Phenol Wastes Treatment by Chemical Oxidation

Findings from a cooperative study conducted by . . .

ARMCO STEEL CORPORATION WALLACE AND TIERNAN COMPANY, INC. WELSBACH CORPORATION, Ozone Processes Division MATHIESON CHEMICAL CORPORATION OHIO STATE DEPARTMENT OF HEALTH U. S. PUBLIC HEALTH SERVICE

. . . under direction of the

OHIO RIVER VALLEY WATER SANITATION COMMISSION

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To the Chairman and Members of the Commission:

This is the final report of a cooperative research project that provides new information on the treatment of coke-plant wastes. The work shows how phenols can be destroyed by three methods of chemical oxidation -- using chlorine, ozone and chlorine dioxide.

This study should prove helpful to industries in meeting problems of phenol-waste control. And it will be of value to the Commission in reaching decisions on the establishment of phenol limits in the Ohio River.

The Commission can take great satisfaction from the manner in which the work was done. The Armco Steel Corporation and three proprietors of competitive oxidation processes -- the Wallace & Tiernan Company, the Ozone Processes Division of the Welsbach Corporation and the Mathieson Chemical Corporation -- joined together as a team with the Ohio State Health Department, the U. S. Public Health Service and your staff to make these fundamental studies.

In terms of money, the combined contribution from industry representatives in this enterprise amounted to more than \$55,000. In terms of accomplishment, the results offer three methods of phenol-waste control, each of which has application merits depending upon conditions to be met.

Coordination of the project was assigned to John E. Kinney, staff sanitary engineer. His devotion to the task and his many technical suggestions were important factors in making this project so fruitful.

Respectfully submitted,

Edward J. Cleary

Executive Director and Chief Engineer

June 15, 1951

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PROJECT PARTICIPANTS

Organizations and their personnel who played a part in this cooperative investigation of phenol-waste treatment were:

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J. B. Whitlock - General Maintenance Engineer

G. A. Pettit - Industrial Waste Control Engineer

- A. Thomas Chief Chemist
- M. Dannis Research Chemist
- F. I. Wilks Coke Plant Superintendent

Wallace and Tiernan Company, Inc.

H. S. Hutton - Sales Manager
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M. Cornish - Assistant Chemist

Welsbach Corporation

Victor Hann - Director, Ozone Processes Div. S. Niegowski - Chemist W. Bowen - Chemist

Mathieson Chemical Corporation

E. F. Fenrich - Manager, Chlorite Div.
R. N. Aston - Chemist, Chlorite Div.
E. Birkett - Chemist

Ohio State Department of Health

F. H. Waring - Chief Engineer
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M. L. Riehl - Chief Chemist
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U. S. Public Health Service

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C. C. Ruchhoft - Chief, Physics and Chemistry Section

M. B. Ettinger - Scientist

Ohio River Valley Water Sanitation Commission

E. J. Cleary - Executive Director & Chief Engineer

J. E. Kinney - Sanitary Engineer & Project Coordinator



RESULTS IN BRIEF

Looking towards methods for the reduction of phenols at their source, a cooperative investigation was made of the oxidation of dephenolized effluent of coke-plant waste with chlorine, ozone and chlorine dioxide. Preliminary laboratory studies -confirmed by pilot-plant operation -- provided information by which performances of these three oxidants could be compared. Here are the findings:

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

ment 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 gramular 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 (DAAP), developed in connection with this research,

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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 phenolwaste problem, but should not be extrapolated for application to that waste problem without additional study.



Chemical oxidation of phenol in coke-plant waste -- successful in the laboratory -- was confirmed by operation of this pilot plant, constructed by Armco Steel Corp.

ABOUT THE PROJECT

This cooperative research project -- which sought to evaluate the possibilities of treating coke-plant wastes by chemical oxidation -- demonstrated:

Phenols in coke-plant wastes can be destroyed by chlorine, ozone and chlorine dioxide; and

The potentialities for integrating the skills and resources of private enterprize and public agencies in promoting industrial-waste treatment.

unselfish teamwork on an industrial waste pollution problems. problem. Principal participants on the team were the Armco Steel Corporation, the various coke-producing plants.

Quite aside from practical merits of project, the Ohio River Valley Water Sani- disappointed. tation Commission takes great satisfaction from the manner in which the investigations Previous knowledge were carried out.

concept held by the Commission: With a had been conducted. mandate and the legal powers for curbing pollution, the Commission also recognizes in good faith the repeated assertion of enlist the services of a technical team for

Teamwork -- What is reported here is responsible members of industry that sinthe outcome of some unusually effective and cere efforts are being made to cope with

Control of phenol-waste discharges is Wallace and Tiernan Company, the Ozone Pro- a case in point. Since it is a generallycesses Division of the Welsbach Corpora- accepted fact that existing methods of tion, the Mathieson Chemical Corporation, reducing phenol discharges are not comand the sanitary engineering division of pletely effective for conditions in the the Ohio State Health Department. The Ohio Ohio River Valley the Commission sought to River Valley Water Sanitation Commission sponsor some new lines of attack. Inspiraserved as coordinator. Assisting the team tion for this particular effort was with advice were many others, notably the furthered by suggestions from Kenneth M. U. S. Public Health Service laboratories in Lloyd, commissioner from Ohio and the exe-Cincinnati, the Dow Chemical Company and cutive secretary of the Mahoning Valley Industrial Council.

In looking to industry to shoulder the technical information originating from this burden of research, the Commission was not

-- This was the sequence of events: The Commission staff first made an evaluation of what had been This finding -- that the Commission done on phenol-waste treatment. This can perform a useful service in inspiring included the usual review of published and coordinating action on industrial waste material. But the important supplement was treatment -- compels attention. It does a personal visit to many places where so because it lends validity to a basic phenol wastes were being treated or research

With this background it was then conthat issuance of a court order is not nec- cluded that chemical-oxidation methods proessarily the quickest or most effective way bably offered the most fruitful field for to secure action. The Commission accepts further development. The next step was to

such an investigation.

Experts consulted -- One of the earliest with whom the possibility of phenol oxidation was discussed was C. C. Ruchhoft, chief of the Physics and Chemistry Section of the U. S. Public Health Service Environmental Health Center at Cincinnati. He thought the idea worth following.

With this expert encouragement, the matter was then explored with William Orchard, general manager and H. S. Hutton, sales manager of Wallace and Tiernan Co. Mr. Orchard's background as a sanitary engineer led him to exhibit genuine interest in what he considered a new approach to phenol-waste treatment. He offered the facilities of his organization in joining with the Commission to promote some research.

Armco helps out -- Looking for a place where the work might be conducted, the Commission discussed the proposition with management of Armco Steel Corporation, represented by L. F. Reinartz, vice president, and J. B. Whitlock, general maintenance engineer. This corporation operates a by-product coke plant at Hamilton, just a few miles from Cincinnati.

In agreeing to collaborate, Armco erected a laboratory adjacent to their byproduct coke plant to facilitate experimental work under actual phenol-production operating conditions. Armco also supplied a research chemist full-time.

Laboratory tests -- At this laboratory chemists from Wallace & Tiernan, Armco and the division of sanitary engineering of the Chio State Health Department began their work with chlorine oxidation." To expedite analytical work the Ohio State Health Department stationed its mobile laboratory at Hamilton for a short time. The Cincinnati Environmental Health Center of the U. S. Public Health Service contributed important help through consultations and specialized laboratory investigations. And the Commission furnished a project coordinator --- John E. Kinney sanitary engineer ---who devoted almost full time to the work.

Following the chlorine tests, invitations were extended by the Commission to the Ozone Processes Division of Welsbach Corporation and to Mathieson Chemical Corporation to apply their proprietary oxidation processes under laboratory conditions of test.

Results from "bottle" experiments were most promising. It was demonstrated that there were at least three methods by which the phenolic constituents could be destroyed. Wallace & Tiernan, for example, explored the potentialities of chlorine oxidation. Ozone oxidation was studied by the Welsbach group. Experimentation with chlorine dioxide was undertaken by the Mathieson Chemical Corporation.

Same conditions, same waste -- It should be noted that this laboratory work was conducted at the same site, with the same waste and under the general direction of the same investigator in each case. This offered the advantage of eliminating many variables and providing continuity and similarity of testing procedures.

After the laboratory results and experiences of all parties were pooled and analyzed, the Armco Steel Corporation agreed with the Commission to carry the work into a pilot-plant stage of investigation. Other members of the team agreed to furnish equipment and technicians to further the work,

Pilot-plant -- Armco installed the required tanks, towers and appurtenances and supplied manpower and other services to operate them. This pilot-plant was operated at successive times by the three companies.

FACTS ABOUT PHENOL WASTES

This investigation concerned itself with phenol wastes. They originated as the effluent from a dephenolized ammonia-still in a coke plant. The dephenolizer was a Koppers Company unit.

Phenols is the broad term applied to the mono-hydroxy derivatives of the benzene ring. Included are phenol, cresols, and xylenols. Coke-oven waste includes a combination of all the phenols. Destructive distillation of coal produces a variable mixture of phenols as well as many other organics, all of which might have an influence on treatment methods.

Variation in the composition of the phenols is a function of coal used, coking time, and temperature. In this study phenol concentration ranged from 28 to 332 ppm.

Additional analyses of the waste showed:

- Cyanides and cyanates -- in low concentration
- Sulfides -- less than 100 ppm
- Chlorides -- ranging between 7,000 and 9,700 ppm

Oxygen Consumed (OC) from 1,400 to 1,800 ppm (about one-half the oxygen consumed as measured by the dichromate reflux method was due to chlorides)

B O D -- ranging from 300 to 400 ppm Ammonia -- from 10 to 2,390 ppm (variation due to drop in pH in fixed leg of

- ammonia still) pH -- fixed leg of ammonia still ordin-
- arily operated above 11.0 for maximum ammonia recovery)
- Temperature -- from the still at 100 deg. C.

Relation to other phenol wastes -- In an effort to define the potentialities of chemical oxidation of phenols in wastes, other than those originating from byproduct coke plant operations, additional laboratory studies were undertaken. These showed that the phenol wastes from plants producing synthetic phenol and a phenolformaldehyde resin would respond to the same treatment. Refinery wastes responded similarly. These tests indicated that chemical oxidation of phenols might have applications in other phenol-producing industries.

Prior studies investigated -- Before laboratory studies were undertaken the work being done at several coke plants, the Mellon Institute, and Dow Chemical Co. was visited and discussed. These contacts provided the information that:

1. Variation in pH in ammonia still wastes, as practiced by the coke plants, caused ammonia content to fluctuate from 10 to 1,500 ppm.

Comment: These data suggested the conditions under which chlorination might be possible. Further it provided the clue why chlorination trials at one place were reported as not worthy of further study. Chlorine has to reach breakpoint potential before it will oxidize phenol. With ammonia present 10 lb. of chlorine are needed for each pound of ammonia before a breakpoint is reached. Thus, the presence of 1,500 parts of ammonia would require 15,000 parts of chlorine for neutralization of ammonia alone. On the basis of economics this suggested why chlorine treatment was not considered feasible.

2. Waste samples used for some experiments were not treated at the source but had been shipped to distant laboratories. Comment: The work at Armco revealed that the oxidant demand of cokeoven waste will vary with time. Fresh waste has less demand.

3. At the Dow Chemical Co., where a full-scale plant for destruction of high concentrations of chlorophenols by chlorine is in operation, it has been demonstrated that control of pH is most important.

Comment: No previous work on cokeoven waste, however, had fully explored variation in pH and temperature.

4. Evidence indicated that only chlorination had been tried as an oxidant. While it was known that ozone and chlorinedioxide were effective in destroying phenolic tastes at water treatment plants. neither had been tried on phenol-containing coke-plant wastes.

Comment: One reason was that the cost of ozone and chlorine-dioxide was considered excessive as compared to chlorine on the basis of available oxygen. Actually, the Armco work showed that the reactions of ozone and chlorine-dioxide were not comparable to chlorine, and therefore previous cost calculations were not reliable. This situation illustrates again the frequent discovery that mass action principles are not fully considered in comparing chemical reactions that are experienced in water treatment with those occurring in industrial waste treatment.

LABORATORY STUDIES

Laboratory work supplied an affirmative answer to the possibility of destroying phenols at the source of the waste. Phenols can be oxidized, and such oxidation can be accomplished with chlorine, chlorine-dioxide or ozone. The oxidation is one of destruction; there is no recovery.

While the main emphasis was on dephenolized coke wastes, the same answers appeared applicable to at least three other types of phenol-containing wastes.

Pretreatment -- Before chlorine studies were undertaken, investigations were made on the effects of pretreatment. These included:

Acidification -- hydrochloric and sulfuric acids were used. There was heavy sludge formation due to the high lime alkalinity, and change in color, due to the organic indicators in the waste, but small reduction in phenol -- up to 6%.

Chemical coagulants -- hydrated lime, ferric chloride and ferrous sulfate in the range from 1 to 250 gpg gave reductions up to 20%.

Permanganate -- maximum reduction of phenols 62%, even with excess permanganate used. Cost is excessive.

Pretreatment before oxidation of the phenols did not appear feasible.

Summary of laboratory studies -- Laboratory investigations then showed:

1. Complete destruction of phenols in ammonia-still wastes as measured by colorimetric chemical tests could be accomplished by oxidation with chlorine, ozone or chlorine dioxide.

2. No pretreatment of the waste is required for oxidation with pzone or chlorine dioxide. Chlorine was applied after pH and temperature reduction. Control of pH appears to have an effect on the degree of the oxidant demand to be satisfied before phenols are destroyed. It should be noted that there is a decrease in the oxidation potential of phenol with increase in pH. This appears to make it easier to oxidize phenol at high pH when other oxidantconsuming compounds are present. That there are other oxidizable constituents in coke plant waste was proved by: (a) variation in results with change in pH; and (b) the impossibility to correlate phenols and oxidant dosage with any stoichimetric relationship. Phenolic content cannot be used as sole basis for determination of required dosage of oxidizing agent in this waste.

3. Undertreatment with ozone and chlorine-dioxide does not result in the formation of objectionable chlorophenols; chlorination requires complete oxidation to prevent such end-products.

4. An excess of several hundred parts per million of chlorine is required for complete destruction of phenols. This excess can easily be removed with granular activated carbon.

5. Oxygen consumed (O C -- noted as C O D in data) and B O D are materially reduced by each of these oxidants.

6. Chlorine-dioxide oxidation causes small increase in chlorides (about 1.5%); chlorination gives increase in chlorides equivalent to dosage.

7. Pilot-plant studies should be undertaken to show the practical and economic considerations relating to the use of these oxidants.

PILOT PLANT STUDIES

A pilot plant was constructed by Armco Steel Corp. to handle a continuous flow of 2 gpm, or to treat in batch operation any quantity up to 350 gallons. Units included:

Holding tank -- 1,000 gal. capacity to provide uniform waste for day's run; equipped with steam coil for temperature control.

Pump and rotometer, which were connected in line between holding tank and reaction tower.

Reaction tower -- 2 ft. dia. 18 ft. high. Tower constructed to permit variation in depth of liquid at 2 ft. intervals. Waste added at top, removed from bottom of tower. Outlet just below diffuser tubes through which ozone and chlorine-dioxide gases were added. Chlorine-dioxide solution, measured by a second rotometer, was added in line to top of tower. Caustic for pH control could be added at any level.

Two 55 gal, drums as reaction tanks for chlorination. Chlorine added directly to the waste in the chlorinator; the waste then passed through the drums before being pumped to tower.

Samples could be taken at various depths of solution in the tower, at inlet and outlet of tower, and at points of addition of chemicals.

Design of the reaction tower was predicated on the volume of gas-in-air solution needed for ozone and chlorine-dioxide treatment of a continuous flow of waste of 2 gpm. Air-lift on the liquid required a larger cross-sectional area than was desired in order to have the waste and gas approximate counter-current flow. Result was continuous mixing with low concentration of phenol. The work suggested several possibilities that should be tried on future work.

Conclusions -- In general, the conclusions

of the laboratory studies were confirmed. However, as might be expected in the larger scale operations, control difficulties were encountered that took time to overcome.

For example, the mixing in the tower caused by the low rate of flow and violent agitation by the ozone and gaseous chlorine-dioxide interfered with the continuous flow studies in both cases. But batch treatment tests confirmed the laboratory studies. Interference due to mixing was also noted in the chlorine detention tanks.

Summary of results -- In addition to the results outlined under laboratory studies, pilot-plant studies with the three oxidants yielded these facts:

Chlorine

1. On the basis of laboratory studies chlorine destroyed phenols completely at some detention time ranging between 10 minutes and an hour. Pilot plant work on continuous flow did not give complete removal in 18 minutes. Plant design and chlorinator capacity prevented exploration beyond this point. Treatment was carried on in two stages; more may be required. Or, it may be that longer contact time is necessary.

2. The initial chlorine dosage acts to satisfy the ammonia demand. Following this there is a substantial decrease in phenol with small increase in chlorine dosage. But increasingly higher dosages are required to give further decreases in the residual phenol.

3. Phenols can be destroyed over a wide pH range -- from 1.8 to 11.0. Wallace & Tiernan recommend pH over 7.0 to speed oxidation of phenols and to minimize nitrogen trichloride formation; and that pH be controlled at a level under 10.0 for economic reasons.

4. Where reductions in phenol (to about 3 ppm) were obtained with substantial chlorine dosages, subsequent treatment with chlorine-dioxide in laboratory tests did not seem feasible.

5. Increase in chlorine dosage caused a decrease in phenol but with increasing chlorine residual.

6. Wallace & Tiernan recommend that temperature of waste be reduced to 45 deg. C. before chlorine is added to prevent formation of chlorates.

Ozone

1. Ozone's greatest affinity for phenol was obtained at pH about 11.8, so no pH adjustment was required. As ozonation proceeded pH dropped but the final pH was on alkaline side.

2. Variation in temperature had no effect on dosage of ozone required.

3. Reaction appears instantaneous; however, contact time must be considered in design of plant because ozone is added as 1 to 2 percent gaseous solution.

4. No residual of ozone is required. Undertreatment with ozone reduces phenols and does not contribute to the formation of other toxic compounds.

5. Ammonia content of waste did not effect ozone dosage.

6. Substantial reduction in phenol with small dosage of ozone was noted but increasingly higher dosages were required as phenol was further reduced.

Chlorine Dioxide

1. No adjustment in pH is necessary. Best results were obtained by starting treatment at pH above 11.5. As the addition of chlorine-dioxide continued, pH dropped to the acid side; best results were obtained when the pH was not held at any controlled level.

2. No adjustment in temperature is necessary.

3. Chlorine and chlorine-dioxide in series did not seem advantageous.

4. But mixture of chlorine and chlorinedioxide simultaneously in ratio of about 2:1 gave greatest efficiency. Chlorinator capacity prevented full exploration of this but at a ratio of chlorine to chlorinedioxide of 2:1 the chlorite dosage was reduced about 50 percent.

5. Ammonia content of waste did not effect chlorine-dioxide dosage.

6. Reaction time for gaseous or aqueous chlorine-dioxide was less than 15 minutes with effective treatment.

7. Residual chlorine-dioxide is not required. Undertreatment reduces phenols but did not cause formation of chlorophenols by colorimetric chemical tests. Spectrophotometer was not used.

8. Reaction curve shows a substantial reduction in phenol attained with small chlorite dosage, but increasingly higher dosages required as phenol is further reduced.

9. This work showed mechanical losses of chlorine-dioxide. Greater efficiency can be expected with improved reaction equipment, which would allow complete utilization of the oxidant.

METHODS OF ANALYSIS FOR PHENOL

Because analytical methods for phenol determination were an important part of the project, considerable thought was given to this. There are 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.,1945, p 216) provides a sensitivity of about 25 parts per billion for a chemist skilled in this technique.

Gibbs test and the 4-aminoantipyrine method have been modified to permit analysis of lower concentrations of phenol -down to 3 ppb -- in river waters by concentration of the phenol through extraction with chloroform or alcohol. Some errors are inherent in this method. Biggest source of error results from the fact that a part of the solvent is soluble in the water and therefore some of the phenol present is not measurable. Series extraction can reduce this loss.

Use of this modification is recommended only for chemists with special training in water analyses. The test is not recommended for industrial waste effluents because of the concentrations of other constituents that could interfere with the results.

This possible interference by other substances should also be considered in applying the modified techniques to riverwater analysis. Just as the solvent adsorbs the phenols, it may also pick up other contaminants that could interfere with the phenol determination. More work is required in correlating phenol waste loads discharged to a stream and the measured concentrations of phenol in the stream.

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Gibbs test does not determine all chlorophenols. In any industrial effluent that would contain chlorophenols, some other method is required.

Greatest objection to the Gibbs test in waste treatment control, however, is the time element. Eighteen hours is too long. to be practical in the control of the volumes encountered in coke-plants. Less time is required for the AAP (aminoantipyrine) method. But correlation between AAP and Gibbs was lacking.

Therefore, when this work was started, the need existed for a technique that would:

> Be fast. Permit reproducible results. Measure chlorophenols.

Michael Dannis, a research chemist at Armco Steel Corp., carried the burden of the analytical work. He has developed a variation on the AAP method that gives excellent checks on Gibbs down to a defined level. Requiring only 45 minutes in contrast to 18 hours for determination by the Gibbs technique, this method gives results to a sensitivity of 0.1 ppm to 0.5 ppm under defined conditions. It has been called the DAAP (distilled aminoantipyrine) since it involves a distillation step.

Agreement with Gibbs was attained on samples of waste from a refinery, synthetic phenol plant and phenol-formaldehyde resin plant. Method and results were reviewed by the Ohio State Health Department and the

U. S. Public Health Service.

It is of interest to report that Weirton Steel Co. independently arrived at the same adaptation of the AAP method.

There is no intention to substitute

the DAAP method for Gibbs. But it is offered as an excellent control for treatment of waste phenols -- especially when chlorinated phenols are present. In this work the DAAP was used as control technique. But Gibbs was employed as a check.



Laboratory studies on chemical oxidation of phenol and pilotplant analyses were carried out in this building -- erected by Armco for this project.

APPENDICES

Appendices I, II and III are abstracts of independent reports relating to the application of chlorine, ozone and chlorine dioxide for chemical oxidation of phenol wastes from a coke plant. These reports were prepared by Wallace and Tiernan Company, Inc.; Ozone Processes Division, Welsbach Corporation; and Mathieson Chemical Corporation, respectively. Copies of the complete reports are available from each of the participating companies.

Data in these reports are limited to research on ammoniastill waste liquors. Additional studies on phenol wastes from other industries are not included in the summaries. A limited amount of work showed that phenol waste from a refinery, synthetic phenol plant and phenol-formaldehyde-resin plant would respond to methods of treatment investigated. But no attempt was made to explore these problems fully.

Data given in the appendices show pilot-plant results only. Laboratory data and reports are not included.

APPENDIX I --- PHENOL WASTE TREATMENT WITH CHLORINE

(An Abstract of the Wallace and Tiernan Co., Inc. Report)

The existing pilot plant was modified to permit use of chlorine as pre-treatment and chlorine dioxide as post-treatment. Pre-treatment units were constructed so that samples could be taken after chlorine-contact intervals of a few seconds and after intervals of 12 - 18 min., depending upon pumping rates. Contact time for post-chlorinedioxide treatment was varied by changing draw-off levels in the post-treatment tower. Due to cold-weather difficulties many chlorine-dioxide applications were conducted on a laboratory basis.

Conclusions:

1. Complete destruction of phenols in still waste can be effected by chlorination.

2. Only a minor portion of the chlorine was actually used in consuming phenols. The major portion of the chlorine applied was actually being used to consume organic matter other than phenols.

3. To obtain a still waste free of chlorophenols, it is essential to apply sufficient chlorine to destroy phenols at all times and to do so at pH greater than 7.

4. Chlorine application required to completely destroy phenols resulted in a high chlorine residual that increased as retention time for complete destruction of phenols decreased. This increase in high chlorine residual was not entirely the result of decreasing retention time, but rather the result of increasing application of chlorine required to completely destroy phenols in a shorter retention time.

5. High chlorine residual resulting from chlorination could easily be dechlorinated by passing chlorinated waste through activated carbon, leaving, at the most, a small chloramine residual in carbon-filter effluent.

6. To effect complete destruction of phenols in still waste in one hour as versus 20 hours, or in 10 min. as versus one hour required increasing applications of chlorine. On laboratory tests, a minimum of 4,375 ppm, 5,000 ppm and 6,250 ppm chlorine were required to completely destroy phenols in respective periods of 20 hours, 1 hour and 10 min., as indicated by the Gibbs Method of phenol analysis.

7. Results obtained in reduction of phenols during a chlorine contact time of 12 - 18 min. in the pilot plant study are identical to those obtained in the laboratory chlorine study, on the basis of the DAAP test.

8. Not more than 5,000 ppm of chlorine in pilot-plant studies were required to reduce phenols in the waste to a minimum of 3.0 ppm or less as in the laboratory study, on the basis of the DAAP test.

9. The same results were obtained for a chlorine-contact time of a few seconds, on the basis of the DAAP test. That phenols could be reduced to this minimum of 2.0 ppm or less was not established in the earlier laboratory tests.

10. Comparative results in the pilotplant study showed that Gibbs test gave results identical to minimum results obtained with DAAP.

11. These results are at variance with those obtained in the laboratory chlorine study where Gibbs results were always lower than minimum AAP results.

12. Apparently, phenols can be destroyed equally well over a wide pH range, that is, from 1.8 to 11.0. To speed oxidation of phenols and to minimize nitrogentrichloride formation, pH in a treatment plant should be kept over 7.0. For economic reasons pH in a treatment plant should be controlled at a level under 10.0.

Where maximum reductions in phenol 13. were obtained with chlorine, about 5,000 ppm or more, subsequent treatment with chlorine dioxide did not effect a significant further reduction of the phenols, as indicated by both AAP and Gibbs tests.

Discussion --- Destruction of phenols, during the laboratory study and pilot-plant study, follows a similar pattern. The first 1,000 ppm of chlorine applied destroy little, if any, of phenol present. (About 100 ppm of ammonia in one pilot-plant test required about 1,000 ppm chlorine.) At the end of the second 1,000 ppm of chlorine applied, phenol destruction becomes appreciable. Between 2,000 ppm of chlorine applied and 4,000 to 5,000 ppm of chlorine applied, depending upon amount of ammonia present, phenol is rapidly destroyed. (Fig. 1) After the phenol drops to a level of about 3.0 ppm by the DAAP method -- in the 4,000 - 5,000 ppm chlorine-applied range -- further removal of phenol with higher applications of chlorine, as indicated by the DAAP test, is gradual.

However, in this last mentioned chlorination range, i.e., 4,000 ppm of chlorine and over, results obtained by the Gibbs test for phenols are dissimilar for the laboratory study and the pilot plant study. In the laboratory study the phenol by the Gibbs test is less than it is for the corresponding AAP test. Furthermore, in the laboratory study phenol present by the Gibbs test is insignificant for the higher application of chlorine for the 10min. chlorine-retention period and becomes absent at all levels of chlorination for 1-hour chlorine-retention period. In the pilot-plant study, phenol by the Gibbs test is never significantly less than it is for the corresponding DAAP test at all applications of chlorine for the 12 - 18 min. contact period.

laboratory study, it was concluded that taste and odor) remained after chlorinachlorine could destroy phenols completely tion. Thus, the difference in the Gibbs in some time interval between 10 min. and test for the two studies could be the diff-

1 hour, (possibly close to 10 min.). On the basis of the Gibbs test in the pilotplant study, it can be concluded that chlorine does not destroy the phenols completely in a 12 - 18 min. time interval.

This difference is the result of some modification, not apparently of the DAAP method (for results by this method are about the same for each study) but rather some modification of the Gibbs method. It is not a result of dechlorination for, where the Gibbs test appears in the laboratory studies, there was no excess of dechlorinating agent (thiosulphate); and where the Gibbs test appears in the pilotplant study, there was an excess of ferrous iron that neither has effect on phenol during distillation nor can be distilled over to adversely affect the colorimetric test. Dechlorination is an important phase of sampling and testing. It is the only method of complying with a stated contact period. By bringing contact period to end through proper reduction of the oxidants, it gives assurance that there will be no further reduction of phenols by oxidants with time at the stipulated pH and temperature or by distillation at an elevated temperature and lowered pH.

Whether one modification or the other is correct, may be of significance. Perhaps of more importance is the meaning of the minimum amount of phenol left by the DAAP method and possibly the Gibbs method. Is this residual phenol a combination of compounds that would affect the taste and odor in a water supply? Since the DAAP is supposed to be a broad method, including various phenols and chlorophenols, and since the Gibbs method is supposedly a narrow method (including phenol and two of the cresols only) it would appear, from the laboratory results that only some high phenols, possibly higher chlorophenols (having no bearing on taste and odor) of some type, remained after chlorination. Giving the same cognizance to the two methods, it would appear from pilot-plant On the basis of the Gibbs test in the results that phenols (having a bearing on

erence between a satisfactory and non- phenol or chlorophenol derivatives were in is realized that whatever the residual dioxide.

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satisfactory chlorinated effluent. This the pilot-plant study, they could not be matter becomes of more importance when it further appreciably destroyed by chlorine



Color changes accompanying reduction in phenol -- as a result of chlorine oxida tion -- are produced by lowering pH.



Date 1950	Run No.	Chlorine dosage ppm	Chlorine residual ppm	Waste flow gpm	Contact time min.	pH Initial	Final	Raw DAAP	Phe AAP	enol Trea DAAP	ated AAP	NH3 (N)
11/8	1 1b 1c	1,000 1,000	0.0	4 4 4	12-15 5	12.0	10.3 4.6	120	165	11.5	164 12.3	18 16 18
11/10	2 2a 2b 2c	2,000 2,000 2,000	$0.0 \\ 0.0 \\ 0.0 \\ 0.0$	n n n n	1 17-18 5	11.8	8.1 6.7 5.5	118	178	108 115 3.7	124 124 5.7	
11/10	3 3a 3b 3c	3,000 3,000 3,000	$51 \\ 0.0$	າ ເນ ເນ	1 17-18 5	11.8	8.1 8.4	118	178	46.5 0.3	41 42 1.4	
11/13	4 4a1 4a2 4a3 4b	3,000 3,000 3,000 3,000 3,000	31 288 27 31	n n n n n	1 1 1 17-18	12.0	8.4 1.8 10.4 8.0	112	177	75 107 82 68	71 121 95 61	61
11/13	5 5a1 5a2 5a3 5b	$\begin{array}{c} 4,000\\ 4,000\\ 4,000\\ 4,000\\ 4,000\end{array}$	218 665 99 142	ວ ວ ວ ວ ວ ວ ວ ວ ວ ວ ວ ວ ວ ວ ວ ວ ວ ວ ວ	1 1 1 17-18	12.0	8.8 4.1 10.5 7.5	112	177	2.1 2.6 3.2 2.1	4.1 8.0 6.0 4.2	61
11/17	6 6a 6b 6b1 6b2 6b3 6b4	$\begin{array}{r} 4,000\\ 4,000\\ 4,000\\ 4,000\\ 4,000\\ 4,000\\ 4,000\\ 4,000\end{array}$	158 140	3	1 17-18 20 20 20 20 20	11.9	8.7 7.8	117		$10.0 \\ 4.7 \\ 4.4 \\ 4.5 \\ 4.3 \\ 5.4$	4.2	
11/14	7 7a1 7a2 7a3 7b	5,000 5,000 5,000 5,000 5,000	270 306 162 151	4	1 1 1 12-15	11.9	9.2 4.1 10.4 8.3	116	156	2.6 2.5 2.1 2.5	3.9	
* 11/18	8 8a 8b 8b1 8b2 8b3 8b4 8b5	5,000 5,000 5,000 5,000 5,000 5,000 5,000 5,000	303 210	4	$ \begin{array}{r} 1 \\ 12-15 \\ 20$	12.0	9.3 7.3	116	-	3.1 3.3 3.2 3.4 3.0 3.1 3.4	3.2* 4.1 2.4*	96
11/14	9 9a 9a1 9b	6,000 6,000 6,000	430 270 283	4	1 1 12-15	11.9	9.5 1.3 9.0	116	156	$2.2 \\ 2.2 \\ 1.3$	$1.6 \\ 1.7 \\ 2.2$	
11/18	10 10a 10b 10c1 10c2 10c3 10c4 10c5	6,000 6,000 6,000 6,000 6,000 6,000 6,000 6,000	460 290	4	$ \begin{array}{r} 1 \\ 12-15 \\ 20$	12.0 1	10.4 7.5	116		$1.7 \\ 1.7 \\ 1.7 \\ 2.1 \\ 1.9 \\ 1.8 $	1.4* 2.3 1.1*	96 14

*Gibbs M

Ca(OH)2 added ppm	Temp. deg. C	Post- treatment NaClO2 added ppm	Chlorine rate of feed lb/day
0	warm	1,380	48
$1,250 \\ 1,250 \\ 1,250 \\ 1,250$	40-45	1,780	72
2,500 2,500 2,500	40-45	1,130	108
2,500 2,500 2,500 2,500 2,500	33		108
3,750 3,750 3,750 3,750 3,750	33		144
3,750 3,750 3,750 3,750 3,750 3,750 3,750	34	240** 480** 720** 960**	144
5,000 5,000 5,000 5,000	37		240
5,000 5,000 5,000 5,000 5,000 5,000 5,000 5,000	34	240** 480** 720** 960** 1,200**	240
$6,250 \\ 6,250 \\ 6,250 \\ 6,250$	30		288
$\begin{array}{c} 6,250\\ 6,250\\ 6,250\\ 6,250\\ 6,250\\ 6,250\\ 6,250\\ 6,250\\ 6,250\end{array}$	34	240** 480** 720** 960** 960**	288
bod	**Lab	oratory tests	

APPENDIX II -- PHENOL WASTE TREATMENT WITH OZONE

(An Abstract of the Report by the Ozone Processes Division, Welsbach Corporation)

Ozone was provided for the test by a Welsbach Type C Ozonator with an ozoneproduction rate of 0.5 lb. of ozone per hour. Ozonized air was dispersed into waste by means of a perforated stainless-steel pipe located at the bottom of the tank.

Runs were made on both a batch and a continuous basis. Continuous runs were made at flow rates in the range of 0.5 to 3.0 gallons a minute.

Discussion of results -- Data developed during the pilot-plant test are collected in Tables 1 and 2. Table 1 contains data based upon continuous operation -- that is, application of ozone to waste as it flowed through a tank at a fixed rate. Table 2 contains data based upon batch-type operation. There is an appreciable difference in results obtained depending upon whether method of application was continuous or batch.

With batch-type operation, it can be seen in Fig. 2 that a dosage of 700 ppm of ozone reduced the phenols remaining to 0.2 ppm. With continuous operation, if there were no mixing, a dosage of 700 ppm should also produce a residual phenols concentration of 0.2 ppm. Actually, the application of ozonized air produces a violent mixing action. Thus, if waste flow and electricity were cut off, in a matter of a few minutes the agitation caused by air going into the mixing tank would produce a uniform mixture.

As a result of this mixing, incoming waste is rapidly diluted with partly oxidized waste and average phenols concentration greatly reduced. The smaller the phenols concentration the more ozone is required to oxidize a unit of phenols (Fig. 2). That this effect causes a very appreciable difference in ozone dosage required for a given phenols removal is evident from the data.

Since batchwise operation in a full-

scale plant would require alternate tanks and automatic controls to allow a continuously flowing volume of waste to be handled, considerable thought was given to use of a more complex type of reactor in which waste could be treated continuously. Obviously, the more complex the reactor, the greater is its cost.

The type of reactor, which seemed most likely to fit the need, was a packed tower. Several experiments on a laboratory scale were run with packed towers. Efficiency approaching that of batchwise operation could not be achieved. Rapid gumming of the packing material also occurred.

The gumming effect was not unexpected as tendency of waste towards gumming had been previously observed. Gumming of packing material in full-scale operation would present serious operating difficulties quite aside from the question of efficiency.

Reactors of more complex design were not investigated because of poor efficiency realized in the packed-tower tests. There is no doubt that the small additional cost of the second tank and controls needed, if operation is batchwise, would be much less than extra cost of a reactor sufficiently complex to treat waste with equal degree of success under the continuous method.

The choice of batch type operation, therefore, would appear to be indicated by economic considerations. It is obvious that any decrease in oxidation efficiency would necessitate an equivalent increase in installed ozone capacity. Since ozone capacity accounts for about 95% and treatment tanks and controls about 5% of the overall cost, it is apparent that an increase of 10% in ozone capacity would increase the overall cost almost 10%. But increases in size of treatment would have a relatively small effect on overall cost.

There is no inherent reason why any volume cannot be handled on a batch basis. It is purely a question of economics. Because of the type of reaction involved, any continuous reactor designed to produce an efficiency approaching batch treatment will have to be designed to operate with near-perfect counterflow conditions and virtually no mixing. This is extremely difficult to do with the large volumes of air involved. It also indicates that the reactor would have to be of expensive and complicated design.

Effect of pH -- It was discovered that the initial pH of the waste had an appreciable effect upon the ozone dosage required to oxidize a given concentration of phenols.

Although small-scale tests had shown some additional advantage in a pH of 12, during pilot-plant work it was found impractical to maintain a pH of more than 11.5 to 11.8 with lime in the hot ammoniastill waste. Attempts to increase pH beyond this range resulted merely in excessive amounts of lime being carried into the settling basins.

By use of sodium hydroxide some further experiments on effect of pH were carried out with initial pH adjusted to 11.8 and 12.8. At pH 11.8 the ozone dosage required to oxidize phenols was significantly less than at pH 12.8.

It therefore appears that increasing initial pH of ammonia-still waste up to about pH 12 favors phenols oxidation, possibly at the expense of some other oxidation reaction. On the other hand increasing initial pH as high as 12.8 appears to reduce efficiency of phenols oxidation. In explanation of the observed effects it has been shown by Conant and Pratt (J. Am. Chem. Soc. 48, 3220 - 32, 1926) that increasing pH decreases oxidation potential of phenols. Thus, at pH 5, apparent oxidation potential of phenol was found by them to be 0.80 and at pH 11, 0.55. Thus oxidation of phenol would be favored by high pH in cases where there were competing ozone-consuming reactions,

The explanation for apparent optimum around pH 12 may be that the known ozonedecomposing effect of high pH is enough to more than offset any gain in oxidation efficiency due to reduction in the oxidation potentials of phenol or other hydroxybenzene compounds.

Reduction in chemical-oxidation demand --Application of ozone to ammonia-still waste resulted in a reduction in chemical-oxygen demand (C O D). In Table 1 data have been collected and reductions in C O D per part of ozone have been computed. Average reduction was 0.7 parts C O D for each part of ozone.

Foaming -- It was noted that the waste had a tendency to foam when ozonized. Foaming occurred only if the waste were allowed to cool to ambient temperature. Since waste is normally hot this did not present any difficulties. Even at temperatures as low as 43 deg. C no serious foam. ing developed.

Since it might at some time be necessary or desirable to treat a cold waste, we believe that the treatment tank should be designed to take care of foaming. The tank, therefore, was fitted with a cover and an overflow to carry foam back to the incoming waste. This appeared to be a satisfactory solution.

Design considerations -- When the data from any of the batch runs (Table 2) are plotted, a graph similar to that in Figure 2 is obtained. The first section of the graph is a straight line (up to an ozone dosage of 200-300 ppm), and the balance of the graph is a curve of rapidly decreasing slope. When the points for the curved portion of the graph are plotted on semilogarithmic paper, it is found in each case that a straight line is obtained, ignoring a small constant residual phenols concentration.

This small residual concentration is apparently an analytical interference in the oxidized ammonia still waste with respect to both the Gibbs and Aminoantipyrine methods of analysis. This is evident from the fact that increasing ozone dosage decreases the phenols content until the concentration is reduced to a point somewhere between 0.2 and 0.5 ppm. After this point has been reached additional ozone dosage fails to reduce the (apparent) phenols concentration. On the contrary, with pure phenol each increment of ozone dosage reduces the phenol concentration by a measurable amount. But, even with pure phenol the red color normally developed with Aminoantipyrine changes to a yellow color when the phenol concentration is reduced to a few tenths ppm by ozone oxidation.

It is not known exactly what causes the interference. It may be a constituent of ammonia-still waste, it may be an oxidation product, or it may be a failure in the analytical method at these very low concentrations.

The phenols-ozone reaction plotted on semilogarithmic paper appears to follow the relation:

y = y'enx

Where, y = phenols remaining x = ozone dosage e = 2.71828+ y' & n = constants

It is apparent that ozone dosage required for a phenols-destruction plant will depend upon permissable phenols concentration limit set up by the regulating authority. When a limit has been established and waste volume and dilution figures are taken into account, the necessary ozone capacity for a phenols-destruction plant can be readily computed.

Cost -- Determination of limits to which phenols concentrations must be reduced, and of volume of waste to be treated are needed to compute the size -- and cost -of the ozone plant required.

High initial costs are offset by the following considerations. Once an ozone plant has been installed, operating costs are constant and predictable since determinative cost elements are fixed charges and charges for electrical energy. There are no freight charges, storage costs, materials handling costs, supply problems and fluctuating chemical costs. Cost of electricity has remained constant or decreased in recent years while cost trends for labor, freight and chemicals have been steadily upward.

Conclusions -- Ozone as an oxidant of a waste containing phenol or phenolic-type compounds has certain important advantages:

1. With ozone, critical control problems are absent. Ozone-phenol reaction products are less objectionable than phenol itself.

2. Examination of phenols-ozone reaction curves shows that a substantial decrease in ozone dosage results in only a disproportionately low concentration of unoxidized phenols. If ozone capacity were occasionally greatly exceeded, still only a small concentration of unoxidized phenols would remain in partially oxidized waste.

3. Ozone can be applied to waste as it comes from the fixed leg of the ammonia still without adjustment of temperature or pH.

4. It is physically possible to build up ozone residuals only to the extent of a

phenols-reaction products are less objec- reduced by use of ozone. tionable than phenols themselves.

5. Ozone will not change original chloride content of a waste.

part per million or so. Even then, ozone- 6. C O D and B O D are materially

7. Operating costs are nearly constant and predictable.



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CONTIN

Date	Sample	Temperature	נמ	H	Ozone		Phenols, p	T
1950	Number		Initial	Final	ppm.	Undistilled AAP	Distilled AAP	D
6-29	1 2 3 4		11.5 11.5 11.5 11.5	11.5 11.3 11.2 10.9	0 530 530 530	140 107 63 47	82	
6-30	1 2 3 4 5	73 63 64 59 73	11.7 11.7 11.7 11.7 11.7	11.7 11.4 11.1 11.2 11.3	0 515 515 515 0	118 51 32 21 119	38	
	7 8 9 10 11 12 13	56 52 52 51 68 50 51	11.7 11.7 11.7 11.7 11.0 11.0 11.0	10.7	515 690 690 690 690 690	25 12 10 9 117 8 7	16	
7-4	1 2 3 4	67 56 49 77 66 61	8.2 8.2 8.2 11.6 11.6 11.6	8.2 7.6 5.6 11.6 11.4 11.4	0 490 1010 0 520 690	170 94 49 168 29 18	47 39 28 58 15 10	
7-5	1 2 3 4 5	67 74 59 56 51	11.8 11.8 11.8 11.8 11.8	11.8 11.5 11.2 10.8	0 520 690 1030	176 32 12 5	77 20 8	
7-7	1234	71.5 48.5 45 43	11.7 * *	11.7 11.2 10.9 10.8	0 700 800 900	118 2.4 2.2 1.6	65 1.8 1.3 1.2	
7-10	1 2 3 4	70.5 51.5 49 48	11.7 11.7 11.7 11.7	11.7 11.2 10.6 10.1	0 800 900 1000	258 29 16 16	206 24 14 13	
7-13	1 2 3 4 5	64 48.5 45 44 45	11.4 11.4 11.4 11.4 11.4	11.4 9.6 9.1 9.2 9.1	0 800 900 900 900	186 25 12 14 16	123 17 11 12 14	

ous runs							
stilled Gibbs	NH3 (as N) ppm.	C.O.D. ppm.	C.O.D. Reduction ppm.	C.O.D. Reduction per part Ozone	Depth of Liquid Feet	Theoretical Detention Minutes	Sampling Time Minutes
78					10.5 10.5 10.5	123 123 123	123 178 208
36				N.,	8.5 8.5 8.5	99 99	30 60 90
10 8					8.5 8.5 8.5 8.5 8.5	99 99 133 133 133	120 165 30 60 90
46 5					8.5 8.5	133 133	120 180
46 37 29 58		2930 2140 1940 2220	790 990	1.6	6.5 6.5	76 152 29	75 165 45
16	45	1970 1650 1960	430 570	0.8	2.5	39	60
	133 119 118	1630 1590 1350	330 370 610	0.6 0.5 0.6	4.5 4.5 4.5	53 71 106	180 75 105
- 1.2	147 140 146	1580 1050 1080 1020	530 500 560	0.8 0.6 0.6	4.5 4.5 2.5	91 106 62	100 106 90
26	87 96 95	2380 1610 1430 1530	770 950 850	1.0 1.0 0.9	4.5 4.5 4.5	82 92 106	100 106 106
	345 320 300 307 290	2490 1810 1570 1690 1730	680 920 800 760	0.9 1.0 0.9 0.8	4.5 4.5 4.5 4.5	89 89 89 89	100 140 215 265

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(CONTI	INUED)						
illed ibbs	NH3 (as N) ppm.	C.O.D. ppm.	C.O.D. Reduction ppn.	C.O.D. Reduction per part Ozone	Depth of Liquid Feet	Theoretical Detention Minutes	Sampling Time Minutes
	422	2290				100	
	397 413 412	2010 2010 1890	280 280 400	0.3 0.3 0.4	6.5 6.5 6.5 6.5	132 132 132 132	90 186 241 301
	782 612 710	2660 2100 1740	560 920	0.4 0.7	6.5 6.5	213 213	240 310
	31 39	1800 1330	470	0.6	6.5		
	16	1930			6.5 6.5	51 51	90 125
	8 21 20	1770 1130 1030	640 740	0.6 0.7	6.5 6.5	175 175	195 255
	9 18 18	1750 1090 1070	660 680	0.5	6.5	205 205	200 260
	8 24 30	1780 960 840	820 940	0.5	6.5 6.5	234 234	200 310
	6 26 26	1400 560 560	840 840	0.5	6.5 6.5	277 277	300 360
	8 27	1470			6.5	277	300
	23	1140	330	0.2	6.5	277	360
	9 17 12 17	1390 930	460	0.5	2.5 2.5 2.5	59 59 65	56 90 120
	67 64 67 65	1920 1460	460	0.9	2.5 2.5 2.5 2.5 (Th (ma	29.5 35 41 41 ese tests were de on a jar	60 65 75 70
					2.5	29.5	29.5

Pate Sample Temperature pH Phenols, ppm. Undistilled Distilled Dis Ozone 1950 OC Initial Final Number ppm. AAP AAP 7-14 1 66 9.5 9.5 0 159 89 2 51 9.5 8.5 900 50 3 50 9.5 8.2 900 40 33 4 46 9.5 8.0 900 34 30 5 48 9.5 8.0 900 35 30 7-17 1 66 7.6 7.6 0 122 45 2 46 7.6 4.5 1300 45 35 3 4.7 44 7.6 1300 40 31 7-21 1 (High) 0 159 107 2 (800)11 9 1 7-24 69 11.6 0 185 168 11.6 11.7 2 11.6 76 51 350 69 3 11.6 11.7 73 48 350 66 7-25 1 70 170 147 11.7 11.7 0 2 49 11.7 11.2 5.3 1100 4.6 3 47.5 11.7 11.3 1100 5.6 4.9 11.8 7-26 1 67 11.8 0 164 135 23 12.9 1300 48 6.0 4.6 * 46 12.8 1300 4.9 3.9 7-27 1 74 11.7 11.7 0 190 157 3.3 3.2 2 48.5 11.7 1530 * 3 45.5 11.8 1530 2.8 2.6 11.7 7-31 1 69 11.7 0 80 58 2 11.5 1800 0.2 45 0.4 * 3 44 11.7 0.2 1800 0.4 8-1 1 70 11.6 11.6 0 172 113 2 11.6 45 10.6 1640 1.0 0.8 Caustic * 43 added 3 11.1 1640 0.9 0.8 11.6 8-2 1 11.6 0 174 131 **2 11.6 10.9 900 0.1 0.6 3 11.6 10.6 900 7.3 6.5 4.3 4 11.6 10.9 1000 3.3 11.2 8-3 1 11.2 0 214 170 2 10.7 11.2 500 51 42 3 10.1 11.2 44 37 600 11,2 4 9.3 700 33 28 5 10.5 700 30 25 9.7 5x1 800 7.9 5x2 9.3 900 2.0 5x3 9.2 1000 0.5 6 11.1 500 41

TABLE 1

TABLE 2

BATCH RUNS

Date	Sample No.	Initial	Final	Ozone, _ppm.	Phenols, ppm. Distilled AAP	Liquid Depth, Feet	Ozonization Time,Minutes
8-7	1 2 3 4 5 6	11.5 11.5 11.5 11.5 11.5 11.5	11.5 11.2 11.2 11.0 10.7 10.4	0 184 275 366 458 550	170 69 29 5.6 1.1 0.5	2.5 2.5 2.5 2.5 2.5 2.5	- 12 18 24 30 36
8-8	0* 1 2 3 4 5 6 7 8 9 10 11	8.5 11.7 11.7 11.7 11.7 11.7 11.7 11.7 11	11.7 11.5 11.4 11.3 11.2 11.1 11.2 11.2 11.2 11.2 11.2	0 100 200 300 400 500 600 700 800 900 1000 1100	89 61 35 12 2.7 0.5 0.3 0.2 0.2 0.2 0.2	- 4.5 4.5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	- 11 21 32 43 54 64 75 86 96 107 118
8-9	0* 1 2 3 4 5 6 7 8 9 10 11	10.9 11.9 11.9 11.9 11.9 11.9 11.9 11.9	11.9 11.7 11.6 11.5 11.5 11.4 11.3 11.3 11.2 11.3 11.2	0 100 200 300 400 500 600 700 800 900 1000 1100	127 86 54 29 12 3.2 0.7 0.3 0.3 0.3 0.2 0.2	- 5555555555555 6666666666 666666666666	- 15 29 44 59 74 88 103 118 132 147 162
8-10	0 1 2 3 4 5 6 7 8 9	11.8 11.8 11.8 11.8 11.8 11.8 11.8 11.8	11.8 11.6 11.5 11.4 11.2 10.8 10.3 9.8 9.6 9.3 9.1	0 100 200 300 400 500 600 700 800 900 1000	103 76 48 25 9 2.4 0.6 0.2 0.2 0.2 0.2 0.1	- 8.5 8.5 8.5 8.5 8.5 8.5 8.5 8.5 8.5 8.5	- 20 40 60 80 100 120 140 160 180 200

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TABLE 2
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(CONTINUED)

Date	Sample No.	Initial	Final C	ppm.	Phenols, ppm. Distilled AAP	Liquid Depth, Feet	Ozonization Time,Minutes
8-11	0 1 2 3 4 5 6 7 8 9 10	11.8 11.8 11.8 11.8 11.8 11.8 11.8 11.8	11.8 11.7 11.6 11.5 11.4 11.2 10.9 10.5 10.1 9.9 9.7 1	0 100 200 300 400 500 600 700 800 900	123 89 59 32 13 3.4 0.9 0.3 0.2 0.2	10.5 10.5 10.5 10.5 10.5 10.5 10.5 10.5	25 50 75 100 125 150 175 200 225 250
8-14	0* 123456789 10	10.2 11.8 11.8 11.8 11.8 11.8 11.8 11.8 11	11.8 11.6 11.5 11.4 11.3 11.2 11.2 11.2 11.2 11.1 11.3 11.2	0 200 300 400 500 600 700 800 900	80 58 34 14 3.9 0.9 0.3 0.2 0.2 0.2 0.2	- 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	- 6 12 18 24 30 36 42 48 54 60
8-14	0A* 1A 2A 3A 4A 5A 6A 7A 8A 9A 10A	10.2 12.8 12.8 12.8 12.8 12.8 12.8 12.8 12	12.8 12.8 12.8 12.8 12.8 12.8 12.8 12.8	0 97 194 292 388 485 582 680 777 874 970	114 81 54 31 15 5.8 2.1 0.8 1.2 1.0 1.0	- 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	- 12 18 24 30 36 42 48 54 60

* Initial pH adjusted on these runs.

APPENDIX III --- PHENOL-WASTE TREATMENT WITH CHLORINE DIOXIDE

(An Abstract of the Report by Mathieson Chemical Corporation)

This work represents the first detailed study of chlorine dioxide on coke-plant waste. The possibilities had been previously recognized due to use of chlorine dioxide in water treatment for removal of phenolic compounds from potable water. It has also been employed for over a year in a chemical-producing plant in the East for treatment of phenolic wastes.

First phase of the work was done by treating waste with a mixture of chlorine- in the second portion of the work. In this dioxide gas and air. Chlorine dioxide was method chlorine was fed through the same generated from a gas generator comparable control panel as above, diluted with a very to those in commercial use. Chlorine from small quantity of air and fed to a chloa cylinder was measured through a control rine-dioxide solution generator. A flow of panel where it was mixed with air at known 1 gal, per min, of water for dilution was rate and passed through a reaction tower. This tower was filled with commercial technical sodium chlorite where chlorine reacts to form chlorine dioxide:

 $C1_2 + 2$ NaClO₂ = 2 ClO₂ + 2 NaCl

The gas-air mixture was then fed to the waste treatment tower.

Disadvantages of this method of generation for this experimental work consisted of such difficulties as inability to directly measure the sodium chlorite consumption and difficulty in obtaining complete adsorption of the chlorine dioxide because of the large volume of air mixed with it, Furthermore the generation of chlorine dioxide as a solution instead of a gas lends itself to simpler commercial operation.

Chlorine dioxide is calculated by measurement of the flow of the chlorine through a rotometer.

The gas feed method of chlorine dioxide generation showed higher consumptions in chlorite than did the more accurate solution feed method. However it was possible to study the effect of many factors during the use of the gas method of treatment.

Solution-feed generation was employed also fed to the generator through a rotometer.

In this case a weighed amount of sodium chlorite was dissolved in a known volume of water in a calibrated container. The chlorite solution was pumped by a proportioning pump to the solution generator where the same reaction as above was employed in aqueous solution. This chlorine-dioxide solution was then added to the discharge side of the pump that lifted waste to the tower.

This method of chlorine-dioxide generation enabled closer measurement of quantity of technical sodium chlorite used in treatment. Although this method permitted only continuous operation, many variables were studied first by the gas method in batch operation.

Conclusions:

1. It has been conclusively shown on pilot-plant scale that chlorine dioxide will oxidize and remove phenolic materials from a complex waste to produce a practically colorless effluent.

2. Treatment with chlorine dioxide does not require any adjustment of pH. It can be used on either the alkaline or acid side. In the waste studied, effective results can be obtained by treating waste without pH adjustment.

3. Chlorine dioxide is effective at all temperatures studied. Therefore waste can be treated without temperature adjustment or control.

4. Reaction time necessary for chlorine-dioxide treatment is short. The shortest time studied in pilot-plant operation was 15 min. Other indications are that reaction is complete in several minutes. Laboratory work showed substantial elimination of phenols in 5 min. or less. This makes unnecessary large or complex treatment works.

5. Ammonia content of the waste studied had no effect on efficiency of treatment. Chlorine dioxide does not react with ammonia as does chlorine, thus variations in ammonia content do not affect treatment.

6. Chlorine dioxide can be used if desired with either pre- or post-chlorine treatment. Post-chlorine-dioxide treatment offers the advantage of removing chlorophenols remaining in effluent as a result of incomplete chlorination. Because of increased complexity of treatment, it does not appear advantageous to use this combination of treatments but rather to use chlorine dioxide alone.

7. It does appear advantageous to feed a mixture of chlorine and chlorine dioxide simultaneously in a ratio of about 2 to 1. This gave greater efficiency in this type waste.

8. Both plant and laboratory work show a reduction in C O D when chlorine dioxide is used, with negligible change in chloride content.

9. Laboratory work on this waste confirms other work elsewhere in indicating definite reduction in B O D due to chlorine dioxide use. 10. Color of a waste treated with chlorine dioxide is considerably reduced. Final color of ammonia-still waste was a pale yellow to colorless effluent.

11. If desired, partial treatment with chlorine dioxide can be employed with a reduction in phenol content without formation of undesirable compounds, such as chlorophenols, due to undertreatment.

12. No problem is foreseen due to overtreatment with chlorine dioxide. Mixing either with other wastes or the stream itself would easily remove this residual.

13. Control and operation of the chlorine-dioxide process would be a simple part-time operation, with automatic operation possible.

14. Greater efficiency would be expected in any treatment works with improved reaction conditions. Chlorine-dioxide losses were continuously experienced in these pilot-plant operations due to poor reaction conditions because of experimental-equipment design.

15. Cost of operation would be primarily cost of chlorite and the small amount of chlorine used. Chlorite consumption is obviously dependent on demand of the waste to be treated.

16. Capital investment for equipment to feed chlorine dioxide is small.

17. As will be seen from a study of curves in Fig. 3 there is an apparent demand for chlorine dioxide in this waste other than phenols. Thus on a waste containing primarily phenols a lowered chlorine-dioxide demand would be expected.

18. It will be further noted in studying the curves that a substantial reduction in phenols can be attained with a small dosage of chlorite, followed by an increasingly higher demand for chlorite to remove last traces of phenol in this particular waste.

19. When required chlorite dosage is

exceeded by variation in demand, resulting increase in phenols is very small.

Discussion of results:

were explored to determine effect of pH on with an accompanying wide variation in cost treatment:

- a high pH.
- b. By addition of acid to permit treatment of the acid side.

Results indicate that best efficiency No marked advantage was seen. for chlorine-dioxide use can be obtained by treatment of waste without pH control. Effect of varying chlorine:chlorite caustic should result in soluble salts.

Effect of temperature -- There was no marked effect due to temperature. Laboratory work showed complete treatment could utilized in forming chlorine dioxide from be obtained with chlorine-dioxide gas at chlorite produced in waste-treatment pro-90 deg. C.

sufficient gaseous chlorine dioxide into this chlorite to form more chlorine dioxwaste in short time.

However, pilot plant and laboratory work indicate contact time necessary to be powerful activating agents for chlorite to definitely less than 15 min. and probably form chlorine dioxide. It might be well to a matter of a minute or two.

Results indicate that ammonia content has could be tried. This type reaction would no effect on chlorite demand and ammonia be expected to effect economy in amount of content is unaffected.

This is one of the reasons, therefore, that it is not felt necessary or advisable to use pre- or post-chlorine treatment with chlorine dioxide. Widely varying ammonia content would necessitate dosage control Effect of pH -- Three major differences and a wide variation in chlorine demand to accomplish satisfactory waste treatment. Chlorine dioxide is independent of this a. By addition of alkali to maintain variable, thus simplifying control and treatment.

Effect of pre- and post-chlorine treatment -- Chlorine dioxide can be used with either pre- or post-chlorination. Prec. Without controlling pH at any level. treatment with 3,000 ppm chlorine dosage did not markedly affect chlorine-dioxide Average waste treated thus was started with dosage necessary for complete treatment a pH of 11.5 to 12.0 and at conclusion of when employed alone. The work has shown treatment had a pH of 2.0 to 4.0. The drop that chlorine dioxide can be used to desin pH is in part probably due to oxidation troy chlorophenols that would result from of phenols to organic acids. Work is in incomplete chlorination. One run was made progress to determine these reactions. where partial treatment with chlorine dioxide was followed by post-chlorination.

Hence treatment is simplified, eliminating ratio -- Varying ratios were tried from need for acid or alkali addition to raw 1 to 0.4, chlorine:chlorite to as high as waste with possible sludge problems. Neu- 2.0 to 1.0, chlorine:chlorite. Indications tralization of resultant acid waste by were that optimum results giving lowest chlorite consumption were obtained by use of a 2 to 1 chlorine to chlorite ratio.

It is believed that excess chlorine is cesses. Chlorine does not react directly with the waste. Chlorine dioxide origin-Effect of time -- It was difficult, due ally added, is reduced by the waste back to limited equipment, capacity, to get to chlorite; excess chlorine reactivates ide.

It is known that there are other more explore these at a later date in a plant operation. For example, addition of small Effect of ammonia content of waste -- amounts of acid anhydrides, aldehydes, etc. chlorite fed to waste.

10. at

33

dioxide gave definite reductions in both portional to chlorite dosage. As phenols COD and BOD.

Effect on chlorides -- Little effect was noted on chlorides due to chlorine dioxide.

Effect on color -- After treatment with chlorine dioxide all samples showed sub- Effect of overtreatment -- Residual of stantial reduction in color.

Effect of undertreatment -- All indications are that undertreatment with chlorine tent would remove chlorine-dioxide residdioxide results in some residual phenol ual. Chlorine-dioxide residual would not content in the waste but without objec- cause chlorophenols or other obnoxious comtionable products such as chlorophenols pounds when mixed with other contaminated being present. The phenol residual versus waters. Control of the process would be chlorite dosage is not a straight line. such that there would be little chance of a See Fig. 3. Reduction in phenol content in chlorine dioxide residual remaining.

Effect on C O D and B O D -- Chlorine this waste, therefore, is not directly proare lowered in concentration, amount of chlorite necessary for further reduction increases disproportionately.

> Resulting end products of oxidation of phenols by chlorine dioxide are much less objectionable than phenols.

> chlorine dioxide in treated effluent causes no difficulty. Mixing with other plant effluent waters that have an organic con-



TABLE I

TREATMENT OF PHENOLIC WASTE WITH CHLORIN

Date	Run No.	Type No.	Gals.Waste Treated	Temp. ^o C	рн	Chlorine Feed Cu.Ft./Hr.	Time (minutes) Cl2 on	Tech.Chlorid consumed Lbs./100 gls.
9/6/50	6-1	B	58.6	31-32	11.8-3.8	3.0	80	3.74
9/7/50	7-1	В	106.	37-39	12.0-11.1	3.0	60	1.66
9/7/50	7-2	в	106.	39-37	11.9-10.1	2.0	120	2.07
9/13/50	13-1	В	58.6	50	11.6- 2.1	3.0	6-0	-
9/14/50	14-1	В	106	57-51	11.4- 2.1	3.0	85	4
9/20/50	20-1	B	106	61-56	11.9-11.9	3.0	20	
9/21/50	21-1	В	58.6	46-45	11.9- 4.7	3.0	60	2.1-2.8
9/22/50	22-1	В	58.6	46-43	12.0- 4.9	1.5	105	1.8-2.5
9/25/50	25-1	В	106	30-43	12.0- 7.8	1.5	160	1.3-2.0
9/26/50	26-1	в	152	55-51	9.2- 3.6	3.0	105	1.9
9/27/50	27-1	в	106	50-45	11.8- 4.3	2.0	105	1.3-1.8
9/28/50	28-1	В	106	55-52	2.5- 2.1	3.0	90	2.4
9/28/50	28-2	В	106	46-45	6.0- 2.5	3.0	75	1.9
9/29/50	29-1	в	106	61-54	11.9-11.8	3.0	140	2.1-2.65
10/17/50	17-1	в	106	63-61	9.3- 9.1	3.0	40	0.78
10/18/50	18-1	c	199	54-50	9.5-8.7	3.0	90	1.3
10/19/50	19-1	c	199	61-57	8.6- 5.1	3.0	60	0.83
10/19/50	19-1B	c	199	54-50	6.9- 4.0	3.0	90	1.25
10/23/50	23-1	c	106	79-60	9.7- 4.9	3.0	115	3.0
10/27/50	27-1	B	106	60-55	11.7-10.7	2.0	55	1.04
10/27/50	27-7	c	106	59-56	11.7- 8.8	2.0	60	3.67
10/31/50	31-1	B	106	75-65	12.0- 9.0	3.0	60	1.57
10/31/50	31-5	c	106	75-64	12.0- 6.1	3.0	60	5.5
10/31/50	31-8	C	106	75-61	12.0- 5.3	3.0	30	3.7
11/2/50	2-1	C	106	54-51	8.2- 2.2	3.0	75	1.95
11/2/50	2-5	C	106	52-46	8.2- 2.3	3.0	60	5.5
11/2/50	2-10	C	106	52-48	8.2-	3.0	45	3.7

Note 1.- Where two figures given for chlorite consumed, First figure is for results at essentially the same as the final result given. Second figure is for total c

Note 2.- B. Batch run C: Continuous run

DIOXIDE GAS

1	Pheno	P Reduct	ion - I DAA	pm P	Ammon	Content	aylses C.	- ppm 0.D.	Chlo	rides		Remar	ke	
ite	Start	Finish	Start	Finish	Start	Finish	Start	Finish	Start	Finish				-
	174	0.2		-		+						Contro	18	OK
	180	31.0	168.	25.0	125	127	1600	970	7800	7900				"
	196	4.5	108	0.8	134	124	1530	1030	7900	8000				.u.
	209	0.8	172	0.9	74	54	1820	610	9700	11300	4	Cl ₂ pr		urehig
	330	4.5	291	2.5	51 (A.									unkom
	183	130											"	30+
	133	0.1	100	0.1	1941							Contro	30	K
	148	0.1	110	0.1										
	96	0.1	58	0.1	14	20			7200	7500				
	80	0.2	54	0.1	408	426								
	160	0.1	134	0.2										
	198	1.9	174	2.4									OB	acid added
	182	3.8	152	3.6										
	131	0.1	105	0.1	5									NaOH
	88	2.1	36	0.8	2160	2390								added
	110	2.0	76	b. 2		-,,,,								
	140	1.0	10	4.1										
	110	60.	61	43.								"		
	86	54.	51	42.									*	
	131	11.	79	9.0										
- *	153	85.	107	63.										
	153	70.	107											
	148	35.	109	25.										
	148	38.	109	32.										
	148	49.	109	40.									=	
	125	2.6	55	1.7									Ħ	
	125	1.6	55	0.8										
	125	1.6	55	0.7										

ntermediate period of time where phenol content is sumed where overtreatment was obtained.

Results	AP AAP Pheno. Corr Factor	3.0	2.0	9 162 2.0	08 118 2.0	73 1.5	3 42 1.66	1.66	2.0	1.66	1.5	1.5	1.5	1.5		1.5	1.5	
Pre Cl ₂ I	ppm DAJ app1.			1000 10	2000 10	3000	3000 4											OLLL
	Cl ₂ : TSC							1:1.5	1:1.25	1:1	2:1	1:2	2:1	1:0.25		1.3:1.0		
	Time	157	451	109	500	09	301	109	157	301	109	109	109	109		109	109	101
ates	Pounds TSC Cons'd/ 100 gals.	2.92	1.9	1.15	1.48	0.66	0.94	0.94	1.23	1.52	0.62	0.66	0.64	0.66		0.66	0.66	
Feed R	Waste gpm	0.5	1.0	1.0	1.0	2.0	1.5	1.5	1.0	1.5	2.0	2.0	2.0	2.0		2.0	2.0	
	Cla C.F.H.	5.0	5.0	2.5	2.5	2.5	2.5	3.0	3.0	7.0	7.0	7.0	8.0	1.5		5.0	5.0	0-2
	Temp. °C	24°	240	42-260	55-240	26°	26°	52-170	* 52-21°	25-18°	25-21°	25-28°	55-38°	55-38°		50-20°	50-28°	50-270
	Hq	7.6 - 2.2	7.6 - 2.0	12.0 - 3.4	11.8 - 2.4	12.0 - 6.5	12.0 - 6.5	12.1 - 6.4	12.1 - 3.8	12.0 - 2.2	12.0 - 2.2	12.0 - 9.2	12.1 - 2.4	12.1 - 2.8-	8.9	12.1 - 4.8	12.1 - 4.9	E C - L CL
AAP	Orig. Final	136 - 1.4	136 - 40	165 - 22	170 - 4.8	170 - 37	170 - 2.1											
DAAP	Orig. Final	75 - 1.8	22	120 - 20	118 - 1.0	118 - 21.0	118 - 0.45	104 - 15.0	104 - 1.3	84 - 2.0	84 - 2.4	84 - 56	144 - 72	744 - 95		143 - 54	143 - 68	7 00 - 511
	n No. Date	(1-5) 11/3	(6-8) 11/3	(1-6) 11/8	(1-4) 11/9	(7-12) 11/10	(13-16)11/10	(1-5) 12/6	(6-10) 12/6	(1-3) 1/2	(4-6) 1/2	(7-9) 1/2	(1-4) 1/3	(5-8) 1/3		(1-4) 1/4	(6-9) 1/4	1/1 (01-01)

Note: In all runs above 1 gpm water was fed with the ClOz. Final DAAP and AAP phenol results are corrected for the above dilution factor.

No NH3 determinations made in this series.

TABLE II

CHLORINE DIOXIDE SOLUTION TREATMENT

APPENDIX IV -- DAAP METHOD FOR PHENOL ANALYSIS

Photometric Method for the Determination of Phenol in Ammonia Still Waste (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 and has a sensitivity of 0.1 ppm.

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, American Public Health Association and American Water Works Association - 9th ed.).

Quinone and hydroquinone interfere slightly by producing a color, 100 ppm of these constituents under the test conditions being equivalent to approximately 1 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 sulfate. (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. Adjust the solution using pH meter to pH of 9.8 (9.6 - 10.0) using a minimum of 1 drop of dilute 1:1 hydrochloric acid and 5 ml. of dilute 1:9 ammonium hydroxide (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 the blank reading (7) on the photometer. (8) Add 2 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 of phenol equivalent to the blank reading and to the total reading.

Calculations:

Without Distillation: micrograms total phenol - micrograms phenol equivalent in blank $ppm phenol = \frac{(total reading - blank reading) x factor (11)}{ml. of sample}$ With Distillation: micrograms total phenol - micrograms phenol equivalent in blank x .93 (12) $ppm phenol = \frac{(total reading - blank reading) x factor x .93}{ml. of sample}$

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, an excess of $FeSO_4$ is added to remove the oxidant. This excess of $FeSO_4$ introduces no difficulties.

(2) $CuSO_4$ 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 H_3PO_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 (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 by adjusting the pH to 9.8 (9.6 - 10.0) using a minimum of 1 drop of dilute 1:1 hydrochloric acid and 5 ml. of dilute ammonium hydroxide. (1:9).

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 is precipitated by addition of an excess of CdCl₂ solution followed by filtration.

(5)	ppm	P	nenol	ml, Sample Taken	
	0.1	-	6	75	
	6	-	20	25	
	20	-	100	5	
	100		500	1	
	500	-	2,500	0.2*	

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

(6) The pH after addition of 4-aminoantipyrine and potassium ferricyanide should be in the range of 9.5 to 10.0. The addition of this amount of hydrochloric acid and ammonium hydroxide acts as a buffer and prevents a large drop in pH. It is more practical to make the pH measurement before addition of reagents instead of afterward.

(7) The volume of solution used for rinsing and for the blank 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 blank has been found to be satisfact-ory.

(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 as the reference solution in an absorption cell having a 1-cm. light path. With the Klett-Summerson photometer Filter No. 52 is used and with the Kromatrol photometer Filter No. 5 (525 mu.).

(9) If there are elements present, such as copper, which react with K3Fe(CN)₆, a 6% (NH₄)₂S₂O₈ solution is used instead. With persulfate the color development is slower (requiring at least 3 minutes for full color development).

(10) The color fades on exposure to light. Therefore, the reading should be obtained within one minute after development of the color.

(11) The calibration curve is prepared by adding various amounts of phenol (up to 500 micrograms) in the form of a standard phenol solution to a beaker, adjusting the pH, and developing the color exactly as directed in the main text. The readings are plotted against micrograms of phenol present. For the most accurate values the calibration curve should be used; however, an average factor may prove sufficiently accurate in most cases.

micrograms

photometer reading

(12) Under the conditions of the distillation it has been found that when 100 ml. of distillate is obtained from 110 ml. sample, approximately 98% of all the phenol present is found in the distillate. Therefore, multiplying by .93 (10 x 100) gives the correct phenol content of the original sample.

Solutions:

4-Aminoantipyrine (2%): Dissolve 0.50 g. 4-aminoantipyrine in 25 ml. phenol-free water.

Factor = -

Potassium Ferricyanide (8%): Dissolve 8.0 g. reagent grade K₃Fe(CN)₆ in 100 ml. phenol-free water.

Standard Phenol Solution (1 ml. = 100 micrograms phenol):

Dissolve 0.200 g. reagent grade phenol in 50 ml. of phenol-free water, dilute to 200 ml. in a volumetric flask and mix. Pipette 20 ml. of this solution into a 200 ml. volumetric flask, dilute to the mark, and mix.

Comments on this method for phenol analysis:

1. Preliminary work showed that a buffer may be used for the adjustment of pH.

2. It is believed the sensitivity of this method is 0.1 ppm phenol, and the reproducibility is better than 5%. Use of an average factor (instead of the calibration curve) on the Klett-Summerson photometer introduces a maximum error of 3%.

3. It was found that many different types of samples gave the same values for phenols with and without distillation. The dephenolized still waste at Hamilton, however, gave different values when samples were distilled than were obtained without distillation.

The various samples which gave the same values for phenol, with and without distillation, were as follows:

Coke plant (Hamilton, O.): total effluent, NH_3 cooling coils, quenching water, light oil condenser water, light oil separator, wash oil cooler, purification liquor, and still feed.

Bakelite waste containing formaldehyde.

Refinery cracking process waste and other units (containing high sulfide).

A paper mill waste which contained high phenol and a large amount of chloroform gave higher values when it was not distilled.

5. Sulfites interfere in this method. Possible methods for removal of sulfites are:

(a) Addition of excess $\mathrm{K_2CrO_4}$ (cold) to sample that is to be determined without distillation.

(b) Digestion with ferric iron below boiling followed by distillation.

(c) Distillation of phenol from slightly basic solution (about pH 8).

6. Good values were obtained on standard solutions when the pH ranged from approximately 9.3-10.5 for color formation. In this work the pH was adjusted to 10.5. But after discussion with the U.S. Public Health Service, the range of 9.6 to 10.0 was employed in this procedure to provide agreement with the extraction modification of the AAP method used on river waters. Later laboratory work showed that a pH range of 9.6-10.0 gave maximum color development and this range is recommended for the procedure. There was close agreement in the phenol values obtained on ammonia still waste at pH 10.5 and at pH 9.8.

7. Much investigation can be made into the reaction between 4-aminoantipyrine and the various phenols with respect to color and intensity. Preliminary studies show:

Phenolic Compound	Color	Color Compared to Phenol (520 mu Filter)*
Phenol	Red	100%
o-cresol	Red	70%
m-cresol	Red	63%
p-cresol	Red	3%
Pentachlorophenol	Green	0 (fades immediately)

*Readings made within one minute after color formation.

8. Investigation may also be made on interference by quinone. Apparently, distillation of the sample at pH 8.0 eliminates quinone and gives satisfactory values for phenol.

9. The same values were obtained by both the Gibbs method and the 4-aminoantipyrine method (utilizing distillation) on all samples analyzed by both methods. These samples were: coke plant wastes (Hamilton, O.), bakelite waste, and refinery waste.

10. When distillation was conducted under the conditions given in the method (100 ml. distillate collected from 110 ml. original sample) the following facts were observed:

Approximate % Solution Distilled	Approximate % Phenol Distilled	
9	18	
18	34	
27	49	
36	62	
46	72	
55	81	
64	88	
73	93	
82	96	
91*	98	
	Approximate % Solution Distilled 9 18 27 36 46 55 64 73 82 91*	

This was done on solutions containing 5-400 ppm phenol. A slightly greater percentage of the phenol distilled over from the more concentrated solution.

*Equivalent to 100 ml. of distillate (110 x .91)

