sulfate deficiencies were limiting the biological oxidation process. The pilot plant was then restarted using the process parameters shown in Table 23. The effluent phenol concentration immediately dropped below 1.0 mg/l and remained there for the duration of the pilot study. As a result of this success, the full scale treatment facility shown on Figure 11 was constructed in 1975. The plant design parameters are given in Table 24. Since going on line, this facility has had great difficulty in maintaining adequate mixing as evidenced by the changing of aerator impellers, the installation of draft tubes, and the installation of a supplemental compressed air mixing system. Even so, the plant

BIOLOGICAL OXIDATION PROCESS SCHEMATIC
FOR COKE PLANT WASTES (2)

WEAK AMMONIA LIQUOR (WAL) STORAGE 1,000,000 gal

FRESHWAL

WAL

STEAM

PHOSPHORIC ACID

DILUTION WATER

BPW

BENZOL PLANT WASTE STORAGE (BPW) 1,000,000 gal

TO COKE QUENCHING

ACTIVATED SLUDGE AERATION SYSTEM 260,000 gal. 35,000 cu. ft.

OXYGEN FROM SURFACE AERATORS

WASTE SLUDGE TO SEWAGE PLANT

RECYCLE SLUDGE

CLARIFIER

40' DIAMETER

EFFLUENT TO STORM SEWER
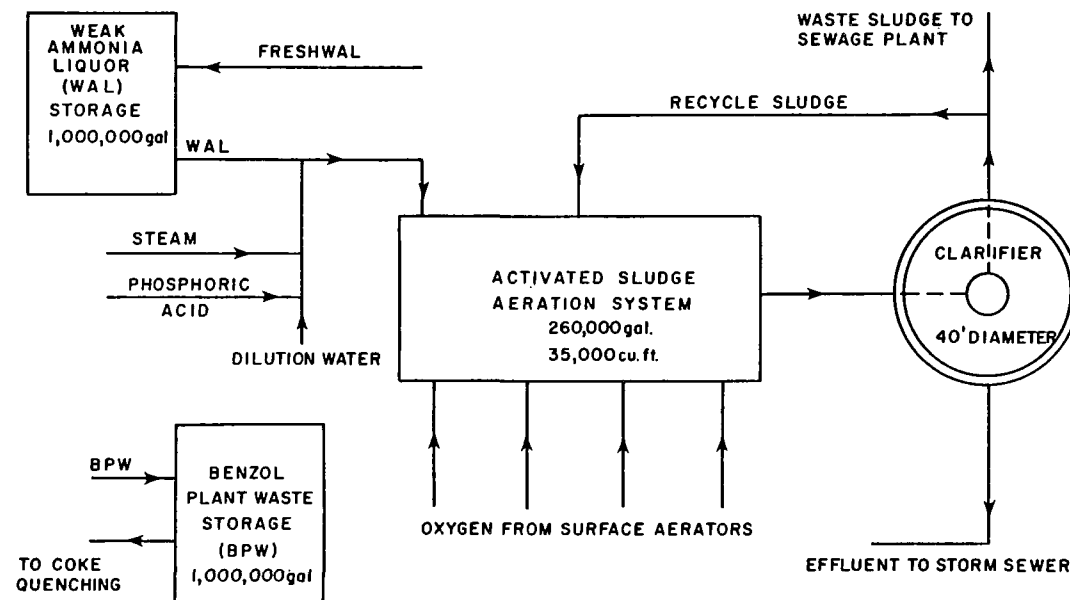
FIGURE 4

BIOLOGICAL OXIDATION PROCESS SCHEMATIC
FOR WOOD PRESERVING WASTES (4)
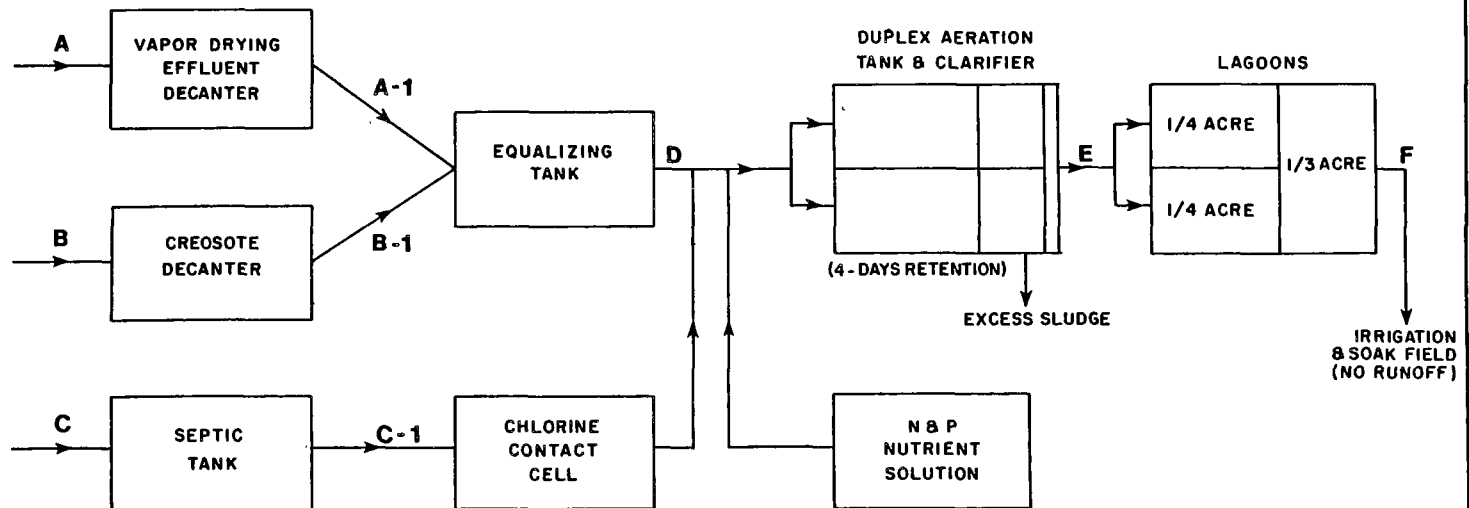
		A-1	B-1	C-1	D	E	F
FLOW		10,000 gpd	2,000 gpd	1,000 gpd	13,000 gpd	13,000 gpd	<13,000 gpd
pH		4.2	4.8	7.5	4.8	6.0	7.5
PHENOLS, ppm		160	1700	—	380	<0.2	0
COD, ppm		2500	11,000	—	3600	300	<50
TOC, ppm		1000	4500	—	1500	100	—

FIGURE 5

40

TABLE 22. OPERATING RESULTS, BIOLOGICAL TREATMENT OF WOOD
PRESERVING WASTES (4)

Date of startup	Influent		Aeration tank					Clarifiers	Lagoon	
	COD	Phenol	pH	Settleable solids	Pro-tozoa	Total organic carbon	Phenol	Phenol	COD	Phenol
3/72	2150	145	6.6	-	0	80	-	-	90	-
4/72	2900	-	7.0	-	Yes	80	0.7	0.2	65	-
5/72	-.	-	7.2	-	"	70	0.4	0.3	130	-
6/72	-	-	7.0	-	"	70	0.1	0.1	45	0.03
8/72	1850	140	7.3	-	"	55	<0.1	<0.1	-	-
2/73	1600	140	6.9	600	"	-	<.05	<.02	40	0.004
3/73	-	-	6.5	-	"	60	-	-	-	-
5/73	1100	80 .	7.0	-	"	-	-	<0.5	35	-
9/73	3200	300	7.2	900	"	-	<1.0	-	65	-
11/73	-	-	6.1	-	."	33	-	-	-	-

41

REMOVAL OF 2,4-DICHLOROPHENOL AND 2,4-DICHLORO-
PHENOXYACETIC ACID FROM SOLUTION IN AERATION
BASIN EFFLUENT BY CONTINUOUS AERATION (6)

Initial Conditions:

64 mg/l 2,4-DCP
174 mg/l 2,4-D Acid
Aeration Lagoon Effluent

pH of acid-phenol mixture
adjusted to 7.00 just before
mixing with effluent

Temperature: 20-21°C.

Constant slow stream of air
bubbled through mixture.

Control samples same as above
without Aeration Lagoon
Effluent. Only distilled
water as solvent.

2,4-D Acid Concentration

2,4-DCP Concentration

Distilled Water Control

Time In Days

FIGURE 6

REMOVAL OF 2,6-DICHLOROPHENOL AND 2,6-DICHLORO-PHENOXYACETIC ACID FROM SOLUTION IN AERATION BASIN EFFLUENT BY CONTINUOUS AERATION (6)

Initial Conditions:

64 mg/l 2,6-DCP

178 mg/l 2,6-D Acid

Aeration Lagoon Effluent

pH of acid-phenol mixture adjusted to 7.00 just before mixing with effluent.

2,6-D Acid Concentration

Temperature: 20-21°C.

Constant stream of air bubbled through mixture.

Control samples same as above without Aeration Lagoon Effluent. Only distilled water as solvent.

Distilled Water Control

2,6-DCP Concentration

Time in Days

FIGURE 7

REMOVAL OF 2,4,5-TRICHLOROPHENOL AND 2,4,5-TRI-
CHLOROPHENOXYACETIC ACID FROM SOLUTION IN
AERATION BASIN EFFLUENT BY CONTINUOUS
AERATION (6)

Initial Conditions:

50 mg/l 2,4,5-T Acid
18.8 mg/l 2,4,5-TCP

Aeration Basin Effluent

pH of acid-phenol mixture adjusted to
7.00 just before mixing with effluent.

Temperature: 20-21°C.

Constant slow stream of air bubbled
through mixture.

Control samples same as above without
Aeration Basin Effluent. Only
distilled water as solvent.

FIGURE 8

44
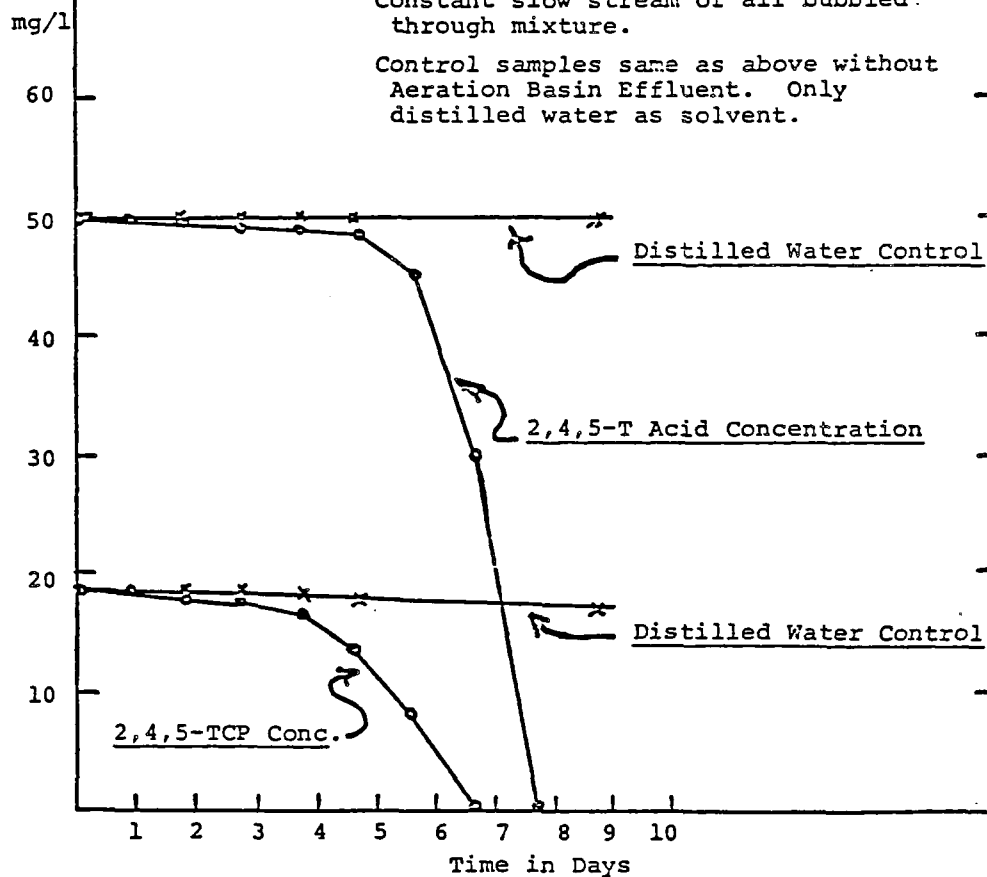
REMOVAL OF 2,4,6-TRICHLOROPHENOL AND
2,4,6-TRICHLOROPHENOXYACETIC ACID FROM SOLUTION IN
AERATION BASIN EFFLUENT BY CONTINUOUS AERATION (6)

Initial Conditions:

18.5 mg/l 2,4,6-TCP

53.0 mg/l 2,4,6-T Acid

Aeration Lagoon Effluent

pH of acid-phenol mixture
adjusted to 7.00 just before
mixing with effluent.

Temperature: 20-21°C.

Constant slow stream of air
bubbled through mixture.

Control samples same as above
without Aeration Lagoon
Effluent. Only distilled
water as solvent.

mg/l

70

60

2,4,6-T Acid Concentration

50

40

30

Distilled Water Control

20

10

2,4,6-TCP Concentration

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

Time in Days

FIGURE 9

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CHANGE IN PENTACHLOROPHENOL CONCENTRATION IN
AERATED SOLUTIONS IN AERATION LAGOON EFFLUENT (6)
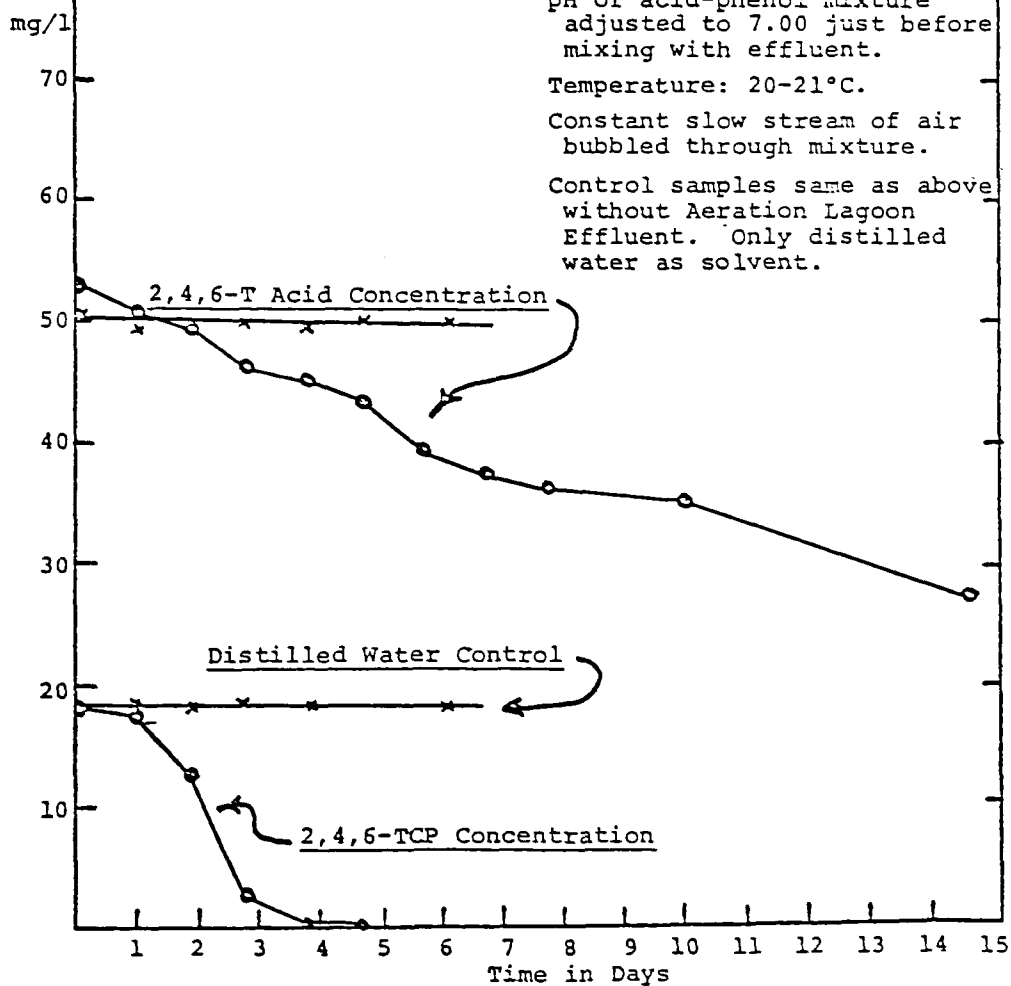
FIGURE 10

consistently removed 99 percent of the influent phenol and 97 percent of the influent BOD.

Halladay et al (9) extensively investigated the phenolic conversion capabilities of 3 types of bioreactors:

1. continuously stirred (CSTBR);

2. packed bed (PBBR); and

3. fluidized bed (FBBR).

The results of these investigations are given in Table 25. Evaluating these results led to the following conclusions:

A. The CSTBR can treat the highest influent feed concentrations, is relatively easy to operate, and the retention time may be varied. It does, however, require the largest volume, is susceptible to shocks and washouts, and is slow to recover from upsets.

B. The PBBR has higher degradation rates and lower retention times than the CSTBR, and recovers quickly from shock loads. It does, however, develop excess biomass which tends to stop flow when the biomass sloughs.

C. The FBBR has degradation rates and retention times similar to the PBBR and has low pressure drop characteristics. The FBBR does, however, yield poor results with compounds requiring long retention times. Solid-liquid disengagement is also difficult.

It should be noted that the lowest effluent phenol concentrations were obtained with the FBBR type bioreactor.

Rotating biological contactors (RBC's) serve as yet another alternative for the biological treatment of pulp and paper mill wastes. Egh and Mueller (10) reported on a laboratory study whereby bleached kraft mill effluents were tested at retention times varying between 2 and 16 hours. BOD_5 removals in all cases exceeded 90 percent. In addition, all acute toxicity to fish was removed at retention times as short as two hours.

Ingols et al(11), in their work with halaphenols, demonstrated that as phenol becomes more substituted, there is an increased resistance to biodegradation. Figure 12 (7) diagrams how this resistance increases with both the level of substitution and position of the chlorine atom. His results, however, showed that in the absence of other organic sources low concentrations of the simpler compounds can be degraded biologically in one to ten days.

TABLE 23. BIOLOGICAL PILOT PLANT PROCESS PARAMETERS (7)

Raw waste characteristics

Phenol	1,000 mg/l
BOD	4,000 mg/l
COD	6,000 mg/l
pH	8.5

Nutrient ratios

BOD:N:SO$_4$	100:5:5

Process parameters

Retention time	24 hr
Volumetric loading	3.92 Kg BOD/m^3
MLSS	6,050 mg/l
SVI	160
Sludge loading	0.6 g BOD/day/g MLSS
Sludge production	0.3 g MLSS/day/g BOD removed

SCHEMATIC OF FULL SCALE BIOLOGICAL
TREATMENT FACILITY OF CAPESTANY (7)

WASTE

pH

200,000 gal.

300,000 gal.

pH

PUMP

NH₃

AERATOR 94,000 gal.

CLARIFIER

TO COLUMBIA RIVER

RAS

DIGESTOR 206,000 gal.

CONTROL BUILDING

TO DRYING BEDS
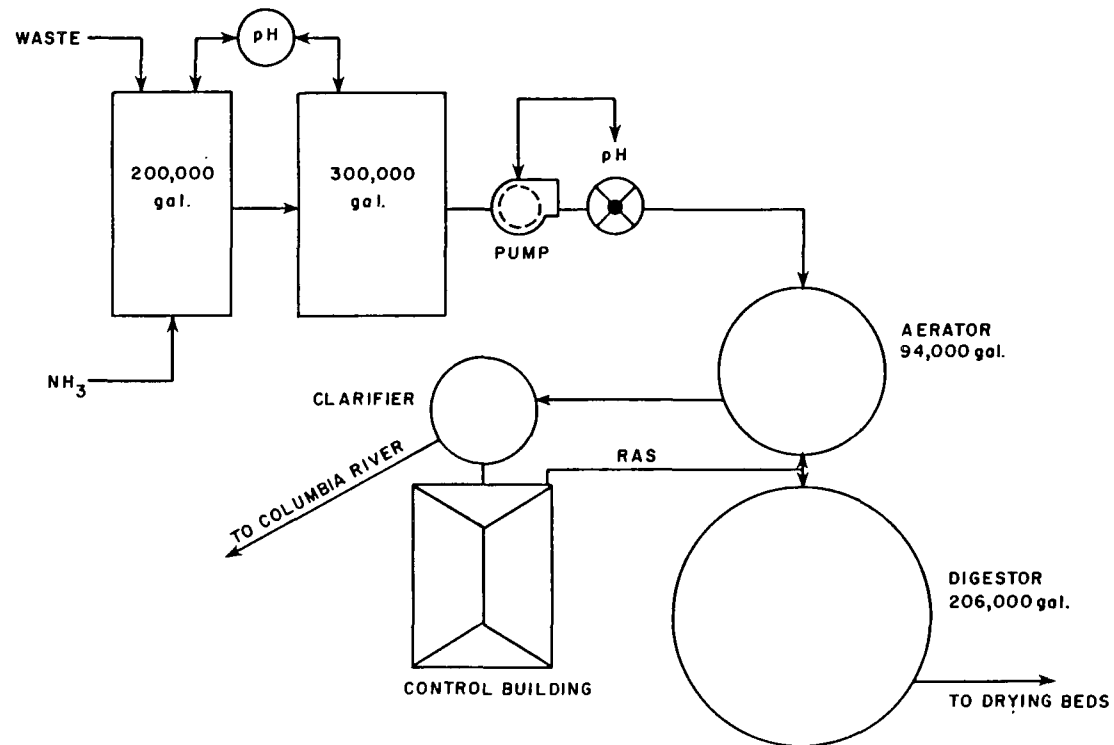
FIGURE II

TABLE 24. FULL SCALE (BIOLOGICAL) TREATMENT FACILITY DESIGN PARAMETERS (7)

General

Flow	72,000	gpd	272,521 l/day
Influent BOD	3,109	lb/day	1,410 kg/day
Influent phenol	1,943	lb/day	881 kg/day

Aeration basin

Volume	93,000	gal	352,006 l
Detention time	31	hr	
Oxygen requirements (@5°C & 2 mg/l residual)	136	lb/hr	61.7 kg/hr
Energy requirements	42/75	hp	31.3/55.9 kW

Clarifier

Overflow rate	360	gal/ft^2	14,656 l/m^2
Solids loading	16	lb/ft^2	78 kg/m^2

Digester

Volume	200,000	gal	757,000 l
Sludge age	20	days	
Energy requirements	15	hp	11.2 kW

Conditions	CSTBR	PBBR	FBBR
Maximum phenol degradation rate for C_i = 500 mg/liter, 0.99 conversion	1.0g of phenol/day/l bioreactor volume	4.7g of phenol/day/l bioreactor volume	8.5g of phenol/day/l bioreactor volume
Maximum phenol degradation rate 0.99 conversion of any feed	2.67g/l d C_i = 1,400 mg/l Q_L^i = 300 ml/h	4.7 g/l d C_i = 500 mg/l Q_L^i = 875 ml/h	11.2 g/l d C_i = 260 mg/l Q_L^i = 18,000 ml/h
Maximum phenol degradation rate any conversion	2.67 g/l d C_i = 1,400 mg/l Q_L^i = 300 ml/h	6.0 g/l d C_i = 800 mg/l Q_L^i = 700 ml/h	21.2 g/l d C_i = 240 mg/l Q_L^i = 42,000 ml/h
Normal effluent phenol concentration at maximum conversion	0.25-1.00 mg/l	0.25-1.00 mg/l	0.01-0.50 mg/l
TOC reduction for 0.99 conversion	0.90	0.90	0.95
Retention time necessary for sizeable thiocyanate conversion	20 h	NDa	ND
Highest C_i successfully degraded	1,400 mg/l	850 mg/l	2200 mg/l
Resistance to step hydraulic shocks	Poor	Good	Fair
Recovery from step hydraulic shocks	Slow 1-5 days	Fast 24 h	Fastest 24 h
Resistance to step organic carbon shocks	Poor	Good	Good

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TABLE 25 (cont'd)

Conditions	CSTBR	PBBR	FBBR
Recovery from step carbon shocks	Slow 1-5 days	Fast 24-48 h	Fastest 24 h
Facility for aeration	Good	Fair	Good
Compatibility with degassing	Good	Fair	Good

[a]Not determined

C_i = Feed concentration in mg/l

Q_L = Liquid feed rate in ml/h

Preliminary investigations by Ashmore et al (12) also suggested that certain dihydric phenols are resistant to bio-oxidation. This conclusion, however, was based on intermittent phenol additions. When a study of continuous treatment under steady state conditions was made, "none of the phenols investigated showed undue resistance to attack." Table 26 shows the results of this study. It will be noted that the degree of purification of both monohydric and dihydric phenols was normally greater than 95 percent. Another interesting finding was that high phenol concentrations cause filamentous sludge bulking. Ammonium chloride was found to suppress the filamentous growth.

PHENOLIC RESISTANCE
TO BIODEGRADATION (II)

PHENOL

O - CHLOROPHENOL

2,4 DICHLOROPHENOL

2,4,6 TRICHLOROPHENOL

PENTACHLOROPHENOL

INCREASED RESISTANCE TO BIODEGRADATION

FIGURE 12

54
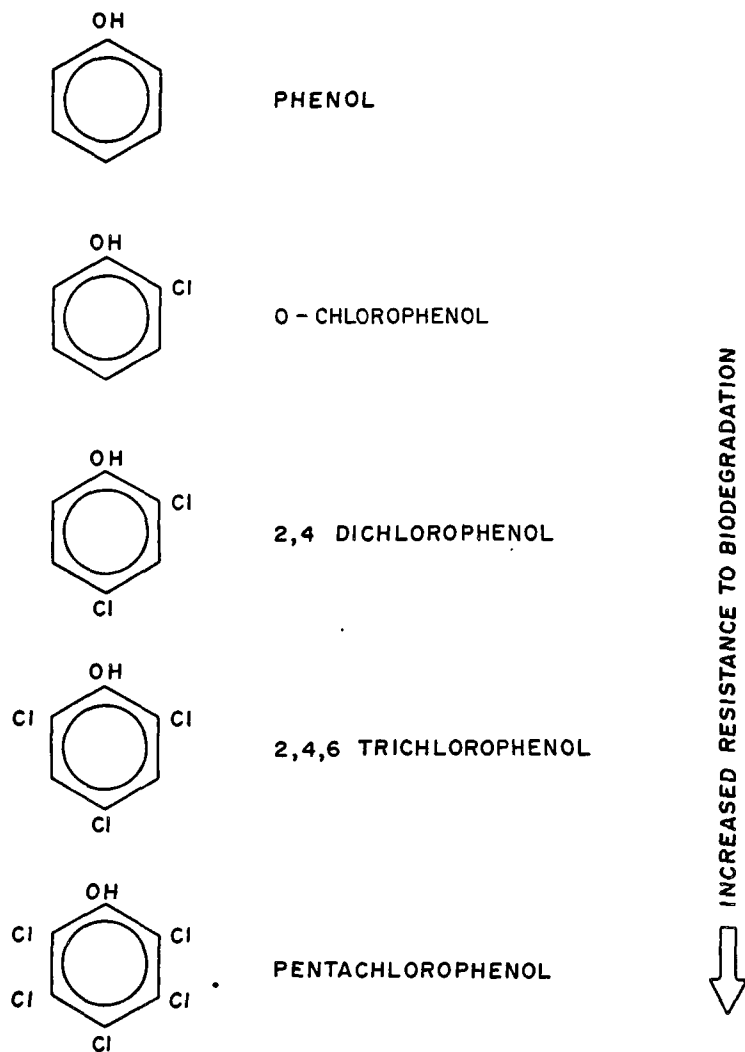
TABLE 26. THE BIOCHEMICAL OXIDATION OF PURE PHENOLS
BY THE ACTIVATED SLUDGE PROCESS (12)

| Compounds used | Amounts in influent(mg/l) | Permanganate value (mg/l) | | |
		Influent	Effluent mean	Percent purification
Phenol	1,680	1,340	17	99.4
O-Cresol	1,120	1,625	10	99.4
m-Cresol	1,120	1,580	8.4	99.5
p-Cresol	1,120	1,535	6.9	99.5
Equal parts of three cresols	1,120	1,580	9.5	99.4
Catechol	1,400	1,875	21.7	98.8
4 Me-catechol	1,400	1,570	55.4	96.5
3 Me-catechol	840	950	120	87.4
Resorcinol	1,400	2,325	18.4	99.2
Synthetic spent liquor - kept in neutral solution				
Phenol	56.0	105		
O-Cresol	4.2	6.1		
m-Cresol	4.2	5.9		
Catechol	231.0	310		
3 Me-catchol	94.8	107		
4 Me-catechol	78.8	88.3		
Resorcinol	179.2	298		
4 Me-resorcinol	16.1	20.6		
5 Me-resorcinol	16.1	19.6		
Quinol	19.6	30.8		
Total	700.0	990	9.4	99.1
Synthetic spent liquor - kept in alkaline solution				
As above	700.0	990	34.2	96.5

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2.0 FOAM FRACTIONATION

Foaming is generally considered a nuisance by the pulp and paper industry. There is benefit, however, in that foam formation tends to concentrate some of the pollutants of interest at the gas/liquid interface. Leach et al reported that this process normally removes only one source of pollution, e.g., suspended solids, color, etc. Therefore, foam separation must be used in conjunction with other unit processes to effect complete treatment.(1) It has also been reported that foam separation, though readily applied to bleached kraft whole mill effluent, is ineffective on newsprint and groundwood mill effluents.(2)

Removal of pollutants in the foam fraction of effluents has been studied for several years.(3, 4) The process requires a large gas-liquid interface area (30 to 50 m^2/l) which may be met by conventional aeration systems such as turbines, jet aerators, and/or porous diffusers. Foam removal also improves the operating efficiency and stability of standard biological treatment systems by reducing toxicity and shock loadings.

Mueller et al (3) noted an increase from between 60 and 70 percent to over 95 percent removal of toxicity on an activated sludge pilot plant with upstream foam separation. The removed foam (generally 2 to 3 percent of the influent volume) was subsequently treated by biological oxidation employing at least three days aeration time. Rubin et al(5) noted 10 to 45 percent reduction (11 to 53 mg/l) in effluent COD values following foam separation, indicating that organic compounds other than the ABS (alkyl benzene sulfonate) under scrutiny were being removed with the foam. In addition, an increase in effluent pH suggested that weakly acidic compounds (such as the phenol group) were being removed preferentially.

More recently, Grieves et al (6) studied the removal of phenols from aqueous solutions over the pH range 10 to 12. Synthetic phenol solutions were used. Foam fractionation was reported to remove 40 percent of the phenol with stoichiometric surfactant concentrations. Removal was found to be strongly influenced by ionic strength.

Ng et al (4) stressed the pH dependency of foam fractionation. Detoxification of whole mill effluents was found to be effective only at pH values greater than 7. Temperature did not appear to have a great effect within the range 25° to 40°C. Efficiency of the fractionation system was found to be improved by using a two-stage system. Ng also reported that interfacial area requirements and thus foam volumes, increased with the increase in toxic compound concentration.

Operating costs for a foam separation facility were estimated at about $1.78 to $2.71/ton at a 25 mgd effluent flow rate, including a biological facility for treatment of the collapsed foam. Capital costs were estimated at $1.0 to $1.7 million (1976). Ranges of costs represent differing foam gener-

ation and collapse methods as shown in Table 27. Ng concluded that if sus-
pended solids removal is not required, use of a turbine system was the process
of choice. The capability to remove solids is part of dissolved air flota-
tion.

TABLE 27. CAPITAL AND OPERATING COSTS FOR VARIOUS FOAM
SEPARATION SYSTEMS (1976) (4)

Foam separation system	Capital ($)	Operating	
		$/1,000 gal.	$/ton
Porous media	1,201,346	6.29	2.10
Turbine aeration	1,012,546	5.34	1.78
Dissolved air flotation	1,664,646	8.13	2.71

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3.0 SOLVENT EXTRACTION

Phenol removal by solvent extraction has been used extensively for the treatment of refinery and coke by-product wastes.(1, 2, 3) Mulligan (2) reported of an extraction process developed by the Jones and Laughlin Corporation which was capable of 99.7 to 99.9 percent phenol removal when treating coke wastes. This process is shown schematically on Figure 13 and is reported to produce an effluent containing 1 to 4 mg/l phenol from an influent feed containing 1,500 mg/l. Even though significant removals are obtained, it was Mulligan's opinion that some form of polishing treatment would be required prior to direct discharge to a stream. This study also evaluated the effect of feed concentration on the cost of phenol recovery. For evaluation purposes, it was assumed that the solvent had a high distribution coefficient (low solvent to wastewater ratio) and that it was easy to strip from the aqueous raffinate. Unfortunately the study did not include capital, maintenance or labor expense, each of which significantly affects the cost of recovery. The results of this evaluation are shown in Table 28. Mulligan concluded that where solvents with a high distribution coefficient are available, phenol recovery through extraction can be economical.

TABLE 28. EFFECT OF FEED CONCENTRATION
ON SOLVENT EXTRACTION PROCESS (2)

Phenol concentration (%)	Energy consumption		Solvent losses @0.15%	
	Steam consumption lb/lb phenol	Cost $/lb phenol	Solvent losses lb/lb phenol	Cost $/lb phenol
1.0	5	$0.018	0.02	$0.004
0.1	50	0.15	0.09	0.018
0.01	500	1.50	0.90	0.18

Earhart et al (1) have done extensive work with the recovery of various organic pollutants through solvent extraction. Important process parameters are summarized below:

1. Solvent solubility should be minimal;

2. The solvent's equilibrium distribution coefficient (K_D) should be high (Table 29 contains experimental values for K_D for various solvents and solutes);

PROCESS SCHEMATIC FOR SOLVENT EXTRACTION
OF PHENOLS FROM COKE PLANT WASTEWATERS (2)
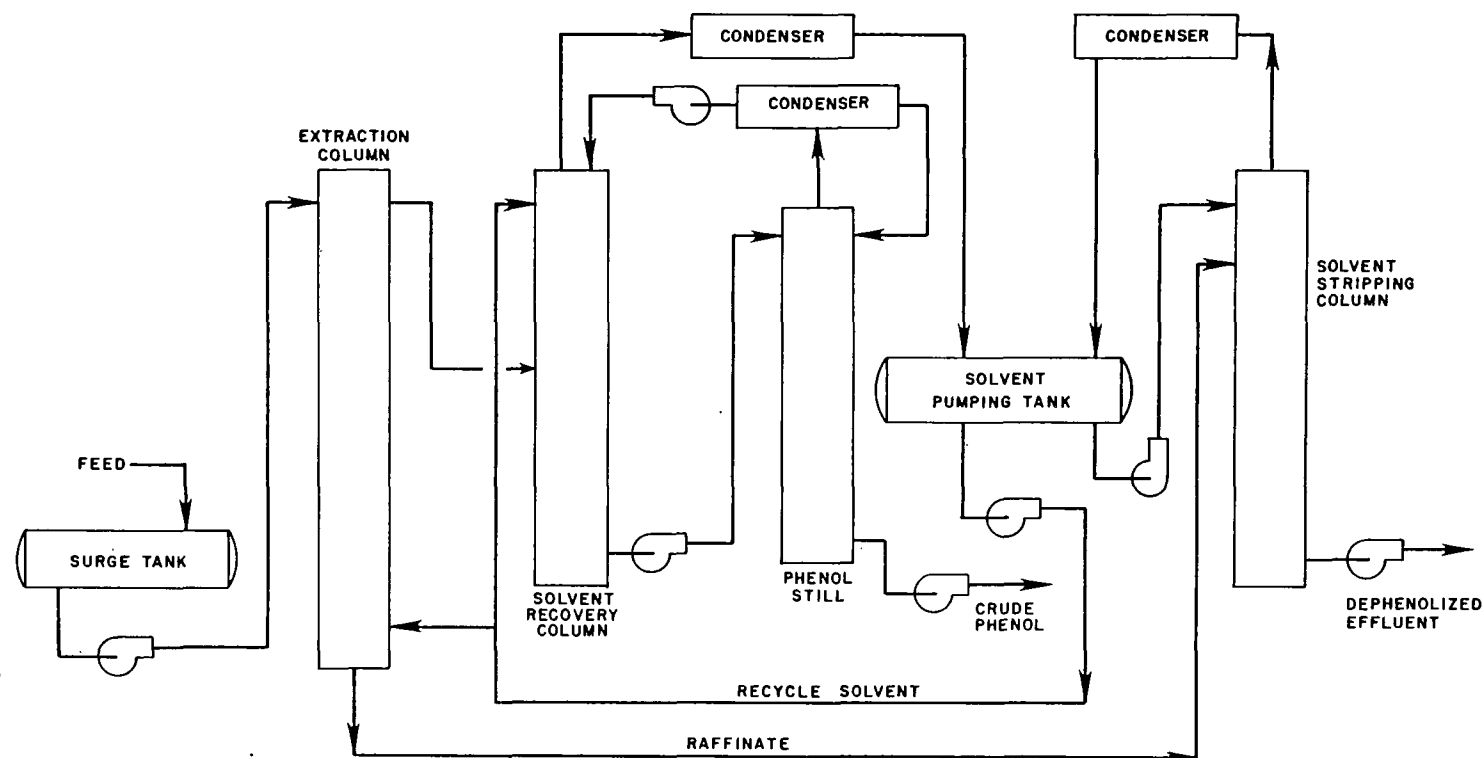
FIGURE 13

3. The ratio K_DS/W should be between 1.5 and 3.0, where

$$K_D = \frac{wt\ fraction\ of\ solute\ in\ solvent}{wt\ fraction\ of\ solute\ in\ water}$$

S = mass flow rate of solvent

W = mass flow rate of water; and

4. The solvent circulation rate should be minimized.

TABLE 29. EQUILIBRIUM DISTRIBUTION COEFFICIENTS
FOR VARIOUS SOLVENTS (20 to 25°C) (1)

Solute	Isobutane	Isobutylene	Benzene	n-Butyl Acetate	Methyl Isobutyl Ketone
Phenol	0.2	0.7	2.9	65	110
o-Cresol	--	4.8	16	--	--
M Cresol	--	2.7	10	150	260
o-Ethylphenol	--	--	63	--	--
o-Chlorophenol	--	--	--	290	490

When removing phenols, it has been determined that lower values of S/W can be used with polar solvents than with volatile hydrocarbons. Unfortunately, with polar solvents, there is considerable carryover in the effluent. These solvents do, however, have a high distribution coefficient for extraction into volatile hydrocarbon solvents. As a result, Earhart et al proposed the processes shown on Figures 14 and 15 for phenol removal. In each case, a polar solvent such as butyl acetate is used for phenol extraction and a volatile hydrocarbon such as isobutane is used to remove residual butyl acetate from the aqueous fraction. The solvents are then regenerated in two distillation columns to isolate the recovered pollutants and recycle the solvents. A mini-pilot plant was used to test this process for treating wastewater from a lube oil refining operation. Two sets of sequential extractions with n-butyl acetate and isobutylene were carried out at a water flow rate of 3.21 gal/hr. Solvent flowrates for each pair of runs were:

Run No.	n-butyl acetate	Iso-butylene
I	0.37 gal/hr	0.55 gal/hr
II	1.11 gal/hr	0.55 gal/hr

DUAL SOLVENT PROCESS SCHEMATIC -
SEPARATE CYCLES (I)

WASTE
WATER

LOADED P.S.

P.S. - POLLUTANTS
SPLITTER

POLLUTANTS

POLAR
SOLVENT
EXTRACTOR

RECYCLE P.S.

V.S. - P.S.
SPLITTER

VOLATILE
SOLVENT
EXTRACTOR

RECYCLE V.S.

V.S. VAPOR

HOLDING
TANK

PURIFIED WATER
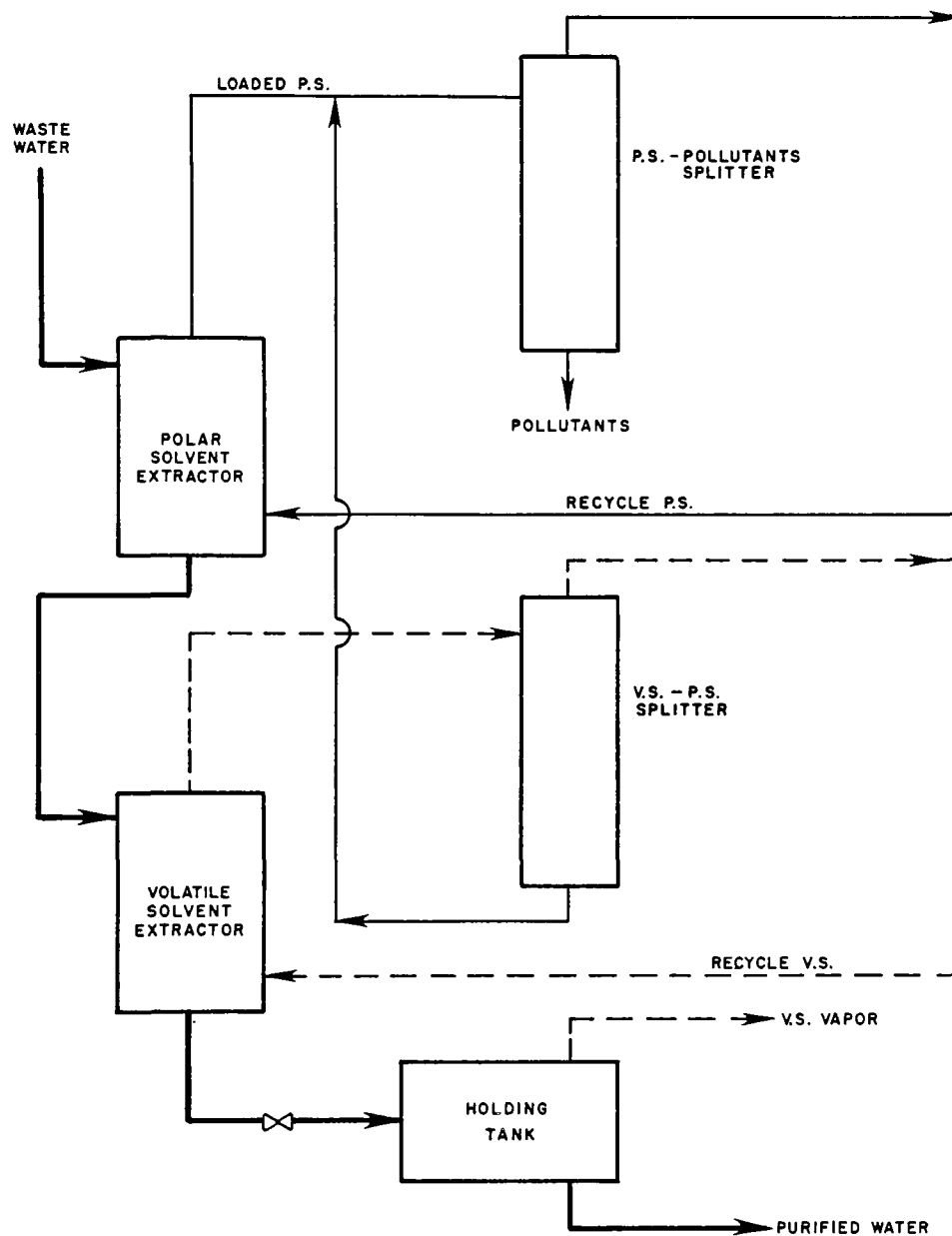
FIGURE 14

DUAL SOLVENT PROCESS SCHEMATIC-
LINKED CYCLES (I)

WASTE WATER

LOADED MIXED SOLVENT

V.S. – P.S. SPLITTER

MIXED SOLVENT EXTRACTOR

RECYCLE P.SS.

P.S. – POLLUTANTS SPLITTER

VOLATILE SOLVENT EXTRACTOR

POLLUTANTS
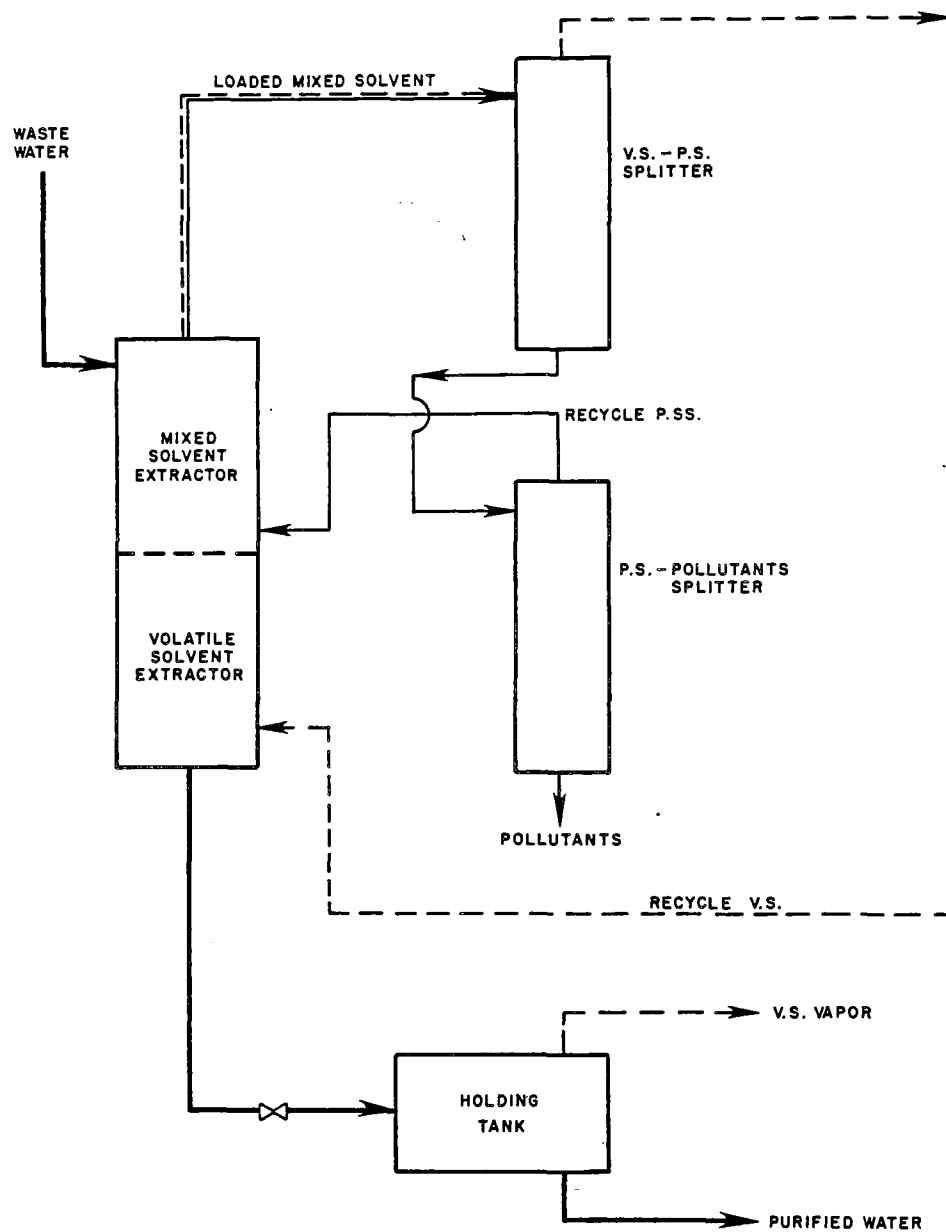
RECYCLE V.S.

V.S. VAPOR

HOLDING TANK

PURIFIED WATER

FIGURE 15

Table 30 summarizes the results of the above pilot plant studies.

Grieves et al (4) compared the relative efficiencies of solvent extraction, solvent sublation, and foam fractionation for phenol removal. Extractions with amyl acetate were found to provide 80 to 95 percent phenol removal over a pH range of 7.0 to 10.7. Removals sharply declined when the pH was above 11.0. Solvent sublation with amyl acetate over the aqueous phase in a cylindrical foam separation column was found to provide removals similar to solvent extraction. However, sublation had two distinct advantages over solvent extraction.

1. There is no equilibrium dissolution of the solvent in the aqueous phase.

2. It permits the use of a lower phase/volume ratio.

Lorton (3) evaluated the economics of three alternative methods of removing phenols from coal gasification process condensate - biological oxidation, solvent extraction, and adsorption. Of the three alternatives, solvent extraction appeared to be the most economical. The evaluation was made using a hypothetical flow rate and phenol concentration typical for gasification processes producing phenols. Manufacturers of commercial processes then developed process designs and cost estimates for use in the evaluation. The results are given in Table 31. The recommended process, as shown on Figure 16, was a product of the Chem-Pro Equipment Corporation. This system has been proven commercially at the Jones and Laughlin Steel Mill in Pittsburgh, Pennsylvania.(1, 2) Though liquid extraction was the recommended process, actual pilot plant data should be obtained for each of the above alternatives before making a firm selection.

TABLE 30. SEQUENTIAL EXTRACTION OF LUBE-OIL REFINING WASTEWATER (1)

	Butyl-acetate Extraction Concentration, ppm				Isobutylene Extraction Concentration, ppm				Overall
Component	KD	Feed	Prod.	%Removal	KD	Feed	Prod.	%Removal	% Removal
S/W for Butyl Acetate Extraction = 0.100:									
Methyl Ethyl Ketone	4.6	12,200	5,900	52	2.5	5,600	3,600	36	69
Phenol	65	8,800	104	98.8	0.7	310	230	26	99.1
o-Cresol		890	6.5	99.3	4.8	24	2.3	91	99.9
n-Butyl Acetate		0	7,100		168	7,100	11.0	99.8	
TOD		52,900					9,350		82
COD		54,500					8,570		84
S/W for Butyl Acetate Extraction = 0.30:									
Methyl Ethyl Ketone	4.6	12,200	2,500	82	2.5	2,800	1,890	33	88
Phenol	65	8,800	77	99.1	0.7	230	190	17	99.3
o-Cresol		890	4.3	99.5	4.8	18.0	2.8	84	99.9
n-Butyl Acetate		0	6,800		168	6,800	15.2	99.8	
TOD		52,900					5,110		90
COD		54,500					4,690		91

TABLE 31. ECONOMIC EVALUATION OF PHENOL REMOVAL FROM PROCESS CONDENSATE (3)

		Incremental capital requirements		
		Extraction	Adsorption	Bio-oxidation
1.	Initial plant investment	base	$9,100,000	$22,500,000
2.	Chemicals & catalysts	base	1,700,000	0
3.	Royalties	base	200,000	0
4.	Startup costs	base	200,000	600,000
5.	Working capital	base	100,000	200,000
	Subtotal	base	$11,300,000	$23,300,000
		Incremental operating costs		
6.	Utilities	base	$ 500,000	$ 900,000
7.	Chemicals & catalysts	base	300,000	600,000
8.	Labor	base	100,000	400,000
9.	Administration & overhead	base	100,000	200,000
10.	Supplies	base	100,000	200,000
11.	Taxes & insurance	base	100,000	500,000
	Subtotal	base	$1,200,000	$ 2,800,000
12.	Credit for sale of phenol byproduct	base	0	(-1,100,000)
	Total	base	$12,500,000	$27,200,000

**NOTE: Plant capacity is 250 x 10^9 Btu/day of pipeline quality gas from western coal at a 90% stream factor

CHEM-PRO SOLVENT EXTRACTION PROCESS SCHEMATIC (3)

C-1(2)-1
RECIPROCATING PLATE
EXTRACTION COLUMN

V-1(2)-1
EXTRACT
SURGE DRUM

C-1(2)-2
SOLVENT
STRIPPER

A-1(2)-1
STRIPPER
CONDENSER

V-1(2)-2
DECANTER
NOTE 3

A-1(2)-2
SOLVENT
CONDENSER

C-1(2)-3
SOLVENT
COLUMN

E-1(2,3)-1
SOLVENT
REBOILER
NOTE 4

A-1(2)-3
PHENOL
COOLER

TK-1-1
SOLVENT
STORAGE TANK

TK-1-2
PHENOL
STORAGE TANK
7 DAYS STORAGE

INERT GAS → TO FLARE

PROCESS CONDENSATE
FROM SOUR WATER
STRIPPER
NOTE 6

TO COAL
SLURRYING

FROM
TK-1-1

TO
TK-1-1

PRELIMINARY

PHENOL PRODUCT

TREATED WATER
TO
COOLING TOWER

NOTES

1 ATMOSPHERIC PRESSURE IS 13.7 PSIA
2 MATERIAL BALANCE IS FOR ONE OF TWO 50% TRAINS
  TOTAL PLANT CAPACITY IS 250×10⁹ BTU PER STREAM DAY OF PIPELINE-
  QUALITY GAS
3 THE DECANTER PROVIDES SURGE FOR THE STRIPPED SOLVENT THE NEED
  FOR A SEPARATE SOLVENT SURGE DRUM WILL BE DETERMINED DURING
  THE DETAILED DESIGN
4 FOULING IN THE SOLVENT REBOILER IS POSSIBLE PILOT PLANT DATA
  WILL PREDICT THE LIKELIHOOD OF FOULING, AND CHEM-PRO MAY
  USE AN ALTERNATE HEATING SCHEME FOR THIS STUDY A COMMON
  SPARE FOR THE REBOILERS IS PROVIDED
5 THE PROCESS CONDENSATE FEED PUMP P-1(2)-1 REPLACES THE PUMP
  SHOWN ON THE SOUR WATER STRIPPING FLOW DIAGRAM IN THE
  FACTORED ESTIMATE DESIGN THE AIR COOLER ON THAT FLOW
  DIAGRAM IS NOT REQUIRED
6 A SURGE VOLUME OF 10,000 GALLONS SHALL BE
  PROVIDED IN THE SOUR WATER STRIPPER UPSTREAM OF THIS FLOW
  DIAGRAM
7 DESIGN DATA PROVIDED BY CHEM-PRO EQUIPMENT CORP
  EQUIPMENT SIZES, DESIGN TEMPERATURES AND PRESSURES, MATERIALS
  OF CONSTRUCTION, UTILITY REQUIREMENTS, EXTRACTION COLUMN
  PRICE

P-1(2)-1A,B
PROCESS CONDENSATE
FEED PUMP

P-1(2)-2A,B
EXTRACTION COLUMN
BOTTOMS PUMP

P-1(2)-3A,B
PREGNANT
SOLUTION PUMP

P-1(2)-4A,B
STRIPPER
BOTTOMS PUMP

P-1(2)-5A,B
DECANTER
SOLVENT PUMP

P-1(2)-6A,B
SOLVENT COLUMN
BOTTOMS PUMP

P-1-7
PHENOL
SHIPPING PUMP

STREAM NUMBER		1	2	3	4	5
COMPONENT	STREAM NAME	PROCESS CONDENSATE	PROCESS CONDENSATE	PROCESS CONDENSATE	PHENOL PRODUCT	TREAT. GATE
WATER	LBS/HR	750,000	500,000	250,000		250,000
PHENOL		12,075	8,050	4,025	4,005	10
OIL & TAR		300	200	100	100	
AMMONIA		120	80	40		
SOLVENT					30	
TOTAL	LBS/HR	762,495	508,330	254,165	4,135	250,020
	GPM	1,590	1,060	530	8	540

FIGURE 16

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4.0 PHYSICAL/CHEMICAL OXIDATION

Numerous researchers have demonstrated the technical feasibility of physical/chemical oxidation of phenols. Their work has been centered primarily around use of the following oxidants:

   o   oxygen

   o   ozone

   o   chlorine

   o   chlorine dioxide

   o   hydrogen peroxide

Additionally, oxidation by ultrasonic, ultraviolet radiation, and catalytic contact treatments has been demonstrated.

Oxygen - Oxygen has been used with and without catalysts as well as in combination with ultraviolet radiation or ultrasound.(1) One such use is the wet air oxidation process in which the waste temperature is increased to the point where air (oxygen) reacts with oxidizable material autogenously. Wilhelm and Ely (2) reported a 99.99+ percent COD removal (Figure 17) when using this process. The Pulp and Paper Institute of Canada reported several additional methods of oxidizing phenols with oxygen.(1) Waste from a lacquer and varnish manufacturer was oxidized using oxygen (in air) and acid treated pyrolusite (MnO_2) as a catalyst. The results are listed in Table 32. Successive uses of the catalyst resulted in a decrease in its activity. It was, however, possible to regenerate the catalyst with a 1.5 to 2.0 percent sulfuric acid solution.

Examples of the photo-oxidation of dilute phenol solutions were also included in the Canadian report.(1) A waste containing 200 mg/l phenol was irradiated with ultraviolet light (300 to 400 nm) using 5,000 mg/l of ZnO as a catalyst. Ninety percent of the phenol was oxidized to CO_2 within 44 to 68 hours, depending on the depth of the waste stream. Even though dissolved oxygen was found to be necessary for oxidation, aeration did not significantly affect the phenol oxidation rate. When TiO_2 was substituted as the catalyst under the same conditions, a maximum 80 percent phenol reduction occurred after 72 hours irradiation. Similar results were also obtained when 300 g/l of beach sand was used as the catalyst.

Ultrasonic irradiation (ultra high frequency sound) was also found to produce significant phenol reductions.(1, 3) Wastes containing 100 mg/l phenol were reported to be completely oxidized in four hours when subjected to a field of 800 KHz at 33 watts/cm^2. When the waste concentration was increased to 500 mg/l, a 70-percent reduction was achieved in 6 hours. As

DECOMPOSITION OF PHENOL
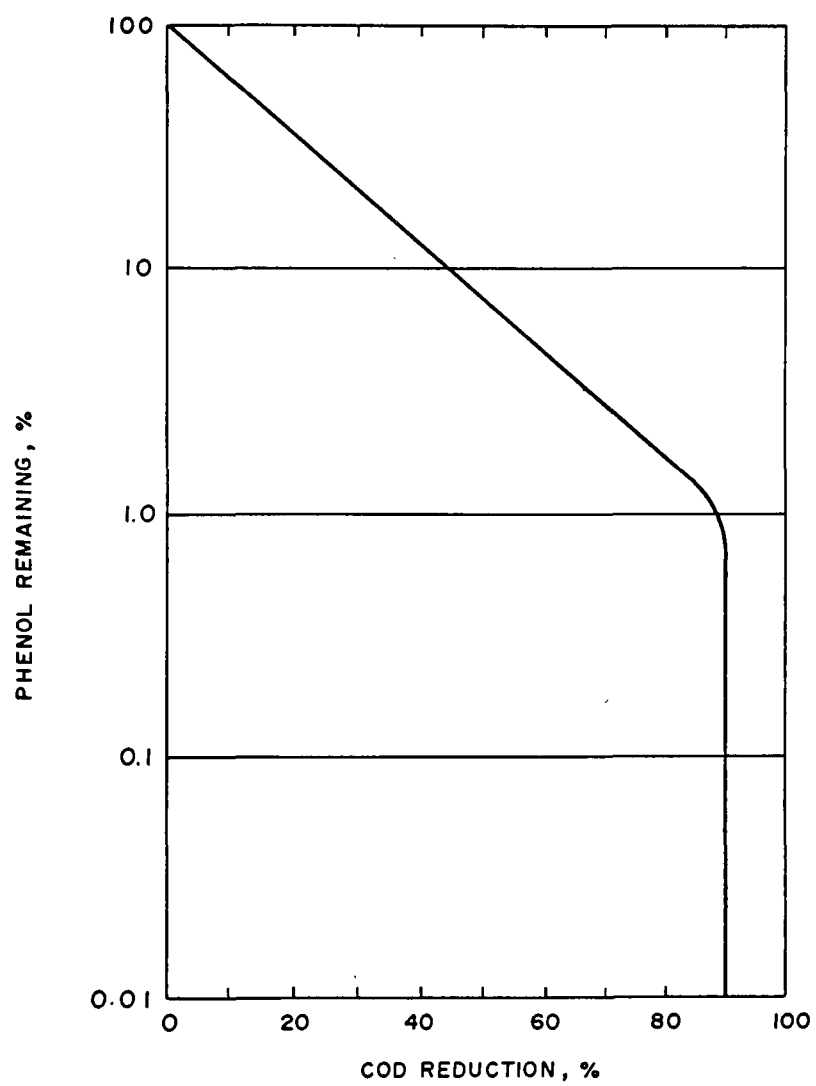# BY WET-AIR OXIDATION (2)

FIGURE 17

shown on Figure 18, phenol reduction was found to be proportional to irradiation intensity. Even though significant phenol reductions were obtained, it was pointed out that this process appears to oxidize phenols to products with a higher oxygen content and not to carbon dioxide. Consequently, this treatment may not necessarily reduce toxicity.

Ultrasonic irradiation in the presence of various catalysts was also investigated by Chen.(4) In experiments with metal oxides, platinum, rhubidium and Raney-nickel, an inhibition of sono-oxidation was noted. However, as indicated by TOC analysis, more complete oxidation occurs since approximately eight percent of the products of oxidation was carbon dioxide (CO_2).

TABLE 32. CATALYTIC OXIDATION OF LACQUER MANUFACTURING WASTEWATER (1)

Phenol concentration (raw waste)	8,000 mg/l
Formaldehyde concentration (raw waste)	1,400 mg/l
pH (raw waste)	7.0
Aeration period	2 hr
Percent removals	
Phenol	99%
Formaldehyde	87 to 95%

Ozone - Ozone has been shown to be extremely effective in the oxidation of many complex organics including phenols. Eisenhauer reported that when ozone initially reacts with phenol, catechol is formed. This compound, in turn, degrades to carboxylic acids and carbon dioxide, as shown on Figure 19.(1, 5)

However, Dence,(6) reporting on the ozonation of spent chlorination and caustic extraction liquors, stated that "in no instance does ozonation cause a substantial reduction in the toxicity . . . and under alkaline conditions, a decided increase is produced." He goes on to state that "it seems safe to assume that the phenolic components of the liquors are not responsible." Apparently, under alkaline conditions, ozone partially decomposes to hydroxyl groups and could form more toxic products.

The phenol content of coke plant effluent has been reduced from 2,000 mg/l to less than 1 mg/l with an average ozone dose of 1.7 g/g of phenol.(5) Cleary and Kinney (7) also worked with coke wastes. Their results, as shown on Figure 20, led to the following conclusions:

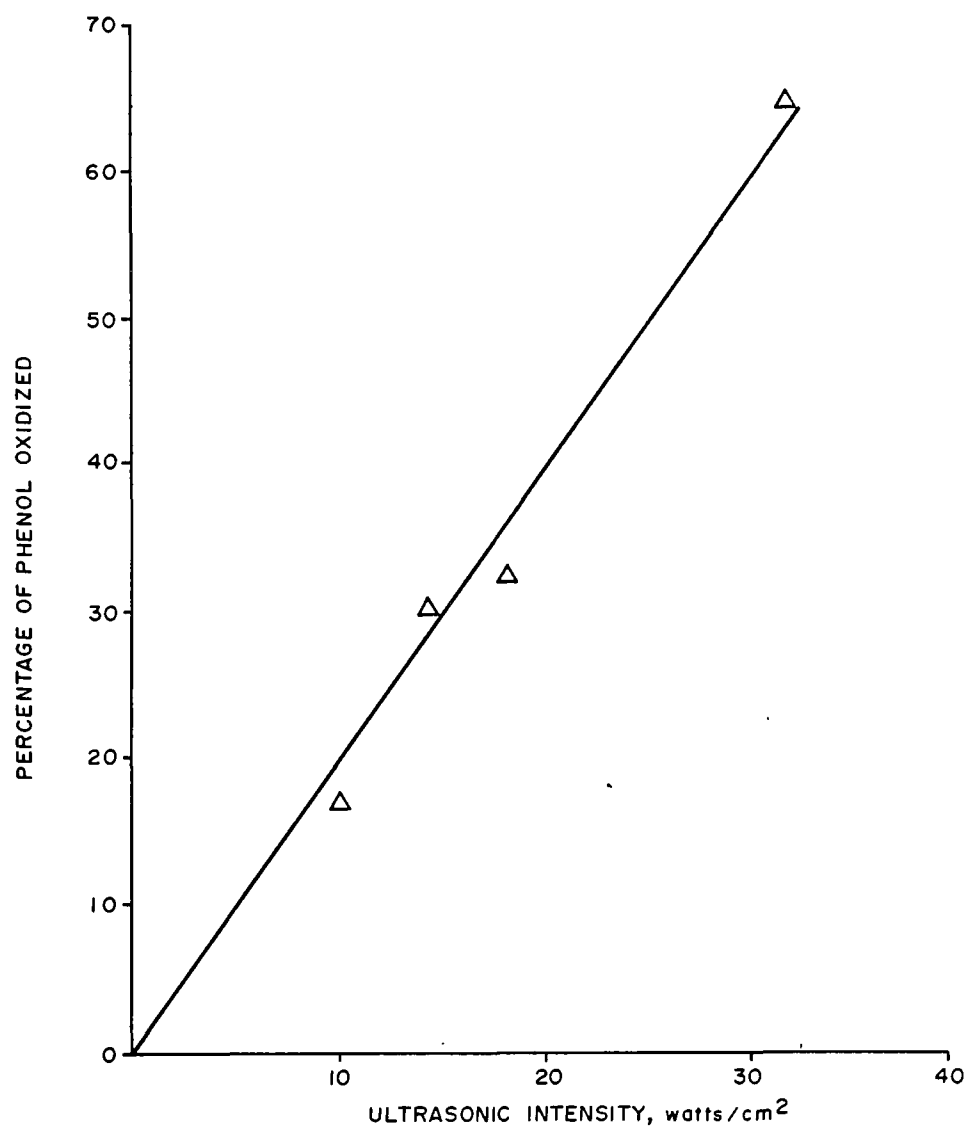PERCENTAGE OF PHENOL OXIDIZED
VS
ULTRASONIC INTENSITY (I)

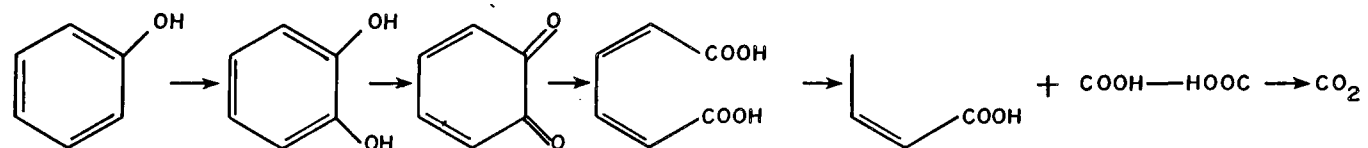FIGURE 18

OZONATION OF PHENOL (1,5)

FIGURE 19

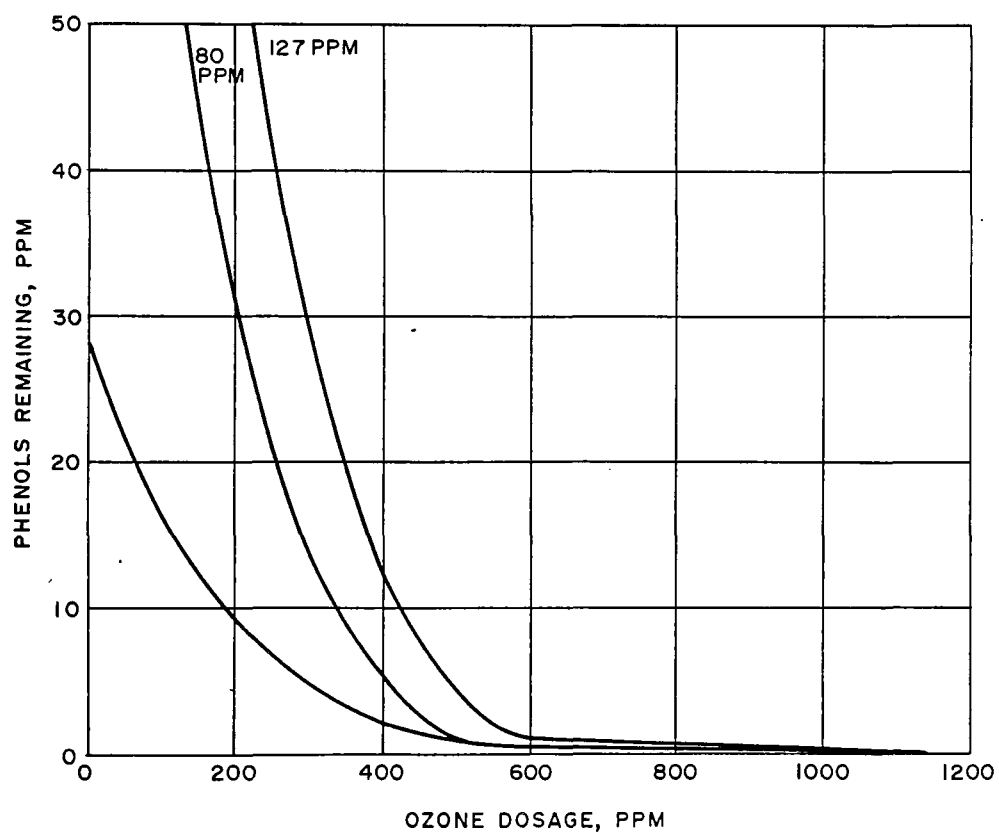OXIDATION OF PHENOL BY OZONE (7)

FIGURE 20

1. Ozone oxidation of phenol is maximized at pH 11.8.

2. The required ozone dose is independent of temperature.

3. Undertreatment with ozone does not form additional toxic compounds.

4. No pretreatment of the waste is required.

Similarly, phenols in refinery wastes have been reduced from 11,600 to 2.5 mg/l with an applied ozone dose of 2.0 g/g of phenol.(5) Gould and Weber (8) evaluated phenol oxidation with ozone and found that near-complete removal was achieved when four to six moles of ozone were consumed per mole of phenol initially present. They also determined that when a plot of COD reduction vs. ozone dosage is made, there is a sharp transition from one linear relationship to another at a much lower rate. The break point between the two functions was found to correspond to the point of near-complete phenol removal.

Little work has been done on the influence of catalysts on phenol removal with ozone. The Pulp and Paper Research Institute of Canada (1) reported that the oxidation rate is increased twofold when Raney-nickel is used as a catalyst.

Many researchers reported that the cost of ozonation is excessive. Dence (9) states that in the case of spent liquors, "other components compete . . . successfully with phenols for the ozone, requiring excessive amounts of ozone for phenol reduction." Eisenhauer(5), in reporting on the work of Peppler and Fern, stated that the cost of ozonation is four to seven times that of biological oxidation. Thompson (10) similarly disregarded ozonation as a viable treatment alternative due to high capital and operating costs. Gould and Weber (8) stated that ozonation for complete removal would be exceedingly costly and time consuming. In general, most researchers said that ozonation would only be economically feasible as a polishing step after some other treatment process.

Chlorine - Chlorine is a powerful oxidant and as such will readily oxidize phenol. Thompson (10) reported that chlorination of phenolic wastes to an excess actually breaks the benzene ring to form organic acids. There is similar evidence to show that chlorine oxidizes pentachlorophenol to chloranil. Thompson did not feel, however, that chlorination alone will adequately treat wood preserving wastes. Too many oxygen demanding substances, including residual phenolic fractions, sometimes remain in the effluent, even after massive chlorine dosages. Frequently a ratio of chlorine to pentachlorophenol of 700:1 is required for near-complete oxidation. This reduces the economic feasibility of such a treatment alternative. Thompson did feel, however, that chlorination could be used as a polishing step for biological treatment plant effluents.

Cleary and Kinney (7) investigated chlorine oxidation of coke wastes at both the laboratory and pilot plant levels.

They found that once the waste's ammonia demand is satisfied, substantial phenol reductions can be obtained with small increases in the chlorine dose. The reaction reaches a point, however, where increasingly larger doses are required for small increases in phenol destruction. The relationship between chlorine dose and phenol remaining is shown on Figure 21.

They also found that phenols can be destroyed at pH values between 1.8 and 11.0. To prevent the formation of chlorophenols and nitrogen trichloride the pH should be between 7.0 and 10.0. Temperature should also be reduced to 45°C to prevent chlorate formation. There is some indication that pH affects the amount of chlorine demand which is satisfied prior to beginning phenol destruction. It seems to be easier to oxidize phenols at a high pH when other chlorine consuming compounds are present.

Based on the above, complete destruction of phenol with chlorine is technically feasible. It does, however, require an excess of several hundred mg/l of chlorine, to accomplish complete destruction.

Oxidation by chlorination, however, may produce harmful side effects. Dence et al, (6) in current research at SUNY-Syracuse, have reported distinct increases in the toxicity of spent chlorination liquors following chlorine treatments, even though up to 70 percent phenol reduction was noted at dosages of 0.8 mgCl/ml spent liquor. Similar results occurred when hypochlorous acid was used as treatment. Phenol reduction of 82 percent was experienced at a dosage of 0.37 mg HOCl/ml spent liquor. Similarly, a sodium hypochlorite treatment at 2 mg/ml of liquor produced at 95 percent reduction in phenol concentration in nine hours at 60°C. A decided increase in toxicity was again noted in the treated samples.

Chlorine Dioxide - Chlorine dioxide is another strong oxidant which can be used for treating industrial wastewater. Unlike chlorine, however, this chemical has been reported to be selective for cyanide, phenol, sulfides, and mercaptans. It does not react with many other organics such as alcohols and organic acids.(11) Cleary and Kinney (7) have found in their work with coke plant wastewaters that pretreatment was not required. They found that the best results were obtained when a 2 to 1 mixture of chlorine to chlorine dioxide was applied together. When chlorine dioxide was used alone, a small chemical dosage was found to produce a large phenol reduction. As shown on Figure 22, additional phenol removal required increasingly higher chemical doses. Mulligan and Fox (11) reported that approximately 1.5 lb chlorine dioxide was required to convert one pound of phenol to quinone. They also reported that "because of its cost, approximately $4/lb, its use will be as a selective polishing treatment for destruction of trace amounts of specific compounds in industrial effluents."
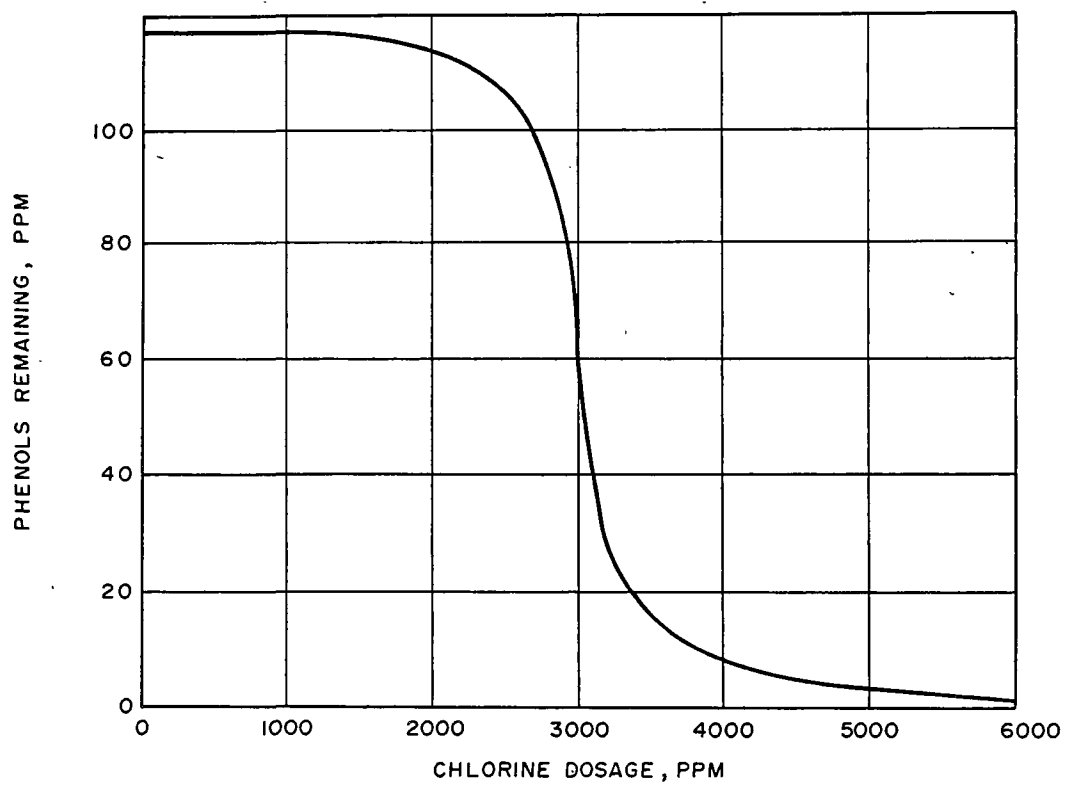
OXIDATION OF PHENOL BY CHLORINE (7)

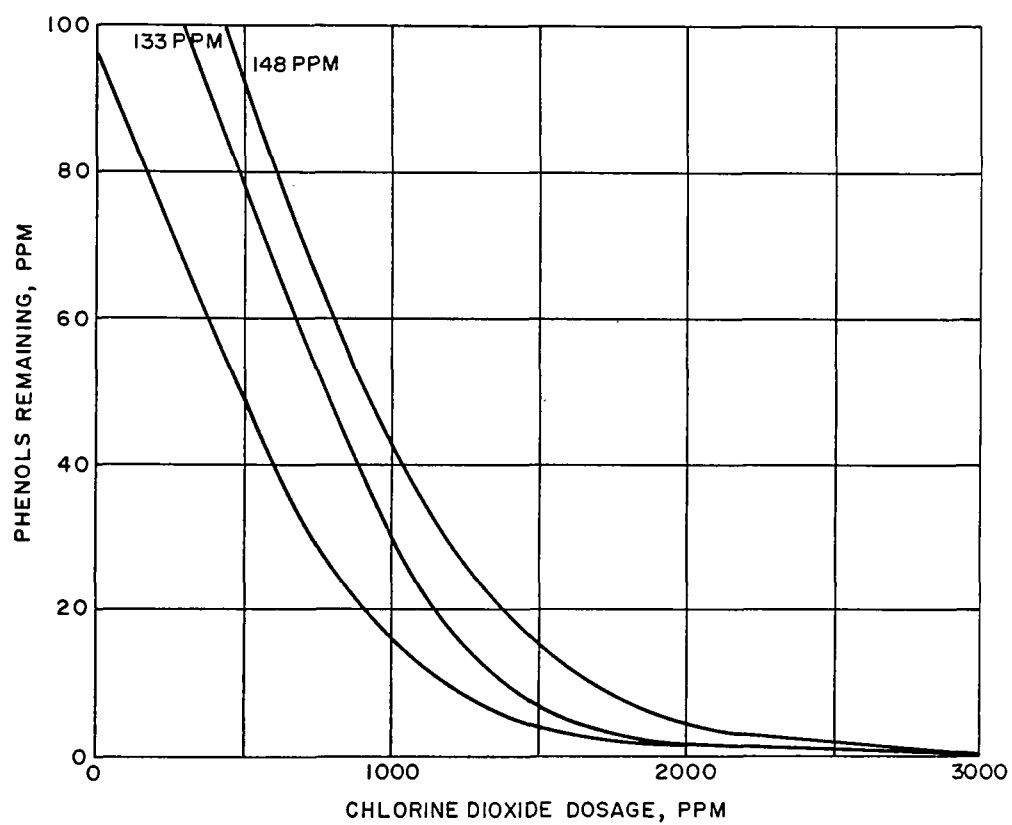FIGURE 21

OXIDATION OF PHENOL BY CHLORINE DIOXIDE   (7)

FIGURE 22

79

Chlorine dioxide, though expensive, has two major advantages over chlorine.(7) First, the ammonia content of the waste does not affect the chemical dose required for phenol destruction. This is significant because approximately 10 mg/l of chlorine is required to oxidize 1 mg/l of ammonia and that all ammonia must be oxidized prior to phenol removal with chlorine. Also, a chlorine dioxide residual is not required. Underdosing reduces phenol concentrations, but according to the colorimetric tests used by Cleary,(7) does not form chlorophenols.

Hydrogen Peroxide - The FMC Corporation, a manufacturer of hydrogen peroxide, has done extensive work with phenol oxidation.(12, 13) They have reported that in the presence of trace amounts of iron salts, hydrogen peroxide will rapidly oxidize phenol first to catechol and hydroquinone, then to dibasic acids, and ultimately to carbon dioxide and water. Eisenhauer, however, has disagreed and stated that the reaction stops with the formation of muconic acid.(14)

As part of their work with phenols, FMC has studied the effect of the H_2O_2/phenol ratio on the extent of phenol oxidation. The results of this work are shown on Figure 23.(12) Similar work also led to the development of a relationship between H_2O_2/COD and phenol reduction as is shown on Table 33 and Figure 24.(12)

TABLE 33. HYDROGEN PEROXIDE TREATMENT OF PHENOL WASTES* (12)

H_2O_2/COD wt ratio	Reduction in phenol (%)	Reduction in COD (%)
0.3	86	28
0.4	94	32
0.6	99	40
0.7	99.8	44
0.8	99.9	52
1.0	100	69

*Initial phenol concentration 2,000 mg/l

Eisenhauer (14) developed a similar relationship using Fenton's reagent; or in other words a combination of hydrogen peroxide and a ferrous salt. Table 34 shows the results of this work.

EFFECT OF INITIAL HYDROGEN PEROXIDE /
PHENOL RATIO ON THE
OXIDATION OF PURE PHENOL (12)

INITIAL PHENOL CONC =
500 Mg / Liter
70° F   5 Minutes
0.1% Fe Catalyst
Initial pH = 5.5

RESIDUAL PHENOL (Mg/ Liter)

HYDROGEN PEROXIDE / PHENOL WEIGHT RATIO
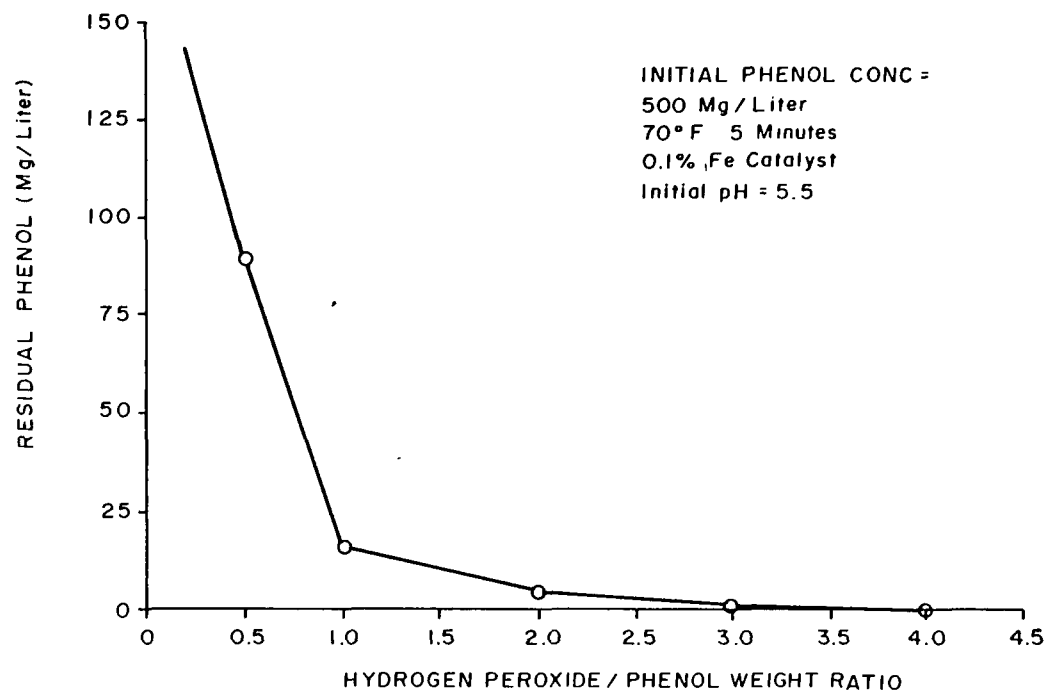
FIGURE 23

EFFECT OF HYDROGEN PEROXIDE / PHENOL RATIO ON CHEMICAL OXYGEN DEMAND REDUCTION OF .PURE PHENOL (12)

INITIAL PHENOL CONC =
500 Mg / Liter
70° F 5 Minutes
.01% Fe Catalyst
Initial pH = 5.5
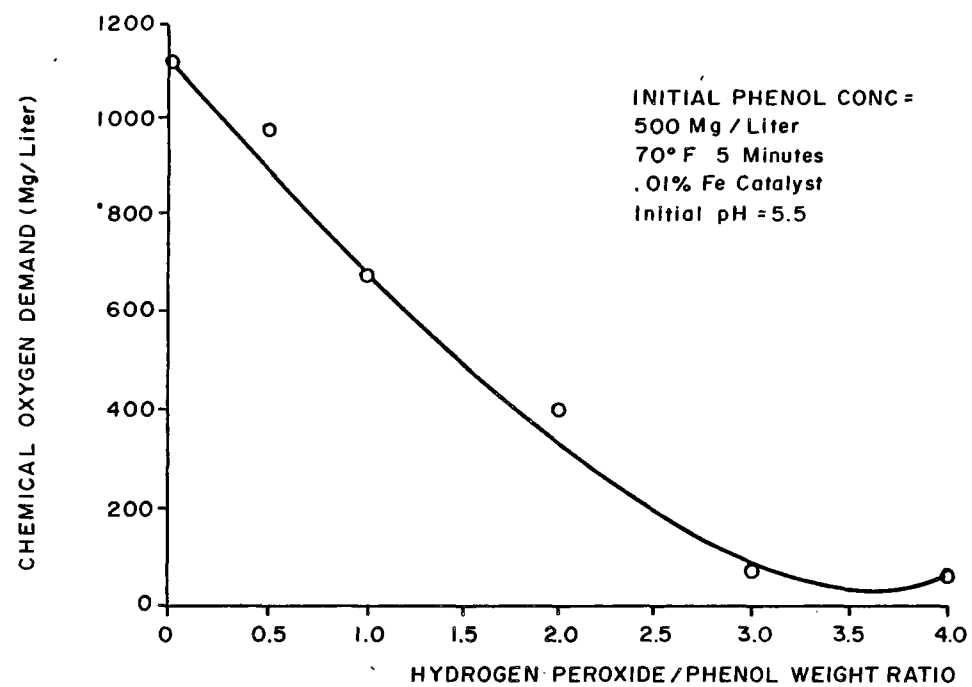
FIGURE 24

TABLE 34. REACTION OF PHENOL WITH FENTON'S REAGENT* (14)

$Fe(NH_4)_2(SO_4)_2$ (moles/mole of phenol)	H_2O_2 (moles/mole of phenol)	Phenol concentration (mg/l)		
		2 min	5 min	15 min
0.1	9	33.6	27.8	8.5
0.25	9	21.2	11.6	0
0.5	9	3.0	0	0
1	9	0	0	0
1	3	2.0	0	0
1	2	13.2	8.8	8.0
1	1	16.0	14.2	13.6
1	0.5	22.4	19.0	16.0

*Solutions containing 50 mg/l of phenol were reacted at pH 3 and 10°C with air agitation.

Eisenhauer concluded that optimum phenol oxidation takes place when the reaction is carried out at a 3:1 mole ratio of peroxide to phenol. Unfortunately, when this reagent was applied to phenolic industrial wastes, the peroxide requirement increased three to six times. This increase was believed to be a result of other organics in the waste. Eisenhauer also reported that cost of phenol removal to be $2.40/lb of phenol (1964 prices), which was too expensive to compete with other removal processes..

In addition to the work described above, the FMC Corporation has also investigated the effect of temperature and various catalysts on phenol oxidation.(13) Temperatures between 70° and 120°F were found to have no practical effect on the reaction. Catalysts such as ferrous sulfate, iron wool, nickel salts and aluminum salts were also evaluated. As shown in Table 35, ferrous sulfate appeared to be the most practical of all the catalysts studied. This finding was also supported by Ross (15) and Keating et al.(16) Keating also compared the effectiveness of ferrous and ferric iron and found no differences with the testing conditions used. He did note, however, that the reaction seemed to begin sooner when ferrous iron was used as evidenced by an earlier color change. FMC similarly tested potassium persulfate both with hydrogen peroxide and alone with an iron catalyst. Even though good oxidaton was obtained, the results were the same as if hydrogen peroxide alone had been used.(13)

A 1961 Russian article, as reported by the FMC Corporation, "gave the following order of catalytic activity for the peroxide oxidation of phenol;

Fe^{++}, Al^{+++}, Cr^{+++}. The catalytic Fe^{+++} and Cu^{++} activity was also said to be enhanced by the presence of Al^{+++}." (13) The previously described work of FMC does not verify this conclusion. FMC has pointed out, however, that the Russian work was performed on a much more dilute solution.

Merour (17) took another approach to the problem and found that oxidizable material may be removed from wastes as follows:

1. saturate the waste streams with oxygen then add hydrogen peroxide;

TABLE 35. EFFECT OF CATALYSTS ON PHENOL OXIDATION (13)

$H_2O_2/$ phenol ratio	Catalyst	Phenol (mg/l)	TOC (mg/l)	COD (mg/l)
none	none	500.0	383	1,105 (theory 1,190)
0.5	none	499.0	365	
1.0	none	493.0	375	
0.5	0.01% Fe	88.0	380	974
1.0	0.01% Fe	7.0	360	679
2.0	0.01% Fe	0.3	310	392
3.0	0.01% Fe	0.2	150	106
4.0	0.01% Fe	3ppb	138	66
0.5	0.03% Fe	118.0	365	1,020
1.0	0.03% Fe	22.0	345	620
2.0	0.03% Fe	0.2	315	418
3.0	0.03% Fe	4.04	210	150
0.5	0.01% Fe, 0.01% Al	79.0	380	971
1.0	0.01% Fe, 0.01% Al	4.0	310	625
2.0	0.01% Fe, 0.01% Al	0.1	300	495
3.0	0.01% Fe, 0.01% Al	0.05	200	172
4.0	0.01% Fe, 0.01% Al	6ppb	196	105
1.0	0.03% Fe, 0.03% Al	5.7	310	510
2.0	0.03% Fe, 0.03% Al	0.3	320	405
3.0	0.03% Fe, 0.03% Al	0.2	225	210
1.0	Steel wool (room temp., 10-min. retention)	16.0		
0.5	0.01% Ni (as $NiCl_2$ $6H_2O$) (room temp. test)	496.0	370	

Initial phenol concentration - 500 mg/l. $120°F$, 30-min. retention time; initial pH = 5.5. Fe added as ferrous sulfate; Al added as aluminum sulfate.

2. adjust the pH to 6-7; and

3. activate the mixture with light having a wavelength of 200 to 500 nm and an energy of 0.5 w/atom of carbon eliminated.

This process was found to require 0.1 to 1.5 atoms of active oxygen per atom of carbon removed.

Keating et al, (16) reported on three commercial installations where phenolic wastes are being successfully treated with hydrogen peroxide. One installation used a batch treatment system. During a typical treatment operation, approximately 10,000 gallons of wastewater were received and tested to determine the phenolic concentration, the H_2O_2/phenol rates, and the required treatment time. The waste was then adjusted to pH 5-6, iron added to equal 15 $\mu g/g$ Fe, and the required amount of peroxide is added. After the necessary treatment time, the waste was retested for phenol; and if found satisfactory, discharged to the receiving stream.

Hydrogen peroxide has also been used as a standby system for biological treatment. At one of the facilities studied, inadequately treated wastewater was diverted to a holding pond where it was stabilized with hydrogen peroxide. It is interesting to note that the amount of hydrogen peroxide required for treatment was well in excess of that required for phenolics (H_2O_2/phenol ratio of 8:1). This was primarily attributed to the presence of other oxidizable compounds. This same treatment system also used hydrogen peroxide to counteract the effects of biological shock loadings. If upstream testing detected a heavy load of phenols, hydrogen peroxide would be added to an equalization basin until phenols were reduced to a level tolerable to the bio-system.

The final commercial application reported by Keating (16) was effluent polishing to remove the last traces by phenol after biological treatment. This type application, however, is necessary only when there are stringent effluent limitations.

Reductive Degradation - Sweeny (9) reported catalyzed iron to be a low cost, effective treatment, replacing substituted chlorine atoms with hydrogen. This removal of chlorine is stated to generally lead to products of greatly reduced toxicity, for example, the degradation of chlorobenzene to cyclohexanol. Use of a column to provide the required contact was investigated in two variations - diluted and fluidized beds. The fluidized bed was found to be most efficient, allowing flow rates as high as 23 gpm/ft^2. A degradation trial with an influent concentration of 2,000 mug/l p-nitrophenol at a flow rate of 22.8 gpm/ft^2 produced an effluent containing only 1.5 mug/l, a 99.8 percent reduction.

An operating pH range of 5.5 to 8.0 was reported to avoid excessive reluctant usage or precipitation in the bed.

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5.0 CARBON ADSORPTION

Carbon adsorption is basically a surface phenomenon (1) and is influenced by such factors as the hydrophobic nature of dissolved organics in the waste stream, and the affinity of the organic for the sorbent.

Adsorption is related directly to a compound's hydrophobic behavior in that organics of low solubility are more readily adsorbed.(1) With respect to phenols, Strier (2) described the order of increasing adsorptivity on activated carbon as:

Compound	Molecular weight	Solubility in water mg/l at 25°C
Phenol	94.1	8.2×10^4
2,4,6 Trichlorophenol	197.5	9.0×10^2
Pentachlorophenol	266.3	3.0 at 50°C

This is also the order of increasing molecular weight and decreasing solubility, which supports the above statement concerning solubility and adsorptivity. The solubilities reported above by Strier, however, do not agree with other published data. The affinity of the organic for the sorbent is due to a combination of electrostatic attraction, physical adsorption, and chemical adsorption.(1) Since activated carbon is negatively charged, it is "more amenable to complexing with increasingly more positively charged aromatic (benzene) compounds such as the more highly chlorinated phenol ico, thereby facilitating adsorption".(2) Strier concluded that:

"...pentachlorophenol could best be removed from industrial waste effluents by oil-water separation and/or by precipitation and filtration at low pH, as pretreatment, followed as necessary by carbon adsorption and/or biological oxidation, to remove other phenolics and organics."

There are basically two techniques for using activated carbon in waste treatment:

1. The waste stream can contact granular carbon in a treatment column; or

2. Powdered carbon can be added directly to the wastewater.

Numerous researchers have reported on the effectiveness of contacting type carbon columns for phenol removal. Zogorski and Faust (3) conducted 25 experiments using laboratory prepared phenol solutions and fixed beds of

granular activated carbon. From their work, they concluded that between 20 seconds and two minutes of contact time is required to reduce phenols below analytical sensitivity. They also found that granular activated carbon rapidly removes phenols, therefore filters with a bed depth of 3-to-5 ft can be as efficient as the much larger units currently being designed. Hager (4) conducted similar laboratory adsorption studies using actual industrial wastewaters and found a 99 percent phenol reduction in all five samples analyzed. He also reported on five full scale adsorption systems installed between March 1973 and March 1975. A brief description of these systems is included in Table 36. Bernardin (5) also reported on two full scale adsorption systems. Plant "A" was a chemical plant manufacturing, among other compounds, phenol. A basic process flow diagram is shown on Figure 25. The carbon adsorption system consisted of two moving bed steel adsorbers, each of which was 12 ft diameter by 36 ft sidewall height. Each contained approximately 124,000 lb of Calgon Filtrasorb granular activated carbon and was designed for a flow rate of 175 gpm. A summary of typical plant operation data is shown on Table 37. Plant "B" manufactured phenolic resins and produced a waste containing floating oils, suspended solids, phenolics, and other organics. A basic process flow diagram is shown on Figure 26. The carbon adsorption system consisted of two fixed bed adsorbers operated in series. Each column was 10 ft diameter by 11 ft sidewall height and contained approximately 20,000 lb of granular activated carbon. A summary of typical plant operating data is shown on Table 38.

TABLE 36. PHENOL ADSORPTION SYSTEMS (4)

Plant No.	Flow (1,000 gpd)	Pretreatment	Contact time (min)	Phenol concentration (mg/l) Influent	Effluent
1	50	Settling, equalization, mixed media filtration	165	200	0.1
2	200	Equalization	41	600	100
3	350	Biological, mixed media filtration	24	800	0.05
4	150	Sand filtration, settling	55	1,200	1.0
5	500	Biological, settling, multi-media filtration	33	80	1.0

PROCESS FLOW DIAGRAM (5)
PLANT "A"

FIGURE 25

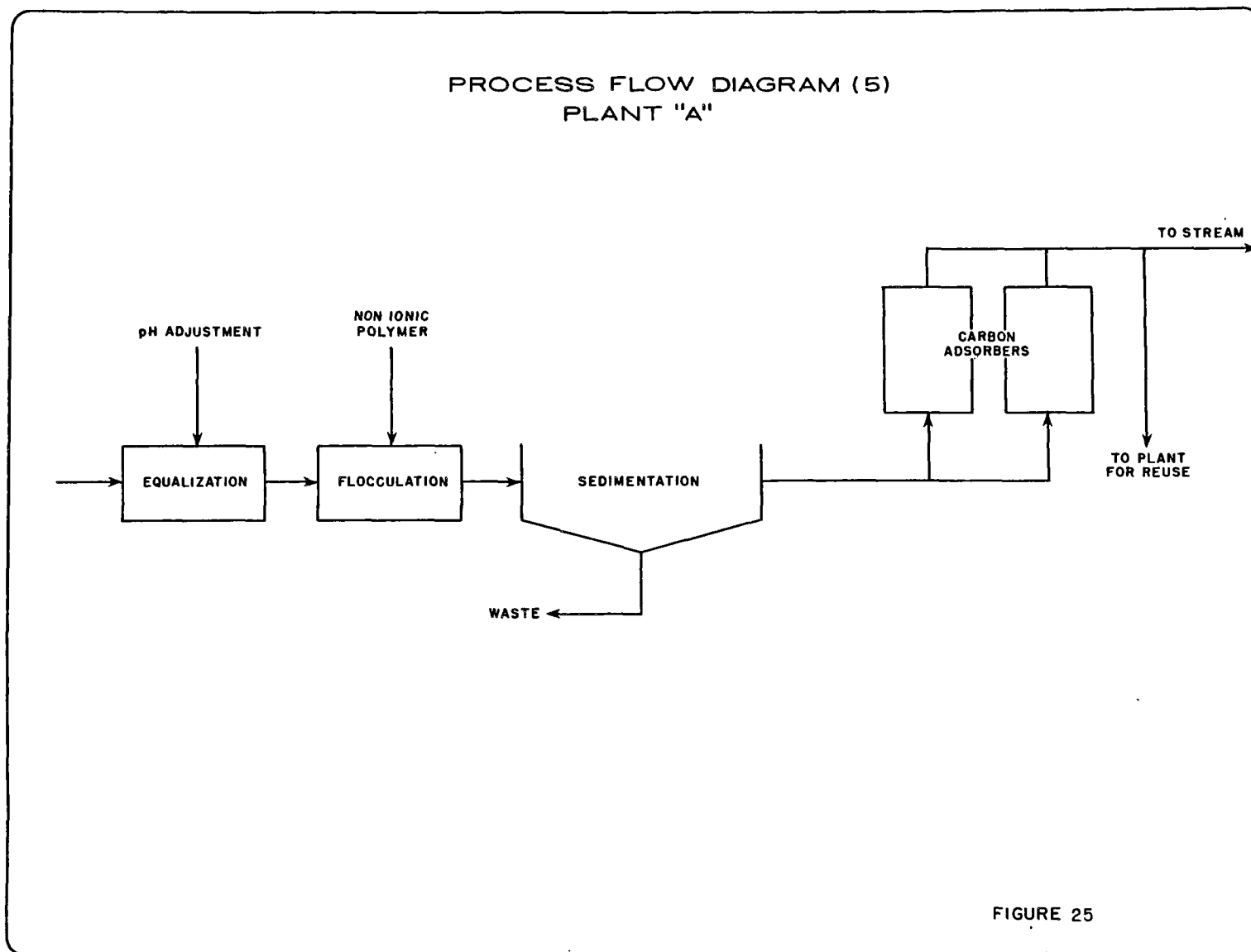TABLE 37.   OPERATING DATA - PLANT "A" (5)

Raw waste characteristics

    Flow   400,000 gpd

    BOD   16,000 lb/day

    COD   27,000 lb/day

    Phenol   1,500 lb/day

Effluent characteristics

    BOD   1,450 lb/day

    COD   2,675 lb/day

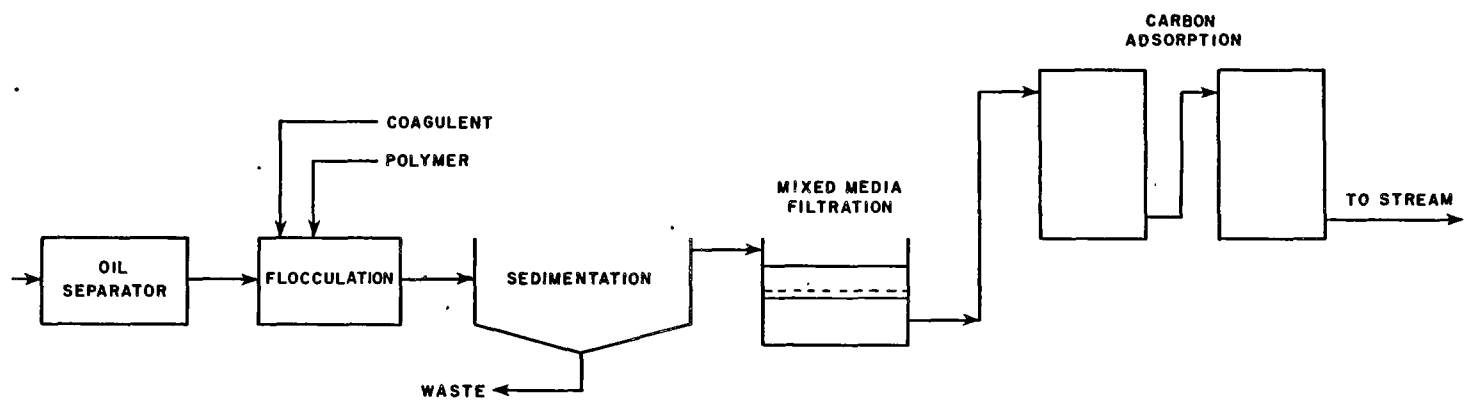   Suspended solids   22 lb/day

    Phenol   0.5 lb/day

PROCESS FLOW DIAGRAM (5)
PLANT "B"

FIGURE 26

TABLE 38. OPERATING DATA - PLANT "B" (5)

	Raw waste	Clarifier effluent	Carbon effluent
Suspended solids	220 mg/l	45 mg/l	10.0 mg/l
Oil/grease	50 mg/l	25 mg/l	5.0 mg/l
TOC	1,200 mg/l	650 mg/l	25 mg/l
Phenol	160 mg/l	130 mg/l	0.1 mg/l

*Plant flow is approximately 100,000 gpd

It is interesting to note that when the raw wastewater toxicity was eval-
uated using bluegill sunfish, all specimens died within the first 15 minutes
of exposure. In a similar test with the final effluent, however, there were
no adverse reactions even after a 10-day exposure test period.

Thompson (6) pointed out that even though activated carbon has been used
to treat various types of industrial wastewaters, it has not been commercially
applied to wood preserving effluents. Laboratory tests have, however, shown
that activated carbon provides good phenolic removals from raw creosote waste-
water. Unfortunately, other organics are also adsorbed and these reduce the
useful life of the carbon to the point where regeneration is essential.
Carbon regeneration equipment is generally too expensive for individual plants
to install.

Carbon regeneration has been shown to significantly affect the adsorption
process. DeJohn and Adams (7) found that the phenol and COD adsorption per-
formance of bituminous coal activated carbon was sharply reduced after regen-
eration. Data supporting this finding are shown in Tables 39 and 40.

TABLE 39. EFFECTS OF CARBON REGENERATION (7)

	Virgin carbon	Regenerated carbon	Percent change
Iodine number	950-1,000	560-680	-27 to -44
Molasses number	230	280	+22
Phenol, % removal	99.9	63	-37
COD % removal	71	13	-82

TABLE 40. IMPURITY REMOVAL DECREASE AFTER REGENERATION (7)

Impurity removal (lb/lb carbon applied)	Virgin carbon	Regenerated carbon	Percent change
TOC	0.17	0.096	-44
COD	0.73	0.35	-52
Phenol	0.01	0.03	-25

As stated, powdered activated carbon added directly to the wastewater serves as a viable carbon adsorption treatment technique. This technique, however, is normally used in conjunction with an activated sludge system. DeJohn and Adams (7) have reported on four full scale activated sludge systems which have tried this treatment alternative. At plant No. 1, a maximum BOD removal of 90-95 percent was achieved with carbon addition vs. 23 percent for the post test control. Similarly, the effluent COD was reduced from an average of 1,800 mg/l without activated carbon to 350 mg/l with addition. At plant No. 2, the raw waste TOC varied between 100 and 1,000 mg/l. After activated carbon addition, however, the effluent TOC was maintained below 20 mg/l, even during shock load periods. Plant No. 3 involved a refinery waste in which effluent TSS and COD removals improved 40 percent when activated carbon was added to the second stage of a two stage conventional activated sludge system. Similar improvements were also noted at plant No. 4. It should be noted that even though the above results are expressed in terms of TOC and COD removals, there was a correlation between such removals and phenol reduction.(8)

Rizzo and Shepherd (9) have outlined the various factors which should be considered in an economic evaluation of a contacting type adsorption system. These factors have been broken down into three general categories:

1. capital cost of the contacting system;

2. capital cost of the reactivation system; and

3. operation and maintenance expenses.

Figure 27 presents estimated equipment costs (installed) for two stage, fixed bed, downflow contacting systems of various capacities. Figure 28 presents the equivalent costs for onsite regeneration facilities. Typical examples of operation and maintenance expenses are presented in Table 41. Since these items are extremely variable and difficult to estimate, no attempt was made to develop typical costs. Instead the report itemized the major components of each cost and provided guidelines to assist in estimating them.

TOTAL INSTALLED COST OF TWO STAGE
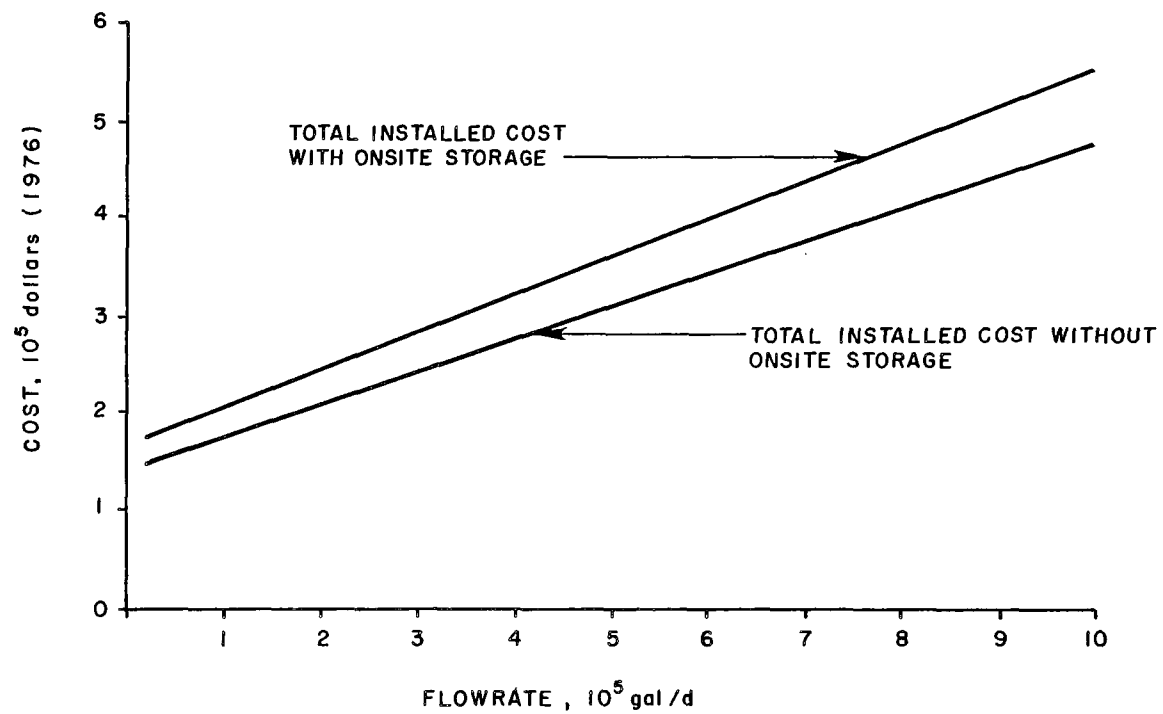ADSORPTION CONTACTING EQUIPMENT (9)

FIGURE 27

TOTAL INSTALLED COST OF CARBON REACTIVATION
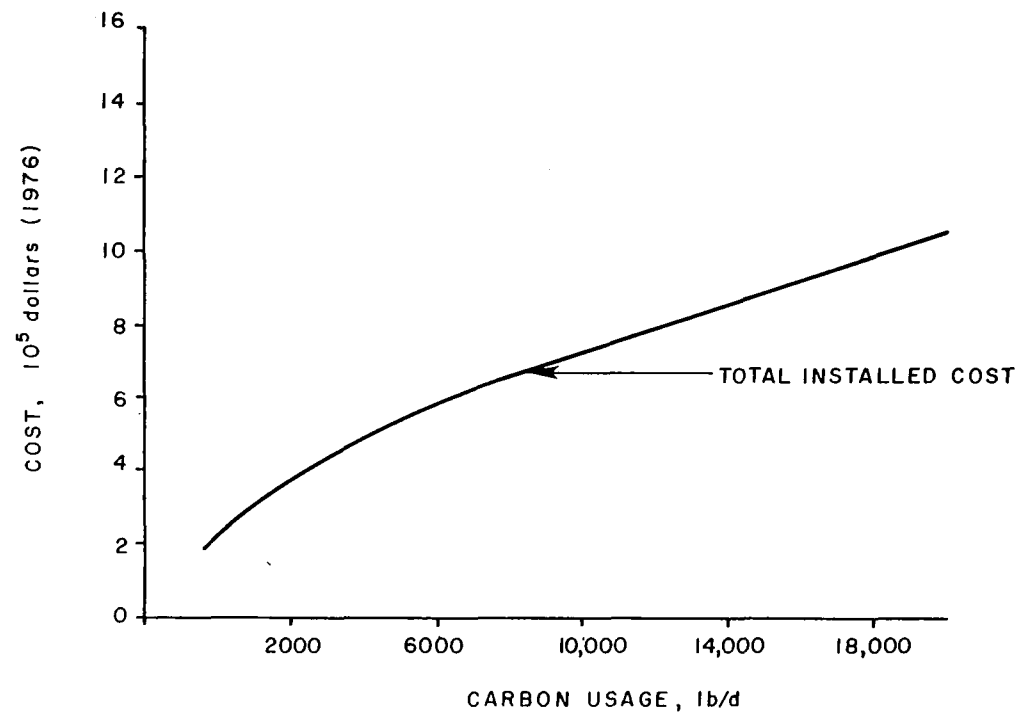AND HANDLING SYSTEM (9)

FIGURE 28

TABLE 41. MAJOR ANNUAL COST CONSIDERATIONS
FOR ADSORPTION OPTIONS (9)

Onsite reactivation	Offsite reactivation	Throwaway carbon	Service
Carbon makeup	Carbon makeup	Carbon disposal	Electricity
Depreciation	Depreciation	Carbon makeup	Labor
Electricity	Electricity	Depreciation	Service fee
Fuel	Interest	Electricity	
Interest	Labor	Interest	
Labor	Maintenance	Labor	
Maintenance	Monitoring	Maintenance	
Monitoring	Reactivation cost	Monitoring	
Steam	Transportation		

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6.0 STRIPPING OPERATIONS

Stripping operations involve passing a gas or vapor through a liquid with sufficient contact that volatile components are transferred from the liquid to the gas phase. The driving force for such an operation is the concentration differential between the liquid and concentrated equilibrium point of the gas. The transferred compound may then be recovered by condensing the stripping vapor.

It may be noted that stripping is essentially the reverse of adsorption. The equipment utilized for stripping operations generally consists of a tower or column containing multiple bubble-cap or perforated plates. Packing of the tower, with a high surface area medium, is also a reported practice.(1) An external condenser cools the gas.

As in many other cases of mass transfer, a more complete separation of components may be obtained through refluxing of one or both of the process streams. In this case, reflux of stripped condensates is a common practice.

The principal processes investigated dealing with wastewater treatment have been air and steam stripping. A single reference was noted (2) reporting favorable phenol removal with carbon dioxide stripping at elevated temperatures (65 to 90°C).

As evidenced by the lack of published data, air stripping has failed to exhibit the capability to remove phenolic compounds from wastewater within reasonable contact times. Air stripping was, however, capable of removing 90 percent of total reduced sulphur compounds and 10 to 20 percent of BOD from contaminated condensate streams.(3) Effective odor removal has also been noted.(1)

Steam stripping is currently practiced at a number of pulp and paper mills, but mainly as an odor control, water reuse, or chemical recovery measure. These mills include Great Northern (Port Edwards, Wisconsin), Mead (Escanaba, Michigan), Weyerhaeuser (Springfield, Oregon), Scott (Somerset, Maine), St. Regis (Rhinelander, Wisconsin), Georgia Pacific (Bellingham, Washington), Flambeau (Park Falls, Wisconsin), and Simpson Lee (Anderson, California). Very little data, however, were found in the search relating to phenol stripping. Work is currently underway in this area.(4)

The relative steam volatility of organic compounds is a complex property involving water solubility, boiling point, vapor pressure and tendency to form hydrogen bonding. Organic compounds that have undergone ionization are not volatile to steam. For example, at alkaline pH, the hydroxyl (OH) groups of phenolic compounds would tend to ionize to the negatively charged phenolate ion and would not be removed by steam stripping. Thus the relative acidities and process pH should be major considerations in attempts to apply steam stripping for phenol removal.

A plot of relative vapor pressures is included as Figure 29 illustrating one aspect of the sequential susceptability to steam stripping of organic compounds. In general, steam volatility increases as boiling point, water solubility and hydrogen bonding decrease.

Steam stripping of pulp and paper mill wastewaters is capable of removing 60 to 85% of the influent BOD while reducing TRS (total reduced sulpher compounds), and toxicity by 95 percent.(3) Recovery of the column streams may also result in salable products such as methanol, ethyl acetate, and furfural.(1)

Operations utilizing steam stripping were reported (3) to maintain a steam usage of about 15 to 18 percent (by weight) of contaminated condensate flow. Rates as low as 6 percent have also been reported.(5) A two percent rate was calculated as the optimal economic rate by Maahs et al. A 1967 cost estimate for a 130,000 lb/hr stripping system was $84,000 with annual operating costs amounting to about $0.32/ADT.

A more recent study (1977) by Guttierrez et al (6) quantified steam stripping efficiency for phenol. Stripper steam/condensate ratios varying from 5.6 to 14.4 percent were noted in a survey of five installations, as shown in Table 42. Table 43 indicates the variability in phenol content of the mills' condensate streams. It was reported that the lower steam/condensate ratios greatly affected BOD_5 removal which decreased from the previously noted 60 to 85 percent to less than 5 percent. Phenol removal ranged from 0.4 to 61 percent, but this variability was attributed to the rectification section rather than the steam ratio. Table 43 presents the removal data. The best phenol removal, 61 percent, still was not considered high enough to qualify steam stripping as an effective removal technology. Continuing work in this area may refute this conclusion.

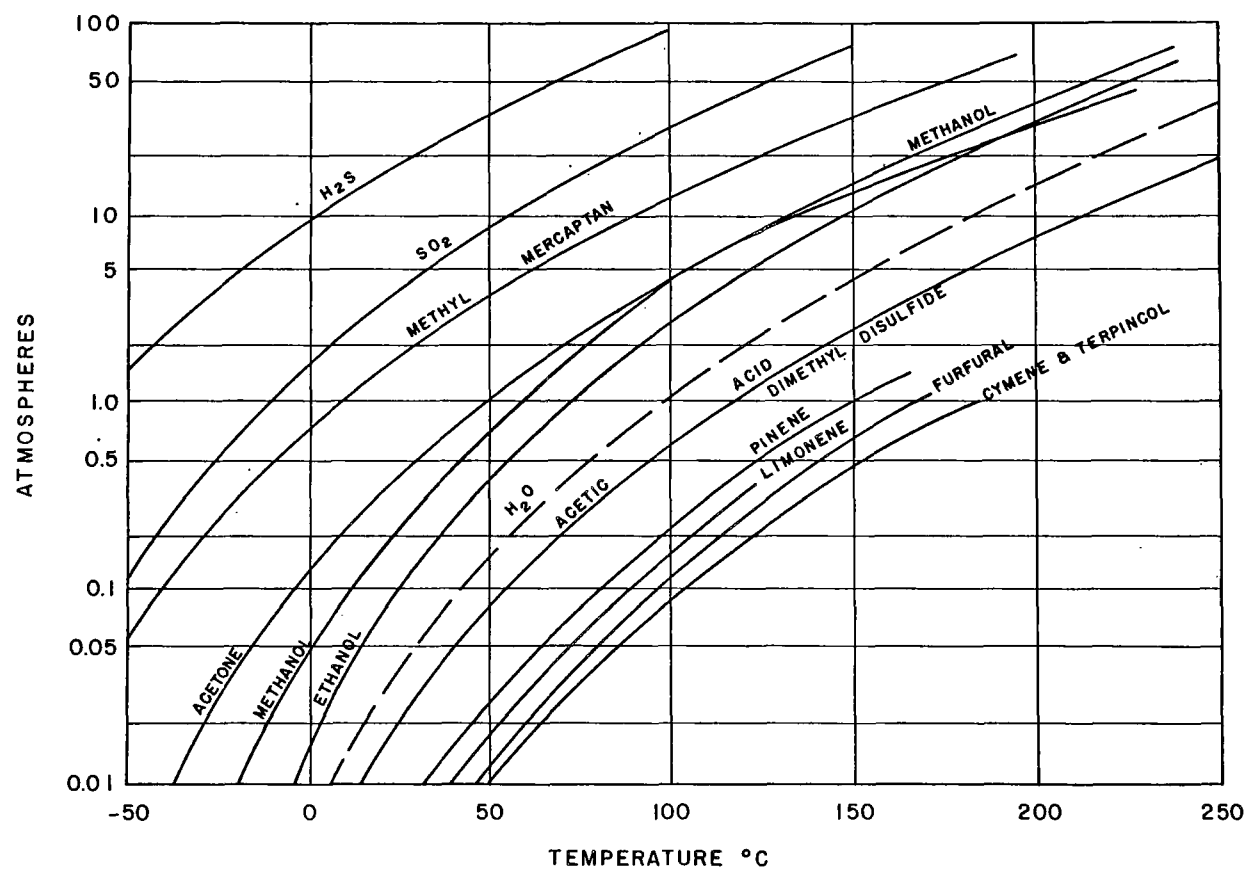VAPOR PRESSURES OF VARIOUS
VOLATILE ORGANIC COMPOUNDS

FIGURE 29

TABLE 42. CHARACTERISTICS OF VARIOUS CONDENSATE TREATMENT SYSTEMS AT
FIVE BLEACHED KRAFT MILLS (6)

Mill code	Production (ADT/day)	Wood furnish (%)	Type of digesters	Contaminated condensates being treated			Stripping system	
				Origin	Flow (gpm)	% of total condensate	General characteristics	Steam Ratio %
A	970	Mixed fir, balsam, hemlock, spruce	Kamyr	Digester area: Steam vessels and #2 flash tank; turpentine decanter underflow; digester area vents. Evaporators area: Evaporator effect #5; evaporator surface condensor & vacuum system.	547	64	Free standing stripper using live steam, no condensor, reflux or decanter.	5.6
B	450	Mixed hardwood	Batch	Digester area: Digesters' blow condensate. Evaporators area: Evaporators' surface condensor and vacuum system.	100	31	Free standing stripper using live steam. Has rectifying section.	6.4
C	510	45% spruce 45% pine 10% balsam fir	Kamyr	Digester area: Steam vessels and flash tank #2. Evaporators area: Secondary surface condensors and vacuum system.	103	12	Free standing stripper using live steam and some digester relief steam, with condensor decanter and reflux.	11.3
D	1100	86-80% Douglas fir 14-20% pine	7-Batch 1-Kamyr	Digesters area: Digesters' blow condensate. Evaporators area: Surface condensor and vacuum system.	493	24	Free standing stripper using live and relief steam. Column has rectifying section.	13.3
E	280	69-70% pine 40-30% hardwood	Batch	Digesters area: Digester's blow condensate and turpentine decanter underflow. Evaporators area: Evaporators' effect #5; surface condensors and vacuum system.	235	46	Stripper built into the evaporator train between 1 and 2 effect. Uses steam from 1st effect and some live steam.	14.4

TABLE 43. POLLUTANT LOAD BY CONTAMINATED CONDENSATES * (6)

Source	pH	Phenol (mg/l)	Phenol (lb/ADT)
Literature range 7.5 to 10.5		4 to 40[6,13]	0.03 to 0.3**
Mill A	8.3	5.8	0.04
Mill B	10.0	33.2	0.09
Mill C	9.6	17.6	0.04
Mill D	8.3	26.6	0.14
Mill E	9.9	29.1	0.29

*Contaminated condensates analyzed are those segregated by the mills for steam stripping.

**Calculated on the basis of foul condensates flow of 1,000 gal/ADT.

TABLE 44. REMOVAL OF PHENOL FROM CONTAMINATED
CONDENSATES BY STEAM STRIPPING (6)

Mill source	Steam ratio (%)	Phenol Feed (mg/l)	Phenol Treated (mg/l)	Phenol Removed (%)*	Phenol Removed (lb/ADT)
A	5.6	5.8	5.0	9.0	0.0036
B**	6.4	33.2	15.8	49.0	0.0441
C	11.3	17.6	13.1	17.0	0.0068
D**	13.3	26.6	10.0	61.0	0.0854
E	14.4	29.1	26.2	0.4	0.0012

*Corrections have been made for the dilution effects by condensed steam.

**Column equipped with rectifier.
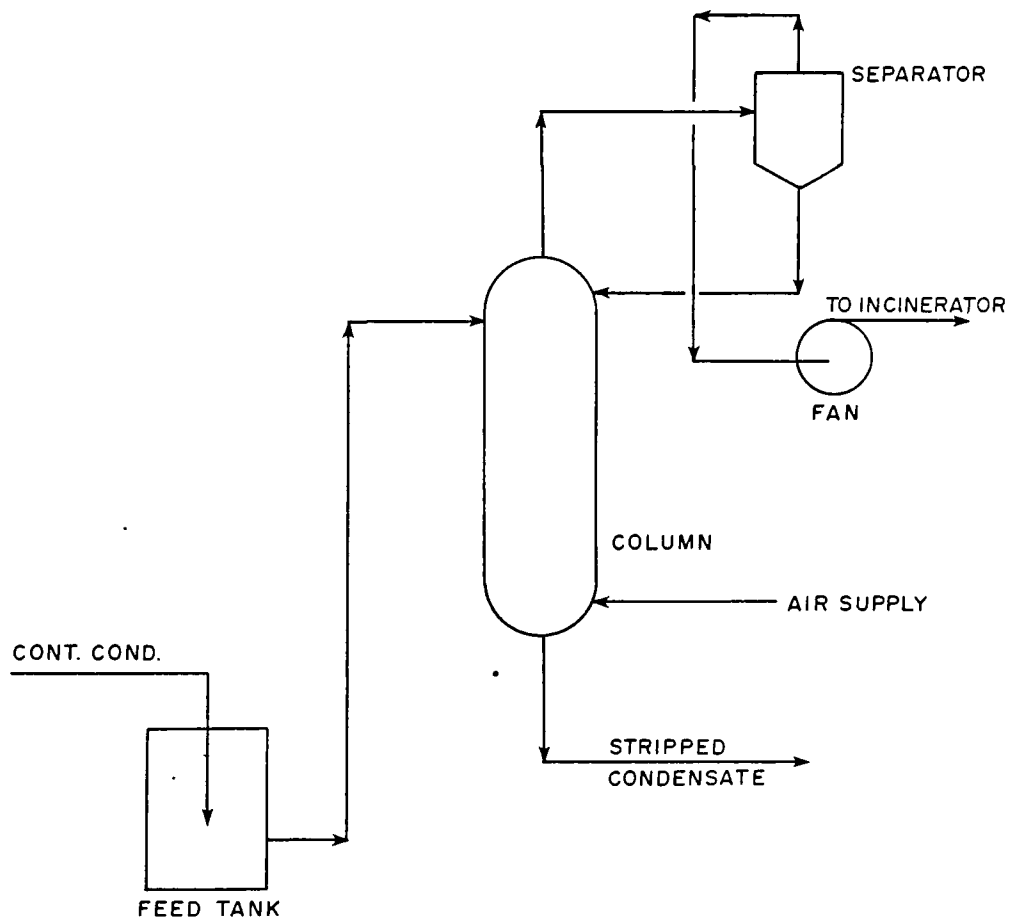
-104-

AIR STRIPPER SCHEMATIC (3)

SEPARATOR

TO INCINERATOR

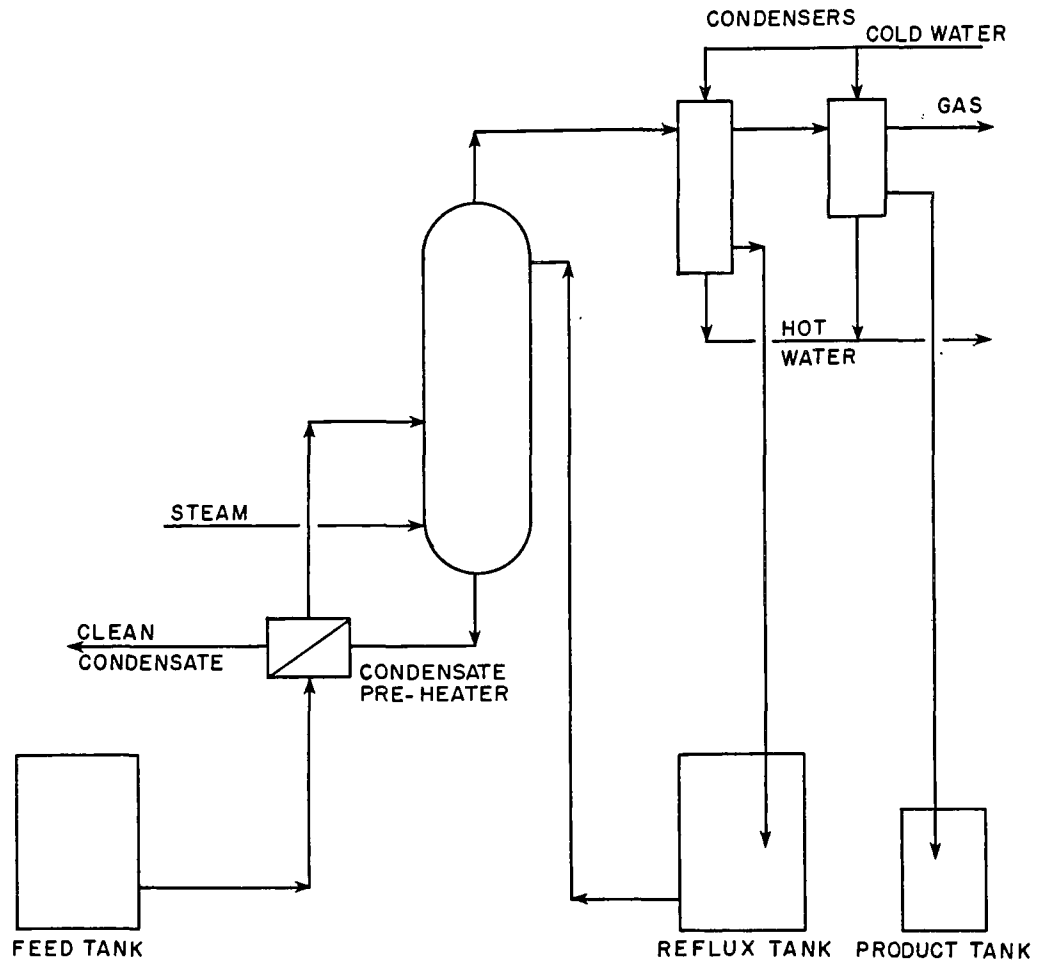FAN

COLUMN

AIR SUPPLY

CONT. COND.

STRIPPED
CONDENSATE

FEED TANK

FIGURE 30

STEAM STRIPPER SCHEMATIC (3)

FIGURE 31

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FLOW DIAGRAM
STRIPPER COLUMN INTEGRAL W/ EVAPORATOR (3)

FIGURE 32

STRIPPING COLUMN DESIGN DETAILS (7)

VAPOR

REFLUX
NOZZLE

MANWAYS
ALTERNATE
PLATES

FEED
NOZZLES

STEAM

BOTTOMS

LIQUID
FLOW

DOWNCOMER

STEEL
SHELL

WEIRS

TRAY

VAPORS
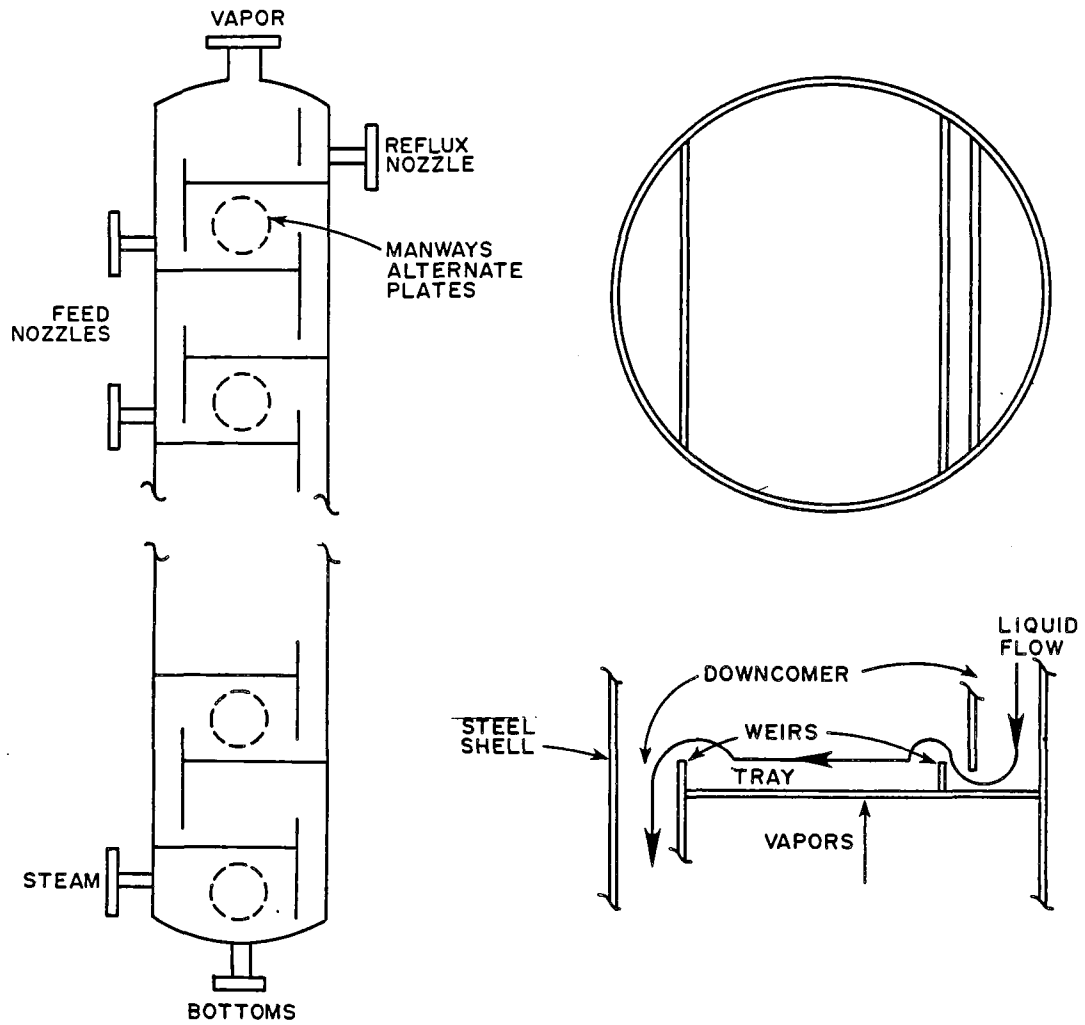
FIGURE 33

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7.0 RESIN ADSORPTION

Synthetic polymeric resins are known to not only effectively remove phenol but also to permit recovery of this valuable chemical. Crook et al, (1) did extensive work with industrial wastewater effluents containing phenol, bisphenol A and p-nitrophenol. One of their studies found that Amberlite XAD-4 reduced the wastewater phenol concentration from 6,700 to less than 1 mg/l. Acetone or methanol was used for regeneration. Both acetone and phenol (99 percent purity) were recovered by subsequent distillation. It was also noted that bisphenol A could be removed by adsorption onto a combination of XAD-4 and XAD-7. Adsorption capacities of each resin for bisphenol A were found to be 34 and 16 g/l, respectively. In this case, resins were regenerated with ethanol. Both Herve (2) and Chamberlain (3) had similar success using resin adsorption for phenol removal.

Rohm and Haas (4) has stated that the phenol adsorption capacity of polymeric resins depends on the type and concentration of phenolics in the wastewater, as well as the pH, temperature, viscosity, polarity, surface tension and background concentrations of other organics and salts. Resin adsorptive capacity changes dramatically with increasing pH. One explanation for this is that the phenolic molecule changes from a neutral, poorly dissociated form at low pH to an anionic, charged form at high pH. Kim et al. (5), based on their work with p-nitrophenol (PNP), support this statement. They also found, with weak acids, however, that as pH decreased below a certain value, the adsorptive capacity was a "maximum in the pH region in which the resin was predominantly in the free base form and the PNP was present as a neutral species." The effect of pH on the adsorption of PNP to a weakly basic resin is shown on Figure 34.

A high salt background has been noted to enhance phenol adsorption. Rohm and Haas conducted experiments in which aqueous solutions of phenol and m-chlorophenol, both with and without salt addition, were passed through columns of XAD-4. The results, as shown in Table 45, clearly indicate that the adsorptive capacity for both solutes was greatly increased by the presence of salt.

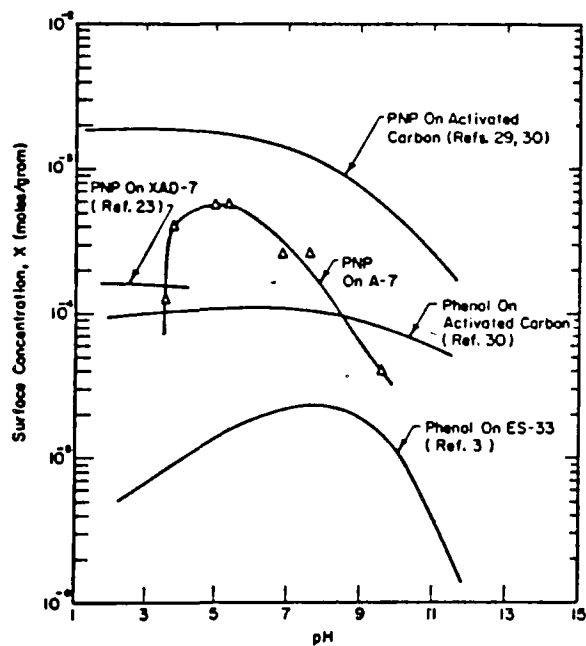# EFFECT OF pH ON ADSORPTION OF P-NITROPHENOL(4)

FIGURE 34

TABLE 45. EFFECT OF SALT CONTENT UPON CAPACITY
OF AMBERLITE XAD-4 FOR PHENOL & m-CHLOROPHENOL ADSORPTION (4)

Solute	ppm	milli-mol/1	Zero leakage	10 ppm leakage
Phenol	250	2.7	0.78	0.83
Phenol with 13% NaCl	250	2.7	0.98	1.09
m-chlorophenol	350	2.7	2.40	2.53
m-chlorophenol with 13% NaCl	350	2.7	3.10	3.43

Header spanning: Solute in influent solute adsorbed, lb/ft^3

As with carbon adsorption, solute solubility is reported to serve as a guide to the adsorptive capabilities of XAD-4. "This is illustrated by the adsorption of phenol, monochlorophenol; 2,4 dichlorophenol and 2,4,6 tri-chlorophenol. The solubility of these compounds in water decreases with the level of chlorine substitution, but the adsorptive capacity exhibited by Amberlite XAD-4 for them increases with the level of chlorine substitution."(4)

As shown in Table 46, the specific adsorption of phenols and chlorinated phenolics on Amberlite XAD-4 resin has been researched. Even with this data, however, column studies should be performed to select the best resin and establish operating parameters for specific industrial wastewaters.

Kim et al, (5) in addition to their work with specific resins, summarized various feasibility studies for using resins for phenol adsorption. One summary reported the work of Anderson and Hansen in which the hydroxide form of strong base resins were found to have much greater adsorption capacity than the chloride form of the same resin or of a weak base resin. They also found that the strong base resin could not be regenerated as efficiently using an alkaline solution or polar solvent as a weak base resin. The work of Pollis and Kunin was also included in the summary. These researchers found that the free base form of weak base resins had an appreciable phenol adsorption capacity and it could be regenerated with either polar solvents or caustic. Adsorption was also found to be independent of the organic salt concentration.
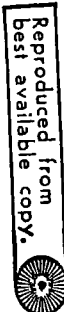
To regenerate a resin adsorbent, the attractive forces between the phenol molecules and the resin must first be overcome. Numerous researchers have stated that this is normally accomplished with either a caustic solution or a polar solvent for non-ionic adsorbents.(1, 2, 4, 5) Kim et al stated that acidic or salt solutions may also be used to regenerate ion exchange resin systems following treatment of phenolic bearing wastewaters.

TABLE 46. ADSORPTION OF PHENOLIC COMPOUNDS ON AMBERLITE XAD-4
AT 25°C AND FLOW RATE 0.5 gpm/ft^3

Compound	Influent concentration (ppm)	Resin capacity (lb/ft^3 at 0.1 ppm leakage)
Phenol	6,700	5.4
Phenol	3,000	4.5
Phenol (in 13% sodium chloride)	250	1.0
Phenol	250	0.8
m-Chlorophenol	350	2.4
2,4-Dichlorophenol	430	5.1
2,4,6-Trichlorophenol	510	12.0

As previously described in the Solvent Extraction section, Lorton (6) evaluated the economics of removing phenols from coke plant process condensate using biological oxidation, solvent extraction and adsorption. Of these three alternatives, solvent extraction was the most economical followed by adsorption and finally, biological oxidation. The results of this evaluation are shown in Table 31. The adsorption system used in the analysis was developed by the Rohm and Haas Company and is shown on Figure 35. This process, with the exception of the superloading step, has been proven at two chemical processing plants. One such plant has been in operation since August 1975 and is reducing wastewater phenolic concentrations from 6,000 to 20,000 mg/l to less than 3 mg/l.

ROHM & HAAS ADSORPTION PROCESS FLOW DIAGRAM (6)

FIGURE 35

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8.0 ELECTROCHEMICAL OXIDATION

Electrochemical oxidation, sometimes referred to as electrolysis, involves the generation of an electrical potential across a cell through which wastewater is flowing. As a wastewater treatment method, this technology dates back at least as far as 1900.(1) Available data indicate that no organic decomposition occurred in these early installations, but it was noted that significant amounts of sodium hypochlorite were generated from lead dioxide, graphite and platinum electrodes. The sodium hypochlorite may have caused interferences with the analytical techniques employed. It was further noted that low conductivity of wastewaters led to uneconomical power consumption.

More recently, Westinghouse Electric Corporation (2) reported 100 percent removal of phenols by electrolysis in the presence of an oxidative catalyst (MnO or CrO_3) suspended as agglomerated particles in the reaction cell. Graphite electrodes were used with a 0.5 to 800 Hz current being passed through the cell. The wastewater, a coking effluent containing 200 mg/l phenol, was treated in this manner for one hour and resulted in the complete elimination of detectable phenols.

A Russian effort (3) investigated electrochemical oxidation on biological treatment plant effluents, black liquor, first stage alkali extraction effluents and evaporator condensates. Additionally, a variety of electrode materials and electroconductive additives were studied. Phenolic removals ranged from 78 to 100 percent. Current densities and pH were noted as major operating parameters; 2 to 4 amp/dm^2 showed marked improvement in COD reduction while a slightly alkaline pH, 7 to 9, was reported as suitable with lead electrodes. Sacrificial aluminum anodes were reported to be useful for a greater range of both current densities and pH. Less power was required with this arrangement also. A major drawback of the process still appears to be excessive power consumption.

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3. Serbodol Skii, E.N., M.I. Anisimova, V.A. Babkin, and G.N. Permyakova. "Purification of Kraft Pulping Effluents by Electrochemical Oxidation." Abstract Bulletin of the Institute of Paper Chemistry, 49(5): entry No. 4099, 1978.

9.0 IONIZING RADIATION

Sufficient excitation of organic compounds in wastewater through exposure to ionizing radiation can lead to their oxidation. Lenz et al (1) studied the effect of gamma irradiation on pulp mill effluent constituents while varying aeration parameters. The studies indicated (via COD reduction data) that oxidation of organic compounds is accelerated by gamma irradiation. It was noted that oxygen transfer rates were the limiting reaction rate factor since turbulent air flow produced better results than static high pressure oxygen. The authors expressed doubts about the economic feasibility of the process due to the high cost of radioactive source materials. Table 47 contains the results of their investigations.

Sunada (2) also reported favorably on the phenol reductions experienced when a chemical plant effluent was exposed to 0.01 Mrad.

Touhill et al, (3) studied the effect of a 175,000 rad/hr dosage of gamma radiation from a cobalt-60 source on oxygenated phenol solutions. The solutions varied in phenol concentration from 10 to 1,000 mg/l. This study also indicated that oxidation was limited by oxygen transfer rates since the rate of phenol removal was relatively independent of initial concentration. Solutions containing 1,000 mg/l phenol required 20 hr for 99 percent phenol destruction. When oxygen was added to the solution 75 percent phenol destruction of a 100 mg/l solution occurred in 60 minutes. At a lower initial concentration of 10 mg/l, an oxygenated solution experienced 95 percent phenol destruction within 30 minutes. No significant difference between the use of air or oxygen was noted, although the rate of degradation was greatly accelerated by the addition of either gas at the lower initial concentrations.

Higher dosages of radiation resulted in higher rates of degradation.

Nenodovic (4) prepared an article setting forth the principles and practical applications of ionizing radiation for wastewater treatment. Reduction of phenols is referred to as a viable application.

Most researchers concluded that the treatment was effective, but too costly. An apparent reason for this was that the chain reactions expected in pulp and paper effluents failed to occur.

TABLE 47. EFFECT OF GAMMA IRRADIATION AND OXYGEN PRESSURE ON pH,
SUSPENDED SOLIDS AND COD OF VARIOUS PULP MILL EFFLUENTS (1)

Sample no.	Irradiation intensity (million rad/hr)	Gas	Pressure (p.s.i.)	Time (hr:min)	pH	Suspended solids (mg/l)	COD (mg/l)	COD removal %
A. Kraft strong effluent								
	Control	O_2^-	-	-	9.08	48	3,218	-
I-1	-	O_2	1,900	4:00	8.19	264	2,846	11.6
I-2	8	O_2	2,100	0:30	7.52	34	2,461	23.5
I-3	8	O_2	2,100	1:00	7.30	60	1,920	40.3
I-4	8	O_2	2,000	1:40	7.33	74	1,379	57.1
I-5	8	O_2	500	2:00	7.05	104	1,092	66.1
I-6	8	O_2	2,100	2:00	7.30	59	1,152	64.2
B. Kraft strong effluent								
	Control	-	-	-	9.08	48	3,218	-
II-1	6	-	-	1:30	8.40	44	2,759	14.5
II-2	8	air	2,100	0:30	7.58	140	2,410	25.1
II-3	4	bubbled	-	2:00	8.64	152	1,260	60.8
II-4	8	air	2,100	2:00	6.06	78	1,841	42.8
II-5	8	Cl_2	2,100	0:30	2.98	642	2,442	24.1
II-6	-	Cl_2 bubbled	-	-	3.73	680	2,875	10.6
C. Kraft weak effluent								
	Control	-	-	-	6.84	166	500	-
III-1	6	-	-	1:30	6.61	128	387	22.6
III-2	4	bubbled air	-	0:20	7.28	152	260	48.0
III-3	-	O_2	1,900	4:00	7.02	160	421	15.8
III-4	4	O_2	2,000	0:20	7.25	120	348	30.4
III-5	8	O_2	2,000	2:00	6.82	174	245	51.0
D. NSSC main mill effluent								
IV-1	Control	O_2^-	-	-	6.02	112	862	-
IV-2	-	O_2	1,500	2:00	6.18	148	715	17.1
IV-3	8	O_2	1,500	2:00	6.78	104	130	84.9
E. NSSC Woodroom Effluent								
V-1	Control	O_2^-	-	-	5.31	680	2,911	-
V-2	-	O_2	1,500	2:00	7.12	236	1,075	63.1
V-3	8	O_2	1,500	1:00	6.51	116	482	83.4

REFERENCES

1. Lenz, B.L. et al. "The Effect of Gamma Irradiation on Kraft and Neutral Sulfite Pulp and Paper Mill Aqueous Effluents." <u>Pulp and Paper Canada</u>, 72(2): 75-80, 1971.

2. Sunada, T. "Wastewater Treatment by Radiation." <u>Chemical Abstracts</u> Vol. 80 (112211), 1974.

3. Touhill et al. "The Effects of Radiation on Chicago Metropolitan Sanitary District Municipal and Industrial Wastewaters." <u>Journal Water Pollution Control Federation</u>, 41(2), Part 2): R44-R60, 1969.

4. Nenadovic, M.O. Micic, O. Gal. "Wastewater Treatment by Use of Ionizing Radiation." <u>Hem. Ind.</u> 28 (5): 217-220, 1974 (Russian).

10.0   ELIMINATION OF POLLUTANT DISCHARGE

To date, the only published technology for the total elimination of phenolic discharges is effective indirectly in that it involves the elimination of any wastewater effluent. A demonstrated technology to accomplish this feat involves the Rapson-Reeve salt recovery process, substitution of chlorine dioxide for a majority of the chlorine used in the bleach plant and major reductions in water usage by complete counter-current bleach plant washing followed by brown stock washing with the same water. This process is currently being pioneered at Great Lakes Paper Company's Thunder Bay installation - an 800 ton/day kraft pulp mill.

In the D/CEDED bleach plant, 70 percent of the chlorine demand is supplied by chlorine dioxide rather than chlorine. This results not only in a reduction in chloride ion within the system (an approximate 80-percent reduction) but also maintains pulp quality at the higher temperatures counter current washing imposes. Water use in the bleach plant is anticipated to drop to 4,000 gal/ton of pulp. This 4,000 gal/ton will be recycled as brown stock wash water.

The major innovation is the Rapson-Reeve salt recovery process. Complete reuse of the bleach plant white liquor would induce the recycle of large quantities of salt. Recycling of the salt would result in a build-up of the salt to saturation levels within the system, ultimately causing problems. The recovery process begins by concentrating the bleach plant white liquor to 26-30 percent $NaOH + Na_2S$. This allows for precipitation of Na_2CO_3 and Na_2SO_4, but not NaCl. Following removal of these crystals, the liquor is further concentrated to 36 to 42 percent $NaOH + Na_2S$ which causes the NaCl to precipitate. The supernatant liquor is then returned to the digestors while the precipitate is purified and stocked for production of NaOH and chlorine/-chlorine dioxide.

Although this method is not specific for the subject pollutants, its use would eliminate their discharge to the environment.
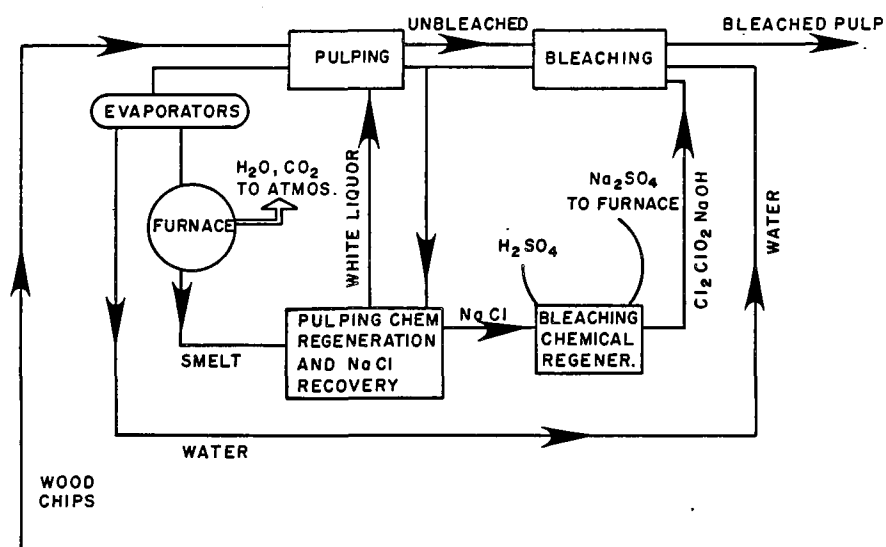
PROCESS FLOW DIAGRAM
CLOSED PULP MILL(1,2,3)

FIGURE 36

PROCESS FLOW DIAGRAM
RAPSON/REEVE SALT RECOVERY PROCESS (1,2,3)

STAGE 1

COOLING
WATER

PC

WHITE LIQUOR
FEED

LEACH LIQUOR
FROM STAGE 2

III

II

I

STEAM

HE

PC

HE

PC

HE

SC

LIQUOR TO
STAGE 2

WATER

SODIUM
CARBONATE
BURKEITE

STAGE 2

LIQUOR FROM
STAGE 1

HE

SC

CONCENTRATED
WHITE LIQUOR
TO DIGESTERS

WATER

WATER

PURIFIED
SODIUM
CHLORIDE

LEACH LIQUOR
TO STAGE 1
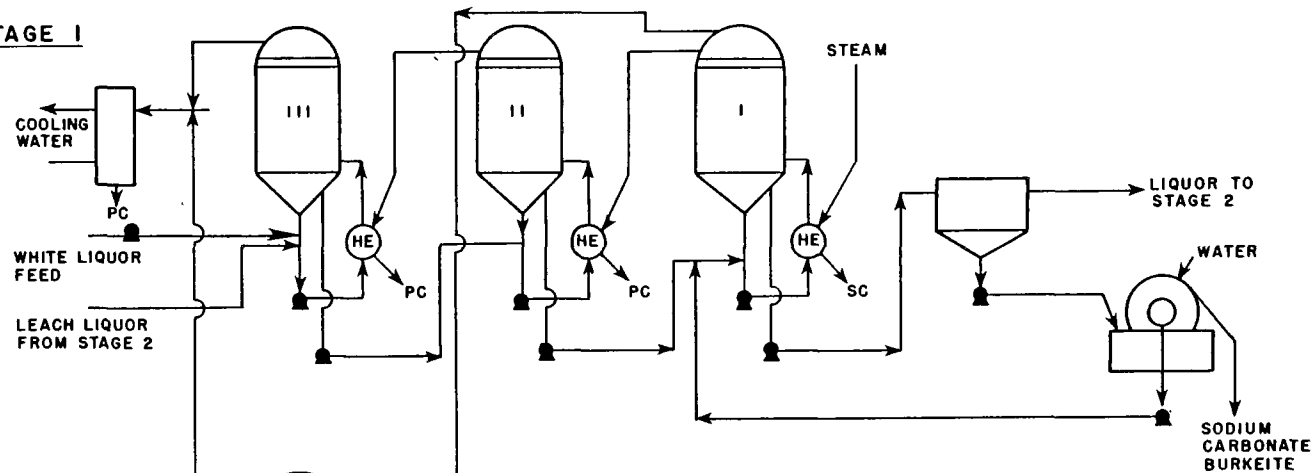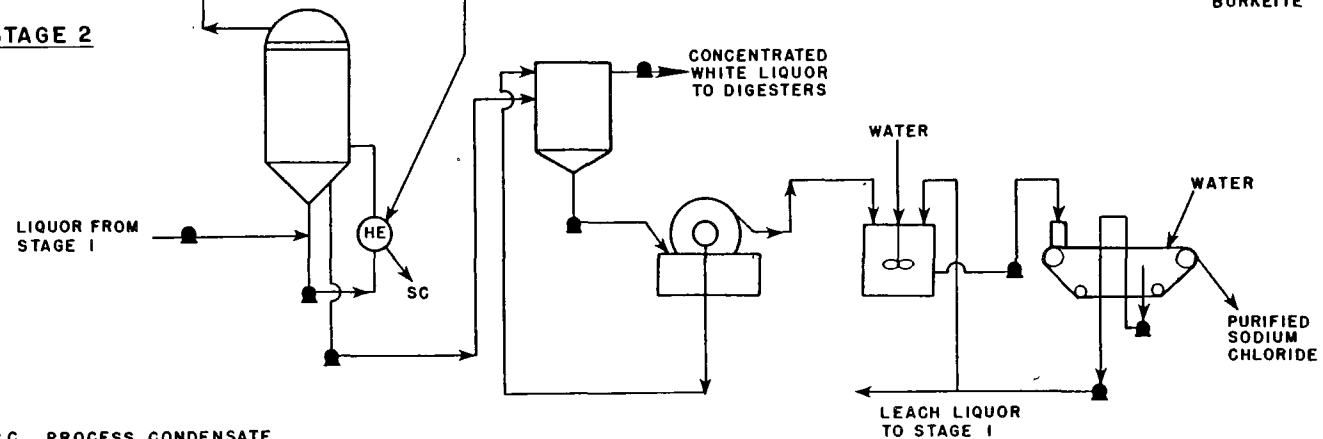
PC   PROCESS CONDENSATE

SC   STEAM CONDENSATE

HE   HEAT EXCHANGE

FIGURE 37

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REFERENCES

1. Stevens, F. "First Pollution-Free Bleached Kraft Mill Gets Green Light." Pulp and Paper Canada, 76(10): 27-28, 1975.

2. Stevens, F. "The No. 2 Kraft Mill, and What's New About It." Pulp and Paper Canada 77(11): 28-32, 1976.

3. Stevens F. "Effluent-Free Bleached Kraft Mill is Pioneered at Great Lakes Paper." Pulp and Paper Canada, 78(3): 94-98, 1977.

APPENDIX B
ANALYTICAL PROCEDURES

B-1

ANALYTICAL PROCEDURES FOR TOTAL PHENOLICS

1.0 TOTAL PHENOLICS

Modified Lowry procedure (Folin-Ciocalteau) of Markwell, Hass, Bieber and Tolbert, Anal. Biochem. 87, 206-210, (1978). Details:

Reagent A:

2.0 percent sodium carbonate

0.4 percent sodium hydroxide

0.16 percent sodium tartrate

1 percent sodium dodecylsulfate

Reagent B:

4 percent copper sulfate pentahydrate

1N Folin phenol reagent:

2N Folin-Ciocalteau reagent (Fisher Scientific) 1:1 with deionized water

In the procedure 100 parts of reagent A are mixed with 1 part reagent B to form reagent C. Standard curve prepared by incubating a sample volume of 1.0 ml containing 10 to 50 micrograms of 2,4-dichlorophenol (a surrogate standard) with 3.0 ml reagent C for 10 to 60 minutes at room temperature. 0.3 ml of 1N Folin reagent is then added, mixed, and incubated 45 minutes at room temperature. Absorbancy is read at 660 nm. Samples are diluted in deionized water to provide readings within the standard range. Note: pentachlorophenol does not react in this analysis.

ANALYTICAL PROCEDURES FOR PENTACHLOROPHENOL - MILL A

The phenol extraction procedure for FID/ECD analysis is as follows:

1. Place a 25 ml to 100 ml aliquot of each sample in a 125 ml or 250 ml separatory funnel and adjust to pH 12 with 10N NaOH.

2. Extract once with 50 ml hexane, drain the water layer into a 250 ml beaker and cover with a watch glass.

3. Back extract the hexane once with 25 ml of 1N NaOH, combine the aqueous layers and discard the hexane.

4. Bring the solution to pH <3 with concentrated HCl (use a hood) and transfer to a 125 ml or 250 ml separatory funnel.

5. Rinse a beaker with 50 ml of nanograde dichloromethane* then add to the separatory funnel. Extract the aqueous layer and dry the chloromethane* layer through anhydrous sodium sulfate washed with chloromethane*. Drain the aqueous portion into a 500 ml flask equipped with an ampule.

6. Perform three extractions with 50 ml of dichloromethane* as described in step 5.

7. Concentrate the organic portion on a steam bath.

8. Adjust the volume to 6 ml and store in a 2 dram vial with Teflon seal cap.

9. Analyze via G.C. using the analytical conditions shown below:

> 1% SP1240DA
> on 100/120 Supelcoport, 3 ft x 2mm I.D. glass
> Helium carrier gas @ 30 ml/min (FID), Argon/methane
> 95:5 @ 30 ml/min (ECD)
> Column temperature 80°C 2 min to 180°C/@ 8°/min.,
>   Det @ 250°C, injector 250°C

All glassware acid washed, rinsed with distilled deionized water, acetone, and CH_2Cl_2.

*Petroleum ether is used instead of CH_2Cl_2 for ECD analyses. Standard curves prepared using authentic PCP.

ANALYTICAL PROCEDURES FOR PENTACHLOROPHENOL - MILL B

1. Place 50 ml sample in 250 ml separatory funnel. Adjust to pH <2 with concentrated HCl.

2. Extract with 50 ml nanograde petroleum ether. Collect organic layer.

3. Repeat step 2 twice with 25 ml nanograde petroleum ether. Combine organic extracts and dry over anhydrous sodium sulfate.

4. Concentrate on a steam bath using a Kuduna-Danish concentrator composed of a 500 ml flask, a 3-state Snyder Column and a graduated 10 ml ampule when necessary for FID analysis.

5. ECD analysis performed on extracts directly or diluted with petroleum ether as necessary.

6. Analyze via GC using the conditions shown below:

   1 percent SP-1240 DA on 100/120 Supelcoport, 3 ft. x 2 mm ID glass.

   A. ECD:

      Argon/methane carrier gas (95/5) at 30 ml/min.
      Injector temperature - 250°C.
      Detector temperature - 350°C.
      Temperature program - Isothermal @170°C.
      Volumes injected - 2-10 microliters.

   B. FID:

      Helium carrier gas at 30 ml/min.
      Injector temperature - 250°C.
      Detector temperature - 350°C.
      Temperature program - 85°C for 2 minutes to 190°C
                            at 10°C/minute increments.

7. Chromatographic performance of underivatized pentachlorophenol was accomplished by the following passification procedure.

A. Glass Column and Injector Sleeve Cleanup

Aspirate 20 to 25 ml of the following slowly through in order given:

1. Chloroform or dichloromethane

2. Acetone

3. Water

4. 50 percent KOH in water

5. Water

6. Concentrated nitric acid

7. Water

8. Concentrated hydrochloric acid

9. Water

10. 85 percent phosphoric acid

11. 200 to 250 ml water

12. Acetone

13. Chloroform .

14. Dichloromethane

15. Dry at 100°C in oven

B. Treatment of Glass Wool with Phosphoric Acid

Place. quantity of silanized glass wool in 85 percent phosphoric acid. Let stand 10 or 15 minutes. Rinse well with water. Soak in acetone, chloroform, and finally dichloromethane. Dry in 100° C oven.

REFERENCES

1. Unpublished information, T.E. Acree and B. K. Wallin.

B-4

ANALYTICAL PROCEDURES FOR PENTACHLOROPHENOL,
GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

EXTRACTION CONDITIONS

1. Adjust pH of 1 liter sample to <2 with concentrated HCl.

2. Spike with deuterated internal standards* (200 to 400 ppb).

3. Serial extraction with nanograde dichloromethane (125x50x50 ml).

4. Break emulsions by glass wool filtration or solvent addition.

5. Dry combined dichloromethane extracts with anhydrous sodium sulfate

6. Concentrate sample by Kuduna-Danish evaporation to 1.0 ml.

7. Add 100 micrograms d_{10} anthracene.

MASS SPECTROMETER - HP 5985

   amu range: 35450
   Scan speed: 300 amu/sec
   A/D per 0.1 amu: 3

GAS CHROMATOGRAPH - HP 5840

   Column: SE-30 SCOT, (SGE D grade 40,000 N_{eff})

   Flow rate: 22 cm/sec at 200°C

   Injection volume: 1 microliter, splitless injection

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*phenol - d_5, octadecanoic acid - d_{35}, naphthalene - d_8

Temperature program: 30 to 260 at 6°C/min.

DERIVATIZATION CONDITIONS

Place 100 microliters sample plus 50 microliters N-methyl N-trimethyl-silyl trifluoroacetamide in conical vial, heat for 15 min. at 70°C, cool to room temperature prior to injection.

QUALITY CONTROL/QUALITY ASSURANCE -
PENTACHLOROPHENOL ANALYSIS

A.   Recovery pentachlorophenol, Gas Chromatography Extraction Procedures:

Trial No.	mg/l pentachlorophenol added	mg/l pentachlorophenol extracted	Percent pentachlorophenol recovery
1	1.0	1.07	107
2	1.0	0.89	89
3	1.0	0.99	99
4	1.0	1.00	100

B.   GC/FID, GC/ECD, GC^2/MS comparison:

Sample No.	GC/FID	mg/l pentachlorophenol GC/ECD	GC^2/MS*
5/21/1	74	76	-
5/22/4	85	98	-
5/22/2	26	26	-
5/22/15	71	82	-
5/23/1	164	128	-
5/23/6	259	293	-
5/23/7	35	40	-
5/23/15	31	37	-
5/23/23B	187	140	-
6/1/15	1.35	.1.55	-
5/31/19	0.18	0.42	-
6/6/13	-	0.112	0.170
6/7/4	-	2.88	2.60
4/26/79	48	50	36.5
5/23/24A	61	57	-
5/23/27A	45	59	-
5/24/6	36	31	-

*Corrected for phenol - d_5 recovery.