


# Reducing Phenol Wastes From Coke Plants

The sources, volumes and concentrations of phenolic wastes  
and methods for reduction by process changes or treatment

*Reference Data Publication compiled by*

**Steel Industry Action Committee**

**OHIO RIVER VALLEY  
WATER SANITATION COMMISSION**





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OHIO RIVER VALLEY WATER SANITATION COMMISSION

January, 1953

Price \$1.00

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## *Foreword*

This is the first of two reports being prepared by the Steel Industry Action Committee on phenol wastes. It reveals the findings from a survey of seventeen plants that produce 80 per cent of the coke in the Ohio River Valley. For the Commission it provides an authoritative summary of sources, volumes and concentrations of by-product coke wastes. For industrial managers it also includes an expert appraisal of process changes and treatment methods by means of which waste discharges can be reduced.

A second report, now being compiled, is designed to serve both the Commission and the steel industry in an evaluation of phenol disposal regulatory requirements.

This report represents the efforts of a sub-committee under the chairmanship of Grant A. Pettit, industrial waste control engineer, Armco Steel Corp. Other members of this group are:

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To all the participants who are contributing in this joint effort to assemble facts on which to promote pollution control in the Ohio River Valley, the Commission makes grateful acknowledgement.

Assisting the sub-committee for the Commission in the assembly and publication of the report were John E. Kinney, sanitary engineer and E. C. Rohmiller, staff assistant.

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Executive Director  
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# *Contents*

BACKGROUND AND SUMMARY .....	4
COKE PLANT OPERATIONS .....	7
Primary Coolers.....	8
Tar Extractor.....	9
Ammonia Absorbers.....	9
Final Cooler.....	9
Gas Scrubbers and Light Oil Recovery.....	12
Coke Quenching System.....	13
Tar Decanter.....	14
Flush Tanks and Storage Tanks.....	14
Ammonia Still.....	14
Dephenolization Equipment.....	14
ANALYTICAL METHODS FOR PHENOL.....	16
DESCRIPTION OF WASTES.....	17
Ammonia Still Wastes.....	17
Light Oil Decanter Wastes.....	17
Quenching Station Wastes.....	18
Other Wastes.....	18
Summary of Contaminated Wastes.....	19
METHODS OF TREATMENT.....	20
Dephenolizing Towers.....	20
Disposal by Coke Quenching.....	23
Chemical Oxidation.....	23
Activated Carbon.....	26
Biological Oxidation .....	26
APPENDIX .....	31
D A A P Method for Analysis of Phenol .....	31
REFERENCES .....	35

## BACKGROUND AND SUMMARY

The Ohio River Valley Water Sanitation Commission in its statement of policy recognized the need of the cooperation by industry located in the Ohio River Basin in order that both the Commission and industry might have a full and comprehensive understanding of the pollution problems involved. The major steel producers of the basin were therefore asked to send representatives to a meeting for a preliminary discussion on this subject. This meeting was held March 2, 1950 in Cincinnati and the Steel Industry Action Committee formed. Realizing the vast complexities of the problem, the Steel Industry Action Committee allocated specific problems to various subcommittees. The function of one of these was to study coke plant wastes.

The Subcommittee on Coke Plant Wastes instituted a complete survey of all the major wastes from the various coke plants of the participating companies. This survey, which required detailed studies by numerous persons, covered seventeen coke plants processing approximately 84,000 tons of coal per day and represents about 80% of the coke producing capacity of the basin. As the phenols seemed to be the most objectionable pollutant in the coke plant wastes, and recognizing that the coke plants in the valley contribute a considerable portion of the phenols in the river, subsequent studies have been concentrated on this phase of the problem.

A proper understanding of the scope of the waste in coke plant operation problems by both regulatory agency and industry is essential. The first report of the committee describes the problems and tells what has and is being done by industry to solve them.

The second report, now in preparation, will tell the effects of phenol wastes on subsequent water users in terms of taste and odor levels, toxicological effects, sensitivities of analytical techniques available, stream purification capacity, and costs of treatment to achieve various degrees of purification of wastes.

These reports are intended to provide basic data that will assist in developing treatment requirements for phenol wastes from coke plant operations.

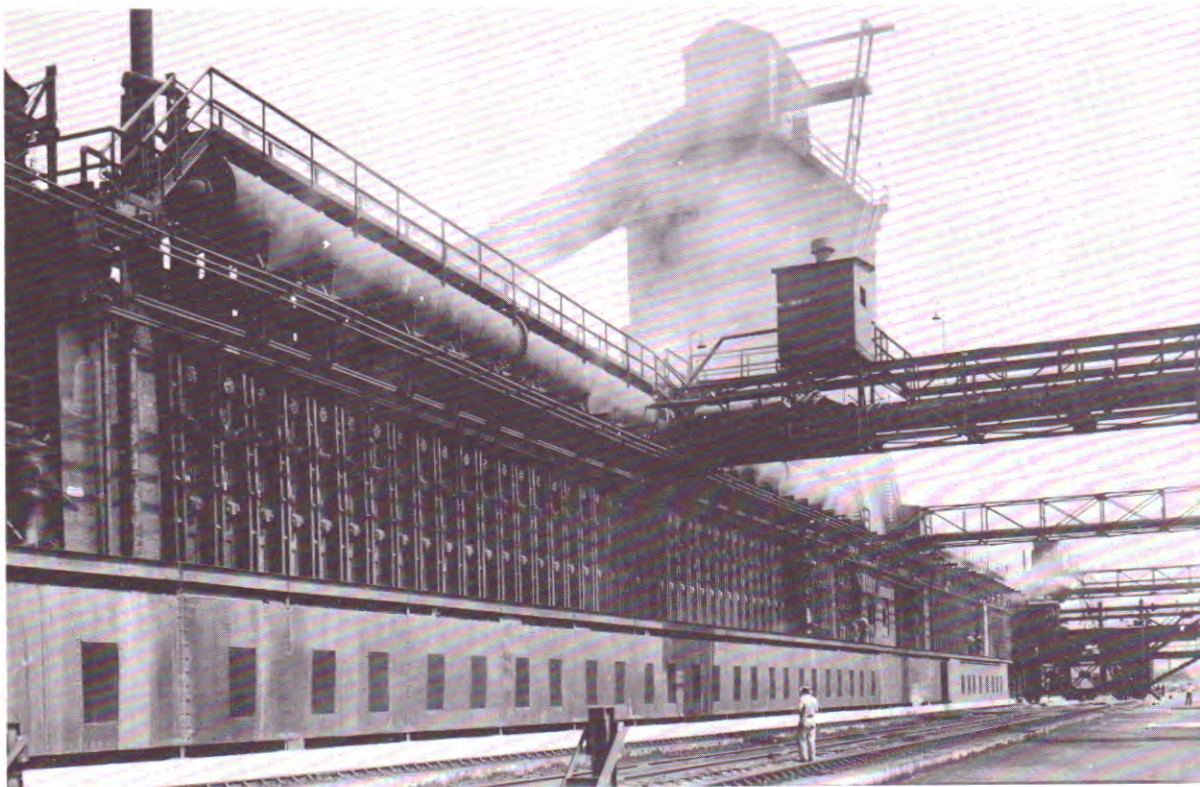
To secure the necessary data to define the amount of phenols being discharged into the various streams, a questionnaire covering individual operations was drafted and sent to the seventeen plants. All the participating companies completed a testing program, using the 4-aminocantipyrine method of analysis, which gave the necessary detailed data. The coordinator of this subcommittee, Grant Pettit, compiled these data. The subcommittee then reviewed the data and when discrepancies appeared, secured rechecks. This has resulted in a definition of the problems at each plant as well as a comparative summary of operating practices.

The sub-committee reviewed each operation, thus obtaining information as to how individual plants were handling various wastes. This review of operations suggested ways to eliminate pollution from all sources except the ammonia still wastes. Most plants have, for example, eliminated pollution from the final cooler by use of atmospheric cooling towers and recirculation of the final cooler water. Others have eliminated contamination from light oil separator condensate by using it as make-up in the final atmospheric cooling tower and pumping the excess to a closed system quenching station.



Quenching coke with phenolic wastes, when permitted, will largely eliminate phenols from this source. However, this process creates a serious corrosion problem within the plant which has not been solved.

Equipment and processes designed to eliminate or reduce pollution of the ammonia still wastes have been studied. These processes are designed to treat ammonia liquor or ammonia still waste for the removal of phenol. Two of these, the liquid extraction and the vapor recirculation processes, are quite well known. The liquid extraction process is designed to treat the ammonia liquor before the ammonia still. It will remove and recover about 98% of the phenol in the liquor. The other process -- vapor recirculation -- will remove about 98% of the phenols, a part of which is recovered. Both of these processes leave a residual phenol content in the still wastes. To reduce this residual phenol content, some additional treatment must be developed. These proposed methods of treatment have been reviewed:



**A battery of ovens for manufacture  
of coke from bituminous coal**

Chemical oxidation -- using chlorine, chlorine dioxide or ozone -- has recently been investigated by laboratory and pilot plant operations and holds promise as a secondary or after treatment method.

The biological oxidation method has been tried, but has not shown much promise with still wastes, except where large quantities of sewage are used as a diluent.

Recently, a pilot plant method using activated carbon seems to have possibilities.

With none of these methods, however, does it appear possible to remove all residual phenol.

It should be recognized that coke plants are not the only source of phenols in streams. Other industries use or produce phenols in their manufacturing processes. Hospitals, institutions, and homes daily use considerable quantities of phenols for disinfection. It is known that decaying vegetation under certain conditions produces phenolic compounds. Phenols from these sources find their way into water courses.



# COKE PLANT OPERATIONS

In general, the manufacture of coke requires equipment for heating bituminous coal out of contact with the air and for recovering the volatile products that are evolved. Each oven is a chamber made of silica brick, the inside dimensions of which are 14 to 19 in. wide, 10 to 15 ft. high, and about 40 ft. long. The ovens are arranged side by side in groups of thirty or more, each group called a battery. The ovens are heated by burning gas in flues between the side walls of the adjacent ovens. The coal is charged through holes on the top of the oven by hopper bottom cars that operate on tracks over the top of the battery. The gases and tars that are evolved from the coal in the ovens (Figure 1) escape through pipes called ascension or standpipes that are located on top of the ovens. To discharge the coke, large doors are removed from each end of the oven and a pushing machine carrying a powerful ram pushes the coke out of the oven into a specially designed car known as the quenching car. The coke leaving the ovens is red hot and is carried by the car to a quenching station, where it is cooled by being sprayed with water. The coke is then delivered to the coke handling equipment for sizing and transportation to the blast furnace. The quenching car returns to receive coke from another oven.

The volatile products of the coal leave the ovens through the standpipes and are collected in a large gas main running the length of the battery. Here the gases are cooled and saturated with water by flushing liquor sprays. The cooling of the gas that occurs in the collecting mains also condenses out most of the tar. The liquor mixed with the condensed tar drains through a decanter to remove the tar.

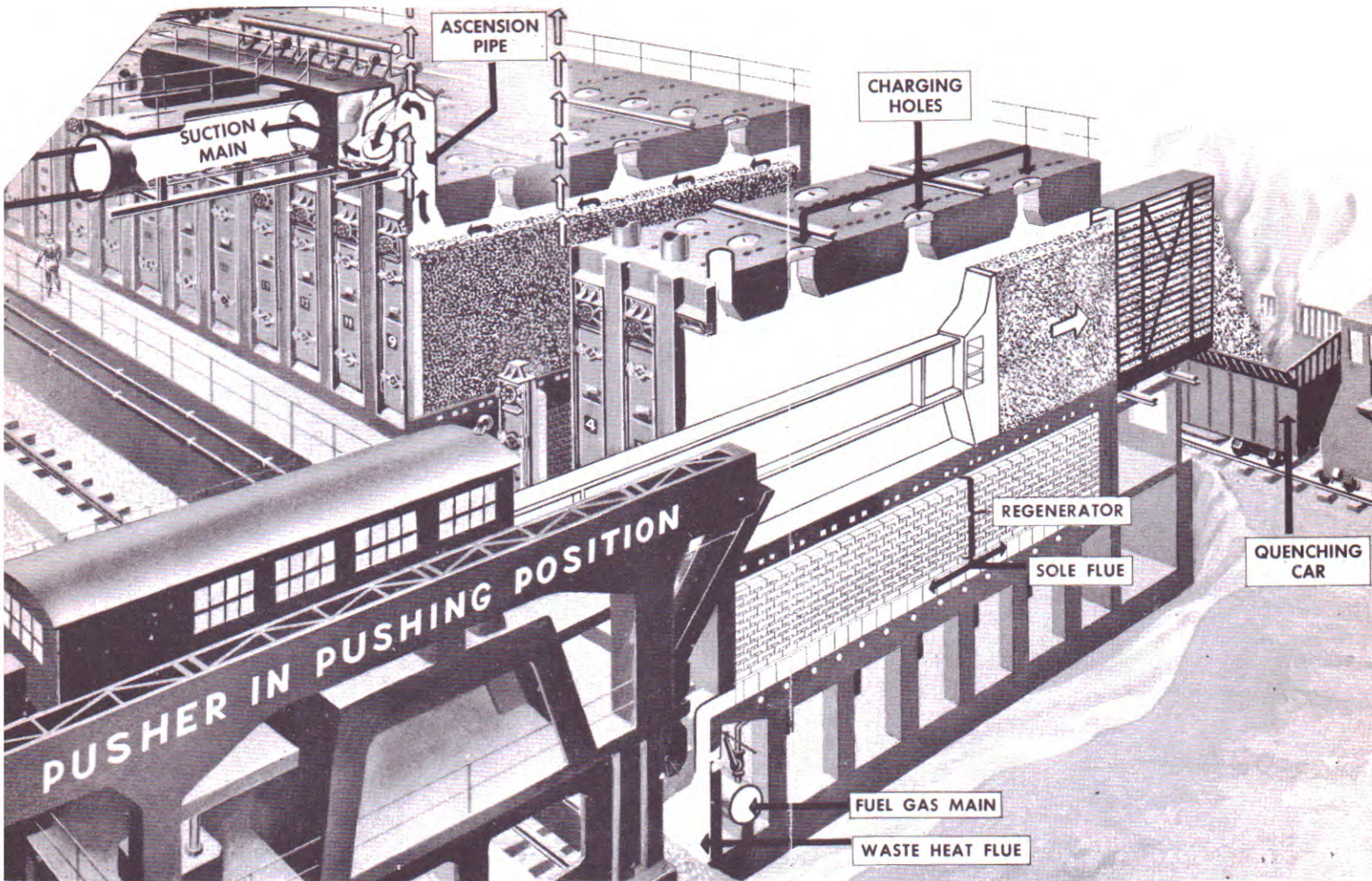
The gas leaving the collecting main is usually about 80°C and is saturated with water vapor. The gas passes through the primary coolers where most of the moisture is condensed and the gas cooled to about 20 to 30°C. This condensate drains into the tar decanter and is mixed with flushing liquor being recirculated through the collector main sprays. This condensate, or ammonia liquor as it is known, contains materials in solution such as ammonia, ammonium chloride, hydrogen sulphide, phenols, etc.

The flushing liquor and the condensate from the primary cooler drains from the tar decanter to a sump, called flush tank, from which it is pumped back to the collecting main. The overflow from the sump is pumped to the ammonia stills in order to remove the free and fixed ammonia and other volatile compounds. In many cases at this point the overflow also passes through a dephenolizing plant for the removal of most of the phenols.

After being cooled in the primary cooler, the gas passes through the balance of the equipment for coal chemical recovery and gas purification, usually in this order:

1. Exhausters draw the gas from the collecting main under suction and force the gas under pressure through the remaining equipment.
2. Tar extractors eliminate tar that would otherwise be carried by the gas as a mist or fog.
3. Ammonium absorbers scrub the gas with dilute sulphuric acid. The ammonia is removed from the gas and recovered as salable ammonium sulphate. Other basic materials are removed and can be recovered at this point in the process.
4. Final coolers remove the heat of compression of the exhausters and the heat of





**Koppers coke-oven construction and operating details**

reaction in the saturators from the gas. A part of the naphthalene is removed from the gas in the final cooler system.

5. Light oil scrubbers remove the benzene and similar oils from the gas. The crude light oil mixture is either sold as such or is converted to refined products such as pure benzene, toluene, xylene, solvent naphtha, and residue.

The use of these processes and their sequence varies among different plants. At some plants, for example, the tar extractors treat the gas before it enters the exhausters although the reverse order is usually followed. A few plants remove the hydrogen sulphide from the gas.

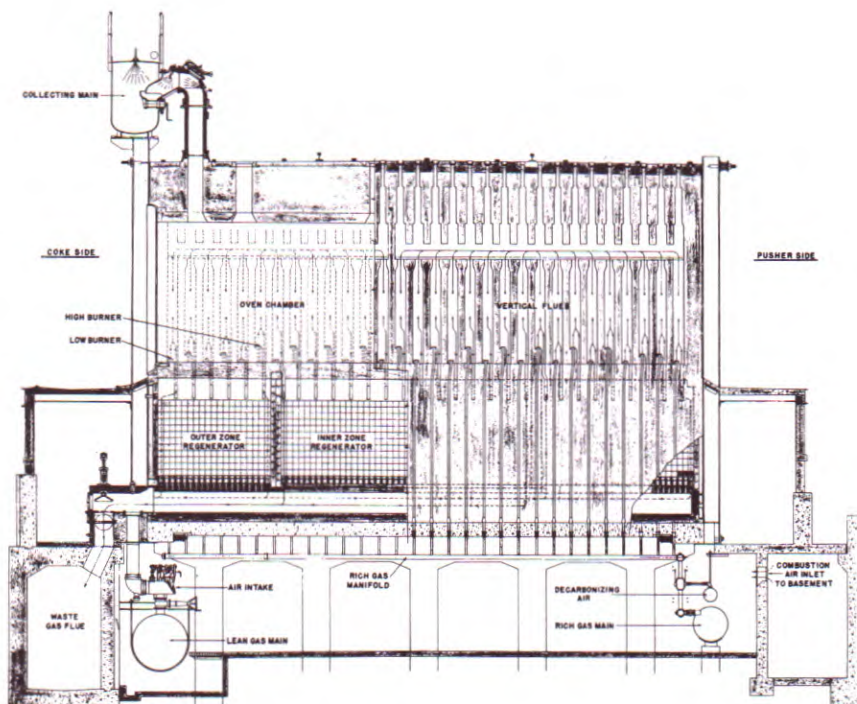
The "Coke-Plant Flow Sheet" in Figure 2 is not intended to be complete in every detail but it covers the major operating equipment of a coke plant and emphasizes the sources of pollution from these operations.

## PRIMARY COOLERS

Two types of primary coolers are in general use: indirect and direct. Neither type contaminates the cooling water used.

In indirect coolers the gas is cooled by passing over a series of cooling coils. The condensate liquor is collected in the bottom of the cooler and pumped to the tar decanter for the removal of tar, ammonia stills for ammonia removal, and sometimes to a dephenolizer for the removal of phenol. The cooling water does not come in contact with the gas and is free from contamination.





**A sectional view of the Wilputte underjet coke oven**

In the direct type of cooler the gas passes up through a tower countercurrent to the cooling liquor being sprayed from the top of the tower. This cooling liquor is pumped through cooling coils and returned to the tower for recirculation. The excess cooling liquor is sent to the tar decanter for further processing as above. The actual cooling water used on the cooling coils is free of contaminants and may be reused in the plant or discharged to the sewer.

## **TAR EXTRACTOR**

Tar and ammonia liquor extracted from the gas in the tar extractor is pumped to the tar decanter for further processing.

## **AMMONIA ABSORBERS**

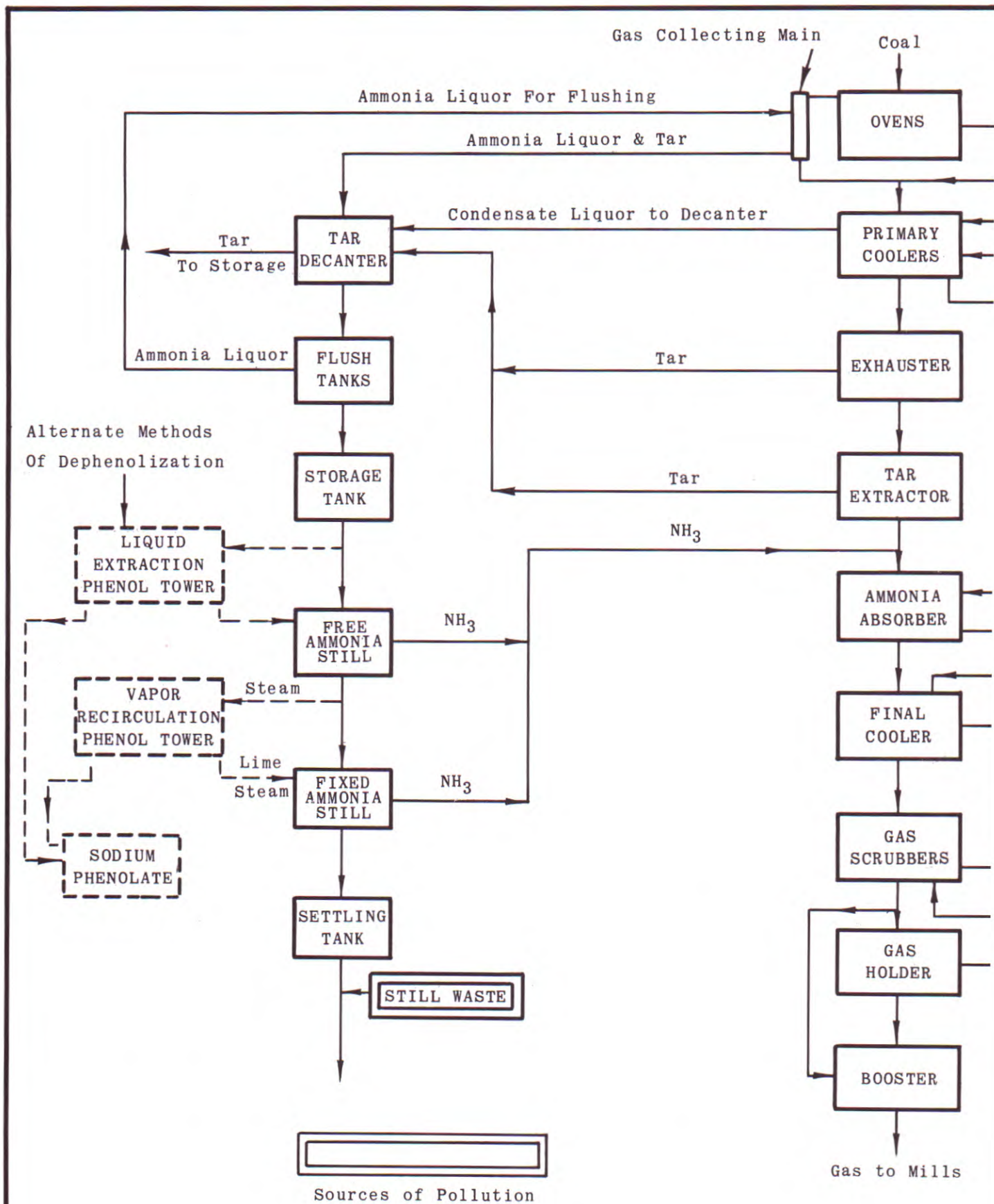
Ammonia absorbers are connected in a closed system. The gas passes through a dilute solution of sulphuric acid which removes the ammonia as ammonium sulphate.

## **FINAL COOLER**

Final coolers all operate on this principle; the gas flows up through the tower countercurrent to the flow of cooling water being sprayed in top of the tower. This liquid, in direct contact with the gas, dissolves water soluble constituents from the gas and carries along the insoluble naphthalene condensed from the gas.

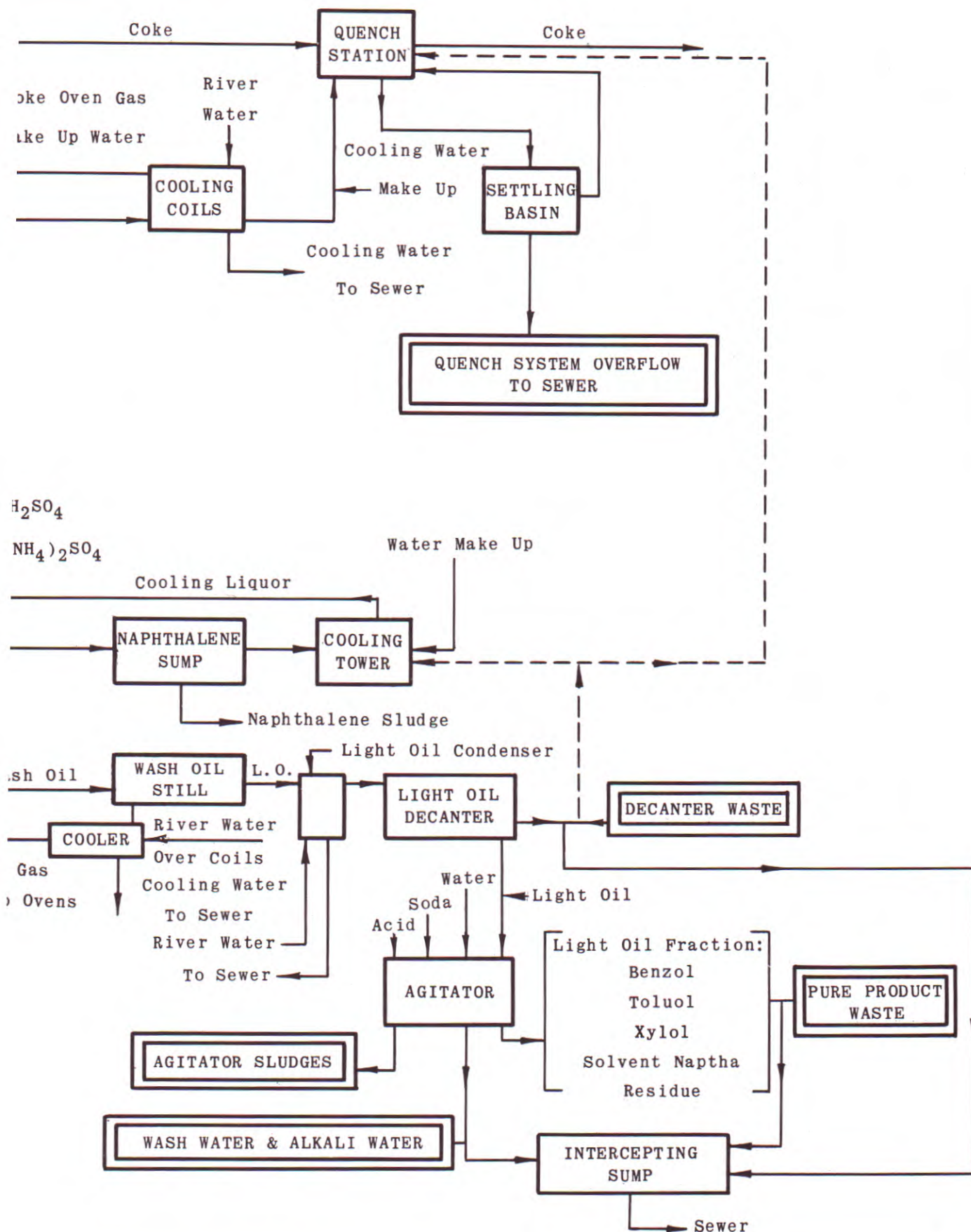
The processing and reuse of this liquid has served to remove the largest source of contamination from coke plant effluents.

Most plants have placed one of two systems in operation to accomplish this job:



## COKE PLANT ...TYPICAL OPERATION





the recirculating closed system and the recirculating system with overflow to quenching station. These systems are basically the same except that one is closed entirely and the other may require a periodic draw-off which may be used at the quenching station or pumped to the ammonia liquor system.

The steps of these systems are as follows: The liquid from the base of cooling tower flows to a sump where the naphthalene is skimmed from the surface. The liquid is then pumped to a cooling tower and returned to the final cooler to complete the cycle. The amount of evaporation in the cooling tower balances the condensation from the gas in the final coolers so that there is little, if any, waste to be discarded. Design of equipment may be such that there is no discharge of contaminated flow except under unusual atmospheric conditions which infrequently occur during the summer. Where there is some periodic discharge it is usually very small and is pumped to the quenching or ammonia liquor system.

Very few plants now use the old straight-through system where cooling water is pumped once through the final cooler and used either for quenching or discharged to the sewer. While the development of the recirculating closed system began about 25 years ago, most of the conversions to this type of operation have occurred within the last ten years. A summary of the final cooler systems of the 17 plants studied is:

Recirculating Closed System	7 Plants
Recirculating System with Overflow to Quenching Station	6 Plants
Recirculating System with Overflow to Sewer	1 Plant
Straight-through System - To Quench	1 Plant
To Sewer	1 Plant
No Final Cooler Used	1 Plant

## **GAS SCRUBBERS AND LIGHT OIL RECOVERY**

The removal of the crude light oil from the gas is accomplished by scrubbing the gas with an absorbent, commonly called wash oil. The light oil is then stripped from the wash oil by steam distillation in the wash oil still. The wash oil is then cooled and returned to the scrubbers. The vapors leaving the still are condensed in the light oil condenser and the water (condensed steam) is then separated from the light oil in a decanter (See C following page)

The balance of the light oil recovery system is devoted to the separation of the light oil into its constituent compounds. This is accomplished by fractional distillation and purification by acid and caustic washing in the agitator.

### **A. Wash Oil Still and Cooler**

The wash oil stripped from its light oil in the wash oil still is passed through an indirect cooler and returned to gas scrubbers. The cooling water does not come in contact with the wash oil and is therefore not contaminated.

Indirect Cooling - 17 Plants

### **B. Light Oil Condenser**

All plants studied use the indirect type of cooling in the light oil condenser



with no resulting pollution of the cooling water.

#### Indirect Cooling - 17 Plants

### C. Light Oil Decanter

The light oil from the decanter is further processed as indicated under Light Oil Recovery. The water (condensed steam) separated from the light oil, being contaminated with phenols and other organic compounds, passes to an intercepting sump and is disposed of as follows:

To Quenching Station	- 8 Plants
To Final Cooler & Quenching Station	- 2 Plants
To Sewer	- 7 Plants

### D. Agitator

In the agitator the crude light oil is washed with sulphuric acid to remove unsaturated compounds. The resulting resinous sludge called agitator sludge is disposed of as follows:

To Dump	- 13 Plants
Burned	- 3 Plants
No Agitator Used	- 1 Plant

After draining the acid sludge from the agitator, some plants wash the light oil with water. The wash water is disposed of as follows:

To Quenching Station	- 3 Plants
To Sewer	- 8 Plants
Not Used	- 5 Plants
No Agitator Used	- 1 Plant

A caustic wash follows the acid and water washes to neutralize the liquid before distillation of the oil into its component fractions. This is disposed of as follows:

To Quenching Station	- 3 Plants
To Sewer	- 13 Plants
No Agitator Used	- 1 Plant

## COKE QUENCHING SYSTEM

In the quenching station the incandescent coke is cooled by large volumes of water sprayed on the coke. The sensible heat of the coke evaporates a substantial portion of the cooling water used, necessitating constant addition of make-up water to the

system. The unevaporated water flows to a settling basin where the fine particles of coke settle and are periodically removed. The clear water from the settling basin is recirculated to the quenching tower. In some cases additions of used water from other sources in the plant cause some overflow from this system. Most plants operate as a closed system without any overflow.

The closed system is recommended as the most desirable method of eliminating pollution from this operation. Survey of the plants showed:

No overflow - 11 Plants

Some Overflow to Sewer - 6 Plants

## TAR DECANter

The tar recovered from the decanter is placed in storage to be either sold or refined by further processing. The ammonia liquor used for flushing runs to the flush tanks from which it is recirculated to the collecting mains.

## FLUSH TANKS AND STORAGE TANKS

As the volume of flushing liquor builds up the overflow is placed in a storage tank from which it is pumped through the balance of the ammonia recovery process.

## AMMONIA STILL

The ammonia still is usually considered as two parts, the free and fixed stills.

In the free still ammonia, hydrogen sulphide, carbon dioxide, and hydrogen cyanide and other low boiling compounds are liberated from the ammonia liquor by steam distillation. In the fixed still the ammonia salts are decomposed by the addition of milk of lime and the ammonia liberated by steam distillation. Vapors from the still are conducted to the gas stream at some point before the ammonia absorber. The ammonia free liquor from the stills, termed still waste, is disposed of as follows for the plants without dephenolizers:

To Quenching System - 9 Plants

To Sewer - 1 Plant

## DEPHENOLIZATION EQUIPMENT

The dephenolizing equipment is used in conjunction with the ammonia stills to reduce the phenol content of the ammonia still wastes. The two processes used commercially are the liquid-extraction process and the vapor recirculation system. A description of these two processes follows:

### A. Liquid Extraction Process

Benzol or light oil is mixed with the ammonia liquor to extract the phenols contained in the liquor. The dephenolized liquor is then processed in the ammonia still.

The phenol in the light oil is absorbed by a caustic soda solution forming sodium phenolate which is a salable product. The dephenolized light oil is reused in the process.



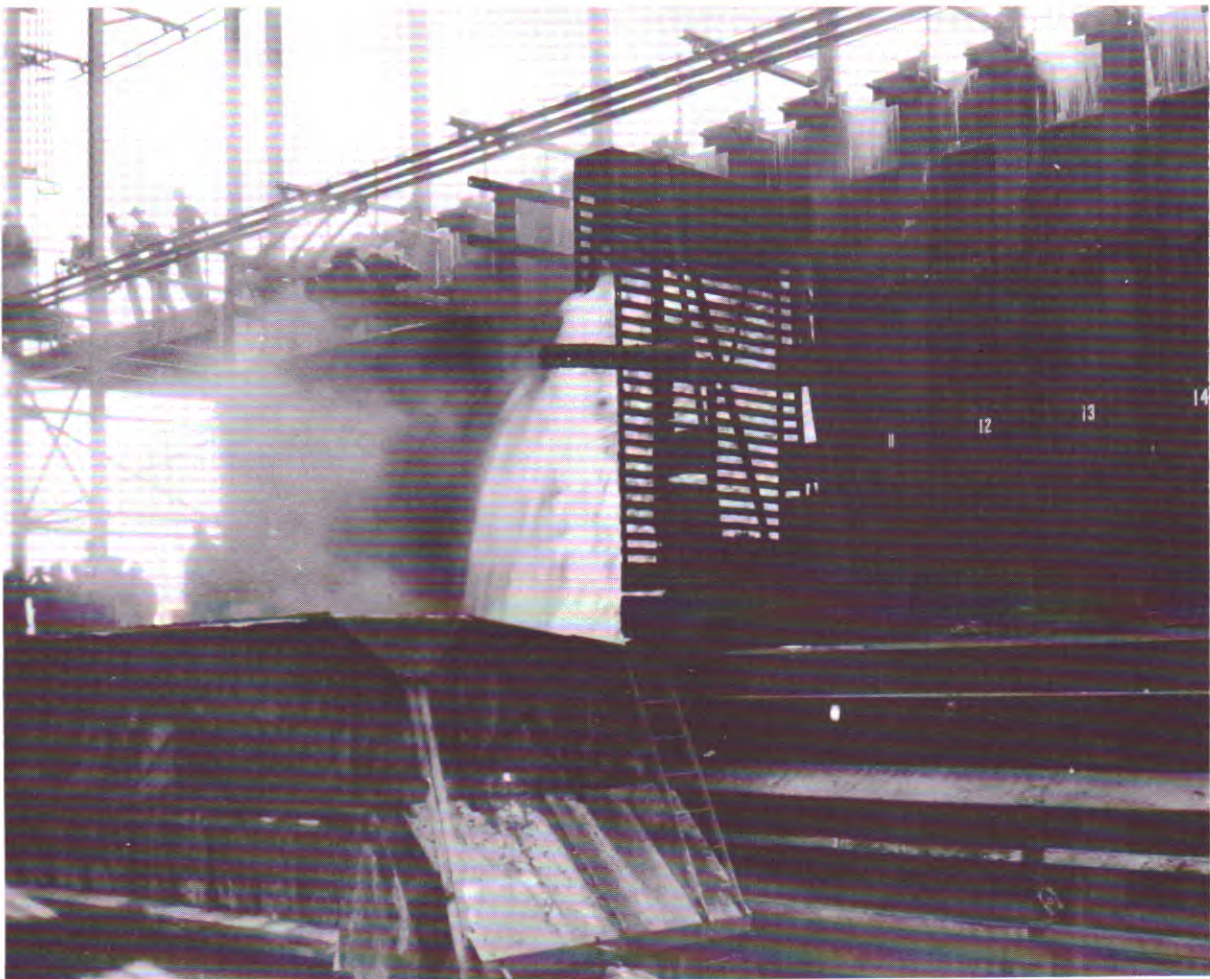
## B. Vapor Recirculation Process

The ammonia liquor, after passing through the free still, is pumped to a tower where the phenols are vaporized by a current of steam. The steam and phenol vapors are then brought in intimate contact with a solution of caustic soda which converts the phenols to sodium phenolate. The steam is reused in the process. The dephenolized liquor is returned to the fixed ammonia still.

After the fixed ammonia still the dephenolized liquor is disposed of as follows:

To Quenching System - 1 Plant

To Sewer - 6 Plants



Coke discharged from the oven to the quenching car



# ANALYTICAL METHODS FOR PHENOL

All components of coke plant wastes reported upon except phenol were determined by using methods of analysis as outlined in "Standard Methods for the Examination of Water and Sewage" (1).

The problems of accurate phenol analysis were aptly presented in the Ohio River Valley Water Sanitation Commission's report on "Phenol Wastes - Treatment by Chemical Oxidation" (2) as follows:

"Because analytical methods for phenol determination were an important part of the project, considerable thought was given to the several accepted methods for determination of phenol. But reproducibility of results with different methods is lacking. Variation in interfering substances found in industrial wastes complicates the correlation of these methods. Further difficulty arises from the desire to have a method with sensitivity applicable to the range of taste and odor production by phenols.

"To date the Gibbs test has been the criterion in determining phenol waste concentrations. Using the method as now outlined in "Standard Methods" (9th Ed., 1946, p 216) provides a sensitivity of about 25 parts per billion for a chemist skilled in this technique."

Several disadvantages of the Gibbs method of determining phenols have been recognized for some time. These disadvantages are:

1. Time required for each determination (18 hours).
2. Failure to detect all phenolic compounds.
3. Lack of sensitivity below 25 parts per billion.

The Subcommittee on Coke Plant Wastes, being aware of these shortcomings, instituted a program of research on analytical methods for determining phenols. A detailed study of several methods of phenol analysis as applied to coke plant wastes was made by the member companies. The results of this work indicate that the distilled 4-aminoantipyrine (D.A.A.P.) method is a rapid method that detects all phenols and is sensitive down to 100 parts per billion. Therefore, the Committee on Coke Plant Wastes has adopted this method for the analysis of all coke plant wastes. The Committee also has recommended that this method be included as an alternate to the Gibbs method in the 1952 revision of "Standard Methods for the Examination of Water and Sewage".

The desirability of having a method sensitive in the low ranges of taste and odor of phenols encountered in the receiving bodies of water has led to the development of a sensitized technique of the D.A.A.P. method by the U. S. Public Health Service. This method is being field tested by the member companies.



## DESCRIPTION OF WASTES

The summary of the data from the 17 plants surveyed indicates the following volumes of contaminated wastes from a coke plant:

TABLE I

Source of Waste	Gallons/Ton of Coal Carbonized		
	Min.	Max.	Ave.
Ammonia Still with Dephenolizer	18.5	41.9	31.4
Ammonia Still without Dephenolizer	23.0	75.0	36.8
Light Oil Decanter	3.0	29.0	13.0
Misc. All Others	.12	.25	.2

### AMMONIA STILL WASTES

The ammonia still wastes produced by processing the ammonia liquor has the following analysis:

TABLE II

Determination	Concentration (ppm)					
	With Dephenolizer			Without Dephenolizer		
	Min.	Max.	Ave.	Min.	Max.	Ave.
Phenols	40	400	158	350	2820	1320
Ammonia	20	255	110	21	470	155
Chlorides	2350	7500	5400	1150	5500	4350
Sulphates	215	1330	744	145	940	468
pH	9.5	11.5	10.0	8.8	12.8	11.3

### LIGHT OIL DECANter WASTES

The analysis of the waste from the light oil decanter are as follows:

TABLE III

Determination	Concentration (ppm)		
	Min.	Max.	Ave.
Phenol	28	164	77
Ammonia	2	34	17
Chlorides	7	107	51
Sulphates	5	135	37
pH	5.2	8.5	6.2



The wide difference between the minimum and maximum results shown in Tables I, II, and III reflects the differences in the processes and materials used in making coke in the seventeen reporting plants. No two of these plants operate with the same equipment or use the same raw materials. The variations are due to the following factors:

Plant Design -- The ages of these plants vary from those built 40 years ago to those just recently completed. Improvements in plant design during these years have resulted in a reduction in the volumes of the contaminated wastes.

Raw Materials -- Coals vary in both chemical composition and physical characteristics from mine to mine and from different sections in the same mine. These variations affect the quantity and quality of liquor produced. For example, each 1% of additional moisture in the coal produces 2.4 additional gallons of ammonia liquor.

Operations -- The operation of a coke plant is determined by the age and design of the plant, the raw materials used, and the coke to be produced. Blast furnace operations require different types of coke to produce the various types of pig iron required in steel production. These types of coke are produced by varying the raw materials and operating conditions such as temperature and coking time.

All these variations affect the quantity and quality of the waste liquor produced. With the best operating practice the control of the quantity and quality of wastes produced is limited by the design of the plant, raw materials used, and coke requirements.

## QUENCHING STATION WASTES

Our survey indicates that any overflow from quenching stations not receiving polluted water from other sources will not contribute to stream pollution, but those stations being used as disposal units for contaminated wastes from other points show a very wide variation of analysis and will contribute to stream pollution if there is an overflow. Therefore, we recommend that all such systems be closed.

## OTHER WASTES

As all agitator sludges are either placed on dump or burned and do not contribute to stream pollution no analyses have been attempted.

The total volume of all the other miscellaneous wastes, which includes pure products, water wash, and alkali wash wastes, is less than 0.2 gallons per ton of coal carbonized and was found to contribute practically nothing to stream pollution.



## SUMMARY OF CONTAMINATED WASTES

This survey resulted in the following summary of the sources, average volumes, and average analyses of the contaminated wastes produced in a coke plant.

TABLE IV

Source of Waste	Phenols ppm	NH <sub>3</sub> ppm	Cl ppm	SO <sub>4</sub> ppm	pH	Gal/Ton Coal Car- bonized	Lbs Phenol /Ton Coal Carbonized
Ammonia Still with Dephenolizer	158	110	5400	744	10.0	31.4	.041
Ammonia Still without Dephenolizer	1320	155	4350	468	11.3	36.8	.404
Light Oil Decanter	77	17	51	37	6.2	13.0	.008
Misc. All Others	53	-	-	-	-	.2	.00008



## METHODS OF TREATMENT

The problem of stream pollution has long been recognized as a major problem by the coke producing industry. Through improvements in operation and by process changes the major portion of the pollution load from coke plants has been eliminated.

The Subcommittee on Coke Plant Wastes made a thorough study of coke plant operations and waste disposal methods. These studies have pointed the way to further reduction in the pollution load through process improvements. The treatment of the remaining residuals is still a problem. This report includes a study of the various treatment methods in use, those on which pilot plant studies have been made, and those still in the laboratory stage. A description of these processes follows.

### DEPHENOLIZING TOWERS

The earlier work on this problem resulted in the development of the patented Tiddy-Heffner and other liquid extraction processes. Tiddy and Heffner extracted the phenols from ammonia liquor with crude benzol or light oil before the liquor goes to the ammonia still, and then separated the phenols from the solvent by distillation.

Engineers at the National Tube Company at the Lorain, Ohio Plant, pioneered a similar liquid extraction process but recovered the phenols from the solvent by extraction with a strong caustic soda solution. This process was further developed and refined by D. W. Wilson for the Iroquois Gas Corporation, by Robert M. Crawford for the Hudson Valley Coke and Product Corporation at Troy, New York, by Hugh E. Jones of the Domestic Coke Corporation at Fairmont, West Virginia, and others.

The recovery of the phenols by caustic extraction proved to be more economical than by distillation; the Tiddy-Heffner Process, involving distillation, therefore gave way to the former. As a result of this early work, liquid extraction plants using benzol or light oil were built at the above plants during the period 1920 to 1926.

The Sharon Steel Plant at Fairmont, although over 25 years old, is in excellent condition and still operates efficiently. Operating data from this plant indicate the consistent removal and recovery of 97 to 98% of the phenols in the ammonia liquor by the dephenolizing unit. Some additional removal in the ammonia still which follows this equipment brings total removal to over 99%.

This equipment has operated continuously since installation with but little repair cost. The only major repair during this period was the recent renewal of the bottoms of both phenol absorbers. The three six-foot-thick banks of coke packing have been replaced only once or twice during this time. The cost of operating this plant is quite low because the ammonia still operator controls it as a part of his job and because the only raw material purchased is utilized efficiently.

Over 85% of the caustic soda in the solution used to extract the phenols from the benzol is converted to sodium phenolate. A part of the remaining 15% reacts with  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and other acidic compounds absorbed by the benzol from the ammonia liquor. The remainder does not combine chemically but remains in the system as caustic soda. Its function is to push the reversible reaction  $\text{C}_6\text{H}_5 + \text{NaOH} = \text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{O}$  as far to the right as possible. When using 23% NaOH solution under the above conditions, only 0.01% (100 ppm) of phenols remain in the benzol after caustic extraction.



At Fairmont about 1.2 gallons of benzol is circulated per gallon of ammonia liquor treated. Each gallon of liquor treated carries about 0.0024 gallons of benzol to the ammonia still. This is about one third more than can be accounted for by the solubility of benzol in water. The excess over that actually dissolved in the liquor is carried along as an emulsion or by entrainment in the liquor.

The benzol carried to the ammonia still by the liquor is not lost but is evaporated and carried by the vapors from the still back to the gas stream from which it is reabsorbed in the gas scrubbers by the wash oil. This recycling of the benzol will add about 2.0% to the light oil vapors to be absorbed from the gas, when about 25 gallons of ammonia liquor is produced per ton of coal coked.

After reviewing the operation of this very simple and efficient plant, the question arises as to why additional plants of this type have not been built. The explanation may be that the industry has depended largely upon contractors for such equipment and that the contractors have promoted only the equipment upon which they had patent protection.

The only recent plants employing liquid extraction is one of the Fairmont type built by the Wilputte Coke Oven Division, of Allied Chemical & Dye Corporation, for their plant at Ironton, Ohio and a plant built at Aliquippa, Pennsylvania for the Jones & Laughlin Steel Company by the Koppers Company.

The plant at Ironton is essentially the same as that at Fairmont, but with a few refinements. One of these is a water washing tower to remove  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and other acidic constituents from the benzol before the caustic soda wash. This is reported to decrease soda consumption. This would, however, produce a contaminated effluent which would require treatment before disposal.

Data from the plant at Aliquippa, Pennsylvania indicated that it was doing an excellent job. This plant appears more complicated than the one at Fairmont but with little increase in efficiency. The plant at Aliquippa uses three stages of centrifugal pumps as contacting apparatus with separators and pump chambers for each stage instead of a coke packed tower. The excessive shearing force in these pumps causes emulsions which are quite a problem. This plant consistently shows a total phenol removal of about 98%.

Liquid extraction plants, using solvents other than benzol or light oil, have been proposed and used. Some of these solvents are tricresylphosphate, and related compounds, petroleum solvents, trichloroethylene, etc. None of these seem to be as economical as benzol or light oil produced in the carbonization of coal. The use of compounds other than those from the coal coking process would entail the construction of special recovery equipment for such compounds, while the usual coke plant gas scrubbers suffice when coal chemicals are used.

Several years after the liquid extraction plants at Fairmont and other points were built, the Koppers Company developed and introduced the vapor recirculation process for phenol removal and recovery. In this process water vapor is recirculated upward through a tower having two or three sections. The vapor first passes through one or two caustic soda scrubbing sections where it is freed of phenols, then on up through the hot ammonia liquor from the free leg of the ammonia still. The vapor removes most of the phenols that remain in the liquor, then passes down through a duct to a blower and is again forced upward through the caustic section or sections where the phenols are again removed.



In this system, 40 to 50% of the total phenol is removed in the free leg of the ammonia still, about 40% in the dephenolizing unit, and the remainder up to about 90 to 95% total removal in the fixed leg. One of the very disturbing facts about this unit is the variability of removal results. A system may run quite well for a few days and suddenly go out of control for no understandable reason.

To remedy this fault, the Koppers Company a few years ago redesigned this unit. The wooden hurdles in the ammonia liquor section were retained but the steel turning packed caustic soda section was replaced by five trays of bubble caps. The use of bubble caps increased the pressure drop through the tower considerably and thus increased the power cost.

Such a plant was built for the Crucible Steel Company at Midland, Pa. and put into operation in early 1950. Early test results seemed quite encouraging. Later operating data were not too good. Results would be good for a few days and then fall off. In the opinion of C. V. Thompson, Superintendent of the coke plant, cleaning the ammonia liquor by providing additional settling time has improved the operation of the tower considerably. He stated that operation during August 1951 had been the smoothest to date. Data covering this period is given in Table V.

**TABLE V - CRUCIBLE STEEL COMPANY DEPHENOLIZER DATA (August, 1951)**

Weak Liquor	Phenol Concentration (ppm)		
	Before Tower	After Tower	Still Waste
1750	930	5	3
1750	700	7	5
1600	350	8	4
1290		6	4
1460	530	50	11
1420	530	33	20
1800	660	22	20
1840			7
2240	720	80	7
1850	700	80	30
1800	740	18	7
1750	930	80	70
1750	550	80	70
1420	440	8	6
1130	580	6	5
1440	890	15	9
1420	750	10	8
1290	530	66	62
1460	440	27	9
1380	740	83	64
Steam to NH <sub>3</sub> Still 2.9 lbs/gallon of ammonia liquor.			



Reference to Table V indicates that results by present day standards are quite good for about 65% of the days for which data are given, for about 10% fair, and for the remaining 25% poor. Mr. Thompson believes that with closer control consistently good results can be obtained.

It should be observed that excessive steam is being used on the ammonia still (2.9 instead of 2.2 lbs. per gallon of liquor to the still). This excessive steam removes phenols from the liquor that usually goes to the dephenolizing tower. Then, too, the liquor at this plant contains less phenols than at many plants. Mr. Thompson plans to reduce steam to 2.2 lbs. per gallon and observe the effect on the effluent from the still.

From the discussion above it will be noted that the liquid extraction dephenolizing process is capable of recovering more than 98% of the phenols entering it. The vapor recirculation process also seems capable of removing about 98% when used in connection with the still but leaves about twice as much chemical oxygen demand as the former process.

In addition to the large capital investment required, the above processes involve high operating cost due to labor, reagents, and power. These costs are such that even in the case of the liquid extraction process the recovered product pays only a portion of the total cost.

## DISPOSAL BY COKE QUENCHING

The use of phenol contaminated wastes for coke quenching has been practiced by several companies for a number of years. This method involves using the contaminated wastes as part of the cooling water necessary to cool the hot coke at the quenching station. With this method the quenching system must be a closed system.

Numerous objections to this method may be cited. It is quite expensive due to the corrosion of coke handling and adjacent plant equipment. This corrosion is due to the high concentration of calcium chloride present in these wastes as shown on page 17 of this report. In addition to the corrosion problem this method presents an air pollution problem and cannot be used where plants are located in densely populated areas.

## CHEMICAL OXIDATION

The report "Phenol Wastes - Treatment by Chemical Oxidation" (2) covers the findings during a recent investigation of the oxidation of phenols with chlorine, ozone, and chlorine-dioxide. This investigation concerned itself with the dephenolized ammonia still waste from the coke plant. Phenols is the broad term applied to the mono-hydroxy derivation of the benzene ring. Included are phenols, cresols, and xylenols. Destructive distillation of coal produces all the phenols as well as many other organics, all of which may have an influence on treatment methods.

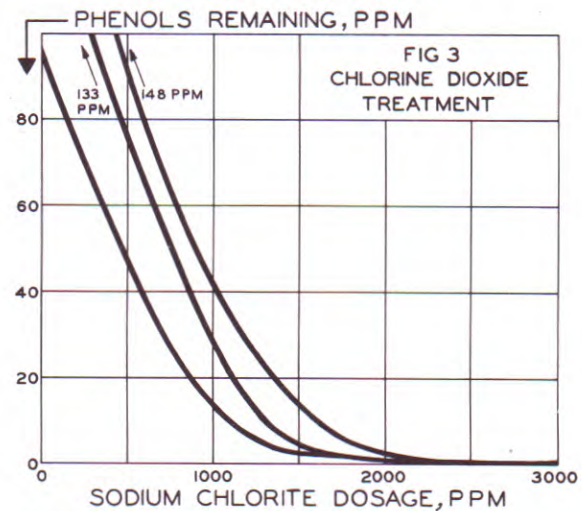
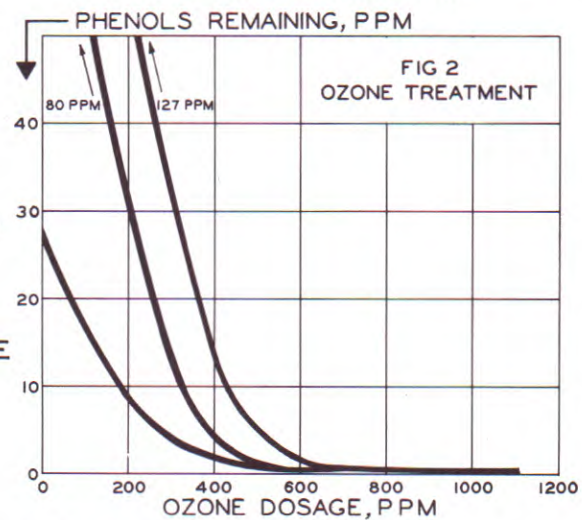
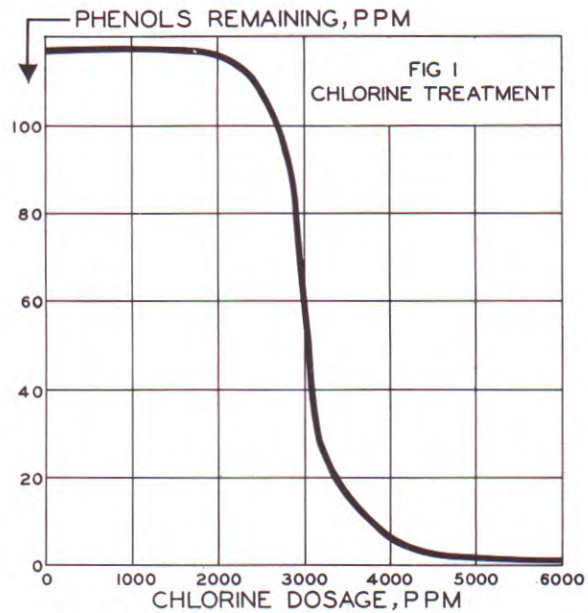
Variation in the composition of the phenols is a function of coal used, coking time and temperature. During these experiments the phenol concentration ranged from 28 to 332 ppm. The preliminary laboratory studies - confirmed by pilot plant operations - provided the information by which performance of the three oxidants, chlorine, ozone, and chlorine-dioxide can be compared. Here are the results in brief as outlined in the above report.

1. Phenols can be oxidized by chlorine, ozone or chlorine-dioxide. Economics and merits of application of each process will depend upon volume and



# TYPICAL REACTION CURVES FOR PHENOL OXIDATION

PHENOLS IN DEPHENOLIZED  
BY-PRODUCTS COKE-PLANT  
WASTE CAN BE EASILY REDUCED  
TO LOW CONCENTRATIONS.  
FURTHER REDUCTION DEMANDS  
DISPROPORTIONATE DOSAGES  
OF CHLORINE, OZONE OR CHLORINE  
DIOXIDE.



OHIO RIVER VALLEY WATER SANITATION COMMISSION

strength of wastes to be handled, the degree of treatment required, and other conditions that are peculiar to each problem. Relative cost of operation may be estimated from the dosage data shown in typical reaction curves with this report.

2. Reaction curves show a substantial reduction in phenol attained with small oxidant dosage, but increasingly high dosages are required as phenol is further reduced.
3. Oxygen consumed and biochemical oxygen demand were materially reduced (over 60%) by each of these oxidants.
4. Phenolic content of coke plant waste cannot be used as sole basis for determination of required dosage of oxidizing agent. Phenols represent but part of the oxidant demand. No correlation was found between oxygen consumed and oxidant demand.
5. No temperature adjustment of waste is required for ozone or chlorine-dioxide treatment. Temperatures above 45 degrees C in chlorination may cause formation of chlorates, thus requiring larger chlorine dosages.
6. Chlorine treatment requires pH adjustment during oxidation, preferably to a range of 7.0 - 10.0. Ozone and chlorine-dioxide oxidized the phenol at all pH's tried; best results were obtained for this waste by adding ozone or chlorine-dioxide to the waste as it came from the still at pH above 11.5 and with no further adjustment in pH.
7. Chlorine treatment requires prior satisfaction of ammonia demand in order to reach the breakpoint potential necessary for phenol oxidation. Ammonia content of the waste has little or no effect on ozone or chlorine-dioxide treatment.
8. Partial treatment is possible with both ozone and chlorine-dioxide without formation of chlorophenols. Chlorination requires complete oxidation to prevent formation of chlorophenols.
9. Residual chlorine in a concentration of several hundred parts per million is required in order to reduce phenol to low concentrations or to effect complete removal. Excess chlorine can be removed by granular activated carbon. Residual ozone or chlorine-dioxide can be controlled to less than one ppm and requires no aftertreatment.
10. Chloride content of waste is increased by an amount equivalent to chlorine dosage. Chlorine-dioxide causes a small increase (about 1.5%) in chlorides; ozone causes no change.
11. Chlorine and chlorine-dioxide in series did not seem advantageous. But a mixture of chlorine and chlorine-dioxide simultaneously gave substantial reduction in chlorine-dioxide dosage.
12. Additional information is required on methods of analysis for phenols to evaluate effects of these oxidants on concentrations less than 0.5 ppm of phenol. But the adaptation of the aminoantipyrine method of analysis for phenols (D.A.A.P), developed in connection with this research, was established as an excellent control for treatment by any of these oxidants.



13. Foaming was experienced with both chlorine and ozone. Chlorine-dioxide did not indicate a foaming problem. Increase in temperature of waste reduced foaming.
14. Most effective utilization of the oxidants can be secured only after certain plant design problems have been overcome.
15. Additional laboratory studies showed that other types of phenol wastes, those originating from synthetic-phenol and phenol-formaldehyde-resin plants as well as those from a refinery, would respond to the same treatment. These tests suggest that chemical oxidation of phenols might have applications in other phenol-producing industries.
16. This study was intended to determine possibilities of oxidizing phenols at the source of waste at reasonable cost. These data should be considered as a basis in evaluating cost for each particular phenol-waste problem but should not be extrapolated for application to that waste problem without additional study.

Further studies by the industrial engineering departments of several member companies indicate that when conditions peculiar to each installation are studied, and high degree of treatment is considered, as shown by the reaction curves, treatment will be expensive. Cost of complete removal of phenol would be prohibitive.

## ACTIVATED CARBON

The Pittsburgh Coke & Chemical Company has built a pilot plant using activated carbon for the reduction of phenols from coke plant wastes by adsorption. Froth flotation cells are used for contact of the waste with the activated carbon. A contact time of from two to four minutes has been found to be necessary. Particle size of the activated carbon is important. Optimum size has been found to be 40 to 100 mesh.

Initially, approximately ten pounds of activated carbon is required to remove one pound of phenol. Reactivation of the carbon results in about a 10% loss of material, or it will finally take approximately one pound of activated carbon to remove one pound of phenol.

It has not been necessary to remove tars from the wastes before treatment. Reactivation has been found to be the critical part of the process and is done in a special furnace, still in the development stage. Approximately 98% of the phenols have been removed from the coke plant wastes of one plant. No work has been done on concentrations other than the wastes from this one plant and work will have to be done at various phenol concentrations. This work is continuing but is not far enough along for complete cost evaluation. It may result in a more economical method of reducing residual phenols from coke plant wastes.

## BIOLOGICAL OXIDATION

It is known that some forms of bacteria will convert organic wastes, including phenols, to harmless compounds such as carbon dioxide and water if these organic compounds are not in too concentrated solution. The activity of these micro organisms is dependent upon temperature. The micro organisms themselves are destroyed by high concentration of some of the chemicals they can convert and by other chemicals which are present in some industrial wastes.



The application of biochemical principles by distributing the solution to be treated over a bed of stones which carry the bacteria capable of using such compounds as food was originally developed by the sewage treatment people. Air supplying oxygen for the process passes upward through the filter bed either by convection or forced draft. It has been particularly successful on dilute solutions of the pure phenols but not on coke plant ammonia still wastes which are a very complex solution of phenols, and other organic and inorganic compounds.

Another application of these principles is in the activated sludge treatment plant in which coke plant wastes diluted with sewage to a very low concentration have been treated.

#### Dow Chemical Company Treatment Plant

The Dow Chemical Company at Midland, Michigan operates trickling filters, primary and secondary aeration chambers, and clarifiers to treat aqueous solutions of phenols and phenolic compounds. It has been found necessary to hold the concentration of phenols to less than 100 ppm by dilution and to control the temperature so as to keep the liquid above 60°F leaving the filters.

#### General American Transportation Co.

The General American Transportation Company has developed a combination absorption biochemical process for the removal of pure phenols from an aqueous solution. In practice the solution is agitated with minus 35 mesh coal for approximately 40 minutes, then passed through a series of flotation cells and a thickener for the removal of the coal. The clarified solution containing less than 50 ppm phenol passes to an equalizing lagoon and is then diluted with sewage and treated on a recirculating trickling filter.

#### Donner-Hanna Coke Plant

The Donner-Hanna Coke Plant constructed a pilot plant for the study of the biological oxidation of dilute still wastes on a trickling filter. The still wastes in this case were diluted with river water rather than sewage and applied to a filter that had been seeded with septic tank effluent. Dilution was such that the still waste-water solution contained not more than 30 ppm of phenol. Preliminary runs indicated poor removal efficiency.

#### Gary Works - U. S. Steel Co.

Activated sludge biological treatment to process Coke Plant Wastes has been recently shown to be feasible by the successful treatment of ammonia still waste from the Gary Coke Works of the United States Steel Company, after approximately 40 to 1 dilution with domestic sewage at the municipal sewage treatment plant in Gary, Indiana. The still waste was diverted, over a period of six months, through the sanitary sewers to the sewage treatment plant, where the material was treated along with the daily flow of sewage. After dilution and biological treatment 99.7% of the phenol was destroyed and five parts per billion of phenol remained in the total effluent from the sewage plant.

The presence of the still waste in the sewage did not interfere with the normal operating efficiency of the sewage works, as was shown by the excellent reduction in biochemical oxygen demand (BOD) and the normal rate of gas production. Interruption of the still-waste flow, and shock loadings of as much as 2,000 pounds per day of phenol, were handled without altering the routine operation of the sewage works.



Permission for the experimental operation at Gary was obtained from the proper city and state officials. W. W. Mathews, Superintendent of the Gary Sewage Treatment Works, had complete authority over the conditions used in the test run which was made to determine whether this activated sludge plant could reduce the entering phenol to an allowable concentration, and whether the addition of ammonia still waste would adversely affect the efficiency of the process. As this is a new possibility worthy of further consideration, additional data on that test run have been included in this report.

Diversion of the still waste to the sanitary sewers began October 24, 1950. The flow was regulated to deliver about 200 lbs. of phenol per day to the treatment plant. The flow was increased to deliver about 400 pounds, then 600 pounds, then 800 pounds of phenol per day on November 3, 1950, December 6, 1950, and January 2, 1951 respectively. This procedure was followed to permit the growth of phenol-consuming bacteria in the activated sludge at the sewage treatment plant. The uninterrupted flow of still waste to the sewage treatment plant and the gradual increase in phenol loading were thought essential to the propagation of these bacteria. However, on several occasions, because of operational difficulties at the Coke Works, the flow of still waste was interrupted for a period of 10 to 20 hours without any apparent ill effect.

For a period of five weeks during the winter months, when the phenol loading was to be 800 pounds per day, the BOD loadings increased to approximately twice the normal loading. Within this period, the coking time at the Gary Works was increased from 17 to 24 hours for one week. This resulted in a higher phenol concentration in the still waste, and the loading at the sewage treatment plant increased to about 1,050 pounds of phenol per day. The phenol destruction averaged above 99.8%, and the reduction in BOD averaged above 94%. These results were achieved despite a complete stoppage in flow of still waste on one occasion, and on another occasion an abrupt increase in phenol loading totaling about 2.5 times the loading of the previous day. On this peak day, 2,090 pounds of phenol were reduced to less than 1 lb. by using only one air blower.

Previous to these results, the superintendent of the sewage treatment plant had begun to use a standby air blower because he believed that more air was needed to destroy the phenol and to reduce the normal BOD loadings. He continued to use this second blower periodically throughout the remainder of the experimental demonstration.

From March 21, 1951 to May 1, 1951 the entire flow of still waste from the Gary Coke Works was discharged to the sewers. At no time during the entire test run did the destruction of phenol or the reduction of BOD drop below 99.7% and 91%, respectively. The addition of the still waste did not interfere with the gas production at the sewage treatment plant. Variations in the volume of gas produced were normal except from February 18 to March 25, 1951. During this period insufficient solids reached the digesters because of a chronic plugging of the lines at the sewage treatment plant. This condition resulted from a cause that was entirely unrelated to the presence of the still waste.

No attempt has been made in this report to show all of the detail in operating conditions, process flow and analytical studies. This information is currently available from Research & Technology, United States Steel Company, Pittsburgh, Pennsylvania. However, some of the significant analytical data, showing effective reduction in phenol and BOD loadings to the activated sludge plant are shown in a table following this report.

Phenol analyses were made according to the modified Gibbs procedure (4). A study of the nitrogen analyses of the sewage flow and of those of the still waste shows that the nitrogen content of the sewage varied independently of the ammonia content of the still waste.



**TABLE VI - SIGNIFICANT ANALYTICAL DATA AT THE  
GARY SEWAGE TREATMENT PLANT**

Date Week Beginning	PHENOL				BOD**		
	Still Waste Lbs.	Clarified Sewage Lbs.	Final Effluent Lbs.	Removal %	Clarified Sewage Lbs.	Final Effluent Lbs.	Reduction %
8/28/50	-	-	-	-	13050	2575	80.3
9/3/50	-	-	-	-	12280	1072	91.3
9/10/50	-	-	-	-	16860	1627	91.3
9/17/50	-	-	-	-	12000	1548	87.1
9/24/50	-	10.54	0.67	93.66	15300	616	96.0
10/1/50	-	4.15	0.97	76.65	9680	578	94.0
10/8/50	-	4.05	0.59	85.45	8900	718	91.9
10/15/50	-	8.00*	0.41	94.86	12680	788	93.8
10/22/50	118	157	0.12	99.92	12900	890	93.1
10/29/50	203	179	0.28	99.84	16380	1078	93.4
11/5/50	369	325	0.17	99.95	17720	824	95.3
11/12/50	337	298	0.39	99.87	14230	892	93.7
11/19/50	324	318	0.42	99.87	14600	903	93.8
11/26/50	332	214	0.57	99.73	14770	1190	91.9
12/3/50	345	318	0.59	99.81	17120	1044	93.9
12/10/50	512	416	0.36	99.91	15750	361	97.3
12/17/50	605	524	0.64	99.88	16900	1288	92.4
12/24/50	514	457	0.54	99.88	15100	1320	91.3
12/31/50	569	591	0.75	99.87	16400	1135	93.1
1/7/51	672	486	1.19	99.76	23190	1810	92.3
1/14/51	759	802	0.53	99.93	18280	1543	91.5
1/21/51	652	690	0.48	99.93	20220	1220	94.0
1/28/51	637	640	0.46	99.93	31400	958	97.0
2/4/51	1098	1067	0.70	99.93	28500	1171	95.9
2/11/51	707	641	0.60	99.91	31820	1012	96.8
2/18/51	783	607	0.23	99.96	17830	780	95.6
2/25/51	714	569	0.33	99.94	16970	581	96.6
3/4/51	643	547	0.33	99.94	13850	804	94.3
3/11/51	804	464	0.43	99.91	21970	1108	95.0
3/18/51	1019	979	0.39	99.96	19050	1105	94.3
3/25/51	1316	1151	0.14	99.91	17720	1552	91.3
4/1/51	1181	1122	0.45	99.96	16280	562	96.6
4/8/51	1485	1316	0.35	99.97	13080	880	94.8
4/15/51	1606	1538	0.30	99.98	16520	995	94.0
4/22/51	1475	1479	0.23	99.98	12880	934	92.7
4/29/51	1236	1399	0.00	100.00	12450	1335	89.3

\* 9-day average, from 10/15/50 to 10/23/50, incl.

\*\* BOD means biochemical oxygen demand



No correlation between the alkalinity of the still waste and that of the sewage flow was obtained. However, a trend toward a slightly higher pH of the raw sewage was indicated.

The superintendent of the sewage treatment plant conducted the experimental run with a large margin of safety to insure the complete treatment of the waste. Some changes were made in the operations, but the phenol destruction and BOD reduction efficiencies were not affected.

In summary, the following should be noted:

1. The entire flow of ammonia-still waste at the Gary Coke Works has been successfully treated for the destruction of phenol by biological oxidation at the Gary activated sludge sewage treatment plant.
2. The still waste did not interfere with the normal operating efficiencies of the sewage treatment plant. The waste was treated in the fall, winter, and spring seasons without difficulty.
3. Interruptions in still-waste flow and sudden fluctuations in phenol loading did not affect the operations at the sewage treatment plant.
4. The alkalinity and nitrogen content of the plant effluent was independent of the alkalinity and nitrogen content of the still waste.
5. No critical data pertaining to the minimum treatment necessary to reduce the still waste to a harmless effluent could be obtained because of the predetermined operating routine at the sewage treatment plant.

Summarizing the report of biological oxidation, it seems possible to treat aqueous solutions of pure phenol successfully on a trickling filter. However, ammonia still wastes have only been successfully oxidized by the activated sludge process when diluted about 40 times with domestic sewage.

# APPENDIX

## D.A.A.P. METHOD FOR PHENOL ANALYSIS

### PHOTOMETRIC METHOD FOR THE DETERMINATION OF PHENOL IN AMMONIA-STILL WASTE (3) (4-AMINOANTIPYRINE METHOD UTILIZING DISTILLATION)

This method is specifically designed for the analysis of phenolic constituents in waste obtained from a coke plant dephenolizer. However, it may be used on other materials with little or no modification. It is based on the color reaction of 4-aminoantipyrine with phenolic constituents in the presence of alkaline oxidizing agents.

On dephenolized ammonia still waste, the values obtained by this method agree very well with values obtained by The Gibbs Method (Standard Methods for the Examination of Water and Sewage, the American Public Health Association, and the American Water Works Association - 9th edition).

Quinone interferes slightly by producing a color, 100 ppm under the test conditions being equivalent to approximately 2 ppm of phenol. Organic compounds such as pyridine, quinoline, formaldehyde, naphthalene, and benzene do not interfere at all. *Sulfites must be absent.*

Ammonia still waste obtained from a dephenolizer yields high values when the sample is not distilled. Therefore, distillation must be employed to separate the phenol from the interfering constituents.

## PROCEDURE

Transfer 110 ml. of the sample (1) to a 250-ml. beaker and add 1 ml. of 10% copper sulphate. (2) Adjust the solution to a pH of approximately 4.0 with 10% phosphoric acid (3) using a pH meter or methyl orange indicator. Transfer the solution (4) to a 500-ml. distilling flask with ground glass joint and connect to a condenser (such as a Graham condenser). Collect 100 ml. of the distillate in a 100-ml. volumetric flask and mix.

If foaming occurs during distillation, a plug of glass wool may be placed in the side arm of the distilling flask. Alternately the original sample may be filtered before distillation.

Pipette a suitably sized aliquot (5) of the distillate (or of the original solution if distillation is not employed) into a 250-ml. beaker and add distilled water to give a total volume of 75 ml. Add 1 drop of dilute (1:1) hydrochloric acid and 5 ml. of dilute (1:9) ammonium hydroxide. Then by further additions of acid or base, adjust the pH to 9.8 (9.6-10.0) using a pH meter (6).

Transfer the solution to a 100-ml. volumetric flask, rinsing the beaker a few times with distilled water. Dilute to 100 ml., mix, add 2.0 ml. of 4-aminoantipyrine



solution and again mix. After rinsing the photometer absorption tube twice with water and once with a portion of the solution, add a sufficient quantity of the solution to the tube and obtain a reference reading (7) on the photometer. (8) Add 2.0 ml. of potassium ferricyanide solution (9) to the remainder of the solution and mix. Rinse the absorption tube with a portion of the solution, add a sufficient quantity of the colored solution to the tube, and obtain a reading (10) on the photometer.

From a calibration curve (11) determine the micrograms ( $\gamma$ ) of phenol equivalent to the reference reading and to the total reading.

## CALCULATIONS

Without Distillation:

$$\text{ppm phenol} = \frac{\gamma_{\text{total phenol}} - \gamma_{\text{phenol equivalent in reference solution}}}{\text{ml. of sample}}$$

or

$$\text{ppm phenol} = \frac{(\text{total reading} - \text{reference reading}) \times \text{factor (11)}}{\text{ml. of sample}}$$

With Distillation:

$$\text{ppm phenol} = \frac{(\gamma_{\text{total phenol}} - \gamma_{\text{phenol equivalent}}) \text{ in reference solution} \times 0.93 \text{ (12)}}{\text{ml. of sample}}$$

or

$$\text{ppm phenol} = \frac{(\text{total reading} - \text{reference reading}) \times \text{factor} \times 0.93}{\text{ml. of sample}}$$

## NOTES

1. If the sample is known to contain oxidizing compounds, such as chlorine, chlorites, etc. which would oxidize phenol when the pH of the sample is adjusted or when the sample is boiled, a slight excess of  $\text{FeSO}_4$  is added to remove the oxidant.
2.  $\text{CuSO}_4$  precipitates any sulfides that are present, resulting in a clearer distillate. It also eliminates the slight interference which results when large amounts of sulfides are present.
3. The volume of sample must be maintained close to 110 ml. (not more than 115 ml.). If the alkalinity is high, it may be necessary to partially neutralize first with concentrated  $\text{H}_3\text{PO}_4$  in order to keep the final volume less than 115 ml.
4. Many samples may be analyzed for phenol without the necessity of making the distillation. This may be done if interfering substances are not present and if the solution is not too highly colored (after dilution of required amount of solution to 75 ml.). It is recommended that several determinations be made with and without distillation on each type of sample to be analyzed. If agreement is good, then the procedure without distillation may be safely employed on future samples of like material. In this case proceed as follows: Pipette the required amount of solution (See Note 5) into a 250-ml. beaker and dilute to 75 ml. If the diluted sample is very cloudy, the original sample should be filtered through a dry filter paper. Continue as directed in the main text with additions of  $\text{HCl}$  and  $\text{NH}_4\text{OH}$  and adjustment of the pH to 9.8.



If a large amount of precipitate forms upon adjustment of the pH to 9.8, the solution should be filtered, and the pH adjusted again if necessary.

If an extremely high amount of sulfide is present (as in some refinery wastes), it may be precipitated by addition of an excess of  $\text{CaCl}_2$  solution followed by filtration.

5.	ppm Phenol	ml. Sample Taken
	0.1 - 6	75
	6 - 20	25
	20 - 100	5
	100 - 500	1
	500 - 2500	0.2*

\* Dilute 10 ml. to 500 ml. in a volumetric flask and take a 10-ml. aliquot

6. The ammonium chloride formed buffers the solution and prevents any appreciable decrease in pH when the 4-aminoantipyrine and the potassium ferricyanide solutions are added.
7. The volume of solution used for rinsing and for the reference reading should be reasonably well controlled in order to avoid gross changes in the final concentration. Use of approximately 5 ml. for rinsing and 10 ml. for the reference reading has been found to be satisfactory.
8. Any good photoelectric photometer may be used employing a color filter having maximum transmittancy near 490-520 mu. The zero adjustment of the photometer is first obtained using distilled water in a cylindrical absorption cell having a light path of about 1 cm. With the Klett-Summerson photometer, Filter #52 (520 mu.) is used and with the Kromatrol photometer, Filter #5 (525 mu.)
9. If there are elements present, such as copper, which react with  $\text{K}_3\text{Fe}(\text{CN})_6$ , a 6%  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution may be used instead. Preferably, the sample should be distilled to separate the phenol from such interfering substances.
10. The color forms immediately when ferricyanide is used. With persulfate the color development is slower (requiring at least 3 minutes for full development). Since exposure to light gradually fades the color, the reading should be made as soon as full color development is obtained.
11. The calibration curve is prepared by adding varying amounts of phenol (up to 500 micrograms) in the form of a standard phenol solution to beakers, adding HCl and  $\text{NH}_4\text{OH}$ , adjusting the pH, and developing the color exactly as directed in the main text. The absorbancies are plotted against micrograms of phenol present. For the most accurate values the calibration curve should be used; however, if a straight line curve is obtained, a factor may be used.

$$\text{Factor} = \frac{\text{micrograms of phenol}}{\text{absorbancy}}$$

All phenolic material will be reported as phenol (carbolic acid). However, if the proportions of the various phenolic constituents in the sample are known, the standard solution may be made to contain the same proportion of these phenols.



12. Under the conditions of the distillation it has been found that when 100 ml. of distillate is obtained from a 110-ml. sample, approximately 98% of all the phenol present is found in the distillate. Therefore, the determined phenol value multiplied by 0.93 (i.e.  $\frac{10}{11} \times \frac{100}{98}$ ) gives the correct phenol content of the original sample.

## ADDITIONAL MANUALS

devoted to waste control in steel plants, which are available from the Ohio River Valley Water Sanitation Commission, are:

### PLANNING AND MAKING INDUSTRIAL WASTE SURVEYS

Detailed instructions for measuring volume of flow, obtaining representative samples and calculating waste loads. The manual is designed to aid those people who have had little or no experience in measuring industrial waste. Diagrams show how to construct and install measuring and sampling devices. Tables are included to assist in computing the rates of flow. The manual was compiled by the Metal-Finishing Industry Action Committee. (44 pp., 27 illus.) Price \$1.00

### DISPOSAL OF SPENT SULFATE PICKLING SOLUTIONS

An evaluation of methods for treating spent solutions resulting from sulfuric acid pickling to reduce stream pollution. Compiled by the Steel Industry Action Committee of the Commission, this manual describes methods for neutralization of acid solutions and for recovery of acid and iron salts. Flow diagrams and a nomograph for determining weight of alkaline agent required to neutralize acid solutions are included. (76 pp., 17 illus.) Price \$2.00



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