United States
Environmental Protection
Agency

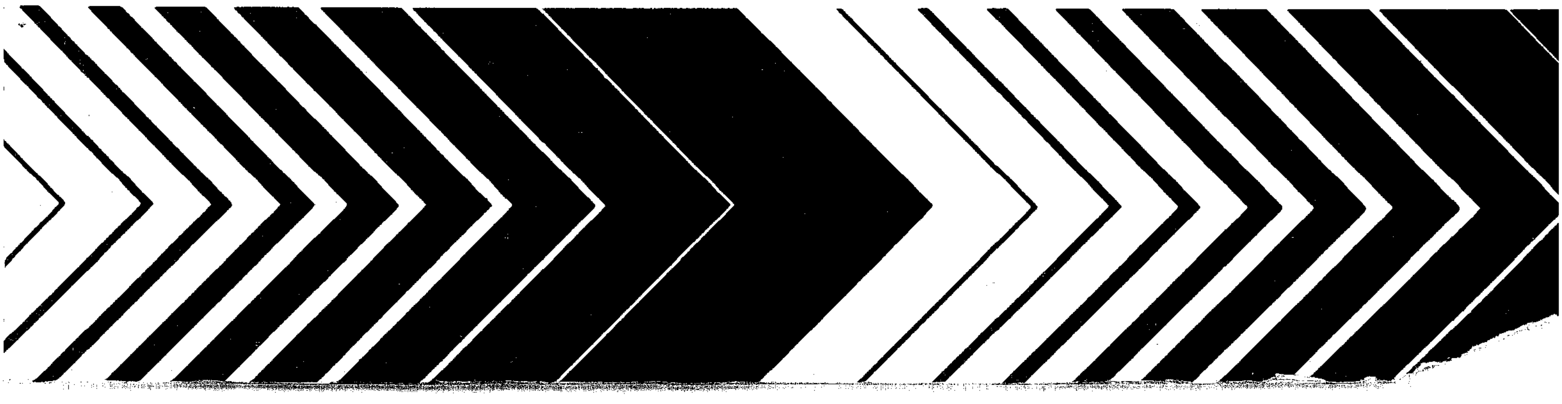
Robert S. Kerr Environmental Research
Laboratory
Ada OK 74820

EPA-600/2-80-060
April 1980

Research and Development

Ozone for Industrial Water and Wastewater Treatment

A Literature Survey



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EPA-600/2-80-060
April 1980

OZONE FOR INDUSTRIAL WATER AND WASTEWATER TREATMENT

A Literature Survey

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DISCLAIMER

FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

Increasing concern over the presence of toxic or nonbiodegradable components in treated effluents has dictated that research be performed to establish technologies for removal or conversion of those components to innocuous or treatable information on the application of ozone technology to control undesirable contaminents in wastewater streams.

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ABSTRACT

This research project and technology transfer effort was initiated in response to growing national concern about the discharge of industrial chemicals and by-products from industrial processing plants into the environment. The technology of oxidation of these chemicals by means of ozone, a very powerful oxidant, offers promise for being able to eliminate some of these chemicals from industrial wastewaters prior to discharge. Therefore this program was initiated to survey the published ozone literature and assess how ozone has been used in the past to cope with specific industrial water and wastewater problems.

This report includes a section on the fundamental principles of ozone technology, which describes the generation of ozone on commercial scale, the various methods of contacting ozone with aqueous solutions and methods of analysis for ozone from the point of view of process controls.

Industries are grouped into 20 individual categories which are discussed separately as to the known uses of ozone in treating waters and wastewaters in each category. More than 500 published articles were reviewed. Some of these articles were abstracted, and these abstracts have been assembled in a companion report entitled, "OZONE FOR INDUSTRIAL WATER AND WASTEWATER TREATMENT, An Annotated Bibliography." A literature survey also was conducted on the subject of the organic oxidation products obtained upon conducting ozonations in aqueous systems. This review is the subject of a separate section of the report.

Finally, a section is included which describes the biological activated carbon (BAC) concept, which is being practiced in certain European drinking water treatment plants. The BAC subsystem involves ozonation to partially oxidize dissolved organic materials so that they will become more easily biodegradable. The ozonized solution then is filtered through an inert medium and passed through granular activated carbon (GAC) adsorbers. Because of the presence of large amounts of dissolved oxygen (DO) and biodegradable dissolved organic materials, aerobic biological activity grows in the inert and GAC media. This biomass is capable of converting dissolved organic carbon to CO_2 and water and of nitrifying ammonia. At the same time, the adsorptive capacity of the GAC for strongly adsorbed, non-polar organic compounds is maintained and the useful life before reactivation is required is greatly extended under certain conditions.

This report was submitted in fulfillment of Grant No. R-803357 by the International Ozone Association, Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 1974 through July 1977.

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ACKNOWLEDGEMENTS

The authors are grateful for the assistance of many people whose efforts were essential to the accomplishment of this work. First, we thank the State of Connecticut, Department of Environmental Protection for their financial contribution in support of this program.

For the gathering and abstracting of the many articles cited, we are appreciative of the efforts of Dr. Archibald G. Hill, William J. Geist, Jane Tofel, James King, Dr. Stanley Padegimas, John Graumann, Teresa Czaposs and Barbara Cowley-Durst.

We also thank Dr. Walter J. Blogoslawski of the National Marine Fisheries Service for critically reviewing those sections of this report dealing with aquaculture and biofouling, Dr. L. Joseph Bollyky of Bollyky Associates for reviewing the sections dealing with cyanides and cyanates as well as electroplating, and Captain Barry W. Peterman of the Army Medical Bioengineering Research & Development Laboratories for reviewing the section on hospital wastewaters.

SECTION 1

INTRODUCTION

Although ozone has been used to treat drinking water at the city of Nice since 1906, and today there are more than 1,000 water treatment plants in Europe alone employing ozone for many different water treatment purposes (Miller et al., 1978), industrial wastewater treatment with ozone is still, relatively speaking, in its infancy.

Current water pollution problems with industrial wastewater discharges have prompted renewed interest in the use of powerful oxidants, including ozone, for treating these wastewaters for recycle and reuse, or prior to discharge to the environment.

In addition, where halogenated oxidants such as chlorine and hypochlorite are currently used to treat municipal and industrial wastewaters, toxicities of these halogenated wastewaters to indigenous aquatic life also have prompted studies on alternative treatment techniques, including ozonation.

In recognition of the potentials for ozone to alleviate certain industrial wastewater pollution problems, the U.S. Environmental Protection Agency, Office of Research & Development, funded a grant (R-803357-01-3) to the International Ozone Institute to conduct a state-of-the-art review of the published literature dealing with the use of ozone. This report will summarize the results of that survey.

This survey is not an exhaustive review of the published literature, in that only the more readily available articles were obtained. In addition, much of the Russian, Japanese and German literature could not be translated due to limitations of time and funding. Nevertheless, some 430 published articles were reviewed and abstracted. Abstracts of the more pertinent articles have been compiled in a companion to this report, entitled, "OZONE FOR INDUSTRIAL WATER AND WASTEWATER TREATMENT, An Annotated Bibliography", published in the National Technical Information System (NTIS).

SECTION 2

CONCLUSIONS

1) Systems for generating and applying ozone to water and wastewater consist of four components:

   a) electrical power generation
   b) feed gas preparation (air or oxygen)
   c) ozone generation
   d) contacting of liquid with ozonized gas

2) When oxygen is used as a feed gas to prepare ozone, provisions usually are made to purify, dry and recycle contactor off-gases to the ozone generator.

3) Ozonation has been used on full commercial scale for treating drinking water since 1906 and today there are more than 1,000 drinking water treatment plants throughout the world using ozone for many purposes. These applications are based upon the strong oxidizing properties of ozone in water and upon its ability to disinfect bacteria and inactivate viruses and are as follows:
   - soluble iron and manganese
   - organically complexed manganese
   - color removal
   - taste & odor-causing components
   - algae removal
   - organics (phenols, detergents, pesticides, etc.)
   - microflocculation of dissolved organics
   - inorganics (cyanides, sulfides, nitrites, etc.)
   - suspended solids removal
   - pretreatment for biological processes
   - bacterial disinfection
   - viral inactivation

4) For treating industrial water and wastewaters, ozone is used for many of the same oxidative purposes as in treating drinking water:
   - disinfection
   - cyanide removal
   - dissolved organics oxidation
   - color removal

   but in addition:
   - recovery and reuse of photographic bleach solutions
   - bleaching of paper pulps

COMMERCIAL WATER & WASTEWATER APPLICATIONS

5) In Aquaculture, ozone is used for (a) disinfecting seawater in European shellfish depuration stations and (b) disinfecting and lowering BOD levels in marine aquaria in the USA (Sea World). Ozonation of seawaters destroys red tide organisms.

6) In Food & Kindred Products, ozone is being used for (a) treating waters for washing baby food bottles and (b) disinfecting water used in the brewing industry in Europe, Canada and the USA.

7) In Metal Finishing, ozone has been used continuously since 1957 at the Boeing Co., Wichita, Kansas for lowering cyanide concentrations in their wastewaters from 0.17 mg/l to below 0.06 mg/l. Since 1973, Sealectro Corporation (Mamaroneck, N.Y.) has been using ozonation of copper and silver plating wastes to lower cyanide concentrations from 60 g/l to below 0.1 mg/l. Ozone coupled with ultraviolet (UV) radiation has been used since late 1976 at a U.S. Air Force base to lower cyanide concentrations in plating wastes from 4,000 mg/l to less than 0.3 mg/l.

8) In Organic Chemicals, two Russian plants manufacturing caprolactam treat their wastewaters biologically, then by ozonation, then store the ozonized wastewaters in biological ponds prior to reuse as cooling waters. Costs for ozonation are about 15% of the total costs of biological treatment at these Russian plants.

9) The only Petroleum Refinery known to be using ozonation is located in Sarnia, Ontario, Canada. Ozone is used as a polishing agent to reduce phenolic levels to below 3 parts per billion (ppb). This low discharge standard is necessary, because the plant outlet is close to the drinking water intake of a nearby city. The ozone demand of this wastewater is 3.5 to 6 pounds (lbs) of ozone per pound of phenol destroyed.

10) In Photoprocessing, ozone is used commercially for the regeneration and reuse of spent ferricyanide bleach. Spent ferrocyanide complexes are so stable to ozonation that they merely are oxidized back to the ferricyanide form, in which they can be reused. This application has been commercial since the early 1970s and is claimed to produce a savings of 2 to 3¢/roll of film processed. Investment costs for a 200 grams per hour (g/hr) ozone bleach recovery system can be recovered in about five years.

11) In Pulp & Paper, ozonation is being demonstrated commercially in Norway for bleaching of pulps. If successful, this bleaching process would eliminate or lower the toxicity of current discharges from pulp bleaching operations to indigenous aquatic life. Similar demonstrations of ozone for pulp bleaching are being conducted in Canada and the USA.

12) Also in Pulp & Paper, the potentials of producing yeast from spent sulfite liquors by ozonation, followed by bacterial fermentation are showing promise.

13) In the Soaps & Detergents category, a car wash in Vienna, Austria has been recycling 19,915 gallons per day (gpd) of washwater since 1970 by aeration, skimming, sedimentation, flocculation, filtration, ozonation and activated carbon filtration.

14) In Textiles, at least nine Japanese dye manufacturing or textile processing plants are known to be using ozone on commercial scale for decolorizing wastewaters. Ozone decolorizes disperse dyes well, without causing increases in turbidity, but has little effect upon chemical oxygen demand (COD) content. Sulfur- or chromium-containing dye wastewaters are not decolorized as effectively with ozone.

15) One of the Japanese plants treats 0.87 mgd of dye wastewaters by 2-stage ozonation (maximum ozone dosage of 50 mg/l) then filtration through granular activated carbon (GAC). The process is free from sludges and cost 34¢/1,000 gallons (gal) in 1974. Operating costs for decolorizing cationic dyes in wastewaters at a second Japanese textiles processing plant treating 1,500 cubic meters per day (cu m/day) [0.36 million gallons per day (mgd)] were 10.19 yen in 1972. Capital costs in 1972 for this treatment plant were 28 million (MM) yen.

GENERAL CONCLUSIONS

16) Ozonation of seawater produces a stable oxidant residual which is toxic to juvenile but not to adult shellfish. This toxicity is caused by oxidation products of bromide ion, and is also formed by chlorination of seawater.

17) Ozonation is being compared with chlorination and other candidate biocides for treatment of power plant cooling waters in a demonstration program at Public Service Gas & Electric Co. of New Jersey.

OXIDATION PRODUCTS OF ORGANIC MATERIALS

18) Complete oxidation of dissolved organic materials to CO_2 and water in aqueous solutions is rare by means of any oxidant. In general, if an organic material is resistant to oxidation by ozone (the most powerful oxidant used in water and wastewater treatment) it will also be resistant to oxidation by any other (weaker) oxidant. Conversely, if partially oxidized intermediates are produced upon ozonation, they also will be produced when using other oxidants.

19) Oxidation products formed by ozonation do not contain halogen atoms, unless bromide or iodide ions are present.

20) Heptachlorepoxide may form upon ozonation of aqueous solutions of heptachlor. The epoxide is stable to further ozonation. However, epoxides also have been isolated as intermediates from reactions of unsaturated organic compounds with chlorine or chlorine dioxide. Thus it is important to know the structure of organic materials being oxidized

with any oxidant, to understand the mechanisms of oxidation of each type of compound, as well as to design sufficient oxidant into the treatment process.

21) Oxidation of some pesticides (aldrin, 3,4-benzopyrene) in clean water proceeds rapidly, but in waters containing suspended solids, the dissolved organics can be adsorbed and "protected" against rapid oxidation.

22) Changing oxidants from chlorine to ozone will eliminate the formation of halogenated organics, but will have little effect upon the formation of non-halogenated organics which are produced by either oxidant.

23) Ozonation of solutions of biorefractory organic materials generally increases the biodegradability of these materials, especially during the early stages of ozonation. Prolonged treatment with ozone then will lower the BOD as well as the COD.

24) Oxidation rates of solutions of organic materials are rapid during the early stages of ozonation, but then the rates slow considerably. This is explained by (a) the concentrations of readily oxidizable organic materials becoming lower and (b) the organic oxidation products of ozonation being more refractory to oxidation.

25) Many compounds which are oxidized slowly with ozone will react 100 to 1,000 times faster in the presence of UV radiation or ultrasonic energy.

26) Ozonation of p-aminoazobenzene produces nitrosoazobenzene and nitroazobenzene as intermediate products and increases the color of the solution. Continued ozonation converts these intermediates into oxalic acid, glyoxalic acid and nitrate ion.

BIOLOGICAL ACTIVATED CARBON

27) The processing sequence of ozonation, followed by filtration through an inert medium (sand, anthracite) then through GAC converts ammonia to nitrate and lowers the dissolved organic contents of drinking waters in several European plants. It also meets current discharge standards of a combined industrial/municipal wastewater in Cleveland, Ohio. However, the process is not known to have been demonstrated on industrial wastewaters. It offers the potential for substituting for breakpoint chlorination (for ammonia removal), thereby eschewing the formation of halogenated organic materials, and for prolonging the useful life of GAC columns. Some European drinking water plants have not had to regenerate their GAC beds or columns for over 2.5 years.

SECTION 3

RECOMMENDATIONS

1) When considering the use of ozonation as part of a water or wastewater treatment scheme, the desired purpose(s) of ozonation should be related to the rate(s) of reaction of the impurities to be oxidized. Oxidation rates of readily oxidized materials will be controlled by the rate of mass transfer of ozone into solution. Oxidation rates of refractory materials will be reaction rate controlled. For optimal use of ozone, different types of ozone contacting devices should be evaluated.

2) In designing an ozonation pilot test unit, always provide for measurement of ozone in the contactor influent and effluent gases and determine the ozone utilized, not just the ozone dosage. More than 95% ozone utilization generally can be attained with full scale ozone contactors, but this efficiency rarely can be obtained in the laboratory or with small pilot scale systems.

3) Always provide for treatment of ozone-containing contactor off-gases, either by recycling or by destruction. Ozone contactors always should be covered.

4) Ozonation studies should be conducted with actual wastewaters whenever possible. Suspended solids in wastewaters may adsorb oxidizable materials and render them more difficult to oxidize than would be indicated by studies in pure solutions.

5) If organic oxidation products are of concern, then it will be important to identify the organic compounds originally present and to understand their mechanisms of oxidation. In addition, it is important to design sufficient oxidant into the process to accomplish the amount of oxidation desired. Some compounds are oxidized first to intermediates which are more toxic than the starting materials, before being further oxidized to innocuous compounds.

6) In comparing the cost benefits of using an ozonation technique versus another process for accomplishing a single pollution control objective, one should also be aware of the additional functions that ozone performs, which many times are advantageous technically and economically. For example, in decolorizing effluents from biologically treated wastewaters with ozone, disinfection also is obtained, as well as an increase in DO content.

7) Demonstrations of the BAC technique (ozonation, filtration through inert media, filtration through GAC should be conducted to determine the potentials of this technique to extend the useful life of GAC and to remove ammonia in industrial wastewater treatment.

SECTION 4

FUNDAMENTAL PRINCIPLES OF OZONE TECHNOLOGY

GENERAL HISTORY (Rideal, 1920)

In 1785 Van Marum, a Dutch philosopher, noticed that the air in the neighborhood of his electrostatic machine acquired a characteristic odor when subjected to the passage of a series of electric sparks. In 1801 Cruickshank observed the same odor in the gas formed at the anode during the electrolysis of water.

In 1840 Schonbein reported the odor as being due to a new substance to which he gave the name ozone, derived from the Greek word "ozein", meaning to smell. Schonbein also was the first to suggest that ozone may occur naturally in the atmosphere.

The present construction of electric discharge ozone generators developed from the apparatus originally designed by Werner von Siemens in 1857 in Germany. Brodie (England) and Berthellot (France) also designed early ozone generators.

Siemens' first ozonizer essentially consisted of two coaxial glass tubes, the outer coated externally and the inner coated internally with tin foil, air feed gas being passed through the annular space. Brodie substituted water as the electrode material in place of tin foil, and Berthollet used sulfuric acid.

The Siemens type of ozone generator has been developed commercially into a form suitable for industrial production of ozone, and today most of the ozone generating systems installed in water and wastewater treatment plants are of this type. Glass tubes are coated internally with a metal dielectric and the individual tubes are cooled by means of water (see Figure 1).

Modifications to the original Siemens generator have been made, primarily dealing with the method of cooling, and today many different types of generators are available. All operate on the same general principle, corona discharge, which requires high voltages and/or high frequencies, thus creating considerable heat. In turn, this requires that the generators be cooled in order to maximize ozone production yields and minimize power consumed. Cooling is usually accomplished by means of water (Siemens and Otto generators), air (Lowther plate type generator) or water and oil (cooling of both electrodes, one with water, the other with oil).

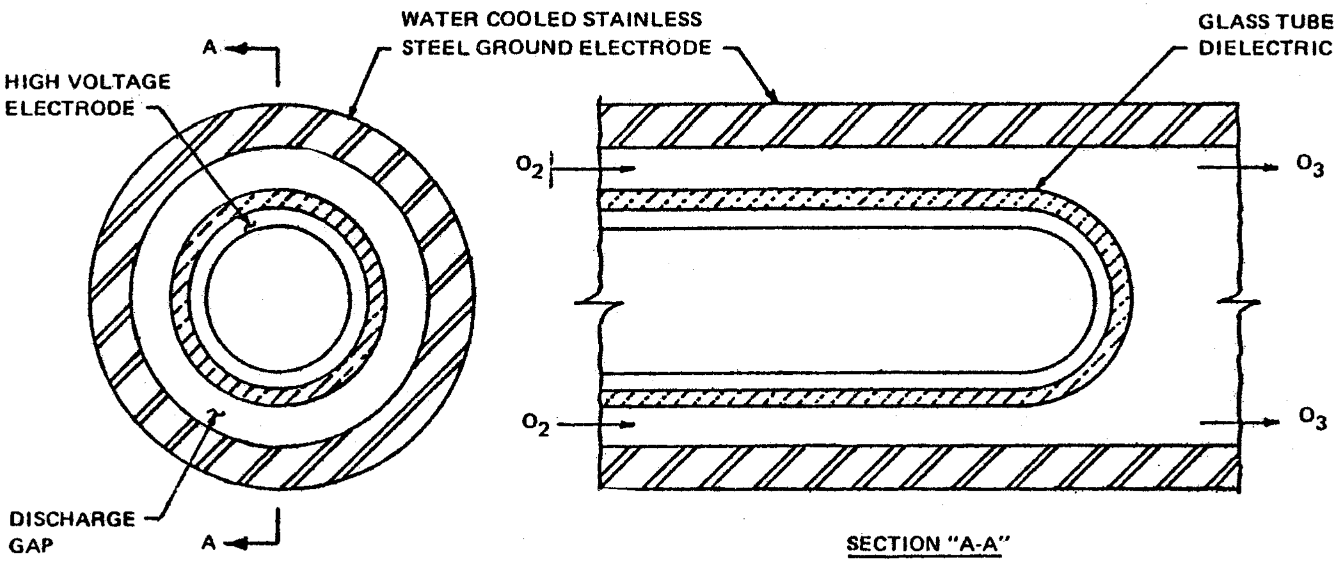

Figure 1. Schematic diagram of tube type, water cooled ozone generator.

PHYSICAL PROPERTIES OF OZONE

Ozone itself is an unstable gas which boils at minus 112°C (-112°C) at atmospheric pressure, is partially soluble in water (more than oxygen -- see Table 1) and has a characteristic penetrating odor, readily detectable at concentrations as low as 0.01 to 0.05 ppm. It is a powerful oxidant, having an oxidation potential of 2.07 volts in alkaline solution, and therefore should be considered a dangerous material, capable of oxidizing many types of organic materials, including human body tissues. In Table 2 are listed the oxidation potentials of many of the oxidants currently used or considered for use in water and wastewater treatment.

TABLE 1. SOLUBILITY OF OZONE AND OXYGEN IN WATER

Temperature °C	Ozone Solubility mg/l	Oxygen (from air) Solubility mg/l
0°	20	6.9
2	10	6.6
20	8.92	4.3
28	1.5	3.7

At the relatively low concentrations of ozone produced by industrial generation equipment (1 to 3% in air; 2 to 6% in oxygen) no explosive hazard exists, but mixtures of ozone concentrated to 15 to 20% or higher in air can be explosive. Available ozone generators cannot generate sufficiently high concentrations of ozone in air to be explosive. On the other hand, ozone is a toxic gas, and unnecessary exposures can be detrimental to humans.

In aqueous solution, ozone is relatively unstable, having a half-life of about 20 to 30 minutes in distilled water at 20°C. If oxidant-demanding materials are present in solution, the half-life of ozone in such solutions will be even shorter.

On the other hand, ozone in air (especially under dry conditions) is much more stable than in water. The half-life of ozone in the ambient atmosphere has been measured by the U.S. Environmental Protection Agency to be on the order of 12 hours. Thus, ozone can be produced in dry air or oxygen, then piped considerable distances to the contactors with no fear of losing the product by decomposition back to oxygen.

HISTORY OF OZONE USE IN WATER TREATMENT (Rideal, 1920)

The earliest experiments on the use of ozone as a germicide were conducted by de Meritens in 1886 in France, who showed that even dilute ozonized air will effect the sterilization of polluted water. A few years later (1891), the bactericidal properties of ozone were reported by Frölich from pilot tests conducted at Martinikenfeld in a drinking water treatment

TABLE 2. OXIDATION-REDUCTION POTENTIALS OF WATER TREATMENT AGENTS*

REACTIONS	POTENTIAL IN VOLTS (E°) 25 °C
$F_2 + 2e = 2 F^-$	2.87
$O_3 + 2H^+ + 2e = O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e = 2H_2O$ (acid)	1.76
$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$	1.68
$HClO_2 + 3H^+ + 4e = Cl^- + 2H_2O$	1.57
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	1.49
$HOCl + H^+ + 2e = Cl^- + H_2O$	1.49
$Cl_2 + 2e = 2Cl^-$	1.36
$HOBr + H^+ + 2e = Br^- + H_2O$	1.33
$O_3 + H_2O + 2e = O_2 + 2OH^-$	1.24
ClO_2 (gas) + e = ClO_2^-	1.15
$Br_2 + 2e = 2Br^-$	1.07
$HOI + H^+ + 2e = I^- + H_2O$	0.99
ClO_2 (aq) + e = ClO_2^-	0.95
$OCl^- + H_2O + 2e = Cl^- + 2OH^-$	0.9
$H_2O_2 + H_3O^+ + 2e = 4H_2O$ (basic)	0.87
$ClO_2^- + 2H_2O + 4e = Cl^- + 4OH^-$	0.78
$OBr^- + H_2O + 2e = Br^- + 4OH^-$	0.70
$I_2 + 2e = 2 I^-$	0.54
$I_3 + 2e = 3 I^-$	0.53
$OI^- + H_2O + 2e = I^- + 2OH^-$	0.49
$O_2 + 2H_2O + 4e = 4OH^-$	0.40

* Handbook of Chemistry and Physics, 56th Edition, 1975-76. CRC Press Inc., Cleveland, Ohio, p. D-141-143.

plant erected by the German firm of Siemens & Halske. In 1893, the first drinking water treatment plant to employ ozone was erected at Oudshoorn, Holland. Rhine River water was treated with ozone, after settling and filtration. Siemens & Halske next built treatment plants at Wiesbaden (1901) and Paderborn (1902) in Germany which employed ozone.

A group of French doctors studied the Oudshoorn plant and its ozonized water and, after pilot testing at St. Maur (in Paris) and at Lille, a 5 mgd plant was constructed at Nice, France (the Bon Voyage plant), which employed ozone for disinfection. Because ozone has been used continuously at Nice since the Bon Voyage plant began operating in 1906, Nice is referred to as "the birthplace of ozonation for drinking water treatment".

Full scale water treatment plants then were constructed in several European countries. As of 1916 there were 49 treatment plants in Europe having a total capacity of 84 mgd (Vosmaer, 1916) in operation, and 26 of these were in France. By 1940 the number of drinking water treatment plants throughout the world using ozone had risen to 119, and as of 1977 at least 1,043 plants are known to be using ozone for drinking water treatment (Miller _et al._, 1978)

APPLICATIONS OF OZONE IN WATER TREATMENT

Because ozone is a powerful oxidant and because many contaminants in water supplies and industrial wastewaters are oxidizable, ozone can be used for many specific applications. The major uses for ozone in modern drinking water treatment processes are listed in Table 3. With the exception of taste and odor control, all of these same polluting parameters listed in Table 3 are encountered in industrial wastewaters. Although the early uses for ozone in treating drinking waters were predominantly for disinfection (bacterial kill and viral inactivation), today oxidative applications account for a significantly increasing number of installations.

In recent years, multiple uses for ozonation in the same water treatment process have been developed. For example, if ozone is applied for color removal near the end of the treatment process, a significant amount of disinfection also will be obtained. The conjunctive use of contactor off-gases from the primary ozone contacting chambers can be effective in such treatment processes. These off-gases (which contain as much as 5 to 10% of the ozone charged to the primary contact chambers) can be recycled to the initial stages of the treatment process to oxidize iron and manganese, to aid in flocculation of suspended solids, or simply to destroy excess ozone while performing useful work.

Alternatively, the ozone in these off-gases either must be destroyed (thermally, catalytically or by passing through moist GAC) or diluted with air before being discharged to the atmosphere. If the volumes of contactor off-gases are not large, it can be cost-effective to recycle them to an early stage oxidation step in the total water or wastewater treatment process.

Another recent application for ozone involves partial oxidation of dissolved organic compounds, which makes them more biodegradable than they were prior to ozonation. At the same time, the aqueous medium is aerated efficiently, thus saturating the solution with oxygen. This provides an aerobic medium containing DO and dissolved, biodegradable organic compounds. When this aerated medium is passed through sand, anthracite or GAC filters, aerobic bacterial growth is promoted in these filter media. As a result, those partially oxidized, biodegradable dissolved organic compounds are converted to CO_2 and water. At the same time, ammonia nitrogen is converted biologically to nitrate ions. Some of the dissolved organics are adsorbed onto the GAC, then appear to be biologically degraded, thus regenerating active adsorption sites.

TABLE 3. APPLICATIONS OF OZONE IN WATER TREATMENT

- Bacterial Disinfection
- Viral Inactivation
- Oxidation of Soluble Iron and/or Manganese
- Decomplexing Organically-bound Manganese (oxidation)
- Color Removal (oxidation)
- Taste Removal (oxidation)
- Odor Removal (oxidation)
- Algae Removal (oxidation)
- Removal of Organics (oxidation)
    - such as pesticides
        - detergents
        - phenols
- Removal of Cyanides (oxidation)
- Suspended Solids Removal (oxidation)
- Increase Biodegradability of Dissolved Organics
- Preparation of Granular Activated Carbon
    - for Biological Removal of Ammonia
    - and Dissolved Organics

This treatment combination of ozonation, followed by sand filtration, followed by GAC has been termed "Biological Activated Carbon" (BAC) by Rice *et al.* (1978). The process was first developed by the Germans and French for treating drinking water. However, the technique also is being employed at the Cleveland Regional Sewer District (Hanna, Slough & Guirguis, 1977) to treat combined industrial/municipal wastewaters. The technology of BAC will be discussed in more detail in Section 8 of this report.

One of the most significant points for the water or wastewater treatment engineer to learn about ozonation is the multiple application aspect. The use of ozone for more than one purpose effectively can reduce the cost of ozone installations. For example, ozone can be installed for disinfection at a cost of X dollars. If this is the only purpose for ozone, then contactor off-gases must be disposed of safely. This can be done catalytically or thermally, but at some additional cost.

Instead, the contactor off-gases can be recycled to the front of the process and utilized for some wastewater treatment purpose such as the oxidation of iron and manganese, or as a flocculation aid, or for color removal, organics oxidation, etc.

In such event, the additional cost for this second ozonation step will be smaller than if the preozonation were the only ozonation purpose. Such dual application of ozone could even require a small amount of additional ozone generation capacity, which might not be economical if only the initial ozonation process step were to have been considered without the later (and primary) ozonation step. As part of a dual ozonation process, the relative costs of ozonation for the terminal ozonation step also will be lowered.

GENERATION OF OZONE

Ozone is made by rupturing the stable oxygen molecule, forming two oxygen fragments, which can combine with oxygen molecules to form ozone:

$$O_2 \rightleftharpoons 2[O]$$

$$2[O] + 2O_2 \rightleftharpoons 2O_3$$

Nature generates ozone continuously by means of sunlight acting upon oxygen in the atmosphere, or intermittently by lightning passing through the air. Man simulates this natural process of generating ozone by passing high voltage electrical discharges, high or low electrical frequencies, or high energy radiation through air or oxygen. Ozone is also generated unintentionally by man as a by-product during operation of electrical power generation, electrostatic precipitators, welding equipment, electrostatic copying machines, UV lights, and a variety of other electrical devices.

Commercial quantities of ozone are generated on-site and as needed in a system which includes gas handling, ozone generation and a cooling mechanism. Generation of ozone is energy intensive, with some 90% of the power supplied to the generator being utilized to produce light, sound, and primarily heat, rather than the desired ozone. Thus, minimizing electrical power requirements is a prime target of the ozone generator manufacturer.

A detailed discussion of the factors affecting ozone generation by the corona discharge technique is given by Rosen (1972). In general, however, type, thinness and surface area of the dielectric medium used, width of discharge gap distance between electrodes, degree of flawlessness of the dielectric medium (no pin-holes), pressure, temperature and rate of flow of feed gas through the ozone generator, composition (air vs. oxygen), and moisture content of the feed gas are among the most important factors (Figure 2). If clean, dry, oxygen-rich gas is fed to the ozone generator, and an efficient method of heat removal is available, then the production of ozone by means of corona discharge under optimum conditions is represented by the following relationships (Rosen, 1973):

$$V \;\alpha\; pg$$

$$(Y/A) \;\alpha\; f\varepsilon V^2/d$$

where: (Y/A) = Ozone yield per area of electrode surface under optimum conditions,
V = Voltage across the discharge gap (peak volts)
p = Gas pressure in the discharge gap (psia)
g = Width of the discharge gap
f = Frequency of the applied voltage
ε = Dielectric constant of the dielectric medium
d = thickness of the dielectric medium

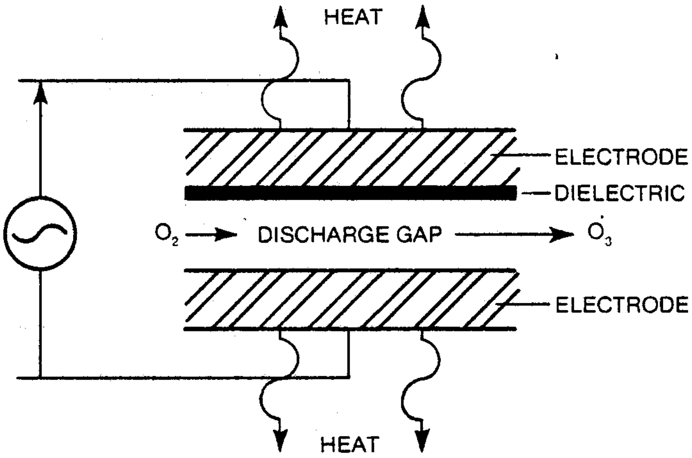

Figure 2. Schematic diagram of corona discharge ozone generator.

Ambient air contains moisture which, if allowed to remain in the feed gas during ozone generation will (a) react with ozone and reduce the yield of ozone per kwhr (kilowatt-hour) of electrical energy applied, and (b) form nitric acid, which can result in severe corrosion of some generator components as well as downstream ozone handling equipment. For these reasons, air to be fed to the generator should be adequately dried. This is the function of the gas handling equipment mentioned earlier. In modern ozone generating systems, air is dried to a dew point of at least minus 40°C (-40°C), and preferably to minus 60°C (-60°C) or below.

When dry air is used to generate ozone, a mixture of 1% ozone in air is produced for the lowest power expenditure consistent with generating ozone at a reasonably rapid rate; when dry oxygen is used to generate ozone, a mixture of 2% ozone in oxygen is produced.

Increasing the rate of feed gas flow through the ozone generator at constant power will increase the amount of ozone generated per unit time and per unit of electrical energy applied, and will reduce the concentration of ozone in the output gas mixture. Reducing the rate of feed gas flow will increase the concentration of ozone per unit of electrical power applied, will increase the amount of ozone produced per kwhr of power applied, but will decrease the amount of ozone produced per unit of time. Proper choice of parameters for the particular ozonizing job at hand will guide the user to produce the optimum amount of ozone for minimal expenditure of power.

Generation of ozone by electrical discharge produces heat, and heat causes decomposition of ozone in the product gas. Thus it is important that the heat generated in producing ozone be removed as quickly and efficiently as possible. This is normally accomplished by water, air or heat transfer fluid cooling of the dielectric media.

In recent years, the efficiency of ozone generation has been increasing. It has been noted that the Bon Voyage plant of Nice in 1906 originally required 33 kwhrs/lb of ozone generated (Gagnon, 1976). By contrast, the Charles-J. Des Baillets drinking water treatment plant of the City of Montreal is now under construction and will house one of the largest ozone generation capabilities in the world (15,000 lbs/day). When this plant is completed in 1980, it will produce ozone for 10.63 kwhrs/lb of ozone generated (Bouchard, 1976).

Use of oxygen as the feed gas rather than air will allow production of essentially double the amount of ozone per kwhr of electrical energy (2% ozone in oxygen), and will also eliminate the need for gas drying. Thus, capital requirements for ozone generation will be approximately halved by using oxygen. The discerning engineer will recognize however, that the gases now exiting the ozone generator will be 98% oxygen and 2% ozone. Therefore, to minimize loss of oxygen, contactor off-gases, still very rich in oxygen, should be recycled to the ozone generator (after removing contaminants and water) or utilized in some fashion. For example, in biological oxygen activated sludge processes, for which dry oxygen is available, ozone can be generated from oxygen and the contactor off-gases can be used to supplement the oxygen supply to the biological reactor (Figure 3).

CONTACTING OF OZONE WITH AQUEOUS SOLUTIONS

Because ozone is only slightly soluble in aqueous media, contacting ozone with water involves bringing bubbles of ozone-containing air or oxygen into intimate contact with the water. Mass transfer of ozone from the gaseous bubbles occurs across the gas/liquid interface into the water.

Factors which affect the mass transfer of ozone into liquids, and which themselves are affected by design and operation of the contactor system, include:

- the miscibility with water and ozone demand of the substance(s) to be ozonized,

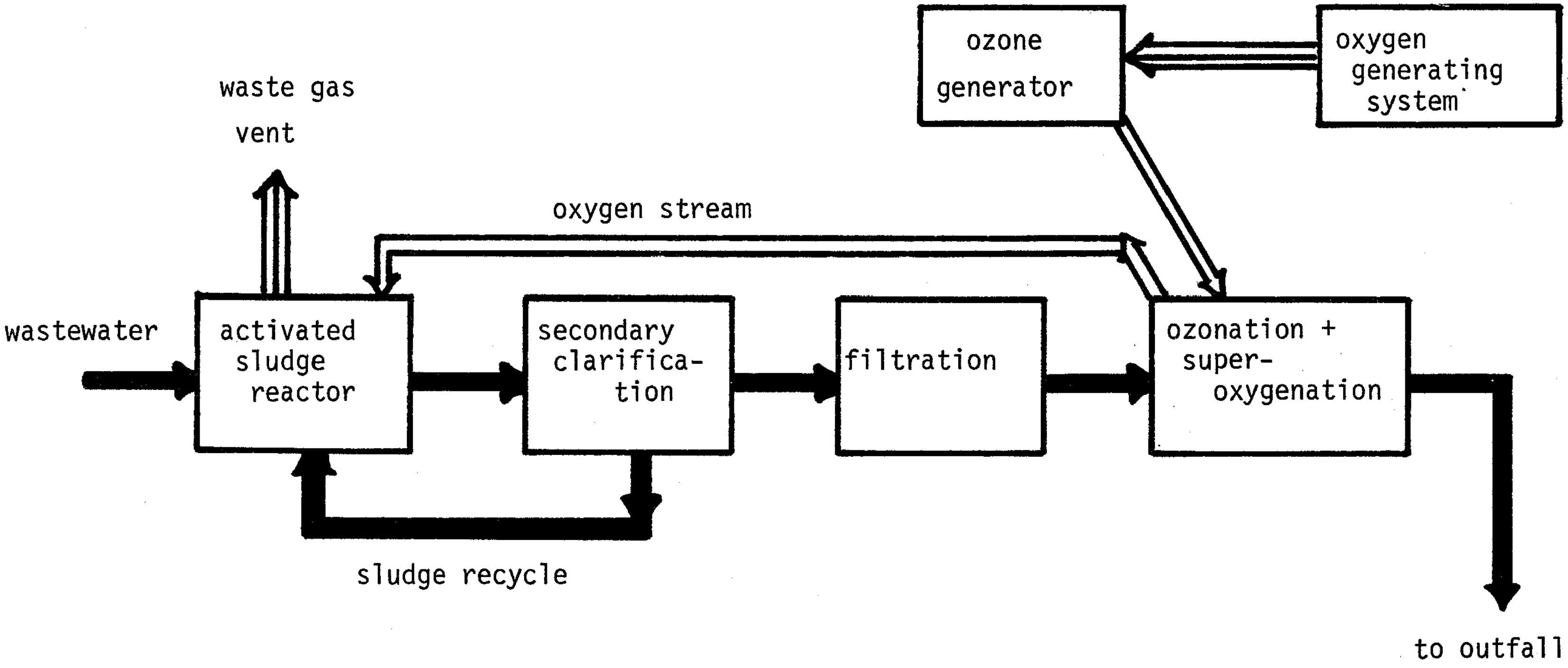

Figure 3. The oxygen activated sludge process.

- concentration of ozone in the gas,
- whether the carrier gas is air or oxygen,
- method and time of contact,
- bubble size, and
- pressure and temperature.

Generally speaking, there are two major categories of reaction which ozone undergoes in solution: (a) those which are so rapid that they are limited only by the rate of mass transfer of ozone into solution, and (b) those which are slower than the mass transfer rate, thus are limited by the reaction kinetics of the material to be ozonized. Reaction rates of such materials as bacteria, nitrites, hydrogen sulfide, phenols, unsaturated organic compounds, etc., are very rapid with ozone, and thus are limited only by the rate at which ozone is "mass transferred" into solution.

Other materials react with ozone very slowly, such as acetic acid, urea, saturated aliphatic alcohols, ammonia, oxalic acid and the like. Even in the presence of large excesses of ozone, the rates of these reactions are very slow, and thus are "reaction rate limited".

Thus, in designing an ozone contacting system, it is important to minimize the amount of ozone required for the specific purpose for which the ozone is to be used. If disinfection only is desired, a contactor which causes rapid mass transfer of ozone should be used. For oxidation of biorefractory organic materials, the rate of ozone mass transfer is less important than maintaining a specific, often low, concentration of ozone for a longer contact period.

These two situations are illustrated graphically in Figure 4. The upper curve shows that a high ozone dose for a short period of time uses the minimum amount of ozone for maximum mass transfer. On the other hand, the lower curve shows that low ozone dosages for long periods of time provide the minimum amount of ozone necessary for reaction rate controlled reactions.

Basically, there are only four different types of gas/liquid contacting systems (Stahl, 1975). These include:

1. Spray towers (liquid sprayed into gas)
2. Packed beds
3. Bubble plate or sieve plate towers (an intermediate situation between 1 and 2)
4. Units for dispersing gas bubbles into liquid.

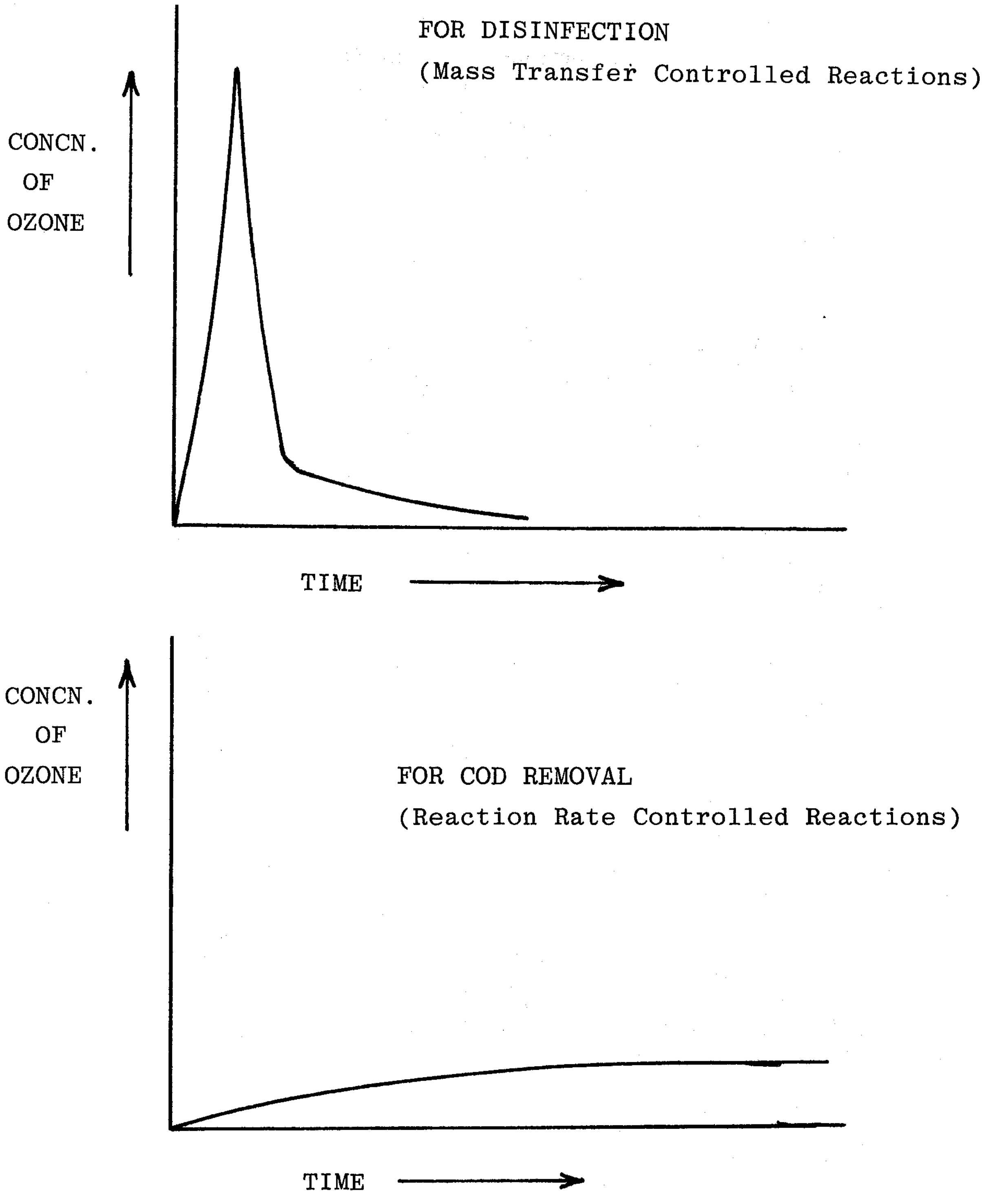

Figure 4. Optimum ozone dosages.

The most common ozone contacting systems are based on some method for dispersing gas bubbles within a liquid (category 4). Generally there are two ways of accomplishing this:

1. Gas is introduced initially into the fluid as bubbles of the desired size, or as smaller bubbles which grow to the desired size as contact time continues, or

2. A massive bubble or gas stream is disintegrated into the fluid.

These two techniques are exemplified by the diffuser (or sparger) and the injector (or eductor) contactors, respectively. Both of these types of contactor were developed originally for treating potable water supplies, and have been utilized throughout the world for this purpose for many years. Many variations of each type have evolved.

With the diffuser, ozone is added at the bottom of the contact chamber, through a porous medium (ceramic, Teflon, stainless steel, etc.), and the gas bubbles rise through the water which is passed co-currently or counter-currently through the chamber. Many installations utilize a multiplicity of diffuser chambers, alternating liquid flow first co-currently then counter-currently with the gas stream. Diffusers can be operated with little energy being added, and are especially useful when large volumes of water are being passed through the plant by gravity flow. Additional power costs to effect contacting thus are minimized. However, contacting chambers to house the diffusers are rather large, because of the relatively long contact time required to achieve maximum mass transfer.

Injectors require added energy, the simplest involving pumping of water to be ozonized rapidly past a small orifice, into which the ozone is either pumped or drawn into the liquid by the vacuum created by rapid flow of water past the orifice. In those installations in which water already is being pumped about the plant, injectors are especially suitable, because of their smaller size and high mass transfer rates.

Ozonation of sewage treatment plant effluents and some industrial effluents recently has pointed up the need to study ozone contacting more carefully. Potable water supplies generally are relatively clean, and do not contain much suspended matter or dissolved organic material. With primary and secondary sewage treatment plant effluents, however, higher concentrations of these types of materials are present. During ozonization, much of the organic material is transformed into more polar oxygenated compounds. Lower valent inorganic ions, such as iron and manganese, are oxidized to higher valence states, at which they will hydrolyze, precipitate, and absorb other material present. The net result is formation of a froth, or scum (Foulds, 1972) and provision for its removal must be made. It has been estimated that for each one mgd of secondary effluent ozonized, 550 gal of sludge will be formed in the froth of an ozonation system (Nebel _et al_., 1974).

In a recent study of disinfection of municipal wastewater (Ward et al., 1976) it was found that disinfection by means of ozonation could be achieved consistently only if the secondary effluent was filtered prior to ozonation.

Thus the mechanical performance of an ozone contacting system is expected to be different when treating secondary sewage and/or industrial plant effluents, than when treating potable water supplies, and the engineer should keep this point in mind in determining the amount of pretreatment the particular wastewater should receive before ozonation.

Detailed discussions of the theory of contacting have been published by Nebel, Unangst & Gottschling (1973); Sherwood & Pigford (1952) and Treybal (1955). For purposes of this report, however, it is sufficient to point out that all contactors have their advantages and their limitations (Table 4), and the engineer is advised to consider the specifics of the ozonation job at hand, with respect to material(s) to be ozonized, volume of liquid to be treated, etc. A pilot study should be conducted with the contactor(s) selected, and the following parameters should be studied over practical and economic limits (McCammon, 1975; Nebel, Unangst & Gottschling, 1973; Masschelein, Fransolet & Genot, 1975, 1976):

1. Liquid head on total pressure at initial point of gas/liquid contact,
2. Distribution of ozone throughout the contact period,
3. Total contact time necessary,
4. Concentration of ozone applied,
5. Gas surface area, or volume rates of liquid to gas,
6. Minimal ozone residual.

Once these parameters have been determined satisfactorily, design of the full-scale ozone contacting system can proceed with a high degree of confidence.

In conducting any laboratory treatability or pilot plant study with ozone, it is essential to measure both the ozone dosed and the amount of ozone remaining in the off-gases from the contactor. The difference between the two values is the value for ozone consumed, which is a much more pertinent number for the wastewater treatment engineer than is the ozone dosage. The significance of this point is as follows.

Mass transfer theory suggests that for porous diffuser contactors, the minimum water column height should be 4 meters (about 13 ft) in order to transfer the maximum amount of ozone from bubbles of ozone-containing air into the water. Only when the ozone contactor system is designed to provide the maximum amount of mass transfer can the ozone dosage be a meaningful number.

TABLE 4. TYPES OF OZONE CONTACTORS

Contactor Type	Advantages	Disadvantages
Spray Towers	- High rate of mass transfer - Uniform ozone in gas phase	- Requires high energy to spray liquid - Solids can plug spray nozzles - Short contact time
Packed Columns	- Wide gas/liquid operating range - Small size and simplicity	- Easily channeled and plugged
Plate Columns	- Same as packed columns, but no channeling and broader gas/-liquid operating range	- Easily clogged, but easier to clean - Best suited for very large installations
Spargers (bubblers)	- Require only gravity feed; no added energy - Wide gas/liquid operating range allows intermittent operation	- Intermittent flows may cause plugging of porous media - Longer contact times require larger housings - Tendency to vertical channeling of gas bubbles, reducing contact efficiency
Agitators, Surface aerators, Injectors, Turbines, Static mixers	- High degree of flexibility - Small sizes - Intimate contact and good dissolution	- Require addition of energy - Narrow gas/liquid operating ranges - Cannot accomodate significant flow changes (injectors and static mixers), therefore require multiple contactor stages

Under laboratory conditions, however, it is rarely practical to employ contactor heights higher than 1.2 to 1.5 m (4 to 5 ft). Therefore mass transfer of ozone to the water will be inefficient, and much of the ozone dosed to the reactor will pass through the contactor unreacted. In such cases of poor mass transfer, the amount of ozone dosage employed to attain a specific amount of oxidative work (color removal, COD removal, disinfection, etc.) will be very high. In the case of diffuser contactors, the shorter the contactor and the faster the ozone is applied, the more ozone will pass through the contactor and the higher will be the apparent ozone dosage.

If the poor mass transfer conditions of laboratory ozone contactors are compensated for, however, by considering the ozone consumed rather than the ozone dosed, a more realistic appraisal will be made of the effectiveness of ozonation. The amount of ozone consumed is determined by measuring the ozone remaining in the contactor off-gases and subtracting this number from the amount of ozone dosed to the contactor:

$$0_c = 0_d - 0_{og}$$

Where: 0_c = Ozone Consumed

0_d = Ozone Dosed

0_{og} = Ozone in contactor off-gases

This point also is of critical importance when reviewing literature articles describing ozonation studies. Laboratory tests reporting only ozone dosages are indicative only of the fact that ozone can or cannot perform a specific function. Ozone dosages for mass transfer limited reactions can never be extrapolated directly to determine full-scale plant conditions for industrial wastewaters unless the test system was designed to attain optimum mass transfer.

OZONE ANALYSIS AND PROCESS CONTROL

The most generally used technique for determing ozone (actually total oxidants) in water is by the starch-potassium iodide (KI) technique. As with other strong oxidants, ozone will liberate iodine from solutions of KI. The liberated iodine then can be titrated, with standard sodium thiosulfate, for example. However, in the presence of other strong oxidants (chlorine, chlorine dioxide, hydrogen peroxide, potassium permanganate, some oxidation products of organic materials, etc.) the total oxidant content of the solution will be determined by this technique.

The orthotolidine-manganese sulfate method is more specific for ozone, being subject to fewer interferences than iodometry.

Perhaps the most accurate and specific method for residual ozone in water involves spectrophotometry [UV absorption at 254 nanometers (nm)] (Hann & Manley, 1952), but the solution must be free of other UV absorbing materials. Many types of residual ozone monitors based upon UV absorption are used in European drinking water treatment plants, because ozonized drinking water is relatively free of extraneous materials which absorb at 254 nm.

Unique to the use of ozone for water treatment is the need to measure ozone in the gas phase, just before the ozonized air or oxygen is added to the contacting system (so as to determine the dosage being applied), and again in the contactor off-gases, so as to be able to determine the amount of ozone utilized, the amount of ozone to be destroyed, to be discharged to the atmosphere, or to be recycled. Ozone in the gaseous phase can be determined by UV absorbance, by iodometry in aqueous solution, or by reacting with gaseous ethylene and measuring the UV absorption of the ethylene-ozone adduct.

An excellent discussion of the various analytical techniques by which ozone can be determined in gaseous and aqueous phases is given by Kinman (1975).

Process control of modern ozonation systems is achieved readily by monitoring residual ozone in the water just after the contacting chamber exit. This technique is employed in many modern European drinking water treatment plants. The analyzer is coupled with the ozone generators so that if the level of dissolved ozone drops below a pre-determined level, the generators are signaled to increase production.

Alternatively, contactor off-gases can be monitored by a gas phase ozone monitor, also coupled with the ozone generators. When the level of measured ozone falls, indicating increased consumption of ozone by the aqueous medium, the generators are signaled to increase ozone production. When the level of monitored ozone in the gas phase rises above a pre-determined level, the generators are signaled to decrease production (Thompson, 1976).

By thus instrumenting, programming and monitoring either dissolved ozone after contacting or contactor off-gases, the normally varying loadings of ozonizable materials in wastewater treatment plants can be handled on an automated basis using minimum quantities of ozone.

In an exactly similar manner, the amount of ozone present in ambient plant atmospheres can be monitored by another analyzer, or series of analyzers. In the event of an ozone leak from the generators, from the contactors or from the associated downstream piping, the ozone sensors will react by signaling the ozone generators to be turned off. Once electricity ceases to pass through the ozone generator, ozone generation ceases.

An outstanding discussion of the engineering details of air preparation equipment, ozone generation equipment, contactors and ozone monitoring equipment is given by Miller et al. (1978) in their "Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies", which was conducted for the U.S. Environmental Protection Agency (EPA 600/2-78-147).

OZONE/UV RADIATION

This recently developed process combines ozone oxidation with photochemical excitation to increase the rate of oxidation reactions considerably over the rates observed with UV radiation or with ozonation applied separately. As a result, compounds normally refractory to ozonation alone, such as acetic and oxalic acids, are rapidly converted to CO_2 and water when subjected to the combination. In addition, cyanide complexes of iron, normally not easily affected by ozonation, are rapidly decomposed by the combination, and the cyanide concentration rapidly is destroyed to below the detectable limit. Finally, solutions of polychlorobiphenyls (PCBs) which are very stable to oxidation, are destroyed rapidly by the ozone/UV combination to concentrations below 0.1 mg/l. The technology has been specified as Best Practicable Control Technology Currently Available (BPTCA) by the EPA (U.S. EPA, Feb. 1977) for PCBs.

The combined ozone/UV process has developed from research efforts initially conducted by scientists at Houston Research Inc., in the early 1970s, under contract to the U.S. Air Force Special Weapons Laboratory, Kirtland Air Force Base, New Mexico (Garrison, Mauk & Prengle, 1974). Initial work was conducted on mixed concentrated cyanide wastewaters (iron, copper and nickel complexed cyanides) and the results were dramatic -- cyanide was destroyed to below the detectability limit (Garrison, Mauk & Prengle, 1975; Mauk, Prengle & Legan, 1976).

Since this initial research using cyanide-containing wastewaters was first conducted, a substantial body of information has been developed on the applicability of the ozone/UV combination to a broad range of inorganic and organic species, including:

- metal cyanide complexes
- organic and amino acids
- alcohols
- pesticides and insecticides
- organic nitrogen, sulfur and phosphorus compounds
- chlorinated organic compounds

Even at this early stage of development, the process has been specified as BPTCA for wastewaters containing PCBs, and is in commercial use at several metal finishing plants for treatment of cyanide containing wastewaters (Prengle, 1977).

A detailed discussion of the theoretical aspects of the ozone/UV process is given by Prengle (1977), and references cited therein, to which the reader is referred. The addition of UV radiation at wavelengths in the 180 to 400 nm range provides energy in the range of 72 to 155 kcal/mole to aqueous solutions. These amounts of energy are quite ample for producing free radicals and other species in varying degrees of photochemical excitement, which are not formed during ozonolysis. Examples are excited atomic oxygen species (O), hydroxy radicals ($HO^{\cdot}$), hydroperoxy radicals ($HO_2^{\cdot}$) and carbon-containing excited species. Significantly, addition of even small amounts of UV radiation to aqueous solutions containing dissolved ozone immediately reduces the dissolved ozone level to zero, yet the oxidative power of the solution is considerably higher than when ozone alone is present (Glaze, 1978).

In practice, UV radiation is applied to aqueous solutions simultaneously with the ozone. Typical reaction schemes for the ozone/UV oxidation of mixed chlorinated aromatics and for cyanides and refractory organics are shown in Figures 5 and 6, respectively. Dosages of UV radiation applied are expressed as 'watts of useful radiation energy per liter'. The amount of UV energy applied normally for this process ranges from 0.44 to 1.32 watts/l at ambient temperatures.

For oxidations which are reaction rate limited, with respect to ozonation alone, the addition of UV radiation requires somewhat more energy. However, because the added UV radiation decreases the reaction time now required to attain the desired degree of oxidation, there is less total ozone required. Therefore, less total energy is required for the reactions involved.

In its current configuration, the ozone/UV process equipment includes high speed agitation and multiple reactor stages for reaction. Those wastewaters which contain materials whose oxidations are both mass transfer and reaction rate limited (for example, free cyanide ion in the presence of iron-complexed cyanide) are treated in the first stage reactor with ozone only (to oxidize free cyanide). The effluent from the first stage reactor then enters the second reactor, in which it is treated with both ozone and UV radiation. Treatability studies on specific wastewaters are recommended to determine the optimum number of stages required, as well as optimum ozone and UV radiation conditions to produce maximum oxidation at minimum energy costs.

Costs for a single stage reactor system, including mixer, UV lights, etc., are shown in Figure 7, and are related to reactor volume. Costs for ozonation equipment are shown in Figure 8, and it should be remembered that about twice the amount of ozone can be generated using oxygen as the feed gas instead of air. Pertinent capital and operating costs for these systems as applied to specific wastewater streams will be discussed in the appropriate industrial wastewater sections of this report.

It has also been shown that coupling higher temperatures with ozonation or with UV/ozonation also increases reaction rates (Garrison, Mauk & Prengle, 1974; 1975).

Because the radiation output from UV bulbs decreases with time, annual replacement costs for these bulbs may turn out to be a major operating cost factor. A promising alternative catalytic process involves the coupling of ultrasonic energy with ozonation. Sierka (1977) has shown that the same increase in rate of oxidation of refractory organic compounds can be obtained by substituting ultrasonic energy for ultraviolet radiation. This research was sponsored by the U.S. Army Medical Bioengineering R&D Command, Ft. Detrick, Maryland.

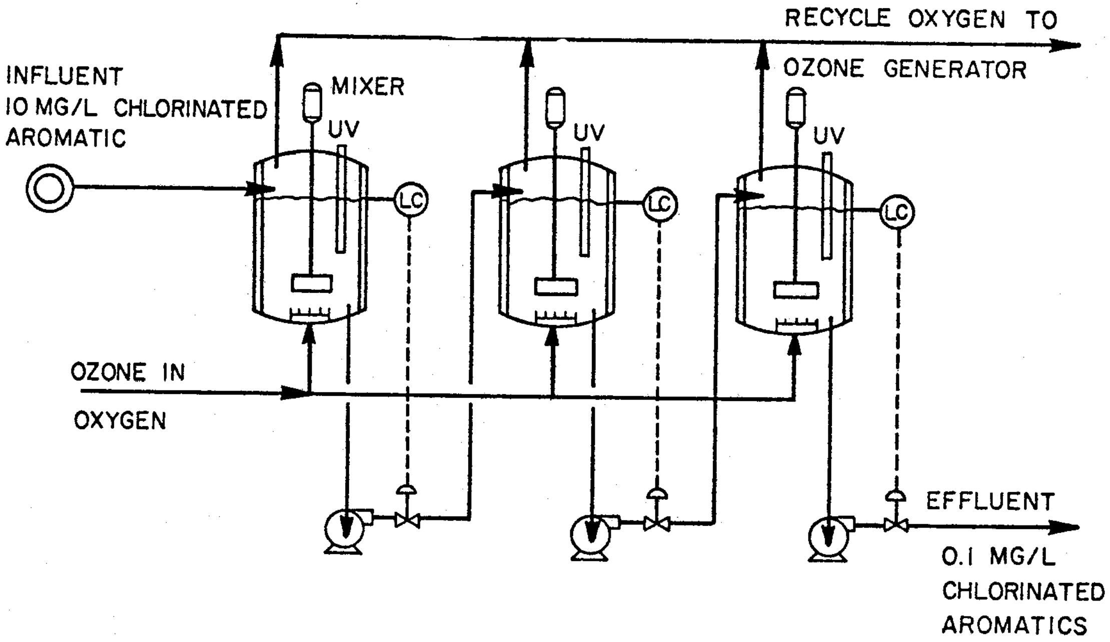

Figure 5. Ozone/UV process flow diagram; mixed chlorinated aromatics.

Source: Prengle & Mauk (1977)

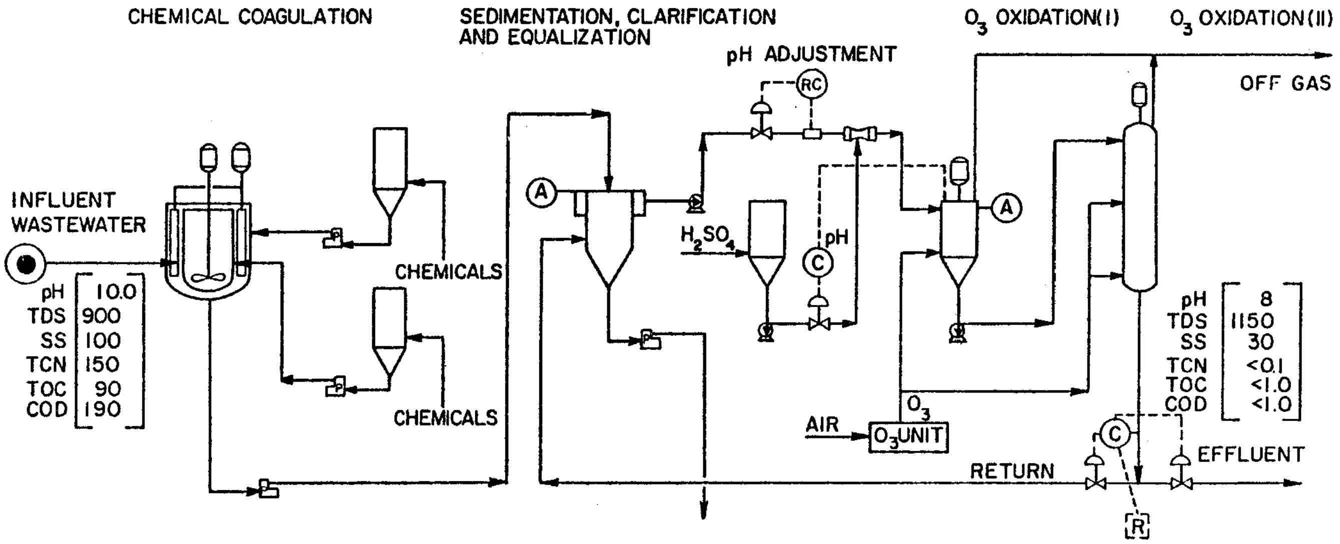

Figure 6. Ozone/UV process flow diagram; cyanides and refractory organics.

Source: Prengle & Mauk (1977)

Further discussion of the ozone/ultrasonics process will be found in Section 5, under Hospital Wastewaters.

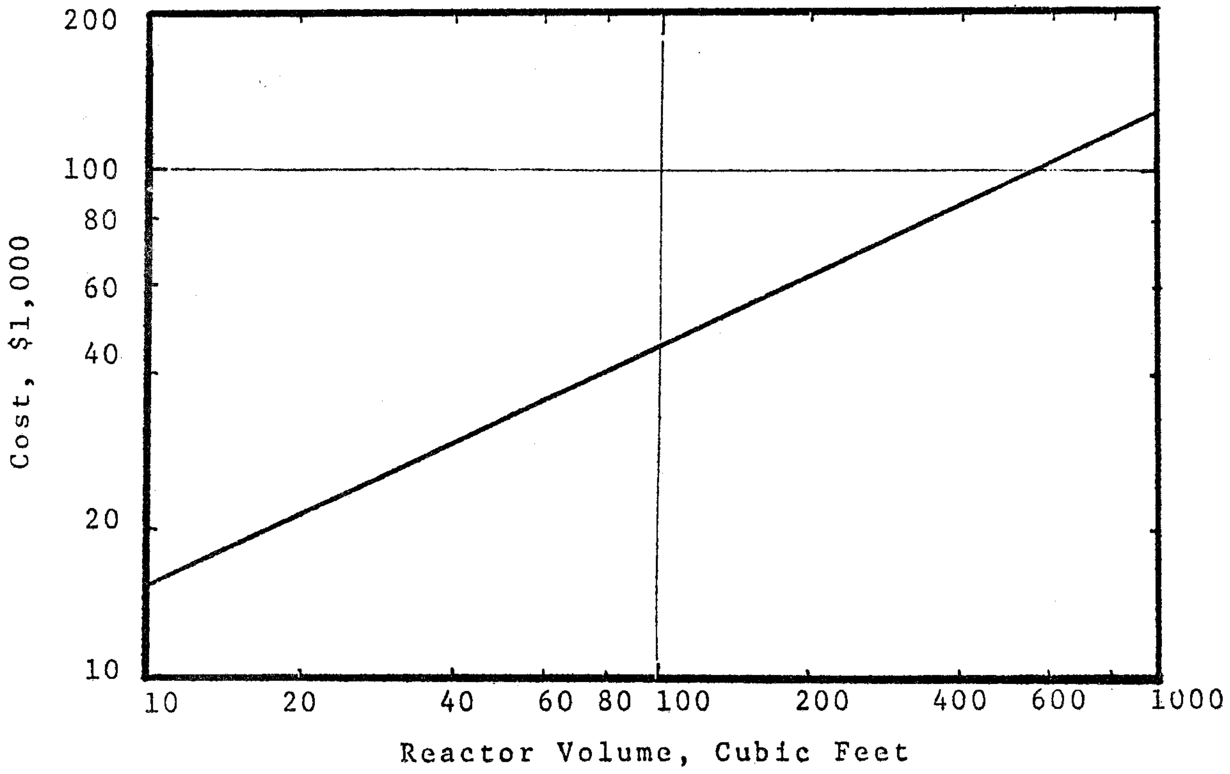

Figure 7. Installed cost of UV/ozone reactor stage.

Source: Prengle (1977)

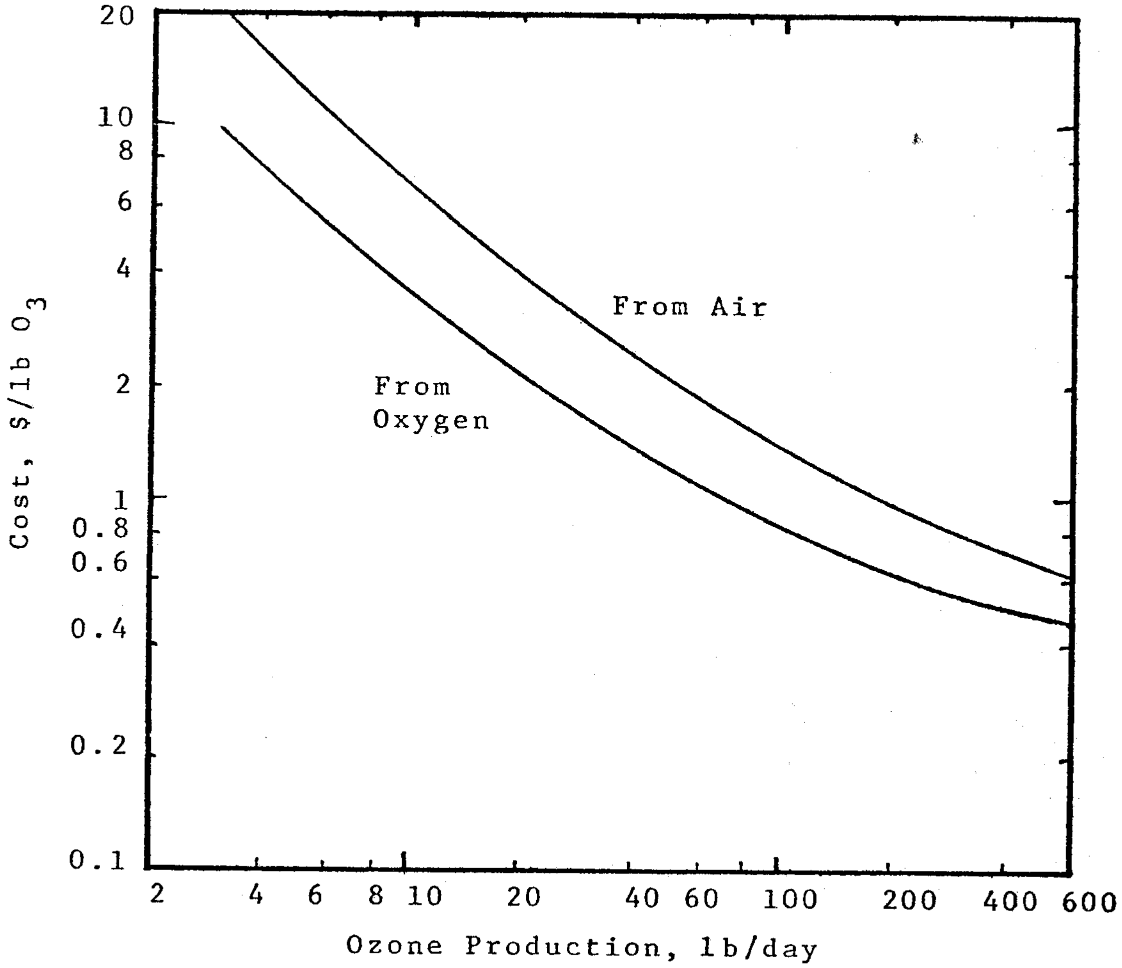

Figure 8. Cost of producing ozone (including oxygen and amortization).

Source: Prengle (1977)

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SECTION 5

INDUSTRIAL WATER & WASTEWATER TREATMENT WITH OZONE

INTRODUCTION AND ORGANIZATION OF SURVEY

In conducting this state-of-the-art survey, the categorization of industrial manufacturing categories which has been adopted by the Effluent Guidelines Division of the EPA was followed. The published literature then was surveyed, and pertinent articles were grouped into the appropriate categories.

Those industrial categories for which pertinent articles were found are listed in Table 1. Many of these articles then were abstracted for content. Originally, the investigators had hoped to find data on actual wastes used, such as raw waste loading, composition of wastewater streams to be ozonized, details of the ozonation equipment and contacting apparatus, data on the contact time, dosage of ozone applied, amount of ozone utilized, analytical data on the ozonized wastewater effluent, etc. The investigators were searching for descriptions of ozonation as applied to actual wastewaters, as opposed to laboratory or pilot plant program discussions.

As the survey progressed, however, it became apparent that very few articles address all of these points, and that there is very little published information dealing with actual full-scale commercial operations. Some published pilot plant and laboratory studies on industrial wastewater treatment with ozone provide pertinent data for consideration, and these articles are included in the survey.

From this point onward, Section 5 is organized by industrial categories. At the end of each subsection dealing with a specific industrial category, the pertinent literature cited for that category is listed. References are arranged alphabetically, according to the senior author. Most of the articles cited have been given a 2-letter code, representing the industrial category, and a number. In many instances, this 2-lettered code plus a number has been asterisked. The asterisk indicates that an abstract for that particular article is included in the companion document to this report, entitled, "OZONE FOR INDUSTRIAL WATER AND WASTEWATER TREATMENT -- An Annotated Bibliography", NTIS Report System. In other instances, the reference cited has not been assigned a category code and number. This is because the reference is a general one, and does not contain information specific to the particular industrial category. These non-category-specific references are included alphabetically as well.

TABLE 5. INDUSTRIAL CATEGORIES REPORTING THE USE OF OZONE

Category	Code	No. of Articles Found	
		Actual Wastes*	Total
Aquaculture	AQ	19	39
Breweries (under Food & Kindred products)	BR	5	9
Biofouling Control	BF	4	10
Cyanides & Cyanates	CY	--	24
Electroplating	EP	17	27
Food & Kindred Products (except Breweries)	FO	5	9
Hospitals	HE	16	30
Inorganics	IC	3	5
Iron & Steel	IS	10	14
Leather Tanneries	LT	0	3
Mining	MI	11	15
Organic Chemicals	OC	25	60
Paint & Varnish	PV	4	4
Petroleum Refineries	RE	22	27
Pharmaceuticals	PC	0	2
Phenols	PH	--	29
Photoprocessing	PF	8	12
Plastics & Resins	PL	4	4
Pulp & Paper	PU	37	60
Soaps & Detergents	SD	7	12
Textiles	TX	30	35
TOTALS		227	430

* also, actual process waters

AQUACULTURE

In this category, the reported literature shows that ozone is being used industrially for (1) treating influent waters to shellfish depuration stations, (2) disease prevention in aquaculture systems through disinfection of holding waters and (3) toxin inactivation. Blogoslawski & Stewart (1977) have reviewed the applications of ozone treatment for these purposes and Blogoslawski (1977) has reviewed the uses of ozone in mariculture. Recent research conducted by the National Marine Fisheries Service, Milford, Connecticut, has shown ozonation to be useful for preventing the detrimental effects normally encountered during "red tide" blooms.

Although ozone decays rapidly in freshwater, doses of ozone in seawater exceeding 0.5 mg/l react with bromide ions to produce a residual "oxidant" which, if not removed through post-ozonation treatment, can be toxic to delicate larval stages of some bivalve shellfish.

Discussion of the use of ozone in the aquaculture field will be divided into five broad areas:

(1) Shellfish Depuration
(2) Marine Water Quality Improvement
(3) Freshwater Quality Improvement
(4) Disease Prevention
(5) Toxicity of Ozonized Seawater

The authors are especially grateful to Dr. Walter J. Blogoslawski of the National Marine Fisheries Service, Northeast Fisheries Center, Milford, Connecticut, for his assistance in the organization and presentation of this section.

Shellfish Depuration

The advantages of using preozonized seawater for the cleansing of shellfish at depuration stations were confirmed by early experiments of Violle (1929) and by Fauvel (1963). Since then, the process has been employed commercially, the most completely described installation being at Sète, on the Mediterranean coast of France (Anonymous, 1972). At present, there are at least 12 other depuration stations in France known to be ozonizing seawater, five in Spain, one in Greece and one in Tunisia (see Table 6). The larger commercial depuration stations process up to 6,000 kg/day of shellfish. Up to 4,800 cu m/day (1.27 mgd) of seawater are disinfected with 1 to 3 mg/l dosages of ozone.

Depuration takes place simply by placing the live adult shellfish harvest in disinfected seawater, and allowing the shellfish to ingest and expell large quantities of water from which they extract their food (Fauvel, 1977). If the water ingested contains bacteria and viruses, these will become concentrated in the shellfish flesh. Depuration in disinfected water (storage up to several days in ozonized water) allows time for the bacteria

TABLE 6. SHELLFISH DEPURATION STATIONS USING OZONE*

Location	Daily Water Flow		Year Ozonation Installed	Amount of Shellfish Processed (kg/day)
	(cu m)	(gal)		
France				
Arromanches	1400		1967	
La Rochelle	1400	369,000	1968	
Harache	1680	444,000	1970	
Le Crotoy			1970	
St. Primel			1970	
Brilemeau			1971	
Viviers (Cote d'Argent)			1972	
Coop le Dauphin (Sète)	2400	634,000	1972	1400
Palavas	500	132,000	1974	
Grandcoup	1900	502,000	1974	
Bouzigues	3600	951,000	1975	1400
Saintes				
Plougosnou				
Other Countries				
Rosas (Spain)	4800	1,268,000	1966	
4 installations in Spain, unknown locations			1969	
Tunis (Tunisia)			1971	
Salonique (Greece)	1450	383,000	1975	

* Sources: (a) Trailigaz, Cie Générale de l'Ozone, Garges-lès-Gonesse, France, Reference List, 1976.
(b) W.J. Blogoslawski & M.E. Stewart (1977).
(c) DEMAG Metallgewinnung, Duisburg, Germany, Referenzliste.

and viruses to be expelled from the shellfish into the water, where the bacteria are killed or the viruses are inactivated by the disinfectant.

At the Sète Laboratory in France, near the Institute of Marine Fisheries (Anonymous, 1972), the depuration station consists of 7 cleansing tanks or troughs, each of which is 20 m long by 2 m wide and 0.95 m high (average), with a capacity of 37 cu m. Metal baskets containing the shellfish to be cleansed are placed on runners longitudinally down the middle and along both sides of the tanks. The floor of each tank has a 2% slope from one end to the other, and ozonized seawater flows through each tank at the rate of 100 cu m/hr.

Shellfish are charged to the tank area at the rate of 35 kg of shellfish/-sq m; the preozonized water in each tank is recirculated and changed daily. One basket from each lot is tested for *E. coli* prior to treatment and after every 24-hr period. The presence of *residual* ozone in the seawater is checked from time to time by addition of a 10% KI solution containing starch to a seawater sample. The blue color (starch/iodine) which develops confirms the presence of ozone or one of its oxidation products capable of liberating iodine from iodide ion. As long as oxidant is present in the water, no fecal coliforms can be detected and the water is presumed to be disinfected.

Seawater is ozonized using an emulsifier contactor, which is a bell-mouthed water tube through which ozonized air is drawn into the water under slight vacuum, or by using a porous tube diffuser contactor.

The depuration of clams and mussels using seawater which is ozonized with varying doses depends upon the initial degree of *E. coli* contamination of the shellfish. The amounts of ozone required to destroy *E. coli* concentrations are shown in Table 7.

TABLE 7. OZONE REQUIREMENTS FOR DEPURATION

Degree of Initial Pollution (E. coli/l)	Ozone Required (g/cu m)
less than 250	0.45 to 0.75
250 to 1,000	0.75 to 1.15
1,000 to 2,000	1.15 to 1.50
2,000 to 5,000	1.50 to 2.10

Depuration times also vary according to the level of shellfish pollution; 2 to 4 days being required for clams and 2 to 3 days for mussels. Cleansing is much more rapid for mussels than for clams. In the more highly contaminated clams, depuration in chlorinated water requires about 50% longer to attain the same degree of purity as when using ozonized water (6 days versus 4 days). With clams having low initial coliform counts, the depuration times in chlorinated or ozonized waters are the same (see Table 8).

Preozonation of seawater is accomplished by supplying ozone until the KI test shows an excess of oxidant. This excess ozone can be eliminated by passing the ozonized water through a desaturator placed at the outlet of the contact tower. The desaturator is a cascading device (Fauvel, 1977), in which ozonized seawater flows over a 6 to 8 ft high dam. At the base of the waterfall, excess gas is eliminated because of the mixing of air with the ozonized water. Thus, disinfected water containing the desired traces of ozone may be prepared for depuration tank addition.

TABLE 8. DEPURATION TIMES FOR CLAMS AND MUSSELS IN OZONIZED AND CHLORINATED SEAWATER

	Degree of Initial Pollution (E. Coli/liter)	Average Cleansing time (days)	Disinfectant
Clams	10,000 or less	2	ozone
	10,000-30,000	3	ozone
	50,000-75,000	4	ozone
	25,000 or less	2-3	chlorine
	30,000-50,000	4	chlorine
	50,000-75,000	6	chlorine
Mussels	25,000 or less	2	ozone
	25,000-75,000	3	ozone

Initial laboratory studies by Violle (1929) were conducted on the depuration of oysters. Seawater was seeded with various strains of pathogenic bacteria and the samples were ozonized to determine the doses necessary to achieve disinfection. Apparently, the doses were the same as those used in ozonizing fresh water (which is 1 to 3 mg/l in European drinking water treatment plants -- Miller et al., 1978). No oxidation of bromide ion was observed even at double the amount of ozone necessary to produce disinfection.

Oysters were kept 18 to 20 days in water using twice the amount of ozone necessary for disinfection, but the ozonized seawater was aerated to remove large excesses of ozone. After 5 to 6 hrs of exposure to the ozonized and aerated seawater, the oysters were free of bacteria. No change in oyster protoplasm was observed visually after exposure to ozonized and aerated seawater for 18 to 20 days. Violle (1929) recommended that the depuration process consist of rapid sand filtration of seawater, ozonation, aeration and flow-through at the rate of 100 ml/hr/oyster.

Salmon, Le Gall & Salmon (1937) reported preliminary test results for oysters and mussels depurated in ozonized seawater. Mussels were cleansed in 24 hrs; oysters and other shellfish were depurated for 48 hrs and showed complete destruction of pathogenic bacteria. These authors also point out that Article 16 of the Decree of 31 July 1923 (France) requires that contaminated shellfish cannot be released to the public until after they have stayed one month in a depuration station. "Since using ozonized seawater can reduce this holding time to 24 to 48 hours, the practical benefits of using ozone can be of great economic significance".

Salmon, Salmon, Le Gall & D'Loir (1937) described tests conducted at the depuration stations at Le Havre (which cleanses 2,000 kg/day of shellfish) and at Boulogne-sur-Mer (6,000 kg/day) using ozonized seawater. Mussels were depurated successfully at an ozonized seawater flow rate of 20 ml/mussel/-hr with 100 mussels/l of water.

Fauvel (1963) compared depuration tests in seawater treated with ozone versus chlorine and conducted on 200 kg lots of bacterially contaminated mussels and on 10 kg lots of clams. He confirmed that depuration rates for clams are slower than those for mussels. After 5 days, clams depurated in ozonized seawater showed zero tissue coliform counts, whereas clams depurated the same length of time in chlorinated seawater gave counts of 1,200 coliforms/-liter. Thus, depuration in ozonized seawater is to be preferred over depuration in chlorinated seawater. In addition, shellfish depurated in ozonized seawater "retain their original taste, whereas those treated in chlorinated water appear soft and chewey". No detrimental health effects were observed in shellfish depurated in ozonized seawater.

A further advantage of ozonation is that a chlorine contact time of 12 hrs is recommended for disinfection, versus 6 minutes for ozone (Fauvel, 1977).

Marine Water Quality Improvement

The economics or physical location of some aquaculture facilities may necessitate the use of water in the hatchery which has been microbially or chemically contaminated. Such facilities must employ an adequate and economically reasonable disinfection system to insure the use of optimal culture waters, preventing waterborne disease in the stock or fouling of the physical operation. Ozone gas has long been recognized as an excellent disinfectant, capable of rapidly killing bacteria, viruses and fungi.

In 1929, H. Violle of the University of Marseille, France, seeking to expand ozone's disinfection capability in freshwater to seawater, demonstrated that the oxidant could easily disinfect seawater seeded with around 1×10^6 bacterial cells/ml within 8 minutes.

More recently, Combs and Blogoslawski (1975) studied the effects of ozonization on seawater suspensions of the marine-occurring yeast, *Sporobolomyces roseus*. No cells survived ozonization periods of 90 seconds and above. In an earlier report, Giese and Christensen (1954) reported that ozone directly affected respiration in yeast cells, often resulting in a complete kill of the cells, thereby reducing yeast respiration. After subsequent tests with other yeasts, Combs and Blogoslawski suggested that ozone was effective in removing both pathogenic and non-pathogenic marine-occurring yeasts. Blogoslawski and Stewart (1977) note that ozonization of hatchery water would prevent the exposure of workers to pathogenic yeasts as well as improve the holding water quality for adult shellfish.

Blogoslawski, Brown, Rhodes & Broadhurst (1975) described a pilot plant seawater disinfection system employing filtration through activated carbon, ozonization, then filtration through activated carbon. The system treated 13,000 gal/day of raw seawater. When the residual ozone concentration reached 0.5 to 0.56 mg/l, no microorganisms were observed on inoculated agar plates incubated 5 days at 18°C. Fish held 90 days in the ozonized seawater showed no fin rot or necrotic lesions and exhibited only limited mortality. Control fish held in non-treated seawater developed fin rot, necrotic lesions, and showed 78 to 100% mortality over the same 90-day period.

The ozone contactors, associated piping and post-ozonation filters did not foul, whereas the non-ozonized seawater pipes became heavily fouled over a 3-day period. This indicates the potential for ozone to control biofouling in cooling water applications.

Honn and Chavin (1976) have noted the necessity for a supplement to regular biological filtration in closed marine systems as bacterial filtration usually is inadequate to deal with the toxic wastes accumulating in these operations. Their work indicates that when ozone is added to the system as a supplementary filtration method, it rapidly stabilizes the system.

Sander and Rosenthal (1975), citing the need for seawater sterilization in mariculture facilities, selected ozone as the most likely method to achieve disinfection without causing physiological damage to the stock being cultured. These authors, basing their work on the studies of Frese (1974), demonstrated that as long as the ozone concentration in air bubbled through holding water is lower than 0.5 mg/l by weight, no harmful effects will occur to gills of fish during treatment procedures lasting less than 6 hrs/day. Sander and Rosenthal (1975) also report that ozonization very often is used in connection with protein skimming in commercial aquaria and aquafarms because of the rapid decomposition of ozone coupled with its oxidative efficiency and simultaneous aeration of the waters during the ozone contacting process. Descriptions of commercial protein skimmers used in conjunction with various ozone contactors are given. To destroy residual ozone before ozonized water is returned to algal or fish tanks, the treated water usually is passed through an activated carbon tower.

Edwards (1975) describes the engineering design of an enclosed raceway for aquaculture, which consists of totally enclosed and insulated raceway tanks complete with an air lift pump system, solid and waste removal system, solid and waste separator and biological filter, water purification unit, pH control and chemical additive system, water heating or cooling system and the necessary pumping equipment. The water purification system can include either ozone or UV light treatment. Blogoslawski (1977) reports that Stopka (1975) has shown that oxidation or foam fractionation degrades dissolved organics in mariculture systems and that Spotte (1970) indicated that ozone is more efficient than air in the oxidation of dissolved organics. The use of ozone in the lift pumps of Edwards' closed raceway culture system effectively removes any dissolved organics from the system.

A critical key to locating oceanaria inland is the ability to recycle the aquatic environment. Murphy (1975) describes the recycling of marine aquaria waters which house the bottlenose dolphins at Sea World of Florida. Continuous chlorination of the recycled water was unsatisfactory because animal irritability increased as the chloramine concentrations increased. In addition, bacterial and algal populations became more and more difficult to control as several species developed resistance to sublethal treatment procedures. Breakpoint chlorination was preferable, but required isolating the animals from the treated water, then dechlorinating. Two small scale studies were conducted successfully using ozonation and a full-scale ozone treatment system was designed and installed in late 1973 for the 2,000,000 gal aquarium housing bottlenose dolphins.

Ozone dosages of 0.8 to 1.0 mg/l are applied through fine pososity Teflon diffusers (0.01 cm bubble size produced) to dolphin tank water which first is passed through high pressure dual media filters. The ozone contact "chamber" is an open, rectangular 330,000 gal tank. The Teflon diffusers are installed in the front one-half of the tank, and the total time water is in contact with ozone is 30 to 40 minutes. The ozone generator is capable of producing 100 lbs/day of ozone from air, but normally is operated at 70 to 90 lbs/day. After ozonation, the water is passed through two ammonia scrubbing towers, stored in a return sump, then sent back to the exhibit tanks. A chlorine dioxide generator is available after the sump in the event of ozonation system failure.

The ozone dosage of 0.8 to 1.0 mg/l maintains BOD in the water at a maximum level of 2 mg/l, even though the marine mammals living in this facility consume nearly 2,000 lbs of food every day. The ozonation facility at Sea World of Florida has been in operation since late 1973. As of June, 1976, the facility was still using the original water, and bacterial populations have remained low (Blogoslawski and Stewart, 1977).

Sea World of Ohio exhibits only marine mammals. Using two ozone generators (capacity 20 to 40 lbs/day of ozone from air), the facility ozonizes 450,000 gal of water in a closed system. The wastewater is ozonized, then passed through a high rate sand filter, after which it is returned to the aquarium tank. Because of the nature of their exhibit, Sea World of Ohio uses only water and sodium chloride. At the doses employed, the facility encounters no ozone residual. The skin integrity of the animals is preserved, the normally yellow colored water in the tanks is turned blue, and no bacterial slime formation is observed (Blogoslawski and Stewart, 1977).

A 170,000 gal coral reef exhibit containing marine fishes, sharks and turtles at Sea World of Orlando, Florida incorporates very efficient physical and biological filter components which negate the need for supplementary treatment for BOD reduction. In this case, ozone is used to eliminate accumulated color from the seawater system. The yellowish color characteristic of recycled aquaria water is removed effectively by treating a side stream with 0.1 to 0.2 mg/l of ozone (1.0 to 1.5 lbs/day of ozone; Murphy, 1975).

Blogoslawski (1977) notes that ozone is of use in the raising of marine animals for experimental purposes. He cites studies of Giese and Christensen (1954) which indicate that ozonized seawater provides a bacteria-free medium for culture of eggs of the sea urchin (Strongylocentrotus purpuratus) without affecting the division of the eggs, and he suggests that this work shows that ozone does not adversely affect the deeper structures of the cell or the nucleic acid components at the dose levels examined.

Tchakhotine (1937) used ozonized seawater to sterilize the external surface of the worm Sabellaria. He found the motility of the sperm destroyed, permitting him to work with the unfertilized eggs necessary for his research.

Ciambrone (1975) described the use of ozonized municipal sewage to grow algae which then was used as food for raising oysters. Municipal sewage was filtered, ozonized, then refiltered and mixed 1:4 with filtered seawater. The ozonized sewage contained 30 mg/l of BOD, 15 mg/l of COD, 20 mg/l of suspended solids (SS) and 20 MPN (most probable number) of coliforms/100 ml. Algae were allowed to grow and stabilize in this medium; then the water was diluted with 18 to 22 volumes of fresh seawater and oysters were raised in this medium. Effluent water from the oyster tanks then was ozonized "to oxidize ammonia to nitrates" (questionable that this occurs) and for disinfection before discharging. It was found that a newly-set oyster spat could be grown to market size oysters by the above procedure in about 1 to 1.5 normal growing seasons (12 to 15 months), or about twice as fast as oysters grown conventionally.

The ozone dosages for treating filtered sewage were stated by Ciambrone (1975) to be 1 mg/l, but this number appears to be too low to produce the quality of ozonized sewage described. A similar municipal sewage at Indiantown, Florida is treated first by a trickling filter, then by chemical precipitation, lamella settling, and still requires ozone dosages of 5 to 6 mg/l to attain fecal coliform counts of 2 MPN/100 ml. Total coliform counts of less than 70 MPN/100 ml are obtained at Indiantown, Florida with ozone dosages of 7.5 mg/l (Novak, 1977).

Freshwater Quality Improvement

The use of ozone to improve water quality long has been recognized in treating freshwaters for drinking purposes (Miller et al., 1978). Its published uses in aquaculture include the hatching of trout eggs and the rearing of fish.

Benoit and Matlin (1966) hatched rainbow trout in ozonized water from two batches of eggs contaminated with mycelial filaments of Saprolegnia. Water was pumped through a temperature controller, then through a head box containing 0.75 inch of glass wool on top of 1 inch of bone charcoal. This water was ozonized with a stream of air containing 26 to 65 mg/l of ozone by volume. Ozone concentrations were increased when the mycelial filaments were observed to be spreading, and were decreased when the mycelia were observed to "shed" from the dead eggs. Ozone dosages were varied by means of a rheostat connected to a Sander ozone generator.

Live eggs of the older group hatched completely, even though a large number of younger eggs were covered with filaments of Saprolegnia. Overall yield of the advanced fry from the older group of eggs was 84% and overall yield of sac fry from the younger group was 34%. Based on these excellent results, the authors recommended that the use of ozone for treatment of fish hatchery waters be reexamined.

Rosenlund (1975) found that residual ozone concentrations of 0.01 to 0.06 mg/l in ozonized lake water influent to aquarium tanks resulted in high mortality of rainbow trout within 4 hrs. However, if the ozonized water was aerated (to eliminate any gas supersaturation) and allowed to stand 11 minutes (to allow excess ozone to decompose), trout could be held successfully with no detrimental effects.

Thompson (1976) reported on the design of an ozonation system to be installed at the Freshwater Institute of Environment Canada in Winnipeg. The Institute plans to import fish diseases for study and requires a means to ensure that these diseases do not escape into the Canadian environment. Design of the treatment process must guarantee total elimination of bacteria and viruses in the fish holding tank effluent, not simply the attainment of "normal" disinfection.

This fish holding tank effluent is of high quality, with the exception of baterial counts. BOD-5 consistently is below 5 mg/l (average 3), suspended solids are rarely above 2 mg/l (average 1), COD averages 21 mg/l and TOC averages 5 mg/l. Total bacterial counts exceed 800,000/ml and total coliforms average 1,500/100 ml.

Pilot ozonation studies were conducted using a 7-ft contact chamber with a sintered polyethylene diffuser. These tests indicated that an ozone dose of 5 mg/l at a 5-minute contact time would meet the required bacterial standards. For assurance, the system design will allow the Institute to apply 22 mg/l of ozone for 44 minutes at average flow and 12 mg/l for 24 minutes at peak flow. Installed ozone generation capacity will be 44 lbs/day by means of 2 units, with a contact tankage of about 3,000 Imperial gal (Igal).

The ozone contacting system to be installed at the Freshwater Institute consists of an ejector device in a first contact chamber and a surface turbine aerator in a second chamber. Ozone and wastewater flow will be countercurrent, so that the incoming wastewater in effect will clean the vent gas of ozone. The time of contacting will be 15 minutes in the first stage and 7 minutes in the second stage at average flow.

It is noteworthy that many European drinking water treatment plants which process polluted surface waters and which incorporate ozonation, monitor their product waters for the presence of toxic pollutants by passing product waters through aquaria stocked with trout. Because there is no residual ozone in the processed drinking water, the trout thrive, unless a toxic pollutant happens to have passed through the water treatment process. If any stress is observed with these trout, the water treatment process is shut down and the cause is investigated (Miller et al., 1978; Poels, 1977).

Haraguchi, Simidu & Aiso (1969) found that the storage lives of fresh jack mackerel and shimaaji fish were lengthened by 1.2 to 1.6 times upon 30 to 60 minute treatment once every 2 days with water containing 0.6 mg/l of ozone.

Disease Prevention Measures

Waters used to support cultured species necessarily must be free from disease. Therefore, aquaculture facilities which draw their waters from areas subject to contamination must use some method of disinfecting the water before exposing the animals to it.

As mentioned earlier, Sander and Rosenthal (1975) have cited the need of aquaculture facilities to prevent disease by sterilizing their intake waters. These authors recommended ozonation as the most efficient method to accomplish this.

Blogoslawski and Stewart (1977) and Blogoslawski (1977) have noted that man is not always responsible for undesirable water conditions for aquaculture, but that blooms of toxic dinoflagellates (including the so-called red tide blooms) occur throughout the world periodically. These toxin-bearing organisms can be lethal to fish or can be concentrated in the tissues of shellfish so as to be poisonous to man.

Blogoslawski, Thurberg & Dawson (1973) first showed that the toxicity of material extracted from Gymnodinium breve cultures is deactivated upon treatment with ozone. After ether extraction of the cultures, the toxic powder was suspended in mammalian saline and injected intraperitoneally into 19 to 21 g of mice and into 6 to 10 g of killifish. Mouse dosage was 6.0 mg of toxin in 0.4 ml of saline and fish dosage was 6.0 mg in 0.2 ml of saline. After data were obtained on the toxicities of the extract, the material was subjected to ozonation. Samples of toxin (3 mg/l) suspended in the appropriate saline were ozonized in 2-dram glass vials by passing 1% ozone-containing air through the solution for 15 minutes by means of a 21-gauge hypodermic needle. At a flow rate of ozone-containing air of 110 ml/minute, the toxicity of the extract was destroyed in 5 minutes.

These authors concluded that ozone treatment of marine aquarium systems could detoxify influent waters containing toxic dinoflagellate blooms provided that the proper dosage was used and would produce no undesirable effects, and provided that no residual ozone remains in the water. Residual ozone may be removed by filtration through activated carbon.

Blogoslawski, Thurberg, Dawson & Beckage (1975) described the successful use of ozone to detoxify the G. breve (red tide) bloom which occurred during April, 1974 on the Florida west coast. However, insufficient data are reported in this article to be able to determine the amounts of ozone utilized.

Dawson et al. (1976) also applied ozonization to the G. tamerensis bloom along the coast of northern New England in September, 1974. Bivalves exposed 8 days in ozonized seawater containing G. tamerensis remained non-toxic.

More recently, Blogoslawski and Stewart (in press) have shown that paralytic shellfish poison (P.S.P.) toxified surf clams (Spisula solidissima) may be detoxified with ozone-seawater treatment. These authors also have indicated the anatomical location of the poison within the clam.

Finally, Stewart & Blogoslawski (1977) have reviewed the status of ozone detoxification of the phytoplankton blooms and another marine toxin, tetrodotoxin. Tetrodon poison, also known as fugu or puffer fish poison, is caused by tetrodotoxin (TTX). Ozonation of 1 mg of crystalline TTX in 25 ml of water 30 minutes with 2% ozone in air at a gas flow rate of 110 ml/min was carried out. All experimental mice injected with 1 ml of the ozonized solution survived, whereas those injected with non-ozonized TTX solution died within 2 to 4 minutes.

Toxicity Of Ozonized Seawater

Although Rosenlund (1975) has shown that exposure to low levels of residual ozone in freshwater can be lethal to rainbow trout, if ozonized lake water is aerated and allowed to stand 11 days, the trout now are not adversely affected. On the other hand, ozonization of seawater produces a much longer residual toxicity.

In 1975, Blogoslawski, Brown, Rhodes & Broadhurst recognized that ozonized seawater prevented fertilized oyster eggs from developing into normal larvae at the ozone dose levels being used (up to 0.56 mg/l). In a 68-hr test, only 44.2% of the eggs developed normally in ozonized seawater. The authors concluded that this toxicity could not be caused by residual ozone because of the short half-life of the oxidant and because residual ozone is destroyed by passage of the treated water through activated carbon. Therefore, they hypothesized that the toxic activity must have been caused by an oxidation product (organic or inorganic).

A more detailed account of the effects of ozonized seawater on fertile oyster eggs is presented by Maclean, Longwell and Blogoslawski (1973). Unfertilized eggs spawned by the same female in the control and ozonized water showed no cytological differences. In ozonized seawater, fertilization occurred less readily. More than double the number of eggs were retarded in their completion of meiosis, a 3-fold increased incidence in abnormal polar bodies was observed, and more than double the number of cleaving eggs had abnormal nuclei. These nuclei showed signs of metabolic difficulties or of degeneration and were pycnotic, pale, diffuse or even fragmented. The cytological and cytogenetic effects of ozone appeared to be radiomimetic, which may be caused by free radical decomposition products of ozone.

These authors concluded that post-ozonation treatment steps, such as activated carbon adsorption, should be developed to remove the offending substances.

Demanche, Donoghay, Breese & Small (1975) made a detailed study of post-ozonation treatments of ozonized seawater and determined the residual toxicities of such samples to oyster larvae. Allowing ozonized seawater to stand up to 4 weeks (by which time residual dissolved ozone no longer could be present) did not reduce the toxicity. Neither did bubbling air through ozonized seawater to remove excess air and/or excess ozone. Treatment with ethylenediaminetetraacetic acid (EDTA) removed heavy metals (iron and manganese) but had no effect upon the residual toxicity. The only treatment technique that was effective in eliminating the residual toxicity of ozonized seawater proved to be filtration through activated carbon, but the effectiveness of different types of carbon was highly variable. Darco D-60 (20 to 40 mesh) satisfactorily removed the toxicity caused by ozonation.

The cause of this residual toxicity in ozonized seawater has been shown to be the oxidation of bromide ion to a bromine-containing species which is long-lived and produces a positive test by the KI-starch test procedure. Blogoslawski et al. (1976) ozonized distilled water solutions of sodium bromide and measured the dissolved ozone by spectrophotometry. When the characteristic ozone peak at 254 nm had disappeared, the KI/starch test procedure still gave a strong positive test.

Pichet & Hurtubise (1976) added bromide ion to artificial seawater and showed that ozonation produced bromine or hypobromous acid. Helz, Hsu & Block (1976) showed that treating natural estuarine water with ozone or with chlorine produces bromoform and negligible amounts of chlorine-containing haloforms. Ingols (1976) also concluded that ozonization of seawater oxidizes bromide ions to bromine and hypobromite, and discusses the mechanisms involved.

More recently, Crecelius (1977) has conclusively demonstrated the formation of bromate in ozonized seawater.

The corresponding oxidation of bromide ion in seawater by chlorination to form hypobromous acid and hypobromite ion is well known (Eppley, Renger & Williams, 1976, and references cited therein). Macalady, Carpenter & Moore (1977) have shown that when seawater is chlorinated (producing hypobromous acid and hypobromite ion) then subjected to photolysis by exposure to natural sunlight, the hypobromite is converted to bromate ion, which is a strong oxidizing agent, but which does not show up well with analytical procedures involving oxidation of iodide ion.

Thus, when ozone is applied to seawater for aquaculture purposes, the dosage levels must be monitored carefully, especially during the susceptible egg and larval stages, so that genetic and physiological damage to the growing animals may be avoided. Alternatively, the oxidized bromine-containing species may be removed from the ozonized seawater by passage through the proper activated carbon adsorbent.

Conclusions

1. Ozonization is an appropriate disinfection treatment for fresh water applications where residual disinfecting agents or toxic oxidation products (such as chlorinated amines) cannot be tolerated, or for seawater used for depuration of shellfish. Ozone dosages to achieve disinfection generally are 1 to 3 mg/l.

2. Coliform or toxin-contaminated adult shellfish cleanse rapidly, without detrimental effects, during depuration in (exposure to) ozonized seawater.

3. Residual dissolved ozone must be removed from the water before exposing fish or eggs; this is normally done by passage of the ozonized seawater through activated carbon. Alternatively, ozonized freshwater can be aerated and allowed to stand for at least 11 minutes (for fresh water juvenile trout).

4. In marine (salt water) applications, ozone doses which exceed 0.5 mg/l will oxidize bromide ion to bromine, which then forms hypobromous acid and hypobromite ions. In the presence of UV light, these will produce bromate ion. All of these oxidized bromine species may cause abnormalities to occur in fertilized oyster eggs and juvenile shellfish. This residual toxicity (after ozonation) can be removed from ozonized seawater by passage through activated carbon, although not all activated carbons give the same performance in this regard.

5. Chlorination of seawater also gives rise to the same oxidized bromine species as does ozonation.

6. Conclusions 4 and 5 imply that if a non-marine water containing both bromide and organic matter is ozonized or chlorinated, bromine-containing organic compounds will be formed.

7. The fact that seawater does not biofoul when it contains 0.50 to 0.56 mg/l of residual ozone, indicates the potential for ozone to be an alternative biofouling control material to chlorination. However, the same long-lived toxicity (from the presence of oxidized bromine species) should be present in seawaters used for cooling purposes when treated with ozone dose levels in excess of 0.5 mg/l as with chlorination.

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BIOFOULING CONTROL

The largest non-consumptive user of both fresh and saline water is the electric power industry. Large quantities of water are used for cooling purposes. Typically, raw water is passed through a steam condenser, heated to a temperature of approximately 8°C above its ambient temperature while performing its cooling function, then is returned to the river, estuary or the sea. Most of this large volume of cooling water is treated chemically to prevent biofouling. Not only can the rapid, undesireable growth of aquatic flora and fauna physically plug the condenser tubing, which can cause failure and plant shutdown, but even thin layers of biogrowth will rapidly decrease the heat transfer efficiencies of the cooling surfaces.

Presently, most power plants add chlorine, either as the gas or as aqueous solutions of hypochlorite, to disinfect or reduce the biofouling which occurs in cooling water systems. The acute and chronic effects of chlorinated compounds on aquatic life are well documented (Brungs, 1973) and residual chlorine levels in cooling water discharges now are subject to the EPA National Pollutant Discharge Elimination System (NPDES) regulation (Chase, 1975).

EPA guidelines have been established requiring that the maximum free available chlorine in once-through condenser and cooling tower blowdown waters cannot exceed 0.5 mg/l for more than 2 hrs/day, without a special state NPDES exemption (Blogoslawski & Stewart, 1976). This has encouraged the electric power industry to search for environmentally and economically acceptable biocides as alternatives to chlorination. One of the biocides under active consideration is ozone.

Toner & Brooks (1975) reported that ozone is an effective biocide at residual concentrations of 0.08 to 1.0 mg/l in seawater for marine plankton, arthropods and fish. They concluded that treatment of cooling water with ozone is just as effective as treatment with chlorine for the indigenous flora and fauna found near the marine intake waters of the Brayton Point Power Station, Massachusetts. Toner & Brooks (1975) also concluded that both oxidants provided equivalent long term toxicity to aquatic life.

On the other hand, Mangum & McIlhenny (1975) compared the use of ozone versus chlorine to prevent the biofouling of influent waters at the Freeport, Texas seawater distillation facilities. These investigators found that chlorine was effective when applied during only 50% of the water flow time at a 1 mg/l concentration. However, to attain the same level of efficiency, ozone had to be applied 85% of the time of water flow at an average dosage of 1.0 mg/l. In addition, both oxidants produced a relatively long-lived oxidant level.

Sengupta et al. (1975) estimated the costs involved in using ozone versus chlorine for power plant biofouling control. They concluded that ozone applied continuously at levels commonly used to disinfect drinking water (2 to 3 mg/l), the costs of ozonation for biofouling control would be considerably higher than those for chlorination. However, if lower levels (1.0 mg/l or less) could be effective, the economics would be more favorable (Sengupta & Chakravorti, 1975).

Siegrist, Tuttle & Majumdar (1976) reviewed the technical and economic factors of biocide system options for cooling water systems. They concluded that for ozonation to replace chlorination on an economic basis alone, the economics of ozone production first must be substantially improved. These authors considered continuous dosing of ozone at 0.75 mg/l as well as intermittent dosing at 2.0 mg/l. Although continuous dosing at the lower level would require less capital investment in ozone generation equipment than would intermittent dosing at a higher level, the operating costs would be higher. Overall, the total costs of ozonation compared with chlorine gas or hypochlorite were estimated to be 10 to 20 times higher. Pertinent data are given in Table 9.

Yu, Richardson & Hedley (1977) have discussed alternatives to chlorination for control of condenser tube biofouling under contract to the U.S. Environmental Protection Agency. They concluded that the high cost of ozonation, poor ozone transfer efficiency, lack of residual protection against downstream contamination for the cooling tower, and lack of field demonstration probably are reasons why ozonation has not been practiced in powerplant cooling water systems in the past.

These authors stated:

> "In view of the more rigorous criteria proposed for residual chlorine content in discharging waters in the future, now is an opportune time for field testing of ozonation for treatment of cooling water. A breakthrough in ozone production technology is required, however, before ozonation can compete economically with other methods....Although ozone is quite efficient in the disinfection of water, the applicability of ozone for the biofouling control of power plants is yet to be field demonstrated".

Finally, Yu, Richardson & Hedley (1977) stated that if ozone could be generated for 10¢/lb, its use could be feasible for use in full-scale power plant cooling water treatment systems in the future, but that at present, "ozone is simply too new, and too untried in the control of biofouling of the powerplant condensers".

The Electric Power Research Institute recently has funded a demonstration contract (No. RP-733-1) to Public Service Electric & Gas Company of New Jersey to compare chlorination with ozonation for biofouling control at an operating power plant (Guerra, 1978). The program began in early 1977 and is scheduled to be completed in early 1979. A mobile trailer has been fitted with three cooling water condensers (connected in parallel) and associated instrumentation and is able to process cooling water flows of 100 gal/min. Each condenser is 9 ft long, contains 9 identical tubes, and is activated by electrical heaters. Instrumentation is available to measure temperatures, pressures and flow rates.

TABLE 9. COMPARISON OF VARIOUS BIOCIDE SYSTEM ALTERNATIVES

System	Capital Cost	Annual Operating Cost
Chlorine Gas	$ 201,000	$ 123,000
Hypochlorite Generators	$ 230,000	$ 144,000
Purchased NaOCl Soln. (15%)	-	$ 223,000
Ozonation		
Continuous	$ 4,306,000	$1,445,000
Intermittent	$ 5,803,000	$ 53,000
Amertap System (mechanical)	$ 920,000	$ 57,000
Copper Sulfate	-	$ 127,000

Bases:

1) Costs estimated based on a 2-unit, 1,220 MWe (each) nuclear power station
2) 1974 price index
3) Interest rate -- 10%
4) Plant life -- 40 years
5) Power cost -- 30 mils/kwhr, 1981 basis
6) Capacity replacement factor for life of plant ignored
7) Chlorine or hypochlorite required -- 1,900 lbs/day
8) Dechlorination with SO_2 included to produce 0.2 mg/l free chlorine residual
9) Continuous ozone dosage -- 0.75 mg/l
10) Intermittent ozone dosage -- 2 mg/l for two 10-minute periods/day
11) $CuSO_4$ dosage -- 4 mg/l for two 10-minute periods/day.

Source: Siegrist, Tuttle & Majumdar (1976)

In the first phase of this demonstration program, the base line performance of the condensers will be assessed using chlorine. Heat balances and the response of the instrumentation under varying simulated power plant operating conditions will be determined, then chlorine will be employed as the biofoulant control and the performances of the "model" condensers, on-site, will be compared with those of the full-scale plant condensers using chlorine.

In early summer, 1978, the program plan is to shift to the use of ozone. The on-site performance of ozone in the model condensers then will be extrapolated to plant-scale performance using as criteria the performances determined using chlorine.

In a parallel program which will be funded by the Department of Energy, bioassays are to be performed on the treated waters to determine the effects of the chlorinated and of the ozonized cooling waters upon selected aquatic species.

Two cooling waters, brackish and fresh, are to be tested by PSEG/NJ under this program, but not full-strength seawater (Guerra, 1978).

A decision as to the applicability of ozonation for control of biofouling of power plant cooling waters thus should be available about mid-1979.

Conclusions

1) Ozone has been shown to be an effective biocide in seawater at residual concentrations of 0.08 to 1.0 mg/l for marine plankton, arthropods and fish in Massachusetts waters.

2) In Gulf of Mexico waters (Freeport, Texas), ozone has been shown to be an effective biocide at a dosage of 1.0 mg/l, but was required to be applied 85% of the water flow time to be as effective as 1.0 mg/l of chlorine applied 50% of the time.

3) Both ozone and chlorine, used as biocides in seawater, produce a relatively long lived oxidant residual and a long-lived toxicity to aquatic life. This toxicity probably is caused by oxidation of bromide ion to higher oxidation states (see Section 5 -- Aquaculture).

4) Total capital and operating costs of ozonation for biofouling control at a continuous dosage level of 0.75 mg/l have been estimated to be 10 to 20 times higher than those for chlorination using chlorine gas or hypochlorite.

5) A definitive demonstration study comparing ozonation with chlorination under actual power plant operating conditions began in early 1977 with results expected in 1979. Effects of the ozonized and chlorinated cooling waters upon selected aquatic species and operating costs are to be determined as part of this program.

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CYANIDES AND CYANATES

Cyanides

The first waste cyanide solutions of any significance were produced in the gold and silver mining industries, where cyanides were used to dissolve these metals from their ores. Since that time, the use of cyanides has expanded significantly into the electroplating industry and photographic bleaches. Cyanides also are found in iron and steel manufacturing (coke oven wastewaters. In addition, certain types of organic chemicals (nitriles and cyanohydrins) contain the cyanide grouping in their structure and some of these compounds can find their way into wastewater discharges.

The known uses of ozonation in each of these major industrial categories will be discussed in the appropriate sections of this report. However, in this section the known chemistries of the basic reactions of ozone with aqueous cyanide and cyanate solutions will be discussed.

The first published account of ozone oxidation of cyanides was by Neuwirth (1933) who treated KCN solutions batchwise with ozonized air and obtained substantial reductions in cyanide concentrations when iron and manganese "catalysts" were present. It is speculated by Sondak & Dodge (1961), however, that the amount of cyanide reported as "lost" by Neuwirth might merely have formed stable (to ozonation) metallic complexes with the catalysts used. That this is highly probable, at least with respect to iron, is indicated by the high degree of stability of iron cyanide complexes to simple ozonation (see Section 4, dealing with Ozone/UV Radiation).

Khandelwal, Barduhn & Grove (1959) investigated the kinetics of ozonation of aqueous cyanide solutions. Using gas phase concentrations of 70 to 90 mg/l of ozone in oxygen and an application rate of 20 to 25 mg of ozone per minute through a 1,500 ml sparged ozone reactor at ambient temperatures, ozonation reaction rates were determined under a variety of conditions for the destruction of cyanide according to the following equation:

$$(CN^-) + O_3 + HOH \longrightarrow (CNO^-) + O_2 + HOH$$

The rate of cyanide disappearance was shown to follow the equation:

$$d(CN^-]/dt = K[CN^-]^{1/3}$$

where: $[CN^-]$ = concentration of cyanide

t = reaction time

K = reaction rate constant

$k_1 = 0.33\ s^{-1}$

The apparent order of the reaction was 1/3. When copper ions were added the reaction rate more than doubled, but higher copper ion concentrations did not further increase the reaction rate. The rate constant for ozonation of cyanide ion increased in the following order with the sulfate salts of the cations added as catalysts: Cd(II), Mn(II), Ni(II) and Cu(II). The rate constant for Cd(II) was practically the same as for the uncatalyzed reaction; the rates were unaffected by the choice of anion, specifically when sulfate, nitrate, acetate or chloride was added as copper salts, over the temperature range 13 to 30°C.

Sondak & Dodge (1961) conducted a detailed investigation of (1) pure aqueous cyanide solutions, (2) synthetic and actual zinc, cadmium and copper plating solutions, and (3) pure aqueous cyanate solutions to examine the kinetics of ozonation reactions.

Ozone was prepared from dried air (compressor, silica gel, dry ice-acetone trap), then passed through dilute sodium hydroxide solution to remove nitrogen oxides. Contacting was conducted in a 4 ft tall by 2.375 inch I.D. glass column containing a porous frit, and usually operated at 2/3 capacity. Ozone in the reactor inlet and outlet gases was measured so that mass balances could be determined.

Experimentation with pure aqueous cyanide solutions showed that 1.84 g of ozone was required to oxidize 1 g of cyanide ion to cyanate:

$$(CN^-) + O_3 \rightarrow (CNO^-) + O_2 \qquad (1.84\ lb\ O_3/lb\ CN^-)$$

In addition, it was shown that:

(1) The rate of ozone absorption was constant at a constant inlet ozone concentration above a limiting ozone concentration,

(2) The rate of ozone absorption increased linearly with inlet ozone concentration,

(3) Because the rate of ozone transfer from the gas film was rate controlling in the region of cyanide concentrations studied (up to 80 mg/l and in the pH range of 10.3 to 12.4), increasing temperature or addition of metal ion catalysts had no effect upon the rate of ozone absorption,

(4) Below a critical value of cyanide ion concentration (about 4 mg/l), the rate of ozone absorption dropped off rapidly and the reaction became rate controlled instead of mass transfer controlled.

Essentially the same results were obtained with synthetic and actual plating solutions, except that the rate constant for copper plating solution was about 15% lower than that for pure aqueous cyanide solutions. In addition, the plot of rate data for cadmium solutions showed a slight curvature, rather than being a straight line.

Bahensky & Zika (1966) studied the effect of copper ion and pH on the ozone oxidation of aqueous cyanide and determined that copper concentrations of 5 to 15 mg/l at pH 10 to 11 are optimum for ozonizing solutions containing at least 100 mg/l of cyanide. At pH values below 7, HCN can be liberated from the reaction mixtures.

Cyanates

Although ozonation of cyanide proceeds rapidly to form cyanate, the oxidative/hydrolytic destruction of cyanate ion proceeds much more slowly upon continued treatment with ozone. Cyanate ion is known to decompose at high or low pH. Kolthoff & Stenger (1947) recommended hydrolysis in strong alkali as a method for determining the concentration of cyanate ion:

$$(CNO^-) + (OH^-) + HOH \longrightarrow CO_3^{-2} + NH_3$$

Resnick, Moore & Ettinger (1958) studied the acid hydrolysis of cyanate at pH 4 and found a half-life for cyanate ion destruction of about 38 minutes.

At temperatures of 30 to 50°C (Sondak & Dodge 1961), the rate of oxidation of cyanate ion was about one-fifth that of cyanide under the same ozonation conditions. At pH 11.0, the rate of cyanate oxidation was fastest, and the ozone demand was 3.06 g/g of cyanate. No hydrolysis of cyanate to free ammonia was observed.

Additional Reactions

Balyanskii, Selin & Kolychev (1972) ozonized 38 to 40 mg/l potassium cyanide solutions under strongly alkaline conditions (pH 12), and identified nitrate as a reaction product. These authors proposed that hydrolysis of cyanate ion first forms ammonia, which then oxidizes quickly at this pH upon ozonation. About 70% of the nitrogen content of the original cyanide was accounted for as nitrate; the remainder was assumed to have been lost as nitrogen gas via direct ozonation of cyanate according to the reaction:

$$2(CNO^-) + 3O_3 + HOH \longrightarrow N_2 + 2HCO_3^- + 3O_2$$

The apparent stoichiometry under the experimental conditions (20°C) could be represented as follows:

$$(CN^-) + 1.3O_3 \xrightarrow{(OH^-)} (CNO^-)$$

$$(CNO^-) + 4.5O_3 \xrightarrow{(OH^-)} 0.7(NO_3)^- + 0.15N_2 + (HCO_3^-)$$

Balyanakii <u>et al</u>. (1972) reported that mass transfer of ozone across the gas/liquid interface was the rate controlling step in both cyanide and cyanate oxidations at 20°C and pH 12.

In reviewing methods for purification of wastewaters containing cyanide ion, Zumbrunn (1971) concluded that using small quantities of ozone produces cyanate, but that with excess ozone, cyanide forms nitrogen and carbonate:

$$2(CN^-) + 5O_3 + 2NaOH \longrightarrow 2(NaCO_3^-) + N_2 + 5O_2 + HOH$$

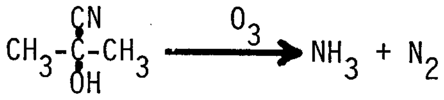
For this reaction to proceed, the pH must be "very alkaline".

Mathieu (1973) describes the ozonation of sodium cyanide solutions, some of which were mixtures with cuprous cyanide. Tests were conducted in a pilot installation capable of treating 2 to 7 gal/min of solution. The ozone contactor system was the sprayer type, in which tiny droplets of solution are sprayed into an atmosphere of ozone in air. Contact time in this type of contactor is about 12 seconds per contacting chamber. The process was more effective at cyanide concentrations of 100 mg/l than at 10 mg/l, removing 91 to 97% of the cyanide. Costs for treating solutions containing concentrations of 50 mg/l of cyanide were estimated to be 5 to 7¢/1,000 gal.

In a more detailed discussion of these tests, Mathieu (1975) states that 98% of the cyanide was eliminated upon optimization of the process. The solution was electro-coagulated to remove suspended solids, then ozonized in three spray contactor chambers (total contact time, about 30 seconds). No cyanate could be detected in the solutions after ozonation.

Fujisawa et al. (1973) ozonized solutions of pure KCN and KCNO at various pH values. Cyanate ion was oxidized by ozone to nitrogen gas.

Ishizaki, Dobbs & Cohen (1978) ozonized aqueous solutions of acetone cyanohydrin at pH 4, 7, 9 and 11. At pH 4, the compound was only slightly oxidized, but at the other values, organic nitrogen content decreased readily, and ammonia and nitrogen were produced, indicating an increase in oxidative decomposition.



$$CH_3-\overset{CN}{\underset{OH}{C}}-CH_3 \xrightarrow{O_3} NH_3 + N_2$$

acetone cyanohydrin

Ikehata (1975) showed that although the destruction of sodium cyanide with ozone is very rapid, ferricyanide and ferrocyanide compounds are very stable to ozone destruction at pH 9 and 25°C. Potassium ferricyanide is a major component in commercial photographic bleaches.

Ozone/UV Radiation

Using synthetic cyanide-containing wastewaters, scientists at Houston Research Inc. (Garrison, Mauk & Prengle, 1974) confirmed that:

(1) Ozonation at pH 11.0 converted all cyanide to cyanate,

(2) Acidification to pH 4 after ozonation immediately hydrolyzed cyanate,

(3) Three lbs of ozone are required to destroy each pound of free cyanide, except when copper ion is present, in which case the ratio is 2.5/1,

(4) Destruction of concentrated cyanide solutions (100,000 mg/l or higher) by ozone is mass transfer limited, whereas ozonation of solutions containing less than 1 mg/l of cyanide is reaction rate limited.

These Houston Research Inc. scientists also discovered the catalytic effect of UV radiation and/or heat upon the rate of ozone oxidation of cyanides and oxidatively refractory organic compounds. Iron cyanide complexes, present in photoprocessing bleach solutions as well as some electroplating wastewaters, normally are quite stable to ozonation. However, by applying both ozone and UV radiation simultaneously, the cyanide concentration can be reduced rapidly to below the limit of analytical detectability.

When employing an actual photoprocessing bleach solution containing 4,000 mg/l of cyanide complexed with iron, and a 6-ozone contacting system (the last 2 with added UV radiation), and using 5.9% ozone in oxygen, the cyanide concentration leaving the last reactor was below 0.3 mg/l. Cyanate ion also was destroyed by this system.

Conclusions

- Ozone reacts rapidly with free cyanide ion and many stable metal cyanide complexes to produce cyanate ions. Iron cyanide complexes are stable to ozonation. Copper ions catalyze the rate of oxidation of cyanide to cyanate.
- The rate of ozone oxidation of cyanate ion is about 20% of the rate of cyanide oxidation under the same conditions. Oxidation of cyanate is fastest at high pH (11.0). Hydrolysis of cyanate proceeds rapidly at acidic pH conditions.
- At pH 12, ozonation of cyanide produces nitrate and (apparently) nitrogen gas from oxidation of the cyanate intermediate.
- Ozonation at pH below 10 to 11 (certainly below 7) might result in HCN gas being stripped out of the reaction mixture and into the reactor off-gases.
- Ozonation of cyanide solutions using a series of 3 spray-tower contactors destroyed all cyanide and all cyanate in about 30 seconds of contact time.
- Ozonation of acetone cyanohydrin solutions at pH 4 is quite slow, but at pH 7, 9 and 11, oxidative decomposition is rapid. Organic nitrogen content decreases rapidly, and ammonia and nitrogen are produced.

- Metal cyanide complexes otherwise stable to ozone oxidation (ferro-, ferri-, etc.) can be decomposed and the cyanide converted to some oxidation stage past the cyanate stage by simultaneous treatment with ozone and UV radiation.

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ELECTROPLATING

The earliest application of ozonation to an actual plating waste was reported by Tyler et al. (1951) who treated cadmium plating solutions with ozone and observed oxidation of cyanide to cyanate, then oxidation of cyanate to bicarbonate and nitrogen:

$$2KCN + 2O_3 \longrightarrow 2KCNO + 2O_2$$

$$2KCNO + HOH + 3O_3 \longrightarrow 2KHCO_3 + N_2 + 3O_2$$

$$2KCN + HOH + 5O_3 \longrightarrow 2KHCO_3 + N_2 + 5O_2$$

Walker & Zabban (1953) studied the use of several oxidants, including ozone, with dilute electroplating wastewater solutions. Samples containing from 200 to 400 mg/l of total cyanide were prepared from the following stocks:

Copper Plating Bath:	Cuprous cyanide 45 g/l; NaCN 68 g/l; sodium carbonate 30 g/l
Zinc Plating Bath:	Zinc cyanide 60 g/l; NaCN 41 g/l; NaOH 79 g/l.

Ozone was generated in a glass tube apparatus with tin foil electrodes, from air which had been dried by passing it through concentrated sulfuric acid and anhydrous calcium sulfate. At the steady state, the concentration of ozone produced was about 1.2% by volume. A 500 ml bottle, with a porous frit, served as the reaction vessel.

In the initial reaction, cyanide ion was oxidized to cyanate, requiring 0.6 to 0.85 mole of ozone per mole of cyanide. The reaction was catalyzed with 10 to 20 mg/l of copper or manganese ions. Without metal ion catalyst, the zinc plating solution absorbed only 50% of the ozone applied; the balance passed through the contactor unreacted. Cyanate ion was not oxidized appreciably under these conditions (initial pH 10 to 12; duration of ozonation 2 to 10 minutes).

For disposal of cyanide-containing plating wastewaters, the alkaline chlorination process is the standard treatment process. However, Selm (1959) points out several disadvantages of alkaline chlorination:

(1) Chlorine must be used in considerable excess -- about 8 lbs/lb of cyanide to be treated. Destruction of 100 mg/l of cyanides results in chloride ion concentrations of 800 mg/l.

(2) Excess chlorine is toxic to aquatic life in rivers, lakes, streams, etc., which may receive the treated wastewaters.

Finally, Selm (1959) suggested that it might be acceptable to stop the reaction of cyanide destruction at the cyanate stage, rather than proceeding to complete destruction, because of the lesser toxicity of cyanate compared with cyanide ion. Recently promulgated U.S. EPA effluent discharge regulations for the electroplating category have supported this concept. EPA has promulgated a cyanide standard, but has not promulgated a discharge standard for cyanate ion in electroplating wastewaters.

The work of Selm (1959) led to the installation of an ozone treatment system for cyanide-containing electroplating wastewaters at the Boeing Aircraft Company, Wichita, Kansas. This wastewater treatment plant was put into operation in 1957 using ozonation, and has been operating satisfactorily ever since (Klingsick, 1975).

The Boeing, Wichita wastewater treatment plant originally installed two 60 lb/day ozone (from air) generators and two cylindical contacting towers packed with Intalox saddles (Klingsick, 1975). These contact towers are 30 ft tall by 4 ft in diameter. Each column contains 18 ft of 2-inch Intalox saddles. Cyanide content is 0.0 to 0.25 mg/l in the wastewater, which first undergoes oil separation, sulfur dioxide reduction of chromates, alkaline precipitation of heavy metals, then clarification. The treated wastes at pH 9 are sent to the first ozonation tower at a flow rate of 20,000 lbs/sq ft/hr. Effluent from the first tower is acidified to pH 7 by carbonation, clarified, then passed through the second tower countercurrent to the flow of gas effluent from the first tower. This technique removes excess sulfur dioxide and disposes of excess ozone in the off-gases from the first tower.

Capital cost for this plant was $70,000, and the ozone production costs are 14 to 15¢/lb (1958 prices). Ozonation is cost-effective over chlorination when the accessories needed to support chlorination (large detention basins, facilities for storing and handling chlorine, railroad spurs and chlorinating equipment) are considered (Anonymous, 1958).

In laboratory studies leading up to the installation of the Boeing plant, Selm (1959) found that 1.75 to 2.00 lbs of ozone were consumed per lb of cyanide oxidized. The initial wastewater solution contained 44.5 mg/l of cyanide at pH 8.8 and at temperatures of 28 to 30°C. The extent of cyanide oxidation with ozone was followed by measuring the oxidation potential of the ozonized solution. While the cyanide was reacting no residual ozone was present, and the redox potential of the solution was low. However, when all cyanide had oxidized, and dissolved ozone was present, the redox potential of the solution rose quickly to a high level.

Klingsick (1975) reviewed the experiences at the Boeing, Wichita plant since its inception. Spot data were taken on an average of 20 daily composite samples in October-November, 1971. The average influent cyanide concentration to the ozone treatment process step was 0.17 mg/l and the average effluent cyanide concentration was 0.06 mg/l; the wastewater flow averaged 175,000 gal/day in 1971 (Klingsick, 1975 - Private Communication).

Serota (1958) reviewed the published literature of the time and noted that cyanide groups in ferricyanide compounds are not attacked by ozone. An appreciable drop in pH occurs during ozonation of cyanide-containing solutions, thus a pH above 10 was recommended for ozonizing electroplating solutions, to avoid the possibility of HCN volatilizing. Lowering the solution pH to about 3 after ozonation allows hydrolysis of cyanate to ammonium ion. Serota concluded that ozonation is a satisfactory treatment technique for large volumes of solutions containing less than 5 mg/l of cyanide, since the cyanate formed will be present in concentrations below 10 mg/l, "which is below the toxic concentration".

Costs for ozonation were estimated by Sondak & Dodge (1961) and compared with those for chlorination for a 100,000 gal/8 hr day wastewater stream containing 200 mg/l total cyanide, 8 mg/l cadmium, 58 mg/l copper and 63 mg/l zinc. Treated effluent would contain less than 0.5 mg/l of cyanide, less than 20 mg/l cyanate and pH of 6 to 8. Equipment for hydrolysis of cyanate was included in the ozonation estimates. Ozonation costs were estimated on the basis of batch or continuous processing and compared with batch processing by chlorination (Table 10).

Ozonation system capital costs were about 67% ($172,000) of the total batch system equipment costs ($250,900), but continuous ozonation capital costs ($194,500) were about 15% lower. Batch chlorination system costs were much lower ($38,400). Operating costs for batch ozonation were $230.40/day, mainly because of the high amortization cost ($126.00/day -- 12 years depreciation at 8%) compared with $120.85/day for chlorination (1956 dollars).

Ikehata et al. (1972) ran batch and continuous tests on silver and copper plating wastewaters with ozone generated from oxygen. Contacting was effected by means of spargers (porous diffusers). For the continuous run studies, contacting was conducted using 3 and 4 stages, so as to allow for complete decomposition of cyanate, which began to decompose rapidly when the total cyanide concentration was lowered to about 60 mg/l (copper plating wastewater) and to about 5 mg/l (silver plating wastewater). Ferrous cyanide complex was the most difficult to be decomposed, whereas nickel and copper cyanide complexes were decomposed rapidly upon ozonation.

Ozone consumption increased considerably as the cyanide concentration decreased. The rate of cyanide decomposition with ozone was zero order between pH 6 and 8, first order with respect to cyanide ion and 0.5 order with respect to hydroxide ion.

Off-gas ozone was recycled to the contactors, thus increasing ozone utilization to 95%. Excess ozone was destroyed by feeding the off-gases into the plant boiler combustion chamber, or by passage through GAC.

Although 6.82 moles of ozone theoretically are required to completely destroy 1 mole of cyanide (past the cyanate stage), in practice, large excesses of ozone are required, and the pH must be kept at 9 or above. The pH for optimum decomposition of cyanic acid by hydrolysis is 6.5 to 7. Thus in destroying cyanides by alkaline chlorination, 2-stage pH control is

TABLE 10. COMPARISON OF INVESTMENT COSTS AND OPERATING EXPENSES FOR A 100,000 GALLON PER DAY PLATING WASTE DISPOSAL PLANT USING OZONE OR CHLORINE (a,e)

Reactant..........	Ozone		Chlorine
System..............	Batch Cost, $	Continuous Cost, $	Batch Cost, $
Equipment			
Storage...............	2,200	-	16,000
Reaction..............	20,600	9,600	10,000
Hydrolyzer............	25,400	6,000	-
Ozonator System (b)....	172,000	172,000	-
Tanks for Chemicals (e)	900	900	900
Pumps & Mixers	3,000	2,000	6,500
Piping (c)............	7,000	3,000	5,000
Total............	250,900	194,500	38,400
	Cost, $/Day	Cost, $/Day	Cost, $/Day
Operations			
Power			
Ozone............	71.20	71.20	-
Pumping..........	0.60	0.60	5.00
Chemicals.............	32.60	32.60	94.50
Amortization (d).......	126.00		21.35
	230.40		120.85

(a) Costs all reduced to a Dec 1956 basis.
(b) Costs from "Ozone Generation for Industrial Application," The Welsbach Corp., 1956, page 9, figure 4.
(c) Fifteen per cent of equipment costs used for this charge.
(d) Twelve year depreciation with money valued at 8 per cent was used.
(e) Cost of sludge handling not included.

Source: Sondak & Dodge, 1961.

required. On the other hand, ozonation of cyanide or cyanate can be conducted under nearly neutral conditions. The CN/ozone mass ratio for first stage oxidation (to cyanate) is 0.542 and for second stage decomposition (of cyanate) is 0.217. In acidic solution, the CN/ozone mass ratio for second stage decomposition of cyanate is 0.361.

Ikehata et al. (1972) concluded that even though the major drawback of ozonation for treatment of electroplating wastewaters is high ozone generator cost, the ozonation of cyanide wastewaters still is somewhat less costly than alkaline chlorination.

Upon reviewing the economics of treating cyanide-containing wastes, Goldstein (1973) concluded that ozonation is economically practical for partial destruction (to cyanate) of 20 lbs/day of cyanide, or for total destruction of 10 lbs/day. Capital costs for ozonation equipment would be $30,000 with $1,200/year annual operating (power) costs. These costs for ozonation compare with $6,000 to $10,000/year annual operating (chemical) costs for alkaline chlorination. Very little capital investment is required for alkaline chlorination, but only 40% as much ozone is required as chlorine to oxidize each lb of cyanide.

Trejtnar (1974) conducted laboratory, then plant ozonation experiments on metal finishing wastewaters in Czechoslovakia and confirmed the two step reaction between ozone and cyanides:

$$2KCN + 2O_3 \longrightarrow KCNO + 2O_2$$

$$2KCNO + HOH + 3O_3 \longrightarrow KHCO_3 + N_2 + 3O_3$$

About 1.1 to 1.6 volumes of ozone are required for each volume of cyanide oxidized to cyanate. However, because of the presence of other oxidizable materials, the practical dosage is 3 g of ozone per g of cyanide. Oxidation with ozone is independent of pH over the range 7 to 12.5, but even at pH 3, the rate is nearly as fast. No sludges or precipitates are formed. The treated wastewater could be used as "service water" (for washing equipment).

Fabjan (1975) concluded that ozone will convert cyanide to cyanate efficiently at alkaline pH, and that cyanate is hydrolyzed to carbon dioxide and ammonium ion at low pH values. At an ozone production cost of 16¢/kg (from air) or 7¢/kg (from oxygen), ozonation is less costly than chlorination. Capital costs for ozonation equipment should be in the range of $1,000 to $2,000/kg/day of ozone generation capacity. Power costs for the generation of ozone represent 75% of the total operating costs. The use of oxygen to generate ozone is recommended for treatment of concentrated cyanide solutions.

Bollyky (1977) describes a 9-month full scale electroplating wastewater plant demonstration project which was conducted for the U.S. Environmental Protection Agency at the Sealectro Corporation, Mamaroneck, New York. This plant discharges 2 wastewaters: an acid wastewater, containing nickel, tin and lead, and an alkaline wastewater containing up to 60 mg/l of cyanide, with copper and silver. The combined plant wastewater flows average 34 gal/min, with peak surges up to 50 gpm.

Sealectro's new wastewater treatment process involves ozonation of the alkaline wastewater without any pH adjustment in the range of 7 to 11, combining the ozone treated alkaline waste with the acid wastewater in a flash mixer, adjustment of the pH with caustic, settling, then discharge to the local sewer. Installed ozonation capacity is 20 lbs/day (from air). Contacting is conducted in a two-compartment, cylindrical chamber, 18.5 ft tall by 30 inches in diameter (total volume 600 gal). The lower compartment contains porous diffusers for treating alkaline wastewaters preozonized in the upper chamber. In the smaller, upper chamber, off-gases from the lower compartment are reintroduced either through a packed column or diffused through the incoming alkaline wastewater. Vent gases from the ozone contactor consistently contain less than 0.05 mg/l (by volume) of waste ozone.

To meet the current EPA/NPDES and New York state discharge standards for BPTCA (0.1 mg/l cyanide oxidizable by chlorine; 1.0 mg/l total cyanide) requires 1.85 to 2.8 mg/l of ozone per mg/l of cyanide at an initial pH of 7.0 to 9.5. The effluent wastewater consistently contains below 0.1 mg/l of cyanide and 6 mg/l of cyanate.

The amount of ozone required depends upon the initial cyanide concentration. At concentrations below 20 mg/l of cyanide, the mole ratio of ozone/-cyanide required to reduce the concentration of cyanide to below 0.1 mg/l is 1:1. At 20 to 40 mg/l cyanide concentrations, the mole ratio required is 2:1 to obtain less than 1 mg/l cyanide, and 3.6 to attain less than 0.1 mg/l.

Plant-scale studies on ozonation of aqueous sodium cyanide showed that ozone/cyanide mole ratios of 2.65 destroyed 97.6% of the cyanide, ratios of 4.3 destroyed 44.8% of the cyanate, and ratios of 14.0 destroyed 97% of the cyanate. For copper cyanide solutions, 1 to 1.5 moles of ozone/mole of cyanide reduced the cyanide concentration to below 0.1 mg/l at initial cyanide concentrations of up to 20 mg/l. As the cyanide concentration rises to 75 mg/l, the mole ratio of ozone/cyanide required to meet the discharge standard increases to 3.0.

Capital plus operating costs at the Sealectro Corporation plant (operated 24 hr/day, 1975 prices, 15 year amortization) are estimated to be $1.31/1,000 gal of combined plant wastewater. Capital investment for the optimized treatment system is $51,200 (Table 11).

The ozone treatment system at Sealectro Corporation began operating in late 1973 and has been treating these electroplating wastewaters satisfactorily since then (Bollyky, 1978). Finally, Bollyky (1977) suggests that with increased ozone dosages (up to 2 moles of ozone/mole of cyanide), plus the addition of flocculant or settling tubes in the settling tank, the treated wastewater could be used to cool the ozone generator or air conditioning equipment.

TABLE 11. SEALECTRO CORPORATION, COST DATA SUMMARY

	operating cost	total cost
combined cyanide + heavy metal waste	\$1.03/1,000 gal	\$1.31/1,000 gal
cyanide waste alone	\$1.43/1,000 gal	\$2.35/1,000 gal \$10.34/kg of CN \$4.70/lb of CN

- combined cyanide + heavy metals waste flow = 49,000 gal/day
- capital investment for optimized ozonation system = \$51,200 (1975 prices)

Ozone/UV Radiation

The ozone/UV wastewater treatment process was initially developed for destruction of cyanides in wastewaters from electroplating and color photographic processes (Prengle, 1977). Cyanides vary in resistance to oxidation from very low (KCN) to very high (complexed ferricyanide). Free cyanide ion is destroyed by ozone essentially as fast as ozone can be added to the solution, and does not require UV input. The reaction rate of free cyanide ion with ozone, therefore, is mass transfer limited, being limited only by the rate at which ozone can be transferred from the gas into the liquid phase.

On the other hand, complexed cyanides of iron, copper and nickel are very difficult to oxidize with ozone alone, but are readily oxidized by the combination of ozone with UV radiation, as shown in Figure 9 for iron complexed cyanide wastewater. Coupling ozone with UV radiation and raising the reaction temperature to 66°C results in the fastest rate of iron cyanide destruction.

The beneficial effect of multistage reactors upon the destruction of complexed cyanides is indicated in Table 12. Iron, copper and nickel complexed cyanide solutions containing 4,000 mg/l of total cyanide treated in 3 to 6 reactor stages to final cyanide concentrations of less than 0.3 mg/l cyanide theoretically should produce 6,500 mg/l of cyanate, if the ozonation proceeds only to the cyanate stage. The fact that much lower concentrations of cyanate actually were found indicates that the ozone/UV process also destroys cyanate ion.

Employing the two-staged reactor system shown in Figure 6, designed to treat an industrial wastewater containing 150 mg/l of free and metal complexed cyanides and 90 mg/l of refractory organics, Prengle & Mauk (1977) were able to reduce total cyanide to below 0.1 mg/l and TOC to below 1 mg/l. The process involves chemical coagulation, sedimentation, clarification, equalization, pH adjustment, followed by a single stage ozonation reactor (for easily oxidized materials) then a multistaged reactor for difficult to

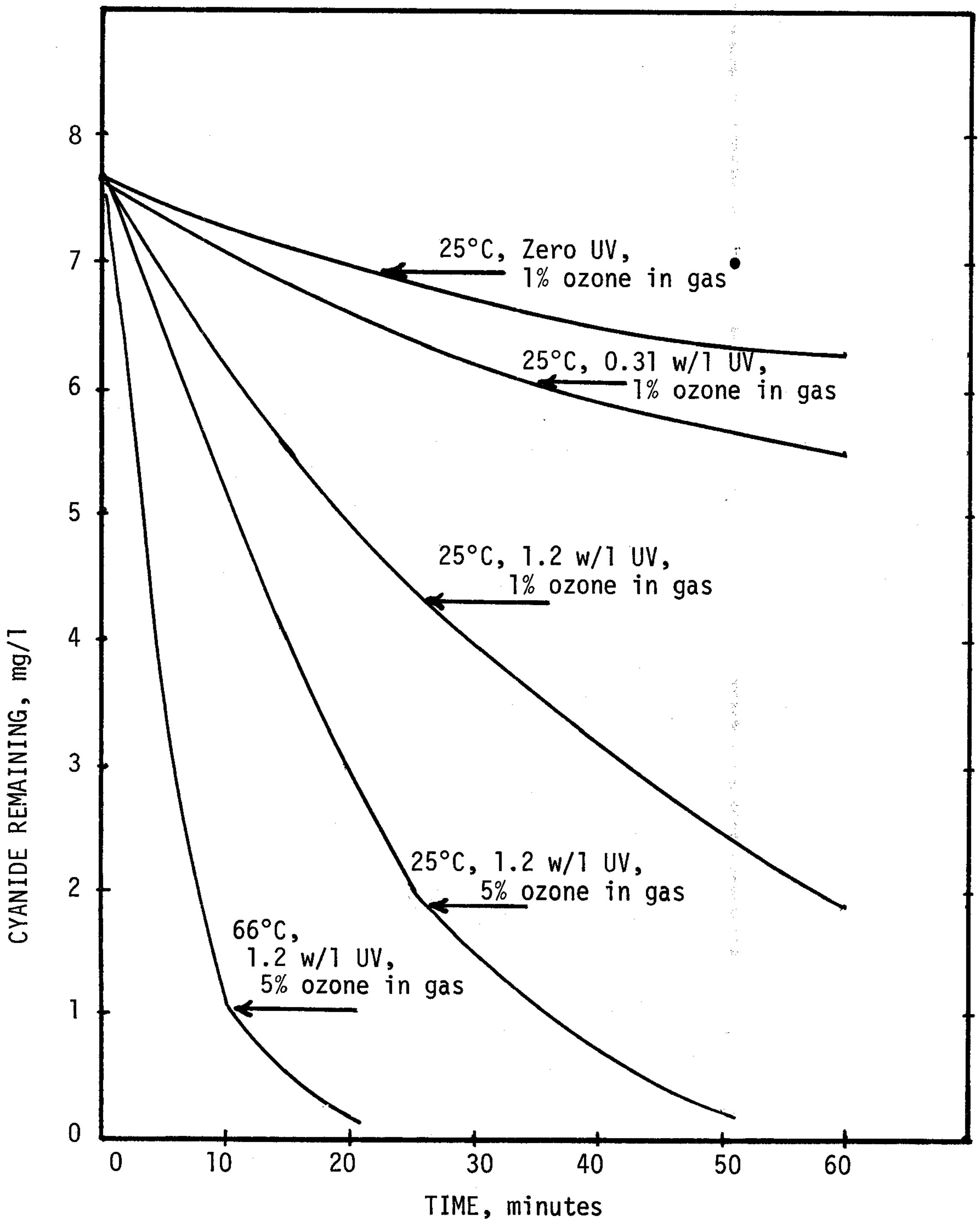

Figure 9. Ozonation of iron complexed cyanide waste.

Source: Garrison, Mauk & Prengle (1975)

oxidize species. The capital costs to treat 100 gal/min of this wastewater are $662,700, and are described in Table 13 (Prengle, 1977).

TABLE 12. TYPICAL CYANIDE OXIDATIONS WITH OZONE AND OZONE/UV

Influent Parameters		Effluent from Reactor Stages:					
		1	2	3	4	5	6
Cu Complexed							
CN, mg/l	4,000	17	0.5	<0.1			
Cyanate, mg/l	0			110			
Temperature, °C	20	20	20	66			
pH	11.5			7.7			
UV, watts/l	--	0	0	1.2			
Ni Complexed							
CN, mg/l	4,000	110	0.6	<0.1			
Cyanate, mg/l	0			470			
Temperature, °C	20	20	20	66			
pH	11.8			8.5			
UV, watts/l	--	0	0	1.2			
Fe Complexed							
CN, mg/l	4,000	2,680	1,630	710	105	13	<0.3
Cyanate, mg/l	0						47
Temperature, °C	20	66	66	66	66	66	66
pH							8.9
UV, watts/l	--	0	0	0	0	0	1.2

Source: Prengle (1977)

As of late 1977 (Prengle, 1977) Houston Research Inc. has installed ozone/UV (the OXYPHOTOLYSIS Process) wastewater treatment systems for metal finishing wastewaters at the U.S. Air Force, Tinker Air Force Base, Oklahoma (metal complexed cyanides), at the French facility of a large American chemical company (cyanide and refractory organics), a similar design for the same company at an American installation, and at Hughes Tool Co., Houston, Texas. This last system has been in full-scale operation since November, 1976, treating metal finishing wastewaters.

Conclusions

1) Ozone treatment of metal finishing, cyanide-containing wastewaters has been in use at the Boeing Company, Wichita, Kansas since 1957. This is the longest known use of ozone for treating these types of wastewaters. The facility treats 175,000 gal/day of wastewaters and ozone reduces the concentration of cyanide from an average of 0.17 mg/l to below 0.06 mg/l.

2) Since 1973, Sealectro Corporation, Mamaroneck, New York has been using ozone treatment to lower cyanide levels in copper and silver plating wastewaters from 60 g/l to below 0.1 mg/l at the rate of 34 gal/min.

The effluent consistently contains less than 6 mg/l of cyanate and meets current discharge standards with respect to other water quality parameters.

TABLE 13. CAPITAL COST ESTIMATE -- OZONE/UV TREATMENT OF AN INDUSTRIAL WASTEWATER

(100 gpm stream containing cyanides and biorefractory organics; e.g., Figure 6)

Item	Amount
Wastewater Evaluation & Treatability Study	$ 17,500
Equipment	
Chemical Coagulation Unit	10,500
Sedimentation-Equalization Unit	45,300
Ozone Generation Unit, with Air Processing	210,000
Ozone Reaction Unit	95,600
Ozone/UV Reaction Unit	144,300
Pumps & Control Valves	7,500
Instrumentation	18,500
Total Equipment	($531,700)
Skids, Piping & Installation	55,000
Design, Engineering & Fee	58,500
TOTAL COST	$662,700

Source: Prengle, 1977

3) Cyanide ion at concentrations of 100 mg/l or less may be oxidized rapidly to cyanate in the presence of copper ions in the pH range of 7 to 12. In this range, pH adjustment is not necessary.

4) Non-transition metal cyanides (Zn, Sn, Cd, Na, K, etc.) are oxidized rapidly in the presence of copper catalyst at room temperature.

5) Iron cyanide complexes are oxidized very slowly by ozone at room temperature. However, these complexes are oxidized rapidly by the combination of ozone with UV radiation and/or coupled with heating to 150°F.

6) Combinations of ozone with UV radiation and/or with elevated temperature have been used to treat metal finishing wastewaters containing iron cyanide complexes since late 1976 at an industrial metal finishing plant, a U.S. Air Force base and at a French affiliate of a large U.S. chemical company. Ozone/UV combinations in multiple staged reactors lower total cyanide concentrations from 4,000 mg/l to below 0.3 mg/l and also destroy cyanate ion.

7) The literature often does not distinguish between mass transfer rate, kinetic oxidation rate and combinations of these. Therefore, the published data often appear contradictory and may not be directly usable for purposes of designing wastewater treatment systems.

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FOOD AND KINDRED PRODUCTS

With the exception of publications dealing with the use of ozone to treat brewery waters, the published uses of ozone in the food and kindred products category have been restricted to sterilization of bottle washing waters in the preparation of baby foods, treatment of sauerkraut brines to reduce COD, treatment of bakery wastes, aiding the extraction of tea solubles from spent tea leaves by oxidation, the artificial aging of wine and the disinfection of poultry processing wastewaters.

Bottle Washing Water

Leavitt & Ziemba (1969) and Leavitt (1972) describe the use of ozonation to sterilize waters on a commercial scale which are used for washing bottles in the preparation of baby foods at Gerber Products Co. In the 1969 article, these authors discuss the reuse of water after ozonation, but also the reclamation of the heating and cooling potentials of the water to be reused.

Water is first sterilized by ozonation in a 25,000 gal tank, after which the ozonized water is pumped through a vertical filter and heat exchanger, then into three water use loops. One of these is 190°F water for bottle washing, a second loop supplies 190°F water for retorting, and the third loop collects water at temperatures below 150°F from the retorts for cleaning floors and flushing gutters.

In the 1972 article, Leavitt discusses the Gerber water treatment system in more detail, emphasizing the instrumentation aspects. Ozone is generated from oxygen feed gas and diffused into water in a 7,500 gal stainless steel tank, 16 ft deep. The entire water treatment system, including ozonation, was purchased for $80,000 in 1968, to which another 30% should be added for installation costs, making a total capital cost of $135,000. The savings in water reuse, steam and sewer charges amounts to $125,000 annually, equating to an 82% return on investment and a payoff period of 1.9 years.

Sauerkraut Brines

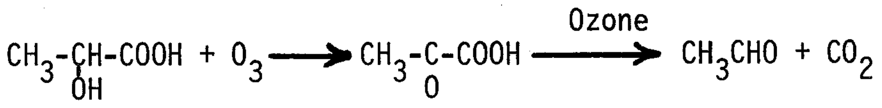
This laboratory work has been conducted by Walter & Sherman (1974, 1976) using samples from lactic acid fermentation of cabbage to produce sauerkraut. BOD of this type of effluent can reach 41,000 mg/l, with lactic acid contents ranging between 14,000 and 16,800 mg/l. Ozonation was conducted in a small, fritted dispersion cylinder (120 mm high and 24 mm diameter which contained 40 ml brine samples. Ozone was generated from oxygen and its concentration was measured both in the inlet and outlet gases, so as to determine accurately the amount of ozone actually used. The contactor off-gases were bubbled through barium hydroxide solution (to form barium carbonate, indicating the presence of carbon dioxide) then through piperazine-nitroprusside reagent, indicating the presence of acetaldehyde. The steady state concentration of ozone being bubbled through the reactor was between 400 and 500 mg/l at 25°. Ozonation was conducted for 24 hr periods under these conditions for a total of 72 hours (1974 paper) and 5 days (1976 paper).

The initial filtered brine solution before ozonation contained 1.30 g/ml of lactic acid, 0 mg/l of pyruvic acid, 0.04 g/ml of sugar, total acidity of 0.17 milliequivalents (meq)/20 ml, was at a pH of 3.3 and gave negative tests for CO_2 and acetaldehyde. As ozonation progressed, the sugar concentration fell to 0 g/ml in 24 hrs, lactic acid concentration was reduced, pyruvic acid concentration rose to 0.28 g/ml (280 mg/l) in 24 hours, then decreased, and the mixture also gave positive tests for acetaldehyde and CO_2. Pertinent data are presented in Table 14.

During the first 48 hrs of ozonation, the COD dropped 48% from an initial value of nearly 15,000 mg/l, and a 78% reduction in COD concentration was obtained after 3 days (about 3,500 mg/l). Thereafter, the relatively higher stability of the remaining organic constituents to ozone oxidation slowed the rate of carbon loss. Upon lime neutralization of the ozonized brines, colloidally dispersed cabbage constituents that were unaffected by ozonation precipitated, resulting in a further reduction in COD content of 1,200 mg/l. The ratio of ozone consumed to COD reduction obtained over the 72 hour period was 2.0.

These authors conclude that where ozone generators already are installed in food processing facilities, and where small batches of refractory effluents are not amenable to biological stabilization, ozonation may be applied as a chemical alternative to lower the concentrations of COD in wastewaters.

Walter & Sherman project the probable chemistry involved in these studies to be represented by the following equations:



$$CH_3\text{-}\underset{OH}{C}H\text{-}COOH + O_3 \longrightarrow CH_3\text{-}\underset{O}{C}\text{-}COOH \xrightarrow{\text{Ozone}} CH_3CHO + CO_2$$

lactic acid pyruvic acid acetaldehyde

and:

$$\text{sugar} + O_3 \longrightarrow CO_2 + H_2O$$

Because of the low boiling point of acetaldehyde (21°C) and because the ozonations were carried out at 25°C, much of the acetaldehyde produced was physically stripped from the reaction mixture by the aeration action in the ozonation reactor. This would explain why oxidation did not continue to produce acetic acid.

In the later paper (Walter & Sherman, 1976), ozonations were conducted over 5 days using sauerkraut brines having two different COD concentrations (35.1 g/l and 17.25 g/l). After 5 days of continuous ozonation, the COD of the higher concentration brine had dropped to 17.5 g/l and that of the lower concentration brine had dropped to 6.75 g/l. However, the efficiency of ozone use over this period of time was higher with the higher concentration brine. This indicates that if ozonation is to be used to treat high COD wastewaters, dilution should occur after, not before, ozonation.

TABLE 14. ANALYTICAL DATA FOR OZONIZED AND NON-OZONIZED SAUERKRAUT BRINE

	Filtered Brine	Oxygenated Brine	Ozonated Brine (24 hr)	Ozonated Brine (48 hr)	Ozonated Brine (72 hr)
pH	3.3	3.5			1.7
Total acidity (meq/20 ml)	0.17	0.17			0.20
Lactic acid (g/ml)	1.30	1.30	0.70	0.20	0.05
Pyruvic acid (g/ml)	0.00	0.00	0.28	0.03	0.01
Sugar (g/ml)	0.04	0.04	0.00		
Total Volatiles (g/ml)	2.0				0.9
Fixed residues (g/ml)	1.9				2.2
Test for*					
NO_3^-	-	-			+
PO_4^{3-}	+	+			+
SO_4^{2-}	+	+			+
Acetaldehyde	-	-	+		
CO_2	-	-	+		

* + indicates positive
- indicates negative

Source: Walter & Sherman (1974)

Bakery Wastewaters

Yim et al. (1975) conducted treatability studies on bakery wastewaters in Hawaii by four methods: chemical coagulation, pressure flotation, chlorine dioxide oxidation and ozonation, and the efficiencies of the treatment methods were determined by the amounts of BOD-5, SS and grease removed by each process.

The ferric sulfate and alum coagulants worked best at pH 8.0, at dosages of 1,300 mg/l and was the only treatment which allowed the high strength wastewaters to meet the local sewer ordinances, with no additional sewer use charges to the bakery (300 BOD-5, 300 SS, 100 mg/l grease; pH 5.5 to 10.0). Poor removal rates were obtained with the pressure flotation unit, which worked best at 50 psig after acidification to pH 1.0.

At the highest chlorine dioxide dosage (200 mg/l) over a 15 minute contact time, only 62.2% removal efficiency was obtained for BOD-5; however, a residual of 9.5 mg/l was present which was considered to be potentially harmful to the receiving sewer stream.

At the maximum applied ozone dosage possible with the ozonation system employed, only 21.2% reduction in BOD-5, 61.5% reduction in SS and 36.8% reduction in grease was obtained using an ozone contact time of 5 minutes. The ozonation system was not described, other than to mention that contacting was accomplished by diffusion, and costs were not discussed. These authors state that increasing the ozone contact time to 15 to 30 minutes, and using a finer air diffuser for contacting, probably would have achieved the desired results. Both chlorine dioxide and ozonation systems had the advantages of minimum space requirements and no sludge disposal.

Pertinent pollutant removal data for the 4 processes studied are given in Table 15.

Extraction Of Tea

Rivkowich et al. (1974) were issued a patent claiming, but not demonstrating by example, the improved extraction of tea leaves to yield soluble solids for instant tea production by oxidation of extracted or spent tea leaves with a solution of ozone in water. Other suitable oxidants are oxygen and hydrogen peroxide, and an example of the process employing hydrogen peroxide is given.

Tea leaves (8 lbs) and 202 lbs of water at 88°C are charged to an atmospheric extractor. After 20 minutes, 175 lbs of liquid extract containing 2.8 lbs of soluble solids are withdrawn. Moist tea leaves (27 lbs) containing 5.2 lbs of soluble solids are fed to a pressure reactor with 4.6 lbs of 30% aqueous hydrogen peroxide solution. The mixture is heated at 240°F and 40 psig pressure for about 50 minutes, producing 74 lbs of liquid extract containing 1.4 lbs of soluble solids. Thus, treatment of spent tea leaves with an aqueous solution of oxidant produces about a 50% improvement in yields of soluble solids.

TABLE 15. COMPARISON OF TREATMENT METHODS ON CAKE SHOP WASTEWATERS

Pollutant	Chemical Coagulation						Pressure Flotation			Chlorine Dioxide			Ozonation		
	Ferric Sulfate			Alum											
	before	after	% Redn.	before	after	% Redn.	before	after	% Redn.	before	after	% Redn.	before	after	% Redn.
BOD-5 (mg/l)	2780	810(1) 960(2)	70.9 65.5	2780	870(1) 110(2)	68.7 60.1	2780	2030	27	3840	1450	62.2	4940	3990	21.1
Suspended Solids (mg/l)	2310	128(1) 173(2)	94.4 92.5	2310	96(1) 26(2)	95.8 98.9	2310	1470	36.4	960	410	57.3	3040	1140	61.5
Grease (mg/l)	1450	96(1) 84(2)	93.4 94.2	1450	47(1) 52(2)	96.8 96.4	1450	493	66	2360	1070	54.7	1260	796	36.8
Optimum pH	8.0	4.3(1) 5.4(2)		8.0	5.2(1) 6.1(2)		1.0			8.4	4.7		8.4		
Dosage (mg/l)	1300 (optimum)			1300 (optimum)						200 mg/l for 15 min. (maximum)			384 mg/l (maximum) (5 min. contact)		
Optimum Pressure							50 psig								

(1) data obtained at optimum pH of ferric sulfate
(2) data obtained at optimum dosage of alum

Source: Yim *et al*. (1975)

Disinfection Of Poultry Processing Wastewaters

Netzer et al. (1977) compared the relative merits of ozonation against those of chlorination for treatment of poultry processing effluents at two plants in Canada, with particular emphasis on the control of salmonella. Both laboratory and pilot scale field evaluations of the two alternative disinfection methods were conducted and the economic implications of using ozone in this application were assessed.

Laboratory ozonation studies were conducted using porous-diffuser contacting in a 12-ft high, 4-inch I.D. contact column. This provided a 13 minute contact time at the wastewater flow rates chosen. Diffusers were located at the base of the column and halfway up, so that ozone could be applied to either diffuser or to both simultaneously. Although only the applied ozone dosages were measured, at least 90% utilization of the ozone added at the base of the column can be expected to be mass transferred into solution to react with the wastewater components. This is because of the height of the column (12 ft).

In laboratory studies, ozone dosages of 20 to 50 mg/l reduced salmonella contents in a biologically treated poultry processing wastewater to below the limit of detection. Standard plate counts were reduced from 6,500 MPN to a range of 265 to 103, fecal coliforms/100 ml were reduced from 220 MPN to a range of 16 to 2, and adenosine triphosphate concentration was reduced from 8.0 nanograms (ng)/ml to 0.37 to 0.17 ng/ml (the higher numbers were obtained at 20 mg/l ozone dosage and the lower numbers at 50 mg/l ozone dosage).

In other laboratory tests using a wastewater significantly more contaminated (BOD 92 mg/l, SS 80 mg/l and bacterial counts 630,000), even 50 mg/l applied ozone dosages were not effective in reducing the salmonella contents, although fecal coliform counts were reduced 99% (from 88,000 to a range of 500 to 600/100 ml). It was concluded that the effectiveness of ozonation for control of salmonella is significantly affected by the chemical and bacteriological quality of the secondary effluent.

Pilot field studies were conducted using ozone generated from oxygen and applied to the base of 2 consecutive 18-ft high contactor columns equipped with cone type diffusers. Liquid flow was countercurrent in column #1 (9.5 Igal volume) and cocurrent in column #2 (21.4 Igal volume). Liquid flow rates were varied from 2.5 to 0.5 Igpm (Imperial gal/min) (equivalent to 15 to 60 minutes hydraulic retention times) and 75% of the ozone was applied to column #2. A high degree of ozone dispersion was confirmed in this system by tracer studies with Rhodamine B and oxygen in process water.

In a parallel chlorination system, NaOCl solution was dosed to a stirred 45-gal contact tank by means of a metering pump.

Ozone efficiency was evaluated at 2 Ontario, Canada poultry processing plants under winter and summer conditions over 2-month periods. At one plant processing 2,500 birds/hr, process waste flows were about 100,000 Igpd. Effluent was screened to remove feathers, grease and gross solids prior to biological treatment. Secondary effluent was dosed with lime and alum to precipitate phosphorus and coagulate residual solids, and this secondary effluent was used to feed the pilot plant studies. Under normal (summer) conditions the secondary effluent contained 20 mg/l BOD and 30 mg/l SS.

Initial pilot studies confirmed the laboratory results, i.e., effective control of salmonella with ozonation is not directly related to disinfection efficiency as measured by other microbiological parameters. Salmonella were detected in some cases where fecal coliform reductions were above 99%. However in other runs, salmonella were not detected, despite low disinfection efficiencies in terms of the other parameters.

Based on these preliminary results, 30 mg/l of applied ozone dosage and 60-minute contact time was chosen for further testing over a 5-day period under winter conditions at this plant. Salmonella were not detected in any of the ozonated secondary effluent samples. Reductions in fecal coliforms approached 3 powers of 10 (99.9%). During all runs under these conditions, salmonella were detected in only 1 of 7 ozonized effluent samples.

These conditions were repeated during the summer at the same plant. Chemical quality of the secondary effluents was somewhat higher. Ozonation efficiency was comparable, with salmonella being detected in only 1 of 5 ozonized samples.

The pilot equipment then was moved to a second poultry processing plant which handles 6,000 chickens and turkeys per hour and process waste flows were about 500,000 Igpd. The effluent was screened, then treated in parallel aeration tanks (5 days retention time). Clarified effluent normally is discharged to a polishing lagoon prior to chlorination and discharge. However, a poor settling, filamentous sludge in the biological reactor resulted in excessive SS carryover from the secondary clarifier, severely limiting the pilot plant ozonation efficiency. In 2 cases, ozonation resulted in negligible reductions in fecal coliform counts. The quality of effluent improved significantly prior to the final 2 runs; in 1 of these runs, salmonella were not present after ozonation.

Comparison of winter and summer runs at this second plant (30 mg/l ozone dosage -- 60 minute contact time) showed 80 to 96% salmonella control efficiency, 98.5 to 99.6% fecal coliform reduction and 55% (winter) to 73% (summer) reduction efficiency of standard plate count numbers. No significant difference related to seasonal effluent variation was observed at this plant.

In fish toxicity tests (96-hr static bioassay procedures), ozonation did not affect the toxicity of secondary effluents. No introduction of toxicity to non-toxic secondary effluents was noted, however, ozonation did not reduce the toxicity in cases where fish mortality was noted in secondary effluents before ozonation.

Economic evaluations were based on disinfecting 1.0 mIgd (million Imperial gal/day) of biologically treated poultry processing plant effluent using ozone prepared from dry air (-40°F dew point). Two types of contacting equipment were costed: (1) columns similar to those used in the pilot studies and (2) a covered baffled tank with gas diffusers. Capital costs of the 2 contactor systems were found to be comparable. Power requirements were estimated to be 10 kwhr/lb of ozone generated. Cost estimates are summarized in Table 16.

TABLE 16. ESTIMATED CAPITAL AND OPERATING COSTS FOR OZONE TREATMENT OF POULTRY PROCESSING WASTEWATERS

1977 Costs -- Capital:	
Air Preparation	$ 70,000
Ozone Generation (300 lbs/day)	140,000
Contacting System (6700 cu ft)	50,000
	$260,000
-- Operating:	
Power (3,000 kwhr/day @ $0.02)	$ 60.00/day
Amortization (15%/yr)	106.85/day
Total Operating Cost	$166.85/day = $0.17/1000 Igal.
Source: Netzer *et al*., 1977	

Netzer *et al*. (1977) concluded the following from this study:

(1) Disinfection efficiency with ozone depends on chemical and bacterial quality of the effluent, the higher quality effluents giving better results,

(2) Ozone at 30 mg/l dosages over 60 minutes of contacting was successful in controlling salmonella 80% of the time in summer and winter,

(3) Disinfection requirements are site-specific and should be ascertained at each site.

Breweries

Ozone has been used in various brewery applications for many years, and particularly in German, French, American and Canadian installations. Du Jardin (1924) reviewed the then current uses of ozonation in breweries, citing the germicidal capabilities of ozone and its property of not leaving an undesirable residue as its primary features. Van Laer (1928) determined that for sterilizing brewing water, 2.25 g of ozone is required per cu m of water provided that oxidizable organic materials are removed first. This author also pointed out that ozonized water is more effective for sterilizing vats and piping than is ozonized air.

Mayrhofer and Steinhart (1955) describe the use of ozonized water in yeast manufacture for the brewing process. Bacteria and coliform counts were reduced to zero, color was diminished and there were no observed detrimental effects on the yeast fermentation ability. Stability of the yeast, baking properties and appearance of the yeast were better than in the preceding year when ozonized water was not used.

Schäuble and Gillardin (1958) determined that 0.5 g/cu m of ozone was sufficient to sterilize waters containing added amounts of various forms of yeasts, rhodotorulae, cocci, short rod bacteria, mold hyphae and spores. Foreign taste and odor problems also were decreased, even though the mechanical ozone contacting system used was inefficient. These authors suggested that the "many advantages" of ozonation should be excellently suited to the fruit juice industry, even though ozonation costs are "slightly greater" than those for chlorination.

Fergason, Harding & Smith (1973) describe a portable ozone test unit assembled at the University of Idaho for field testing of the ozonation unit process. One such test was conducted by a major brewery to eliminate tastes and odors from its brewery waters. As a result of successful testing with this unit, the brewer was reported to be installing a full-scale ozonation plant to treat a portion of the brewery water. Preliminary estimates for the cost of ozonation at a full-scale plant based on tests with this portable test unit were 30¢/1,000 gal for decolorization and deodorization. The portable test unit contained a 2 gallon reactor capable of varying contact times from 1 to 20 minutes. The contactor was a Venturi nozzle (injector). Ozone production capability of the unit was 12 g/hr and the treatment rate was 1.5 gal/minute.

Tenney (1973a) points out several barriers to broader acceptance of ozonation in breweries. In the early days of useage, ozone often was asked to perform oxidation functions that could be accomplished more economically by first removing reactive materials using less expensive procedures, such as filtration, GAC, etc. Ozone certainly is too expensive an oxidant to be considered for the total treatment of heavily contaminated waters, even though it can perform many oxidations that other oxidants cannot accomplish alone.

Ozone has several applications in treating brewery waters, even though in solution ozone has a short half-life. Tenney (1973a) recommends that a brewery considering the use of ozone for multiple applications should plan to install several small ozone generators, one at each point of use, rather than to install a single unit in some central location. Once ozone has been contacted with water, the water should not be pumped to some distant point in the plant, but should be used immediately after ozone addition, so as not to lose any ozone by decomposition.

Tenney (1973a) also points out that one of the early designs of ozone generators used in breweries had a fan blowing air across electrically charged plates spaced so as to create a corona discharge. However, as dust built up on the plates during prolonged use, short circuiting occurred, causing malfunction of the equipment. This particular design of ozone generator also incorporated a heater to dry the incoming air (rather than a compressor and/or desiccant tower). The efficiency of such units diminished quickly and most of them were soon inactivated. Unfortunately, a number of these devices were sold to American breweries during the late 1940s. Their ineffectiveness has contributed to distrust of other, more reliable types of ozone generators.

Tenney (1973a) concludes that with electricity costs of 1.5¢/kwhr and at ozone generation rates of 10 g/hr, costs for ozone generation should be less than 30¢/kg. Capital costs for ozone generators capable of generating 5 to 10 g/hr from air range from $2,000 to $3,000.

In a second review article, Tenney (1973b) discusses the existing and potential uses of ozonation in breweries. In brewery water treatment, yeast washing is conducted with freshly ozonized water containing 1 to 3 mg/l of ozone for destruction of the easily oxidizable substances in the yeast mass, including melanoidins which create color in the beer residue. Bacteria also are destroyed with minimal damage to the yeast.

Final rinsing of bottles or cans by means of water containing dissolved ozone will remove trace materials and eliminate beer-spoiling organisms. The maximum amount of oxygen introduced to the beer by using this technique is 0.000009 g/bottle, which will have negligible influence on the product. Normal variations in air content provide more oxygen variation than this small amount caused by ozonation.

Beer fillers and process equipment such as filters, tanks, pipelines, etc., are sterilized before use by circulating hot solutions through the equipment. The cooling water which follows must be sterile, and water containing 1 mg/l of ozone is effective for this application. Final rinsing of brewery filter mass with ozonized water just before packing new pads will assure sterility at this point in the process for plants still using this type of equipment (Tenney, 1973b).

Brewers have used ozone to purify air in rooms used by taste panels and for controlling mold growth and odors in brewery cellars. Ozone also can be used for purifying air in yeast handling areas, in wort cooling and aeration, and might replace chemical scrubbing of CO_2, such as with permanganate (Tenney, 1973b).

Geminn (1974) describes the processing of concentrated wort as practiced at the Genessee Brewing Co., Rochester, New York, which involves the use of ozonation in the preparation of dilution water. Municipal tap water is filtered at the rate of 63 gal/min through a combined sand and gravel filter, then through activated carbon. Ozone then is diffused through the filtered water at 2 mg/l over 3 to 5 minutes contact time to sterilize and remove tastes, odors and possible entrained bacteria. The 0.2 mg/l ozone residual decays in about 6 minutes.

Ozonized water is deaerated by spraying, passing through a packed column, then is recarbonated and stored under CO_2 for blending with the concentrated wort. Power requirements for the 3-electric cell ozone generator, equipped with air filter, motor compressor set and dual tower desiccator are "about the same as burning a 200 watt bulb, plus an additional cost of about 15 gal/hr of tap water to cool the electrodes".

A survey of available literature from various ozonation equipment vendors located in Europe shows that ozonation systems are installed in the breweries listed in Table 17.

TABLE 17. EUROPEAN BREWERIES USING OZONE

Installation	Process Flow	Amt. of Ozone	Year Installed
Bayerische Bierbrauerei Aschaffenburg, Germany	40 cu m/hr	40 g/hr	1959
Stadtbrauerei, Göttingen, Germany	35 cu m/hr	25 g/hr	1962
Brauerei Bock, Finland		100 g/hr	
Oy Kaukas, Finland		500 g/hr	
M.M. Braun, Belgium (plant in Katanga)		150 g/hr	

In addition, it is known from private communications that Brauerei Beck (Bremen, Germany), Molson's (Canada), Schlitz, Coors and Genessee Breweries in the United States have incorporated ozone into their beer manufacturing processes.

Wine Making

An English patent (Coffre, 1931) describes the ozonation of oak chips, which then are soaked with fermenting wines. By alternately soaking and aging ozonized oak chips 15 to 20 times at 24-hour intervals and then reozonizing, the aging wine acquires the same characteristics in three weeks as wines aged 10 to 15 years. However this process has been banned in France, because of the importance of the wine-making industry there and its dependence upon vending of naturally aged wines (Béchaux, 1977; Le Pauloüe, 1977).

Yeast Production

Very recently, Jurgensen & Patton (1977) at Michigan Technological University, have reported studies on the growth of yeast in ozonized spent sulfite liquors from the pulp and paper industrial category (see Section 5, under Pulp & Paper). Short term ozonation (10 minutes) of spent sulfite liquors converts biorefractory organic materials into more readily biodegradable organic materials by partial oxidation. Early in this project, yeast production yields of 0.5 to 5.0 g of dry yeast per liter of ozonized effluent were obtained in laboratory scale studies.

This program is being conducted under contract to the U.S. Department of Energy, Division of Industrial Conservation. The primary objective of this work was to generate methane from spent sulfite liquors, but the yeast-producing potentials are believed to be economically feasible now (Jurgensen, 1978) and pilot plant scale studies to prove engineering feasibility are being planned.

Conclusions

(1) Ozonation is in commercial scale use for treating bottle washing waters at Gerber Products Co. and in several breweries for treating bottle washing and process waters (Genessee Brewing, Rochester, N.Y.; Coors, Golden, Colorado; several in Germany, Canada, Katanga and Finland).

(2) Capital costs for the ozonation system at Gerber Products ($135,000) were repaid in 1.9 yrs by the savings obtained from water reuse and lower steam and sewer charges ($125,000/yr).

(3) Ozonation has been described for treating brewery atmospheres to control mold growths and odors in brewery cellars and in yeast handling areas. Ozonized water is more effective for sterilizing brewing vats and piping than is ozonized air.

(4) Laboratory and pilot plant studies have been conducted recently on the use of ozonation for treating sauerkraut brines (to reduce levels of COD), bakery wastewaters and to disinfect poultry processing wastewaters. Estimated costs of salmonella control in Canadian poultry processing secondary effluents upon ozonation are $0.17/1,000 Igal.

(5) Ozonation of spent sulfite liquors from pulp and paper mills provides an oxygenated medium conducive to the growth of yeast. This potential application for ozonation appears to be economically feasible on a laboratory scale and currently is being pilot plant tested on larger scale.

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HOSPITAL WASTEWATERS

Although there are no reported applications of ozonation for treating actual hospital wastewaters, a very comprehensive research & development program was conducted by the U.S. Army Medical Bioengineering R&D Laboratories, Ft. Detrick, Maryland, from the early 1970s until late 1977. This program developed a large volume of fundamental information which is of great significance to all wastewater treatment applications involving ozonation. In particular, the combination of ozone with UV light was optimized for oxidation of refractory organics under this program (McCarthy, Lambert & Reuter, 1977).

The objective of this Army program was to develop a wastewater treatment system for a mobile field hospital, named MUST (Medical Unit, Self-Contained, Transportable). MUST wastewaters from the hospital X-ray laboratory, clinical laboratory, kitchen, operating room, shower and laundry facilities (all non-sanitary wastewaters) were to be treated to such a high quality that the waters could be reused for non-consumptive human purposes. Therefore, the Army defined the COD of such reuse water to be 10 mg/l and TOC to be 5 mg/l, with no toxicity to humans.

In conducting research to define a candidate wastewater treatment process for pilot testing and prototype development, considerable effort was expended on the characterization of these wastewaters. Sufficient quantities of actual field hospital wastewaters were not available for extended treatability studies, so that realistic wastewater recipes had to be developed to allow representative wastewaters from any hospital activity to be synthesized as needed (Lambert & Reuter, 1976).

MUST hospital composite wastewater has the following composition:

Shower	51% (by volume)
Operating Room	26%
Kitchen	12%
Clinical Lab	8%
X-Ray Lab	3%

and the following characteristics:

TDS	1240 mg/l
SS	70 mg/l
pH	6.6
COD	870 mg/l
TOC	229 mg/l

MUST laundry composite wastewaters have the following characteristics:

TDS	1630 mg/l
SS	194 mg/l
pH	10.5
COD	1740 mg/l
TOC	457 mg/l

As stated earlier, the wastewater treatment objectives were to attain waters having a COD of 10 mg/l and a TOC of 5 mg/l, which are the maximum allowable concentrations of these parameters in the 1962 U.S. Public Health Service drinking water standards. The Army's Water Processing Element (WPE) was designed to treat 4,200 gal/day, and to recover 85% of the wastewater for reuse. Initially, reuse was for non-consumptive purposes (showers, laundries, washing, toilet flushing), but eventually the process could allow for potable reuse as well.

Unit processes for the WPE treatment train are, in sequence: hydraulic equalization, 40-mesh screening, ultrafiltration, reverse osmosis, UV-ozonation followed by hypochlorination. Much of the remainder of this discussion will center on R&D efforts directed toward design of the UV-ozonation unit operation.

Army R&D efforts were concentrated in 4 areas:

- characterization of wastewaters before, during and after treatment,
- understanding of ozone oxidation mechanisms and kinetics of reaction with wastewater consituents,
- design and scaleup of a UV-ozonation reactor which optimized mass transfer and reaction of ozone in a multi-component liquid,
- development and evaluation of control and monitoring instrumentation for the ozonation unit operation.

The combined UV-ozonation step was chosen because many of the wastewater components are refractory organic compounds which are only slowly oxidized by ozone, and the necessity to convert contained COD and TOC into CO_2 and water in order to meet the stated objectives of 10 and 5 mg/l, respectively. Much emphasis was placed by the Army on development of automatic control and monitoring capability for process parameters, detecting component failures, sequencing actuators for mode transitions and reducing operator errors to assure trouble-free operation in the field.

Initial studies aimed at selection of treatment process steps consisted of comparison of ozonation, activated carbon, ion exchange and biological oxidation as potential candidates alone or in combination. Ozonation proved to be the only unit operation which satisfactorily treated all wastewaters tested (Bryce _et al._, 1973; Sierka, 1975; Reuter, 1975; Chian, Kuo & Chang, 1977). Next, development of suitable analytical methods and techniques for wastewater characterization were initiated, including the identification of intermediate and final oxidation products to allow the study of mechanisms of the ozonation process and to identify potentially toxic products. Methanol and acetone were found to comprise a large fraction of the reverse osmosis (RO) permeates from hospital laboratories. o-Toluidine and N,N-diethyl-m-toluamide (DEET) were present in most other RO permeates (Chian, Kuo & Chang, 1977; Mix & Scharen, 1975).

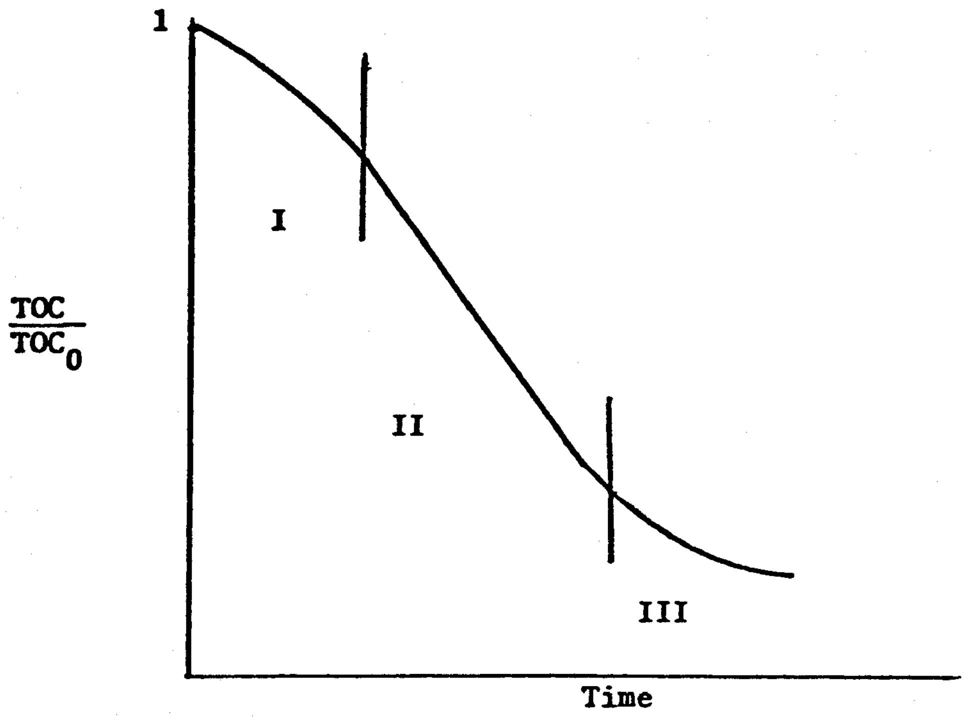
Ozone oxidation kinetics were monitored in the various wastewaters to gain insight into how to enhance removal of the organic compounds. Wastewater oxidations exhibited initial periods of rapid TOC removal and low dissolved ozone values, indicating that initial removal was principally mass transfer controlled. There was a subsequent period of slower TOC removal and stable dissolved ozone values, indicating that the reaction rates of the organics with the dissolved ozone were controlling the TOC removal rates (Figure 10). It was noted that, depending on the wastewater, gas stripping of components was significant in various degrees during mass transfer controlled oxidations. The pH of the wastewater was significant in the reaction rate controlled cases. Oxidation increased with increasing pH, supporting an hypothesis of free radical mechanisms (Sierka, 1975; Reuter, 1975; Chian, Kuo & Chang, 1977; Gollan et al., 1976).

A portion of the wastewaters, and especially RO permeates from clinical laboratory wastes, remained refractory to ozone oxidation. UV radiation was investigated extensively in response to indications that aqueous ozone oxidation kinetics are accelerated by addition of UV (Chian, Kuo & Chang, 1977; Hewes et al., 1974; Zeff et al., 1976).

Treatability studies also allowed identification and quantification of variables affecting the ozonation process. These included temperature, pH, ozone concentration, mixing speed, gas flow, contact time and organic composition. It became difficult to compare results obtained by each of the investigators who, in addition to using different reactors, employed different experimental conditions in their approach to the problem. Nevertheless, general trends were recognized and served as bases for further work closer to optimum ozone oxidation conditions (Lambert & McCarthy, 1977).

During the next phase (1975-1976), ozonation of Army field hospital wastewaters was investigated on laboratory and pilot scales. Most attention was focused on 2 wastewaters studied as RO permeates. One was called composite waste, a time-averaged composite of all the non-sanitary field hospital wastewaters which reasonably could be expected in an actual field situation. The composite waste represented the "average" wastewater. The second was the hospital laboratory wastewater which represented the worst case because of large concentrations of organics refractory to UV/ozone oxidation.

Analytical techniques were refined to measure selected compounds at low concentrations and to identify unknown compounds. Additional compounds identified in composite or laboratory RO permeates included phenolic compounds, chloroform, diethyl ether, methyl ethyl ketone and propanol (Chian, Kuo & Chang, 1977; Cowen, Cooper & Highfill, 1975).



I Initial period (Mass transfer control)
- Fast reaction with large TOC

III Tail end (Reaction rate control)
- Slow reaction with small TOC

II Major reaction (Both important)

Source: Lee & See (1977)

Figure 10. UV/ozone oxidation of hospital composite wastewater.

As analytical techniques became more precise and "routine", additional studies on ozonating or UV-ozonating single model compounds in aqueous solution were better able to follow the intermediate and final oxidation products with minimum interferences. Compounds at significant concentrations in the wastewater were studied, including those listed above as well as important intermediate oxidation products. Major ozonation end products were found to include formic, glyoxylic, oxalic, and acetic acids (Chian, Kuo & Chang, 1977; Cowen & Cooper, 1975).

$HCOOH$	$HOOC\text{-}CHO$	$HOOC\text{-}COOH$	CH_3COOH
formic acid	glyoxylic acid	oxalic acid	acetic acid

Advantages or disadvantages of adding UV light in the oxidation reaction also were studied. Within the conditions studied, methanol and urea showed little or no improvement to ozonation when UV was added, and are among the most ozone-refractory organic compounds. o-Toluidine and DEET were easily oxidized whether UV was present or not. Methyl ethyl ketone and acetic acid showed distinct increases in the rates of oxidation when UV light was added. Although the benefit of UV addition varied among compounds, its overall effect on the composite and laboratory wastewaters was a positive one, especially during the latter stages of ozonation. UV intensity was shown to attenuate rapidly (reduced 95% within 5 inches from the bulb) however, underscoring the need for good mixing (Chian, Kuo & Chang, 1977; Gollan et al., 1976; Zeff et al., 1976; See, Yang & Kacholia, 1976).

Measurement of ozone oxidation kinetics and comparison of data obtained under mass transfer controlled conditions versus reaction rate controlled conditions suggested that mass transfer conditions dominated, unless ozone dose concentrations were approximately 2% or more by weight. Hospital laboratory wastes continued to be those most refractory to ozone oxidation. Shower wastes were easiest to treat. For most cases, COD was shown to be the limiting factor in meeting the water quality specifications, rather than TOC removal. This underscored the industrial nature of the wastewater (Chian, Kuo & Chang, 1977; Gollan et al., 1976; See, Yang & Kacholia, 1976).

Further refinements were made to study the effects of different variables. The most rapid TOC removal was found to occur between a pH of 8 and 10 and was hypothesized to be related to free radical production. Rapid TOC removal also occurred between 45° and 60°C, but fell off on either side in the 30° to 80°C range for most wastewaters. This variation in removal rate is believed to be a result of the combination of an increase in the oxidation reaction rate with temperature and a simultaneous decrease in ozone solubility (Gollan et al., 1976).

During this time period 3 pilot scale contactors were developed and constructed. One was a stirred, 2-chamber contactor with multiple UV lamps. A second used only gas sparging for mixing and had multiple compartments and multiple UV lamps. A third was also gas sparged and utilized completely mixed columns in series, each with a UV lamp down the middle. All contactors were tested and evaluated to varying degrees (Gollan et al., 1976; Zeff et al., 1976; See, Yang & Kacholia, 1976). A comparison of the efficiency of ozone/UV oxidation by the three reactors is given in Table 18 (Lee & See, 1977).

The third or last contactor (preceeding paragraph) was selected for extended testing prior to full scale pilot evaluation (Figure 11 shows a schematic), using the synthetic hospital composite wastewater shown in Table 19 (Lee & See, 1977). Six reactor columns are arranged in series through which wastewater alternately flows concurrently then countercurrently to ozone-laden gas. The gas containing ozone is bubbled up through each column via a sparger in the bottom and a UV lamp extends down the middle of each column. The columns operate at about 15 psig pressure (aiding mass transfer) because all off-gases are collected and routed to a precontactor or scrubber. The precontactor aids in transferring remaining ozone into the fresh incoming wastewater while stripping out volatile organics from solutions (See, Yang & Kacholia, 1976). Figure 12 is a photograph of the pilot scale ozone/UV contactor built for this program.

TABLE 19. ORGANIC CHEMICAL COMPOSITION OF SYNTHETIC MUST HOSPITAL COMPOSITE WASTEWATER

	RO Permeate	TOC, mg/l	COD, mg/l
Kodak X-Omat Developer	283 µl/l	18.42	64.80
Kodak X-Omat Fixer	283 µl/l		
Methanol	16 µl/l	4.76	19.05
Acetone	5 µl/l	2.50	8.70
Urea	12.0 mg/l	2.40	9.60
Acetic Acid	2.8 µl/l	1.15	3.15
Phenol	0.4 mg/l	0.31	0.95
Ethanol	0.5 µl/l	0.20	0.82
N,N-Diethyl-m-toluamide (DEET)	0.2 mg/l	0.15	0.52
Oleic Acid	0.1 µl/l	0.06	0.23
Diethyl Ether	0.1 µl/l	0.05	0.18
TOTAL		30.0	108.0

Source: Lee & See, 1977.

In parallel with this Torricelli-type contactor design, considerable planning and effort was devoted to control and monitoring instrumentation. A proposed control and monitor panel connected to a computer which activates an ozone oxidation unit process simulation panel was built (See, Yang & Kacholia, 1976).

During the summer of 1976 an investigation of the feasibility of combining ultrasound with ozone was begun. Within its small scale, generally favorable results were noted, especially for the more refractory laboratory RO permeate. Urea, however, still resisted ozone oxidation with or without

TABLE 18. COMPARISON OF OZONE/UV OXIDATION OF ETHANOL BY VARIOUS TYPES OF REACTORS

	Parameter	gas sparged, completely mixed columns, each with a UV lamp down the middle	gas sparged, multiple compartments, multiple UV lamps	stirred, 2-chamber, with multiple UV lamps
Test Condition	● Reactor Volume, liters	35	12	10
	● Initial TOC, mg/l	57.7	65	67
	● O_3 Concn., wt %	1.4	2.6	3.0
	● UV Intensity, Watts/l	1.52	2.69	1.50
	● O_2 Flow Rate, l/min/l Water	0.18	0.11	0.10
Performance	● Half-life of Reaction ($t_{0.5}$) Min	92	214	175
	● Ozone Dosage, mg O_3/mg TOC Oxidized	12.8	22.0	22.8
	● Energy Consumption, kW-hr/g TOC Oxidized	0.40	0.83	0.97
Efficiency	● Ozone Eff., mg TOC Oxidized/g O_3 Dosed	78.1	45.5	43.9
	● Energy Eff., g TOC Oxidized/kW-hr	2.5	1.2	1.0

Source: Lee & See, 1977.

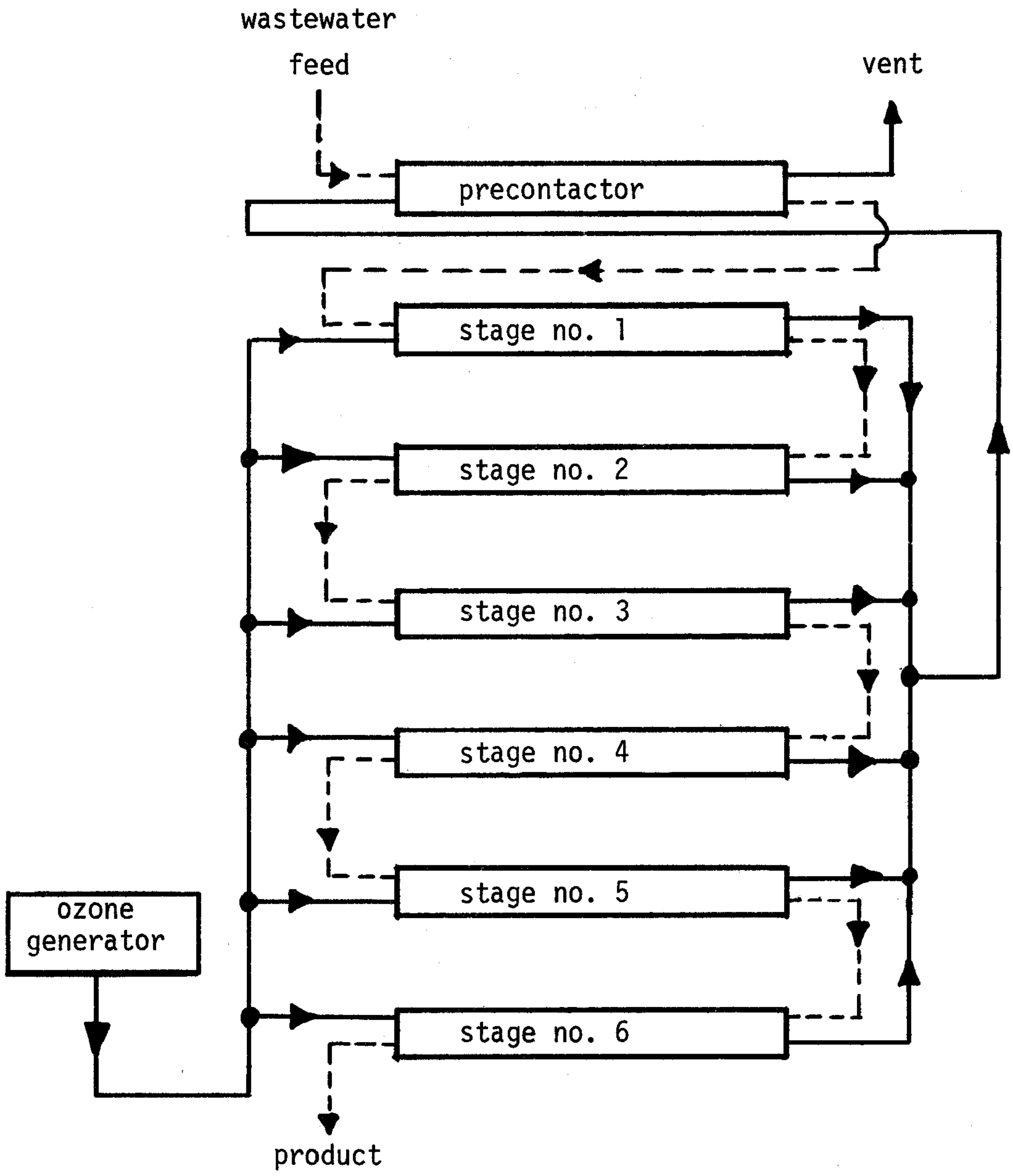


Figure 11. Modified Torricelli ozone contactor for U.S. Army MUST hospital wastewater treatment

<u>Source</u>: McCarthy, Lambert & Reuter (1977)

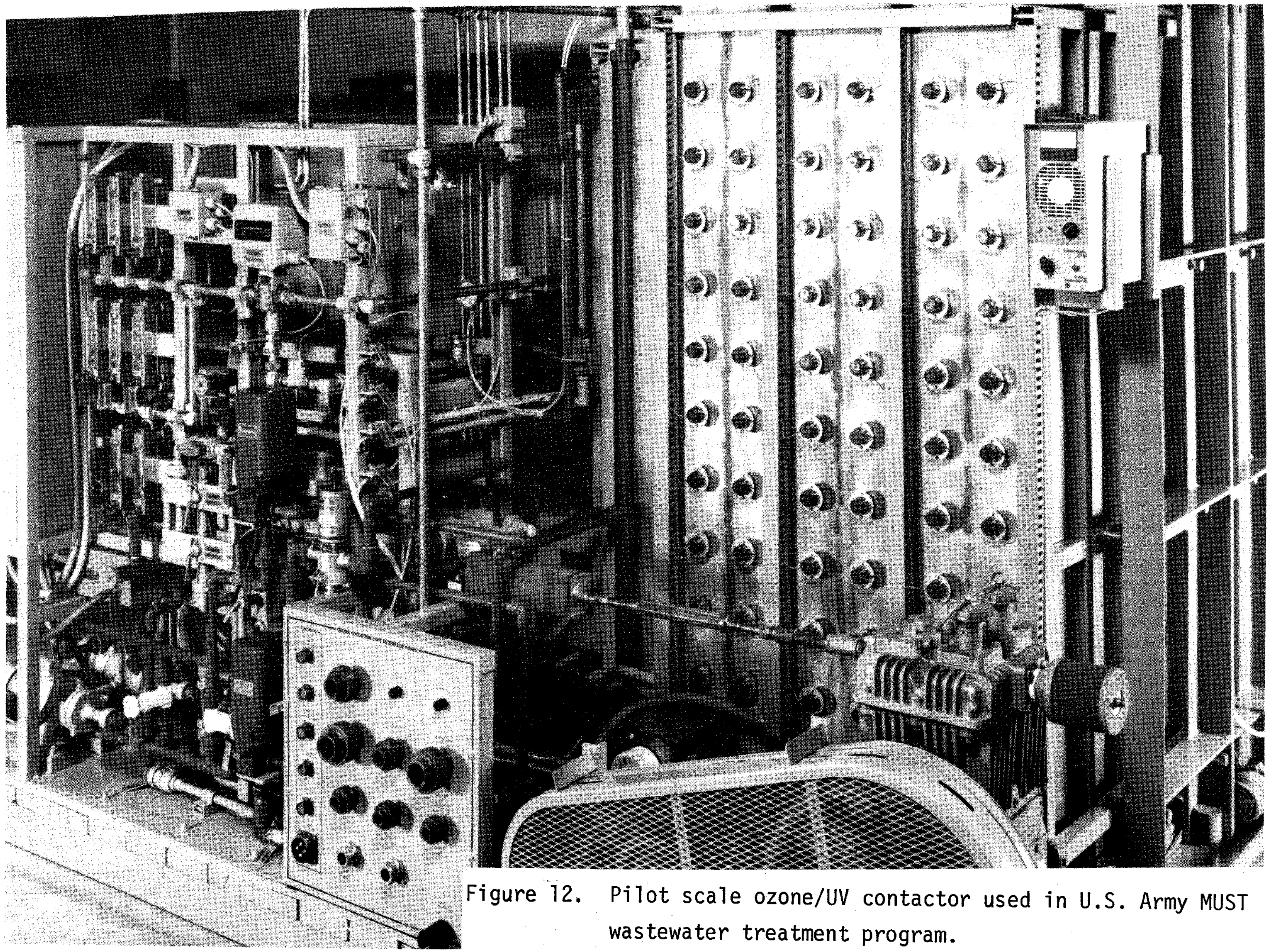


Figure 12. Pilot scale ozone/UV contactor used in U.S. Army MUST wastewater treatment program.

ultrasound. When ultrasound was used, ozone mass transfer rates into solution were found to be faster. Increasing TOC and COD removal rates indicated that ozone oxidation rates were enhanced for laboratory and composite wastewaters (Sierka, 1976, 1977; Sierka & Skaggs, 1977).

In this 1976 to 1977 period, efforts were focused on ozonating laboratory and composite RO permeate wastewaters using the pilot scale Torricelli contactor or contact chambers of similar dimensions. Detailed information needed for scale up to full pilot size was obtained and studies were made on the stripability of the wastewater components.

Composite and laboratory wastewaters were subjected to extended stripability tests. It was believed that maximizing the amounts of contaminants removed by the stripping operation would minimize the more costly ozonation operation. However, tests on composite wastewater showed little tendency to strip volatiles from solution within the range of conditions studied. Tests with hospital laboratory wastewaters were more encouraging. At 50°C and relatively high gas flows, 11% of the TOC was stripped the first hour and about 6% during the second hour. A model was developed which predicts the amount of stripping experienced by the laboratory wastewater at 50°C as a function of the oxygen transfer coefficient, k_La, in any gas sparged reactor (McCarthy _et al._, 1977).

The Torricelli pilot contactor was characterized extensively using worst case hospital laboratory wastewaters. Variables explored were UV intensity, ozone concentrations, gas flow, mass transfer, hydraulic mixing, and prestripping. At 1% by weight ozone concentration in air, about 10 hrs were required to reduce the TOC level of 138 mg/l and COD level of 535 mg/l to 5 mg/l and 10 mg/l respectively. Time to attain these same results was cut to about 6 hrs when 1.5% weight concentration of ozone in air was used (McCarthy _et al._, 1977).

Development of analytical methods and techniques continued, and glyoxal, methyl glyoxal and dimethyl glyoxal were identified as major end products of ozonation. Oxalic acid, an important oxidation end product, showed an improved rate of oxidation to CO_2 when UV light was added. Surprisingly, its most rapid removal came under acidic and not alkaline conditions. It was postulated that the accumulation of inorganic carbon in solution at high pH retards the oxidation of oxalic acid to CO_2. When the pH of the solution was lowered to less than the pK value, most of the bicarbonate remained in the unstable carbonic acid state, resulting in a substantial improvement in the reaction rate (Chian, Kuo & Chang, 1977).

Mixtures of compounds in aqueous solution were ozonized. Methanol and acetone were investigated because these were the 2 most abundant compounds in laboratory RO permeates. Methanol was removed rather rapidly but acetone was difficult to remove. Within the conditions studied, the refractory nature of the acetone apparently was a result of competition for ozone among the methanol, methanol oxidation products, and acetone. It apparently was not a result of interactions among the organic compounds (Chain, Kuo & Chang, 1977).

There have been suggestions in the literature that once generated, ozone can decompose catalytically in diffusers made from different porous materials before it has a chance to contact the aqueous stream to be ozonized. To determine the validity of these suggestions, several different diffuser materials were evaluated with respect to ozone decomposition. They were fritted glass, stainless steel, fused aluminum, and Teflon. All materials used resulted in negligible gas phase decomposition of ozone (Chian, Kuo & Chang, 1977).

Design equations and criteria necessary for scale-up to a full size pilot contactor were determined using composite wastewater and subsequent construction of the reactor has been accomplished. Contactor configuration is basically the Torricelli type configuration shown in Figure 11. In design, it was recognized that there are 3, not 2, mass transfer states to consider. These are the first phase where the rate of reaction (oxidation) is mass transfer controlled, a long second phase where both mass transfer and reaction rate are important, and finally a third phase which is principally reaction rate controlled (Lee & See, 1977, Figure 10).

The full-scale pilot ozone contactor was delivered to the Army Medical Bioengineering R&D Laboratories at Ft. Detrick, Maryland in September, 1977. Information from strategically placed probes and sensors can be transferred onto computer tape or a print-out recorder. The pilot contactor has UV lights in all reactor chambers and an ultrasound horn in the first. It has provisions for temperature, pH, and gas flow monitoring and control, and can be operated manually or in an automatic mode. Variable ozone concentrations (within flow and pressure limits) are available from the attached 26 lb/day ozone generator (Figure 13).

A mathematical model simulating a sparged ozone contactor for the removal of low concentrations of organics in aqueous solution has been developed. Given a fixed residence time and well mixed conditions, expected variables of the model are ozone partial pressure and superficial gas velocity. The model is designed to be independent of contactor geometry or size. When completed, it can be tested against empirical results from the full size pilot contactor and can be an aid to prototype unit design (McCarthy, 1977).

Further investigation of ultrasound with ozonation was conducted. Unlike the first feasibility effort which was bench-scale (Sierka, 1976) later work was conducted in a Torricelli chamber geometrically similar to one in the quarter scale contactor which preceeded full scale-up. Laboratory and composite RO permeates were ozonated in combination with ultrasound. Special attention was paid to the effects of column length to diameter ratio (Sierka & Skaggs, 1977).

A feasibility study of ozonation under high pressure also was completed and is to be reported in the near future. Pressures to 100 psig were explored. Ozone losses due to heat of compression and gas "blow-up" were monitored. High pressure ozonation is looked upon as an alternative (or supplement) to higher ozone gas feed concentrations. Larger amounts of ozone are expected

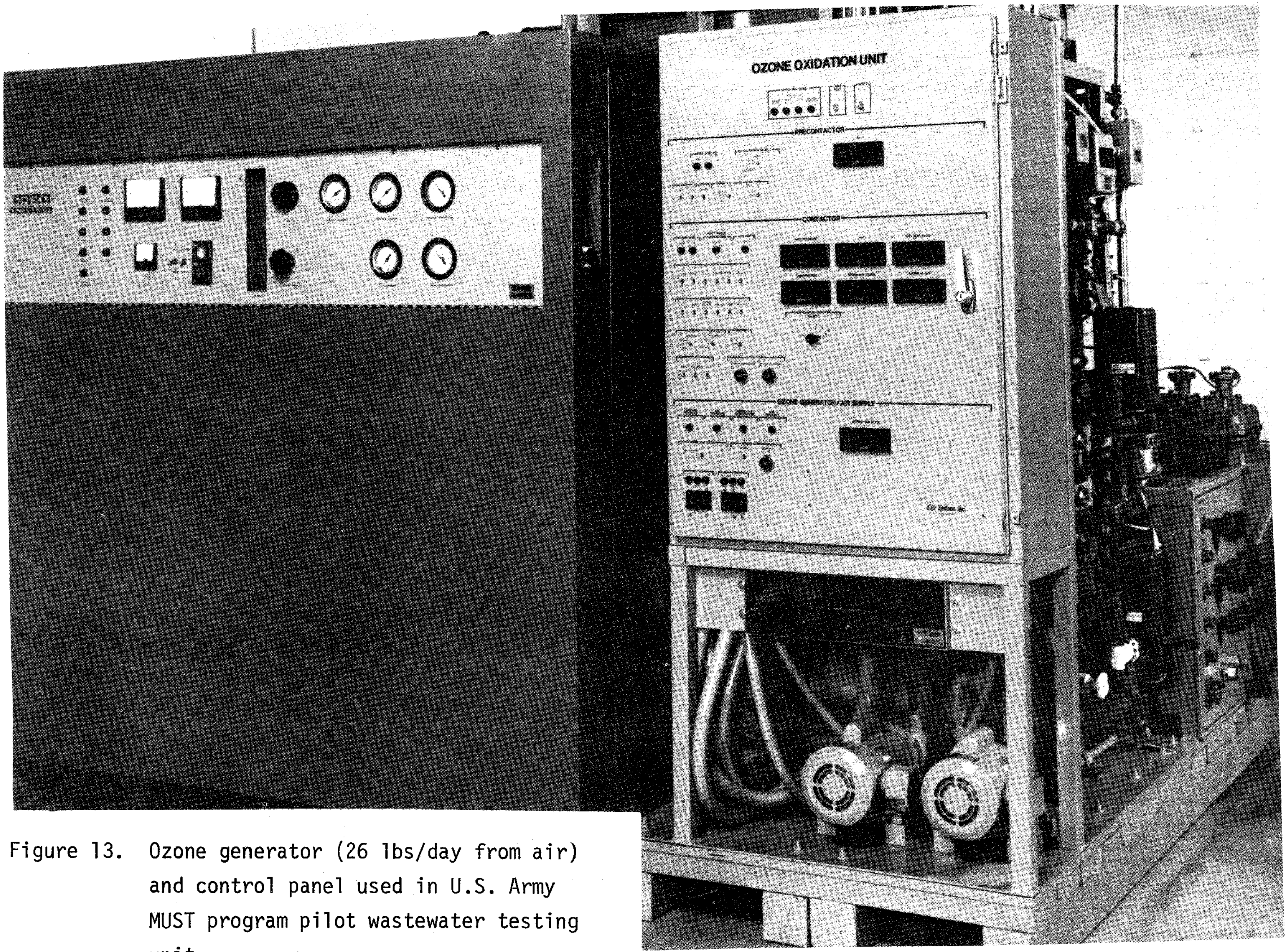


Figure 13. Ozone generator (26 lbs/day from air) and control panel used in U.S. Army MUST program pilot wastewater testing unit.

to dissolve into solution according to Henry's law. Heat transfer problems (for the small-scale studies) were minimal. Verification of the feasibility of the process would come with treatability studies which show increased rates of oxidation under high pressure conditions (Hill & Howell, 1977).

Contractor and in-house reports which have emanated from the Army's MUST program provide some of the most complete information available on ozonation, UV/ozonation and UV/ultrasonics systems for oxidation of refractory organic compounds, identification of oxidation products of organic compounds and oxidation reaction kinectics. Considerable advances strides also were made in the development of monitoring and control instrumentation for small scale ozonation systems.

In late 1977 the Army terminated its program pointed at developing field operational and deployable MUST hospital units. This has resulted in a change in the wastewater treatment R&D program being conducted by the Army Medical Bioengineering R&D Laboratories at Ft. Detrick, Maryland.

Current priorities of the Army involve studies pointed at wastewater reuse, as can be made applicable to the total needs of the Army, rather than being restricted to hospital wastewaters alone. Medical-specific wastewaters (X-ray lab, clinical lab and operating room) from Army installations are of insufficient volumes to consider treatment for reuse as being practicable. Discharges of these wastewaters to the environment are regulated satisfactorily under PL 92-500 and the Clean Water Act of 1977.

On an Army-wide basis, the Army Medical Bioengineering R&D Laboratories currently are characterizing laundry and shower wastewaters for the ability to be treated for reuse. Standards and criteria for these raw and treated wastewaters are being developed and toxicological parameters are being determined (Peterman, 1978).

Conclusions

1) The Army Medical Bioengineering R&D Laboratories MUST program was unique in that techniques were being developed to treat hospital wastewaters for at least non-consumptive human reuse.

2) Results of this program generally are applicable to hospital wastewater components which are classified as "toxic to receiving bodies of water or sewer systems".

3) Major ozonation products of organic wastewater components are formic acid, glyoxylic acid, oxalic acid and acetic acid. All of these are biodegradable.

4) Increasing the concentration of ozone in air from 1% to 1.5% reduces the time necessary to attain the target TOC and COD concentrations (of 5 and 10 mg/l, respectively) by 40%.

5) Three pilot ozone/UV reactors were tested and one design was scaled up for extended pilot scale evaluation. This reactor consists of 6 columns, each having a UV bulb extending the length of the column and each having a porous diffuser for ozone at its base. Water flow is alternately cocurrent then countercurrent to the gas flow. The unit operates under 15 psi pressure of ozone-containing gas, and off-gases from the 6 columns are sent to a preozonation contactor where ozone demand is highest. The precontactor also allows volatile organics to be air-stripped from solution.

6) Porous ozone diffusers made from glass, stainless steel, fused aluminum and Teflon gave the same performances. No gas phase decomposition of ozone was observed with any of these diffuser materials.

7) Studies conducted at gas pressures of ozone in air up to 100 psi show promise as an alternative means of increasing the concentration of dissolved ozone, thus reducing required reaction times.

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INORGANICS

All easily oxidized inorganic anions and cations can be oxidized by ozone under aqueous conditions. Specific ions which have been ozonized under wastewater treatment conditions include cyanides, cyanates, thiocyanates, nitrites, sulfides, sulfites, thiosulfates, cations of Mn(II), iron(II), Hg(I), arsenic, aluminum, lead, nickel, chromium. copper, cobalt, barium, zinc, cadmium and organic complexes of some of these metals.

Details of the ozone oxidation of cyanide, cyanate and thiocyanate ions already have been discussed under Cyanides and Cyanates. Sulfides will be discussed to some extent under Leather Tanneries and under Petroleum Refineries, iron and manganese oxidation will be discussed to some extent under Mining and sulfites and thiosulfates in sections dealing with Photoprocessing and Textiles. Other literature dealing with oxidation of these inorganic materials will be discussed in this section, along with the ozonation of aqueous solutions of ammonia.

Some drinking water supplies contain small amounts of sulfides (groundwaters which contain sulfate and anaerobic bacteria), cyanides and iron and manganese. There are many operating drinking water treatment plants throughout the world using ozone for coping with these specific problems. The recently started (Spring, 1978) 13 mgd drinking water treatment plant at Monroe, Michigan installed ozonation mainly for tastes and odors, but also for cyanide oxidation (Le Page, 1976).

Iron and Manganese

German water treatment plants along the lower Rhine River in the Düsseldorf area draw well waters which have been filtered through the sand banks located along the Rhine. During this process of river sand bank filtration, levels of iron and manganese in the raw waters rise considerably, and ozonation was installed in the early 1950s to oxidize these cations from the divalent to the trivalent (iron) and tetravalent (manganese) states. In the trivalent state ferric ion now hydrolyzes, forming insoluble ferric hydroxide. As this material coagulates it serves as a flocculating agent for dissolved organic materials which are polar in nature:

$$Fe^{+2} + O_3 \longrightarrow Fe^{+3} \xrightarrow{H_2O} Fe(OH)_3$$

Ozonation of manganous ion produces insoluble manganese dioxide, which precipitates much more rapidly than does ferric hydroxide. Continued ozonation of manganese-containing solutions can form the septavalent permanganate ion, which is quite soluble and which imparts a pink color to the solution:

$$Mn^{+2} + O_3 \longrightarrow Mn^{+4} \xrightarrow{H_2O} MnO_2 \xrightarrow{O_3} MnO_4^-$$

If a pink color is obtained during drinking water treatment, indicating over-ozonation of manganese-containing solutions, the ozonized waters are held about 30 minutes, during which time the permanganate slowly oxidizes extraneous dissolved organic materials, being reduced back to manganese dioxide, and the pink color disappears. Alternatively, the slightly pink solution can be passed through GAC, which reduces permanganate ions to manganese dioxide.

Details of the use of ozonation for iron and manganese oxidation in drinking water treatment can be found in Miller et al. (1978). Other references on this subject include Whitson (1947), Sergeev (1964), Marcy & Metthes (1967), Sengaki & Ikehata (1968) and Rohner (1969).

Other Heavy Metals

Lizunov, Leontovich & Skripnik (1972) ozonized wastewaters from chlor-alkali production containing mercury. An air mixture containing 22 to 24 mg/l of ozone was passed through a 50 mm x 2 mm column containing 0.124 mg/l Hg for 6 to 32 minutes. The oxidation rate of mercury increased with decreasing pH and "was complete" at pH 4. No metallic mercury vapor was produced. No further details were given in the English abstract of this work.

Yakobi, Galstyan & Galstyan (1975) studied the oxidation of Cr(III) solutions with ozone. In the absence of transition metals, $Cr(OH)_3$ was not appreciably oxidized by ozone-air mixtures. Addition of manganese compounds to the solutions, however, allowed the oxidation to proceed smoothly, giving a quantitative yield of Cr(VI). The mechanism proposed by these authors for the accelerating effect of manganese is that ozone first reacts with bivalent manganese ions, producing trivalent manganese and hydroxyl radicals. Both the trivalent manganese and the hydroxyl radicals then are postulated to oxidize Cr(III) to Cr(IV), which then disproportionates to Cr(VI) (33%) and Cr(III) (67%).

Netzer, Bowers & Norman (1972) described a bench scale system for removing trace metals from solution by treatment with lime and ozone. Stock solutions of metals were prepared at 100 mg/l concentrations. Lime was added to adjust pH to 7 to 9, then ozonation was conducted to saturation in a 120 x 6.5 cm column. Metals removed from solution were above 99.5% for Al, As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn. Removal of mercury "was lower". This preliminary work showed that these metal cations precipitate in aqueous solutions as a result of the formation of insoluble hydroxides and oxides.

In a more detailed report, Netzer & Bowers (1975) showed that a large percentage of these metals are removed by lime adjustment to pH 7.0, 8.0 and 9.0, and that the remaining dissolved metals are precipitated by ozone at these pH levels. Stock solutions containing 100 mg/l of the metal cations were treated with lime in a rapid mix reactor, from which the mixture was passed into a flocculation/sedimentation tank with a residence time of about one hour, then to a clearwell holding tank prior to ozonation.

Ozone was produced from dry oxygen, then passed through a porous stone in a 120 x 6.5 cm perspex column with solution being pumped cocurrently to the ozone flow. Ozone was analyzed in the inlet gases and in solution, but not in the contactor off-gases. Ozonation was carried to saturation and only the effect of pH was examined experimentally. To show that removal of metals was due to ozonation, duplicate experiments were conducted with nitrogen, air and pure oxygen under conditions identical to those involving ozone. No removal of metals was found unless ozone was present.

Greater than 99.5% removal was achieved for all the metals studied, except mercury which was removed only to the extent of 2% at pH 7 and 8, and 1% at pH 9. Furthermore, the pH for complete removal of all metals except cadmium and iron was lower by this process than the pH necessary for complete removal by lime treatment alone. Lime treatment alone would require recarbonation to lower the pH of an effluent prior to discharge. Costs for the lime/ozonation process are estimated to be 1¢/1,000 gal at pH 8 and 1.4¢ at pH 9. By comparison, lime treatment alone at pH 10 is estimated to cost 1.7 to 3.6¢/1,000 gal (cost estimates are based on a 10 mgd wastewater flow containing 25 mg/l heavy metal content).

Weber & Waters (1973) showed that ozonation (ozone generated from oxygen) of aqueous solutions of dimethylmercury "destroyed" the mercurial compound from its solubility of 0.0005M to below its limits of detection (0.00005M) and that at least 90% of the material originally present reacted in 10 minutes. The ozonation reaction was too fast to allow calculation of a rate constant.

Shambaugh & Melnyk (1978) studied the removal of heavy metals from solution by means of ozonation. Aqueous solutions of lead, manganese, cobalt, nickel, barium and zinc were studied, as were aqueous solutions of EDTA complexes of manganese, cadmium, nickel and lead.

Ozone was generated from oxygen and applied to the solutions through a sintered glass sparger contained in a 1-liter glass reactor 21 cm high. Solutions of the metals (100 mg/l) were buffered with 6.6×10^{-4}M sodium tetraborate. Following ozonation, the pH was raised with NaOH and any material which precipitated was filtered. Concentration levels of solutions of uncomplexed Mn, Co and Ni then were too low to be measured by flame atomic absorption spectroscopy, but no lowering in concentrations of Ba and Zn was observed. These last two metals have only one known oxidation state in solution, which is incapable of being changed by ozonation.

The concentrations of lead were lowered very rapidly upon ozonation at pH 8, 9, 10 and 11. At the 3 higher pH values, lead concentrations decreased to less than 0.1 mg/l within 3 minutes after ozonation began. During the course of these runs, the pH changed by no more than 0.2 pH unit. At pH 8 (borate buffered), however, the pH dropped to 3.6 during the course of ozonation over 10 minutes, after which the concentration of lead was 0.1 mg/l. This behavior at pH 8 is explained on the basis of maintenance of pH by the buffer for the first few minutes of ozonation, after which it decomposes and the pH then drops slowly.

Shambaugh & Melnyk (1978) concluded that ozonation times on the order of 1 minute will suffice for lowering the concentrations of uncomplexed metals (which can be oxidized to higher valence states by ozone) to levels below the current EPA maximum allowable discharge concentrations. For EDTA complexes of Mn, Cd, Ni and Pb, ozonation times of 10 minutes are required to reach the same levels.

For ozonation of the EDTA-metal complexes, a simple second order rate expression describes the disappearance of metal complexes. It was also shown that ozone decomposes at least 50 times faster than it reacts with EDTA and that the rate of destruction of EDTA-metal complexes is an order of magnitude faster than that of the simple attack of ozone on EDTA alone.

Ammonia

Singer & Zilli (1975) studied the effects of ozonation on the ammonia content of municipal wastewater and evaluated the effects of pH and concentrations of ammonia, ozone and residual COD on ammonia removal with ozone. Ozone was generated from oxygen and the contactor was a plexiglass column 43 cm high and 9.5 cm in diameter, which contained a porous diffuser stone. Concentrations of ozone were measured in the influent gas from the generator and in the contactor off-gases so that the amount of ozone actually consumed (or decomposed) could be determined.

In the first phase of this program, buffered solutions of ammonium chloride (NH_4Cl) were ozonized to determine the products of the ammonia-ozone reaction and to establish the kinetics of the reaction. Solutions buffered at pH 9 (boric acid-borate) containing 10 to 50 mg/l of NH_4Cl were ozonized for 30 minutes (the gas stream contained 5.7 to 5.8 weight % ozone) and samples were collected periodically and analyzed for ammonia, nitrite and nitrate. No nitrite was found and the rate of increase of nitrate ion paralleled the rate of decrease of ammonia concentration on a 1:1 basis.

To confirm that the disappearance of ammonia could not be attributed to air stripping or to oxidation by oxygen, one of the experimental runs was conducted under the same ozonation conditions, but with the power to the ozone generator turned off. Thus only oxygen gas was being passed into the solution. No changes in concentration of ammonia were observed at pH 9 under these conditions.

The rate of disappearance of ammonia during ozonation decreased as the ammonia concentration decreased. The half-life for ammonia at an initial concentration of either 10 or 50 mg/l was about 12 minutes, indicating that the reaction is first order with respect to ammonia over the pH range 7 to 9. However, the rate of oxidation is pH dependent, being 10 to 20 times faster at pH 9 than at pH 7. The buffered test solutions never decreased more than 0.2 pH unit during ozonation.

Ozonation of solutions of ammonium sulfate gave the same results, indicating that with NH_4Cl there was no oxidation of chloride ion to chlorine (by ozone) followed by chlorine oxidation of ammonium ion.

In the second phase of the study, secondary sewage treatment plant effluent was spiked with NH_4Cl to produce ammonia levels of 30 mg/l. The spiked effluent was treated with lime to the pH test level(s), SS were allowed to settle and the clarified liquid was drawn off and ozonized in the same manner as were the samples of NH_4Cl. Ozonized samples were analyzed for ammonia, nitrate and COD. When no buffering was employed and no adjustment of the pH was made, ozonation lowered the COD 34% (from 66.1 to 43.9 mg/l). However, only a slight decrease in ammonia concentration was observed after 60 minutes of ozonation, during which time the pH fell from 7.55 to 7.20.

When the pH was raised by addition of lime or NaOH, ozonation caused a depression of pH which limited effective ammonia oxidation. The pH dropped from an initial value of 9.2 to 8.3 within the first 15 minutes of ozonation, after which subsequent oxidation of ammonia was negligible. After 60 minutes of ozonation, the pH had dropped to 7.4.

When secondary effluent was buffered at pH 9 with boric acid-borate, ammonia removal was appreciable (70% being oxidized in 60 minutes), although the COD remained unchanged. Measurements of the rate of nitrate ion increase confirmed that nitrate was the only oxidation product of ammonia, and that for each mole of ammonia which disappeared, one mole of nitrate was produced. However, the rate of oxidation of ammonia in wastewaters containing 66 mg/l of COD was slower than in simple NH_4Cl solutions.

In one experiment, a large lime dose was added to the wastewater to elevate the pH to 11.6 and the settling step was omitted. Despite the drop in pH to 7.7 upon ozonation, the ammonia concentration decreased 89% to 3.3 mg/l and the COD concentration also decreased by 69%.

Stoichiometrically, the oxidation of 1 equivalent of ammonium ion to produce 1 equivalent of nitrate ion requires 4 equivalents of ozone, according to the following equation:

$$NH_4^+ + 4O_3 \longrightarrow NO_3^- + 4O_2 + H_2O + 2H^+$$

In actuality, a slightly greater amount of ozone was required because some of the ozone added decomposed before it could react with the ammonium ions.

Singer & Zilli (1975) concluded that ozone oxidation of ammonia in wastewaters can be attractive when the wastewaters are pretreated with lime to produce high pH values.

Somiya, Yamada & Goda (1977) studied the ozonation of aqueous solutions of ammonia, nitrite and several organo-nitrogen compounds. Ozone was generated from oxygen and the contactor was an acrylic column 100 cm high and 5 cm in diameter, one end of which contained a fritted glass plate. Then 1.2-liter samples of 0.5 mM (millimolar) nitrogenous compounds were adjusted to alkalinities of 100 mg/l of bicarbonate and to test pH values with 0.1N sulfuric acid or NaOH. Solutions were ozonized 30 to 60 minutes and the samples were analyzed for ammonia, nitrite, nitrate, pH, alkalinity and TOC.

During the ozonation of ammonia solution starting at pH 11.58, nitrite ion concentration increased rapidly to a peak concentration in 2 minutes, then decreased to zero during the next eight minutes. Nitrate was formed stoichiometrically with decrease in ammonia concentration, indicating that none of the ammonia was physically stripped out of solution during ozonation. The rate of formation of nitrite from solutions containing 7 mg/l of ammonia-N is about 0.02 mg/l/min at pH 7, increasing to about 0.95 at pH of 11.58; 1.0 mg of ammonia-N consumed 7.14 mg of alkalinity.

Nitrite

Ozonation of potassium nitrite solutions containing 7 mg/l of nitrite-N at initial pH values of 5.0, 7.0 and 10.0 oxidized all nitrite ion to nitrate ion within two minutes. The rate of formation of nitrate increased at the same rate as the concentration of nitrite decreased. A decrease in alkalinity was not observed and the pH of the solutions was not changed upon ozonation.

To confirm that the disappearance of nitrite was not caused by oxygen oxidation (as opposed to ozone oxidation), an "ozonation" experiment was conducted at pH 7 without power being supplied to the ozone generator. No change in nitrite concentration was observed after 30 minutes of passing oxygen through the solution (Somiya, Yamada & Goda, 1977).

Conclusions

1) Sulfide, cyanide, thiocyanate and nitrite ions are oxidized rapidly by ozone.

2) Ozonation of water supplies to remove iron and manganese has been a common practice in many European drinking water treatment plants for many years.

3) Pure solutions of Cr(III) are not appreciably oxidized by ozone, but addition of manganese compounds allows the oxidation to Cr(VI) to proceed smoothly.

4) Metals which can exist in more than one oxidation state in aqueous solution (Cd, Co, Cr, As, Cu, Fe, Pb, Mn and Ni) can be removed from solution by ozonation with or without prior treatment with lime. Greater than 99.5% removal of these metals can be achieved starting with concentrations of 100 mg/l by lime treatment followed by ozonation, and at a lower pH (9) than that required for removal using lime treatment alone. Mercury cannot be removed from solution effectively by the lime/ozonation procedure.

5) Concentrations of uncomplexed Pb, Mn, Co and Ni at initial pH values of 9, 10 or 11 can be lowered from 100 mg/l to less than 0.1 mg/l within 3 minutes of the start of ozonation. EDTA complexes of these same metals react more slowly, requiring 10 minutes of ozonation to reach concentrations below 0.1 mg/l.

6) Aqueous pure solutions of ammonia at initial pH values of 7 to 11.58 react with ozone to produce nitrite ion as an intermediate, which rapidly oxidizes to nitrate. Even at pH values above 9 (where ammonium ion exists as free ammonia), one equivalent of nitrate is formed for each equivalent of ammonia-N removed from solution by ozonation. Thus, no gas stripping of ammonia occurs during ozonation.

7) Ozonation of ammonia in secondary sewage treatment plant effluents produces nitrate stoichiometrically. The rate of oxidation with ozone is very slow at an initial pH of 7.55 but more rapid at higher pH values. However, the presence of COD levels of 66 mg/l apparently lowered the ammonia oxidation rates considerably over those observed with pure solutions of ammonium compounds.

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IRON AND STEEL

In this category, wastewater pollutants which have been treated by ozonation include:

- Cyanide
- Thiocyanate
- Phenols
- Thiosulfates
- Sulfide

In addition, it is possible to consider ozonation for the removal of manganese and ammonia. Manganous and ferrous ions are easily oxidized by a number of strong oxidizing agents, including ozone, and the use of ozonation for this specific purpose in many European drinking water treatment plants (Miller _et al._, 1978) since the mid-1950s attests to its efficacy.

Preozonation of GAC columns and beds has been incorporated into some German and French drinking water treatment plants specifically to promote biological growth in the carbon adsorbent. Nitrifying bacteria develop in the carbon adsorbent, and thus the preozonized carbon now is capable of converting ammonia to nitrate biologically. Whether or not this technique can be transferred from the rather dilute ammonia concentrations found in drinking water supplies (up to 8 mg/l) to iron and steel wastewater effluents (up to 2,400 mg/l) is not known at this time. Nevertheless, the applicability of Biological Activated Carbon (BAC) (Rice, 1978) to iron & steel and other industrial categories whose wastewaters are likely to contain ammonia should be determined by experimentation and pilot studies. A more detailed discussion of the status of BAC is given in Section 7.

Ozonation of wastewater containing phenols will be discussed in detail in this section, but ozonation of specific iron and steel industry wastewaters will be discussed at this point. The chemistries involved upon ozonation of cyanides have been discussed under Cyanides and Cyanates.

Thiocyanate ion, $(NCS)^-$, also is oxidized upon treatment with ozone, producing cyanide ion first, which then further oxidizes to cyanate, then to CO_2 and nitrogen:

$$(NCS)^- + O_3 \longrightarrow (CN)^- + (SO_4)^{-2} \longrightarrow (CNO)^- \longrightarrow CO_2 + N_2$$

The oxidation of thiocyanate to cyanide by means of ozone is faster than the oxidation of cyanide to cyanate.

Phenols in Coke Plant Effluents

The total amount of phenols in coke plant discharges (ahead of dephenolizing) usually is between 0.25 and 0.50 lb/ton of coal carbonized, and the total amount of waters containing phenols to be discharged may be on the order of 35 to 50 gal/ton of coal processed. Approximately one-half of this is condensate from the gas coolers. Representative concentrations of phenol in this effluent may range from 1,000 to 2,000 mg/l. In the discharges from light oil decanters, phenol concentrations may be 50 to 150 mg/l and 10 to 50 mg/l in the effluents from miscellaneous plant sources. If it is assumed that most coke plants employ efficient dephenolizers which will remove 95 to 99% of the phenol in the gas cooling condensate, and then add the discharge from the light oil decanters (without passing it through the dephenolizer), the combined effluent from the coke plant that will have to be treated will have an average concentration of phenol of about 100 mg/l (Nebolsine, 1957).

Marechal (1905) was the first to patent the use of ozone for oxidation of phenols in iron & steel industry wastes. Later, Leggett (1920) obtained a U.S. patent for the same purpose. Although the use of ozonation for phenol oxidation was well known, the first detailed study of its use in the iron & steel industry was not published until 1951, when a consortium of companies and agencies participated in a program directed by the Ohio River Valley Water Sanitation Commission (ORSANCO) and later described by several authors (Anonymous, 1951a, 1951b; Cleary & Kinney, 1951; Murdock, 1951).

In the ORSANCO study, phenol wastewaters originating as the effluents from a dephenolized ammonia still in the Armco Steel Co. (Hamilton, Ohio) coke plant were tested first in laboratory experiments, then in an on-site pilot plant. Three treatment processes were studied: chlorination, chlorine dioxide and ozonation. Phenols present in the wastewater stream included phenol, cresols and xylenols, and the characteristics of the dephenolizer effluents are given in Table 20.

TABLE 20. ANALYSES OF PHENOL-CONTAINING WASTEWATERS

Phenol	28 to 332 mg/l
Cyanides and cyanates	in low concentration
Sulfides	less than 100 mg/l
Chlorides	between 7,000 and 9,700 mg/l
Oxygen Consumed (OC)	1,400 to 1,800 mg/l (about one-half the OC as measured by the dichromate reflux method was due to chlorides)
BOD	300 to 400 mg/l
Ammonia	10 to 2,390 mg/l (variation due to drop in fixed leg of ammonia still)
pH	fixed leg of ammonia still ordinarily operated above 11.0 for maximum ammonia recovery
Temperature	from the still at 100°C

Source: Cleary & Kinney, 1951

Laboratory investigations showed the following:

(1) Complete destruction of phenols in ammonia still wastewaters could be achieved by oxidation with chlorine, chlorine dioxide or ozone.

(2) No pretreatment was required for oxidation with ozone or chlorine dioxide, but for chlorination, the pH had to be adjusted to 7.0 to 10.0 and the temperature reduced to 45°C.

(3) Under-oxidation with ozone or with chlorine dioxide did not result in the formation of chlorophenols; chlorination required complete oxidation to prevent the formation of such end products, requiring an excess of several hundred mg/l of chlorine. This excess chlorine then could be removed easily with GAC.

(4) Ozonation caused no increase in chloride content; chlorine dioxide caused about 1.50% increase; chlorination caused an increase equivalent to the amount dosed for complete oxidation.

Based on these laboratory experiments, a pilot plant was constructed at Armco Steel which was capable of handling 2 gal/min continuous wastewater flows, or 350 gal in batch operations. A 1,000 gal holding tank provided uniform wastewater for a 1-day run, and the water was heated by means of a steam coil. A reaction tower 2 ft in diameter and 18 ft high allowed variation in liquid depth at 2 ft intervals. Wastewater was pumped to the top of the tower, and ozone was added through stainless steel diffusers at the bottom of the tower. Chlorine dioxide was added in-line at the top of the tower. Caustic could be added at any level for pH control. Two 55-gal drums served as chlorination reactors, after which the chlorinated wastewater was pumped to the tower.

In general, the laboratory results were confirmed in this pilot plant. Chlorine added during continuous flow did not provide complete phenol removal in 18 minutes. The initial chlorine dosage first had to satisfy the ammonia demand, after which there was a significant decrease in phenol concentration with small increases in chlorine dosage. Chlorine destroyed phenols over a wide pH range (1.8 to 11.0). The recommended pH was above 7.0 (to avoid formation of chlorophenols and nitrogen trichloride) and under 10.0 for economic reasons. It was found that the temperature should be reduced to 45°C before chlorine is added, to avoid the formation of chlorates.

Ozonation was effective at the ambient pH level of 11.8, so that no pH adjustment was required. As ozonation proceeded the pH dropped, but the final pH was on the alkaline side. Variation in temperature had no effect upon the dosage of ozone required, and because ozone does not react rapidly with ammonia, the concentration of ammonia had no effect on the ozone dosage. Substantial reduction in phenol concentration was obtained with small dosages of ozone, but increasingly higher dosages were required as phenol concentration was further reduced.

Best results were obtained from chlorine dioxide starting at pH above 11.5 when it was not controlled. The pH fell to the acid side during treatment. No temperature adjustment was necessary. A 2:1 chlorine:chlorine dioxide ratio resulted in the best efficiency in less than 15 minutes of treatment. Ammonia content also had no effect on the dosage of chlorine dioxide required.

During these ORSANCO studies, the distilled ammonantipyrine (DAAP) method for measuring phenol with a sensitivity of 0.1 to 0.5 mg/l was developed (Cleary & Kinney, 1951).

In reporting results of the ORSANCO work (Anonymous, 1951b) the following performance data were cited:

(1) Only 600 mg/l of ozone reduced phenol concentration to less than 1 ppm; however 1,000 mg/l of ozone or more were required to attain 5 ppb, the taste-producing limit for drinking water supplies.

(2) Pure phenol required less ozone for complete oxidation, probably because of the presence of other oxidizable materials (thiosulfate, cyanide, thiocyanate) in the actual wastewaters. The average reduction in COD concentration was 0.7 part/part of ozone.

(3) Foaming occurred during ozonation if the wastewater was allowed to cool to ambient temperature. However no serious foaming developed at 43°C.

In this same article (Anonymous, 1951b), costs for ozonation are discussed. Capital installations for chlorine and chlorine dioxide are much less than those for ozonation, but operating costs for chlorination are 2 to 3 times those for ozonation and 6 to 8 times higher for chlorine dioxide. The low operating costs for ozonation should offset the first cost differential in 2 to 5 years. It is estimated that coke plant phenolic wastes can be treated with ozone for about $1.00/gal (1951 costs) generating ozone from air, and $0.35/gal if oxygen is used as the feed gas.

Murdock (1951) in reporting results of the ORSANCO study showed that ammonia still wastewaters containing 118 mg/l of phenol required 6,000 mg/l of chlorine to reduce the phenol concentration to 3 mg/l. Costs for ozonation of ammonia still wastewaters in a 100-oven coke plant would be about 3¢/ton of coal carbonized, which would drop to 2¢/ton of coal carbonized for a 300-oven plant. If low cost oxygen were available, this 2¢/ton figure would drop further to 1.25¢/ton of coal carbonized. The capital equipment was amortized over 12 years in these costs calculations. Murdock concludes that where quick write-offs are allowable in new facilities, a large plant could expect a cost of 1¢/ton of coal carbonized after a 5-year amortization period.

In reviewing the ORSANCO work, Nebolsine (1957) concluded that chemical costs to reduce phenol concentrations to 20 to 50 mg/l from raw wastewaters are not large, although the equipment required to generate chlorine dioxide or ozone is "extensive and costly". To reduce phenol concentrations much below the concentrations just mentioned would require more elaborate facilities and disproportionately larger dosages of chemicals, "and no new designs have been reported that have overcome this difficulty". "Getting rid of the last trace of phenols is like trying to squeeze the last drop out of a toothpaste tube -- there always seems to be a little more".

Hall (1958) reported the results of detailed laboratory investigations on the effects of ozonation of ammoniacal waste liquors from 15 coke oven effluents in Britain. In addition to phenols, these effluents also contained thiosulfates, thiocyanates and sulfides. In ozonation experiments, the amounts of ozone in the influent gas stream and in the contactor off-gases were measured so that the amount of ozone actually used could be determined. Ozonation was conducted using a sintered glass frit, and gas flow was countercurrent to the flow of effluent being treated. Ozone dosages employed were 200 to 300 mg/l, and confirmed that the amount of ozone required to destroy one part of phenol becomes greater at the lower phenol concentrations.

For 13 raw wastewaters tested at the Durham coke plant, an average of 17 lbs of ozone was required per 1,000 gal of wastewater. Maintaining the pH at about 10 caused a 25% increase in the efficiency of ozone useage, thus lowering treatment cost. During these tests, thiosulfates, even at 4,000 mg/l initial concentrations, were 98% converted to sulfuric acid (or sulfate) during the early stages of ozonation.

Oxidation of thiocyanate by ozone was found to occur in three steps, going first to cyanide, then to cyanate, then to CO_2 and nitrogen. Monitoring the cyanide content of effluents being treated showed that cyanide concentration passed through a maximum of 25 to 50 mg/l, which appeared at the point of thiocyanate disappearance. However, although thiocyanate was converted rapidly to cyanide during the early stages of ozonation, once it had formed, cyanate remained "stable" to further ozone additions until the phenol concentration dropped to low values. Only then did ozonation of cyanide become rapid.

When the pH was increased to above 8.0, reaction of ozone with thiocyanate became slower, and at an initial effluent pH of 11.5, the time required for thiocyanate destruction in cokeworks spent liquor was nearly 10 times longer than when conducted below pH 8.0. It was shown experimentally that there was practically no accumulation of cyanide as long as the pH was maintained above 9.0.

Sulfides were easily oxidized to sulfuric acid, but ferrocyanides were little affected. Oxalic acid was found in ozonized solutions of catechol and of coke works spent liquor, in concentrations up to 800 mg/l.

Pretreatment by froth flotation reduced the phenol concentrations to 30 to 100 mg/l, and the amount of ozone now required to destroy all phenols dropped to less than 1 lb of ozone/1,000 gal. When pretreated by an activated sludge process, the effluent now contained about 10 mg/l of phenol, and even less ozone was required to destroy these quantities of phenol. However, ozonation of the contained thiocyanate again produced cyanide, which would be removed more economically by final treatment with ferrous sulfate or chlorine than by ozone.

Using an assumed cost of tonnage quantities of ozone of 10 to 15¢/lb (1958 USA prices), Hall (1958) considered the costs for ozonation in Britain to be 42¢/lb for a plant producing 10 lbs/hr. This is comprised as follows:

Depreciation & Interest	14¢
Power	14¢
Labor	7¢
Maintenance, replacements, etc.	7¢
Total	42¢

Although these costs might be "a bit high," Hall concluded that ozonation costs never will drop below 28¢/lb of ozone.

Therefore, to ozonize coke works effluents directly, requiring an average of 17 lbs of ozone/1,000 gal would vary from 14¢ to 49¢/ton of coal processed, with an average cost of 28¢/ton of coal carbonized. Although this is much cheaper than most other chemical processes suggested, "it would still be a very big burden to a coke works", and would include only a portion of the total treatment costs anyway.

The economics become much more attractive if ozonation is considered as a finishing step following pretreatment by dephenolization, by froth flotation or by biological oxidation. Amounts of ozone required then would be about 3 lbs/1,000 gal for dephenolized liquor, 1 to 2 lbs/1,000 gal for froth plant effluent, and 1 lb/1,000 gal for activated sludge effluent. This final treatment, therefore, would average about 3d/ton of coal.

Hall (1958) also suggests the use of ozonation as a pretreatment step to oxidize thiocyanate and thiosulfate before treating phenols biologically.

Hall & Nellist (1959) describe the laboratory apparatus used for developing the ozonation data in the earlier article (Hall, 1958). The reaction tube was 3 ft long and 3 inches in diameter, holding 1,500 ml samples. Effluent from a froth flotation plant required less than 1 lb of ozone/1,000 gal of liquor to destroy all phenols present at an ozone/phenol ratio of 3/1, and an ozone concentration in air of 5 mg/l. At an ozone production cost of 42¢/lb, the cost of ozonizing this effluent would add about 3.4¢ to 6.7¢/ton of coke to the plant costs. These authors concluded that dephenolization should be the first treatment step for coke wastes high in phenols, followed by biological treatment or froth flotation to reduce phenol concentrations to 10 to 50 mg/l. If further treatment still is necessary, then ozonation should be incorporated as the terminal step.

Hall & Nellist (1965) describe further ozonation experiments utilizing a more efficient contactor. This apparatus consisted of an outer tube 30 inches long and 2.5 inches internal diameter, containing an inner tube 19 inches high and 1.5 inches in diameter. Eleven circular plates spaced evenly in the annular space between the tubes were fixed firmly on the inner tube and sloped slightly downward, and were divided into 6 equal sectors by 0.1-inch wide slots. The discs were staggered so that the slots in the next lower disc were below the sector blades of the disc above, each disc being rotated through 30° compared with the adjacent discs above and below.

The following conclusions were reached from ozonation studies using this apparatus and air containing 6 mg/l of ozone:

(1) It should be possible to produce an effluent with a residual permanganate value of about 30 mg/l from a coke works spent liquor previously treated by a biological process. The ozone consumption should not exceed 1.5 lb/lb of permanganate value destroyed.

(2) Assuming ozone costs at 42¢/lb and also that the original waste liquor was diluted by a factor of 3 with clean water in the biological treatment step, the cost of ozonation would be about $1.12/1,000 gal of ammoniacal spent liquor, or 6¢/ton of coal carbonized.

Kucharski, Ladouceur & Le Clair (1976) reported bench-scale studies on the ozonation of scrubber waters from blast furnace gas cleaning operations containing cyanide, phenol, ammonia, heavy metals and SS. Ozonation was studied for simple and complex cyanide destruction. Total cyanide concentration in the untreated, recycled blowdown water did not exceed 1 mg/l, and in the water from the once-through system total cyanide concentration fluctuated in the 10 to 16 mg/l range.

Simple cyanide was readily removed to below 0.05 mg/l, however similar reductions in total cyanide concentration were possible only through the use of catalysts [Cu(II), Mn(IV)]. Phenolic compounds were oxidized to less than 0.02 mg/l before cyanide was removed. Removal of ammonium ion by ozonation was feasible, but only after raising the pH to above 9. Following cyanide and phenol oxidation by ozonation, then raising the pH, air stripping of ammonia and removal of heavy metals became feasible.

Prober, Melnyk & Mansfield (1977) presented preliminary results obtained on ozone/UV destruction of ferricyanides in coke oven and blast furnace effluents at pH 4.5 to 9.5, temperatures of 8 to 50°C, ozone feed rates of 0 to 65 mg/l and UV intensities of 0 to 10 watts/l. Effective destruction of ferrocyanide was observed, but ozone consumption was 5 to 80 fold greater than stoichiometric requirements, due to parasitic reactions of ozone.

Throop, 1977 showed that ozone dosages of 5.32 mg/l produced non-detectable quantities of phenol in five minutes of contact, starting with 110 ppb concentrations of phenol in a presettled and decanted foundry wastewater. He also compared the costs for treatment of foundry wastewaters to reduce phenol concentrations to 1.5 ppb at flow rates of 2.89, 1.3 and 2.4 mgd. In 1974 dollars, the costs estimated were as follows:

Chlorination:	Chlorination contact tanks	$125,000
	Annual chlorine cost	40,000
Permanganate:		$ 65,000/year
Peroxide:		$ 75,000/year

Carbon Adsorption:	Capital cost	$9 million
	Operating cost	$1,100/year
Ozonation:	Generation & contacting	$80,000-$125,000
	Power cost	$4,000 - $9,000/year @ 2¢/kwhr

Conclusions

1) Coke plant wastewaters contain phenols (phenol, cresols) thiocyanate, thiosulfate, cyanide, sulfide and ammonia at pH above 11. All of these except ammonia are readily oxidized by ozone.

2) Upon ozonation, thiosulfates and sulfides are oxidized rapidly to sulfuric acid, which is partially responsible for causing the pH to be lowered.

3) Thiocyanate then oxidizes to cyanide, which remains "stable" to further ozonation while phenols are oxidized. Once phenols are destroyed, ozonation of cyanide to cyanate, then to CO_2 and nitrogen proceeds rapidly.

4) At pH above 8, reaction of ozone with thiocyanate becomes slower. With an initial pH of 11.5, the time required for thiocyanate destruction is nearly 10 times longer than at pH 8.0.

5) Oxalic acid (HOOC-COOH), is produced by ozonation of phenols. Complete destruction of phenol by ozone can be achieved at a 3/1 ratio of ozone to phenol.

6) Phenol oxidation by means of ozone is independent of pH (starting at about 11) temperature (above 43°C) and ammonia concentration.

7) Maintaining the pH at 10 results in a 25% increase in oxidation efficiency, thus reducing ozonation costs by 25%.

8) Foaming occurs during ozonation at ambient temperatures, but not at 43°C or higher.

9) As phenol concentration becomes lower, more ozone is required for its oxidation.

10) Ozonation of raw coke plant wastewaters requires large quantities of ozone for oxidation (17 lbs of ozone/1,000 gal of wastewater). If the raw wastewaters are pretreated to reduce phenol levels, the amount of ozone required to destroy the remaining phenols will be decreased significantly to: 3 lbs of ozone/1,000 gal for dephenolized liquor, 1 to 2 lbs/1,000 gal for froth flotation and 1 lb/1,000 gal for activated sludge effluent. Thus ozonation is less costly as a terminal polishing step.

11) Ferro- and ferricyanides are stable to ozonation, but the combination of ozone with UV radiation destroys these complexes. On the other hand, ozone consumption to accomplish this appears to be high (5 to 80 times greater than the stoichiometric amounts).

12) To date, ozonation has not been utilized to oxidize manganese and other heavy metals in iron and steel wastewaters, nor has BAC been tested for ammonia removal.

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LEATHER TANNERIES

Only a few attempts have been made to study the use of ozone for treating tannery wastes, and investigators so far have concluded that ozonation is more costly than other methods available. Eye (1956) suggested the use of ozone for color reduction in spent vegetable liquor. However, Eye concluded that the applicability of any oxidant to color removal is limited because of the large amounts required.

Eye & Clement (1972) studied the oxidation of sulfide in lime-sodium sulfide unhairing wastewaters using direct chemical oxidation with ammonium persulfate or ozone, precipitation with ferrous sulfate and the use of air oxidation catalyzed by manganous sulfate, chromium(III) and potassium permanganate. Ozone, as well as air oxidation with manganous sulfate or permanganate, rapidly oxidized sulfide, while the other techniques were unsuccessful. The permanganate reaction then was applied to a hair-burning wastewater containing about 5,000 mg/l of sulfide. At a total permanganate concentration of 500 mg/l, complete oxidation of the sulfide was obtained in 90 minutes in a 2-stage treatment system. Pertinent data regarding these experiments are listed in Table 22. The purpose of removing sulfide from this wastewater is as a pretreatment to biological treatment, with which high concentrations of sulfide are known to interfere.

TABLE 22. COMPARISON OF SULFIDE OXIDATION SYSTEMS

Treatment Method*	Initial [S] (mg/l)	Final [S] (mg/l)	Contact Time (sec)
$KMnO_4$ + air	100	0	290
$MnSO_4$ + air	100	0	1800
O_3 - 3.0 l/min	100	0	220
O_3 - 6.4 l/min	100	0	180

* 100 mg/l reagent concentration, except ozone which was of unknown concentration

Source: Eye & Clement, 1972

Eye & Clement (1972) reported that the concentration of ozone used was not measured, but was present "in excess, as evidenced by the odor of ozone at the surface of the reaction solution". These authors concluded the following:

> "Ozone is only very slightly soluble in water and technical problems in efficiently applying this oxidant prevented further study. An efficient contact device might make ozone a feasible means for sulfide elimination, especially in applications where treatment space is limited. Ozone generation equipment currently is expensive and its use must be evaluated carefully".

This kind of statement made without reporting how the ozone was generated (from air or oxygen), what type of contacting was used, a description of the contactor nor determining the ozone dosage and amount of ozone in the contactor off-gases, makes evaluation of this work very difficult. The statement "technical problems in efficiently applying this oxidant prevented further study" implies that these authors did not have access to technical assistance in the proper application of ozone.

The wastewaters from an actual hair-burning operation have the characteristics as shown in Table 23. The waste typically smells strongly of ammonia and decaying organic matter, is of a brown-black color and contains large quantities of short, stiff pieces of hair about 0.25 inch long. Compositions listed for Effluents #1 and #2 are those obtained by the 2-stage permanganate/-air oxidation process.

TABLE 23. CHARACTERISTICS OF TANNERY HAIR BURNING WASTEWATERS*

	Raw Water	Coarse Screened	Effluent #1**	Effluent #2***
BOD-5	78,000	-	-	10,560
COD	-	130,000	73,000	42,400
TS	123,000	-	-	-
TVS	43,600	-	-	-
SS	39,300	83,000	25,500	7,800
VSS	20,500	-	-	-
pH	11.7	11.7	11.7	11.7-12.2
TKN	6,200	-	-	-
[S-2]	5,000	4,800	500-800	0

* all concentrations in mg/l

** after $KMnO_4$ aeration and clarification

*** after a second $KMnO_4$/aeration, clarification step

Source: Eye & Clement, 1972

Costs for the successful permanganate treatment were estimated to be \$4.20/gal of wastewater treated, based on 1971 prices.

One can develop an estimated cost for ozonation, assuming efficient contacting and that sulfide is oxidized to sulfur trioxide which then hydrolyzes to sulfate by the following reactions:

$$S^{-2} + O_3 \longrightarrow SO_3 \xrightarrow{H_2O} SO_4^{-2}$$

If the reaction proceeds in this fashion, then for each mole of sulfide (molecular weight of 32), 1 mole of ozone (molecular weight of 48) will be required. Therefore, stoichiometrically 5,000 mg of sulfide will require 7,500 mg of ozone. At an ozone cost even as high as \$1.00/lb (most ozonation equipment purveyors cite 25 to 50¢/lb generation and contacting costs) the amount of ozone required to oxidize 5 g of sulfide to sulfate ion would be 7.5 g and would cost about 0.65¢/liter, or 2.6¢/gal.

On the other hand, some of the applied ozone will be consumed in oxidizing other components of the wastewater, particularly BOD and COD, even though sulfide ion should be the most readily oxidized component. If it is assumed that 90% of the ozone added would react with components other than sulfide, then the total amount of ozone for sulfide oxidation would increase 900% to about 742 g, which would raise the ozonation cost to $1.60/gal of wastewater treated. This is considerably less than the permanganate costs and indicates that ozonation still should be considered as a viable candidate to be further evaluated.

Successful use of ozone for sulfide oxidation in this wastewater would show other advantages in:

(1) partially reducing BOD and/or COD levels and
(2) not forming manganous sludges (which form with permanganate oxidation), therefore reducing sludge disposal costs.

Conclusions

1) Ozonation has been studied once for oxidation of sulfides in hair-burning wastewaters and without reporting the key parameters sufficient for proper evaluation of the work. The investigators rejected further evaluation of ozonation due to "technical problems" of contacting. Instead, potassium permanganate was shown to be successful in removing sulfide at levels of 5,000 mg/l in the raw water, but at a cost of $4.20/gal of wastewater treated.

2) With contact efficiencies equivalent to those obtained in ozonation plants for disinfection of sewage, estimates of costs for ozonation of sulfides are well under $2.00/gal of wastewater treated and should produce no manganous sludges. Therefore the use of ozonation should be reconsidered.

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MINING

There are two types of mining wastewaters which have been treated by ozonation,

(1) acid mine discharges from coal mines
(2) cyanide discharges from gold mining operations

Actual acid coal mine drainage wastewaters have been ozonized but only synthetic cyanide-containing solutions in the gold mining category have been ozonized.

Acid Coal Mine Wastewaters

Mine drainages from coal mines are characterized by high levels of dissolved iron and manganese at low pH values. This type of pollution is a result of bacterial oxidation of pyrites (iron sulfides) in the mines by oxygen in the mine water. Acid is produced by the oxidation of sulfide to sulfate, and much of the soluble iron remains in the ferrous state. Manganous compounds are leached into the mine waters and rise to fairly high levels, sometimes 20 to 100 mg/l. Such discharges can contaminate downstream water supplies. Compositions of typical discharges from a Pennsylvania anthracite field are given in Table 24, along with analysis of a typical culm runoff from either anthracite or bituminous regions of Pennsylvania.

TABLE 24. ANALYSES OF MINE WATERS IN WYOMING VALLEY, PENNSYLVANIA

Mine Water	pH	Fe(mg/l)	Mn(mg/l)
Discharge I	3.4	295	22
Discharge II	5.8	153	10.6
Culm Bank Runoff	2.5	1044	83.2

Source: Rozelle & Swain, 1975

Ozone is stable at low pH and is used for removal of iron and manganese in many European drinking water treatment plants (Miller *et al*. (1978). In the process, soluble ferrous and manganous ions are oxidized to the ferric and manganic states, respectively, at which they hydrolyze to insoluble products which are readily removed by filtration:

$$Fe^{+2} + O_3 \longrightarrow Fe^{+3} \xrightarrow{H_2O} Fe(OH)_3$$

$$Mn^{+2} + O_3 \longrightarrow Mn^{+4} \xrightarrow{H_2O} Mn(OH)_4 \longrightarrow MnO_2 + 2H_2O$$

Rozelle *et al*. (1968) first compared the use of oxygen and of ozone for the oxidation of ferrous to ferric iron in mine wastewaters. For complete hydrolysis using oxygen, the pH must be raised to a value of 10; however, ozonation was found to be effective at pH 3, and this would require sufficient neutralizing agent to raise the pH only to between 5 and 7 after ozone treatment, to allow coagulation and precipitation of insoluble iron hydroxide. Thus, limestone requirements would be less as would the amount of sludge produced.

Under an EPA funded program, Bellar, Waide & Steinberg (1970) conducted an engineering design and economic study to evaluate the feasibility of ozone oxidation followed by limestone neutralization of acid mine drainage (AMD). No experimental studies were performed. AMD flows which were considered ranged from 0.25 to 6 mgd and contained ferrous iron concentrations varying from 50 to 1,000 mg/l. Treatment cost values developed are given in Table 25.

In this table the lowest cost values apply to the highest flow rates. These data also assume ozone production of 200 tons/day by a chemonuclear process and ozone packaging (compressed and stored in Freon F-11) and shipment from a centrally located point in the coal fields.

TABLE 25. OZONE/LIMESTONE TREATMENT COSTS FOR ACID MINE DRAINAGES

ferrous iron, mg/l	¢/1,000 gallons
50	9-13
300	18-34
1,000	40-78

* flow variation from 250,000 gpd to 6 mgd

Source: Bellar, Waide & Steinberg, 1970

For a specific case of an AMD containing 150 mg/l of ferrous iron, the conventional aeration/limestone process would cost $0.17/1,000 gal at an investment cost of $350,000. The ozone/limestone process would cost $0.13 to $0.16/1,000 gal and require $280,000 for an on-site ozone/limestone treatment system. The investment cost using ozone produced in a central plant, and including on-site ozone storage equipment would be $184,000.

The investment cost to treat the entire AMD of southwestern Pennsylvania (estimated at 486 mgd) would be $182 million, based on the use of a 200 ton/day central chemonuclear plant generating ozone.

Also under EPA funding Swain & Rozelle (1974, 1975) and Rozelle & Swain (1975) conducted laboratory studies on ozonation of actual acid mine drainage waters. The aeration/lime neutralization method had been found by Rozelle et al. (1968) to be more cost-effective than ozone for removing iron, but ineffective for removing manganese. In order to remove Mn(II) effectively by aeration and lime, one would have to overtreat considerably with lime (Swain & Rozelle, 1975) to precipitate manganous hydroxide.

Ozone was generated from oxygen and the effects of variables on the oxidation rate of Mn(II) with ozone were studied (Swain & Rozelle, 1975) at ozone gas phase concentrations of about 2 mg/l. At pH 7 to 8 the oxidation was about twice as fast as at 3 to 4, but was temperature independent. At the higher pH values, Mn concentrations below 0.1 mg/l were obtained, but only 0.5 mg/l Mn concentrations could be achieved at pH 3 to 4. A minimum concentration was reached, indicating that upon continued oxidation the Mn(IV) was being converted to higher oxidation states which are more soluble. It is well known in European drinking water treatment plants using ozone for iron and manganese oxidation that overdosage with ozone forms soluble permanganate. The European practice is to allow ozonized water to stand 15 to 30 minutes to allow hydrolyzed Fe(III) and Mn(IV) oxides to coagulate and precipitate as well as to allow Mn(VII) to decay back to Mn(IV) by oxidizing dissolved organics (Miller et al., 1978). Filtration through GAC completes the process of reducing permanganate to MnO_2.

Swain & Rozelle (1975) also showed that at pH 1.4 to 2.0, oxidation of Mn(II) to Mn(IV) by ozonation occurred only after all Fe(II) had been ozidized to Fe(III). They also found that chlorine gas will not oxidize Mn(II) at pH 1, 3, 5 or 7. On the other hand, ozone use efficiencies were only 10% in the work described, indicating the necessity for better ozone contactor design.

In later work, Rozelle & Swain (1975) compared ozone, hypochlorite and chlorine gas for oxidation of Mn(II) in acid mine drainage to Mn(IV). Reverse osmosis was shown not to reduce the Mn levels to below 0.05 mg/l (the potable water limit). Chlorine gas at pH 2, 4, 6 and 7.9 showed no significant oxidation of Mn(II).

The experimental ozonation setup included a 500 ml suction flask which contained a bubbler and the sample to be ozonized. The amounts of ozone in the feed gas and in the out-gases from the suction flask were measured, so that the efficiency of ozone use could be determined. Using a single reactor, the ozone use efficiency was found to be only 2 to 3%. Using 5 such reactors in series, the ozone use efficiency rose to 10%. Since ozone use efficiencies greater than 90% are obtained in full-scale ozonation systems for oxidizing iron and manganese in drinking water treatment (Miller et al., 1978), it is apparent that the ozone contacting reported during this work was quite inefficient.

Reaction rates of ozone with Mn(II) at pH 7 to 8 were found to be about 2 to 3 times faster than at pH 3 to 5. In addition, the ozonation reaction was temperature independent over the range 2° to 56°C. There was little difficulty in lowering total Mn levels to below 1 mg/l with ozone at pH 3 to 8, but levels below 0.05 mg/l were obtained only in the more neutral solutions (pH about 7). This is because in the more acid solutions, secondary oxidation of Mn(IV) occurs upon ozonation, probably forming permanganate, Mn(VII).

On the other hand, hypochlorite was not found to cause secondary oxidation of Mn(IV), and thus can be used to reduce Mn concentrations to very low values. The hypochlorite oxidation of manganous ion occurs by the following equation:

$$Mn^{+2} + 2(OCl)^- \longrightarrow Cl_2 + MnO_2$$

Two equations were developed for determining the amounts of ozone required to oxidize Mn in acid mine drainage, as a function of ozone contacting efficiency. Both are based on the following oxidation reaction:

$$Mn^{+2} + O_3 + 2(OH)^- \longrightarrow MnO_2 + O_2 + H_2O$$

To oxidize 1 mg/l of Mn(II) would require 7.2×10^{-6} lbs of ozone, or 8.6×10^{-4} g. Thus the two equations for calculating costs become:

$$(7.2 \times 10^{-6})(\text{gal of AMD})[\text{mg/l of Mn(II)}])/(\text{Efficiency}) = \text{lbs of ozone}$$

$$(8.6 \times 10^{-4})(\text{liters of AMD})[\text{mg/l of Mn(II)}])/(\text{Efficiency}) = \text{g of ozone}$$

NaOCl oxidation requires 2.2×10^{-5} lb or 2.6×10^{-3} g per mg/l of Mn(II), and similar equations are developed. In the Rozelle & Swain (1975) work, the efficiency of use of hypochlorite was at least 60% when 45 mg/l of NaOCl was used, which was much more efficient than the ozonation experiments conducted. Even with these differences in use efficiencies, however, it was concluded that when the acid mine drainages contain more than 2 mg/l of manganese, the ozonation process is less costly than is hypochlorite, depending upon the total volume of discharge to be treated. At manganese concentrations below 2 mg/l, the hypochlorite process is less costly.

Gold Mining

Mathieu (1977) has compiled an excellent summation of the published literature on cyanide oxidation with ozone and has evaluated the potentials of applying ozone to the treatment of Canadian gold mill effluents. A private communication is cited by Mathieu which reports the destruction of one part of cyanide with one part of ozone in treating a sample of bled solution from Giant Yellowknife Mines Ltd. which contained 450 mg/l of cyanide, of which about 220 mg/l were metal-cyanide complexes. Only 2 mg/l, probably in the form of ferricyanide, was left in solution after 20 minutes of ozonation by bubbling, for a decomposition rate of more than 22 mg/l/minute. This value indicates that the ozonation reaction probably is autocatalytic, meaning that reaction of cyanide with ozone catalyzes the reaction of cyanide or cyanate with the oxygen present.

In 1973, the Sumitomo Metal & Mining Co. of Japan reported studies on cyanide-containing wastewaters at their Konomai gold mine. Filtrate from the Merrill press operation was diluted to about 110 mg/l cyanide concentration, and the filtrate also contained Cu = 7.7, Zn = 41.4, Fe = 0.14 and Mn= <0.1 mg/l. The data from 6 ozonation tests on this filtrate are reported in Table 26.

TABLE 26. OZONE TREATMENT OF KONAMAI MINE MERRILL PRESS LIQUID (DILUTED)

pH		CN (mg/l)		Time (min)	CN destruction rate (mg/min)		O_3 (mg/l)	
Initial	Final	Initial	Final		Average	Increment	Added	Absorbed
11.9	11.5	109	65.3	3	14.5	14.5	130	130
11.9	11.1	109	34.9	5	14.8	15.2	215	215
11.9	9.9	109	9.6	7	14.2	12.1	300	300
11.9	9.0	109	0.5	10	10.8	3.6	430	349
11.9	8.7	109	0.3	12	9.1	0.1	515	365
11.9	8.6	109	0.3	15	7.2	0.0	645	400

Source: Sumitomo Metal & Mining Co. (1973)

Mathieu (1977) considers the 99.5% cyanide decomposition obtained in 10 minutes to be particularly encouraging in view of the shortcomings and adverse conditions of ozonation during the tests, namely:

(1) use of a low frequency ozone generator delivering only 1% ozone in air,

(2) use of a conventional ozone diffuser contactor, rather than a spray drier contacting system (see Mathieu, 1975),

(3) lack of pH adjustment to prevent its decrease during reaction to a level at which the reaction rate becomes slow,

(4) lack of UV light to destroy the residual 0.3 mg/l CN present as iron-cyano complexes.

The same is said by Mathieu (1977) about published Russian studies to date. The Russians claim good success in ozone oxidation of cyanide complexes of zinc, copper, nickel and iron in the wastewater from Lemnogorskii, Zodskii and Zyryanovskii dressing plants, but give practically no information on the cost projections and economics of a full-scale application under optimum conditions. For instance, Chernovbrov and Rozinoer (1975) have only this to say about test work on cyanide removal by ozone in the pilot plant at Zodskii:

> "Wastewater from the processing of mixed ore from the Zodskii deposit gave the following analysis (mg/l): Cu - 20, Zn - 40, Ni - 15, Fe - 4 to 8.5, As <0.4, Sb <1.5, Pb - 16 to 20, SCN - 9 to 10, and CN - 70 to 100 (free and bound in complexes). An ozone-oxygen mixture with a pH of 11 to 12 was used for the ozonization (37 to 56 mg/l of ozone). After 10 to 20 minutes there was a complete removal of simple and complex cyanides from the wastewater. By the time 100% dissociation of cyanides was achieved, 90 to 98% of heavy metals (Cu, Zn, Ni, Pb) were removed. Pilot plant experiments at the Zodskii plant have shown that cyanide-containing wastewater treated with ozone can be used for recycling".

The main features of the tests in the USSR appear to be the use of oxygen as the carrying gas, the high concentration of ozone, the presence of transition metal ions (catalyst), and a favorable pH. These conditions probably are responsible for the rapid and complete destruction of all the cyanides. Recent papers by Kvyastkovskii et al. (1975) on the use of catalysts for purification of cyanide-containing wastewaters with ozone and by Bespamyatov et al. (1975) on decomposition of cyanides from wastewaters of a concentration plant by ozonation (with separate use of non-ferrous metals) may go further on optimization and practicability of the ozonation method for purifying mill cyanide-barren effluents. As of this writing, however, translations of these articles had not become available.

Mathieu (1975) described ozonation experiments on synthetic solutions of sodium cyanide and of copper complexed sodium cyanide solutions using the spray drier type of contactor system. In this contacting system, fine bubbles of solution are sprayed into an atmosphere of ozone in air or oxygen. A portable pilot plant capable of treating 2 to 7 gal/minute was employed, which had a series of 3 spray drier contacting units. Contact time in each chamber was about 12 seconds. Two levels of cyanide concentration were tested: 10 mg/l and 100 mg/l. The lower concentration is representative of gold mill tailing pond overflows and the higher concentration is representative of those found in solutions bled from the same type of mill. Cyanide solutions were fed through the pilot unit at 2 gal/min. Ozone was generated in oxygen at the rate of 0.4 g/min.

It was found that 91 to 97% of the cyanide was decomposed in less than 2 minutes of contact with ozone in this type of contacting apparatus, irrespective of the starting cyanide concentration. Additionally, analysis of the ozonates for cyanate showed this material to be absent; therefore, Mathieu (1975) concluded that ozonation converts cyanide past the cyanate stage in the spray type contactor.

Incorporation of an electrocoagulation step prior to ozonation decreased the time required to attain 98% cyanide destruction from 2 to 3 minutes to less than 1 minute. On the other hand, about 4 parts of ozone were required to destroy 1 part of cyanide at initial cyanide concentrations of 10 mg/l. Therefore, several experiments were conducted with electrocoagulation and addition of copper ion as catalyst in attempts to reduce this high ozone/CN ratio required at the lower cyanide concentrations.

Pretreatment by electrocoagulation allowed 98% of the initial cyanide to be decomposed within 36 seconds (on passing through three contact chambers) with or without the presence of copper ions as catalysts. However, cupric ions favored elimination of some cyanide during the electrocoagulation stage, 34.7% of the cyanide being removed in the presence of copper sulfate (1:1 by weight with NaCN) and only 8.1% being removed in its absence. In the first contact stage, ozone was completely utilized and nearly all the cyanide present was destroyed.

Mathieu (1977) also compared the costs for ozonation of cyanide today with the analysis made by Sondak & Dodge (1961). These 1961 authors concluded that the cost for treating 100,000 gpd of copper plating wastewaters (200 mg/l CN) would be nearly twice that of chlorine treatment ($1.27 to $1.38/lb of CN for ozone, versus $0.72/lb of CN for chlorine). Bollyky (1975) determined ozonation costs to be $0.94/lb of CN in 100,000 gpd plating wastes containing 100 mg/l CN. Mathieu (1977) extrapolated cost data developed for ozonation systems by Bowers, Netzer & Norman (1973). Assuming that (1) oxidation with oxygen is cheaper than oxidation with ozone, (2) maximum oxygen losses would be 5% and (3) a conservative ratio of 2.5:1 (ozone/CN) would be required to destroy cyanides, the total cost for ozonation would be lower than $0.80/lb of cyanide decomposed using a 200 lbs/day ozone generation (from oxygen) plant. By using air instead of oxygen, the operating cost would drop to $0.60/lb, but the capital costs would increase from $28,200 to $46,600.

Goldstein (1976) analyzed costs for destruction of 140 lbs of cyanide per day by ozonation and by chlorination. Capital costs for ozonation were $100,000 and were $30,000 for chlorination. Operating costs were $0.74/lb for ozonation (including amortization, interest at 20%, no labor and electricity at 1¢/kwhr), versus $1.94/lb for chlorination (chlorine at 10.25¢/lb and caustic at 6¢/lb). Since the chlorination process is more labor intensive than is ozonation, the total operating costs for ozonation are about 33% of those for chlorination.

The fact that 25 years ago, the cost of ozonation per lb of cyanide decomposed was nearly twice that of chlorination attests to the progress made in ozone technology. However, the higher capital investment required for ozonation still discourages its use for cyanide destruction.

Conclusions

1) Ozonation has been studied for oxidation of iron and manganese in acid mine drainage solutions and has been tested for destruction of cyanide in gold mining wastewaters.

2) In acid mine drainage, ozonation has the technical advantages of being able to oxidize iron and manganese at low pH. Addition of limestone to a pH of 5 to 7 now allows coagulation and precipitation of the metal hydroxides.

3) When acid mine discharges contain more than 2 mg/l of manganese, the ozonation process is less costly; however, when the discharges contain more than 2 mg/l of manganese, oxidation with hypochlorite is less costly than ozonation.

4) In cyanide-containing gold mining wastewaters which also contain copper and zinc (but little iron), 99.5% cyanide decomposition was obtained in 10 minutes of ozonation using a conventional bubbler contactor and without pH adjustment.

5) Synthetic cyanide-containing gold mining wastewaters ozonized using a spray drying type of contactor system showed 91% to 97% cyanide destruction past the cyanate stage in less than 2 minutes of ozonation. Incorporating a prior electrocoagulation step decreased the ozonation time necessary to attain 98% cyanide destruction to 36 seconds in this contacting system.

6) Operating costs for ozonation of cyanide-containing wastewaters to destroy 140 lbs/day of cyanide are lower than for treatment by alkaline chlorination ($0.74/lb of cyanide removed by ozonation vs $1.94/lb by chlorination). However, capital costs for ozonation are higher ($100,000 vs $30,000).

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ORGANIC CHEMICALS

Although there are many published articles dealing with the ozonation of aqueous solutions containing specific organic chemicals, there are very few published accounts of ozonation of actual wastewaters from plants manufacturing organic chemicals. Nevertheless, the chemistries involved in ozonizing pure solutions of specific organic compounds are reasonably similar to those which can be expected when actual wastewaters are ozonized, and so the subject will be reviewed here.

For more details on the chemistry of oxidation of organic materials with ozone, the reader is referred to the proceedings of a workshop on Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, recently published (1978) by the International Ozone Association. The subject of this workshop was identification of organic oxidation products formed upon ozonation and determination of their toxicities (or potential toxicities). In an early presentation at this workshop, Oehlschlaeger (1978) reviewed the known chemistries involved in oxidizing organic compounds with ozone. Most of the published literature on the subject deals with ozonation in non-aqueous solvents, and water and wastewater treatment engineers need to know that non-aqueous chemistry is or is not applicable to reactions which occur in dilute aqueous solution.

By the end of this workshop, it had become quite clear that when organic compounds are ozonized in aqueous solution, their reaction products generally are the same as when the ozonation reactions are carried out in non-aqueous solvents. The same oxidation products have been identified, although in lower concentrations, from ozonations in dilute aqueous solution as from ozonizing more concentrated non-aqueous solutions of the same organic compounds, then quenching the solutions in water. There are exceptions to this general statement, but the conclusion is generally applicable.

For a more detailed discussion of the organic oxidation products formed upon ozonation, the reader is also referred to Section 6 of this report, to Section 12 in "An Assessment of Ozone and Chlorine Dioxide Technologies for the Treatment of Municipal Water Supplies", a Final Report by Miller et al. (1978) to the EPA Water Supply Research Laboratory, EPA 600/2-78-147. Also, Rice & Miller (1977) have discussed the types of organic materials formed when drinking water supplies containing organic materials are ozonized.

A later part of this section, Phenols, contains a detailed discussion of the organic oxidation products obtained upon ozonizing aqueous solutions containing specific phenolic compounds.

Actual Organic Wastewaters

Gregersen (1971) studied color reduction by ozonation of 4 unidentified chemical plant wastewater streams which included (1) a combined wastewater, (2) a process wastewater, (3) an arsenic wastewater and (4) a low pH nitrification process wastewater containing primarily a salicylic acid derivative. In addition, a number of nitro-aromatic compounds in water were ozonized.

The first 2 wastewaters lost considerable color after 10 minutes of ozonation, but the last 2 wastewaters seemed to be unaffected. Some organic carbon was eliminated. Activated carbon was recommended for treating these wastewaters, primarily because the technology needed to design treatment systems already existed. Ozonation followed by biological treatment was selected second, but it was not known to what degree the ozonized organic compounds truly are biodegradable. The process of ozonation followed by biological treatment potentially is less expensive to operate than a GAC column (Gregersen, 1971).

Livke, Velushchak & Plysynk (1972) describe ozonation of wastewaters from caprolactam synthesis at two different Russian chemical plants. Ozonation was applied after biological treatment, both for chemical oxidation and disinfection, then the ozonized effluents were stored in biological ponds prior to reuse as cooling water.

Tables 28 and 29 show the results of ozonation of caprolactam wastewaters at the 2 Russian plants which had received secondary biological treatment. At ozone consumptions of 10 mg/l, "complete clarification" of the wastewaters was obtained. Increasing ozone consumptions to 15 to 25 mg/l provided "complete removal of resins" from the wastewaters as a result of oxidative degradation of the resins to simpler compounds. This is indicated by the fact that during ozonation, the BOD values increased as the COD values declined, and the ratios of BOD:COD changed from 0.1 to 0.5.

TABLE 28. OZONE TREATMENT OF SERVERODONETSK CAPROLACTAM WORKS, BIOLOGICALLY TREATED CAPROLACTAM WASTEWATERS

parameter	after secondary treatment	after ozone treatment ozone consumption (mg/l) 10	15	20
COD (mg O_2/l)	92	82	74	68
BOD (mg/l)	11	13	16	24
BOD-5 (mg O_2/l)	78	30	30	25
DO (mg/l)	5.2	5.0	4.5	4
NH_3 (mg/l)	0.25	0.05	traces	n.d.
nitrites (mg/l)	4.5	4.6	4.8	5.1
nitrates (mg/l)	24	13	9	traces
microbe no. 1 0_3 os/ml	6.2	5.0	3.0	2.4
Coliform titer	0.004	0.04	0.43	0.43

n.d. = not detected

Source: Livke, Velushchak & Plysynk (1972)

TABLE 29. OZONE TREATMENT OF SHCHEKINO CHEMICAL WORKS, BIOLOGICALLY TREATED CAPROLACTAM WASTEWATERS

parameter	after secondary treatment	after ozone treatment				
		ozone consumption (mg/l)				
		5	10	15	20	25
COD (mg O_2/l)	120	106	96	92	56	42
BOD-5 (mg O_2/l)	9.7	13	16	17	22	43
DO, mg/l	3.5	12.8	25.8	26.4	27.0	29.1
NH_3, mg/l	15.9	15.9	15.4	14.7	14.3	13.5
nitrite, mg/l	0.5	0.2	0.11	0.1	none	none
nitrates, mg/l	14.7	14.8	15.3	16.0	16.8	17.4
urea, mg/l	7.3	6.2	4.9	none	none	none
caprolactam, mg/l	2.8	1.2	0.9	0.5	none	none
hydroxylamine, mg/l	0.9	0.1	none	none	none	none
cyclohexanol, mg/l	0.7	0.5	none	none	none	none
Microbe no, 1 0_3 os/ml	30	22	4	1.5	none	none
Coliform titer	0.004	0.004	0.04	0.43	4.3	4.3

Source: Livke, Velushchak & Plysynk, 1972

These authors concluded that the cost of ozonizing biologically treated caprolactam wastewaters, producing water that can be reused in place of river or well waters for plant purposes, is about 15% of the cost of the biological treatment. The ozone contactor off-gases should be recirculated to provide these results, as should used oxygen (if ozone is generated from oxygen).

Kanebo Ltd. and the Japan Organo Co. announced on March 22, 1973 the joint development of a treatment process for colored wastewater using ozonation followed by powdered activated carbon. The process is installed at a chemical plant of Kanebo in the Nagahama factory (Shiga Prefecture). Wastewater is treated to an almost colorless clean water, containing less than 50 mg/l of BOD and COD. The process is reported to have the advantages of : (1) excellent decolorization and no foaming during treatment due to quick decomposition of surfactants, (2) decomposition of phenols, (3) no sludge production, (4) less installation space, (5) automatic operation and (6) lower running costs. No published technical account of this plant has been found as yet, however, to be able to evaluate performance and cost data.

Lapidot (1975) describes pilot studies on the ozonation of wastewaters from a major chemical plant manufacturing silicones. Ozone was generated from oxygen, and contactor off-gases were passed through a catalytic burner to prevent the buildup of flammables, then through 2-stage drying prior to recycling to the ozone generator. A value of 3.75 lbs of ozone was found to remove each lb of total oxygen demand (TOD) of the wastewater (with 25% losses), and an engineering estimate was made of the costs for utilizing ozonation to remove 1,000 lbs/day of TOD at this plant at the rate of 2,000 gal/minute. This would require 3,750 lbs/day of ozone generation capacity.

Assuming 10-yrs amortization, 1.8¢/lb for oxygen, 1¢/kwhr for power and 100% ozone use efficiency, the total costs for ozonation were determined to be $253,000/yr, or $0.72 to remove each lb of TOD by ozonation ($0.25/1,000 gal treated). This cost was considered excessive, and the project was abandoned.

Prengle, Mauk, Legan & Hewes (1975) reported the use of ozone in combination with UV light at an unidentified plant which treats wastewater first by secondary biological treatment, then by activated carbon adsorption. A 1 mgd wastewater stream contains 10 mg/l TOC which must be lowered to less than 0.1 mg/l. The organics in the wastewater are not identified, but are referred to as "potentially toxic, refractory organic compounds remaining after secondary treatment and carbon adsorption". The influent stream from the previous treatment units is flow controlled to a multistage ozone/UV reaction unit (described in Section 4) where the organic compounds undergo oxidation to CO_2 and water. Ozone is generated from dried air, its concentration is adjusted automatically by an effluent monitor, and the installed cost of the entire ozone/UV facility was $505,000.

Davis, Magee, Stein & Adams (1976) ozonized wastewaters from the production of several alkyl amines using a submerged turbine contactor. Pertinent data are given in Table 30. Parameters of primary interest were the COD and TOC concentrations. Residual COD of the isobutyl amine wastewater <u>increased</u> during the first two hours of ozonation, indicating structural <u>alteration</u> of some of the wastewater components, but then dropped to about 33% of the original content after an additional two hours of ozonation. Thus a relatively high ozone utilization rate will be required to substantially reduce the organic content of these wastewaters.

These authors also ozonized a wastewater generated from a synthetic organic chemicals plant manufacturing chelating agents. Ozonation was tested for removing COD, nitrogen and cyanide compounds after biological pretreatment. A net increase in ammonia-N was observed under acid conditions, probably due to degradation of organic nitrogen compounds to ammonia. At a pH of 8.8, removal of ammonia by ozonation was very low. Ozonation appeared to <u>increase</u> the free cyanide content, and this behavior was ascribed to ozone decomposition of complexing agents containing cyanide moieties. Finally, ozonation had little effect on the COD of the wastewater before biological treatment, but significantly decreased the COD of biologically treated wastewater (Table 31).

Finally, Davis <u>et al</u>. (1976) ozonized a wastewater generated in an organic chemicals plant producing organic dyes and resins. The purpose of ozonation was to remove color. For the raw wastewater, ozonation generally decreased the total and soluble TOC and BOD, but increased the volatile suspended solids concentration. This means that ozonation precipitated and coagulated soluble wastewater constituents.

TABLE 30. SUMMARY OF BATCH OZONATION RESULTS FOR ORGANIC CHEMICALS INTERMEDIATE WASTEWATERS

Wastewater	Influent Ozone (mg/l-min)	Reaction Time (min)	Effluent pH	Effluent Adj pH	Effluent Ozone (mg/l-min)	Effluent COD (mg/l)	Effluent TOC (mg/l)
Isobutyl Amine	39.0	0	7.6(a)	--	2.0	1,000	800
	39.0	15	7.6	--	0.8	1,300	770
	39.0	30	7.6	--	0.8	1,500	740
	39.0	60	7.6	--	0.5	1,600	690
	39.0	120	7.6	--	3.8	1,180	420
	39.0	240	7.6	--	14.1	360	180
Isopropyl Amine	39.0	0	8.8	--	0.6	9,250	--
	39.0	15	6.6	--	6.0	9,290	--
	39.0	30	5.8	--	8.6	9,210	--
	39.0	60	3.8	--	16.6	8,050	--
	39.0	120	2.8	--	--	7,760	--
	39.0	240	2.5	--	32.1	6,080	--
Isopropyl Amine (Pretreated)(b)	39.5	0	8.0	--	1.3	6,820	1,920
	39.5	15	7.0	--	3.2	8,370	1,920
	39.5	30	5.5	9.5	6.7	7,830	1,890
	39.5	60	5.2	10.7	7.3	6,940	1,820
	39.5	120	4.6	9.5	12.3	5,780	1,610
	39.5	420	4.3	--	16.6	4,800	1,320

(a) pH maintained at 7.6

(b) Activated sludge pretreatment.

Source: Davis et al. (1976)

TABLE 31. SUMMARY OF COD REMOVAL FROM A CHELATING COMPOUND PLANT WASTEWATER

	Run No. 1 (b)		Run No. 2 (c)		Run No. 3 (d)	
Time (min)	Raw	Biologically Pretreated	Raw	Biologically Pretreated	Raw	Biologically Pretreated
0	8,340	--	8,340	4,620	8,340	--
15	8,650	3,500	--	3,630	8,740	4,340
30	8,340	--	8,200	3,670	8,900	4,030
60	7,930	3,140	8,270	3,580	8,820	3,950
120	--	--	--	--	8,670	--
240	7,680	1,800	--	1,680	--	--

(a) Values shown are total COD concentration in mg/l.
(b) pH adjusted to 6.0.
(c) pH not adjusted ≈ 8.0.
(d) pH adjusted to 11.0.

Source: Davis *et al*. (1976)

Biologically treated wastewater from the dye and resin plant was ozonized with dosages up to 626 mg/l (Table 32). Only marginal changes in TOC content were observed, but approximately linear increases in BOD (up to 2,900%) were found with ozone doses of up to 200 mg/l.

Laboratory Studies

Polynuclear Aromatic Hydrocarbons (PAH)--

Il'nitsky, Khesina, Cherkinsky & Shabad (1968) ozonized water solutions of 3,4-benzpyrene, 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, pyrene and 9,10-dimethyl-1,2-benzanthracene and showed that all these compounds were destroyed. 3,4-Benzpyrene was the most ozone-resistant, and the last named compound showed the least ozone resistance.

Il'nitsky (1969) showed that the concentration of 3,4-benzpyrene was reduced about 200 times after 5 minutes of ozonation, and that it could no longer be detected after 7.5 minutes of ozonation. The starting concentrations of BP in water were 0.038 to 1.2 mg/l, and ozonation conditions were those generally used in treating drinking water (1 to 3 mg/l dosage; contact time 5 to 10 minutes).

Reichert (1969) and Il'nitsky & Khesina (1969) showed that 3,4-benzpyrene concentrations of 1 to 100 μg/l in double distilled water are more than 99% decomposed in 30 minutes ozonation time with ozone dosages of 0.5 to 1.5 mg/l. However, incorporation of natural materials, which can adsorb the 3,4-benzpyrene, into the waters will lengthen the required ozonation time to achieve the same degree of decomposition.

Sforzolini *et al*. (1974a; 1974b) studied the chlorination and ozonation of pyrene, 1,2-benzanthracene, 3,4-benzpyrene, 3,4-benzofluoroanthene and

TABLE 32. OZONATION RESULTS FOR TREATMENT OF A FILTERED, BIOLOGICALLY PRETREATED WASTEWATER FROM A RESIN AND DYE PLANT

Ozone Applied	TOC (mg/l)				Change in TOC (a)		BOD (mg/l)				Change in BOD		Solids (mg/l)				Change in Solids (a)	
	Inf		Eff		%		Inf		Eff		%		Inf		Eff		%	
(mg O_3/l)	Tot	Sol	Tot	Sol	Tot	Sol	Tot	Sol	Tot	Sol	Tot	Sol	SS	VSS	SS	VSS	SS	VSS
40	134	137	154	144	14.9	-5.1	13	6	23	17	-76.9	-183	41	16	45	23	-9.8	-43.8
88	136	126	129	120	5.1	4.8	13	7	30	23	-131	-229	75	26	48	25	36.0	3.8
98	146	144	169	147	-15.8	-2.1	7	2	27	23	-286	-1,050	39	36	40	32	2.6	11.1
106	139	134	140	131	-0.7	2.2	11	5	26	25	-136	-400	27	11	20	10	25.9	9.1
187	129	119	149	116	-15.5	2.5	12	5	34	27	-183	-440	46	25	26	13	43.5	48.0
154	137	120	137	135	0.0	-12.5	7	1	30	30	-329	-2,900	25	--	36	27	44.0	--
166	138	126	152	142	-10.1	-12.7	6	4	32	30	-433	-650	45	27	44	29	2.2	-7.4
303	129	120	146	136	13.2	13.3	11	5	41	38	-273	-660	41	20	53	33	-29.3	-65.0
295	128	122	132	128	-3.1	-4.9	13	6	44	38	-238	-533	42	20	33	17	21.4	15.0
356	139	131	139	129	0.0	1.5	10	4	42	38	-320	-850	24	19	53	35	-121	-84.2
626	141	123	93	93	34.0	24.4	7	2	39	36	-457	-1,700	29	12	50	24	-72.4	-100

(a) Negative sign designates an increase upon ozonation

Source: Davis *et al.*, 1976

11,12-benzofluoroanthene. Chlorination produced new peaks observed spectrophotometrically, but ozonation produced no new peaks. Ozonation destroyed 100% of the 3,4-benzopyrene and 11,12-benzofluoranthene, but only major proportions of the other compounds. Variability of results was high in river water samples spiked with the PAH compounds, probably because of adsorption of these compounds onto naturally contained colloidal materials.

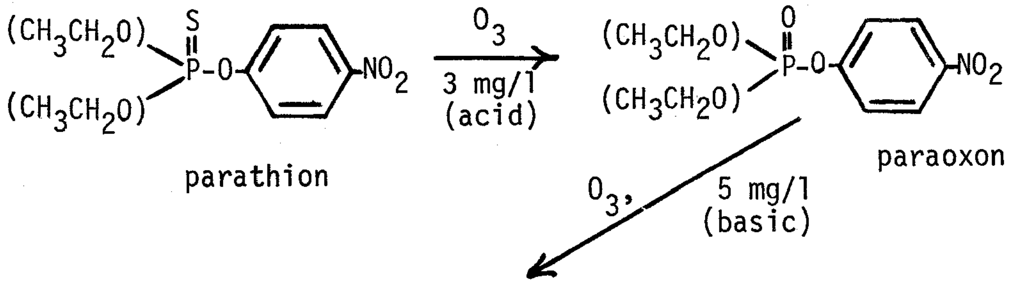
Pesticides--

Buescher, Dougherty & Skrinde (1964) studied the ozonation of aqueous solutions of lindane, aldrin and dieldrin. Ozonation markedly affected the lindane concentration, but did not remove it completely. Aldrin was completely removed by ozonation. Dieldrin was 90% removed by a combination of air stripping and ozonation.

Robeck, Dostal, Cohen & Kreissl (1965) ozonized aqueous solutions of lindane, dieldrin, DDT and parathion and found that dosages of 10 to 38 mg/l of ozone were required to destroy these pesticides to levels acceptable for drinking water. These dosages were considered to be too high to be practical. These authors also concluded that the more usual drinking water treatment plant ozone dosages of 1 to 2 mg/l probably would oxidize parathion to paraoxon, a compound which is more toxic than is parathion.

Gabovich & Kurinnyi (1966) showed that ozone actively oxidizes such organophosphorus pesticides as carbophos, methaphos, M-81 and trichloromethaphos-3. Using 26 mg/l doses of ozone, it was possible to completely disintegrate 10 mg/l concentrations of carbophos, and with net 8 to 10 mg/l doses of ozone, initial 10 mg/l concentrations of trichloromethaphos-3, methaphos and M-81 were reduced in value to 0.7, 0.1 and 0.0 mg/l, respectively

Richard & Brenner (1978) confirmed that ozonation of parathion with 3 mg/l ozone dosage does form paraoxon, a more toxic material than parathion itself. The reaction proceeds fastest in acid medium. Continued ozonation of paraoxon (5 mg/l ozone dosage) proceeds slower, with destruction of paraoxon and formation of 2,4-dinitrophenol, picric acid, H_2SO_4 and H_3PO_4:



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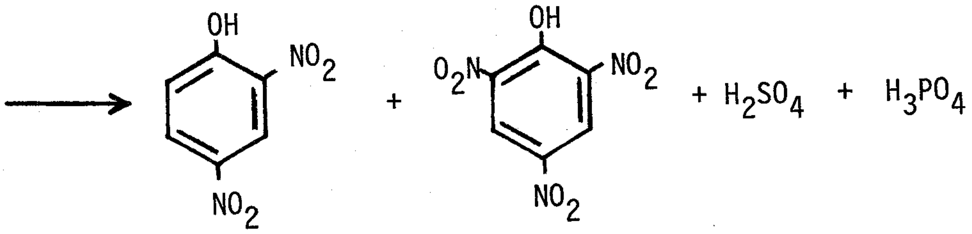
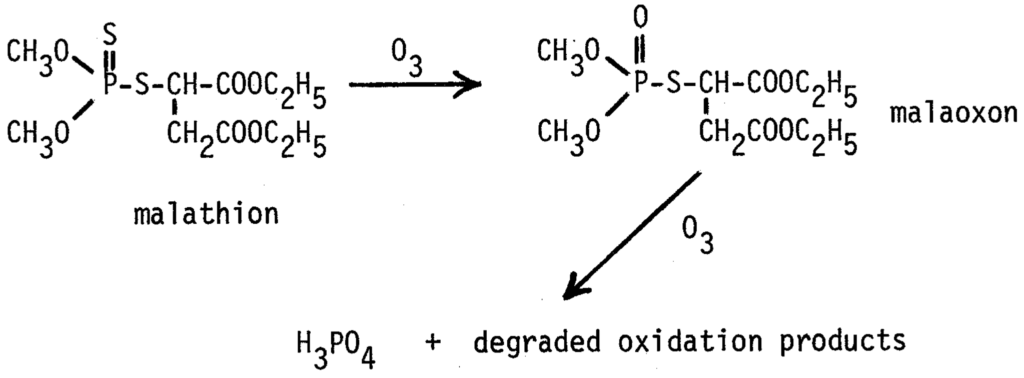
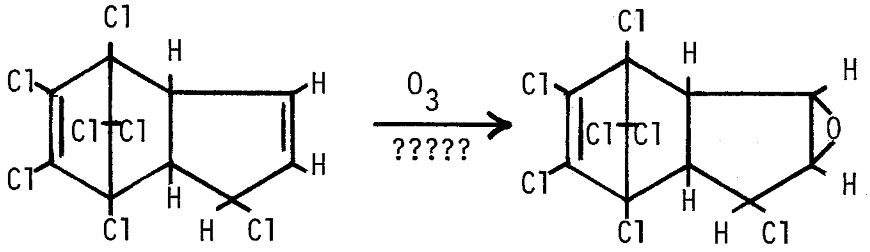


Similarly, Richard & Brener (1978) ozonized malathion and isolated malaoxon as the first stage intermediate. Continued ozonation destroyed the malathion, producing H_3PO_4 and unidentified, degraded organic compounds.



It is apparent, therefore, that under-ozonation of some organic materials can produce other organic materials that are toxic. It is therefore critical to know the chemical content of waters to be treated with ozone (or any other oxidant) so that sufficient oxidant dosages can be provided.

Hoffmann & Eichelsdörfer (1971) dissolved various pesticides in hexane or acetone, then diluted with water to make aqueous solutions as high as 2 mg/l in pesticide concentrations. These were ozonized over 45 minutes with total ozone dosages of up to 240 mg/l. At these dosages, aldrin and heptachlor were "quantitatively" destroyed, but oxidation products were not identified. On the other hand, solutions of dieldrin, heptachlorepoxide, chlordane, lindane, DDT and endosulfan were hardly affected by ozonation at all. This raises the question as to whether the ozonation of heptachlor produces heptachlor epoxide. If so, the epoxide will be stable to further ozonation and is a toxic material. Neal (1978) has advised that experiments conducted in his laboratories have confirmed that ozonation of aqueous solutions of heptachlor produced heptachlorepoxide.

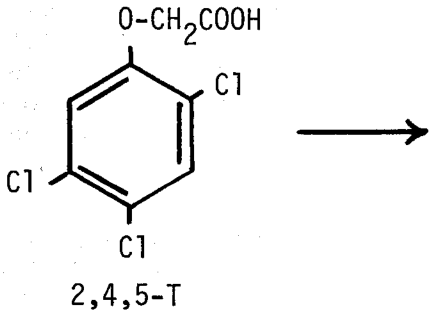


heptachlor heptachlorepoxide

Mallevialle, Laval, LeFebvre & Rousseau (1978) ozonized aqueous solutions of aldrin, and found this compound to be easily degraded by ozone. On the other hand, when aldrin was added to aqueous solutions containing humic acids, 0.45 µg/l of aldrin was detected even after 10 minutes of ozonation. These researchers concluded that ozonation studies on organic compounds conducted in pure solutions can be misleading. It is necessary to know the humics or soils content of water to be ozonized, since these materials can adsorb dissolved organics and thereby "protect" them from the oxidizing action of ozone.

Prengle & Mauk (1978) showed that ozonation of DDT in water proceeds very slowly, but the oxidation rate is accelerated by combining UV radiation with ozonation.

Weil, Struif & Quentin (1977) ozonized 0.0001M solutions of 2,4,5-T with 0.048 mole/hr of ozone and identified oxalic acid, glycolic acid, dichloromaleic acid, chloride ion and CO_2 as oxidation products. No ozonides or polymeric peroxides could be found. The concentration of dichloromaleic acid peaked after 8 to 9 minutes, that of glycolic acid peaked after 12 minutes and that of oxalic acid peaked after 20 minutes of ozonation, after which the concentrations of all three intermediate products decreased with time of ozonation. The concentration of dichloromaleic acid became zero in 25 minutes:



2,4,5-T

$HOOC\text{-}\underset{Cl}{C}H\text{-}\underset{Cl}{C}H\text{-}COOH$ peaked in 8 to 9 minutes

+ $HOOC\text{-}CH_2OH$ peaked in 12 minutes

+ $HOOC\text{-}COOH$ peaked in 20 minutes

+ $Cl^- + CO_2$

Miscellaneous Organic Chemicals--

Rogozhkin (1970) ozonized wastewaters containing dimethylamine in an alkaline medium and concluded that this amine is oxidized to formaldehyde, formic acid, CO_2, nitrites and nitrates.

Kandzas et al. (1970) ozonized 50 mg/l concentrations of cyclohexane in water for 90 minutes of ozonation at pH 11.5 to 12.5. The COD value was reduced from 120 mg/l to 5.95 mg/l (in the case of pH 11.5) and to 13 mg/l (in the case of pH 12.5), and almost complete oxidation to CO_2 was attained with 5 to 7 mg of ozone/mg of cyclohexane.

Krasnov, Pakul & Kirillova (1974) studied the ozonation of aliphatic alcohols, using ethanol as the model compound. Ozonized air was cleansed of nitrogen oxides by passing through a dilute alkali absorber before entering the ozone contact chamber. Ethanol, butanol and octanol gave acids (through aldehyde intermediates), the rate of oxidation increasing with increasing pH. Secondary alcohols produced acids, forming ketones as intermediates. Hydrogen peroxide was produced as a by-product of the decomposition of the intermediates. Formation of acids upon ozonation was considered to be more environmentally acceptable than discharge of alcohols, since acids are more readily biodegradable.

Tencza & Sierka (1975) studied the ozonation of aqueous solutions of butyric acid, which was easier to oxidize than butyl or isobutyl alcohols, methyl ethyl ketone or butyraldehyde. Oxidation was faster with increasing ozone concentrations in oxygen (fastest at 5.67 wt %), with increasing temperature and with increasing pH (fastest at 12.0).

Organo-Nitrogen Compounds--

Somiya, Yamada & Goda (1977) studied the ozonation of aqueous solutions of organo-nitrogen compounds such as amino acids, proteins, ethylamine and urea. Ozone was generated from oxygen and applied at 20°C through a porous diffuser contactor chamber 100 cm high and 5 cm in diameter. Off-gases were analyzed for excess ozone. Solutions 0.05 mM in nitrogen compound (1 liter) and buffered with 1/30M phosphate or 0.02M carbonate were ozonized 30 to 60 minutes. Samples were analyzed periodically for the starting compound, nitrite, nitrate, pH, TOC and alkalinity.

Ozonation of 0.2, 0.5, 1 and 2 mM/l solutions of glycine (H_2NCH_2COOH) at pH 5 produced ammonia, nitrite (in very small amounts and as an intermediate only) and nitrate. The concentrations of ammonia and nitrate increased during ozonation, and it was concluded that both are formed initially and simultaneously during ozonation, then the ammonia is oxidized to nitrate, but only above pH 7. No hydroxylamine ($HONH_2$) was detected during these ozonation studies. At the higher concentrations, most of the applied ozone was utilized for oxidizing the carbonaceous chain, rather than for oxidation of ammonia.

During ozonation of the aliphatic amino acids glycine, leucine, isoleucine and glutamic acid, increasing the pH from 5 to 10 linearly increased the rate of formation of ammonia. About 90% of the nitrogen in the starting aliphatic amino acids was detected as ammonia and nitrite ion after 40 minutes of ozonation. With aromatic amino acids, the rate of ammonia formation was independent of pH, and only 50% of the nitrogen was detected as ammonia and nitrite after 40 minutes of ozonation.

Solutions of aromatic amino acids containing side chains gave varied rates of TOC concentration decreases. With tryptophan and glutamic acid, the carbon was easily oxidized by ozone and the rate was independent of pH. With aromatic amino acids, only 50% decreases in TOC were observed during the ozonation period. Aliphatic amino acids decomposed rapidly during the initial stages of ozonation with increasing pH, but these rates slowed drastically during the later stages of ozonation, even at high pH. In general, TOC levels were lowered the most in neutral solutions after 40 minutes of ozonation.

Oxidative decomposition rates of ethylamine upon ozonation were one-half those of glycine (which contains the same number of carbon atoms) and these rates increased with increasing pH.

Ozonation of an aqueous solution containing 50 mg of a protein, bovine serum albumin, was found to be independent of pH. Nitrate was detected in the ozonate, but only 10% of the starting nitrogen was found as nitrate ion after 40 minutes of ozonation.

Urea was not appreciably oxidized with ozone at pH 6.1, 7.8 or 9.6.

Ozone/UV Studies

A general discussion of this technology already has been given in Section 4. Specific applications also were discussed earlier in this section under Hospitals. Others will be discussed at this point and later in this section under Photoprocessing.

Prengle, Hewes & Mauk (1976) discuss the treatment of refractory organic compounds, such as ethanol, acetic acid, glycine, glycerol and palmitic acid, with ozone/UV in a multistage reactor. The addition of UV radiation during ozonation increased oxidation rates for these compounds 100 to 1,000 fold. Ethanol was oxidized to acetaldehyde, then to acetic acid, then to CO_2.

Fochtman & Huff (1976) ozonized wastewaters containing small amounts of trinitrotoluene (TNT) in the presence of UV light. About 85% of the carbon lost from solution was isolated as CO_2, and the ozone utilization was 12 lbs/lb of carbon removed. The initial TOC of 63 mg/l decreased to 56 mg/l using ozonation alone for 3.5 hrs. With concurrently applied UV, the TOC decreased to 17 mg/l in 2 hrs.

Farrell _et al_. (1977) reported studies leading to the design of a 5,000 gpd pink-water pilot plant using ozone/UV treatment technology. Pink water is a wastewater from TNT manufacturing, and contains TNT plus dinitrotoluenes as its major contaminants. This 5,000 gpd pilot plant is said to be capable of being scaled up to a 100,000 gpd plant simply by adding modules.

Engineering data were gathered by Farrell et al. (1977) using a 1,000 gpd pilot test unit after bench-scale tests using a 5-stage, 25 gal reactor in which water flow alternated cocurrently, then countercurrently, to the direction of the rising ozone bubbles. Each of the 6 ozonation stages also contained five 40-watt UV lamps and ozone was introduced in equal amounts to each reactor chamber through two spargers per stage. Wastewater could be exposed to ozone and to UV radiation simultaneously. This pilot test unit was 15 inches x 15 inches x 30 inches high.

Levels of 54 mg/l TNT in tap water (analyzing 20 mg/l TOC) could be lowered to below 1 mg/l TOC at a 16/1 ratio of ozone/TOC in 95 minutes of ozone/UV treatment using 2 reactor stages which contained 3 UV lamps in the first stage and one in the second; the ozone concentration was 1.4% in oxygen. The initial pH was 7.6 and the operating temperature was 31°C. Repeating this experiment with actual pink water (10 mg/l initial TOC, pH 9, operating temperature 25°C) gave less than 1 mg/l of TOC in 86 minutes of treatment at an applied ozone/TOC ratio of 18.8/1 and using 1.3% ozone in oxygen.

The 1,000 gpd pilot test unit was 28 inches wide, 45 inches long and 45 inches high and contained 6 chambers, which held up to 30, SL36G low pressure UV lamps and porous diffusers to allow introduction of ozone into each chamber. Water flow also alternated cocurrently then countercurrently. Pink water flow rates were varied between 0.2 and 2 gpm, allowing retention times to be varied from 37 to 375 minutes in the reactor. The pink water to be tested contained 140 mg/l of TNT, 72 mg/l of RDX (a reaction product of hexamethylenetetramine and fuming nitric acid, also called "cyclonite"), 10 mg/l of wax and 68 mg/l of TOC. Therefore, for initial screening a synthetic TNT solution was prepared at 140 mg/l concentration. At this high level, undissolved TNT was present in the mixture, but this dissolved and reacted as oxidation progressed.

This synthetic TNT mixture was treated using 2% ozone in oxygen at a feed rate of 1 g of ozone/minute and 29 UV lamps were turned on in the reactor. A TOC value of 4 mg/l was obtained after a residence time of 140 minutes. Further testing of 140 mg/l TNT solutions showed that TOC levels of 5 to 10 mg/l could be obtained in the first 3 reactor stages using 9 to 13 UV lamps and residence times of 118 minutes. In order to lower the TOC level further (to 1 to 3 mg/l), 9 to 14 UV lamps were necessary in the last 3 stages and an additional 118 minutes of residence time also was required.

Actual pink waters showed greater resistances to oxidation in the 1,000 gpd test unit than did solutions of TNT in water. The TOC of pink water was lowered only to 17 mg/l after 240 minutes of residence time and the number of UV lamps used had to be increased.

Results obtained in the 1,000 gpd reactor on actual pink waters are summarized in Table 33. Less than 1 mg/l each of TNT and RDX remained in all effluent samples analyzed. On a volume basis and starting with a TOC level of 70 mg/l, the ozone requirement to obtain these results is 910 mg/l and the UV requirement is 770 watts/l. Theoretically, assuming no reaction of the oxygen carrier gas with the organic components, the amount of ozone required to oxidize all organic carbon to CO_2 and water is 813 mg/l. Thus, the stoichiometric requirement of ozone/TOC was 1.12/1, or, the ozone use efficiency was 89.3%.

Engineering analyses of the data obtained in the 1,000 gpd pilot test unit were performed to derive design and operating parameters for a 5,000 gpd (18.9 cu m/day) larger pilot test unit. These parameters are listed in Table 34. Estimated installed capital costs ($97,255) for this size ozone/UV reactor system are detailed in Table 35. Operating costs will include 600 kwhrs of electrical power/24 hrs of operation plus 2 hrs of supervisory and 6 to 8 hrs of technician time for each 8-hr shift.

For a 100,000 gpd ozone/UV system based on the results of Farrell *et al.* (1977) and for pink water assuming an optimum ozone requirement of 800 mg/l, the total ozone generating capacity required will be 660 lbs (302 kg)/day. An ozone/UV unit using this amount of ozone is said to be capable of being constructed from 15 modules, each 5,000 gpd in size, if the optimum residence time is 150 minutes. This size system will require 1,080 UV lamps and will involve $962,500 installed capital cost and an annual operating cost of $91,300 ($2.61/gal), based on 350 days of operation/yr. The operating expenses are comprised of $48,200 power cost for ozone generation (@ $0.02/-kwhr), $12,400 UV light power cost plus $30,700 maintenance, of which 70% is for UV lamp replacement.

Polychlorinated Biphenyls (PCBs)

The combination of ozone with UV radiation has been specified by EPA as BPTCA for treating wastewaters which contain PCBs. Based upon work performed for EPA by Versar, Inc. (1976) at Houston Research and at Westgate Research, EPA has adopted the use of ozone/UV for treating wastewaters containing PCBs. At Houston Research, a 1,000 mg/l solution of Arachlor 1254 in methanol was employed to prepare a 514 ppb aqueous solution. Ozone (2% in oxygen) was sparged into 21 liters of this solution at 3 l/min. At the same time, a high pressure, 650-watt mercury UV bulb generating 253.7 nm radiation was present in the reaction flask. In 1 hr, about 67% of the PCBs had been decomposed; in 3 hrs, only 7% of the PCBs remained; in 4 to 5 hrs, nearly complete destruction to CO_2 and water had occurred.

At Westgate Research, a 3-liter reactor was used with the same UV energy, and ozone was fed into the 200 ppb PCB solution at the rate of 3.4 l/min of 1.4% ozone in oxygen. More than 99% of the PCBs was destroyed in 4 hrs of exposure to ozone/UV, and the final PCB concentration in solution was about 1 ppb. Both Arochlor 1254 and 1016 were destroyed satisfactorily in this manner. With the more reactive Arochlor 1016, the initial concentration

TABLE 33. UV/OZONATION OF PINK WATER*

Parameters	Test Number		
	1	2	3
Residence time (min)			
Stages 1, 2 & 3	118	177	177
Stages 4, 5 & 6	118	177	177
Weight % ozone	2.2	2.1	1.8
Ozone mass flow (mg/min)			
Stages 1, 2 & 3	850	942	721
Stages 4, 5 & 6	850	942	721
TOA at steady state (mg/l)			
Influent	68	67	70
After 3 reaction stages	22	6.5	5
After 6 reaction stages	17	5	3
No. of UV lamps/stage			
Stage 1	5	5	5
2	5	5	5
3	3	5	5
4	3	4	4
5	3	4	5
6	3	3	5
Average pH value			
Influent	6.2	6.2	6.2
Effluent	3.8	3.8	3.8
Average effluent temperature (°F)	85	86	86
Ozone/TOC mass ratio (mg/mg)			
Stages 1, 2 & 3	10	18	13
Stages 4, 5 & 6	32	181	180
UV/TOC input, watts/mg			
Stages 1, 2 & 3	6	11	11
Stages 4, 5 & 6	14	85	140

* containing 140 mg/l TNT, 72 mg/l RDX and 10 mg/l wax

Source: Farrell *et al.*, 1977

TABLE 34. DESIGN & OPERATING PARAMETERS OF PROPOSED 5,000 GPD UV/OZONE REACTOR FOR PINK WATER (TO OBTAIN <1 mg/l TNT + RDX)

Volume :	675 gal (2.6 cu m)
Flow rate :	5,000 gal/day (18.9 cu m/day)
Retention time :	180 minutes
Dimensions :	3 x 6 x 5 ft (0.9 x 1.8 x 1.5 m)
UV lamp specs :	G64T6, 64" long, 0.75" diam. Draws 65 watts. Av UV power output 25.5 watts. Lamp life 7,500 hours
No. of UV lamps :	144
Ozone requirements :	37.5 lbs/day (17 kg/day) at 1 wt % from air
No. of reactor stages:	3 minimum, up to 6

* containing 140 mg/l TNT, 72 mg/l RDX and 10 mg/l wax

Source: Farrell *et al*. 1977

TABLE 35. ESTIMATED INSTALLED COSTS FOR 5,000 GPD UV/OZONE REACTOR FOR PINK WATER

Engineering		
Supervision	$	1,120
Engineering		3,000
Technicians		3,900
Materials		16,000
Outside Services		2,500
Packing & Shipping		2,000
Travel		2,000
Sub-total		30,520
G & A @ 75%		22,890
Fee @ 7.2%		3,845
Ozone Generator (40 lbs/day from O_2		40,000
TOTAL COST	$	97,255

Source: Farrell *et al*. 1977

was 237 ppb. Within 45 minutes of exposure to ozone/UV, the PCB level had dropped to 1 to 2 ppb (99+ % destruction); after 2 hrs the PCB concentration was less than 100 parts per trillion.

Based upon these results, EPA adopted ozone/UV treatment as BPTCA for PCBs for both existing and new sources in February, 1977.

Conclusions

1) Oxidation products of organic materials subjected to ozonation generally are the same whether they are synthesized in aqueous or non-aqueous solvents. The major exception to this statement are those compounds produced when water participates in the reaction itself, such as in hydrolysis of intermediates. This conclusion is important because there is a great deal of published literature regarding the reaction of organic materials with ozone either neat, in non-aqueous solvents or in the gas phase, much more than is available in dilute aqueous solutions.

2) Oxidation of pure organic materials in clean water usually proceeds at faster rates than in wastewaters. Even small amounts of suspended solids can adsorb dissolved organics and increase their apparent resistance to oxidation by ozone.

3) At 2 Russian chemical plants manufacturing caprolactam, ozonation has been applied to the effluents from biological treatment on full scale since 1972. Ozone is used both for chemical oxidation and disinfection, and the ozonized effluents are stored in biological treatment ponds prior to reuse as cooling waters. Complete clarification of the secondary effluents is obtained with ozone consumptions of 10 mg/l. Complete destruction of remaining resins (by converting them to simpler compounds) is obtained with ozone consumptions of 15 to 25 mg/l. Ratios of BOD/COD increase from 0.1 to 0.5 after ozonation at these plants. Costs for ozonizing these biologically treated caprolactam wastewaters are about 15% of the costs for the biological treatments themselves.

4) A Japanese chemical plant installed ozonation followed by powdered activated carbon in 1973. The wastewater is unidentified, but contains surfactants and phenols; ozone is used for decolorizing. The ozonized wastewater is colorless and contains about 50 mg/l of BOD and COD.

5) Ozonation of wastewaters from the manufacture of alkylamines showed an increase of COD content during the first 2 hrs of treatment, followed by a drop to about 33% of the initial value after an additional 2 hrs of ozonation.

6) Ozonation of biologically treated wastewaters from a synthetic organics plant manufacturing chelating agents produced an initial increase in cyanide content -- probably by destruction of the chelating compound. Ozonation of the wastewater before biological treatment had little effect upon COD levels, but ozonation after biological treatment lowered

the COD to about 20% of its initial value after 4 hrs of treatment. The COD level was reduced about 60% during the first 15 minutes of ozonation.

7) Ozonation of wastewaters from an organic dyes and resins manufacturing plant for color removal decreased total soluble BOD and COD, but increased volatile suspended solids. This confirms that ozonation can produce a flocculation effect, and indicates that a filtration step should be considered after ozonation in such cases.

8) Biologically treated effluent from a dye and resin manufacturing plant treated with up to 626 mg/l dosages of ozone showed only marginal changes in TOC levels. However with ozone doses of up to 200 mg/l, BOD levels increased as much as 2,900%. This confirms that ozonation of biorefractory organic materials forms oxidized materials which can be much more biodegradable.

9) In wastewaters, methylamine produces formaldehyde, formic acid, nitrite and nitrate ions and CO_2 upon ozonation. Amino acids produce ammonia, nitrite and nitrate ions. Glycine oxidizes faster with ozone than does ethylamine. Acetic and oxalic acids are quite stable to oxidation with ozone. Cyclohexene oxidizes completely to CO_2 with ozone doses of 5 to 7 mg/l.

10) 3,4-benzopyrene, 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, pyrene and 9,10-dimethyl-1,2-benzanthracene all are destroyed rapidly upon ozonation, with the last compound being the most reactive and the first being the least.

11) The pesticides aldrin, carbophos, M-81, methaphos and heptachlor are completely oxidized to other products upon ozonation. Dieldrin, lindane, trichloromethaphos and 2,4,5-T are about 90% oxidized with ozone. On the other hand, dieldrin, heptachlorepoxide, chlordane, lindane, DDT and endosulfan are hardly affected by ozonation. Combinations of ozone with UV radiation will oxidize these refractory compounds at faster rates.

12) Ozonation of the pesticides parathion and malathion proceeds through the corresponding oxons as intermediates. These are more toxic than the starting thions. Continued ozonation decomposes the oxon intermediates. Thus it is important in designing ozonation systems for chemical oxidation to know as much as possible about the chemistries of the materials to be oxidized.

13) Combining ozone with UV radiation increases the oxidation rates for refractory materials such as ethanol, acetic acid, glycine, glycerol and palmitic acid by 100 to 1,000 times. Oxidation rates of many refractory pesticides and halogenated organic compounds also can be increased by this combination. Ozone/UV has been specified as BPTCA by EPA for PCBs.

14) Ozone/UV treatment systems for pink waters from TNT maunfacturing are being developed under sponsorship of the U.S. Army Armament R&D Command.

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PAINTS AND VARNISHES

Only 4 published papers have been found in this category. Two of these discuss treatment of paint and varnish plant wastewaters with ozone and two deal with treatment of aircraft paint stripping wastewaters (which contain phenols) with ozone.

Paint and Varnish Plant Wastewaters

Ballnus and Leiss (1968) describe a treatment scheme involving ozonation of a paint plant wastewater at pH 12 to 13, which was highly colored and contained 1,100 to 10,400 mg/l BOD-5, 10 to 40 mg/l of phenols, 1,300 to 14,200 mg/l permanganate number and divalent Zn, Pb and Cu ions. The BOD consisted of melamine and acrylate polymers. The raw wastewater was acidified to pH 5.0 with HCl, flocculated with $FeSO_4$ for 1 hr, then treated with lime to pH 10.5, filtered, then then ozonized. This produced a clear, colorless wastewater with the permanganate number now less than 80 mg/l and which could be discharged to the local receiving canal. Chemical costs for this treatment process totalled 0.40 Deitsch Marks (DM)/cu m (20¢/cu m at an exchange rate of 2 DM/$1.00), of which ozonation cost (77 g/cu m) was 0.31 DM, HCl cost (0.7 l/cu m) was 0.06 DM and lime cost (7.4 l/cu m lime water) was 0.03 DM.

Bauch & Burchard (1970) reported rather extensive studies of treatment of a varnish plant wastewater in Wuppertal, Germany (on the Rhine, near Düsseldorf). Wastewaters were preclarified with $FeCl_3$ and/or $Al_2(SO_4)_3$, then neutralized and ozonized. Pertinent data are presented in Table 36. The residue on evaporation was reduced by 210 mg/l (from 2,400), but the residue on ignition remained the same, indicating that ozonation converted about 10% of the organic content to CO_2. In addition, the permanganate oxidizability was lowered significantly (from 1,940 to 340 mg/l), BOD-5 was lowered from 1,400 to 190 mg/l), and concentrations of volatile hydrocarbons, volatile phenols, non-volatile phenols and fats and oils also were reduced significantly by 30 minutes of ozonation (20 mg of ozone/l of air) at 19°C.

Even better results were obtained by Bauch & Burchard (1970) when they pretreated the wastewaters with chlorine, then ozonized. The $KMnO_4$ number was lowered to 120 mg/l and BOD-5 to 80. In Table 37 are presented data showing the same varnish plant wastewaters treated by several techniques. Table 38 shows similar data obtained by treating canal water near the discharge outlet of this paint & varnish plant. Hot and cold aeration without ozonation provided some improvement, but not nearly as much as did ozonation.

Bauch & Burchard (1970) reported that flocculation followed by filtration through activated carbon is acceptable for treating small volumes of paint & varnish wastewaters, but that activated carbon costs were too high for consideration when treating large volumes of these wastewaters. In addition, they stated that the carbon cannot be regenerated, implying that it becomes too fouled. They also stated that treatment with chlorine was not acceptable, due to formation of chlorinated organic materials which interfered with

TABLE 36. TREATMENT OF WASTEWATER FROM A VARNISH PLANT BY GASSING WITH OZONE (20 mg/l) FOR 30 MINUTES AT 19°C

Analytical Parameters	Before treatment	After treatment
Capable of settling after 2 hrs	6 ml/l	6.3 ml/l
Appearance after settling	slightly turbid, yellow	slightly turbid, almost colorless
Odor	intensively of varnish	stale, faintly of varnish
Odor threshold	1:600	1:16
pH value	6.0	5.3
Conductivity in microsec	4,900	4,950
Residue on evapn	2,400 mg/l	2,190 mg/l
Residue on ignition	1,010 mg/l	1,040 mg/l
Chlorides as Cl^-	150 mg/l	155 mg/l
Sulfate as SO_4^{-2}	320.0 mg/l	335 mg/l
Sulfide as H_2S	8.0 mg/l	not traceable
Overall hardness in ° dH	15.6 mg/l	14.2 mg/l
Calcium as CaO	128.0 mg/l	130.0 mg/l
Iron II	20.0 mg/l	not traceable
Iron III	11.0 mg/l	36.0 Mg/l
Zinc as Zn	131.0 mg/l	135.0 mg/l
Lead as Pb	18.0 mg/l	16.0 mg/l
Copper as Cu	3.5 mg/l	3.0 mg/l
Volatile hydrocarbons	140.0 mg/l	20.0 mg/l
Volatile phenols	24.0 mg/l	4.0 mg/l
Nonvolatile phenols	14.0 mg/l	not traceable
Fats and Oils	62.0 mg/l	32.0 mg/l
Oxidizability ($KMnO_4$ consumption)	1,940.0 mg/l	340.0 mg/l
BOD-5	1,400.0 mg/l	190.0 mg/l

Source: Bauch & Burchard, 1970

TABLE 37. WASTEWATER DISCHARGE OF A PAINT & VARNISH PLANT TREATED 25 MINUTES WITH OZONIZED AIR*

	Appearance	Odor	Odor Threshold	$KMnO_4$ Consumption	BOD-5 mg/l	Lead mg/l	Zinc mg/l	Volatile Components mg/l	Fats & Oils mg/l
Untreated sewage after 24 hrs settling	milky turbid, brownish	Intensively of varnish and esters	1:1,000	2,850	1,860	40.0	200	80	98
Sewage acidified with sulfuric acid (pH 3.6) addition: 0.05 g iron as $FeCl_3$ + 0.05 aluminum as $Al_2(SO_4)_3$, neutralized milk of lime up to pH 8.1	clear yellowish	intensively of varnish and esters	1:900	2,800	1,900	--	--	80	15
Clarified sewage gassed cold with air	clear yellowish	intensively of varnish and ester	1:500	2,400	1,600	--	--	30	14
Clarified sewage gassed hot with air	clear yellowish	intensively of varnish, faintly of ester	1:150	1,400	1,050	--	--	15	16
Clarified sewage treated with ozone	clear yellowish	faintly of varnish	1:18	110	180	--	--	--	16
Clarified sewage pretreated with Cl_2, then treated with ozone	clear, strongly yellowish	stale, somewhat of benzene	1:8	120	80	--	--	--	12

* 20 mg ozone/liter of air

Source: Bauch & Burchard, 1970

TABLE 38. WASTEWATER FROM THE CANAL NEAR THE OUTLET OF A PAINT & VARNISH MANUFACTURING PLANT, PRETREATED BY PRECIPITATION AND TREATED WITH OZONE* (30 MINUTES) AND CHLORINE

	Appearance	Odor	Odor Threshold	$KMnO_4$ Consumption mg/l	BOD-5 mg/l	Lead & Zn mg/l	Volatile Portions mg/l	Fats and Oils mg/l
Untreated sewage after 24 hrs settling	milky, turbid	intensively of varnish	1:800	3,850	1,800	114.3	110	80
Sewage acidified to pH 5.0 with sulfuric acid addition: 0.1 g/l iron as $FeCl_3$, precipitated with milk of lime at pH 7.6	clear yellowish	intensively of varnish	1:700	2,900	2,600	traces	70	18
Clarified sewage gassed cold with air	clear yellowish	intensively of varnish	1:500	2,720	2,100	traces	60	16
Clarified sewage gassed hot with air	clear yellowish	intensively of varnish	1:240	1,800	1,400	traces	10	19
Clarified sewage gassed cold with ozonized air	clear, almost colorless	faintly of varnish	1:20	190	260	traces	--	16
Clarified sewage pretreated cold with excess Cl_2, then ozonized air	clear, almost colorless	stale, indefinable	1:4	82	150	traces	--	5

* 20 mg ozone/liter of air

Source: Bauch & Burchard, 1970

later clarification processes in municipal wastewaters treatment plants. However, pretreatment with chlorine before ozonation was justified on the basis that ozone will oxidize any residual chlorine to perchlorate, which itself is a powerful oxidant capable of destroying organic compounds.

Phenolic Aircraft Paint Stripping Wastewaters

Kroop (1975) reported the removal of phenols by ozonation of aircraft paint stripping wastewaters, which generally contain the following components:

Phenols	1,000-3,000 mg/l
Methylene Chloride	1,000-3,000 mg/l
COD	5,000-30,000 mg/l
Chromium	50-200 mg/l
Suspended Solids	100-1,000 mg/l
Oils	100-2,000 mg/l
pH	8.0-8.5

Some 71.5% of the COD is contributed by the phenols.

In batch ozonation experiments on these wastewaters, it was found that 99.7% of the phenol could be destroyed by ozonation, but that COD values were reduced only 57%. Formation of CO_2 was only 10% of that stoichiometrically expected on the basis of phenol being oxidized completely, thus intermediate oxidation products probably are formed which were not detected by the analytical method (4-aminoantipyrine) used to determine phenol. Controlling the initial pH at 11.0 lowered the amount of ozone required to remove phenol to 3.46 moles/mole of phenol (or 1.77 g of ozone/g of phenol). Ozone concentrations were measured in the inlet gas and in the contactor off-gases. Lowering of the COD during the initial 30 minutes of ozonation was shown to be a result of air stripping of the volatile methylene chloride solvent.

Continuous flow ozonations then were conducted in a 2-stage diffuser reactor system at an influent pH of 11.5. Wastewater flowed first to Reactor #1, where it was treated with 40 mg/min of ozone (in air) and all ozone was consumed. Effluent from Reactor #1 then flowed into Reactor #2 along with the off-gases from Reactor #1. An additional 17 mg/min of ozone in air was added to Reactor #2.

Using this 2-stage reactor system, Kroop (1975) found that to attain 99% destruction of phenol (30 mg/l residual phenol) required 200 minutes of ozonation; to attain 3 mg/l residual phenol (99.9% removal) required 300 minutes of ozonation. After 240 minutes of ozonation, even though the residual phenol concentration was below 20 mg/l, the COD was 3,500 mg/l (a 65% reduction in COD value). To attain 99% phenol removal by ozonation required 5.2 moles of ozone/mole of phenol (2.66 g/g); to attain 99.9% phenol removal required 8.0 moles of ozone/mole of phenol (4.50 g/g).

Kroop (1973) reported the capital and operating costs to treat 29,000 gal/day of phenolic aircraft paint stripping wastewater to the two levels of treatment (99% and 99.9%) as follows:

	concn. of residual Phenol	
	20 mg/l	2.0 mg/l
Capital Cost	$389,000	$505,000
Operating Cost	$400/day	$548/day

Conclusions

1) Ozonation of a colored paint and varnish wastewater having a permanganate number of 1,300 to 14,200 and containing melamine and acrylate polymers, phenols, Zn, Pb and Cu produced an effluent having a permanganate number of 80 mg/l and which could be discharged to the environment. Chemical treatment costs totalled 20¢/cu m, of which ozonation costs were 15 to 16¢/cu m.

2) Ozonation of varnish plant wastewaters which had been preclarified with $FeCl_3$ or $Al_2(SO_4)_3$ and neutralized, lowered permanganate numbers from 1,940 to 340 mg/l and BOD-5 from 1,400 to 190 mg/l in 30 minutes. Pretreatment of this wastewater with chlorine allowed permanganate and BOD-5 values of 120 and 80 mg/l, respectively, to be obtained upon ozonation.

3) Aircraft paint stripping wastewaters containing 1,000 to 3,000 mg/l of phenol when ozonized in a 2-stage diffuser reactor produced 99% removal of phenol (to below 30 mg/l) over 200 minutes and required 5.2 moles of ozone per mole of phenol. To attain 99.9% phenol removal (to less than 3 mg/l) required 300 minutes of ozonation (8.0 moles of ozone/mole of phenol).

4) Total capital and operating costs to treat 29,000 gal/day of phenolic aircraft paint stripping wastewaters to phenol levels of 20 and 2.0 mg/l have been estimated to be $400/day and $548/day, respectively.

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PV-02* Bauch, H. & H. Burchard, 1970, "Experiments to Improve Highly Odorous or Harmful Sewage with Ozone", Wasser, Luft & Betrieb, 12(5):289, 292-293.

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* Abstracts of asterisked articles will be found in EPA 600/2-79-   b.

PV-03 Kroop, R.H., 1973, "Treatment of Phenolic Aircraft Paint Stripping Wastewater", USAFWL Rept. 72-181, Jan. 98 pp. U.S. Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico.

PV-04* Kroop, R.H., 1975, "Ozonation of Phenolic Aircraft Paint Stripping Wastewater", in *Proc. First Intl. Symp. on Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, Editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 660-673.

PETROLEUM REFINERIES

Wastewater Characteristics

Table 39 shows the wastewater characteristics from 10 specific petroleum refinery processing steps, as listed by Carnes, Ford & Brady (1973). Typically, refinery BOD and COD is composed of oils, hydrocarbons (saturated and unsaturated), nitrogen-containing organics, phenolics (comprised of phenols, cresols and xylenols), plus sulfides and mercaptans. In addition, ammonia also is present in many refinery wastewaters.

Ozonation Studies on Refinery Effluents

As early as 1951, Murdock studied the ozonation of phenolic and sulfide components of refinery wastewaters containing 470 mg/l of phenols. Treatment with 1500 mg/l of ozone reduced the phenols content to 0 mg/l (at pH 12.0). Prior aeration of this wastewater, followed by pH adjustment to 12.0, reduced the ozone requirement to 1,200 mg/l for the reduction of phenol content to 0 mg/l. The amount of sulfides present in this wastewater is not mentioned, but oxidation of sulfides present will occur before the ozone demand of phenol is satisfied. A detailed discussion of the chemistry observed during the ozonation of phenols is given later in this section under Phenols.

Peppler & Fern (1959) conducted a laboratory ozonation study of refinery wastewaters at the Sarnia, Ontario, Canada refinery of Imperial Oil Ltd. Cat-cracker condensates containing sulfides, mercaptans and phenol were ozonized and it was confirmed that sulfide oxidation proceeds initially to the exclusion of phenol oxidation. Therefore, cat-cracker condensates should be stripped prior to ozonation in order to remove the volatile sulfides. This will reduce the amount of ozone required, since 1 g of H_2S requires about 1.33 g of ozone to be oxidized to sulfate.

Refinery effluent from a biological treatment unit containing 900 ppb of phenols required 345 mg/l of ozone to lower the phenols content to 60 ppb. This corresponds to an ozone consumption of about 400 g of ozone/g of phenol removed. This very high ozone "requirement" can be explained on the basis that the amount of ozone present in the contactor off-gases was not measured. Therefore this was the amount of ozone dosed to the reaction mixture, not the amount consumed.

Comparative costs for phenol removal from refinery effluents were estimated by Peppler & Fern (1959). Costs for steam and flue gas stripping are $0.91/lb of phenol removed, for biological oxidation, $0.24/lb (at the rate of 800 lbs/day of phenol removed) and for ozonation, $0.95 to 1.65/lb of phenol removed. These cost projections are based on an initial cost of 27.3¢/lb for ozone and a phenol ozone demand of 3.6 to 6 lbs of ozone/lb of phenol. The actual ozone demand of the Sarnia refinery sour waters was shown to be in the range of 3.5 to 6 lbs of ozone/lb of phenol removed. This range corresponds well to the range discussed later under Phenolics.

TABLE 39. TYPICAL WASTE LOADINGS FROM REFINERY PROCESSES

TYPICAL TECHNOLOGY

Fundamental Process	Wastewater Characteristics							
	Flow, gal/bbl	pH	BOD lb/bbl	COD lb/bbl	Oil lb/bbl	H_2S lb/bbl	NH_3 lb/bbl	TDS lb/bbl
Crude Desalting	2.1	6.7-9.1	0.003	0.032	0.012	0.008	0.009	0.250
Crude Fractionation	26	8.6	0.0002	.005	0.017	0.001	--	0.035
Catalytic Cracking	15	8.3-9.7	0.015	0.018	0.100	0.036	0.040	0.090
Thermal Cracking	2.0	6.4	0.001	0.003	0.001	0.001	--	--
Hydrocracking	2.0	7.3	0.002	0.045	--	0.002	--	0.002
Hydrotreating	1.0	9.0	0.010	0.050	--	0.002	0.030	0.035
Delayed Coking	1.0	8.8-9.1	--	0.032	0.006	--	--	0.030
Reforming	6.0	7.6	--	0.040	0.050	0.001	--	0.125
Sour Condensates	3.0	4.5-9.5	0.100	0.200	0.100	1.00	0.75	--
Alkylation	60	8.1-12	0.001	0.010	--	0.010	0	0.300

Primary Effluent Quality From Refineries

REFINERY CLASSIFICATION		CONTAMINANTS, mg/l					
	gal/bbl crude throughput	BOD	COD	Oil	TDS	Sulfide	Ammonia-N
A	13	113	-	76	2,980	2	--
B	17	326	956	64	2,380	57	351
C	50	112	332	34	597	21	35
D	90	148	391	46	2,100	21	40

Source: Carnes, Ford & Brady (1973)

Popov (1960) showed that 75 to 80% of the petroleum products present in wastewater could be removed in 16 hrs using ozone generated in air. Aeration alone removed only 60% of these materials during the same time. The remaining materials imparted little odor to the treated wastewater, and 4 to 5-fold dilution removed this completely.

Alekseeva & Karelin (1963) ozonized a refinery wastewater containing soluble petroleum products which they judged to be amenable to treatment only by oxidation. The wastewaters contained 180 to 259 mg/l of BOD, 20 to 50 mg/l of oil residues and 0 mg/l of dissolved oxygen. Ozonation with 1540 g of ozone/hr (in air) produced an effluent containing 2 to 4 mg/l of petroleum residues having a BOD of 8 to 15 mg/l and 1.8 to 2.7% dissolved oxygen. The abstract of this article does not list the time of ozonation, the type of contacting apparatus used, nor how much ozone actually was consumed to give these results.

Malkina (1971) studied the ozone oxidation of demulsifiers present in refinery wastewaters and evaluated the toxicities of the ozonized wastewaters to _Daphnia magna_ (water fleas). The Russian demulsifiers NChK, OP-10 and disolvane-4411 present in the wastewaters at concentrations of up to 50 mg/l were 92 to 99% oxidized upon ozonation. The ozonized wastewaters were not toxic to _Daphnia magna_.

A 1975 article by the Tungfanghung Oil Refinery describes the use of ozonation in the treatment of wastewaters from a refinery in the Peoples Republic of China. After desulfurizing, removal of oil, flotation, biological treatment and aeration, the wastewater now can be "purified to surface water quality" by single stage or 3-stage ozonation. "Good results" also were obtained by ozone treatment of the flotation tank effluent, showing the feasibility of replacing the biological treatment by a chemical method.

Ioakimis _et al_. (1975) studied ozonation of three different refinery wastewater streams: (1) a mixed waste before biological treatment, (2) a contaminated storm-drain effluent and (3) a desalter waste after mechanical treatment. The most effective method of ozonation involved multi-stage contacting, which produced a maximum 60% reduction in COD concentration. When the wastewater streams were ozonized in a countercurrent flow column, the COD and BOD concentrations were found to decrease during all stages of contacting, but the original ratio of BOD/COD hardly changed at all. A first order linear differential equation predicting the ozonation reaction mechanism was tested on a Minsk-22 computer, and confirmed the hypothesis of formation of oxidized intermediates.

Zaidi & Tollefson (1976) studied the physical-chemical treatment of sour gas plant wastewaters using activated carbon, chemical clarification, incineration, steam stripping, chlorine/UV oxidation and ozonation. Treatment by these last 2 techniques "did not appear to be capable of meeting the current wastewater quality standards".

The Trafalgar Plant (near Toronto, Ontario, Canada)--

Dabine (1959) describes the wastewater treatment system which was installed in 1957 at the then Cities Service (now British Petroleum) refinery, located on Lake Ontario, at the city of Trafalgar, which is between Hamilton and Toronto. The initial plant treatment capacity was 20,000 bbls/day, and ozonation was installed as a polishing step to remove phenols, or to reduce their concentrations to a sufficiently low level (0.003 mg/l) so that the city of Bronte, whose drinking water intake is close to the refinery wastewater discharge, would develop no undesireable tastes and odors during potable water treatment, which includes chlorination.

Dabine (1959) describes some of the initial studies on the Trafalgar refinery wastewater treatment system, which includes ozonation as a polishing step for phenol removal. Biological treatment first reduces the phenol concentrations from 55 mg/l to 0.38 mg/l, after which ozonation lowers this level to 0.012 mg/l. At the time this article was written, the suggested local wastewater discharge standard for refinery phenols was 0.015 mg/l. Following ozonation, the original treatment process included addition of 2 mg/l of powdered activated carbon, followed by sand filtration to remove the activated carbon, before discharge to Lake Ontario.

The Trafalgar plant wastewater treatment system was designed to handle 300 gal/minute, but Dabine states that it has handled up to 600 gpm "satisfactorily". Total ozone generating capacity initially installed was 190 lbs/day. Ozonation was chosen over chlorine dioxide treatment for phenol removal because of the lower operating costs for ozonation (although the capital costs would be much higher for ozone generation and contacting than for chlorine dioxide).

In 1962, McPhee & Smith reported on the first 2 years of operation of the Trafalgar refinery wastewater treatment system. The effluent standards set as objectives for the refinery wastewaters were:

Phenolics	less than 20 ppb
Iron	17 mg/l
pH	5.5-10.6
Oil (Total)	15 mg/l
Floating Solids	none
Settlable Solids	none

The Trafalgar refinery installed a 10-step wastewater treatment consisting of:

(1) Stripping of sulfides and ammonia
(2) Separation of oil and tank bottoms
(3) pH adjustment
(4) Temperature adjustment (required because of low temperatures encountered during winter months)
(5) Chemical coagulation and precipitation
(6) 2-Stage biological oxidation
(7) Final settling

(8) Ozonation (for phenols)
(9) Activated carbon adsorption
(10) Filtration through sand

Data reported in this paper by McPhee & Smith were gathered during the summer of 1960, when the wastewater flows averaged 225 Igpm. The phenolic design loading was 200 lbs/day and averaged 56 mg/l in the raw wastewater.

Trafalgar's oil separators operate at 85 to 94% removal efficiencies and the aerated equalization basin converted the phenolic concentrations from a range of 40 to 80 mg/l to constant feeds of about 40 mg/l. Also, the oil concentrations were lowered from a range of 270 to 400 mg/l to 50 to 100 mg/l. Flocculator/clarifier units complete oil separation, lowering its concentration to below 15 mg/l. This also reduces COD from a range of 1,200 to 2,350 mg/l to 240 to 440 mg/l and BOD from 1,600 mg/l to 160 to 260 mg/l. Activated sludge treatment further reduces BOD from an average of 200 mg/l to about 50 mg/l, COD from 400 to 150 mg/l and phenols from 40 to 1 mg/l (in 10 hrs) and to 0.35 mg/l in an additional 3 hrs of activated sludge treatment (13 hrs total).

Wastewater streams fed to the ozonation step contained 0.16 to 0.39 mg/l concentrations of phenols which are oxidized to concentrations of less than 0.003 mg/l. Because the ozonation step meets the effluent discharge standards for phenols, the use of the activated carbon step was discontinued after the first few months of plant startup and after steady state operation had been attained. Rapid sand filtration now is sufficient to remove any turbidity that may be present after ozonation. The treated plant wastewater is said to be "as good as the Lake Ontario raw water", except that the total solids are higher (1,606 mg/l versus 116 to 224 mg/l for the raw lake water). Ozone dosage rates to attain this amount of phenol oxidation are 20 to 40 mg/l, and the diffuser contactors provide a total detention time of 80 minutes.

Hoffman et al. (1973) describe a computerized simulation program for the Trafalgar wastewater treatment process at steady state operation. Using operational plant data obtained since 1960, zero or first order kinetics were assumed and plug flow or continuous stirred reactor hypotheses were assumed. A first order reaction combined with a plug flow reactor gave the most consistent results.

In 1977, the Trafalgar plant was visited by EPA Effluent Guidelines officials (Schafer, 1977). Because of a process upset, these visitors were not allowed into the plant. The plant originally was a 20,000 bbls/day refinery, but today is an 80,000 bbls/day plant. Plant officials confirmed the discontinuance of powdered activated carbon after ozonation for phenols oxidation, but also the discontinuance of the following sand filter as well. This had been installed originally to filter activated carbon and prevent it from being discharged into the lake.

Current ozonation capacity at Trafalgar is 120 lbs/day, provided by 4 individual ozone generating units. Ozone contactors are 14 ft x 20 ft, epoxy-lined stainless steel vessels, normally fed 50% of the 550 to 650 Igpm biologically treated effluent. The installed cost of ozonation in 1958 was $150,000. The maintenance costs for ozonation today are $40/lb of phenol removed by ozonation, and the normal operating cost is $12/lb of phenol removed. These costs are based upon 550 Igpm being fed to ozonation step.

It should be realized that with an influent phenol concentration of 30 to 100 ppb and an ozonation effluent concentration of 10 to 20 ppb, no more than 0.25 lb/day of phenol is being removed by ozonation at this plant. Therefore, 1 lb of phenol requires 4 days of ozonation at Trafalgar. The seemingly high operating cost of $12/lb is not unreasonable on this basis. For comparison, see Eisenhauer (1971) later in this section under Phenols, who estimates that at an ozone cost of 7¢/lb, the cost to obtain 98% removal of phenol by ozonation is 18¢/lb (1971 Canadian dollars).

Trafalgar plant personnel reported (Schafer, 1977) that reliable operation of the ozone generators at this plant "is very difficult" and depends upon obtaining uniform cooling of the stainless steel generator tubes as well as upon absolute control of the inlet air (to the ozone generator) at a -60° dewpoint. A nearby Texaco refinery studied the use of ozone for removing phenols in 1976 or 1977 and chose activated carbon instead, because of higher costs for ozonation.

Ozonation of Used Cutting Oils

Filtration and ozonation of lubricating oils containing microorganisms at a rate of 50 g/hr allowed a French automobile manufacturer to recycle cutting oil and obtain one year total use from the oil, which previously had been changed up to seven times per year (Anonymous, 1973).

Another article (Anonymous, 1974) also discusses the rejuvenation of used cutting oil by treatment with ozone. With an ozone consumption of 50 g of ozone/cu m of used oil, filter pressing allows recovery of 5% fuel oil in addition to regeneration of the cutting oil. When regeneration is not possible, the used oil is refined by decantation and filtration to recover fuel oil.

Effects on Drinking Water Supplies

Gabovich & Kurinnoi (1967) showed that ozonation of drinking water supplies containing petroleum product contaminants can be used to eliminate or greatly reduce the concentrations of these contaminants. About 45 mg of ozone was required to break down 1 mg of petroleum at an original concentration of 10 mg/l of petroleum. Ozone also eliminated gasoline from water at an ozone consumption ratio of 0.023 mg ozone/mg of gasoline, although the result probably is due to air stripping of the gasoline rather than by chemical oxidation by means of ozone. Dosages of 5.1 mg/l of ozone fully deodorized the gasoline-containing water (50 mg/l) in 5 minutes.

Diehl et al (1971) reported on a study conducted in 1969 at the Baton Rouge (Louisiana) Humble Oil Refinery to define the refinery's contribution to taste and odor problems in drinking waters taken from the lower Mississippi River. Laboratory treatability studies were conducted on particular wastewater streams using several treatment techniques.

Although ozonation generally was responsible for some lowering of COD and BOD levels, threshold odor levels decreased to a minimum value, then increased again. The character of the odors changed upon ozonation from hydrocarbon odors to a sweet/sour odor similar to that of acetic acid. No quantitative information on the use of ozone is given in this article, but formation of acetic acid as a stable end product of ozonation is entirely reasonable in light of the known organic oxidation chemistries.

Diehl (1976) amplified on the earlier results, showing that ozone dosages of 20 to 30 mg/l over 30 minutes of diffuser contacting produced 90% reduction in threshold odor number, from just over 1,000 to just over 100. On the other hand, simple oxygen stripping provided about 85% removal.

Upon continued ozonation (1 to 1.5 hrs of contacting, the threshold number of the samples again rose to 200 to 250 after 5 to 7 hrs of ozone contacting time.

Conclusions

1) Ozonation has been used commercially to polish effluents from a refinery in Sarnia, Ontario, Canada since the late 1950s. This is the only refinery currently known to be using ozone for treating actual wastewaters. The plant wastewater discharge is close to a water supply intake, therefore the plant must produce a very high quality effluent, and has a 3 ppb phenols discharge limitation.

2) Ozone demand of sour waters at the Sarnia refinery is in the range of 3.5 to 6 lbs of ozone/lb of phenol destroyed. This corresponds to ozonation costs of $0.95 to $1.65/lb of phenol destroyed (at 27.3¢/lb ozone cost).

3) In cat-cracker condensates containing sulfides, mercaptans and phenol, ozonation oxidizes sulfides initially to the exclusion of phenol oxidation. Thus, stripping prior to ozonation will reduce the amount of ozone required to treat this type of refinery wastewater.

4) Used cutting oils can be rejuvenated by treating with ozone to a consumption of 50 g of ozone/cu m of used oil. This treatment, followed by filter pressing, allows recovery of 5% fuel oil as well.

5) Pilot tests at Humble Oil's Baton Rouge refinery showed that threshold odor numbers of various ozonized wastewaters decreased at first, then increased. The character of the odors changed from those of hydrocarbons to those of esters, acids, ketones, aldehydes, etc.

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PHARMACEUTICALS

Although the wastewaters from this industrial category are organic in nature, remarkably little interest in the potentials for ozonation has been shown, as indicated by the paucity of published literature. A study initiated in 1972 by the Pharmaceutical Manufacturers Association compiled information on the sources, volumes and characteristics of the industry's wastes, current treatment processes and future treatment needs (Lederman *et al.*, 1975). In the section dealing with "Future Treatment Needs", the PMA points to the need to understand and utilize carbon adsorption, reverse osmosis, ultrafiltration and ozonation.

A French patent issued in 1974 describes the bleaching and clarification of wastewater from the synthesis of Vitamin B_2. The decolorization/-clarification is accomplished by injecting ozone (4 to 6% in air) into the waste stream. Chlorine also may be added, but only to the extent of about 50% of the ozone added. Otherwise the ozone will be destroyed.

Conclusion

Ozonation has been used to bleach and clarify wastewater from the synthesis of vitamin B_2. The processing employed 4 to 6% ozone generated in air.

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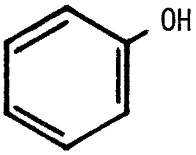
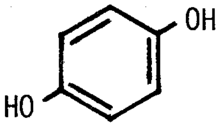
PHENOLS

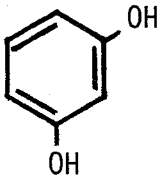
Phenols are a class of organic compounds which contain an aromatic ring upon which is substituted at least one hydroxyl group. The simplest phenol is phenol itself:

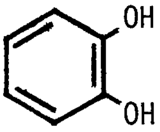

phenol

Other phenols include those in which more than one hydroxyl group is substituted onto the single aromatic ring, or multiple and/or fused aromatic rings which contain one or more hydroxyl groups:

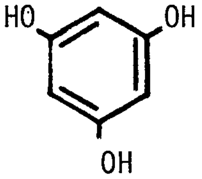

hydroquinone

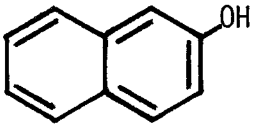
resorcinol




catechol

phloroglucinol




β-naphthol

Phenols as a class are present in the wastewaters from a number of industrial categories, in particular:

Organic Chemicals
Plastics & Synthetics
Petroleum Refineries
Iron & Steel (Coke) plants
Soaps & Detergents
Photoprocessing (hydroquinone)
Pulp & Paper
Textiles

When treated with chlorine, phenol first forms chloro-substituted phenols, which are known to impart disagreeable medicinal tastes and odors to drinking waters. As a class, however, these compounds generally are rather easily oxidized by strong oxidants, such as ozone, chlorine dioxide and potassium permanganate. Even continued additions of chlorine itself eventually will destroy the aromatic ring moiety.

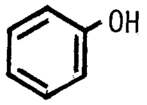
It must be borne in mind, however, that even though phenols as a class are readily oxidizable, this does not necessarily mean that they will be easily oxidized completely to CO_2 and water. Phenol oxidation under water and wastewater treatment conditions can stop at some stage after rupture of the aromatic ring, far short of all of the organic carbon being converted to CO_2, particularly if insufficient oxidant is used.

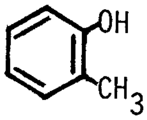
In much of the water and wastewater literature there are references to the "destruction of phenol" by ozone oxidation and by other powerful oxidants. The reader should note, however, that the "destruction of phenol" is followed by an analytical procedure which usually is specific only for the phenolic compound, or for an aromatic oxidation product, and is not necessarily specific for any of the aliphatic, ring-ruptured oxidation products that will be formed.

In this section, we will discuss the organic chemistry of ozone oxidation of phenolic compounds in some detail so that the reader will gain a greater appreciation of these points. Many of the experiments reported here were performed with the objective of isolating and identifying intermediate oxidation products, and not necessarily of optimizing ozonation conditions for destruction of phenols. Details of ozonation of specific phenol-containing wastewaters will be discussed in the sections dealing with pertinent industrial categories.

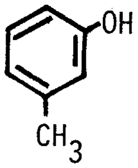
Reactions Of Ozone With Phenol

Niegowski (1953) ozonized aqueous solutions containing 100 mg/l concentrations of phenol, o-cresol and m-cresol at pH 12. These compounds





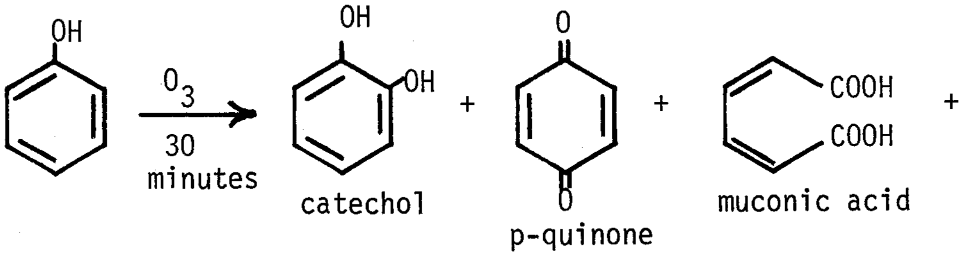
o-cresol

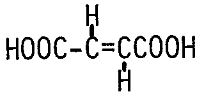


m-cresol

required ozone dosages of 200 to 260 mg/l to be 99+% destroyed. Niegowski (1953) also ozonized phenolic-containing wastewaters from 8 iron and steel coke plants, from 1 chemical plant (containing 2,4-dichlorophenol) and from 2 refineries. With the exception of 2 of the coke plant wastewaters, the ratios of ozone to phenol required to lower the phenol concentrations from a range of 100 to 11,600 mg/l down to 2.5 mg/l or below ranged from 1.0 to 8.8. For the 2 coke plant wastewaters containing 38 and 51 mg/l of phenols, dosages of 18 to 20 mg/l of ozone were required/mg of phenol to attain residual phenol concentrations of 0.4 and 0.1 mg/l, respectively.

Eisenhauer (1968) ozonized aqueous solutions of phenol for 30 minutes (until phenol was "destroyed" by the analytical test used) and isolated catechol, hydroquinone, p-quinone, cis-muconic acid, oxalic acid and fumaric acid as organic oxidation products:




$\mathrm{HOOC\text{-}\overset{H}{C}{=}\underset{H}{C}COOH}$ (fumaric acid) +

HOOC-COOH (oxalic acid)

After 4 moles of ozone/mole of phenol had been consumed (up to 1 hr of ozonation time), substantially all of the phenol originally present had disappeared, but very little CO_2 had formed.

When ozonation was conducted for only 10 minutes, Eisenhauer (1968) isolated a 20% yield of catechol, but only 70% of the phenol was destroyed. This indicates that upon oxidation of phenol, other organic compounds (10%) or CO_2 are produced along with the catechol.

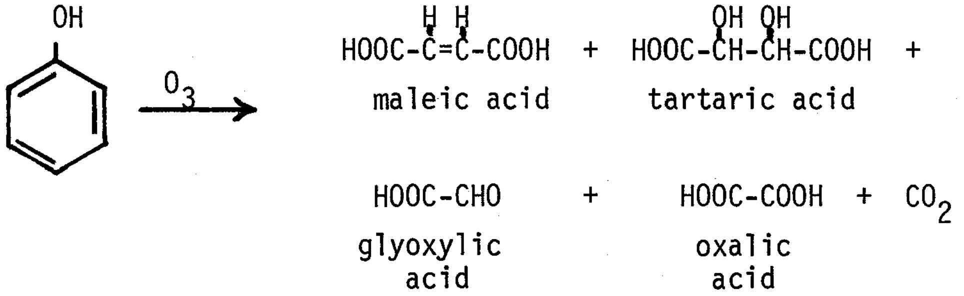
Eisenhauer (1971a) ozonized 50 to 300 mg/l concentrations of phenol at pH 3 to 9 and 20°C. As the ozonation reactions proceeded, the TOC of the solutions decreased, but no CO_2 formed until after 1.5 moles of ozone/mole of phenol had been consumed. When 33% of the theoretical CO_2 had formed, CO_2 production ceased. At 50°C, about 65% of the theoretical CO_2 was produced under the same conditions.

Eisenhauer (1971a) concluded that if the first stage of phenol oxidation (destruction of the aromatic ring) is sufficient to satisfy a pollution control problem, then 98% of the phenol can be "destroyed" using 5 moles of ozone/mole of phenol. The phenol was "destroyed" according to the analytical test employed, but 67% of the original dissolved organic carbon still was present in the form of other organic oxidation products. Eisenhauer (1971a; 1971b) concluded that at an ozone cost of 7¢/lb, a treatment cost of 18¢/lb of phenol "destroyed" is required.

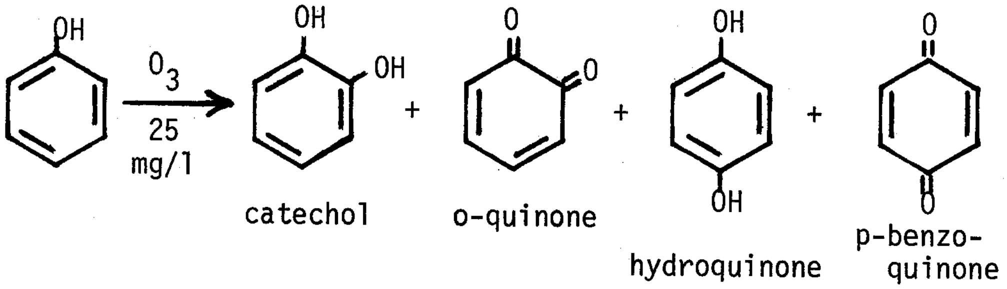
In further studies of the ozonation of aqueous solutions of phenol, Eisenhauer (1971b) showed that 1 mole of CO_2 is formed for 7.3 moles of ozone consumed. Complete oxidation of phenolic effluents to CO_2 and water cannot be achieved economically with ozonation alone. The maximum rate of ozonation of phenol occurs at pH 11 and 50°C, but its oxidation products are not as reactive under these conditions.

Bauch, Burchard & Arsovic (1970) found monobasic and polybasic (aliphatic) acids upon ozonation of water solutions of phenol. They concluded that oxidation of phenol by ozone proceeds via the ozonide and produces hydrogen peroxide. Initial phenolic oxidation products themselves consume additional ozone.

Bauch & Burchard (1970) ozonized aqueous solutions of phenol and isolated and identified maleic acid, tartaric acid, glyoxylic acid, oxalic acid and CO_2:

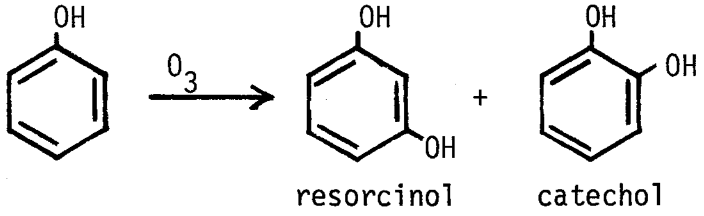


Mallevialle (1975) ozonized 100 to 200 mg/l aqueous solutions of phenol with 25 mg/l ozone doses and identified catechol, o-quinone, hydroquinone and p-quinone as oxidation products:

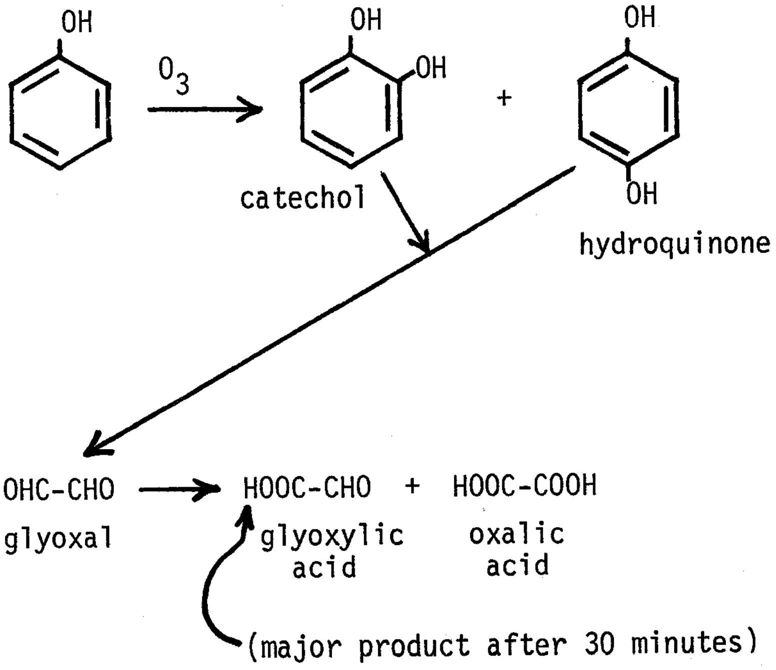


Mallevialle (1975) also showed that ozonation of aqueous solutions containing naturally occurring humic acids produces phenolic compounds as intermediates (analyzed chromatographically), which then oxidize upon further ozonation. Thus it is possible to increase the concentrations of phenols in water by insufficient ozonation. Waters containing 525 mg of humics required 100 mg of ozone to destroy 95% of the color and 320 mg of ozone to destroy 95% of the polyhydroxyaromatic compounds. Mallevialle (1975) concluded that it is necessary, therefore, to add 380 and 500 mg of ozone to lower the COD and TOC values, respectively, by 75%.

Spanggord & McClurg (1978) were the first investigators to identify resorcinol as an initial oxidation product, along with catechol, upon ozonation of phenol in water:



Gould & Weber (1976) have made the most complete study to date on the ozonation of phenol. They found that the early oxidation products (catechol and hydroquinone) are further oxidized as ozonation continues, and fall to relatively insignificant concentrations as the reactions proceed. Glyoxal is formed by ring rupture, but its concentration decreases to a low level as the reactions proceed. Glyoxylic acid is the main oxidation product isolated after 30 minutes of treatment with ozone, together with smaller amounts of oxalic acid.



Ozonation of aqueous phosphate buffered solutions containing 1.4 to 1,106 mmoles/l of phenol required ozone dose rates of 0.774 to 8.076 moles of ozone/mole of phenol. During the early stages of reaction, the combined concentrations of catechol plus hydroquinone reached a maximum of about 10% of the initial phenol concentration, indicating that hydroxylation of phenol is not the most important reaction of the ozone.

Gould & Weber (1976) also showed that addition of 24 moles of ozone/mole of phenol lowered the COD of the solution 77%. An additional 24 moles of ozone were required to lower the COD an additional 3%. Therefore, to attain 90% reduction in COD values requires greater than 150 moles of ozone/mole of phenol. These authors concluded that ozonation beyond the stage of aromatic ring rupture is not economical. This point is quite acceptable, however, since the oxidation products are considered to be "inoffensive" and are biodegradable. Therefore, dosages of 4 to 6 moles of ozone/mole of phenol will assure virtually complete removal of phenol and its aromatic oxidation by-products, will leave about 33% of the initial organic carbon in the form of glyoxal and glyoxylic acid (about equal amounts) and a 70 to 80% reduction in COD levels will be attained. Gould & Weber (1976) recommend that the aromatic breakpoint can be used as an indicator of the optimum ozone dosage, and this can be followed by a COD or TOC monitor.

Throop (1977) showed that ozone dosages of 5.32 mg/l produced non-detectable quantities of phenol in 5 minutes of contact, starting with concentrations of 110 ppb of phenol in a presettled and decanted foundry wastewater. This dosage is equivalent to 48 parts ozone/part of phenol. However, ozone dosages of 25.5 mg/l (200 parts ozone/part phenol) were required to produce a measureable (trace) amount of residual ozone in the solution. This confirms the fact that although ozone rapidly destroys phenol itself, significant amounts of ozone-demanding oxidation products are formed.

Throop (1977) compared the costs for treatment of foundry wastewaters to reduce phenol concentrations to 1.5 ppb at flow rates of 2.89, 1.3 and 2.4 mgd. In 1974 dollars, the costs estimated are as follows:

Chlorination: Chlorination contact tanks $125,000
annual chlorine cost 40,000

Permanganate: $65,000/yr

Peroxide: $75,000/yr

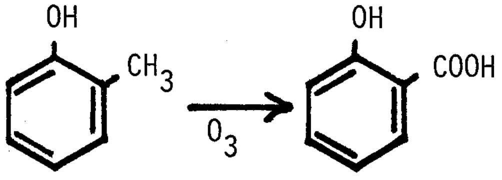
Carbon Adsorption: $9 million capital cost
$1,100/yr operating cost

Ozonation: $80,000 to $125,000 ozone generation and contacting cost
$4,000 to $9,000/yr power cost (@ 2¢/kwhr).

Reactions Of Ozone With Other Phenols

Bauch, Burchard & Arsovic (1970) compared the rates of ozonation of phenol with cresols and xylenols, and also isolated and identified ring ruptured oxidation products in all cases. The 3 cresol isomers decomposed more rapidly than did phenol, and the m-cresol isomer decomposed faster than did either the o- or p-isomers. Cresols reacted faster with ozone in acid solution than in basic solution. A decomposition of 80% for cresols was attained with 2 moles of ozone/mole of cresol (85 g ozone/100 g cresol). Chlorophenols gave HCl, indicating splitting of C-Cl bonds by ozonation.

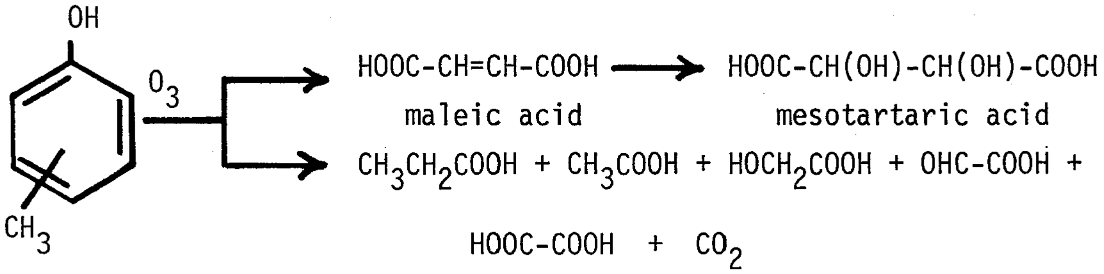
Upon initial ozonation, the methyl group of each cresol isomer oxidized to the corresponding carboxylic acid. For example, o-cresol produced salicylic acid:



salicylic acid

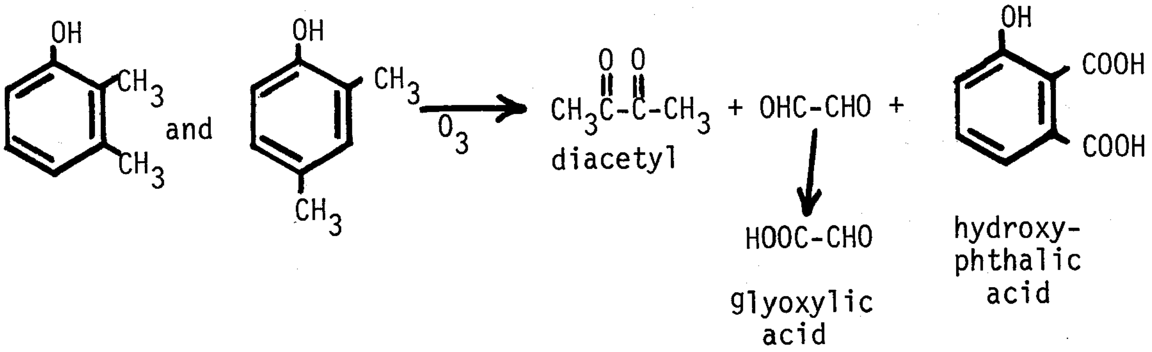
o-cresol

Continued ozonation of cresols ruptured the aromatic ring and produced maleic acid (which further oxidized to mesotartaric acid), acetic acid, propionic acid, glycolic acid, glyoxylic acid, oxalic acid and CO_2:

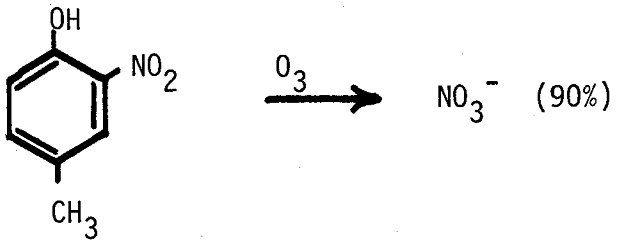


All 3 cresols (o-, m- and p-) formed the same oxidation products upon ozonation. Only the rates of oxidation varied.

Xylenols with ortho or para hydroxy groups reacted fastest with ozone and produced the same oxidation products as the cresols (Bauch, Burchard & Arsovic, 1970). In addition, 1,2,3- and 1,2,4-xylenols produced diacetyl, glyoxal (which disproportionates to glyoxylic acid), hydroxyphthalic acid and ketoaldehydes:



Gilbert (1978) ozonized 1 mmole/l of 2-nitro-p-cresol with 10 mg of ozone/minute until the cresol was destroyed. He found that 90% of the original nitrogen was converted to nitrate ion, indicating rupture of the aromatic ring as well as cleavage of the C-N bond.



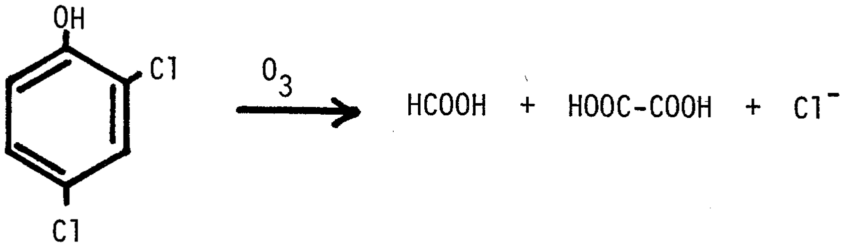
Finally, Hillis (1977) ozonized aqueous solutions containing 30 mg/l concentrations of 14 phenols and found that with ozone concentrations of 22 g/cu m (in oxygen) and 10 minutes of dosage, the concentrations of these phenols could be brought to below 0.5 mg/l (in many cases to below 0.1 mg/l), except for pentachlorophenol. Some 2 to 3 g of ozone/g of phenol (4 to 6 moles/mole) is required, and the COD levels are reduced 50 to 67%, but are not eliminated, indicating that organic compounds remain in the solution after ozonation has been completed.

Reactions Of Ozone With Chlorinated Phenols

Shuval & Peleg (1975) followed the rate of formation of chloride ion during ozonation of aqueous solutions of o-chlorophenol. In all experiments, about 80% of the aromatic chlorine was converted to chloride ion upon ozonation, indicating that covalent C-Cl bonds on the aromatic rings are broken with ozone. There was an induction period during which the concentration of o-chlorophenol decreased, but without formation of chloride ion. On the other hand, after all o-chlorophenol had disappeared, chloride ion still was being produced upon continued ozonation. This indicates that the active oxidation species attacks the aromatic ring at a site or sites other than the chlorine site, producing chlorinated aliphatic compounds as intermediates. These then decompose upon continued ozonation.

Gilbert (1976) ozonized aqueous solutions of 2-chloro-, 4-chloro-, 2,3-dichloro-, 3,5-dichloro- and 2,4,6-trichlorophenols until the phenols could not be detected by gas chromatography and no phenolic functionality could be detected by the 4-aminoantipyrine method. This required 3.2 to 5 mmoles of ozone/mmole of phenol. The rate of oxidation increased from mono- to trichlorophenol. After ozonation, 60 to 95% of the chlorine was found as chloride ion. Ozonation of 4-chlorophenol produced chloride ion at the start of ozonation; chloride ion was first detected only after 40% of the 2-chlorophenol had been degraded. The different rates of dechlorination are explained by Gilbert (1976) in terms of different electron density distributions on the aromatic rings.

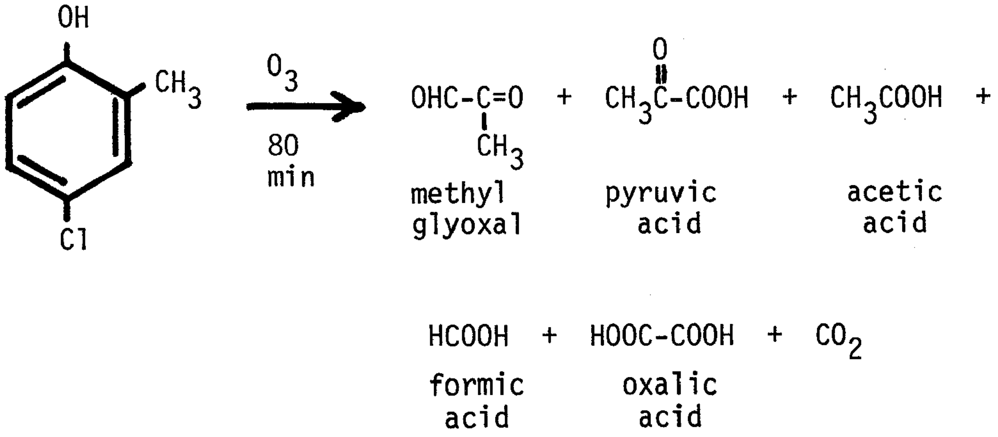
The compound 2,4-dichlorophenol produced formic and oxalic acids upon ozonation, in addition to chloride ion:



Biodegradability of the ozonized products became higher with increasing degrees of oxidation and with decreasing chlorophenol concentration. After total oxidation of the phenols, the COD level had been reduced from 200 to 100 mg/l and TOC concentration had been reduced from 72 to 59 mg/l.

After chlorophenols had disappeared, thin layer chromatography techniques indicated the presence of carbonyl or carbonyl/carboxylic acid functionalities. In instances of incomplete dechlorination, chlorinated aliphatic moieties were isolated but not identified.

Gilbert (1978) ozonized 4-chloro-o-cresol and identified 67% of its oxidation products. After 80 minutes of treatment with ozone (800 mg of ozone total dosage added to 1 mmole of chlorocresol) none of the starting cresol was present and 100% of the chlorine was found as chloride ion. In the ozonate, methylglyoxal, pyruvic acid, acetic acid, formic acid and oxalic acid were isolated and identified, along with CO_2. The course of reaction is as follows:



Methylglyoxal was produced from the beginning of the reaction, its concentration reaching a maximum after 60 minutes of reaction, then slowly decreasing. This means that its rate of formation from the cresol is faster than its rate of oxidation.

Pyruvic acid and acetic acid concentrations increased steadily during ozonation, even after complete elimination of the cresol, indicating that these two acids are produced from the initial oxidation products of the cresol. All TOC was accounted for by these organic compounds at various times during ozonation. Therefore, the above compounds, plus CO_2, water and chloride ion are the only oxidation products of this cresol.

Figure 14 summarizes the known reactions of phenols with ozone to produce organic oxidation products before complete conversion to CO_2 and water.

Catalyzed Ozonation

Chen & Smith (1971) reported the first studies on coupling sonocatalysis or Raney nickel catalysis with ozonation for the treatment of solutions containing phenol and of o-chloronitrobenzene. Aqueous solutions of phenol (500 mg/l) were ozonized for 3 hrs and samples were withdrawn every 0.5 hr for analysis. Ozonation alone (65 mg/hr) decreased the phenol concentration 31% in 3 hrs. Ultrasonics alone caused a 60%, almost linear, decrease in phenol concentration, and this decrease was unaffected by the addition of 160 g of Raney nickel. However, combined sono-ozonation decreased phenol concentration by 95%.

In later studies, Smith, Chen & Seyffarth (1973) showed that Raney nickel plus ultrasound caused a 60% decrease in phenol concentration in 3 hrs, which is about the same rate as for ultrasound alone. However, combining Raney nickel with ozonation decreased the phenol concentration 68% in 3 hrs; compared with 28% for ozonation alone. The lowest phenol concentration found after 3 hrs of treatment was obtained using the combination of ultrasonics, ozone and Raney nickel. The combination of ozone with Raney nickel caused a substantial loss in dissolved carbon, suggesting that more of the phenol is converted to CO_2, while the other treatments merely produce more highly oxidized species.

Finally, Chen, Hui, Keller & Smith (1975) showed that catalytic ozonation allows at least two oxygen atoms from each ozone molecule to be utilized in the oxidation reaction with phenol. Steady state oxidation of aqueous solutions of phenol was reached in 90 minutes using ozone alone, but was reached in 60 minutes using catalytic ozonation (using a special Fe_2O_3 catalyst). At initial COD concentrations of up to 900 mg/l, total removal of COD was obtained by catalytic ozonation, whereas in the same ozone contact time only 65% (at 200 mg/l initial COD concentration) and 30% (at 900 mg/l initial COD) of the initial COD was removed by ozonation alone (0.2 l/min; 30 mg/l ozone concentration).

Conclusions

1) Ozonation of phenol in aqueous solution proceeds rapidly, to produce aliphatic, ring-cleaved, oxidation products at an ozone/phenol molar ratio of 4 to 5. These ring-ruptured oxidation products are biodegrad-

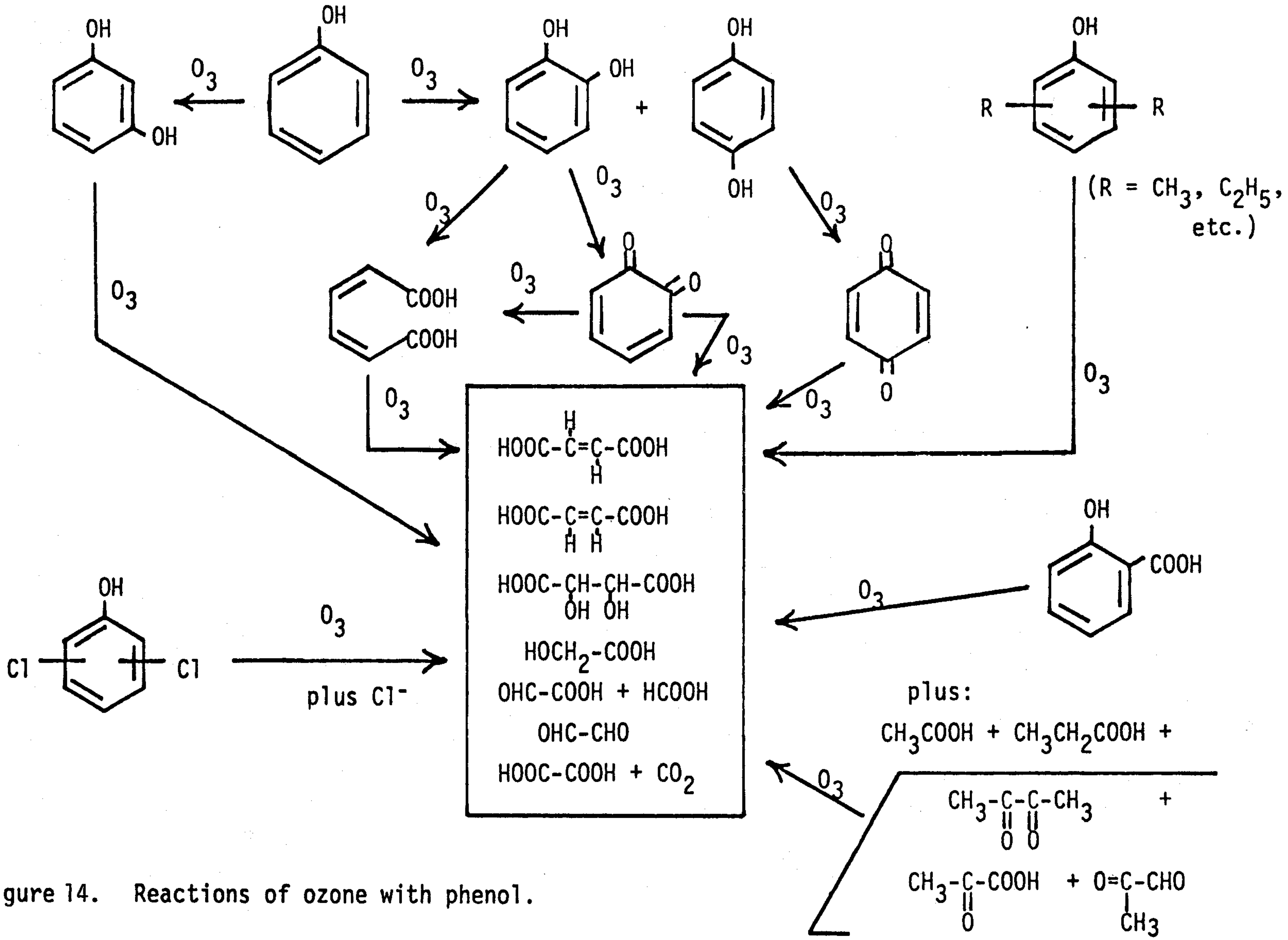


Figure 14. Reactions of ozone with phenol.

able. About 33% of the theoretical amount of CO_2 is formed, and the final TOC value is about 67% of the original.

2) Under-ozonation of phenol will produce intermediate oxidation products which still contain the aromatic ring. These include: catechol, resorcinol, hydroquinone, o-quinone and p-quinone. To avoid having these compounds in the ozonized solution, sufficient ozone should be provided to allow their oxidation to aliphatic materials.

3) Aliphatic oxidation products of the ozonation of phenol include: muconic, fumaric, oxalic, formic, maleic, tartaric and glyoxylic acids and glyoxal, in addition to CO_2.

4) Cresols and xylenols oxidize faster than phenol to produce aromatic ring-containing oxidation products initially (salicylic acid from o-cresol, for example). Continued ozonation ruptures the aromatic ring to form maleic, mesotartaric, acetic, propionic, glycolic, glyoxylic and oxalic acids, plus CO_2.

5) Chlorinated phenols react slower with ozone, producing chloride ion after ring rupture, and non-chlorinated aliphatic oxidation products.

6) Catalytic ozonation with ozone/ultrasonics/Raney nickel, ozone/Fe_2O_3, ozone/ultrasonics or ozone/UV will increase the rate of oxidation of phenols.

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PHOTOPROCESSING

Wastewater Composition

Wastewaters from photographic processing establishments contain a complex variety of organic and inorganic pollutants. The wastewaters generally are characterized by a pH between 7 and 9, numerous toxic organic compounds and inorganic salts, heavy metals, phosphates and nitrates which promote algae growth, and high biochemical and chemical oxygen demands. Table 40 shows an analysis of EA-4 photographic wastewaters (including wash waters). In addition to the materials listed in this table, organic compounds such as ethylene glycol, benzyl alcohol, acetic acid, N,N-dimethyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene, 4-amino-N-ethyl-N-[β-hydroxyethyl]-aniline, p-dimethylaminophenol, 1-phenyl-3-pyrazoline, EDTA, hydroxylamine, formaldehyde and methanol also can be present in color film developer formulations. Some of these react readily with ozone; others (acetic acid and methanol, for example) are refractory to ozone (see section on Hospitals).

The majority of photographic bleaches contain ferricyanide salts and are used primarily in color reversal processing. In doing its bleaching job, ferricyanide ion is reduced to ferrocyanide. Both iron cyanide complexes are very stable to oxidative destruction, therefore the spent ferrocyanide bleaching solution can be treated with an oxidizing agent so as to regenerate the ferricyanide solution for recycle and reuse:

$$2[Fe(CN)_6]^{-4} + H_2O + O_3 \longrightarrow 2[Fe(CN)_6]^{-3} + 2(OH)^- + O_2$$

There are commercially available ozonation systems which are designed to regenerate ferricyanide bleaching solutions as well as to reduce the concentrations of oxidizable organic and inorganic constituents. Thus the major objective of treating photoprocessing wastewaters is to remove toxic components. A second objective is to regenerate, recycle and reuse ferricyanide bleaching agents, and a third is to reduce the pollutional load of the wastewaters before being discharged to local community sewers. It has been estimated (Dougherty _et al_., 1976) that 95% of all photoprocessing plants discharge wastewaters _to_ municipal sewer systems, rather than to free bodies of water.

Treatment of Bleach Solutions

Lotz (1972) conducted a questionnaire survey of wastes generated by photographic processing at U.S. Air Force major civil engineering installations and Air National Guard units within the continental USA and abroad. Because the survey was conducted from June, 1970 to June, 1971, several operational air bases in Viet Nam were surveyed. At the time, it was concluded that over 26 million gal/month of photographic wastewaters were discharged by these 2 service branches. Over 70% of the installations responding in the U.S.A. discharged 10,000 to 1,000,000 gal/month.

TABLE 40. ANALYSIS OF WASTE DISCHARGED FROM EA-4 PHOTOGRAPHIC PROCESS, SHAW AIR FORCE BASE

Constituent	Concentration (mg/l)
COD	2,234
Dissolved Solids	5,942
Suspended Solids	70
Volatile & Fixed Suspended Solids	70
Oils & Greases (as Heptane)	22
Surfactants (as Linear Alkyl Sulfonate)	13
Phenols	0
Nitrates	48
Phosphates	380
Sulfates	1,100
Cyanides	260
Silver	6.70
Iron	1.96
Zinc	0.20
Copper	0.08
Manganese	0.05
Chromium	0.05
Lead	<0.05
Cadmium	<0.01

Source: Lotz, 1972

Lotz concluded that wastewaters should be desilvered before biological treatment or discharge because of the toxic effects of silver, but there is also the strong economic incentive to recover silver for reuse. Additionally, Lotz found that only 3 of the 311 installations submitting completed questionnaires regenerated the ferricyanide bleaches for reuse. All 3 regenerating installations used chemical oxidation, rather than ozone oxidation.

Hendrickson & Daignault (1973a, 1973b) conducted a detailed investigation of the treatment of complex cyanide compounds at the Berkey Photo film processing plant at Fitchburg, Massachusetts. The objective of this investigation was to evaluate electrolytic and ozone oxidation techniques for the regeneration of ferrocyanide for reuse of photoprocessing bleach baths, and to evaluate ozonation, precipitation and chlorination for the treatment of waste solutions containing complex cyanides from film processing waste discharges. A maximum residual ferrocyanide concentration of 0.4 mg/l was the goal established during this work for the treated wastewater.

These authors concluded that "ozonation is the best choice for control of complex cyanide pollution". Both ozonation or electrolysis could be used with similar process cost savings for the recovery and reuse of ferricyanide bleaches, and the recovery is economically justifiable. Copper and zinc can precipitate ferro- or ferricyanide from solution, and complex iron cyanide destruction can be achieved by either ozone or chlorine oxidation in acid solution.

Hendrickson & Daignault (1973a, 1973b) studied the regeneration of spent ferrocyanide bleach solutions in bench-scale systems using electrolysis, chlorination and ozonation, then in pilot-scale systems using ozonation, before installing a full-scale ozonation system at Berkey Photo. For bench-scale ozonation studies, 1 liter of 10 g/l potassium ferrocyanide solution was ozonized until the odor of ozone could be detected above the solution surface. The reaction was followed by analyzing for pH and ferricyanide. A second bench-scale study was conducted at constant pH, in which concentrated HCl was added to the ozone reactor (a sparger column, 18.5 inches high and 2.5 inches in diameter).

In these bench-scale regeneration experiments, the rate of oxidation of ferro- to ferricyanide was found to be zero order with respect to ferrocyanide concentration. The ozonation reaction was rapid, mass transfer controlled, and pH independent. The stoichiometry is:

$$2K_4Fe(CN)_6 \cdot 10H_2O + O_3 \longrightarrow 2K_3Fe(CN)_6 + 2NaOH + O_2 + 10H_2O$$

For each unit weight of ozone, 20.2 unit weights of ferrocyanide are regenerated to form 11.7 unit weights of ferricyanide. The ozone oxidation efficiency is 100% at ferrocyanide concentrations above 1 g/l. Below this concentration, ozone escapes from solution and the ferricyanide complex begins to decompose. Therefore, detection of ozone in the exhaust gases indicates the reaction end point. Pertinent data are given in Table 41.

These bench-top ozonation studies were conducted using used Ektachrome ME-4 and Kodachrome K-12 bleaches. No apparent decrease in ozone efficiency was observed for simulated or actual photoprocessing bleaches. The authors stated that in some commercial installations using ozone regeneration of ferricyanide bleach, the solutions have been regenerated up to 40 times with no adverse effects observed as to their bleaching capabilities.

TABLE 41. RESULTS OF BENCH TOP OZONATION OF USED PHOTOPROCESSING BLEACH AT BERKEY PHOTO*

Process	Time of Reaction (min)	Ozone Feed Rate (g/hr)	Initial Ferricyanide Concn (g/l)	Final Ferricyanide Concn (g/l)	Efficiency of Ozone Use (%)
K-12F	40	0.665	113	123	100%
ME-4	30	2.36	101	128	98%
ME-4	50	1.40	104.2	131.6	100%
ME-4	40	2.00	97.7	126.0	91%

* All solution volumes are 0.5 liter

Source: Hendrickson & Daignault, 1973a

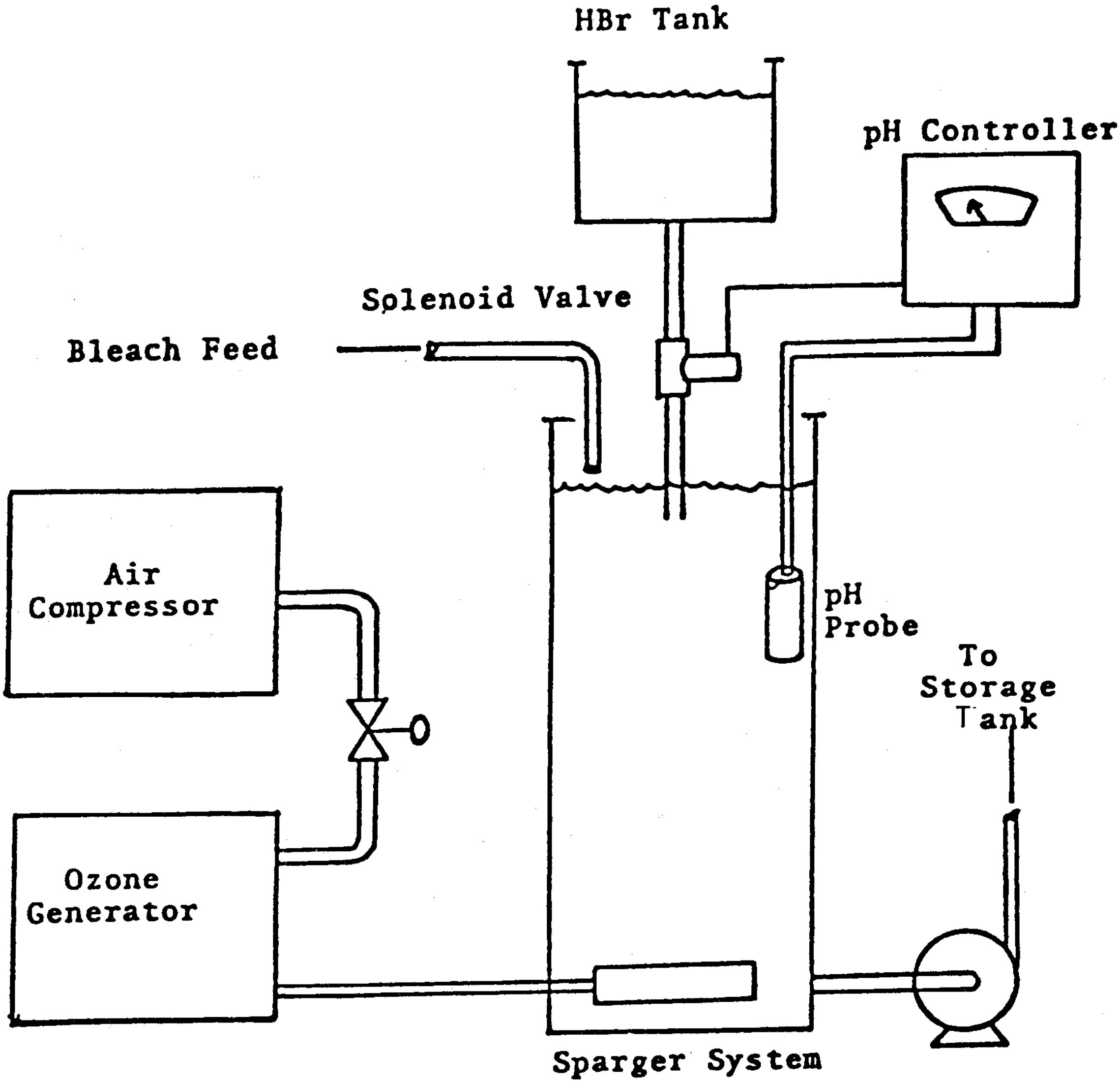
Bench top ferricyanide destruction experiments were conducted using 500 ml of 0.01M potassium ferrocyanide solutions in a 1 liter flask, and pH was adjusted by adding HCl or NaOH solution. Three treatment schemes were studied: (1) ozonation without pH control, (2) addition of 20 ml of concentrated HCl and 5 g of steel wool (catalyst), then ozonation, (3) acidification with 20 ml of HCl, heating to 70 to 90°C, then ozonation. At room temperature, ozonation had little effect on the ferricyanide destruction rate. Under alkaline conditions, ozonation produced a dark red color after the stoichiometric amount of ozone had been added. This red color disappeared when the mixtures were acidified. Some ferricyanide decomposition occurred with the steel wool catalyst. Below pH 3.0, the reaction proceeded rapidly to produce iron hydroxide and cyanate. Above pH 3.0, the reaction ceased. Under hot, acidic conditions at 70 to 90°C, there was only a small initial effect of ozonation, but as the reaction proceeded, the continued addition of ozone promoted more rapid and complete destruction.

Chlorine destruction of ferricyanide was studied by adding 500 ml of Chlorox to 500 ml of 10 g/l potassium ferricyanide, and adjusting the pH to 11.0. At room temperature, little destruction was observed. However at 90°C, destruction was complete in 4 hrs. In a second technique, chlorine gas was bubbled into 1 liter of a 10 g/l ferricyanide solution with and without the addition of NaOH to maintain the pH at 11.0. Sodium sulfite was added to quench the reaction whenever the reaction mixture was sampled. This process destroyed 85% of the ferricyanide. When the mixture then was made alkaline again and filtered, an additional 85% of the remaining ferricyanide could be destroyed. This second method (2) was found to be the best chlorination method for ferricyanide destruction.

Pilot studies of ferrocyanide ozonation for bleach regeneration were conducted in a continuous flow apparatus (see Figure 15). Ozone (2% in oxygen) was sparged into the bottom of a column 52 inches high and 3.5 inches in diameter. A 50-gal synthetic bleach solution containing 30 g/l potassium ferrocyanide was pumped through this ozonation reactor at the rate of 50 to 150 ml/minute. Samples were analyzed periodically for ferrocyanide, ferricyanide and pH. Results obtained in the pilot unit confirmed those obtained in bench top studies. At a constant flow of ozone into the reactor, the rate of conversion of ferrocyanide to ferricyanide was found to be inversely proportional to the flow rate of solution.

Pilot ferricyanide destruction experiments also were conducted in a continuous flow apparatus. Waste ferrocyanide solution and HCl were heated and ozonized. The overflow was filtered, and the filtrate was neutralized with NaOH and sewered. The precipitate was treated with NaOH to extract the metal complexed cyanides; this slurry was filtered and the filtrate was recirculated to the ozonation reactor. The final products from this destruction scheme are NaCl and iron hydroxide, at the rate of about 6 lbs/day from the average processing machine.

Costs were analyzed by considering the wastes from an hypothetical photographic processing machine. The chosen machine was a "combined average" of various processes which included: Kodacolor Color Negative (process C-22), Ektacolor Color Paper (process Ektaprint C), Ektachrome Reversal Film (process E-4) and Ektachrome Paper (process Ektaprint-R). Table 42 shows the flow rate, concentration of sodium ferricyanide and approximate costs



Source: Hendrickson & Daignault (1973a)

Figure 15. Flow schematic of a photographic bleach regeneration system using ozone.

for the individual bleaches and the "combined average". During film processing, about one-sixth of the replenisher ferricyanide was assumed to be reduced to ferrocyanide. An average year was taken as 260 days (8 hrs/day), and a "combined average" machine was assumed to handle 800 rolls of film per day.

TABLE 42. COSTS FOR THE "COMBINED AVERAGE" HYPOTHETICAL PROCESSING MACHINE

Process	Replenisher Flow Rate (ml/min)	Replenisher $Na_3Fe(CN)_6$ Concn (g/l)	Bleach Cost $/100 gal
Kodacolor (C-22)	275	25	$ 87.00
Ektacolor Paper (Ektaprint-C)	260	25	$ 48.00
Ektachrome Film (E-4)	115	120	$238.00
Ektachrome Paper (Ektaprint-R)	150	30	$ 72.00
Combined Average*	200	50	$111.00

* Assumed to handle 800 rolls of film/8 hr day -- 260 days/year

Source: Hendrickson & Daignault, 1973a

Costs for regeneration of bleach from the "combined average" processor in the continuous flow mode were calculated to be $7,200 capital to recover 90% of the bleach used, saving $22.90/day, or 2.85¢/roll of film processed (Table 43). Costs for ozone destruction of complex cyanides were calculated to involve $25,680 capital equipment costs, and daily operating costs were $17.50 (equipment amortized over 10 years), or an increase of 2¢/roll of film processed (Table 44).

On a comparative basis, alkaline chlorination for complex cyanide destruction would involve $6,000 in capital costs and a daily cost of $16.25, or 2¢/roll processed.

Comparative savings for ferricyanide bleach treatment from the "combined average" processor by the several techniques studied are listed in Table 45. The authors concluded that ozonation appears to be the best choice for control of complex cyanide pollution because of its versatility of use, both in chemical recovery and waste treatment.

Based on these bench top and pilot scale studies, Hendrickson & Daignault (1973a, 1973b) describe the installation of a full-scale combined ozone bleach regeneration and waste destruction treatment system at Berkey Photo Inc., Fitchburg, Massachusetts. A schematic of the installed system is shown in Figure 16. The system incorporates 2 ozone generators, one produces up to 100 g/hr, the other up to 60 g/hr of ozone from dried air. The smaller generator handles ferrocyanide bleach regeneration and waste cyanide treatment. Analytical tests are made for ferro- and ferricyanide concentrations, then the proper amount of ozone is fed into the reactor and bleach is regenerated.

TABLE 43. COSTS FOR BLEACH REGENERATION BY THE "COMBINED AVERAGE" PROCESSOR

Equipment	Cost
Ozone Generator (10 g/hr output, from air)	$2,000
Dry Air Supply System	$ 350
50 Gallon Polyester Tank	$ 100
Mixer: 2 HP rubber-coated steel	$ 550
Spargers & Acid Tank	$ 300
Pumps	$ 250
pH Controller with Automatic Probe, Solenoid & Metering Valve	$3,000
Labor & Maintenance (10% of cost)	$ 650
TOTAL	$7,200
Calculated present bleach cost/8 hr day	$ 28.20
Cost of O_3 equipment/day for 10 yr amortization	$ 2.50
Savings at 90% bleach recovery	$ 25.40
Daily savings = Daily bleach savings - Daily equipment cost = $25.40 - $2.50 =	$ 22.90
Savings/roll @ 800 rolls/day	$ 2.85/roll

Source: Hendrickson & Daignault, 1973a

TABLE 44. COSTS FOR OZONE DESTRUCTION OF COMPLEX CYANIDES

Equipment	Cost/Unit
Reactor vessel; glass lined steel, 50 gal	$ 2,000
Mixing tanks, polyester, 50 gal	$ 200
Portable mixers, 2 HP rubber coated steel	$ 550
Heating coil, Teflon immersion coil	$ 1,000
Pumps, corrosion resistant	$ 250
Filter presses, plate & frame	$ 1,200
Ozone generation unit (200 g/hr)	$ 14,000
Labor & maintenance (19% of cost)	$ 2,480
Total	$ 25,680

Daily Chemical Costs	Quantity	Cost
1) Oxygen	200 cu ft	$6.60
2) HCl	1 liter	$0.75
3) NaOH	1 lb	$0.30

Daily cost of destruction (equipment amortized 10 years)	$17.50
Increase in cost of processing per roll of film	$ 0.02/roll

Source: Hendrickson & Daignault, 1973a

TABLE 45. ESTIMATED SAVINGS ON TREATMENT OF FERROCYANIDE BLEACH. "COMBINED AVERAGE" PROCESSOR

Method of Treatment	Daily Savings, $/roll
Electrolytic Regeneration	0.029
Ozone Regeneration	0.0285
Ozone Destruction	-0.022
Acid Chlorination	-0.020
Alkali Chlorination	-0.075
Daily Saving = Daily Bleach Savings - Daily Costs of Equipment using 10 year amortization	
<u>Source</u>: Hendrickson & Daignault, 1973b	

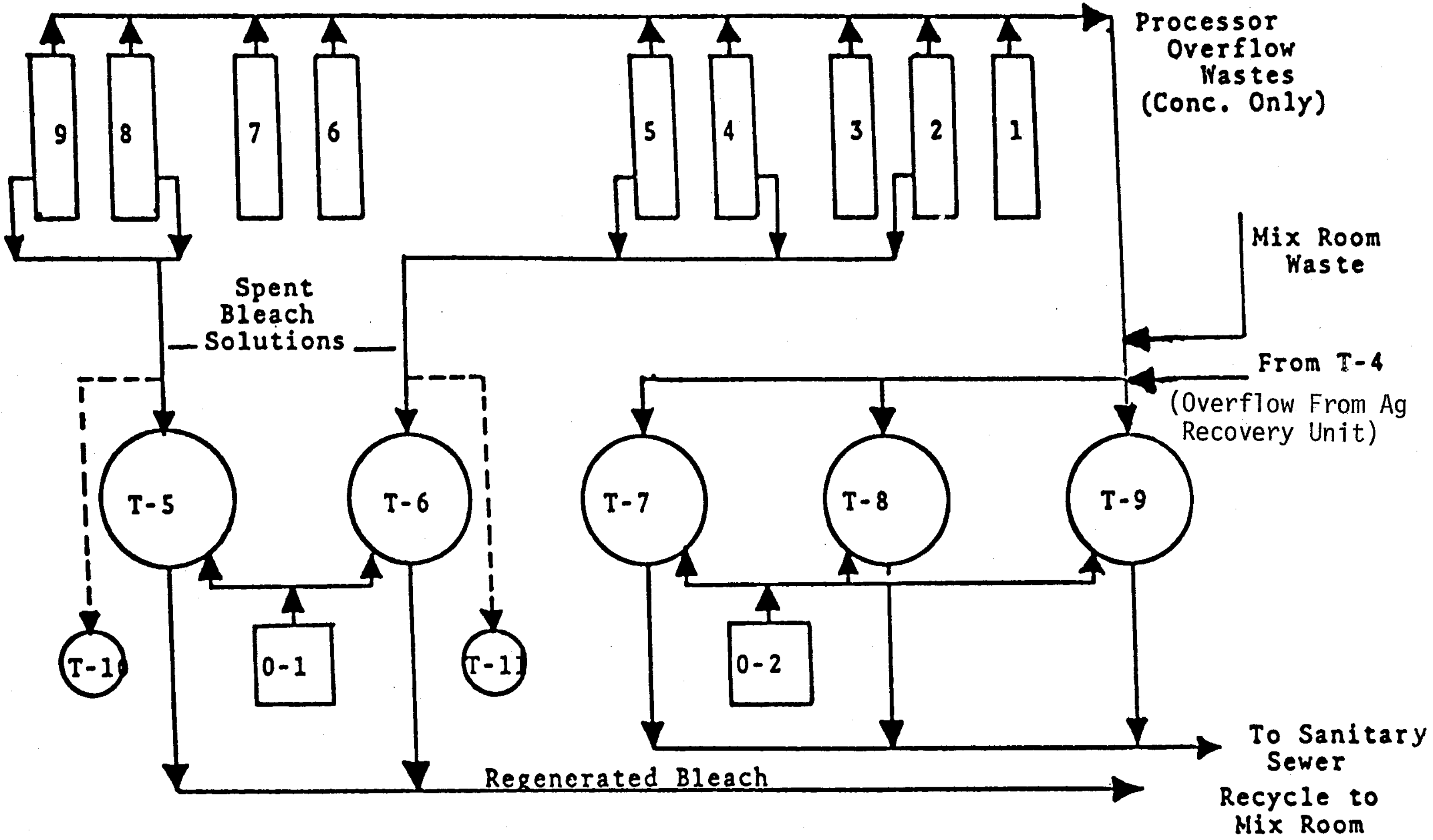
The larger generator distributes ozone to 3 tanks which hold the overflows from the various photoprocessors, plus desilvered waste fixing solutions. In these wastewaters, organic constituents plus easily oxidized inorganic components (thiosulfate, sulfite, etc.) are destroyed before discharge of the wastewaters to the local municipal sewer system.

Hendrickson (1975) has reviewed the applications of ozonation in the treatment of photoprocessing wastewaters, and has cited case histories of several operational photoprocessors who have installed ozonation equipment. Ozone is used to regenerate ferricyanide bleach and to destroy complex cyanides and other waste materials (organics, thiosulfate, sulfite).

In 1971, Photographic Corporation of America, Matthews, North Carolina, installed a 100 g/hr ozonation system to lower the oxygen demand of its wastewaters and/or to recover ferricyanide bleach for reuse. Ozone is sparged through 100 micron ceramic diffusers and destroys the metal chelating capability of EDTA present. The same ozonation system also is used to regenerate bleach solutions. In 1973 the ozone generation capacity at this plant was doubled so as to handle the increased volume of processing. Ozone output can be varied from 20 to 200 g/hr at 0.75 to 1.5 weight % in dried air. The total cost of this ozonation system at its current output capacity of 200 g/hr is $42,000 -- and this cost should be returned, through bleach recovery, in about 5 years (Hendrickson, 1975).

The Berkey Photo system at Fitchburg, Massachusetts (Hendrickson & Daignault, 1973a, 1973b), has been operational since mid-1971. As of November, 1973, about 220 consecutive 100-gal batches of the same ferricyanide bleaches had taken place, which amounted to an annual savings of about $9,000. The 2 ozone generation units at Berkey Photo cost approximately $41,000 (excluding installation), and the system should return its investment in about 5 yrs, based upon recovery of ferricyanide bleach alone.

CBS Television News, New York, N.Y. processes between 100,000 and 200,000 ft of 16 mm film per week. In 1971 an automated ozonation system was installed. When the photoprocessor is turned on, the ozone generator



Key:
1-Black & White Paper Processor
2,4,5-Ektacolor Paper Processor
3-Ektachrome Paper Processor
6-Black & White Film Processor
7-Ektachrome Film Processor
8,9-Kodacolor Film Processor

T-5 thru T-9 - 250 Gallon Holding Tank
T-10, T-11 - 55 Gallon Holding Tank
0-1, 0-2 - OzPAC Ozone Generators

Source: Hendrickson & Daignault (1973a)

Figure 16. Flow diagram of bleach regeneration system and concentrated waste oxidation system at Berkey Photo, Fitchburg, Massachusetts.

automatically pumps ozone to the waste treatment tank to destroy concentrated waste overflows from the film processing machine. When the processing machine is turned off, the ozonator operates automatically until the waste is completely destroyed and then shuts down, unless the spent bleach tank is full. In this instance, ozone is directed to that tank for bleach regeneration, prior to automatic ozone generation shutdown. This equipment has paid for itself in less than 2.5 yrs (Hendrickson, 1975).

JSOR-TV, Nagano City, Japan, processes 80,000 ft/month of 16 mm television movie film. In late 1972 an ozonation system was installed to pretreat photoprocessing wastewaters before discharge to a biological treatment lagoon. Before the ozonation system was installed, effluent from the aerated lagoon had a BOD-5 of 1500 mg/l. With ozonation installed, the effluent BOD-5 now is about 12 mg/l, and all iron, cyanide, zinc, silver and cadmium concentrations are within local discharge concentrations. The total investment for the ozonation system and biological lagoon was $34,000. Annual savings generated are approximately $6,000/year, resulting in a total payoff time for this installation of about 6 yrs.

Hendrickson (1975) concludes that for bleach regeneration only, a properly designed ozonation system will return its entire investment in approximately 24 months. For both chemical recovery and waste treatment, the ozonation system will return its investment in 60 months (5 yrs).

Bober & Dagon (1974) compared ozone regeneration of spent ferricyanide bleach with persulfate regeneration. Appreciable salt buildup, commonly resulting from the traditional persulfate treatment process, is eliminated by use of ozone. For a photoprocessing lab operating 5.5 days/week, a total of 465 lbs of sodium ferrocyanide would have to be regenerated. This would require 224 lbs of potassium persulfate or 39 lbs of ozone, assuming 100% efficiency in both cases.

Capital costs for ozonation were estimated at $18,700 (1970 prices, exclusive of installation) and operating costs are $650/yr. Persulfate operating costs are $4,070/yr, at 20¢/lb for persulfate. The cash flow rate of return for the ozonation system was estimated to be 9%/yr.

These authors concluded that ozone can be used economically to regenerate bleaches from Kodachrome film process K-12 and Ektachrome process CR1-1, but that the high capital costs for ozonation equipment make it uneconomical for treating other bleach baths. Malfunction of equipment was not found to be a serious problem.

Some unidentified Japanese authors (Anonymous, 1975) studied the waste bleaching solutions from 7 Japanese printing and 9 film developing plants. Heat decomposition reduced cyanide concentrations to less than 0.5 mg/l. Electrolytic oxidation of COD was unsatisfactory, removing only 11% of the COD. Ozone oxidation attained 74% COD removal only if the COD content was low, but removal efficiency decreased with increasing COD content. BOD and COD could be removed at 100% efficiency by the combustion method, but this forms sulfur oxides, and results in secondary pollution problems.

Treatment of Organic Components

Bober & Dagon (1975) report a detailed study of the ozonation of organic constituents of photoprocessing wastewaters. Although most of the organic chemicals found in these wastewaters are biodegradable, certain color developing agents are biorefractory, and conventional biological treatment has little effect on their removal. The objectives of this study were to determine if:

(1) ozonation can be used in place of biological treatment,
(2) the use of ozone as a tertiary treatment (disinfection after biological treatment would be applicable,
(3) the use of ozone to selectively treat individual processing solutions would be practical.

Bober & Dagon (1975) studied the ozonation, in detail, of solutions of more than 25 individual processing chemicals and several photoprocessing effluents. They concluded that ferro- or ferricyanides cannot be destroyed effectively with ozone, but ozone can be used to regenerate ferricyanide bleach solutions. Also, ozonation is not an effective substitute for biological treatment. Thiosulfate, acetate, sulfite, hydroquinone and benzyl alcohol respond well to biological treatment.

Ozonation of solutions of ethylene glycol produced 30 to 35% reduction in COD content in 4 hrs, but had no effect thereafter during an additional 20 hrs. Hydroxylamine sulfate was easily attacked by ozone, 70% of the COD being destroyed after 6 hrs of ozonation. The COD of a solution of benzyl alcohol was 90% destroyed after 24 hrs of ozonation. No reduction in COD content was observed after 24 hrs of ozonation of acetate. Thiosulfate solutions (3 to 10 g/l) were 70% to 80% oxidized after 8 hrs of ozonation, and 95% in 14 to 24 hrs. Sulfite was 100% oxidized in 1 hr of aeration, without the need for ozone.

Color developing agents produced some spectacular color changes upon ozonation. The material CD-3 (4-amino-N-ethyl-N-[β-methanesulfonamidoethyl]-m-toluidine) turned from a pale pink to opaque purple, then scarlet within 15 minutes, then to a deep yellow, then orange, then lemon yellow, then to creamy off-white, and then colorless. After 8 hrs of ozonation, the COD had decreased 60% and then became stable to further ozonation.

The COD level of a 1 g/l solution of CD-1 (N,N-diethyl-p-phenylenediamine.HCl) was reduced 70% after 43 hrs of ozonation. Similarly, the COD level of CD-2 (2-amino-5-diethylaminotoluene.HCl) was reduced 60% after 8 to 16 hrs of ozonation. The COD level of CD-4 (4-amino-3-methyl-N-ethyl-N-[β-hydroxyethyl]aniline sulfate) was reduced 65% in 8 hrs of ozonation, after which the COD content remained constant.

Glycine was unaffected by ozonation over 24 hrs. Hydroquinone was 60% to 70% decomposed in 8 hrs and 95% decomposed in 16 to 24 hrs. The pH dropped from 10 to 4 during the course of ozonation, probably because of the formation of organic acids (oxalic, formic, maleic, etc.). The COD of a solution of Elon (p-dimethylaminophenol sulfate) was lowered 60% to 70% after 8 hrs of ozonation, but remained constant thereafter.

The chemical phenidine (1-phenyl-3-pyrazoline) exhibited an initial lag period upon ozonation, after which there was a rapid decrease in COD concentrations (to about 60%) in 4 to 8 hrs. COD removal then slowed, and 90% was removed in 23 hrs.

EDTA was slowly decomposed initially (20% decrease in COD after 14 hrs), then decomposition became rapid (70% COD decrease in 14 to 20 hrs of total ozonation; 90% after 30 hrs total ozonation). The COD of sodium formate was 90% removed in 4 hrs of ozonation. This material was not degraded biologically. The COD of formalin (formaldehyde in water and methanol) was decreased 50% in 4 to 6 hrs and 85% in 24 hrs. Methanol showed a 37% decrease in 23 hrs, and KCNS showed greater than 90% decrease in COD in 2 hrs. Ferrocyanide oxidized to ferricyanide very rapidly, but ferricyanide showed no significant decomposition after 38 hrs of ozonation (9% in 20 hrs). After 100 hrs of ozonation, only 30% of the ferricyanide had decomposed.

During ozonation studies with a sparger contacting system, foaming of solutions caused serious mechanical problems. However, the authors believe that the foaming can be designed around to minimize its disruptive effects on the treatment system.

Bober & Dagon recommended regeneration of bleach, the use of squeegees, silver recovery and installation of a ferrocyanide precipitation system (using ferrous sulfate) to prevent ferrocyanide from being carried out with the overflow fix and subsequent wash. Since acetate comprises 52% of the BOD-5, is biodegradable, but is not readily oxidizable by ozone, biological treatment should precede ozonation.

Simulated wastewater effluent from the standard ME-4 processor (motion picture Ektachrome) using ammonium rather than sodium thiosulfate contains 4,700 mg/l COD. Ozonation of this waste for 4 hrs provided 41% decrease in COD concentrations (3 liters of ME-4 waste treated with 1.5 g/hr of ozone).

Finally, Bober & Dagon (1975) ozonized 3-liter samples of effluent from an activated sludge system treating photoprocessing wastes solely. Samples were ozonized 5, 10, 15, 30 and 60 minutes (1 liter/min gas flow; 1.5 mg/l/min of ozone) and obtained complete disinfection in 30 minutes. At the same time, the COD levels dropped from 50 to 30 mg/l. After 1 hr of ozonation, the COD level of the effluent had dropped to 17 mg/l.

Treatment With Ozone/UV Light

Garrison, Mauk & Prengle (1974, 1975) first described the conjunctive use of UV light with ozonation and heat for the destruction of complex cyanides contained in photographic processing wastewaters. Under contract to the U.S. Air Force Weapons Lab at Kirtland Air Force Base, New Mexico, these investigators at Houston Research Inc., Houston, Texas, studied the destruction of both electroplating and photoprocessing wastewaters with the ozone/UV/heat system. Treatment of electroplating wastewaters by these techniques already has been discussed earlier in this section. Ozone/UV treatment of pink waters from TNT manufacturing has been described earlier in this section. under Organic Chemicals.

A laboratory-scale semi-batch reactor (Figure 17) was designed, fabricated and operated to obtain data from which ozone mass transfer constants, ozone decomposition constants and reaction rate constants were obtained. From these data, a continuous pilot-scale, multi-staged reactor was designed (Figure 18) which was fabricated and used to treat actual photographic bleach and photographic fixer wastewaters which contained high cyanide concentrations. In all cases, the concentrations of cyanide in the final effluents were below the limits of detection.

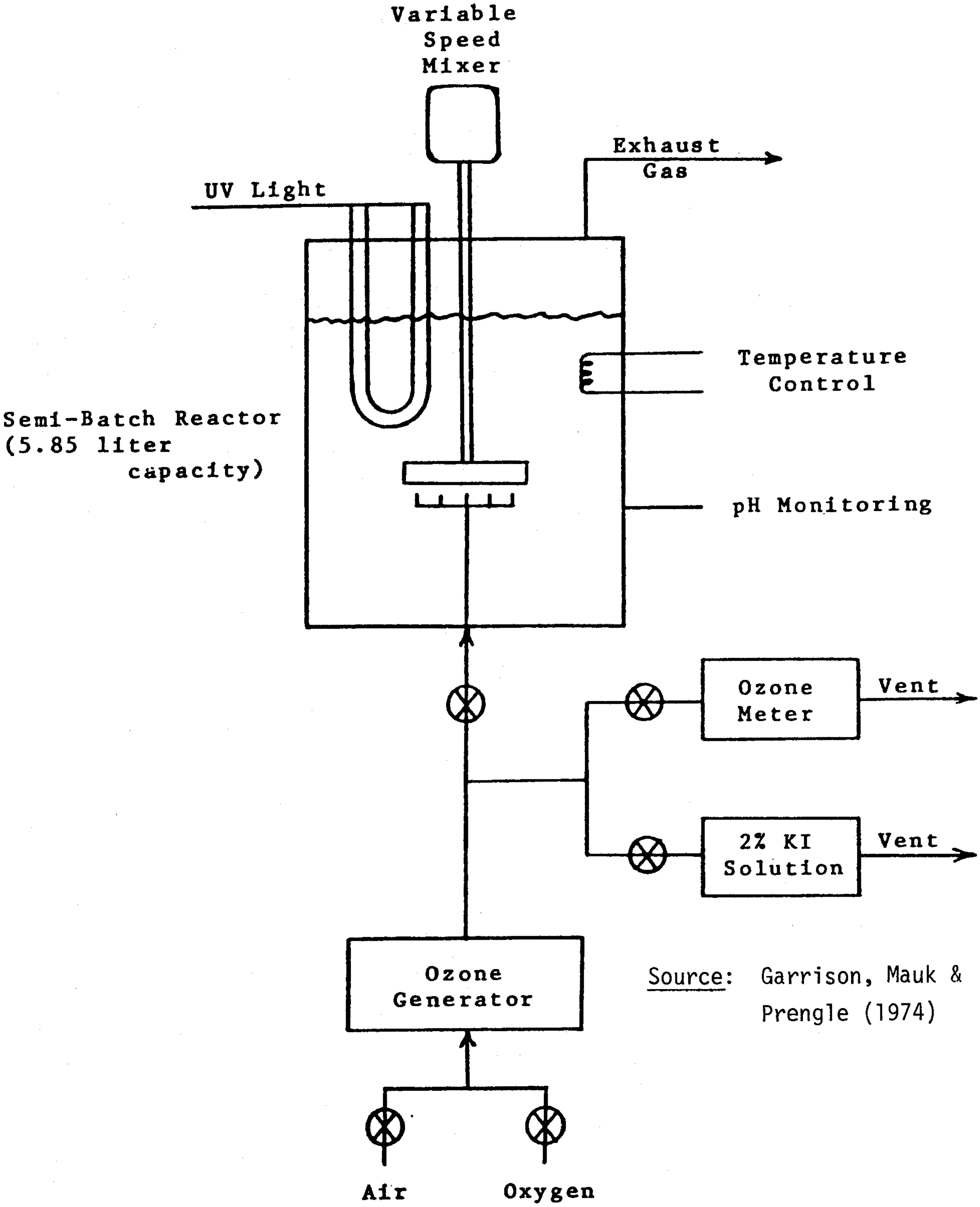
Preliminary oxidations using 3% ozone without added UV radiation lowered the cyanide concentration in a diluted fixer bath from 5.8 mg/l to 0.4 mg/l in 4 hrs of ozonation (2.42 l/min of 3% by weight ozone -- 103 mg/min), and the initial pH dropped from 7.6 to 3.9, due to the formation of sulfurous acid from oxidation of the thiosulfate. Ozonation of bleach (also 6 mg/l initial cyanide concentration) under similar conditions lowered the cyanide concentration to 1.3 mg/l in 7 hrs of ozonation. However, conversion of ferrocyanide to ferricyanide occurred during the first few seconds of this run (by visual observation of color change).

At a higher cyanide concentration (665 mg/l), bleach waste was ozonized using 1.3 weight % ozone (18 mg/min) and gave appreciable cyanide destruction (about 300 mg/l in 11 hrs of ozonation), but the weight of ozone required per weight of cyanide destroyed was large. The fact that about one-half of the cyanide was destroyed in 11 hrs using this high speed agitation ozone reactor should be compared with the results obtained by Bober & Dagon (1975) who used a sparger contactor and decomposed only 9% of the ferricyanide after 20 hrs of ozonation with 1% ozone in air.

Addition of cupric ion to the 665 mg/l cyanide bleach solution after 26 hrs of ozonation did not have any effect on the oxidation rate.

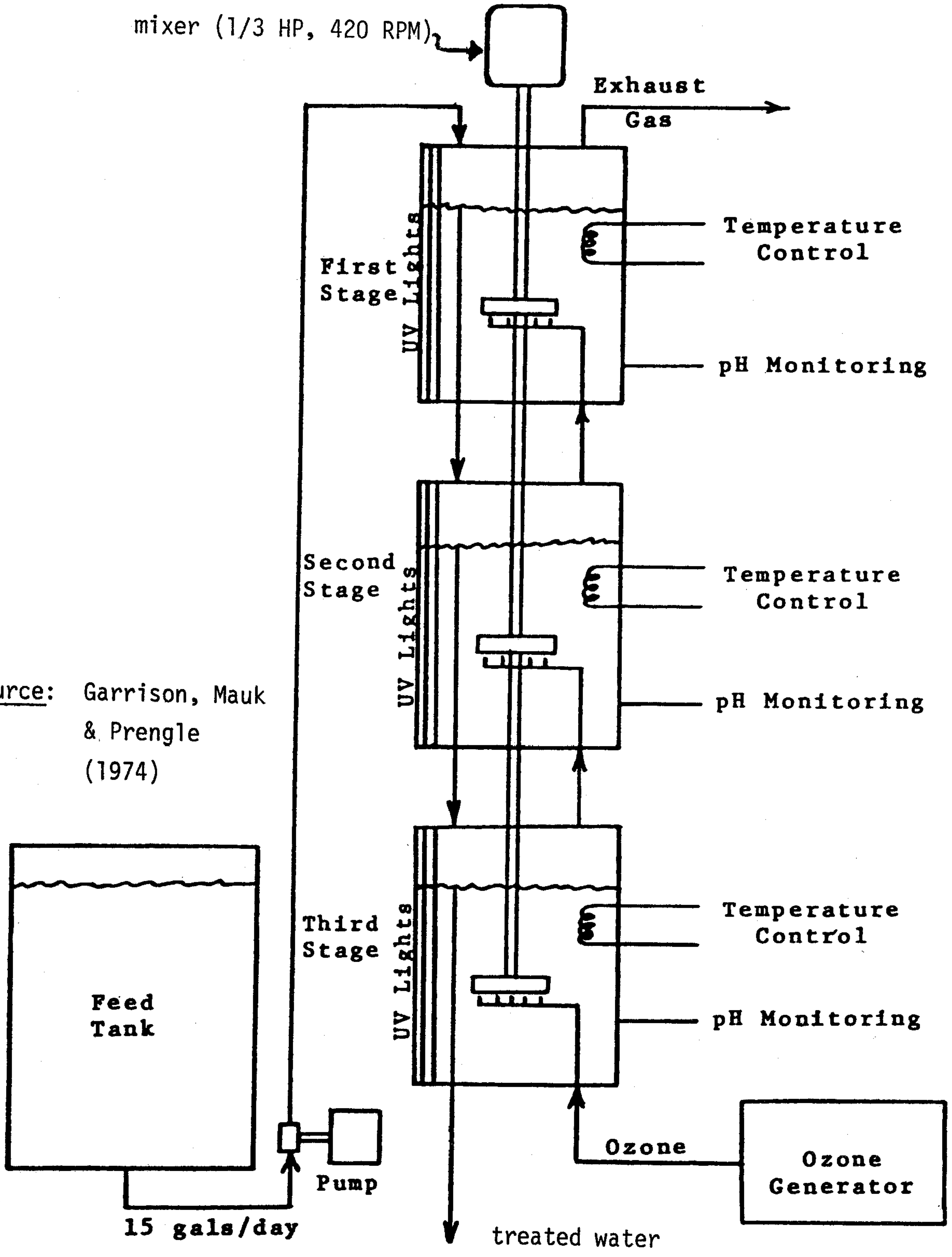
A full strength bleach waste, containing 73,000 mg/l of cyanide was ozonized at a rate of 1 liter/min with 1.2% by weight ozone (16 mg/min). Cyanide concentration decreased by 40,000 mg/l during the first 600 hrs of ozonation. After 1,600 hours of ozonation, the cyanide concentration was 1.8 mg/l.

Maximum reaction rates of these cyanide-containing wastewaters occurred at pH 7.0. The initial reaction rates were much faster when higher ozone concentrations in air or oxygen were used. No improvement in reaction rate was observed upon filtration during ozonation, upon addition of copper or silver ions as catalysts, or whether the ozone was added in air or oxygen (as long as it was at the same concentration in the gas phase and added at



Source: Garrison, Mauk & Prengle (1974)

Figure 17. Schematic diagram of lab scale apparatus for mass transfer and reaction kinetics tests......ozone/UV.



Source: Garrison, Mauk & Prengle (1974)

Figure 18. Schematic diagram of prototype cyanide disposal system based on ozone/UV treatment.

the same flow rate). However, reactions conducted at 65°C were much faster than those at 25°C.

A UV light shined on top of the liquid being ozonized caused some increase in reaction rates, but substantially faster reactions occurred when the UV bulb was totally immersed in the aqueous medium being ozonized. The UV light source used drew 4 watts and produced 253.7 nm wavelength UV light. Using this combination of UV with ozone at various concentrations (from 1% to 5% by weight) in the carrier gas, substantial increases in cyanide destruction rates were obtained. For example, the initial reaction rate of 1% ozone with UV light in a solution containing 53 mg/l of bleach cyanide was about equal to that obtained with 5% ozone without UV light, until a cyanide concentration of about 16 mg/l (70% conversion) was obtained, after which the reaction rate with 1% ozone with UV was far superior to that of 5% ozone without UV (Figure 19).

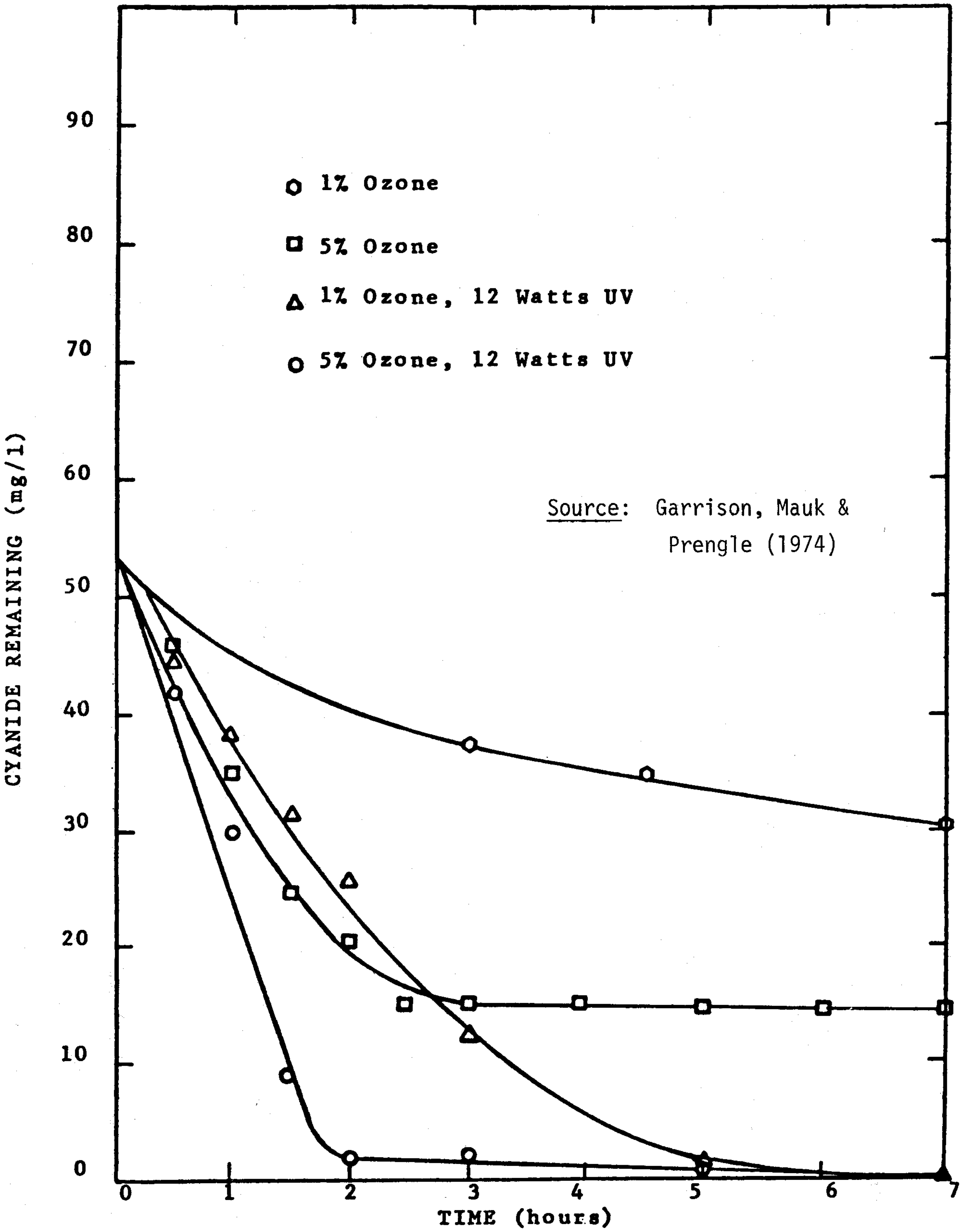
Studies then were conducted in the continuous flow, prototype reactor (Figure 20) using dilute, 10 mg/l cyanide concentrations in photo bleach and photo fixer baths (Runs P-1 and P-2, Table 46). The feed rate was 20 gal/24 hr day, which provided 18 hrs retention time equally divided over the 3 stages. Six 15 watt UV lights were used in each of the 3 stages, and the electrical heaters were not used. Ozone was generated from oxygen, producing 1.4 lbs/day of 3.2 wt % of ozone in oxygen. The prototype was operated continuously on each wastewater for 32 hrs, to allow steady state concentrations to be attained in each stage, before final cyanide sampling for analysis was made. During the photo fixer runs, additions of small amounts of caustic to the first stage were required to maintain the optimum pH level of 7. The second and third stages had steady pH which did not require caustic for its control. The photo bleach runs did not require pH control in any of the 3 stages.

TABLE 46. OZONE MATERIAL BALANCES IN PROTOTYPE UNIT RUNS

Run No.	Type of Waste	Ozone Charged (lbs/day)	Ozone Discharged (lbs/day)	Ozone Consumed (lbs/day)	Original CN concn (mg/l)	Cyanide Reacted (lbs/day)
P-1	bleach	1.71	0.40	1.31	10	0.00167
P-2	fixer	1.71	0.43	1.28	10	0.00167
P-3	fixer	2.10	0.54	1.56	700	0.088
P-4	bleach	2.52	0.16	2.36	4,000	0.501

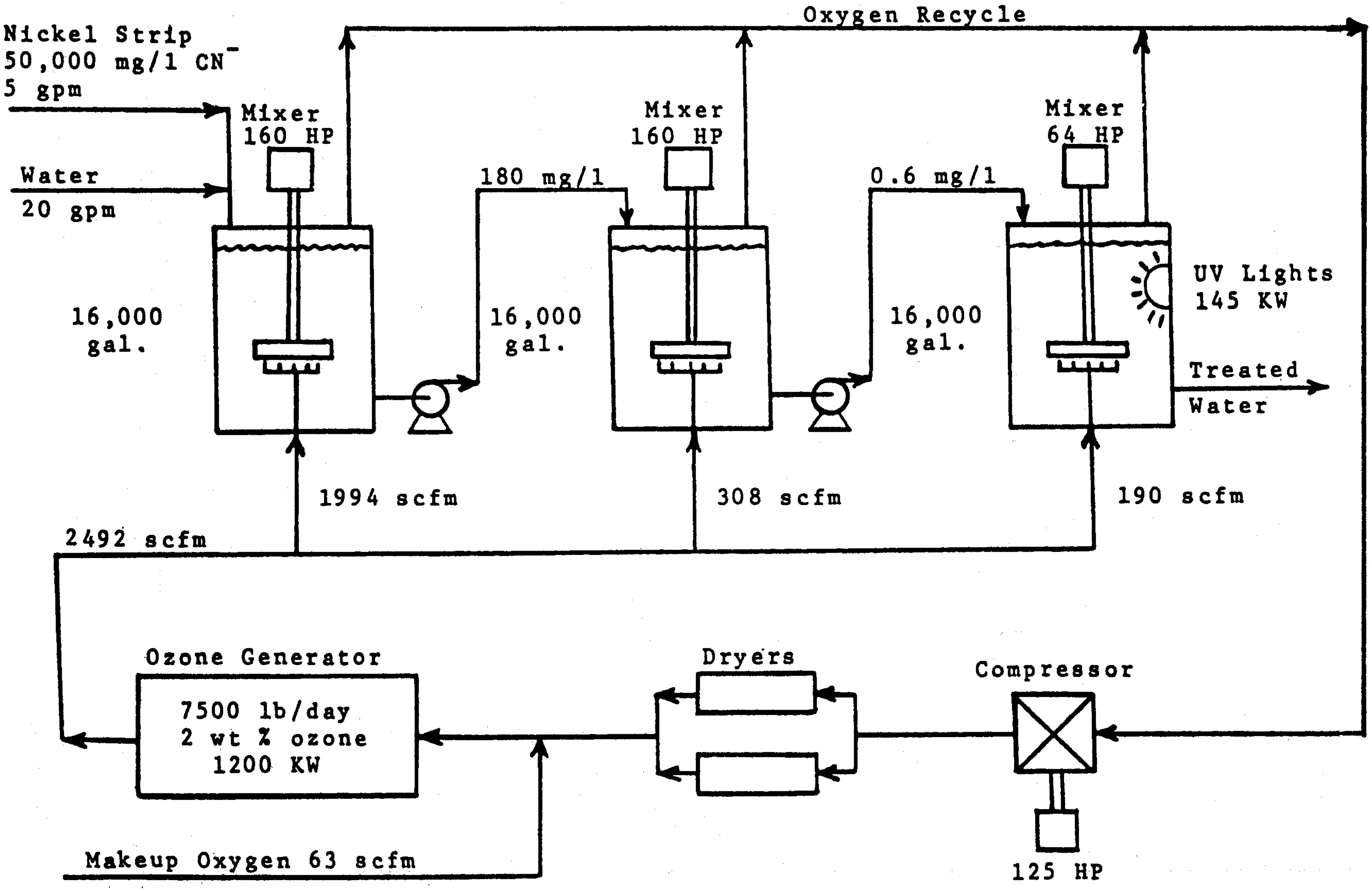
Source: Garrison, Mauk & Prengle, 1974

Other prototype experiments were conducted using higher cyanide concentrations, in which the gas feed contained 2.4 wt % ozone and was applied at the rate of 2.1 lbs/day. For fixer experiments, of the total ozone charged, 0.43 lb/day was fed to stage 3, 0.43 lb/day to stage 2, and 1.23 lbs/day to stage 1. Five 15-watt UV lamps were used in stage 3, and no UV lamps were used in stages 1 or 2. The temperature in all 3 stages was maintained at 65°C. The liquid feed contained 700 mg/l cyanide ion complexed with iron at a pH of 8.4. The pH of stage 1 was controlled at 7 using NaOH solution (Run P-3 of Table 46).



Source: Garrison, Mauk & Prengle (1974)

Figure 19. Effect of UV light and ozone concentration on ferricyanide at 77°F. Starting bleach cyanide concentration: 53 mg/l.



Source: Garrison, Mauk & Prengle (1974)

Figure 20. Full-size cyanide disposal system based on ozone/UV.

The discharge from stage 3 of the experiment starting with fixer waste containing 700 mg/l of cyanide complexed with iron contained no detectable cyanide (limit of detection: 0.2 mg/l). Cyanide concentration was reduced to 550 mg/l in stage 1 and to 70 mg/l in stage 2. The treated water from stage 3 contained 625 mg/l SS, and the effluent was clear and colorless.

A photo bleach solution containing 4,000 mg/l of cyanide complexed with iron also was treated in the prototype reactor system. After three stages of treatment, the level of complexed cyanide had dropped to 700 mg/l. Therefore, the effluent was reprocessed through the same three stages, but only after all wastewater had received 3-stage treatment. This gave the effect of a 6-staged reactor system (Run P-4 of Table 46).

Ozone concentration in the feed gas was 5.9%, and 0.50 lb/day was fed to stages 1 and 4 and 0.38 lb/day was fed to the other 4 stages. Five 15-watt UV lamps were employed only in stages 5 and 6 and no UV was used in the first 4 stages. The temperature in all 6 stages was controlled at 65°C.

The discharge from this prototype run contained no detectable cyanide (limit of detection: 0.3 mg/l). The cyanide concentrations leaving stages 1, 2, 3, 4 and 5 were 2,680, 1,630, 710, 105 and 13 mg/l, respectively. Approximately 1,900 mg/l of SS were formed during this run; after filtering, the resulting liquid was clear and colorless.

During these prototype runs, discharge gases from each run were collected and the amount of ozone remaining was measured. The difference between the ozone charged and the ozone discharged was taken to be the amount of ozone consumed (see Table 46). For the dilute cyanide runs (P-1 and P-2) the amount of cyanide plus other oxidizable components was nearly negligible. Thus, it appears that most of the ozone "consumed" can be attributed to decomposition. For the concentrated runs, P-3 and P-4, it is less certain how much ozone decomposed. For run P-3, fixer, considerable ozone reacted with the thiosulfate present. But unless ozone also reacted with cyanate, over one-half the ozone "consumed" might be attributed to decomposition.

More recent studies by Glaze et al. (1977) on ozonizing dilute solutions of humic acids in water in the presence of UV light have shown that UV rapidly decomposes ozone. Passage of ozone through pure water develops a measureable residual of ozone which has a certain stability. In the presence of UV light, 0 mg/l of zero residual ozone can be detected in solution. On the other hand, the power to oxidize humic materials is higher in the solution which has been treated with ozone and UV than in the solution containing the residual ozone which was not also treated with UV radiation. Thus the "decomposition of ozone", apparently without performing useful work, as observed by Garrison, Mauk & Prengle (1974), might have been the other way around, i.e., the ozone definitely was decomposed by the UV radiation, but to some species which apparently is a more powerful oxidizing agent than is ozone itself.

Studies pointed at identifying the mechanisms of UV/ozone oxidations are just beginning, and any further comments at this point would be merely conjectural.

Garrison, Mauk & Prengle (1974, 1975) developed the conceptual design for full scale cyanide disposal systems based on their studies of Air Force electroplating and photoprocessing wastewaters containing complexed cyanides. Estimated equipment costs for a 5 gal/min treatment system are $2,481,700, plus the cost of liquid oxygen storage for generating ozone from oxygen (Table 47). The major operating cost is 1.35 megawatts of power (probably per yr), with labor and makeup oxygen being in relatively minor proportion.

A reduced scale system capable of continuously processing 1,000 gal in five 24-hr days/week, and in which ozone is generated from air, was estimated to cost $217,000 capital (Table 48). The 3 reactors would each hold 450 gal. The first 2 mixers would have a 5 HP motor and the third would have a 2 HP motor. The third stage would require 4.1 kw for UV light. An 18 HP air compressor would drive 350 scfm of ambient air through driers into the ozone generator, which would require 34 kw to produce 210 lbs/day of ozone. The first reactor would receive 280 scfm of 1% ozone in air, the second would receive 43 scfm and the third 27 scfm. The system requires only 2 ozone generators of 105 lbs/day capacity, but a third generator is specified as backup. Major operating costs would be 8 man hrs/week labor, 60 kw of electrical power and $5000/year in replacement UV lights.

TABLE 47. COST ESTIMATE FOR 5 GPM CYANIDE TREATMENT BY UV/OZONE

Item	$ 000
Ozone generators, 9 ea., 840 lbs/day units @ $120,000	$ 1,080
Gas drying units for recycle @ $40,000 ea.	360
UV lights (tubes only), 8,050 @ 35.35	280
125 HP compressor	30
160 HP mixer, 2 @ $1,700	3.4
64 HP mixer	1
Glass lined reactors, 3 @ $12,000	36
Pumps, 3 @ $500 ea.	1.5
Total Hardware	$ 1,791.9
Engineering @ 10% of hardware	179.2
Ozone installation	180
Other installation @ 30% of hardware	105
TOTAL	$ 2,256.1
Fee @ 10% of total	225.6
	$ 2,481.7
plus cost of liquid oxygen storage	

Source: Garrison, Mauk & Prengle, 1974

Mauk & Prengle (1976) discuss this same Air Force contract work, but report data for UV/ozone destruction of ferricyanide bleach solution given in Table 49.

TABLE 48. COST ESTIMATE FOR 1,000 GAL/WEEK CYANIDE TREATMENT WITH OZONE/UV

Item	$ 000
Ozone generators, 3 ea., 105 lbs/day units @ $22,000	$ 66
Gas drying units @ $15,000 ea.	45
UV lights (tubes only), 500 @ $9.70 ea.	5
Compressors, pumps, etc. (from 0.7 power rule)	6
Hardware	$ 122
Engineering @ 10% of hardware	12
Ozone installation	60
Other installation @ 30% of other hardware	3.3
TOTAL	$ 197.3
Fee @ 10% of total	19.7
	$ 217.0

Uses air, not oxygen

Source: Garrison, Mauk & Prengle, 1974

TABLE 49. CYANIDE BLEACH DESTRUCTION WITH OZONE/UV
FERRICYANIDE BLEACH SOLUTION

Item	Influent Stage 1	Effluent From Stage					
		1	2	3	4	5	6
Total CN, mg/l	4,000	2,680	1,630	710	105	13	<0.3
CNO, mg/l	0						47
Temp., °C	20	66	66	66	66	66	66
pH							8.9
UV light, watts	--	0	0	0	0	0	75
Liquid flow, l/hr	2.36	2.36	2.36	2.36	2.36	2.36	2.36
Ozone added, g/hr	--	9.45	7.18	7.18	9.45	7.18	7.18

Source: Mauk & Prengle, 1976

Dougherty et al. (1976) studied the photographic processing subcategory of the photographic point source category for the purpose of developing effluent limitations and guidelines for existing point sources and standards of performance and pretreatment standards for existing sources and new sources, to implement Sections 301(b), 301(c), 304(b), 304(c), 306(b), 307(b) and 307(c) of the Federal Water Pollution Control Act, as amended. This subcategory is defined to include commodities listed under Standard Industrial Classifications (SIC) 7221, 7333, 7395 and 7819. An estimated 95% of all photoprocessing plants discharge their wastewaters to municipal sewer systems. Regeneration of photoprocessing bleach solutions is recognized and is specified by EPA as BPTCA for cyanide control in existing plants. For the 1983 discharge standards requiring application of Best Available Control Technology Economically Achievable (BATEA) and for New Source Performance Standards, oxidation of BOD-5 and COD is specified, along with filtration and ion exchange.

These investigators found 2 plants, one discharging 50,000 gal/day and the other plant discharging an unknown quanity of wastewaters (out of 237 plants surveyed) which are currently using ozonation to recover and reuse photographic bleach solutions. The EROS Data Center in Sioux Falls, S.D. has installed an ozonation system to regenerate used bleach. In addition, as the tenth of 11 wastewater treatment steps, ozonation in a series of tanks reduces COD levels from an average of 25,000 mg/l to less than 5,000 mg/l. The ozonized water then is discharged to treatment ponds, which subsequently reduce the COD to 30 mg/l, ferrocyanide to 0.05 mg/l and total silver to 0.006 mg/l.

In reviewing the literature, Dougherty et al. (1976) concluded that the photoprocessing chemicals could be grouped as shown in Table 50: those treatable by ozonation, those marginally treatable, and those not treatable. Only glycine and acetate ion are non-treatable, but both are biologically susceptible.

Conclusions

1) Ozonation is a commercially practiced technique for regeneration of spent photoprocessing bleaches, which are composed of iron cyanide complexes. These complexes are so stable to oxidation by ozone that spent ferrocyanide bleaches are oxidized upon ozonation only to the ferricyanide forms.

2) Savings of 2 to 3¢/roll of film processed are being obtained at commercial photoprocessing houses using ozone for bleach recovery. Investment costs for a 200 g/hr ozonation bleach recovery system should be recovered in 5 yrs or less, depending upon the amount of film processed.

3) Such ozone/bleach recovery systems have been operational since 1971 at photoprocessing plants. Television studios have been using ozone systems to recover bleach solutions and/or to destroy photoprocessing wastewaters since 1972. Annual savings in chemicals amount to $4,000

to $9,000 per yr, depending upon system size and amount of photographic materials processed.

TABLE 50. TREATABILITY OF PHOTOPROCESSING CHEMICALS BY OZONATION

Treatable Chemicals	Non-treatable Chemicals
HAS	Glycine
Benzyl Alcohol	Acetate ion
Color Developing Agent	
Thiosulfate	
Sulfate	
Hydroquinone	
Kodak Elon Developing Agent	
Phenidone	Marginally Treatable Chemicals
EDTA	
Ferric EDTA	
Formate ion	Ethylene Glycol
Maleic Acid	Methanol
Eastman Color Print Effluent	Ferricyanide
Ektaprint 3 Effluent	Ethylenediamine
Flexicolor Effluent	Ektachrome ME-4 Effluent
Synthetic Effluent from Combined Process	

Source: Dougherty et al, 1976

4) Hydroxylamine sulfate, benzyl alcohol, thiosulfate, sulfite, hydroquinone, phenidine, EDTA, sodium formate, formaldehyde and potassium thiocyanate all are readily oxidized by ozone.

5) Organic developing agents CD-1, CD-2, CD-3 and CD-4 all are decolorized upon ozonation, but COD levels are reduced only 60% to 70% over 8 hrs of ozonation, after which COD levels become constant. This implies that the original organic molecules are oxidized to simpler organic materials, but which are more refractory to ozone oxidation.

6) Glycine and acetate ion are not treatable with ozone (for wastewater discharges), but both of these can be treated biologically.

7) As the tenth in a sequence of 11 wastewater treatment steps in an operating photoprocessing center, ozonation reduces COD levels from an average of 25,000 mg/l to less than 5,000 mg/l. The ozonized water then is discharged to biological treatment ponds which subsequently lower COD levels to 30 mg/l.

8) Immersion of UV light bulbs in ozonation reactors increases the rate of oxidation of components of photoprocessing wastewaters. For example, 1% ozone with UV radiation gave about the same amount of oxidation of bleach cyanide as did 5% ozone.

9) In a 6-stage ozone/UV reactor, a photographic bleach solution containing 4,000 mg/l of iron-complexed cyanide, the level dropped to 700 mg/l after passing through 3 treatment stages. After 6 treatment stages, no

cyanide was detected (less than 0.3 mg/l).

10) Estimated equipment costs for a 5 gal/min ozone/UV system designed for treating photoprocessing or electroplating wastewaters are $2.48 million.

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PLASTICS AND RESINS

Four pertinent publications have been found dealing with this category. Wastewaters treated with include:

Phenol-formaldehyde manufacturing
Synthetic Polymers
Synthetic Leather
Synthetic Rubber

Phenol-formaldehyde Manufacturing

Linevich et al. (1972) discuss the ozonization of wastewaters containing phenol and formaldehyde. However, the original article could not be obtained and the only information at hand in English is a short abstract which notes that both the phenol and formaldehyde components were oxidized.

Synthetic Polymers

Kwie (1969) reported a laboratory study using wastewaters from an unidentified synthetic polymer plant. Although the plant product was not identified, the wastewaters contained unsaturated organics and some sodium 8-alkylnaphthalene sulfonate-2 (SANS) which is very resistant to biodegradation. Ozone was generated from oxygen and the ozone content of the oxygen used was 101 to 106 mg/l. Ozone was determined in the inlet gas and in the contactor off-gases. The contactor was a 100 ml bubbler vessel.

Ozonation just to the point of oxidizing all the unsaturated organics (which react readily with ozone) lowered the COD content from 3,340 mg/l to 910 mg/l and 5,400 mg/l of ozone was absorbed by the solution in an unspecified contact time.

An ozonized wastewater sample which had a COD of 1,380 immediately after ozonation had a COD of 450 mg/l after 7 days of storage. This is attributed to the further reaction of aldehydes (initially formed upon ozonation) with dissolved oxygen to form acids. Biological oxidation of this ozonized sample is ruled out because of its very high salt content.

In all samples studied, foaming ability, color and odor levels were reduced upon ozonation. Colloidal orange substances were converted upon ozonation into an easily settleable sludge. One aromatic ring of SANS was cleaved during ozonation, but the remaining ring-containing compound was resistant to further ozonation. Ozonation of SANS did not increase its biodegradability.

Synthetic Leather

Bauch & Burchard (1970) ozonized the wastewater from an artificial leather plant in Wuppertal, Federal Republic of Germany. The wastewater from the plant had been mixed with municipal sewage. Data of Table 51 show

TABLE 51. WASTEWATER FROM AN ARTIFICIAL LEATHER PLANT, MIXED WITH SEWER WATER. TREATMENT WITH OZONIZED AIR: 30 MINUTES. (20 MG OZONE/AIR)

	Appearance after preliminary clarification	Odor	Odor Threshold	$KMnO_4$ Consumption mg/l	BOD-5 mg/l	Heavy Metals Zn, Cu, Pb mg/l	Volatile Hydrocarbons mg/l	Phenols		Petroleum Ether Soluble mg/l
								Volatile mg/l	Not Volatile mg/l	
Untreated sewage after 24 hours of settling	milky turbid	strictly of solvent and amyl	1:800	950	720	20 mg Zn	90	25	30	70
Sewage after precipitation by means of iron chloride and sodium hydroxide (NaOH) at pH 8.0	clear yellowish	strictly of solvent and amyl	1:700	910	830	--	80	28	20	32
Clarified sewage gassed cold with air	clear yellowish	strictly of solvent and amyl	1:600	800	790	--	60	29	19	34
Clarified sewage gassed hot with air	clear yellowish	strictly of solvent and amyl	1:180	620	580	--	20	8	22	30
Clarified sewage treated with ozone	clear yellowish	faintly of phenol	1:20	250	200	--	not detectable	not detectable	11	24
Clarified sewage, after pretreatment with Cl_2 & treated with ozone	clear yellowish	faintly of ester	1:16	180	120	--	not detectable	not detectable	5	18

Source: Bauch & Burchard, 1970.

the results obtained. For comparison, data also are given after flocculation with iron chloride and caustic at pH 8.0, after cold and hot aeration, after treatment with ozone (30 minutes using 20 mg/l of ozone in air) and after pretreatment with chlorine, followed by ozonation.

Ozonation lowered the permanganate number from 950 to 250 mg/l and the BOD-5 from 720 to 200 mg/l. Pretreatment with chlorine followed by ozonation lowered the permanganate number to 180 and the BOD-5 to 120 mg/l, and is therefore the preferred treatment process.

Synthetic Rubber

Chen & Okey (1977) describe a 10 gpm pilot study using actual wastewaters from emulsion polymerization of GRS rubber. These wastewaters contain butadiene, styrene, K rosin soap, detergent, sodium phosphate, caustic, Cerelose, ferrous sulfate, potassium pyrophosphate, cumene hydroperoxide, tertiary mercaptans, hydroquinone and N-phenyl-2-naphthylamine. The BOD and COD of the alum coagulated and settled wastewater from the latex filtering step were 70 and 365 mg/l, respectively, and were only about 20% biodegradable.

Ozonation was conducted under undefined conditions, except that a bubbler contactor was employed and flow rates of ozonized air were 1.0 or 1.5 scfm. At the higher ozone flow rate, COD concentration in the plant effluent was lowered from 365 to 160 mg/l in 40 minutes. Addition of 360 mg/l $NaHCO_3$ under the same conditions lowered the COD to 85 mg/l in the same 40 minutes of ozonation. At 1.0 scfm the COD concentration was lowered 47% and 70% without and with added bicarbonate, respectively. The optimum pH for ozonation of these wastewaters was 6.0 to 8.5.

Effluents treated with ozone exerted substantial influence on oxygen uptake, whereas untreated effluents did not. This indicates that ozonation of biorefractory organic materials followed by biological treatment would be a better way to treat such organic materials.

Upon ozonation, the distinct odor of butadiene-styrene was replaced by a milder scent. Turbid solutions became clear and suspended matter settled within 10 to 20 minutes of ozonation.

Conclusions

1) Wastewaters from a synthetic polymer plant containing SANS and unsaturated organics and ozonized just to the point of oxidizing all unsaturated organics, lowered the COD content from 3,340 mg/l to 910 mg/l. One aromatic ring of the SANS molecule was cleaved during ozonation, but the remaining ring-containing compound was resistant to further oxidation by means of ozone.

2) Ozonation of wastewater from a synthetic leather plant, which had been mixed with municipal sewage, lowered the permanganate number from 950 to 250 mg/l and the BOD-5 from 720 to 200 mg/l. Prechlorination,

followed by ozonation, further lowered the permanganate number to 180 mg/l and the BOD-5 to 120 mg/l, and is a preferred treatment process for this wastewater.

3) Ozonation of wastewaters from emulsion polymerization of GRS rubber for 40 minutes at pH 6.0 to 8.5 lowered the COD level from 365 to 160 mg/l and to 85 mg/l when bicarbonate was added. Ozonized effluents were biodegradable, whereas the unozonized effluents were not.

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* Abstracts of asterisked articles will be found in EPA 600/2-79- b.

PULP AND PAPER

In this category, ozone has been studied for four major purposes:

- Pulp bleaching
- Pulp and paper mill wastewater treatment
- Odor control at paper mills
- Treatment of spent sulfite liquor to generate methane and to grow yeast

Pulp Bleaching

Although initial studies of the use of ozone for bleaching of paper pulps were conducted by Dorée & Cunningham in 1913, it has only been during the past decade that the process has shown promise of becoming commercial (Abadie-Maumert, Fritvold & Soteland, 1977; Liebergott, 1975). When fluffed wood pulp is treated with ozone, both the cellulosic and lignin portions can be oxidized. However, oxidation with ozone never is complete (to produce CO_2 and water). In fact, if more than initial oxidation occurs, the properties of ozone-bleached wood pulps degrade, due to over-oxidation of the cellulosic and/or lignin portions of the pulp fibers. The key to successful use of ozone for pulp bleaching appears to involve the judicious selection of ozonation conditions such that only partial oxidation occurs. This forms additional oxygen-containing sites on the fibers, and these are capable of being tightly bonded to each other or to other paper-making ingredients added later in the paper-making process.

Successful bleaching of wood pulps with ozone would mean that use of the polluting bleaching agents (sulfite, chlorine, etc.) could be reduced or even eliminated, thus reducing what today is a severe water discharge problem in many parts of the world.

The bleaching process with ozone involves passing ozone in the gas phase (usually in oxygen) saturated with water through fluffed wood fibers. The fibers are not suspended in water.

Samuelson _et al_. (1953) showed that the degree of polymerization of cellulose diminishes appreciably upon exposure to ozone. Initial degrees of polymerization (DP) of about 1,300 rapidly reach a levelling off DP of just over 100.

Osawa _et al_. (1963a; 1963b) showed that gas phase ozonation of fluffed wood pulp using ozonized gas 100% saturated with water degrades the carbohydrate fraction of the wood fiber, without penetrating the cellulose crystallites. The odor of acetic acid was noted.

Lantican et al. (1965) showed that ozone in oxygen first degrades the incrustation on cellulosic walls, then attacks the secondary wall itself, beginning at the lumen, then progresses slowly through the secondary wall until it reaches the middle lamella, resulting in pulping of the wood. The water soluble fraction of wood increases with duration of ozone treatment, and the cell wall is progressively delignified as ozonation continues.

Katai & Schuerch (1966) showed that the attack of ozone upon cellulosic fibers follows 2 mechanisms:

(1) A free radical chain mechanism (slow) which forms peroxides, hydroperoxides, carbonyl and carboxy groups and, presumably, lactones,

(2) Electrophilic attack which liberates the anomeric carbon of glucosides via an ozone catalyzed hydrolysis of glycosidic linkages.

Ozonation of several sugars was studied and ozone was found to attack ketonic, aldehydic and alcoholic groups. At the same time, however, ozonation of cellulose introduces oxygen atoms into the polymeric structures to form these same groups, as well as to cause depolymerization of the cellulose and lignin structures.

Moore et al. (1966) studied the gas phase ozonation of wood fibers for time periods of up to 30 hrs. Significant portions of the hemicelluloses containing xylose and mannose were found to persist in wood fibers during the extensive degradation of wood shavings by ozone (in oxygen) in the presence of cold water under a variety of conditions. Three types of reactions were observed to occur:

(1) Ozonolysis of aromatic and unsaturated structures,

(2) Ozone-initiated chain oxidation of aliphatic functional groups to yield a variety of oxidized carbohydrate residues,

(3) Hydrolysis of glycoside linkages, with both ozone and proton (H^+) participating as electrophilic catalysts.

Glucose was found to be the wood sugar most resistant to ozone oxidation. In addition, the average degree of polymerization of the fibers decreased to 250 to 300, before the fiber started to delignify. High water soluble fraction losses were found under these conditions.

Neimo et al. (1967) treated bleached pine sulfate pulp with ozone in the gas phase and found that ozone reacts with the cellulose to form peroxide and hydroperoxide groups. These slowly decomposed into free macroradicals by heat treatment (to 80°C). Most of these radicals were found to be located in the cellulose phase. After ozonation of cellulose, polyacrylamide (1 to 33%) or polyacrylonitrile (1 to 13%) can be grafted onto the cellulose by these macroradicals.

Ozonation of cellulose by Neimo et al. (1967) gave impaired paper making properties; however, when grafted with polyacrylamide the paper making properties were almost restored. The wet breaking length rose, in fact, to a value 150% above the initial length after grafting.

Ancelle (1966) was issued a patent claiming that when chopped wood pulp (dry and at pH 6 to 7.5) is ozonized in a stream of air saturated with water (15.5 mg/l ozone in the gas phase), a bleached pulp is obtained having improved whiteness, rupture length, bursting index and tearing index.

Hatekeyama et al. (1967) studied the reactions with ozone of the model lignin compounds vanillyl alcohol and veratryl alcohol in aqueous solution. The primary oxidation product from each of these model compounds (under acidic conditions) is a muconolactone methyl ester. In both cases the aromatic ring was opened, Demethylation also occurred in the position para to the side chain. Under alkaline conditions the reactions were faster (Figure 21). These authors concluded that when free hydroxyl groups are present on aromatic rings, the ring will open upon ozonation, producing muconic acid derivatives, then maleic and/or oxalic acid derivatives.

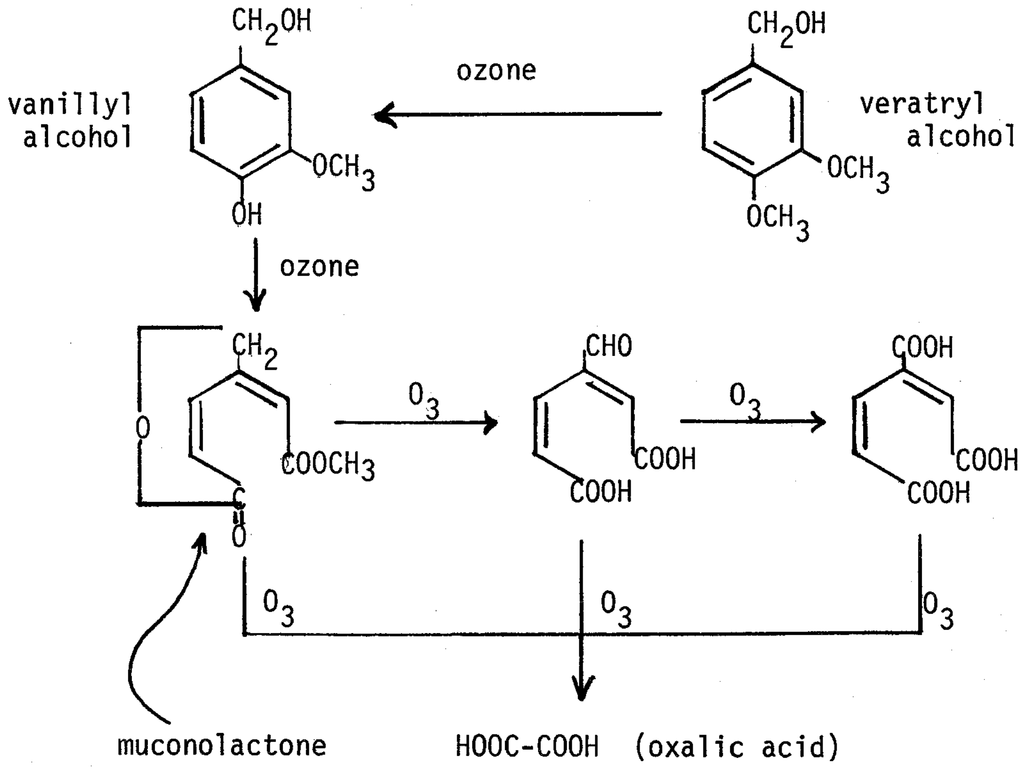


Figure 21. Ozonation of model lignin compounds.

Katuscak et al. (1971a) studied the ozonation of various lignins. Methanol lignin, HCl-lignin and diazomethane methylated HCl-lignin were ozonized either as the dry solids or suspended in protogenic solvents (water, acetic acid or methanol). The objective of this work was to prepare lignin containing as many hydroperoxide groups as possible. Methanol lignin ozonized fastest of the three, and oxidation occurred faster in acetic acid. The ozonized lignins were capable of initiating polymerization of unsaturated monomers by free radical reactions.

In later work, Katuscak et al. (1971b) studied the ozonation of low molecular weight methanol lignin in greater detail. Ozonation increased the active and total oxygen contents, decreased molecular weight, formed carbonyl groups and attacked aromatic rings. Bleaching took place within about 10 to 15 minutes of the start of ozonation with methanol lignin in the dry state and no further color change occurred. Molecular weight reduction was fastest during the first five minutes of ozonation. The number average molecular weight dropped from 1,700 to 800 in 5 minutes, then dropped to 550 after 1 hr of ozonation. Aromatic rings were destroyed and carbonyl content increased within the first 5 minutes of ozonation. These authors concluded that since the active oxygen in the ozonized lignin initiated radical polymerizations, the active oxygen must be in the form of hydroperoxides, since ozonides and quinonoidal structures cannot initiate this type of polymerization.

In Canada, studies of the bleaching of mechanical pulps with ozone have been described by Liebergott (1969), Clayton, Liebergott & Joachimides (1971) and Liebergott (1975). In 1969, Liebergott found that addition of 0.2 to 0.6% H_2O_2 to groundwood pulp, followed by treatment with 1% ozone in air increased the brightness of the bleached pulp 4 to 9 points, and also gave substantial increases in textile and bursting strengths. The ozonation technique was applied successfully to 6 representative stone and refiner groundwood pulps.

In 1971, Clayton, Liebergott & Joachimides confirmed that the new process improved the strength of mechanical pulps, and that the ozone-bleached mechanical pulps could be used in newsprint furnishes, with a corresponding reduction in the amount of chemical pulp normally added. This would reduce the amount of chemical pulp required by the newspaper industry, thereby reducing the amount of pollution in aqueous discharges from chemical pulp mills using zinc hydrosulfite bleaching.

Finally, in 1975, Liebergott described the results of continuous run pilot plant operation of the PAPRIZONE pulp bleaching process. Groundwood is sprayed with H_2O_2, then ozonized in the gas phase to produce a bleached mechanical pulp suitable for incorporation into newsprint furnishes. The mechanical pulp is adjusted to 30 to 40% consistency, fluffed to form loose fiber aggregates, sprayed with 4 lbs of H_2O_2/ton of pulp, then treated with 4% ozone (in oxygen) (20 lbs of ozone/ton of pulp). Following ozonation, the material is retained 15 to 30 minutes before further processing. This treatment leads to improved breaking lengths, improved burst factors, improved brightness and lowered opacities. Liebergott (1975) concluded that even if ozone were to cost 50¢/lb, the process is economical, saving $2.50 to $10.00/ton of $12.50/ton mechanical pulp (depending upon the amount to be produced) and lowering the requirements for chemical pulps in newsprint.

Similar studies were initiated at the Norwegian Institute of Paper Research in the late 1960s. Soteland & Kringstad (1968) showed that the oxidative treatment of high yield paper pulps can double the breaking length of a spruce mechanical or chemical pulp with a loss in yield no greater than 5%. They concluded that the improved strengths result from increased hydrophilicity caused by ozone modification of the lignin structure.

Soteland & Kringstad (1968) found that ozone did not reduce the specific absorption coefficients of the mechanical or chemical pulps studied, probably because of secondary reactions between water and the initial reaction products of ozonation of the pulps. However, if the ozonation was carried out in acetone/water (90/10) suspensions, the specific absorption coefficients were reduced to levels comparable to those of a fully bleached chemical pulp. On the other hand, very strong ozonation was required to attain this effect, indicating that some chromophoric groups are very stable to ozone. When the ozonized pulps then were treated with water, colored products were formed and the brightness dropped below that of the unbleached pulps., This indicates that hydrolytic reactions were forming or reforming color-causing chromophoric moieties.

Soteland (1971) ozonized groundwoods of western hemlock, eastern spruce, cottonwood and poplar in 90/10 (vol/vol) acetone/water, or pre-extracted these pulps with acetone, then ozonized them. Strong ozonation conditions resulted in increased losses of yield. Alkaline treatment after ozonation drastically increased pulp yield losses. Wet storage of ozonized pulp produced colored material in the pulp. The production of these chromophoric groups became higher as ozonation treatment was increased. All ozonized groundwoods showed high brightness reversion upon heating.

Soteland (1974) reviewed the progress made to that time on pulp bleaching with ozone. Attempts to develop ozone bleaching did not begin in earnest until about 1963. Ozonation produces marked drops in viscosity and acts more like a delignification agent than a bleaching agent. A chemical pulp cannot be bleached with ozone to high brightness before most of the residual lignin is removed. Nevertheless, research on bleaching of pulps with "environmentally acceptable" agents (oxygen, ozone and H_2O_2) was continued.

Soteland & Lorås (1974) showed that ozonation of mechanical pulps produced considerable increases in tensile strengths. Softwood mechanical pulps decreased in brightness upon ozonation, but hardwood pulps increased in brightness. Drainage properties of mechanical pulps are little influenced by ozonation. Some fiber components are solubilized by ozonation, resulting in yield losses.

Studies at the Norwegian Institute of Paper Research (NIPR) have culminated in a semi-commercial pilot plant which is described by Abadie-Maumert, Fritzvold & Soteland (1977). The results of laboratory studies at NIPR on bleaching mechanical and chemical pulps have been so promising that five of the largest Norwegian paper companies and a mechanical engineering company have collaborated in the construction of this demonstration plant.

The plant capacity is 200 kg of pulp processed/hour with 6 kg of ozone produced from oxygen. The plant is located at an existing paper pulp factory so that the products can be blended and/or used to produce papers in production lots and in commercial equipment. The plant has been operational since May 1976. Newspapers have been prepared from ozone-bleached pulps without the use of chemical pulp.

NIPR personnel apparently are concerned now only with the quantities of ozone which will be required if the ozone bleaching process is adopted by the Norwegian paper industry. For example, a newspaper pulp production plant producing 250,000 tons/year could replace 30% of its chemical pulp (75,000 tons) with thermomechanical pulp prepared by ozone treatment (using 2% ozone in oxygen). This 75,000 tons/year of ozone bleached pulp would require 1,500 tons/year of ozone, or 5 tons/day. For a sulfate bleaching plant producing 300,000 tons/year the pulp would require treatment with 0.8% ozone. This equates to 2,400 tons of ozone/year or 8 tons/day (Abadie-Maumert, Fritzvold & Soteland, 1977).

These quantities of ozone are very much within the current capabilities of the companies which manufacture ozone generation systems. For example, the city of Montreal, Canada is installing a new drinking water treatment plant which when completed in the early 1980s will be capable of generating 15,000 lbs of ozone per day from air in 1% concentration. This will be the largest drinking water treatment plant in the world at that time to use ozone (Miller et al., 1978). If oxygen were to be used as the feed gas in the Montreal ozone generators, the ozone generation capacity would be doubled to 30,000 lbs/day (15 tons/day).

In the United States, ozone bleaching of wood pulps was first reported by Secrist & Singh (1971). In 1974 a news release (Anonymous, 1974) announced that successful demonstration of ozone bleaching of hardwood pulps on 15 ton/day scale had been conducted at the Scott Paper Company, Muskegon, Michigan plant. The economics as well as the pollution abatement potentials of the ozone bleaching process "appear to make the process an attractive alternate for conventional hardwood bleaching". To date, however, full scale commercial adoption of ozone bleaching has not yet been announced.

Wastewater Treatment

Experiments to eliminate or reduce pollution-causing components in wastewaters from the pulp and paper industry did not begin seriously until the early 1970s. Huriet & Gelly (1970) patented a process for totally decolorizing kraft black liquors using ozonized air in aqueous media, the concentration of ozone in the air being controlled as a function of color intensity. The ozonation step preferably should follow partial color removal using lime.

In the laboratory, Tyuftina (1971) applied ozone to residual liquor from yeast cultivation before and after biological treatment. In both cases, a reduction in color intensity was obtained. The best results were obtained by ozonation of the residual liquor at 37°C in an alkaline medium -- the reduction in color intensity was 84.5% at an ozone consumption of 3.24 g/l. Treatment of purified residual liquor with 0.2 g/l of ozone reduced the color intensity by 78%.

Buley (1973) discussed the coming application of high purity oxygen to numerous process applications in the pulp and paper industry, and also discussed the potentials of ozonation in treating pulp mill wastewaters.

Furgason et al. (1973) describes a potable test unit for treating liquid materials with ozone. Basic characteristics of the unit include:

Reactor Volume	2 gal
Reactor Residence Time	1 to 20 min
Wastewater Feed Rate	0 to 1.5 gal/min
Ozone Production Rate	12 g/hr

Contacting is by Venturi nozzle (vacuum injection) so as to have the unit size as small as possible and still have good mass transfer of ozone to the liquid phase. Ozone is prepared from oxygen and contactor off-gases are passed through a molecular sieve column (to destroy excess ozone) before discharging to the atmosphere.

Extensive field work using this portable test unit was reported (Furgason et al., 1973) on kraft pulp mill effluents, which are dark brown, pungent wastewaters. Contaminating materials originate from lignin and its derivatives, which are complex organic molecules containing phenolic structures and other configurations which are not easily biodegraded. Therefore, wastewaters from a pulp mill can pass through normal primary and secondary treatment facilities without the color and odor being significantly reduced. In fact, color may become even worse (Furgason et al., 1973).

Effluents from the Potlach Forests kraft mill at Lewiston, Idaho were treated with ozone (Furgason, Smith & Harding, 1973). Wastewaters from the bleach plant, total plant, primary clarifier and extended aeration secondary system were tested with ozone. Little differences were noted between the ozonized streams with regard to color, odor, and COD removals. Therefore, the bulk of the ensuing data were taken on the primary clarifier output material with the following results:

The color of the sulfite liquor changed dramatically from a dark chocolate brown to light straw yellow after about 5 minutes in the reactor. During this time, the strong sulfur-laden odor disappeared entirely. Also during this time, COD removal usually was 10 to 15%, but occasionally rose to 30%, even though less than this amount of CO_2 was formed. This suggested to Furgason et al. (1973) that ozone should not be used as a post- or tertiary treatment, but should precede secondary biological treatment.

These tests with ozonation of kraft mill wastewaters definitely established the utility of ozone as a decolorizing or deodorizing agent. Preliminary estimates indicated that ozonation costs for a full scale plant would be in the range of 30¢/1,000 gal.

Nebel, Gottschling & O'Neill (1974) reviewed the decolorization of pulp and paper mill secondary effluents by chemical coprecipitation, adsorption, reverse osmosis and chemical oxidation with $KMnO_4$, H_2O_2, chlorine and ozone. Experiments were conducted on pulp and paper mills from four unidentified plants using ozone generated from air or oxygen. Contacting was conducted in a 6.5 inch I.D. x 10 ft column using porous plastic (type not specified) diffusers. Ozone was analyzed at the entry and at the exit of the contactor. Since normally no ozone was found in the off-gases, the authors concluded that the numerical amount of ozone dosed to the contactor was the amount of ozone absorbed by the secondary effluent. Color was determined by the NCASI (National Council of the Paper Industry for Air and Stream Improvement) procedure at pH 7.6 and 465 nm wavelength. Results obtained on each plant effluent are discussed below.

Plant A: this was a kraft mill producing fine papers. To remove color from 520 to 100 APHA units in the wastewater required 70 mg/l of ozone dosage. This ozone dosage also produced a 37% reduction in COD values (298 to 188), 98% total bacteria removal (240,000/100 ml to 4,900/100 ml) and 93% total coliform removal (24,000/100 ml to 1,600/100 ml).

Plant B: also was a kraft mill producing fine papers. The ozonation objective at this plant was to reduce color levels from 900 APHA units to 200, and this required 81 mg/l dosages of ozone. At the same time, this dosage of ozone provided 29% reduction in COD values (248 to 176 mg/l) and lowered turbidity by 50% (950 to 479 JTU).

Plant C: was a bleached board plant using kraft and neutral sulfite pulps. To reach the goal of 200 APHA units (from 1,600) required 143 mg/l ozone dosages, which also lowered turbidity 67% (620 to 207 JTU), COD by 21% (275 to 217 mg/l), BOD by 16% (147 to 124 mg/l), total bacteria 99% (130,000,000 to 1,180,000) and fecal streptococci 100% (40 to zero). During ozonation of Plant C effluent, the BOD was found to decrease initially upon ozonation, then increased to a peak value corresponding to an ozone dosage of 143 mg/l (Figure 22). This is the same dosage which removes the maximum amount of color. Therefore, the color of this effluent is associated with the COD and not the BOD.

Plant D: is a paper mill making paperboard from reclaimed paper. There is no pulping operation at this plant. Six samples were ozonized, 3 of which contained dyes and required the highest ozone dosage levels (29 mg/l) to reduce color levels to 50 APHA units (from 170). At the same time, COD levels were reduced 51% (67 to 33), turbidity was lowered 63% (230 to 85 JTU), tannin and lignins were 67% removed (3.3 to 1.2 mg/l) (note: original article says 33% removal) and total coliforms were 99.99% removed (20,700 to 2/100 ml). This same wastewater required 150 mg/l of chlorine to achieve the same level of color removal. Costs for chlorination of 2.5 mgd (@ 5.25¢/lb for chlorine) were $164.50/day, whereas ozonation costs were $48.40, including amortization, with ozone being generated from air.

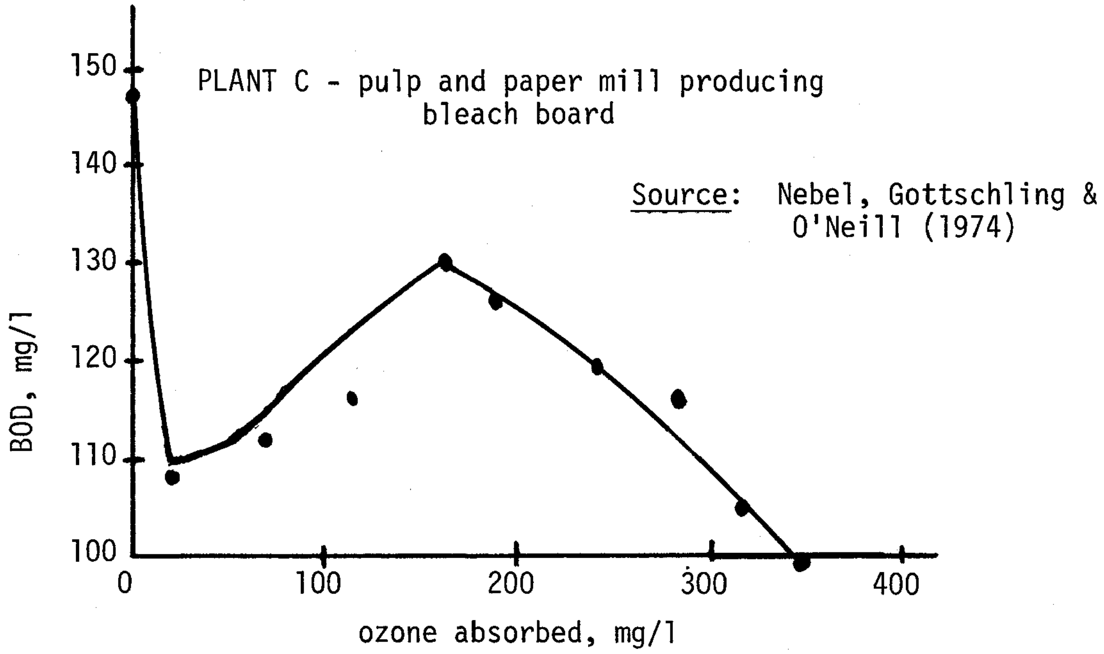


Figure 22. Reduction in BOD values by ozonation.

Table 52 shows the estimated daily operating expenses and capital investments required to attain the color removal objectives (using ozone) at the 4 plants, and Table 53 shows the treatment costs/1,000 gal at these plants using ozone.

TABLE 52. DAILY OPERATING COSTS & CAPITAL INVESTMENT

Plant	Daily Ozone Requirements	Feed Gas to Ozone Generators	Daily Operating Expense	No. of Ozone Generators	Capital Investment for Ozone Generators
A	8,750 lbs	Oxygen	$ 393.75	4	$315,000
B	10,800 lbs	Oxygen	$ 486.00	5	$372,000
C	29,780 lbs	Oxygen	$1,340.10	14	$976,000
D	605 lbs	Air	$ 48.40	1	$ 95,000

Source: Nebel, Gottschling & O'Neill, 1974.

TABLE 53. OZONE TREATMENT COSTS

Plant	Capital Investment for Ozone Generators	Installed Cost	Annual Debt Retirement	Cost per 1,000 gal
A	$315,000	$ 378,000	$30,220	3.1¢
B	$372,000	$ 446,400	$36,370	3.2¢
C	$978,000	$1,173,600	$96,180	6.4¢
D	$ 95,000	$ 114,000	$ 7,706	2.8¢

Source: Nebel, Gottschling & O'Neill, 1974.

These data were obtained by applying ozonation after secondary treatment. The additional advantages of disinfection, COD and BOD removals and turbidity reductions also are obtained upon ozonation for the primary objective (color removal), at least partially. Also, since the DO content of the wastewater is greatest after ozonation, a reaeration step will not be required. The authors also point out that using ozonation processes for color removal in these types of effluent will not result in sludges being formed during this treatment step.

Moergli (1973) reported on the treatment of paper and board mill effluents by flocculation, followed by filtration (to remove 95% of the SS, then ozonation, which reduced levels of dissolved organic materials by 55% and was "very effective" in color removal. Further treatment with activated carbon reduced the SS content to 1 mg/l and permanganate consumption to less than 60 mg/l, producing a water which could be recycled.

Kamishima and Akamatsu (1973,1974) attempted to improve color removals after activated sludge treatment of alkaline extracted effluents from the bleaching of kraft pulp. Ozonation of the effluents resulted in improved removals of TOC, COD, lignin and color, compared with conventional activated sludge treatment. Subsequent activated sludge treatment of the ozonized effluent showed "adequate" BOD removal. Activated carbon adsorbed very little lignin from the ozonized effluent.

Watkins (1973) studied coliform bacteria growth and control in aerated stabilization basins. The majority of this study involved chlorination of secondary treated effluents from the Crown Zellerbach plant at Camas, Washington. A small section of this report was devoted to "Evaluation of Miscellaneous Bacteriocides" -- ClO_2, NaOCl and ozone.

In the ozonation studies an ozone generator was used which generated ozone from oxygen. Secondary effluent was passed through a <u>rubber hose</u> (1.5 inches I.D.) which contained an ozone sparger and was used as the ozone contactor. Ozone dosage rates were calculated from the output of the ozone generator. Reactions between the effluent and ozone were "monitored" by smelling the treated wastewater for ozone. "Since ozone at concentrations of 0.1 mg/l or less can be smelled -- the absence of an ozone odor was considered to be evidence that most, if not all, of the applied effluent had reacted with the effluent".

Apparently Watkins was unaware that ozone reacts very rapidly with rubber and with plasticizers for rubber and plastics. Therefore, with this rubber hose ozone contactor, very little dosed ozone would be expected to survive for reaction with effluent constituents.

The original ozone concentration was 0.46 mg/l and the flow rate of gas through the ozone generator was adjusted so that the applied dosage of ozone was varied between 0.46 and 4.6 mg/l. After 30 minutes of treatment under these conditions, Watkins found no effect upon bacterial motility and no reduction in the concentration of bacteria.

Watkins then increased the rate of oxygen flow through the ozone generator by 5 times, in an attempt to increase the ozone dosage to 21 mg/l. However, no mention is made of increasing the power applied to the ozone generator as the oxygen flow rate was increased. If power were not increased, then the total amount of ozone generated in five times the gas volume would be slightly more, but the concentration of ozone in that increased volume of gas would have been lowered considerably.

Thus the results of Watkins (1973) should be disregarded as meaningless.

Smith & Furgason (1976) studied the effect of ozonation on the ability of microorganisms to biodegrade kraft pulp mill liquid wastes. Four different examination procedures were utilized. First, oxygen uptake rate experiments were conducted in a 1,600 ml system using full strength, undiluted pulp mill wastewater. These tests illustrated the combined effects of biodegradability and toxicity upon biological treatment of both non-ozonated and ozonated waste materials. Then oxygen uptake rate studies were made on diluted wastewater in 300 ml bottles. Dilution eliminated the effects of toxicity and allowed examination mainly of biodegradation. Two extended aeration biological systems, one treating ozonated waste and the other treating non-ozonated waste, were examined in a small pilot plant system. Finally, NMR (nuclear magnetic resonance) spectra of the original and ozonated wastes were examined to determine changes in the basic chemistries of the wastewaters due to ozonation.

Wastewaters from the Potlatch Corporation kraft mill at Lewiston, Idaho were studied. The materials were ozonized in simple batch diffusion, with ozone concentrations being measured at the entrance and exit of the contact column (contactor details are not given). From the difference in ozone concentrations before and after, the gas flow rates and times of contact, ozone utilizations (usually 190 to 800 mg/l) were calculated for each sample. The pH of the raw wastewaters (3 to 3.3) was adjusted to 7 to 7.5 before a run was made. Activated sludge cells were acclimatized to the waste before measuring oxygen uptake at 2,000 to 3,000 mg/l of mixed liquor suspended solids (MLSS).

Results of the oxygen uptake studies showed that ozonation of full strength raw wastewater increased its biodegradability. However, ozonation of the diluted wastewaters produced little change in biodegradability. Therefore, Smith and Furgason (1976) concluded that the original inhibition of biodegradability of the full strength wastewater is caused by toxic components, which are destroyed by ozonation and/or are rendered less toxic upon dilution.

During extended aeration studies comparing ozonated and non-ozonated kraft mill wastewaters with normal sewage being treated by activated sludge organisms, in every category (MLSS, BOD and COD removals and in sludge volume indices) the ozonated wastes were more biodegradable than the non-ozonated wastes. The differences were not large, however, and were of about the same magnitude as those obtained during the oxygen uptake studies. In nearly every measure, the normal sewage system was much more biodegradable than either the ozonated or non-ozonated pulp mill waste.

The NMR spectra taken of the non-ozonated and ozonated wastes showed that the major peaks remained unchanged, except for one peak which was absent after ozonation. This peak could have been due to a Cl or S group, either of which would have had a distinct toxic effect upon the biodegradation of the waste material.

Smith and Furgason (1976) concluded that since ozonation reduces color by about 70 to 80%, eliminates noxious odors and destroys inherent toxicity of full strength kraft pulp mill wastewaters, rendering them more biodegradable, it would be advantageous to have the ozonation treatment step incorporated prior to a biological treatment step. Prolonged ozone treatment is required in order for the ozone to actually sever the lignin molecules and break them into much smaller, more readily biodegradable materials. Such prolonged ozone treatment probably is outside of the range of economic feasibility. On the other hand, if wastewater stream recycle is contemplated, ozonation should be studied in more detail.

Melnyk and Netzer (1976) conducted a kinetic study of the reactions between ozone and those lignin compounds which produce an intense color in wastewaters originating from kraft pulping and pulp bleaching processes. For the ozonation studies, a 1 liter sparged reactor was employed and ozone was generated from oxygen. Analyses were conducted for ozone in the contactor influent and effluent gases. Ozonized wastewaters were analyzed for changes in pH, COD, biodegradability and color content. Wastewater studies included caustic bleachery (softwood), unbleached pulp washer (softwood), combined caustic chlorine bleach stages (softwood) and caustic bleach stage (hardwood).

For development of the kinetic model, it was assumed that color is contributed by 2 unidentified species, each of which differs in its reactivity with ozone. Each species was assumed to react with soluble ozone independently and as a first order rate process. The 2 species differ in their reactivity with ozone, and it is concluded that the more reactive (to ozone) species also is responsible for most of the initial color (65 to 87%). The rate of color removal was found to be linearly dependent upon the soluble ozone concentration. Decreases in COD values were observed to parallel decreases in color intensity in the ozonated samples, but the amount of COD reduction is significantly smaller than the amount of color removed.

Melnyk & Netzer (1976) also monitored the oxygen uptake rates of ozonated wastewater samples. It was not clear that ozonation enhanced biodegradability. Ozonation clearly increased the amount of material which could be oxidized biologically, but this new material was degraded at a slower rate.

Nebel et al. (1974a) discussed pilot plant studies with ozone treatment of kraft mill effluents for color removal. Examples are presented of color, COD and BOD level reductions in kraft mill effluents by ozonation at various dosages, and the economics of ozone treatment and generation by using air or oxygen are compared.

Nebel et al. (1974b) discussed experimental data indicating the cost of color removal by ozonation in 4 different pulp and paper mill secondary effluents. Costs were in the range of \$0.007 to \$0.017/cu m (2.65 to 6.44¢/-1,000 gal) of wastewater treated, with the predominating factor being the cost of electrical power. Both of these last two articles appear to be very similar in content to that of Nebel, Gottschling & O'Neill (1974).

Kamishima and Akamatsu (1974a,b) studied the mechanism of BOD removal in an ozonated diluted black liquor subjected to activated sludge treatment. With BOD levels of 600 mg/l, the removal rate approximated a first order reaction, and at BOD levels of 100 to 200 mg/l the reaction followed second order kinetics. BOD removals of 90% were obtained at loadings less than 0.5 kg BOD/day/kg of mixed liquor volatile suspended solids (MLVSS), and sludge yield was the same or lower than that for other pulp mill effluents. For liquors treated with 4 to 15 mg/l of ozone, BOD removal efficiency decreased at higher loadings, but not at loads less than 0.4 kg/day/kg of MLVSS. In 2-stage ozone/activated sludge treatment, total permanganate COD and BOD removals depended upon the efficiencies of the individual stages, which were 61.6% and 87.5%, respectively, even with ozone residuals of 0.4 mg/l. Lignin and color removal efficiencies depended upon ozonation effectiveness and were 66.6% and 81.5%, respectively.

Bauman and Lutz (1974) ozonized effluent from the P.H. Glatfelter Co., Spring Grove, Pennsylvania integrated kraft mill making 500 tons/day of fully bleached pulp and 600 tons/day of fine papers using a 5 gal/minute pilot plant on the total mill effluent after primary and secondary biological treatment. The primary objective of this study was color removal, but the effects of ozonation upon COD, BOD, SS, bacterial counts and DO also were studied.

Ozone was prepared from oxygen at 80 g of ozone/hr using 3.5 kwhr of electrical energy per lb of ozone. Contacting was conducted in four 8-inch, schedule 40 steel pipes, each 13 ft high. Ozone was introduced through 2 inch stainless steel spargers, 1 per tower, located about 1 ft from the base of the contact towers. The liquid heights in each tower, therefore, were about 11 ft. Most of the pilot studies were conducted at 4 gal/min, which provided about 30 minutes total retention time, or about 7 minutes per tower. The inlet gas flow was divided and regulated so that 40% of the ozone was applied in Tower #1, 30% in Tower #2, 20% in Tower #3 and 10% in Tower #4. Liquid samples could be taken from each tower effluent and the gas streams also were sampled. Contactor vent gases could be tested for ozone and gas flow rates to each tower were adjusted so that no ozone was "wasted out the vents". This means that the ozone added to each tower was utilized, but not necessarily that the ozone demand of the liquid was satisfied.

For each sample, a minimum of 2 hrs running time was conducted for each level of ozone applied. For reduction in color level, little was gained by applying more than 30 mg/l of ozone, and nothing was gained at dosages above 40 mg/l. Almost no bacteria were killed at ozone dosages up to 20 mg/l. When bacteria began to be killed by ozone, the coliform organisms were destroyed selectively first. At 30 mg/l of ozone, significant reductions in coliform levels (60 to 80%) were observed, and at 40 mg/l ozone dosage, nearly 100% coliform kills were obtained. However, the bacterial counts remained surprisingly high, even after addition of 40 mg/l of ozone.

Initial experiments were conducted with air feed to the ozone generator, and 5 μ mean pore size spargers quickly became plugged after only a few hours of running time. A brown deposit which adhered tenaciously was shown to be almost entirely $CaCO_3$. This was soaked with HCl to remove the deposit, but this required removing the spargers.

Therefore the 5 μ spargers were exchanged for 20 μ mean pore size diameter spargers, which allowed 72 hrs continuous runs with air feed. However, when oxygen feed was used, even the 20 μ spargers became plugged within 24 hrs of use. Therefore, daily cleaning with acid was required.

At equivalent ozone dosages, no differences in color level reductions were observed due to the different (5 and 20 μ) pore sizes of the spargers.

Ozone at 20 to 40 mg/l doses consistently increased the BOD-5 about 100% (BOD of the secondary effluent was about 10 mg/l). When ozone was prepared from air, the DO level became about 8 mg/l. Oxygen dissolves in direct relation to its proportion in the mixture of gases. Since the concentration of oxygen in air is about 21%, only 20% of its ultimate solubility in water is attained. But when ozone is prepared from oxygen, the DO attained approaches 40 mg/l, the ultimate oxygen solubility in water. The doubling of BOD-5 was obtained by Bauman & Lutz (1974) regardless of whether ozone was generated from air or from oxygen.

By varying the power applied to the generator, the concentration of ozone in the feed gas was varied as follows:

0.45% at 10 mg/l dosage
0.90% at 18 mg/l dosage
1.35% at 30 mg/l dosage
1.8 % at 38 mg/l dosage

The color remaining after ozonation depended upon the amount of ozone applied, not on the concentration of ozone in the gas stream. On the other hand, there was a significant decrease in the time necessary to apply the required amount of ozone at the higher ozone concentrations. Bauman and Lutz (1974) recommend that this relationship should be investigated in detail before capital expenditures for a full scale plant treatment system are made.

Multiple regression analyses were conducted during 48 hrs of continuous running at 20 mg/l of ozone dosage and over 48 hrs at 30 mg/l ozone dosages. The % color removed was related to the BOD levels (which increased 105%), COD (decreased 12%) and SS (decreased 22%). For an initial color of 600 mg/l, COD of 225 mg/l, BOD of 10 mg/l and SS of 25 mg/l, the regression equation predicted that 100 mg/l of ozone dosage would be required to provide 80% color removal.

Extended ozonation runs then were conducted using ozone dosage levels up to 300 mg/l. Color removals of 80% were obtained at 80 mg/l, but even after addition of 300 mg/l of ozone, 30 mg/l of color remained. The BOD rose from 10 to 24 mg/l at 40 mg/l of ozone, remained at 20 to 25 mg/l up to 200 mg/l ozone dosages, then dropped back to 10 mg/l by 280 mg/l ozone dosages. About 99% of the coliform bacteria were killed by 40 mg/l ozone dosages and 99% of the total bacteria were killed at 100 mg/l ozone dosage.

Cost estimates were made on an ozonation installation designed to treat 15 mgd and providing up to 40 mg/l of ozone generated from oxygen. Capital investment would be $1 million - $1.25 million and 5 kwhr of electrical energy/lb of ozone generated would be required (at a power cost of $0.015/-kwhr). Table 54 shows the estimated operating costs for treating 15 mgd of pulp mill secondary effluent containing less than 1,000 mg/l of color, about 200 mg/l of COD and less than 50 mg/l of SS (the plant would be sized to process 500 tons/day of pulp).

Whittemore & McKeown (1974) conducted preliminary laboratory studies to determine the oxidation and disinfection properties of ozone applied to a variety of pulp and paper mill effluents. Specific objectives of the study were to determine the amount of color reduction attainable by ozonation with and without prior lime decolorization treatment, the amounts of ozone required, changes caused in COD and BOD, then to define ozonation conditions (amounts and contact times) required to disinfect selected pulp and paper mill effluents.

The ozone contactor was a 90-cm high x 5 cm-diameter column of 1.8 liter total volume, but samples to be ozonized all were 1 liter in volume. A fritted-glass diffuser was installed at the base of the column, but was covered with an inverted polypropylene funnel to restrict the gas phase from being drawn out of the reactor by the downflowing liquid. The column was designed originally to be packed with glass beads, but preliminary observations showed that bubble sizes were smaller and overall turbulence was greater without the packing. The beads seemed to coalesce the bubbles and promote gas phase channeling. Foaming was reduced when beads were removed.

TABLE 54. ESTIMATED OPERATING COSTS FOR TREATING 15 MGD OF PULP MILL SECONDARY EFFLUENT WITH OZONE

mg/l of ozone	Color of Ozonated Effluent (mg/l)	Operating Cost	
		Annual	per ton of pulp
--	1,000	---	---
10	300-450	$121,500	$0.675
20	250-350	$243,000	$1.35
30	150-200	$364,500	$2.03
40	125-175	$486,000	$2.70

Source: Bauman & Lutz, 1974.

Ozone was generated from oxygen. Off-gas ozone was passed through a KI trap for determination of the amount of unused ozone, and ozone material balances were determined so as to calculate the ozone utilization of the system. After completion of each run the residual ozone was determined in the ozonized solution by addition of KI and determining the amount of liberated iodine. In nearly all cases this was 0.0 mg/l of ozone, so that ozone utilization could be calculated simply by subtracting the concentration of ozone in the off-gases from that in the feed to the reactor.

Using unbleached kraft pulp mill effluent synthesized from weak kraft black liquors, hardwood caustic stage bleaching effluents (CE), softwood chlorination stage bleaching effluents (Cl_2E) and biologically treated bleached kraft total mill effluents (TTME), in all four cases, effluent color decreased with increasing ozone useage (up to 800 mg/l of ozone utilized). Where the amount of ozone dosed was sufficient to satisfy the ozone demand, the percent color reduction was time-dependent -- about 45 minutes residence time being required to produce more than 80% reduction consistently (residual color levels of less than 100 APHA units). In most cases, lime-decolorized effluents required substantially less ozone to attain a given level of color reduction. Pertinent data are summarized in Tables 55, 56, 57 and 58.

Color reversion also was investigated. This is defined as the return of color 24 hrs after ozone treatment. Generally, it was found to be in the 0 to 10% range, but in some cases it was greater. The median amount of color reversion was 5 to 8%, but this did not occur consistently with any one effluent or with any single class of effluent.

TABLE 55. ESTIMATED OZONE REQUIREMENTS FOR SYNTHESIZED UNBLEACHED KRAFT BLACK EFFLUENT DECOLORIZATION

Waste Description	Initial Color, APHA Units	Ozone Requirements (mg/l) Color Reduction 50%	75%	90%
Hardwood - Black Liquor, Diluted 1/100	4,800	500	650	>700
Hardwood - Black Liquor, Diluted 1/100, Lime Decolored	370	300	400	>600
Softwood - Black Liquor, Diluted 1/100	2,200	400	500	>750
Softwood - Black Liquor, Diluted 1/100, Lime Decolored	145	250	350	450

Source: Whittemore and McKeown, 1974.

Kraft total mill effluents were disinfected (determined by total coliform densities) rapidly with 70 to 90 mg/l of ozone utilization. Eighty percent total coliform reduction was obtained at about 40 mg/l ozone dosage, 90% reduction at about 50 mg/l and 100% reduction at about 80 mg/l. However, boxboard mill effluents showed total coliform densities reduced to zero with only 25 mg/l dosages of ozone.

Effluent color appeared to be a significant factor in the amount of ozone required for disinfection. Primary settled total mill effluent containing coliforms was split and 1 portion was spiked with color in the form of kraft bulk liquor. After 7 days of biological oxidation, both samples were ozonized and the degree of disinfection tested by determining the total bacterial and total coliform counts. Complete coliform kills were not attained at levels of 190 to 300 mg/l dosages. An increase in color (from 800 to 4,000 APHA units) retarded disinfection efficiency. In the ozonated sample, levels of added color, bacteria and total coliform organisms were reduced 15% and 57%, respectively, at 300 mg/l ozone dosage. The sample with fewer color bodies gave 99% bacterial and 97% coliform kills at 190 mg/l ozone dosage. It was also shown (by filtering a biologically treated kraft total mill effluent) that lowering the SS will reduce the ozone demand for effluent disinfection following biological oxidation (75 mg/l dosage versus 190 mg/l).

TABLE 56. ESTIMATED OZONE REQUIREMENTS FOR CAUSTIC STAGE BLEACH EFFLUENT EXTRACT DECOLORIZATION

Waste Description	Initial Color, APHA Units	Ozone Requirements (mg/1) Color Reduction 50%	75%	90%
Mill A - Hardwood	3,900	200	360	>450
Mill B- Hardwood	2,600	200	300	>400
Mill B - Hardwood Lime Decolored	425	60	100	130
Mill C - Softwood	7,250	200	>250	>300
Caustic Extract D - Softwood	15,000	300	625	775
Caustic Extract E - Softwood	7,200	220	275	350

Source: Whittemore and McKeown, 1974.

Ozonation generally lowered the COD by as much as 30% (occasionally up to 50%). Boxboard, integrated kraft ASB (aerated stabilization basin) effluents and sodium base NSSC (neutral sulfite semi-chemical) total mill effluents produced significant increases in BOD-5 (boxboard effluents showed a 60% increase; integrated kraft ASB effluents showed a 200% increase). With other effluents the BOD generally decreased slightly (0 to 20%) or increased slightly (0 to 10%).

Ozone decolorization had negligible effects upon the subsequent rates of biodegradability of effluents.

Less than 3 lbs of ozone were required to remove 1 lb of COD from various pulp mill effluents. Actual data ranged from 0.3 to 33 lbs, with an average value of 1.61 lbs. In theory, if only 1 oxygen atom in the ozone molecule is utilized in oxidation of the COD, then 3 lbs of ozone should be required to remove 1 lb of COD. Those wastes in which less than 3 lbs of ozone were required per lb of COD removed indicates that more than 1 atom of oxygen in the ozone molecule is utilized in the oxidation process.

Whittemore & McKeown (1974) concluded from this preliminary laboratory study that:

- Ozone is capable of removing color from a wide range of process streams and total mill effluents,

- 15 to 20 color units are removed per mg of ozone dosage in caustic bleach effluents; 4 to 5 color units are removed/mg of ozone dosage in total kraft mill effluents and less than 1 color unit/mg of ozone is removed in lime treated effluents,

TABLE 57. ESTIMATED OZONE REQUIREMENTS FOR CHLORINATION STAGE BLEACH EFFLUENT DECOLORIZATION

Waste Description	Initial Color, APHA Units	Ozone Requirements (mg/l) Color Reduction 50%	75%	90%
Mill A - Hardwood	220	>275	---	>900
Mill A - Hardwood Lime Decolored	45	185	260	325
Mill B - Hardwood	590	65	200	>275
Mill B - Hardwood Lime Decolored	100	45	95	175
Mill C - Softwood	175	80	150	>250
Mill C - Softwood Lime Decolored	175	110	>150	175
Mill D - Softwood	700	75	190	225
Mill D - Softwood Lime Decolored	80	160	200	>300

Source: Whittemore & McKeown, 1974

- 24 hour color reversions usually are less than 10%, and average 5 to 8%,

- 90 percent or greater total coliform reductions are attained at about the same ozone requirements as the one hour chlorine demand for integrated kraft mill effluents, but are several times the chlorine dose required for disinfection. Color bodies and SS both showed preferential ozone demand, thus increasing the amount of ozone required for disinfection.

Ng et al. (1978) reported results of ozonizing kraft mill wastewaters. Ozone was generated by passing 0.3 cu m/hr of oxygen at 3 psig through an air-cooled plate type generator (W.R. Grace & Co.). Ozonations were conducted in a dynamic system and in a batch system. In the dynamic system, the

TABLE 58. ESTIMATED OZONE REQUIREMENTS FOR TOTAL MILL EFFLUENT DECOLORIZATION

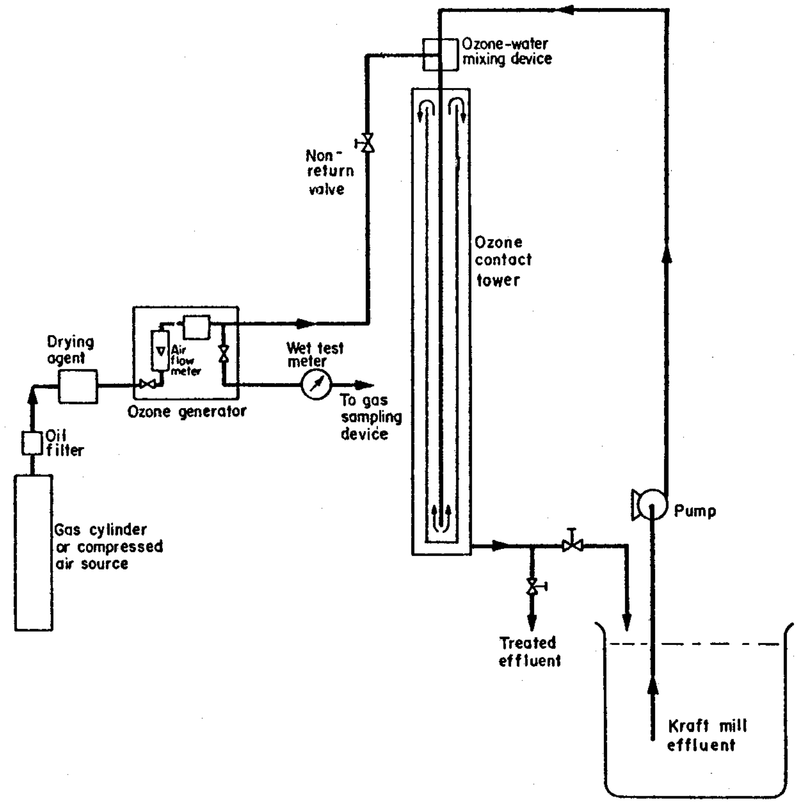
Waste Description	Initial Color, APHA Units	Ozone Requirements (mg/l) Color Reduction 50%	75%	90%
Boxboard Secondary Total Mill Effluent (ASB)	180	20	100	>600
Boxboard Secondary Total Mill Effluent After Settling	140	30	150	>175
NSSC Total Mill Effluent, Na Base	7,500	>850	---	---
NSSC Total Mill Effluent, NH_3 Base	40,000	Color Increase noted at 1,200 mg/l		
Sulfite Secondary Total Mill Effluent	1,620	550	>800	---
Kraft A Secondary Total Mill Effluent	400	38	70	>125
Kraft B Secondary Total Mill Effluent	540	18	85	>300
Kraft C Primary Total Mill Effluent	1,180	>260	---	---
Kraft D Secondary Total Mill Effluent	1,150	70	88	250

Source: Whittemore & McKeown, 1974.

contact tower was a polyvinyl chloride column 3 m (10 ft) high and 15 cm (6 inch) diameter containing a concentrically mounted 10 cm (4 inch) diameter pipe sealed to the 15 cm pipe at the lower end. A centrally mounted dip tube extending to the base of the 10 cm pipe was connected at the top to the ozone/effluent mixing device (Figure 23). Effluents adjusted to pH 3, 7 and 9 were pumped at 5 gal/min into the mixing device where they were treated with 1% ozone in oxygen. The ozonized effluent then entered the 15 cm diameter contact column through the annular opening and passed through the contact column within two minutes. Each passage allowed an ozone dosage of 8.8 mg/l. Residual ozone could not be detected at the top of the contact column, thus it was assumed that all ozone applied to the effluent was consumed by the effluent.

The batch system consisted of a 40 liter polyethylene container fitted with a porous gas dispersion tube. Ozone (1% in oxygen) was dispersed into the effluent which had been adjusted to the desired pH value and was stirred by means of a magnetic stirrer. Ozone was determined in the inlet and off-gases.

Four batches of bleached kraft whole-mill effluents were obtained from a British Columbia interior bleached kraft mill (1 sample) and a coastal bleached kraft mill (3 samples). Samples were composited over 24 hours, shipped immediately to the laboratory and stored at 4°C. Coarse particles and fibrous materials were removed prior to ozonation by straining. Toxicity of treated effluents to juvenile rainbow trout (Salmo gairdneri) was measured as medial survival time (MST), the time to death of 50% of the fish population exposed to 100% effluent. For bioassays, the effluents were neutralized to pH 7.0 ± 0.1, DO was kept at saturation and temperature was controlled at 15° ± 1°C. All samples were toxic to fish, except the one taken from the interior mill. The MST values ranged from 290 to 420 minutes, color varied from 1,780 to 3,200 APHA units, BOD-5 values ranged from 190 to 250 mg/l and TOC from 270 to 330 mg/l.



Source: Ng et al. (1978)

Figure 23. Dynamic ozone treatment system.

In batch experiments, detoxification of the effluents by ozonation was marginal at pH 4.2; detoxification was significantly better at pH 7.0 and was substantial at pH 9.0. However, detoxification in the control samples was as effective as with ozone, and also gave the best toxicity lowering at pH 9.0. Removal of color by 8.8 mg/l of ozone averaged 10% and was of similar magnitude at all three pH ranges tested. Color was not improved in the control. At the low level of 8.8 mg/l, ozonation did not significantly affect BOD-5 and TOC.

Sequential removal of pollutants was studied at pH 9 as a function of ozone dosage by dosing up to about 50 mg/l of ozone. Initial color levels of 2,080 and 1,880 APHA units were lowered to 1,500 and 1,250, respectively. The rate of color removal was fastest during initial stages of ozonation. A mathmatical relationship was developed which predicted the ozone dosage required for various levels of color removal:

$$\ln (\text{color removed}) = 0.72 \ln (\text{ozone applied}) + 3.78.$$

No color was removed in the control samples, indicating that color removal was due to the ozone.

Upon initial treatment with 4 mg/l of ozone, the BOD-5 values increased by 5 to 6%, but as ozone dosages were increased, BOD-5 values peaked, then decreased as a function of ozone dosage. Treatment of effluents with 48 mg/l of ozone reduced BOD-5 values from 180 and 190 mg/l to 145 and 150 mg/l, respectively, or showed 20 to 22% reduction. The removal of BOD-5 could be expressed as:

$$\ln (\text{BOD-5 removed}) = 0.86 \ln (\text{ozone applied}) + 0.26.$$

About 260 to 270 mg/l of ozone would have to be applied to lower the BOD-5 by 90% (to 20 mg/l). If 150 to 175 mg/l of ozone were to be applied, as would be necessary to remove 90% of the color, then about 61 to 66% of the BOD-5 also would be removed.

Concurrent with BOD-5 removal, some reduction in TOC was observed, averaging 0.25 to 0.3 mg/l TOC removed/mg of ozone applied. The ratios of BOD-5/TOC removed per unit of ozone applied ranged between 3:1 and 4:1, suggesting that the carbon removed by ozone treatment is oxidized to CO_2 and water and that BOD-5 removal is congruent with the carbon removal. In the control experiments, oxygen had no effect upon BOD-5 and TOC.

Color was attacked most readily by ozone, followed by BOD-5. TOC was attacked slightly by ozone and toxicity was not affected. However, oxygenation conditions prevailing during ozonation resulted in toxicity removal. Segregated sequential attack of ozone did not occur; color and BOD-5 were destroyed concurrently.

Ozonation For Deodorizing Kraft Mill Gaseous Emissions

Tuggle (1972) studied the effects of ozone on 4 odorous, reduced sulfur compounds associated with kraft mill gaseous emissions: hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (CH_3SCH_3) and dimethyl disulfide (CH_3S-SCH_3). He concluded that at least double the theoretical dosage of ozone is necessary for complete oxidation of these 4 compounds and that residence times in contact chambers in excess of plant exit stack residence times are required for total oxidation. Excluding cost considerations (which were not conducted), Tuggle concluded ozone to be effective in eliminating methyl mercaptan, dimethyl sulfide and dimethyl disulfide from actual kraft mill emission sources (smelt, tank and vent gases). Complete removal from these three gases was achieved at an ozone/-total reduced sulfur ratio of about 2.5.

In these experiments, ozone was generated from oxygen and nitrogen was used as the carrier gas. For both laboratory and field studies, the contact times ranged from 10 seconds to 1 minute.

Oxidation of H_2S with ozone was found to be much more rapid than that of the other 3 gases. Methyl mercaptan oxidation with ozone produced dimethyl disulfide with slightly more than the theoretical amount of ozone required. Subsequent reaction of the dimethyl disulfide required more than double the theoretical amount of ozone for complete oxidation.

An additional 23 references for the use of ozone for deodorizing pulp and paper mill gaseous effluents are given by Rice & Browning (1976). In this publication, abstracts of each article cited are included.

Ozonation Of Spent Sulfite Liquor To Generate Methane And To Grow Yeast

Jurgensen & Patton (1976-77; 1977a) describe a laboratory feasibility program, funded by the U.S. Department of Energy, Industrial Energy Conservation Division, to study the production of methane and protein by fermentation of spent sulfite liquor (SSL) from pulp mills. Although anaerobic fermentation of carbonaceous materials is well known for the production of methane, as is the growth of yeasts and algae on wastewaters, the use of ozonation to convert SSL to substrates more amenable to these biological processes is novel.

It has been estimated (Mueller & Walden, 1970) that 2,100 gal of SSL are produced for every ton of sulfite pulp manufactured. This waste material can be treated mechanically or biologically before discharge. However, the general lack of success with biodegradation of lignosulfonates has suggested that some pretreatment should be utilized to degrade the SSL, or to transform it into a state which can be better metabolized by biologically functioning organisms.

Stern & Gasner (1974) have shown that ozonation of kraft mill waste liquors causes a shift in the molecular weight distribution of lignins to lower molecular weight fractions. Ozonation also was shown to increase the susceptibility of waste liquors to biological decomposition.

Jurgensen & Patton (1977b) are testing a multistage treatment process in the laboratories of Michigan Technological University, Houghton, Michigan. This process involves 3 fermentation stages, ozonation, steam stripping and centrifugation, to harvest useful products from SSL.

Raw waste pulp mill effluent enters the primary yeast fermenter where all assimilated organics are converted to protein and CO_2. Effluent from the primary fermenter is centrifuged to harvest protein and the centrifugate is ozonized to modify the sulfur bonds and to break down the high molecular weight organics. Ozonized effluent is cooled and fed to the anaerobic digester, which contains a mixed bacterial culture and Desulfovibrio, which are needed to transform ozonized fragments into substrates satisfactory for methane synthesis.

Effluent from the anaerobic digester still may contain unassimilated ozonated fragments which can be utilized by Torula yeast. Therefore, the effluent is fed to the secondary yeast fermenters, then to centrifugation for protein removal. Any BOD-5 still present is removed by activated sludge treatment or soil infiltration.

During initial phases of the Michigan Technological University study, ozone was prepared from oxygen and ozonation was carried out in a 1 inch I.D. x 6 ft tall glass column (500 ml volume) packed with berl saddles. The pH was monitored and controlled automatically. Preliminary experiments were conducted by bubbling ozone through 300 ml of SSL for 1 to 6 hrs. After 6 hrs, ozone consumption had reached minimum values and significant quantities of ozone were present in the off-gases. Infrared analyses of the raw and ozonized SSL samples showed significant transformation of aromatic structures to carboxylic acids.

Samples ozonized 6 hrs also were analyzed for BOD, COD and sulfur. Concentrations of metabolizable organics increased by 100% when ozonations were conducted at pH = 3, but very little increase in BOD was obtained at alkaline pH. The COD values were reduced about 23% upon ozonation under either acid or alkaline conditions, but no change in the sulfur content was found.

Continuous reactor studies were conducted initially at pH = 3 over 3 hours (the point at which ozone became just detectable in the contactor off-gases). Ozone consumption averaged 12.8 g/l of SSL, which theoretically should have reduced the COD value by 8,500 mg/l (from an initial value of 101,000 mg/l) on the basis of only one oxygen atom in the ozone molecule reacting. The actual reduction in COD value observed was 13,000 mg/l, indicating that at least part of the oxidation occurs by means of a second oxygen atom in the ozone molecule.

Methane production was consistent with the change in concentration of BOD-5 (10,500 mg/l in raw water; 11,600 mg/l in ozonized water; 8,400 mg/l in fermented, ozonized SSL). Methane was produced at the rate of 17 ml/hr (423 ml/day) from a 700 ml volume fermenter with 2.8 days retention time. Fermenter gas was comprised of 65% methane and 35% CO_2 and gas yields decreased with detention time in the fermenter. About 75% of the ozone consumed was expended in the production of CO_2, rather than in producing biodegradable fragments.

In continuation of these studies, Jurgensen & Patton (1977c; 1977d) have shown that the gas composition from ozonized SSL averages greater than 80% methane, while that from non-ozonized SSL effluent is mostly CO_2. Initial ozonation times of 3 hrs have been shortened to 10 minutes, and maximum yields of yeast growths have been obtained under these conditions. Yields of methane gas at 2 to 6 day fermenter residence times have stabilized at 10 ml/hr (70 to 80% methane), and the fermentation process has been shown to be carbon-limited.

Current work on this program at Michigan Technological University is scheduled to be completed in June, 1979. The investigators currently believe that the production of yeast from ozonized SSL is economically feasible, but that the economics of methane production are marginal (Jurgensen, 1978, Private Communication).

Conclusions

1) Ozonation has been studied for:

- Pulp bleaching
- Pulp and paper mill wastewater treatment
- Odor control of pulp and paper plant gaseous exhausts
- Treatment of spent sulfite liquors to produce methane and yeasts

In Pulp Bleaching:

2) Ozone can produce pulps which give satisfactory physical and papermaking properties. Aqueous effluents from ozone bleaching processes therefore are free of chlorine, hypochlorite or sulfites.

3) Ozone partially degrades cellulosic polymers and wood sugars, liberating lignin. However, over-ozonation of wood pulp liberates sufficient lignin so that the physical properties of fabricated paper products can be unsatisfactory.

4) Norwegian Institute of Paper Research personnel have been developing pulp bleaching processes with ozone since the late 1960s. Since May, 1976, the NIPR process has been operating on semi-commercial scale at a Norwegian paper pulp factory. This demonstration is being co-sponsored by 5 major Norwegian paper companies and a Norwegian mechanical engineering company. Similar studies are being conducted in Canada and the USA.

In Wastewater Treatment:

5) Ozonation has been studied for color removal, reduction in levels of BOD and COD, for bacterial disinfection and for removing toxicity of effluents to juvenile rainbow trout. The use of ozonation either for removal of color or COD or for disinfection also provides partial lowering in levels of the other parameters as well as SS. BOD levels generally increase (up to 100%) upon ozonation. High suspended solids and color contents appear to reduce the disinfection effectiveness of ozone. Detoxification of ozonized effluents is effective at pH 9, partially effective at pH 7.0 and only marginal at pH 4.2. However, oxygenation at pH 9 was as effective as ozonation for detoxification.

6) The increased biodegradability of ozonized pulp and paper mill effluents generally has been attributed to the partial oxidation of cellulosic polymers by ozone. However, a recent paper indicates that this may be caused by ozone destruction of materials toxic to biological organisms, rather than by formation of more biodegradable materials upon ozonation.

7) Because of the increased biodegradability of ozonized pulp and paper mill effluents, it appears advantageous to incorporate ozonation before biological treatment rather than after, for removal of BOD, COD and perhaps color.

8) Ozonation reduces color levels 65 to 90%, but up to 10% reversion of specific wastewaters can occur within 24 hrs.

9) For color removal, about 30 mg/l of ozone dosage (assuming 100% ozone utilization) are required. Ozone dosages of 40 mg/l provide 100% kills of fecal coliforms, but total bacterial counts remain high. These ozone dosages effect 100% increases in BOD-5 and lower COD levels 15 to 20%. About 3 lbs of ozone are required to remove 1 lb of COD in this type of wastewater system.

10) Color is attacked most readily upon ozonation, then BOD-5, then TOC. However, segregated sequential attack by ozone does not occur; color and BOD-5 are destroyed concurrently.

11) Costs for ozone treatment of pulp and paper mill wastewaters have been estimated from as low as 3 to 6¢/1,000 gal for color removal to as high as 30¢/1,000 gal for color removal and other purposes. Ozone dosages of 20 and 40 mg/l would cost $1.35 and $2.70, respectively, per ton of pulp produced in an integrated kraft mill manufacturing 500 tons/day of fully bleached pulp and 600 tons/day of fine papers.

12) For deodorizing gaseous emissions from pulp and paper plants, the odorous components are hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The amount of ozone actually required for complete oxidation of these compounds is about 2 times the theoretical amount. Contact times of 10 to 60 seconds are required, which are

longer than those normally found in plant exhaust stacks. The oxidation rate for H_2S with ozone is much faster than for the other compounds.

13) Ozonation of spent sulfite liquor (SSL) to produce substrates suitable for anaerobic production of methane and/or for the growth of yeast is a new concept just being studied. Laboratory results to date show that 10 minute ozonation of SSL allows methane production at the rate of 10 ml/hr in a 700 ml fermenter with 2 to 6 day retention times. The gas composition is 70 to 80% methane. At the present stage of this research, it appears that production of yeast from ozonized SSL is economically feasible, but that methane production is only marginal.

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SOAPS AND DETERGENTS

Ozonation Of ABS (Alkylbenzene Sulfonate)

The first reported studies of ozonation of wastewaters containing synthetic detergents were reported by Buescher & Ryckman (1961) who ozonized settled raw sewage and activated sludge sewage treatment plant effluent samples which contained ABS (tertiary AlkylBenzene Sulfonate) detergents. The objectives of this work were to reduce the foaming observed in aeration basins of activated sludge plants caused by ABS (sometimes 2 to 5 ft deep) and to remove ABS from surfactant-laden wastewater solutions. Foam properties were observed in ozonized sewage treatment plant waters and distilled water solutions of ABS were ozonized to determine the extent of ABS oxidation. Ozone was generated from air and concentrations in the reactor feed gas and off-gases were measured. The ozonation reactor was a flask (unspecified size, but larger than 2,500 ml) through which ozone was bubbled by means of a glass tube (not fritted).

Two types of measurement were made. The first was an aeration test under conditions similar to those existing in an activated sludge aeration basin. Foam heights above a 1,500 ml sample in a tall column were measured after 10 minutes of aeration. The second method was the shake test, in which a 50 ml sample in a 100 ml Nessler tube was shaken 25 times. The foam volume and time for the foam to break were determined, giving measures of foam production and foam stability.

Settled raw sewage containing 168 mg/l of BOD and an ABS concentration of 21 mg/l was ozonized (2.5 liter samples) for 2.5 hrs each, and subjected to 10 minute aerations before and after ozonation. Of the 1,057 mg/l ozone dosage, only 342 mg/l was absorbed, thus the contacting efficiency was only 32%. After about 300 mg/l of ozone (per 2.5 l) had been absorbed, the samples produced no foam upon subsequent aeration. Before ozonation, the foams produced were 10.5 inches in height. The sewage changed color during ozonation from an opaque gray to chalky white, and the odor changed to a chemical odor which was judged to be "not objectionable". Foam reduction and ABS removal proceeded at the same rates as ozonation progressed.

Additional quantities of ABS (10 mg/l) were added to sewage treatment plant effluents containing 13 mg/l of BOD. This gave ABS concentrations of 6.8 and 16.8 mg/l. Effluents containing 6.8 and 16.8 mg/l of ABS were ozonized 20 and 40 minutes, respectively. Both samples absorbed about 50% of the applied ozone. The amounts of absorbed ozone required to reduce ABS concentrations in the effluents were less than those needed for the raw sewage. By the shake test, foaming ceased when 24 mg/l of ozone had been absorbed. Ozonation to this level also eliminated foaming (23 inches in height before ozonation).

To halt foaming, raw sewage required 135 minutes of ozonation, whereas activated sludge effluent required only 5 minutes of ozonation. The ABS-spiked activated sludge effluent required 10 minutes of ozonation to eliminate foaming. As ozonation progressed, the foams became progressively less stable.

Solutions of distilled water containing 50 mg/l of ABS (62.4% + 31% Na_2SO_4) were ozonized and the degree of oxidative destruction of ABS was followed by determining the amount of inorganic sulfate formed (above the starting level). ABS concentration decreased linearly up to about 90 mg/l of ozone absorbed (about 80% ABS destruction) and then levelled off up to 125 mg/l of ozone absorbed (88% ABS destruction). During the linear portion, from 2 to 4 parts of ozone absorbed were required to remove 1 part of ABS in either sewage effluent or distilled water.

Buescher & Ryckman (1961) concluded that ozonation of activated sludge effluent to eliminate foaming caused by ABS would be economical if the ABS concentration is not greater than about 4.5 mg/l. This would require 12 mg/l of ozone absorbed at 4.5 mg/l of ABS (2.67 mg of ozone/mg of ABS). They also concluded that ozonation of activated sludge effluents from sewage treatment plants has additional advantages, such as color and odor removal. Ozone oxidized the ABS molecule, but "apparently not completely to CO_2 and water, though there are indications that the para-substituted benzene rings and the sulfonate rings are removed".

Evans & Ryckman (1963) reported further studies on the ozonation of Highland, Illinois sewage containing ABS detergents. In this work, 45 gal samples of primary and secondary treated sewage (containing 6.4 mg/l ABS), of sewage treatment plant effluents containing an additional 10 mg/l ABS (16.4 mg/l total) and distilled water containing 50 mg/l of ABS were ozonized. Biochemical behavior of the ozonized samples was observed by following the changes in BOD.

For this study, the ozone contactor was a single column 10 ft tall with a vertical mixing recirculating system in the lower section. Samples (3.8 liters) were ozonized for 2 to 120 minutes. The amount of ozone absorbed was determined by subtracting the amount of ozone found in the contactor off-gases from the amount of ozone dosed. Ozonized liquids were analyzed for ABS, COD and BOD. Secondary effluent samples and those with 10 mg/l of added ABS were ozonized in duplicate for 2.5, 10, 20, 30, 45, 60, 90 and 120 minutes. The sample of 50 mg/l ABS in distilled water was ozonized at an ozone/air flow rate of 0.1 cu ft/min for periods up to 120 minutes.

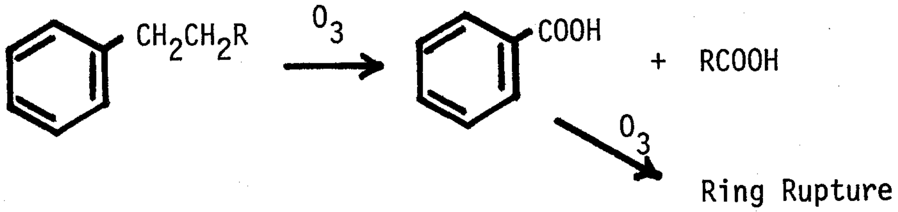
Removal of ABS was rapid at first for the sewage samples, then began to taper off at 45 mg/l of ozone dosage (sample spiked with 10 mg/l of ABS) and 25 mg/l (unspiked sample), respectively. Reduction of ABS concentration from 6.4 to 1.0 mg/l (unspiked sample) required 150 mg of ozone; reduction of ABS concentration from 16.4 mg/l (spiked sample) required 250 mg of ozone (in 3.8 liters of sample). The additional 10 mg/l of ABS in the spiked sample required 100 mg of ozone. Stated another way, 2.64 mg/l of absorbed ozone was required to eliminate 1.0 mg/l of ABS from the samples.

The greater the starting concentration of ABS, the greater the amount of ABS that was removed while maintaining ozone transfer efficiency at 86 to 90%. As the quantity of ozone utilized increased, the COD of the samples decreased.

The BOD-5 of sewage treatment plant effluent samples was reduced to 0 mg/l after absorption of 180 mg/l of ozone, but twice as much ozone was required to reduce the BOD of the ABS-spiked sample to 1 mg/l. The BOD of the spiked sample increased with increasing ozonation until the point at which ABS no longer was detectable, then fell. Thus at low concentrations, ABS was converted to intermediates which were biodegradable. At higher concentrations of ozone, the ozonation products were oxidized further, such that the products no longer exerted a BOD.

For the first 10 minutes of ozonation, the distilled water sample containing 50 mg/l of ABS inhibited activated sludge organisms, but this effect disappeared after 10 minutes of ozonation. By increasing the amount of applied ozone, the rate of biological reaction increased.

Evans & Ryckman (1963) postulated that when alkylbenzenes are ozonized, the alkyl group is converted to a carboxyl group, the point of attack being the carbon attached to the benzene ring. Upon continued ozonation, the aromatic ring is ruptured:



Evans & Ryckman (1963) concluded that ozonation of wastewaters containing ABS lowers both COD and BOD concentrations and destroys the biological inertness of ABS.

Kandzas & Mokina (1968, 1969) confirmed that ozonation easily oxidizes ABS compounds. They studied sewage which contained ABS and sodium dodecylbenzene sulfonate. Both of these compounds were readily oxidized upon ozone treatment.

On the other hand, Kwie (1969) found during the ozonization of SANS that only 1 aromatic ring of its molecule was ruptured, which did not improve the biodegradability of this compound.

Other Surface-Active Agents

Verde, Meucci & Vanni (1969) and Kuiz (1970) established that ozone effectively oxidized several anionic surface active agents in water. The extent of oxidative destruction depended not only on the properties of the treated substances and their concentrations, but also upon the dose of ozone and the time of ozonation.

Mal'kina & Perevalov (1970) ozonized solutions of the Russian-made nonionic surface active agents OP-10, OZhK and Disolvan 4411 and noted that these materials were destroyed effectively by ozonation.

Recycle Of Car Wash Waters

Baer (1970) described a Viennese car wash wastewater treatment and recycling system which uses ozonation. The city of Vienna would only allow this car wash facility to draw 793 gal/day of potable water, although initial needs were forecast at 12,417 gal/day. The solution to the problem in this 700-car parking garage was to install a wastewater treatment system capable of treating 19,915 gal/day of wastewater and add to it the 793 gal/day of potable water allowed by the city.

The treatment process involves collecting car wash water in an open 3,963 gal tank. In an oil separator, an upward gush of compressed air causes foaming. After the foam has been skimmed off, the solution is transferred to a solids separator and held for three hours to allow sediment to settle. Flocculating agents can be added at this point to promote further separation of colloidal matter. The intermediate solution contains soluble detergents and very fine sediment, which is trapped in a gravel filter as the solution is transferred to the ozonation tank.

Both the contaminated water and some fresh water enter the ozonation tank countercurrently to the upward flow of ozone gas being applied at 4 to 6 atmospheres pressure. This causes high turbulence in the reaction vessel during the 15 to 20 minute contacting time. Water is drawn out of the bottom of the tank and reinjected at the top. In the final step, the treated water is passed through a charcoal filter on its way to a storage tank.

One alternative to this treatment process would have been to dig a well, however the groundwater level at this location is about 820 ft below the surface, and the cost of installing a well this deep was estimated at $61,500. In addition, there would have been the added cost of wastewater disposal. The cost for the ozonation process was about $23,000 and there is zero discharge of wastewaters.

This car wash wastewater treatment system is described in detail in 2 U.S. patents issued to Marschall (1973, 1974).

Conclusions

1) Ozonation of sewage treatment plant effluents containing ABS eliminated the tendency to foam in 5 minutes (1 mg of ABS required 2.67 mg of ozone). Ozone oxidizes the ABS molecule, but not completely, to CO_2 and water. The reaction products of ozonation are biodegradable.

2) A Vienese car wash has recycled 19,915 gal/day of its wastewaters by aeration, skimming, sedimentation, flocculation, filtration, ozonation and charcoal filtration since 1970.

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SD-10* Marschall, K., 1973, "Process of Treating and Purifying Sewage, Particularly of Sewage Contaminated with Detergents." U.S. Patent 3,733,268, May 15.

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TEXTILES

Wastewaters from dye manufacturing and textile dyeing plants normally are highly colored and contain organic dyestuffs, sizing agents (organic and inorganic), surface active agents, organic acids and inorganic acid salts. Depending upon the season, different organic dyes are employed. Therefore, the specific causes of color, BOD and COD change seasonally in this industry. Ozonation of textile industry wastewaters, primarily for the elimination of color, began to be reported in the early 1970s.

Bauch & Burchard (1970) studied the ozone treatment of odorous and "harmful" wastewaters from a number of industries, including a textile processing plant. Textile plant wastewaters treated in various manners showed the properties listed in Table 59. The ozone contactor employed was a perpendicular glass tube 2 m long and 40 mm in diameter, which contained a porous G-3 frit. The sample volume was 1.5 liters.

TABLE 59. TREATMENT OF TEXTILE WASTEWATERS WITH OZONE

Treatment	$KMnO_4$ No. (mg/l)	BOD-5 (mg/l)	Fats & Oils (mg/l)	Foaming
After 2 hrs sedimentation	460	300	43	Strong
After pptn with $FeCl_3$ + NaOH	430	---	traces	Distinct
After 2 hrs settling, + 10 min chlorination	590	---	---	Slight
After 2 hrs sedmtn, + ozone*	81	70	32	Slight
After 2 hrs settling + 10 min Cl_2 + 20 min ozone*	42	40	20	Hardly

* 20 mg/l of ozone in air

Source: Bauch & Burchard, 1970.

From the data of Table 59 it can be seen that treatment of the settled wastewater with chlorine increased the permanganate number 20 to 25%, whereas treatment with ozone lowered the permanganate number about 82% and the BOD-5 by 77%. However, treatment with chlorine followed by ozonation lowered these values by 91% and 87%, respectively.

Smirnova _et al_. (1972) studied the use of ozone for removing sodium thiocyanate from an acrylic fiber wastewater stream. An ozone dosage of 1.2 to 1.3 mg/l of ozone/g of NaCNS "was effective under alkaline conditions".

Maeda _et al_. (1972) described a field test at an industrial plant "for the first time in the world" involving ozonation of a dyeing wastewater.

The test unit had a wastewater treatment capacity of 100 cu m/hr and followed coagulation. It was installed at the Kurokawa Kogyo Jyoyo plant in Japan in 1971.

GAC alone was found to be effective for color removal, but required frequent regeneration. Ozonation of the wastewaters followed by GAC adsorption was effective and "sludgeless". The time for ozonation was 20 to 30 minutes and no pH adjustment was required during ozonation.

Hydrophilic dyes (reactive, cationic or acidic) were shown to be quite reactive to ozone, less than 1 g of ozone being required to decolorize 1 g of this type of dye. For disperse dyes, however, more than 1 g of ozone was required to decolorize 1 g of dye, although the exact amount of ozone required depended upon the individual dye.

The Kurokawa test unit contained three ozonizers, each capable of producing a maximum of 2.4 kg/hr (normally 1.8 kg/hr) of ozone from air. The wastewater treatment process steps in this installation were: lime addition, coagulation, polymer flocculation, precipitation, ozonation, first stage aeration and second stage aeration. The normal addition rate of ozone ranged from 19 to 22 g/cu m. Injection of ozone also could be accomplished after the first treatment step of aeration, after the second aeration step, or both, either in parallel or in series. Wastewaters tested contained about 140 mg/l of BOD.

The pH was adjusted to 9 with NaOH, coagulant and polymer were added, the mixture was sent to a sedimentation tank, then to the aeration tank where it was ozonized using an injector contactor. The BOD level was lowered from 150 to 78 mg/l and the percent transmission increased from 80.5 to 96.2%.

Ozone concentrations in the gas phases were monitored before and after two stage injection into the wastewater. The ozone contacting efficiencies were 83 to 100%, the amount of decolorization obtained was 79 to 98% and the mg of ozone consumed per mg of TOC destroyed was 0.105 to 0.225.

Maeda _et al_. (1972) make the point that one cannot determine the ozone capacity that will be required to treat textile wastewaters simply by determining the concentrations of pollutants. One must test the actual wastewaters to be treated, which vary quite widely in composition. Therefore, the best approach is to sample at different time intervals, then mix these samples. This will provide a sample of "average" wastewater quality.

Although ozonation was effective for decolorization, it was not effective with sulfide dyes nor with chromium-containing dyes at this pilot facility.

Table 60 summarizes the cost data presented by Maeda _et al_. for the Kurokawa test facility.

TABLE 60. COSTS FOR TREATMENT OF DYEING WASTEWATERS BY OZONATION

Wastewater to be treated	From synthetic fiber plants, mainly cationic dyes
Volume of water to be treated	1,500 cu m/day (360,000 gal/day)
Installation cost (pretreatment + ozonation)	About 28 million yen
Ozonizer	Mitsubishi Model OS-1200
Operating Costs	Yen/cu m
Chemicals	7.47
NaOH	1.62 (54 mg/l, 30 yen/kg)
PAC	5.00 (200 mg/l, 25 yen/kg)
Polymer Coagulant	0.85 (1 mg/l, 850 yen/kg)
Electrical Power	2.72
Pretreatment	0.96 (32 kW, 4.5 yen/kWhr)
Ozonation	1.76 (58 kW, 4.5 yen/kWhr)
Total	10.19 yen/cu m

Source: Maeda *et al.*, 1972

Stuber (1973, 1974, 1975a,b,c) studied the ozonation of carpet dye wastewaters after secondary biological treatment at the Dalton, Georgia municipal wastewater treatment plant. Ozone was generated from oxygen and the contactor was a 5.5 inch diameter x 8 ft tall cylindrical plexiglass column which contained a polyethylene diffuser. The contactor volume was 10 gal (37 liters).

The Dalton, Georgia municipal wastewater treatment plant is a 40 mgd activated sludge plant. Approximately 90% of its wastewater feed originates from more than 200 carpet producing and tufted dyeing plants. Table 61 lists the characteristics of the wastewater influent and Table 62 lists the characteristics of the secondary treated effluent.

TABLE 61. SELECTED INFLUENT CHARACTERISTICS: DALTON, GEORGIA PLANT

Constituent	Concentration (mg/l)
BOD-5	200
COD	540
Total Solids	850
Total Suspended Solids	125
Volatile Suspended Solids	100
Alkalinity (Methyl Orange)	73
pH	6.8

Source: Stuber, 1973

TABLE 62. SELECTED EFFLUENT CHARACTERISTICS: DALTON, GEORGIA PLANT

Constituent	Concentration
True Color, APHA units	300
Total Phosphate,	50 mg/l
COD	150 mg/l
Total Coliforms	3,000,000 per 100 ml
Fecal Coliforms	2,000,000 per 100 ml
BOD-5	20 mg/l
Total Suspended Solids	30 mg/l
Volatile Suspended Solids	30 mg/l
Total Solids	580 mg/l
Ammonia Nitrogen	0.3 mg/l
MBAS	3 mg/l
Biphenyl	2.0 mg/l

Source: Stuber, 1973

For this study, Stuber used 20 gal grab samples which were refrigerated until the ozonation experiments were conducted, which was always within 24 to 48 hrs of sampling. Ozone was monitored in both the contactor influent and effluent gases; ozone transfer efficiencies were 79% to 100%, depending upon the dosage applied. Pertinent data are listed in Table 63.

TABLE 63. OZONE TRANSFER EFFICIENCIES INTO DALTON, GEORGIA WASTEWATER TREATMENT PLANT EFFLUENT

Ozone Applied	Transfer Efficiency
0 - 28 mg/l	100%
28 - 58 mg/l	85 - 100%
58 - 100 mg/l	82 - 95%
100 - 150 mg/l	79 - 85%

Source: Stuber, 1973.

Stuber (1973) drew the following conclusions from ozonation studies of the Dalton, Georgia wastewaters:

1) Reductions in COD concentrations of 40% were attained at ozone dosages of 45 mg/l. SS removal prior to ozonation did not enhance COD removal by ozonation.

2) No fecal coliforms were present at ozone dosages above 25 mg/l.

3) Total coliforms were less than 100 MPN/100 ml at ozone dosages of 45 mg/l.

4) True color levels were reduced to less than 30 APHA units at ozone dosages of 40 mg/l. Lowering of SS levels prior to ozonation lowered the ozone dose necessary to attain less than 30 APHA color units to 26.5 mg/l.

5) Soluble organic carbon levels increased slightly with increasing ozone dosages when SS were present, but eventually decreased at extremely high dosages.

6) SS levels were reduced about 90% by ozonation.

7) The BOD-5 increased 150% at ozone dosages of 8 to 15 mg/l, but was essentially unchanged at dosages above 25 mg/l. Therefore, biorefractory organics were being converted into biodegradable organics during the early stages of ozonation.

8) Biphenyl concentrations were reduced from about 2 mg/l to less than 0.1 mg/l at ozone dosages of 89 mg/l.

9) Anionic detergent levels were reduced from about 0.6 mg/l to below 0.1 mg/l at ozone dosages of 15 mg/l.

10) Foaming problems were reduced with increasing ozone dosages and were eliminated in the range of 50 to 100 mg/l ozone dosage.

11) DO residuals were on the order of 40 mg/l when oxygen was used to generate ozone.

12) Ozone residuals could be measured up to 20 minutes after contacting.

13) The transfer efficiency of ozone into solution was 85% to 100% at ozone dosages up to 58 mg/l.

Nebel and Stuber (1976) expanded upon the earlier work of Stuber (1973, 1974, 1975a,b,c) of ozonation of Dalton, Georgia municipal wastewater secondary effluents. Grab samples 20 gal in size were stored under refrigeration and treated within 48 hrs of collection. The ozonation contactor was a plexiglass column having a height of 8 ft, a diameter of 5.5 inches and a capacity of 37 liters (10 gal). Ozone was generated from oxygen and sparged into the column through a 60 μ, high density polyethylene diffuser. Ozone was analyzed both in the contactor feed gas and in the off-gases. GAC adsorption was tested to compare the amount of reduction in color and COD levels.

The major sources of colors in Dalton's wastewaters are synthetic organic dyes which are not destroyed by activated sludge treatment. These produce color levels of about 300 APHA units. Filtered and unfiltered wastewaters were ozonized to determine the amount of ozone necessary to attain a target color removal to levels of 30 to 60 APHA units. The amount of ozone required to lower the color of filtered secondary effluent to 20

APHA units was 32.5 mg/l; that required to lower the color of unfiltered effluent to 30 APHA units was 45 mg/l of ozone.

At these ozone dosages, the levels of COD decreased rapidly as ozone dosages rose to 45 mg/l, then slowed and approached 40 to 45% total reduction in value. There was no significant advantage to removing SS to effect higher COD removals. This indicated that the SS present in this effluent were attacked by ozone at a much slower rate than was the dissolved COD.

The BOD-5 increased from 21 to 53 mg/l as the ozone dosage increased from 0 to 13.6 mg/l, then decreased to 21 mg/l at an ozone dosage of 34 mg/l. The COD concentration decreased in the range in which BOD-5 increased, proving that an oxidation process was taking place. Soluble organic carbon increased from 48 to 58 mg/l up to an ozone dosage of 75 mg/l, then decreased to about 33 mg/l at an ozone dosage of 165 mg/l. Samples containing SS showed increased levels of soluble organic carbon after ozonation, while samples which showed decreased levels of soluble organic carbon contained no suspended material.

SS levels were lowered significantly upon ozonation, from 20 mg/l to 2 mg/l. Total coliform counts were reduced from 850,000 MPN/100 ml to 2,500 MPN/100 ml at ozone dosages of 28.6 mg/l. Fecal coliform counts were lowered from 8,000 MPN/100 ml to 0 MPN/100 ml at 22 mg/l ozone dosages.

Table 64 shows the changes in wastewater parameters obtained by treating unfiltered Dalton, Georgia secondary effluent with 45 mg/l of ozone, to reach 30 APHA units of color level -- considered to be acceptable by the local regulatory agency since background levels of the receiving river are about 20 APHA units.

TABLE 64. TREATMENT OF UNFILTERED DALTON, GEORGIA EFFLUENT WITH 45 MG/L OZONE

Parameter	Initial	Final	Change
Color,	275 APHA	30 APHA	- 89%
COD	156 mg/l	94 mg/l	- 40%
BOD	21 mg/l	21 mg/l	0%
DO	2 mg/l	8.5 mg/l	+ 325%
Organic Carbon	53 mg/l	54 mg/l	+ 2%
Inorganic Carbon	3 mg/l	5 mg/l	+ 67%
Suspended Solids	20 mg/l	3 mg/l	- 85%
Biphenyl	1.85 mg/l	0.90 mg/l	- 51%
Anionic Detergents	0.6 mg/l	0.05 mg/l	- 92%
Fecal Coliforms	8,000/100 ml	0/100 ml	- 100%
Total Coliforms	850,000/100 ml	>1,000/100 ml	-99.99%
pH	6.8	7.1	+ 4%

Source: Nebel & Stuber, 1976

Economic comparisons between ozonation treatment at dosages of 45 mg/l and GAC treatment to attain the same degree of color removal are shown in Table 65. Assumptions made in this comparison were as follows: 12 mgd wastewater flows require generation of 4,500 lbs/day of ozone and 780 lbs/day makeup GAC; the cost of GAC is 50¢/lb; 5% of the GAC is lost during reactivation; reactivation cost is 8¢/lb; ozone is generated from air and requires 11 kwhr/lb @ 1.5¢/kwhr. Over a 20 yr period, the total costs for GAC treatment are estimated to be double those of the ozonation process. In addition, ozone treatment also disinfects, but credit was not taken for this (Nebel & Stuber, 1976).

TABLE 65. PROJECTED ECONOMICS OF OZONE AND CARBON AT DALTON, GEORGIA

Item	Ozone	Granular Activated Carbon
lbs/day	4,500	780
Capital, total project cost	$1.86 million	$11.2 million
Amortize 20 yrs @ 7%	$237,860	$1.06 million
Annual operation & maintenance	$296,495	$29,893
Total costs over 20 yrs	$10.7 million	$21.8 million

Source: Nebel & Stuber, 1976

Urushigawa, Kurata & Noji (1974) ozonized dyeing wastewaters pretreated by trickling filters at two Japanese dyeing mills. The trickling filters were 4.5 m deep, 0.2 sq m in cross section, 0.9 cu m in volume and the specific surface of the plastic filter media was 140 sq m/cu m. The ozone treatment tank was 0.1 cu m in volume and the ozone generator capacity was 30 g/hr (feed gas not identified in the English abstract). The degree of organics removal and decolorizing effects were studied at different hydraulic loadings without recirculation and the following observations were made:

1) BOD removal efficiency was 55% to 65% at 2.4 cu m/sq m/hr at a BOD loading of 2.0 kg/cu m/day.

2) Greater than 60% efficiency of BOD removal on the trickling filter was difficult without recirculation.

3) COD removal efficiency on the trickling filter was about 25%.

4) Decolorization efficiency was maintained at 80% by use of ozonation.

5) In the total treatment system, involving ozonation, removals of BOD, COD and color were 73%, 53% and 80%, respectively.

Maeda (1974) studied ozonation of reducing waste liquids discharged from a Japanese dye and dye intermediate manufacturing plant. These wastes contained sodium sulfide, sodium sulfite, sodium thiosulfate, p-aminophenol, p-nitrophenol and various organic intermediates as major constituents; the plant discharged 15 tons/day of wastewater. Soluble organic substances accounted for about 50% of the initial 60,000 mg/l COD values.

Ozonation was conducted in either of 2 tanks, a 6-liter tank and a 14-liter tank, using gas dispersion tubes. Ozone was generated from air and could be measured in the contactor inlet and off-gases. Alkaline oxidation of 60 g of $Na_2S_2O_3.5H_2O$ plus 20 g of NaOH (in 6 liters) over 7 hours used 25.87 g of ozone (1.47 g of thiosulfate/g of ozone). Sodium sulfite was produced as an intermediate, which was oxidized to sodium sulfate. When the concentration of thiosulfate was less than 7.0 g/6 liters, the solution contained 5 to 7 g of sodium sulfite at all times during ozonation as long as thiosulfate was present (Figure 24).

A 3-liter sample containing 171.65 g of sodium thiosulfate was treated with 107 g of sulfuric acid and the solution was aerated for 2 hrs. Under these conditions, SO_2 was produced and the COD dropped from 20,670 to 10,500 mg/l (49.2% reduction in COD level; 79.3% reduction in thiosulfate concentration). This solution then was ozonized for 1 hr and the COD dropped to 7,500 mg/l (total COD reduction of 63.7%; total thiosulfate reduction 99.9%).

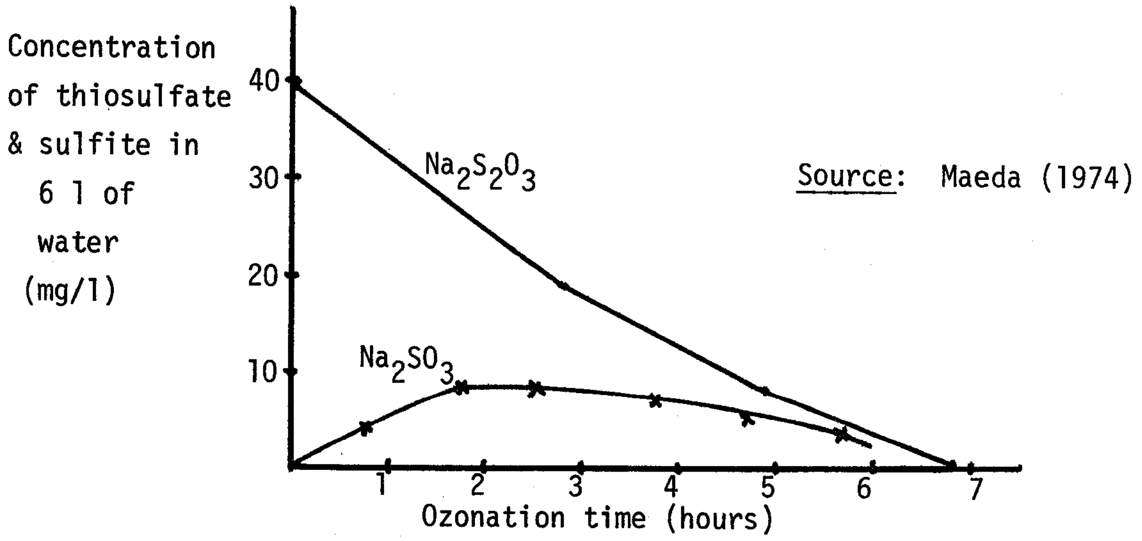


Figure 24. Ozonation of thiosulfate solution.

Three treatments were conducted on 1 liter samples of reducing waste liquids at pH 9.5 to 10.5: (1) ozonation alone; (2) addition of 10 ml of formalin, stir, heat (to promote condensation polymerization of phenolics), filtration and ozonation; (3) 4 liters of liquid treated with formalin, condensation products filtered, $FeSO_4$ added to remove sulfite, H_2SO_4 added to pH 3.0 to 3.5, aerated to remove thiosulfate, then pH re-elevated and ozonized. Pertinent results are shown in Table 66. Method (3) gave the best removal of COD.

Maeda (1974) concluded that initial treatment of this type of wastewater (at pH 9.5 to 10.5) with formalin will remove some soluble organics by condensation polymerization, and the corresponding reduction in COD levels can reach 50%. Adjustment of pH to 3.0 to 3.5 will remove some sulfide and some condensation polymers which were soluble at elevated pH levels; COD removal then will reach 63%. Thiosulfate then can be removed by ozonation, chlorine oxidation or aeration at pH 1, giving 6,000 to 10,000 mg/l COD (83% to 85% overall reduction). Readjustment of pH to the alkaline side, followed by ozonation now should produce a wastewater having a final COD value of 3,000 to 4,000 mg/l.

TABLE 66. OZONATION OF REDUCING WASTE LIQUID FROM DYE MANUFACTURING*

Treatment Method**	Total Ozonation Time	Initial COD (mg/l)	Final COD (mg/l)	Ozone Consumption (g)	% Reduction of COD value
1	11 hrs, 55 min	40,000	7,800	42.5	80
2	8 hrs	45,000	4,400	29.6	90.3
3	2 hrs	7,650	3,230	----	57.8
4	7 hrs	7,650	981	----	87.2

* Initial pH: 9.5 to 10.5

** Method 1: Ozonation alone

Method 2: Polymerization with formaldehyde, filtration, ozonation

Method 3: Polymerization with formaldehyde, filtration, add $FeSO_4$ (for sulfite), add H_2SO_4 to pH 3.0 - 3.5, aerate (for thiosulfate removal), elevate pH and ozonize.

Source: Maeda, 1974

Snider & Porter (1974) described the ozone treatment of selected wastewater streams from dyeing operations. Ozone was generated from air and the contactor was a 750 ml gas washing bottle with a sintered glass dispersion stone. Then 500 ml samples were ozonized. The off-gases were collected in a second gas washing bottle and analyzed for ozone. The time required for ozone to penetrate into the second bottle ranged from less than 1 to about 30 minutes.

All experiments were conducted at room temperature and the usual ozone contact time was 1 hr. Three pH ranges were studied: near neutral, acidic and basic. Ozone was generated at the rate of 0.5 g/hr. Dye wastewaters were analyzed for COD, color, total solids, volatile solids and dissolved solids both before and after ozonation. In addition to actual wastewater streams, solutions of 2 commercial disperse dyes also were ozonized (Disperse Red 60 Foron Brill Red E-2BL and Eastman Fast Blue B-GLF #27).

Data obtained confirmed the complexity and variability of the wastewater systems studied, but pointed out some general trends, for which there were exceptions observed in almost all cases. Ozonation normally lowered the COD levels from a few percent to more than 50%. No significant decreases in total solids, dissolved solids or volatile solids were observed after ozonation, indicating that complete oxidation of the organics to CO_2 and water did not occur to any great extent. In most cases, the solids contents increased after ozonation, mostly as a result of addition of sulfuric acid or NaOH to adjust the pH before ozone was added.

The amount of visible color decreased dramatically in all cases, but in some cases turbidity increased and contributed to the color readings. Disperse dyes showed the most dramatic color decreases with no turbidity formation. Color reduction occurred even though the COD decreases were small. Thus, either ozone or hydroxyl radicals selectively attacked the dye molecules, or only 1 or 2 bonds in the dye molecules needed to be broken to render the dye colorless.

Snider & Porter (1974) concluded the following:

1) There was no steadfast relationship of pH to efficiency of color removal by ozonation. The highest COD removal occurred at low pH in several cases.

2) In all cases, use of low concentrations of ozone alone for removal of the majority of the organics was not feasible (maximum removals were 55% by low level ozonation, compared with above 90% by conventional treatment).

3) Color was reduced dramatically by application of about 1 g/l of ozone, but in most cases this led to an increase in turbidity which contributed significantly to color as measured spectrophotometrically.

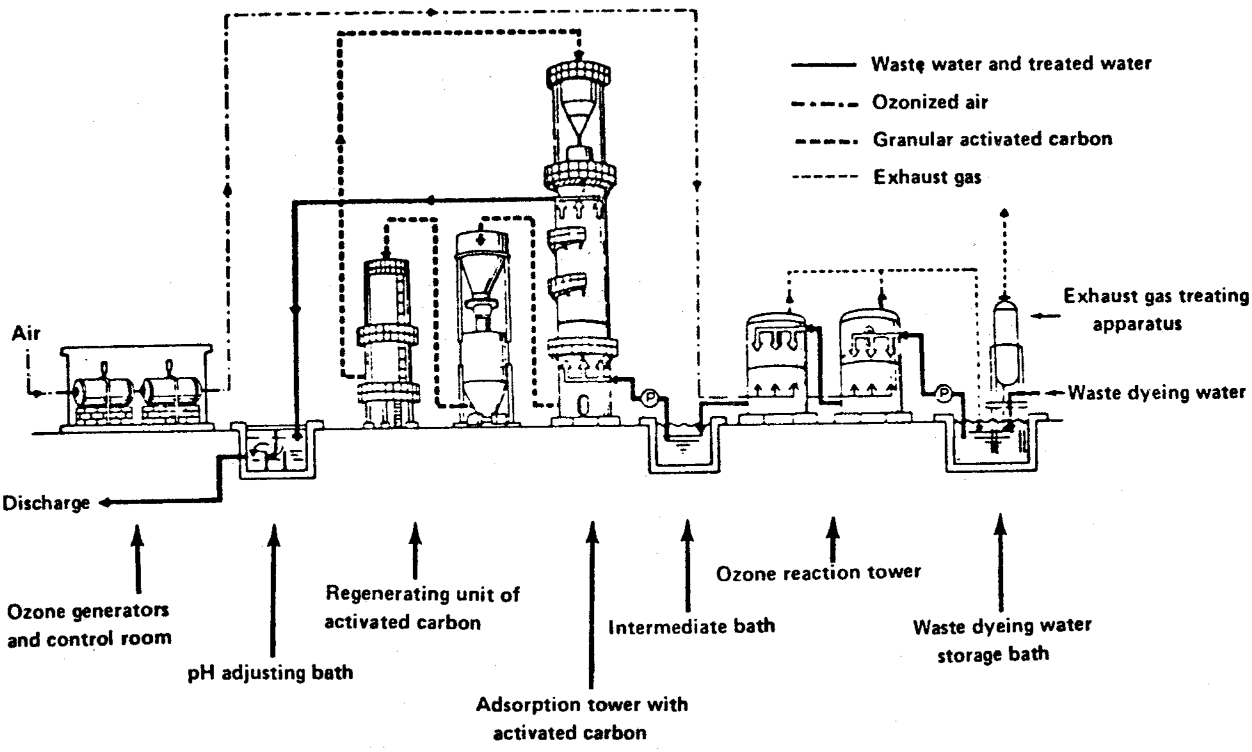
4) Ozone was best applied to textile wastewaters as a polishing agent to remove dyes which were inert to conventional treatment.

In Japan, the Kanebo Company installed an ozone/GAC treatment system at its Nagahama factory in 1974 (Anonymous, 1974). This system handles 3,300 cu m/day (0.87 million gal) of dyeing wastewaters. A "synergistic effect" of the sequential combination of ozonation followed by GAC is noted in this article, which also states that "the combined use of ozone and activated carbon, as compared with the separate use of each, will often produce a doubled effect and result in low investment costs." This statement is not expanded upon further, however.

At the Nagahama factory, dyeing wastewaters are sent to a 600 cu m holding tank from whence it is passed, consecutively, through 2 ozone reaction towers, each 2,800 mm in diameter and 5,000 mm in height. The specifics of ozone contacting in this installation are not described, but ozone is supplied by means of 3 generators, each capable of producing 2.4 kg/hr of ozone from air (7.2 kg/hr total ozone generation capacity). At its maximum addition rate, ozone dosage is 50 mg/l, and dye colors and dissolved organic substances are decomposed at this point.

Ozonized wastewater then passes through an intermediate tank and is sent upflow at 17 m/hr through a carbon adsorption tower (pulse head type) packed with GAC. The carbon adsorption tower is 3,200 mm in diameter and 7,500 mm in height and contains 38 tons of GAC. After carbon adsorption, the pH of the treated wastewater is adjusted and the water is discharged. A schematic of this system is shown in Figure 25.

Exhaust gases from the ozone contacting tower are heated and passed through a 500 liter tower packed with activated carbon. This treatment destroys residual ozone remaining in the contactor off-gases.



<u>Source</u>: Anonymous (1974a)

Figure 25. Dye wastewater treatment plant at the Kanebo Company, Japan.

Pertinent wastewater parameters obtained on these dyeing wastewaters using the ozone/GAC process are listed in Table 67. Major points to be noted are that the BOD values of the ozonized wastewaters are about the same as those of the raw wastewater, and that COD values are lowered 10 to 15% by ozonation. After GAC adsorption, both BOD and COD values have been reduced 60% to 80% from those of the raw water.

The Nagahama factory ozone/GAC installation is claimed to be completely free from sludges (normally produced by coagulative precipitation methods or activated sludge treatment), only a small plant area is required for the installation (about 500 sq m) and the costs of operation of the process are 34¢/1,000 gal of wastewater treated (Anonymous, 1974a).

TABLE 67. DYEING WASTEWATER TREATMENT BY OZONE/GAC AT KANEBO CO., JAPAN

Parameter	Initial	After Ozonation	After GAC
Color*	0.2-0.35	0.05-0.1	0.02-0.05
pH	6.0-8.0	6.0-7.0	6.5-7.5
SS (mg/l)	8-15	5-10	0.6-2
BOD (mg/l)	110-160	100-140	20-50
COD (mg/l)	120-170	100-150	20-50
Phenol (mg/l)	1-2	0.1-0.2	0

* color determined by average of absorbance at 430, 530, 550, 610 and 660 nm.

Source: Anonymous, 1974a.

The synergistic effect of following ozonation with granular activated carbon adsorption also was noted by Mizumoto and Horie (1974). They concluded that the overall cost of a treatment plant using both ozone and GAC in sequence would be less than 1 using either process alone, to attain the same level of treatment. Ozone treatment removed only about 10% of the BOD, while activated carbon removed 60% to 80%. Ozonation removed most of the color and GAC adsorbed that which remained.

Even earlier, Kawazaki (1965) had studied the ozonation of surface active agents and found that greater than 90% decomposition of these materials could be obtained using a 5-fold excess of ozone. On the other hand, these same surface active agents also could be adsorbed onto activated carbon, which then could be "regenerated" using ozone. Further details of the "ozone regeneration" of activated carbon were not given in the abstract available.

Matsuoka (1973) in reviewing the uses of ozonation in the treatment of drinking water and industrial wastewaters, describes 7 Japanese dye manufacturing plants which were using ozone at that time for treating their wastewaters. The plants and their treatment processes are as follows:

Mitsubishi-Denki: Press & Float. Ozonation of 12,000 cu m/day of wastewater; installed August, 1973.

Mitsubishi-Kurogawa Industries: Coagulation, then ozonation of 100 cu m/hr of wastewaters; installed October, 1971.

Kyoshenski-Mitsubishi: Filter, activated carbon, ozonation of 50 cu m/hr of wastewater; installed April, 1973.

Organo-Shobo (Ozone Fuji-Denki): Ozonation, activated carbon treatment of 3,300 cu m/day; installed summer, 1973.

Nishimo-Mitsubishi: Press & Float. Ozonation then activated sludge treatment of 200 cu m/day of wastewater; installed January, 1973.

Fukui-Senkyoshi: Spray filter beds, then ozonation.

Mitsubishi-Juko (Ozone Mitsubishi-Denki): Secondary treatment, coagulation, sand filtration, ozonation then activated carbon treatment of 1,800 cu m/day of wastewater.

Sato, Yokoyama & Imamura (1974) studied the organic oxidation products formed when representative azo dyes were decomposed by ozone. Azobenzene and its derivatives substituted in the para-position with $-NH_2$, $-NMe_2$, -OH or -OMe groups were studied as water-insoluble dyes. Methyl orange was the only water soluble dye studied.

Ozonation of water-insoluble azo dyes was conducted in a 100 ml bottle containing 20 ml of CCl_4 plus 10 ml of water. Ozonation of methyl orange was conducted in a 300 ml bottle containing 100 ml of methyl orange-water solution. The amount of ozone fed was 24 mg/l/min and ozone consumption was determined by the KI technique.

Major oxidation products isolated and identified are listed in Table 68.

TABLE 68. PRODUCTS OF OZONATION OF AZOBENZENES

Starting Azobenzene Compound	Oxidation Products Identified
azobenzene (I)	azoxybenzene, oxalic + glyoxalic acids
p-amino-I and p-dimethylamino-I	nitrosoazobenzene, nitroazobenzene, oxalic + glyoxalic acids, NO_3^-
p-hydroxy-I	oxalic + glyoxalic acids
p-methoxy-I	oxalic + glyoxalic acids, NO_3^-
methyl orange	oxalic + glyoxalic acids, NO_3^- + HSO_4^-

Source: Sato, Yokoyama & Imamura, 1974.

Ozonation of p-aminoazobenzene initially formed nitroazobenzene and other products neither soluble in water nor in CCl_4, but resulted in a temporary increase in color. Prolonged ozonation finally caused decolorization with concomittant decomposition of the oxidation products.

Ikehata (1975) described batch and continuous ozonation studies on aqueous solutions of nearly 100 dyes having various chemical structures. These dyes comprised direct dyes, acid dyes, basic dyes (which were rapidly and completely decolorized by ozonation) and insoluble and disperse dyes which were removed by chemical coagulants. In addition, the wastewater from a dye printing works was nearly completely decolorized by injection of less than 30 g of ozone/cu m. The purpose of this study was to develop a conceptual design of an ozonation process for treatment of dye wastewaters and to evaluate costs.

For batch tests, ozone was prepared from oxygen, but for continuous ozonation tests and plant wastewater studies, ozone was generated from air. In the batch tests, ozone was sparged into the dye wastewater solutions and the rate of decolorization was measured spectrophotometrically. Ozone in both the feed gas and contactor off-gases was measured so that ozone utilization efficiencies could be determined.

For the continuous tests the concentration of ozone in air was 20 g/cu m. An Otto type injector contactor* was employed in two contacting columns. The dye solution flow rate was 0.5 cu m/hr, but different flow rates for ozone in air were used. Ozone in the contactor feed and off-gases also was determined.

Pilot tests were conducted on the effluents from the printing dye works at Jyoyo Kogyo Ltd. (near Kyoto city) which began operating in 1972. Prior to the ozonation step, the wastewaters were sent through clarification to remove suspended organic materials and colloidal substances. The flow rate was 100 cu m/hr.

Ozonation was conducted by 3 different contacting techniques. In Method A, all ozone was injected into the water in a packed, cylindrical steel chamber of 4 cu m volume and having 5 Otto injector units* on its lower side. In Method B, the wastewater to be ozonized was divided. One-half was ozonized in the steel chamber and the other one-half was ozonized in a 15 cu m concrete chamber containing a single Otto injector contactor*. In method C the wastewater again was divided and ozonized in each of 2 single injector concrete chambers. Method C gave the best performance results of the 3 (more than 95% decolorization and more than 80% ozone utilization).

Decolorization reactions were found to follow first order kinetics up to almost 90% removal of color. Cleavage of the -N=N- (azo) bonds probably was involved, since NO and NO_2 were formed during ozonation. More than 95% decolorization of dyes was obtained in all cases. The ratio of dye to ozone necessary to obtain 85% decolorization was less than 1. Preflocculated and filtered rayon wastewaters required only 33% of the amount of ozone to provide 85% decolorization as did untreated wastewater. BOD and COD values of these wastewaters decreased by 10% and 25%, respectively.

Costs for ozonizing by all 3 methods are given in Table 69, and were 1152.7 yen/100 cu m of wastewater treated by Method A, 1367.5 for Method B and 1203.4 for Method C. By comparison, costs for chemical clarification were 2475.5 yen/cu m to attain a similar level of treatment.

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* An Otto type contactor is an injector (such as a Venturi nozzle) apparatus in which a small portion of the water initially is treated with all of the ozone to be dosed. Then this small portion of water (now containing all of the added ozone) is drawn into the balance of the water to be ozonized by means of the injector.

TABLE 69. COST OF OZONE TREATMENT OF JYOYO KYOGO DYE WASTEWATERS*

Item	Cost for Method A	Ozonation by Method B	Contacting By Method C
Capital Cost (Yen x 10,000)	2,400	2,800	2,600
Operating Cost (Yen/100 cu m)			
Amortization, 15 yrs @ 7%	628.5	775.5	680.5
Power	319.5	382.5	315
Maintenance	4.5	9.5	7.5
Total Operating Cost (Yen/100 cu m)	1,152.7	1,367.5	1,203.4

* Plant Capacity: 100 cu m/hr

Source: Ikehata, 1975.

Tsukabayashi (1975) studied various methods of treating textile dyeing wastewaters and concluded that "ozone treatment is excellent, but very expensive; it can be used as a secondary treatment method".

Anonymous (1975b; TX-05) concluded that for destroying color, ozonation is excellent for textile wastewaters containing reactive dyes, but inefficient for those containing threne, naphthol and/or sulfur dyes. However, since about 90% of the dyes used in the towel dyeing industry in the Ehime Prefecture of Japan are reactive dyes, treatment with ozone is a viable method. Treatment with activated carbon also was effective in removing color, but the decolorization effect was greatly enhanced by the combined use of activated carbon and ozone.

Anonymous (1975a; TX-04) studied the treatment of various dyeing wastewaters containing oil/water emulsions used in the oiling process of fiber dyeing. These were treated with ozone and inorganic coagulants and the process removed about 100% of the oil emulsion and colored organic compounds. The sludge formed in using the ozone/inorganic coagulant process was about 33 to 50% that of the "normal volume".

Anonymous (1975c; TX-06) studied the decolorization of wastewaters containing dyes by ozonation. The amount of ozone required for decolorization was higher for effluents containing disperse dyes than for wastes containing hydrophilic dyes. The weight ratio of added ozone to dye ranged between 0.5 and 1.0 for wastes containing hydrophilic dyes, but was 1 for wastes containing disperse dyes. This author states that "disperse dyes which have a high solubility can be decolorized with a smaller amount of ozone because of the higher contacting efficiency of dyes with ozone during treatment".

Pretreatment, such as coagulation/precipitation, used before ozonation, removed most of the disperse dyes from solution. However, removal of hydrophilic dyes could not be accomplished by coagulation/precipitation, and ozonation was effective in these instances. The presence of reducing substances, such as dithionites, interferred with ozone decolorization of these dyes by reacting with the ozone before the dyes reacted. Therefore, such reducing agents should be removed prior to introduction of ozone (Anonymous, 1975).

Rinker (1975) studied the treatment of textile wastewaters by activated sludge and alum coagulation. These produced an effluent from a mill producing a synthetic knit fabric for the apparel and automotive markets which needed additional treatment to meet anticipated discharge limitations. Research studies were conducted using carbon adsorption, resin adsorption and ozonation for color removal.

Netzer et al. (1976) described the ozonation of dye wastewaters. Exhausted dyebath effluents were collected from 3 different Canadian textile mills which produced dyed fibers for carpets, hats and yarns. These samples were filtered through Whatman #54 filter paper and stored at 4°C prior to use.

Ozonation was conducted in a 3 liter glass vessel containing a sparger. Ozone was generated from oxygen at a concentration of 25 ppm and was passed through the sparger tube at the rate of 1 liter/minute. Contacting time was 15 minutes, but the off-gases were not analyzed for excess ozone. After ozonation, the samples were filtered and analyzed for TOC, COD, heavy metals and color.

Foaming was persistent during ozonation, but usually subsided by the end of the ozonation experiment. After analyses were made, the samples were split. One-half of the samples were treated with lime to a pH of 11 to 12, and the second one-half were treated with 3,000 mg/l of powdered Nuchar C-190N activated carbon. The mixtures then were stirred 0.5 hr and filtered.

In a second set of experiments, the sequence was reversed. Powdered activated carbon treatment preceeded ozonation. Ozonation did not lower the amounts of free or complexed heavy metals appreciably. The most notable effect observed was nearly complete color removal.

The ratio of TOC/COD for untreated and treated samples remained essentially constant, but in several cases the ratio of TOC/COD of ozonated wastewaters was greater than in the raw effluent. Netzer et al. (1976) concluded that no firm conclusions could be drawn as to the effect of ozonation on the content of TOC or COD. Therefore, neither TOC nor COD are appropriate parameters to gauge the effectiveness of ozonation of textile wastewaters.

Powdered activated carbon alone gave good decolorizations and good TOC and COD removals in nearly all cases. Lime was effective in precipitating heavy metals, such as zinc, and also resulted in good color removals and some lowering of TOC and COD values. However, none of the hat dyeing effluents was decolorized to any appreciable extent by lime addition.

Powdered activated carbon followed by ozonation gave better TOC and COD removals in all but one case. Lime addition followed by ozonation was superior to ozonation followed by lime addition with carpet mill effluents. Hat dyeing wastewaters were decolorized by lime followed by ozonation, but showed little removal of TOC or COD.

In conducting similar studies, Netzer (1976) characterized effluents from dyehouses of various textile mills in Canada and studied the removal of color, soluble organics and heavy metals from these wastewaters by massive lime coagulation, by activated carbon adsorption, by ozonation and by resin adsorption. Ozone was generated from oxygen (25 mg/l of ozone in oxygen) and the gas mixture sparged into 100 ml samples of effluent in a 250 ml gas washing bottle for 20 minutes, after which the samples were filtered and analyzed. Lime coagulation achieved excellent removals of free heavy metals and very good color removals in some cases as well. Substantial soluble organics and color removals were obtained with activated carbon and resin adsorption. Ozonation was "very potent" for decreasing color intensities, but not for reducing the concentrations of soluble organics.

Anonymous (1976b; TX-08) treated dyeing factory wastewater by activated sludge immobilized on polyurethane sponge. Although this process with extended aeration was sufficient to lower the BOD to acceptable levels, it was necessary to inject ozone into the aeration bath in order to obtain acceptable COD values.

Anonymous (1976c) tested ozonation for treating dye bath, scour and rinse waters from the dyeing processing of cotton. Reactive and basic dye colored waters were successfully decolorized with ozone, but it could not adequately decolorize wastewaters containing disperse dyes.

A Dutch patent (Anonymous, 1976a) describes a process for recycling dye works effluents. Neutral wastewaters containing organic dyes and auxiliary agents are subjected to continuous oxidative degradation with ozone in several stages, with strong agitation.

Conclusions

1) At least 9 Japanese dye manufacturing or textile processing plants are known to be using ozonation on commercial scale for treating their wastewaters. The major purpose for ozone in these wastewater treatment processes is decolorization.

2) Hydrophilic dyes (reactive, cationic or acidic) are quite reactive with ozone, less than 1 g of ozone being required to decolorize 1 g of this type of dye. This ozone requirement has been determined with actual plant wastewaters treated by the sequence of lime coagulation, polymer flocculation, precipitation, ozonation and 1- or 2-stage aeration. BOD levels were lowered from 150 to 78 mg/l and 79 to 98% decolorization was obtained.

3) With the above wastewaters (of conclusion 2), ozonation was not effective in treating sulfur-containing or chromium dyes.

4) For a synthetic fiber plant using mainly cationic dyes and treating 1,500 cu m/day (360,000 gal/day) of wastewater (the plant of conclusion 2), capital costs in 1972 were 28 million yen and operating costs were 10.19 yen/cu m.

5) Ozonation of unfiltered secondary treated combined municipal/industrial wastewaters (90% being wastewaters from carpet producing and tufted dyeing plants in Dalton, Georgia) with 45 mg/l dosages of ozone lowered the effluent color from 275 to 30 APHA units. At the same time, this 45 mg/l ozone dosage also lowered COD levels by 40%, SS by 85%, biphenyl by 51%, detergents by 92%, fecal coliforms by 100% and total coliforms by 99.99%. BOD levels increased during the early stages of ozonation, but at the 45 mg/l total dosage level, there was no overall change in BOD level. Cost comparisons between ozonation and GAC to achieve the same amount of color reduction at the 12 mgd Dalton, Georgia wastewater treatment plant and taken over a 20-yr period showed ozonation costs to be about 50% of those of activated carbon.

6) Japanese dyeing plant wastewaters treated by trickling filter, then ozonation showed 80% lowering of color, 73% lowering of BOD and 53% lowering of COD levels.

7) Reducing waste liquids from a Japanese dye manufacturing plant were pretreated with formaldehyde to polymerize phenolics, filtered, ferrous sulfate added to remove sulfite, adjusted to pH 3.0 to 3.5, aerated (to oxidize thiosulfate), the pH increased and the waste ozonized. This treatment lowered a starting COD value of 7,650 by 58% in 2 hrs of ozonation and by 87% in 7 hrs.

8) Laboratory studies on 500 ml samples of wastewaters from a U.S. dyeing plant showed that disperse dyes are decolorized best upon ozonation with no increase in turbidity and little reduction in COD levels. With other types of dyes, ozonation increased turbidity.

9) An 0.87 mgd Japanese dyeing plant uses 2-stage ozonation (maximum dosage 50 mg/l) followed by GAC adsorption. The process is free of sludges and total operating costs are 34¢/1,000 gal. The combined process of ozone followed by GAC is lower in cost than the cost of using either treatment process alone.

10) Ozonation of p-aminoazobenzene in water initially formed nitrosoazobenzene, nitroazobenzene and gave an increase in color. Continued ozonation decolorized the solution and formed oxalic acid, glyoxalic acid and nitrate ion.

11) Wastewaters from a Japanese dye printing works were nearly completely decolorized by injection of less than 30 g of ozone/cu m (after clarification). Double-stage ozone injection gave greater than 95% decolorization and greater than 80% ozone utilization. Preflocculated and filtered rayon wastewaters required 33% of the ozone to provide 85% decolorization as untreated wastewater. The ozone/dye ratio necessary to obtain 85% decolorization was less than 1. Ozonation costs for treating 100 cu m/hr were 26 million yen (capital) and 1,203 yen/100 cu m (operating).

12) Ozonation is viable for decolorizing wastewaters containing reactive dyes, but is inefficient for those containing threne, naphthol or sulfur-containing dyes.

13) Dyeing wastewaters containing oil/water emulsions used in the oiling process of fiber dyeing were successfully treated with ozone and inorganic coagulants; about 100% of the oil emulsion and colored organics were removed. Only 33 to 50% of the sludge normally produced by conventional processing was formed by this ozonation/inorganic coagulant process.

14) The ozone/dye ratio required to decolorize wastewaters containing hydrophilic dyes is 0.5 to 1.0, but 1 or greater for disperse dyes. Reducing agents (such as dithionite) should be removed prior to ozonation.

15) Neither TOC nor COD are appropriate parameters to gauge the effectiveness of decolorization of dye-containing wastewaters. Decolorization occurs, but without causing significant changes in TOD or COD.

16) In decolorizing Canadian dye mill wastewaters, lime addition followed by ozonation was more effective than ozone followed by lime with carpet mill effluents.

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SECTION 6

OXIDATION PRODUCTS OF ORGANIC MATERIALS

INTRODUCTION

There does not exist a great deal of literature in which the investigators deliberately attempted to isolate and identify the oxidation products of organic compounds from actual wastewaters or drinking water supplies. Most of the research has been directed toward determining the dosage of oxidant necessary to reduce the concentration of a particular organic compound to below a limit detectable by means of an analytical technique specific for that compound. It has not been generally recognized that oxidation products formed from these materials still may be present, may not be detectable by the analytical technique used to determine the original compound, and may pose a public health concern. It has been only recently that Rook (1974) has shown chloroform to be a product of the chlorination of drinking water supplies containing humic materials. Since then, research into the formation and nature of organic oxidation products under drinking water and/or wastewater treatment conditions has accelerated.

Most of the experiments dealing with organic oxidation products from ozonation and other oxidation processes have not been conducted under controlled water or wastewater treatment plant conditions, i.e., dilute aqueous solutions of compounds, low dosages of oxidant, short contact times, absence of pH control, etc. At the rather low concentrations of organic materials normally encountered in water and wastewater treatment plants, oxidation of o organic compound usually produces other compounds in even lower concentrations. Therefore, recent research studies have utilized the approach of starting with relatively concentrated solutions of organic compounds, and using high dosages of oxidants for prolonged periods of time, in order to force the oxidations to proceed to later stages. Others have started with high concentrations of organic compounds, but have deliberately underdosed with oxidant in order to be sure of producing partially oxidized, early intermediate materials for isolation and study.

Miller et al. (1978) and Rice & Miller (1977) have reviewed the available literature on the use of ozone and chlorine dioxide with the intent of determining specific oxidation products which have been isolated and identified without regard to the relationship of their experimental synthetic conditions (mostly laboratory studies) to actual wastewater or drinking water treatment plant conditions under which ozone and chlorine dioxide normally are employed. A list of specific organic chemicals known to be formed upon oxidation by ozone and/or chlorine dioxide would be useful to toxicologists and other water and wastewater treatment scientists.

Similarly, once it is known with certainty which specific organic compounds can be formed upon oxidation with ozone, reaction conditions can be designed for wastewater treatment processes which will minimize their formation.

BACKGROUND

The capability of one substance to oxidize another is measured by its "oxidation potential", normally expressed in volts of electrical energy (referenced to the hydrogen electrode). The oxidation potential is a measure of the relative ease by which an atom, ion, molecule or compound is able to lose electrons, thereby being converted to a higher state of oxidation. If the oxidation potential of substance A is higher than that of substance B, then substance B will be oxidized in the presence of substance A. Oxidation potentials of representative oxidants encountered in drinking water treatment are listed in Table 70.

Although the relative position of an oxidant in this table is indicative of its ability to oxidize other materials, it does not indicate how fast 1 material will be oxidized by another, nor how far toward completion the oxidation potentials alone whether a specific organic compound will be oxidized completely (to CO_2 and water) or only to the first of several intermediate stages.

One significant fact can be learned from this table, however, at this point. As will be discussed in detail later in this section, it is rare that organic compounds treated with an oxidant as powerful as ozone will be converted totally to CO_2 and water, under conditions normally encountered in wastewater treatment plants.

Therefore, no other commonly employed and less powerful water treatment oxidant (such as chlorine, bromine, chlorine dioxide, etc.), all of which have lower oxidation potentials than ozone, will oxidize an organic material completely to CO_2 and water if ozone will not.

All oxidants weaker than ozone will be less effective than ozone in converting organic compounds to carbon dioxide and water, and thus may produce higher quantities of partially oxidized organic materials under wastewater treatment plant conditions. It is important, therefore, for the wastewater treatment engineer to understand the chemistry of the organic components of the wastewater when considering the use of ozone or other oxidants in the processing.

FUNDAMENTAL PRINCIPLES

All oxidants react with organic materials by 1 or more of 3 different mechanisms:

- Addition
- Substitution
- Oxidation

TABLE 70. OXIDATION-REDUCTION POTENTIALS OF WATER TREATMENT AGENTS*

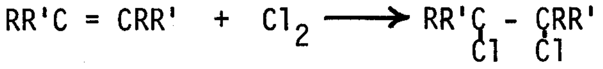
REACTIONS	POTENTIAL IN VOLTS (E°) 25°C
$F_2 + 2e = 2F^-$	2.87
$O_3 + 2H^+ + 2e = O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e = 2H_2O$ (acid)	1.76
$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$	1.68
$HClO_2 + 3H^+ + 4e = Cl^- + 2H_2O$	1.57
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	1.49
$HOCl + H^+ + 2e = Cl^- + H_2O$	1.49
$Cl_2 + 2e = 2Cl^-$	1.36
$HOBr + H^+ + 2e = Br^- + H_2O$	1.33
$O_3 + H_2O + 2e = O_2 + 2OH^-$	1.24
ClO_2 (gas) $+ e = ClO_2^-$	1.15
$Br_2 + 2e = 2Br^-$	1.07
$HOI + H^+ + 2e = I^- + H_2O$	0.99
ClO_2 (aq) $+ e = ClO_2^-$	0.95
$ClO^- + H_2O + 2e = Cl^- + 2OH^-$	0.9
$H_2O_2 + H_3O^+ + 2e = 4H_2O$ (basic)	0.87
$ClO_2^- + 2H_2O + 4e = Cl^- + 4OH^-$	0.78
$OBr^- + H_2O + 2e = Br^- + 4OH^-$	0.70
$I_2 + 2e = 2I^-$	0.54
$I_3^- + 2e = 3I^-$	0.53
$OI^- + H_2O + 2e = I^- + 2OH^-$	0.49
$O_2 + 2H_2O + 4e = 4OH^-$	0.40

*Handbook of Chemistry & Physics, 56th Edition, 1975-76. CRC Press Inc., Cleveland, Ohio, p. D-141-143.

In some cases, oxidants will react with organic compounds by all 3 mechanisms, although in sequential steps.

Addition

Addition occurs with organic compounds containing aliphatic unsaturation, such as olefins. Chlorine can add across an olefinic double bond to produce a dichloride:

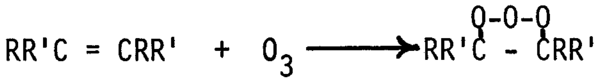


$$RR'C = CRR' + Cl_2 \longrightarrow RR'\underset{Cl}{C} - \underset{Cl}{C}RR'$$

Hypochlorous acid can add across a double bond to form a chlorohydrin:

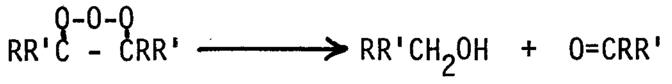
$$RR'C = CRR' + HOCl \longrightarrow RR'\underset{Cl}{C} - \underset{OH}{C}RR'$$

Ozone can add across a double bond to form an ozonide:



$$RR'C = CRR' + O_3 \longrightarrow RR'\overset{O-O-O}{C - C}RR'$$

This last reaction occurs readily in non-aqueous solvents, but as soon as water is added, the ozonide hydrolyzes to other products, with cleavage of the former double bond:

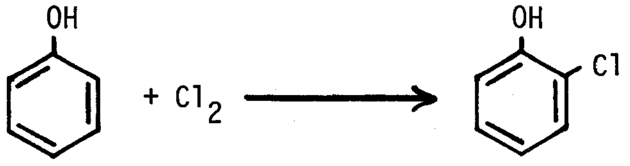


$$RR'\overset{O-O-O}{C - C}RR' \longrightarrow RR'CH_2OH + O=CRR'$$

ozonide alcohol ketone

Substitution

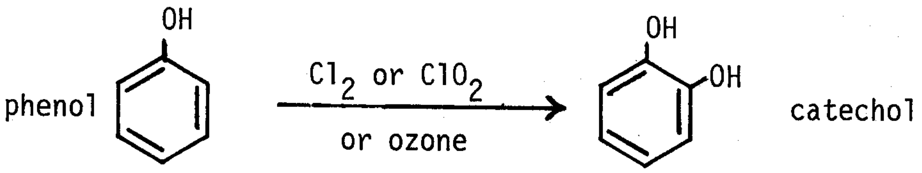
Substitution involves replacement of 1 atom or functional group with another. For example, chlorine can react with phenol to produce o-chlorophenol. In this reaction the ortho-hydrogen atom is replaced by chlorine:



phenol o-chlorophenol

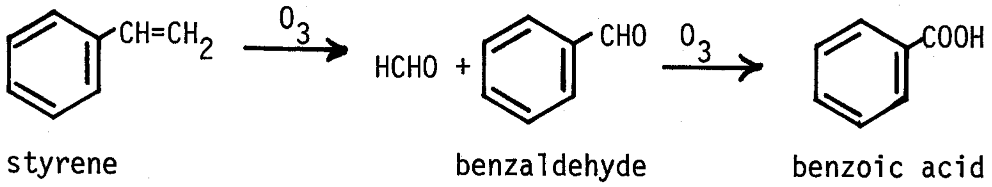
Oxidation

Oxidation involves the introduction of oxygen into the organic molecule, with or without degradation of the organic compound. For example, oxidation of phenol with either chlorine, chlorine dioxide or ozone can produce catechol as a first oxidation product:



This specific reaction also can be viewed as an <u>insertion</u> reaction, whereby oxygen is inserted between the ring carbon and hydrogen to form the hydroxy group on the ring.

Oxidation also can involve cleavage of carbon-carbon bonds to produce fragmented organic compounds. For example, ozonation of styrene produces formaldehyde, benzaldehyde, and benzoic acid (Yocum, 1978):



At the last stage in treatment of organic compounds with oxidants, oxidation also can involve production of CO_2 and water:

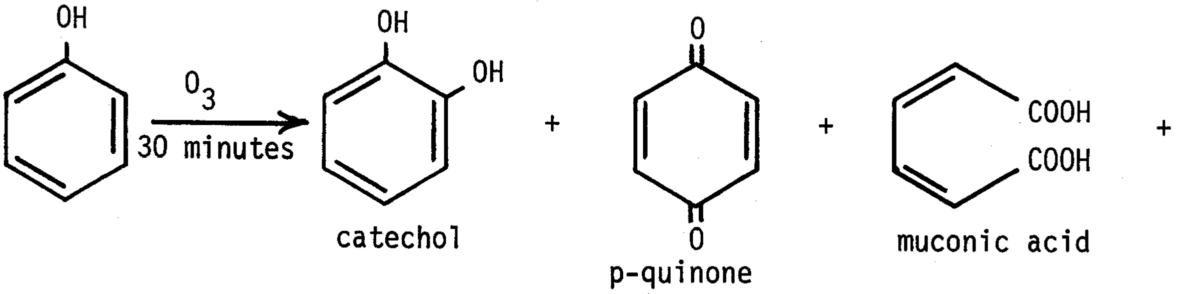
$$HCOOH + O_3 \longrightarrow CO_2 + H_2O$$

formic acid

REACTIONS OF ORGANIC COMPOUNDS WITH OZONE

<u>Reactions With Phenol</u>

Eisenhauer (1968) ozonized aqueous solutions of phenol for 30 minutes (until phenol was destroyed) and isolated catechol, p-quinone, <u>cis</u>-muconic acid, oxalic acid and fumaric acid:



\+ (equation continued)

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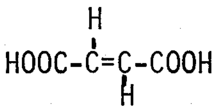


$\mathrm{HOOC}-\overset{H}{C}=\underset{H}{C}-\mathrm{COOH}$ (fumaric acid)

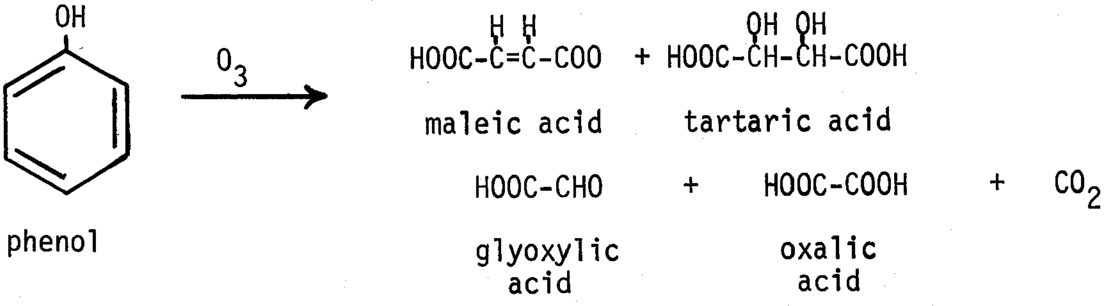
+ HOOC-COOH (oxalic acid)

When ozonation was conducted for only 10 minutes, Eisenhauer isolated a 20% yield of catechol, but only 70% of the phenol was destroyed. This indicates that upon oxidation of phenol, other organic compounds (10%) or CO_2 are produced along with the catechol.

Gabovich et al. (1969) treated 10 mg/l aqueous solutions of phenol with ozone dosages of 0.7 to 2.3 mg/l. To attain 90% destruction of phenol (to 1 mg/l concentration) required 1.85 mg of ozone/mg of phenol; complete destruction of phenol required 2.3 mg ozone/mg phenol.

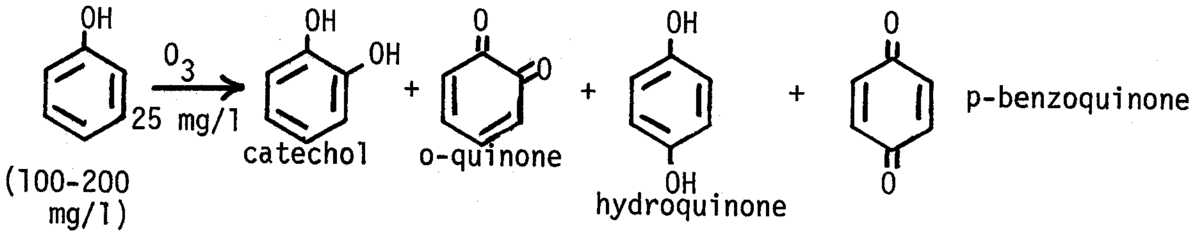
Bauch et al. (1970) found monobasic and polybasic (aliphatic) acids upon ozonation of water solutions of phenol. They concluded that oxidation of phenol by ozone proceeded via the ozonide and produced hydrogen peroxide. Initial phenolic oxidation products themselves consumed additional ozone.

Bauch & Burchard (1970) ozonized aqueous solutions of phenol and isolated and identified maleic acid, tartaric acid, glyoxylic acid, oxalic acid and CO_2:

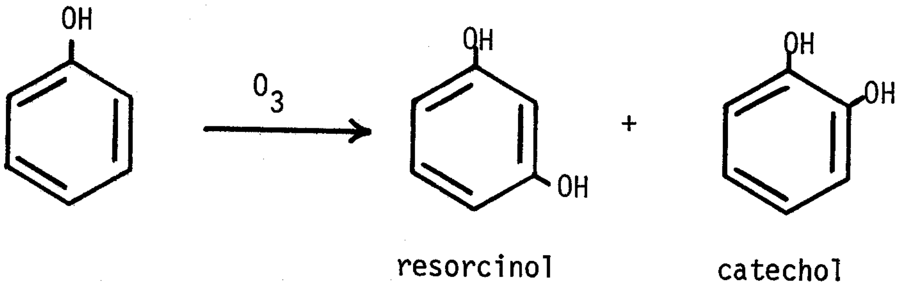


Smith et al. (1972) found that the rate of disappearance of phenol upon ozonation in water is increased by combining ultrasonics and/or Raney nickel with ozonation. After 2.5 hours of ozonation, an initial solution of 500 mg/l phenol showed the complete absence of phenol. On the other hand, the COD of the original solution decreased only slowly, and was still fairly high after the phenol had disappeared, indicating the presence of intermediate oxidation products. Considerable carbon loss indicated the formation of some CO_2.

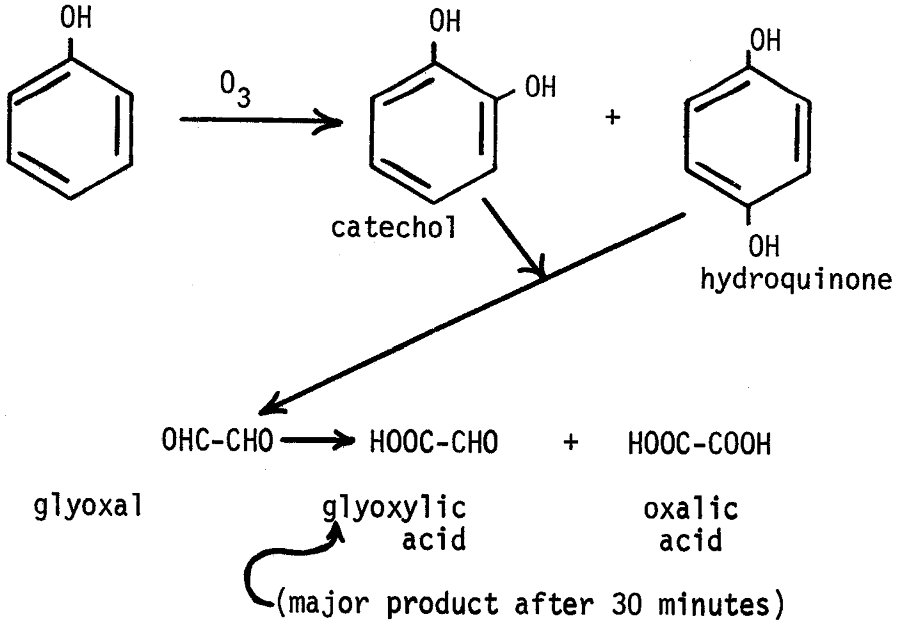
Mallevialle (1975) ozonized 100 to 200 mg/l aqueous solutions of phenol with 25 mg/l ozone doses and identified catechol, o-quinone, hydroquinone and p-quinone as oxidation products:



Spanggord & McClurg (1978) were the first investigators to identify resorcinol as an initial oxidation product, along with catechol, upon ozonation of phenol in water:



Gould & Weber (1976) have made the most complete study to date on the ozonation of phenol. They found that the early oxidation products (catechol and hydroquinone) are further oxidized as ozonation continues, and fall to relatively insignificant concentrations as the reactions proceed. Glyoxal is formed by ring rupture, but itself decreases to a low concentration level as the reactions proceed. Glyoxylic acid is the main oxidation product isolated after 30 minutes of treatment with ozone, together with smaller amounts of oxalic acid.



Throop (1977) showed that ozone dosages of 5.32 mg/l produced non-detectable quantities of phenol, starting with concentrations of 110 ppb of phenol in water. This dosage is equivalent to 48 parts of ozone/part of phenol. However, ozone dosages of 25.5 mg/l (200 parts ozone/part phenol) were required to produce a measureable (trace) amount of residual ozone in the solution. This confirms that although ozone rapidly destroys phenol itself, significant amounts of ozone-demanding oxidation products are formed.

Reactions With Other Phenols

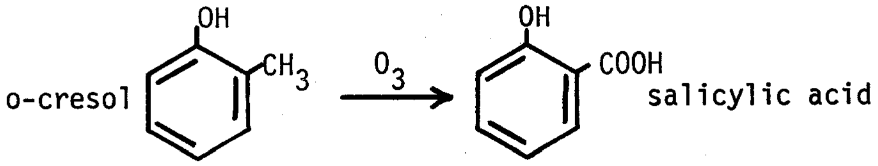
Hillis (1977) studied the oxidation of 14 phenols with ozone over the pH range 4 to 10, but did not identify oxidation products. With 30 mg/l concentrations of phenols and ozonation conducted 4 to 12 minutes [except for pentachlorophenol (PCP), which required 35 minutes], residual concentrations of phenols of less than 0.10 mg/l were obtained. However, COD values were reduced only about 50%, indicating that organic carbon-containing oxidation products were still present.

With solutions of phenol, phenolsulfonic acid, hydroquinone and pyrogallol, COD was destroyed steadily upon ozonation. However, with pentachlorophenol and β-naphthol, there was a steady rise in COD values during the first few minutes of ozonation, followed by a steady reduction in COD values.

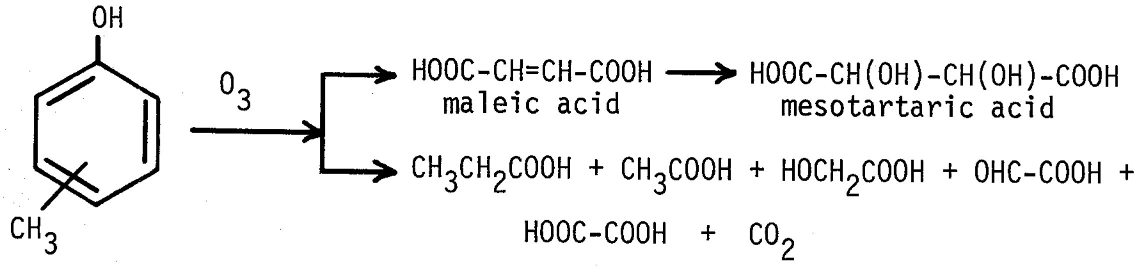
The amount of ozone required to lower the concentration of these phenols from 30 mg/l to below 0.5 mg/l in 10 minutes (except for PCP) was 2.0 to 3.0 g/g phenol (4 to 6 moles ozone/mole phenol).

Bauch, Burchard & Arsovic (1970) compared the rates of ozonation of phenol with cresols and xylenols, and also isolated and identified ring ruptured oxidation products. Cresols decomposed more rapidly than phenol, and m-cresol decomposed faster than did the o- and p-isomers. Cresols reacted faster with ozone in acid solution than in basic solution. An 80% decomposition of cresols was accomplished with 2 moles of ozone/mole of cresol (85 g ozone/100 g cresol).

Upon initial ozonation, the methyl group in cresols oxidized to the carboxylic acid. The compound o-cresol, for example, produced salicylic acid:

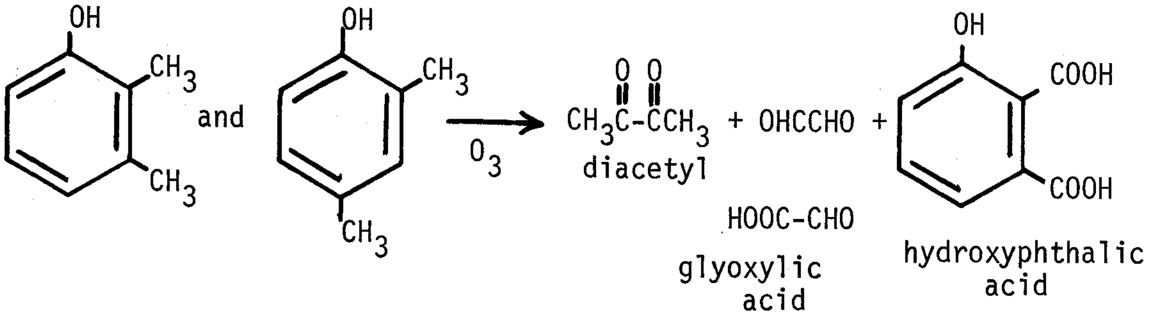


Continued ozonation of cresols ruptured the aromatic ring and produced maleic acid (which further oxidized to mesotartaric acid), acetic acid, propionic acid, glycolic acid, glyoxylic acid, oxalic acid and CO_2:

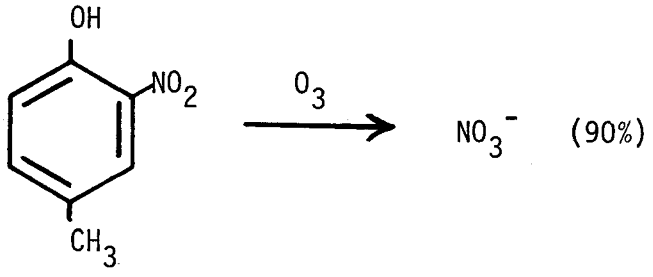


All 3 cresols (o-, m- and p-) formed the same oxidation products upon ozonation. Only the rates of oxidation varied.

Xylenols with ortho or para hydroxy groups reacted fastest with ozone and produced the same oxidation products as the cresols (Bauch, Burchard & Arsovic, 1970). In addition, 1,2,3- and 1,2,4-xylenols produced diacetyl, glyoxal (which disproportionates to glyoxylic acid), hydroxyphthalic acid and ketoaldehydes:



Gilbert (1978) ozonized 1 mmole/l of 2-nitro-p-cresol with 10 mg of ozone/minute until the cresol was destroyed. He found that 90% of the original nitrogen was converted to nitrate ion, indicating rupture of the aromatic ring.



Reactions With Chlorinated Phenols

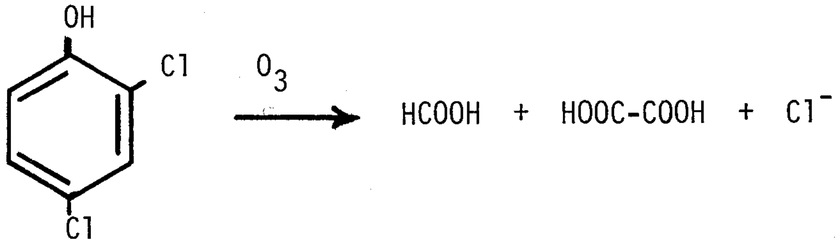
Shuval & Peleg (1975) compared the ozonation of phenol with o-chlorophenol. At the same initial pH, the rates of oxidation with ozone are the same for both compounds, but the rate is fastest at higher pH. Starting at pH 10 the reactions are faster when the pH is maintained at 10, rather than letting it drop (to 2.5) as ozonation proceeds.

In addition, the rate of formation of chloride ion was followed during ozonation of chlorophenol. In all experiments, about 80% of the aromatic chlorine was converted to chloride ion upon ozonation, indicating that covalent C-Cl bonds are broken with ozone. There was an induction period during which the concentration of o-chlorophenol decreased but without formation of chloride ion. On the other hand, after all o-chlorophenol had disappeared, chloride ion still was being produced upon continued ozonation. This indicates that the active oxidation species attacks the aromatic ring at a site or sites other than the chlorine site, producing chlorinated aliphatic compounds as intermediates.

Gilbert (1978) ozonized aqueous solutions of 2-chloro-, 4-chloro-, 2,3-dichloro-, 3,5-dichloro- and 2,4,6-trichlorophenols until the phenols could not be detected by gas chromatography and no phenolic functionality could be detected by 4-aminoantipyrine. This required 3.2 to 5 mmoles of ozone/mmole of phenol. The rate of oxidation increased from mono- to trichlorophenol.

After ozonation, 60% to 95% of the chlorine was found as chloride ion. Ozonation of 4-chlorophenol produced chloride ion at the start of ozonation; chloride ion was found only after 40% of the 2-chlorophenol had been degraded. The different rates of dechlorination are explained in terms of different electron density distributions on the aromatic rings.

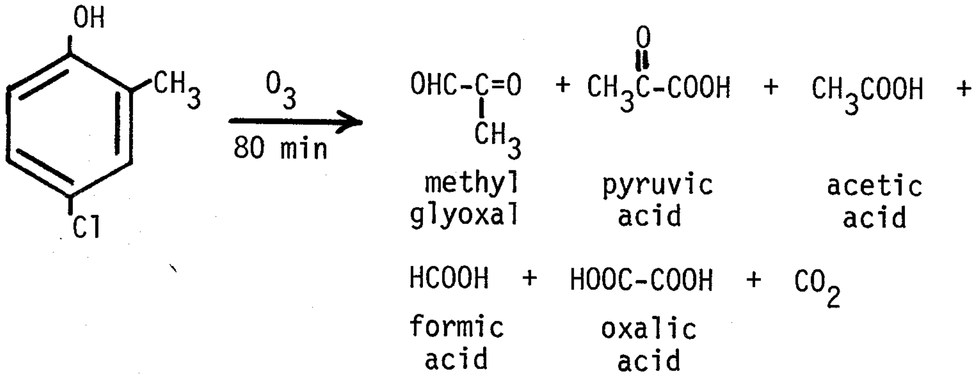
Ozonation of 2,4-dichlorophenol produced formic and oxalic acids and chloride ion:



Biodegradabilities of the ozonized products were higher with increasing degree of oxidation and with decreasing chlorophenol concentration. After total oxidation of the phenols, the COD level had been reduced from 200 to 100 mg/l and the TOC level had been reduced from 72 to 59 mg/l.

After chlorophenols had disappeared, thin layer chromatography techniques indicated the presence of carbonyl or carbonyl/carboxylic acid functionalities. In instances of incomplete dechlorination, chlorinated aliphatic moieties were isolated but not identified.

Gilbert (1978) ozonized 4-chloro-o-cresol and identified 67% of its oxidation products. After 80 minutes of treatment with ozone (800 mg of ozone total dosage added to 1 mmole of chlorocresol) none of the starting cresol was present and 100% of the chlorine was found as chloride ion. In the ozonate, methylglyoxal, pyruvic acid, acetic acid, formic acid and oxalic acid were isolated and identified, along with CO_2. The course of reaction is as follows:



Methylglyoxal was produced from the beginning of the reaction, its concentration reaching a maximum after 60 minutes of reaction, then slowly decreasing. This means that its rate of formation from the cresol is faster than its rate of oxidation.

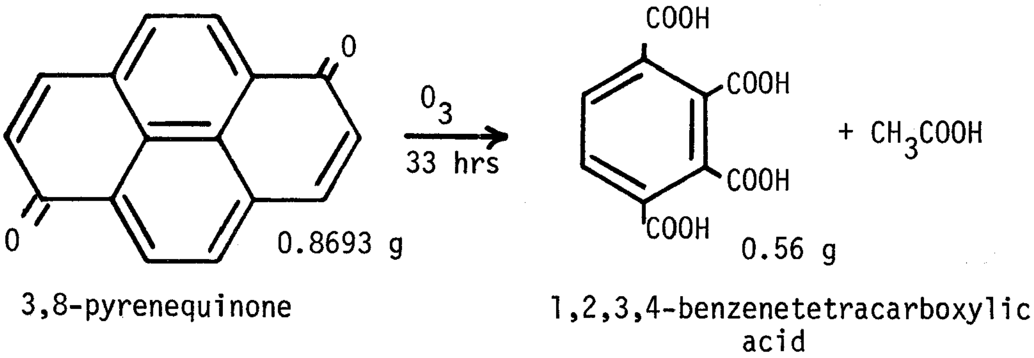
Pyruvic acid and acetic acid concentrations increased steadily during ozonation, even after complete elimination of the cresol, indicating that these two acids are produced from the initial oxidation products of the cresol.

All TOC was accounted for by these organic compounds at various times during ozonation. Therefore, the above compounds, plus CO_2, water and chloride ion are the only oxidation products of this cresol.

Figure 26 summarizes the reactions of phenols with ozone.

Reactions With Other Aromatics

Ahmed & Kinney (1950) ozonized 0.8693 g of 3,8-pyrenequinone for 33 hrs in water and isolated 0.56 g of 1,2,3,4-benzenetetracarboxylic acid plus acetic acid:



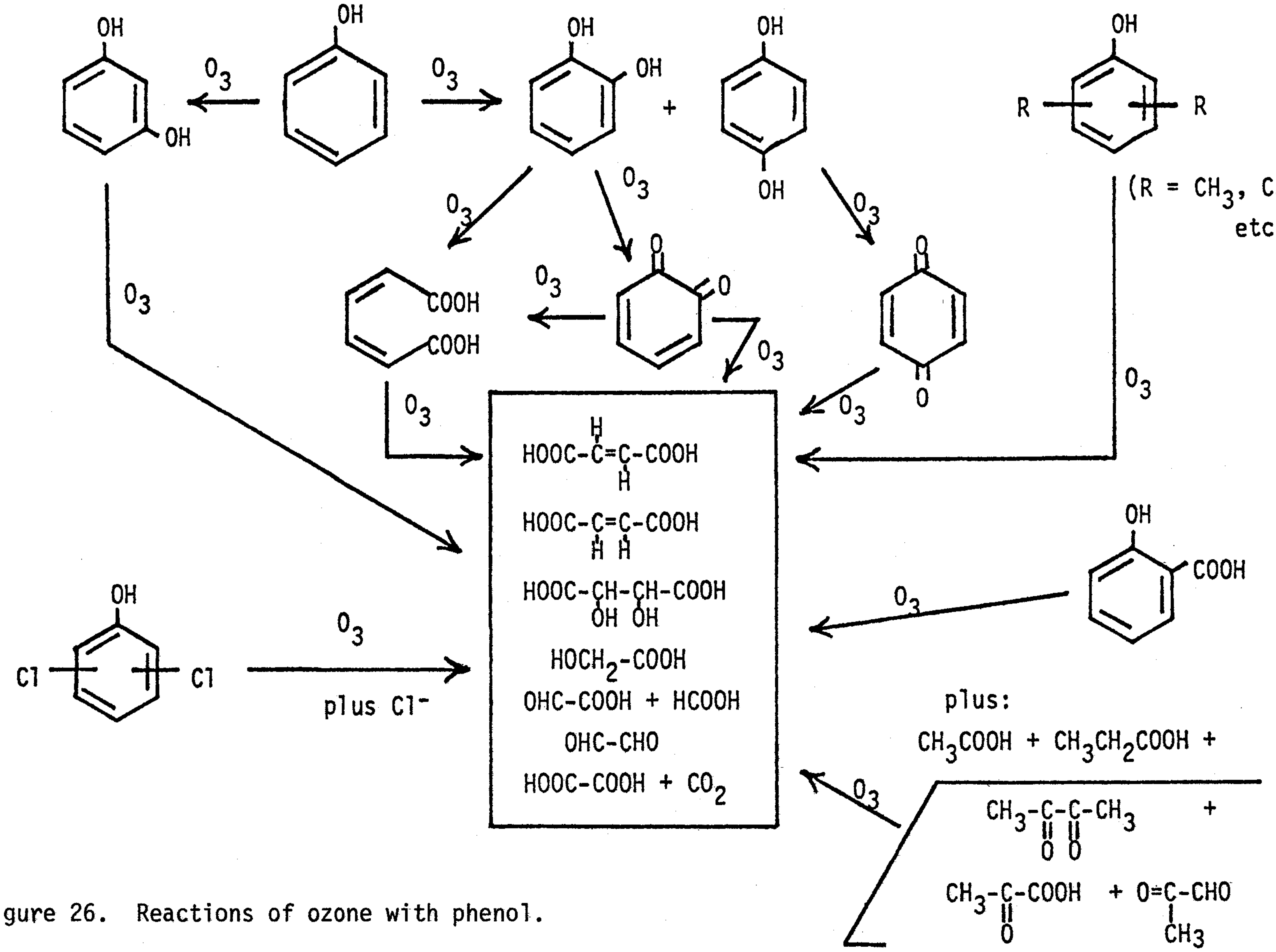
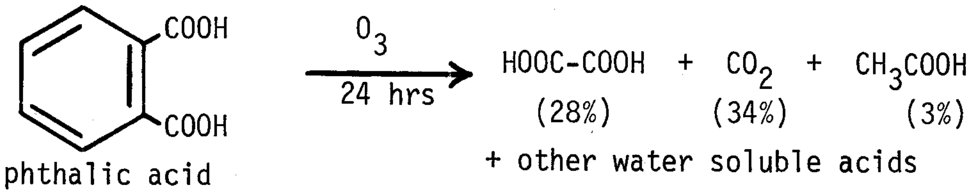
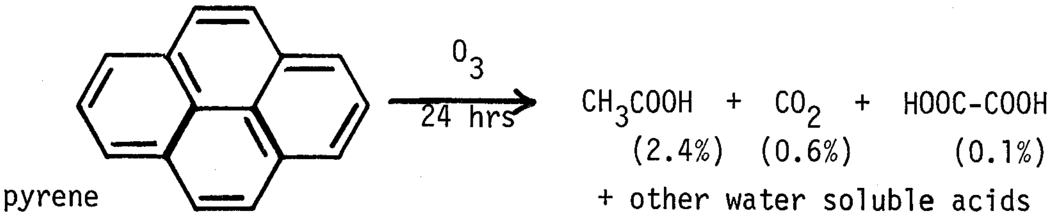


Figure 26. Reactions of ozone with phenol.

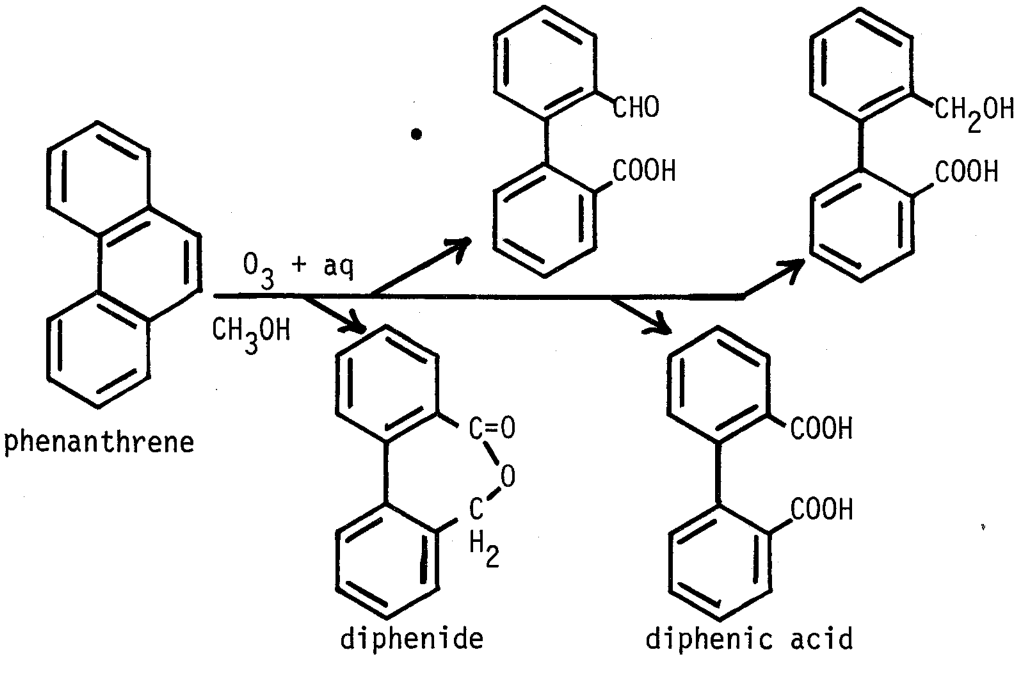
Kinney & Friedman (1952) ozonized an alkaline solution of phthalic acid for 24 hrs and isolated 28% of the carbon as oxalic acid, 34% as CO_2, 3% as acetic acid and 35% as other water soluble acids:



Kinney & Friedman (1952) also ozonized a solution of pyrene for 24 hrs and isolated 2.4% of the carbon as acetic acid, 0.6% as CO_2, 0.1% as oxalic acid and 19.9% as water soluble acids.



Sturrock et al. (1963) ozonized phenanthrene in a 1/1 water/methanol solution (methanol is resistant to ozonation). Water was used to avoid the formation of explosive ozonides or peroxides, which are formed under neat or non-aqueous solvent conditions. After ozonation of 15 g of phenanthrene, 1.3 g of unreacted phenanthrene was recovered, along with 16.4 g of oxidation products. These were identified as 2'-formylbiphenylcarboxylic acid, 2'-hydroxymethyl-2-biphenylcarboxylic acid, diphenide and diphenic acid.



It is of significance that only 1 ring in phenanthrene was opened by treatment with ozone. This indicates that the material is fundamentally resistant to ozone.

Il'nitskii et al. (1968) found that 3,4-benzopyrene in distilled water was destroyed much more rapidly than when the pyrene was added to raw drinking water containing added soil particles. In 1 minute, ozone destroyed 61% of the pyrene in distilled water, but only 33% in naturally occurring raw water. In 2.5 minutes of ozonation, 100% of the pyrene was destroyed in distilled water, but only 60% was destroyed in this time (same concentration) in raw water containing added soil particles.

These investigators concluded that 3,4-benzopyrene is adsorbed onto fine soil particles and thus is "protected" from oxidation. In designing the ozonation treatment for waters containing 3,4-benzopyrene, an effective filtration step should precede ozonation. Protection of organic compounds from oxidation by naturally occurring colloidal materials also was noted by Mallevialle et al. (1978) in studies with aldrin (see-- "Reactions With Pesticides").

Il'nitskii (1969) ozonized 0.6 to 1.2 mg/l concentrations of 3,4-benzopyrene in water maintaining a 0.4 mg/l residual of ozone. In 7.5 minutes the pyrene had been oxidized to below the detectable limit.

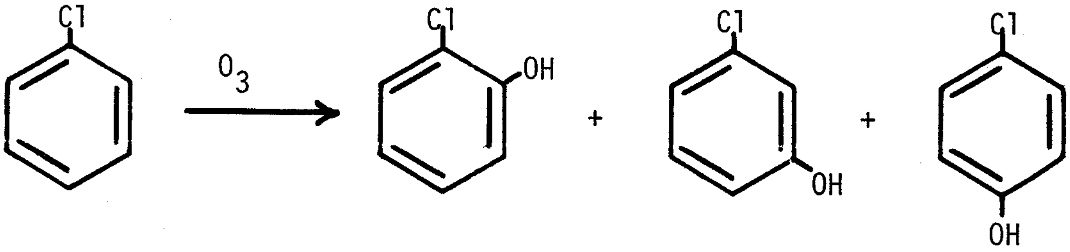
Gabovich et al. (1969) compared the oxidation rate of 3,4-benzopyrene when treated with chlorine and with ozone. Chlorine reduced the concentration of the pyrene 5 to 10 times in 0.5 to 2 hrs. Ozonation for 3 to 5 minutes reduced the concentration 10 to 50 times.

The compound 3,4-benzopyrene (4 μg/l) treated 3 minutes with 2.5 mg/l of ozone was reduced in concentration to 0.06 μg/l; treating the same concentration 3 minutes with 4.5 mg/l of ozone dosages lowered the pyrene concentration to 0.04 μg/l (Coin et al., 1964, 1967).

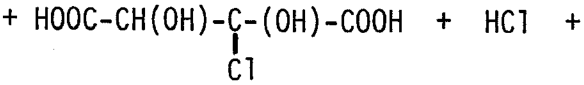
Reichert (1969) dissolved 3,4-benzopyrene in 1 ml of acetone, then diluted this to 1,000 ml with water. Samples containing 1 to 100 μg/l of pyrene were ozonized with 0.5 to 1.5 mg/l doses. In 30 minutes of ozonation, 99% decomposition of the pyrene was observed.

Gabovich et al. (1969) also studied the rates at which ozone would reduce the concentrations of other aromatic compounds in water. Diethylbenzene in concentrations of 10 to 100 mg/l upon treatment for 7 to 10 minutes with quantities of ozone similar to those used in drinking water treatment (1 to 5 mg/l) was reduced in concentration to 0.5 to 0.8 mg/l. The compound 2,4-dinitrophenol at 50 mg/l was reduced in concentration to 0.35 mg/l using 2 mg of ozone/mg of phenol; using 5 mg of ozone/mg phenol, the final concentration of 2,4-dinitrophenol was lowered to 0.05 mg/l.

Chlorobenzene reacts with ozone slower than does phenol, probably because of its lower solubility in water, but gives the same oxidation products as does phenol. In addition, HCl, chlorotartaric acid and o-, m- and p-chlorophenols are formed (Bauch, Burchard & Arsovic, 1970):



(o- m- and p-chlorophenols)



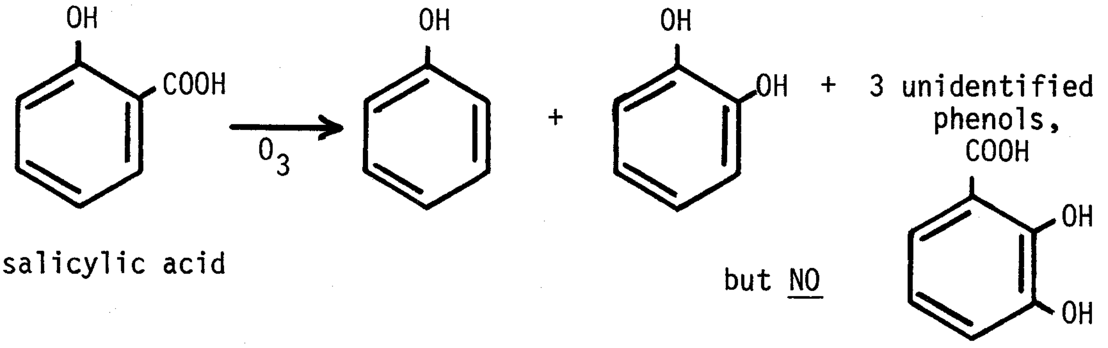
$$+\ HOOC\text{-}CH(OH)\text{-}\underset{\displaystyle Cl}{\underset{|}{C}}\text{-}(OH)\text{-}COOH\ +\ HCl\ +$$

the same ring-ruptured, aliphatic
oxidation products as from the
ozonation of phenol

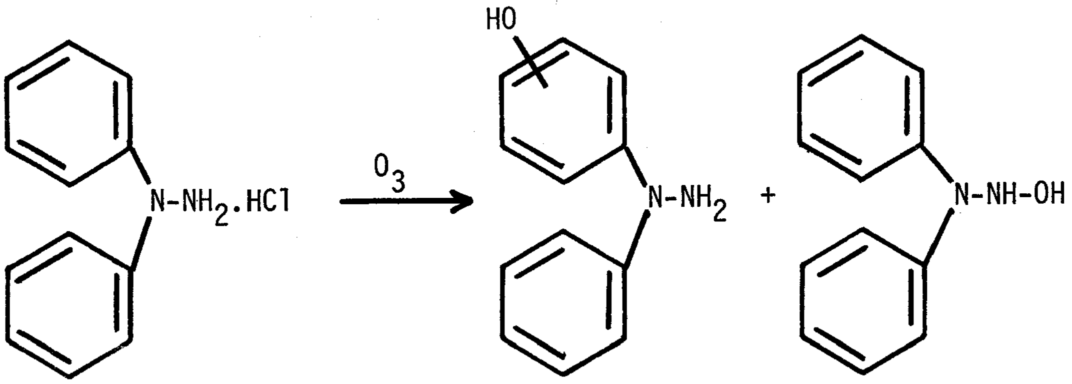
Chlorocresols, chlorophenols, naphthols, thiophenols and polyhydroxyphenols give similar oxidation products as do phenols upon ozonation (Bauch, Burchard & Arsovic).

Hoigné (1975) showed that ozonation of benzoic acid caused 10% decarboxylation to produce CO_2.

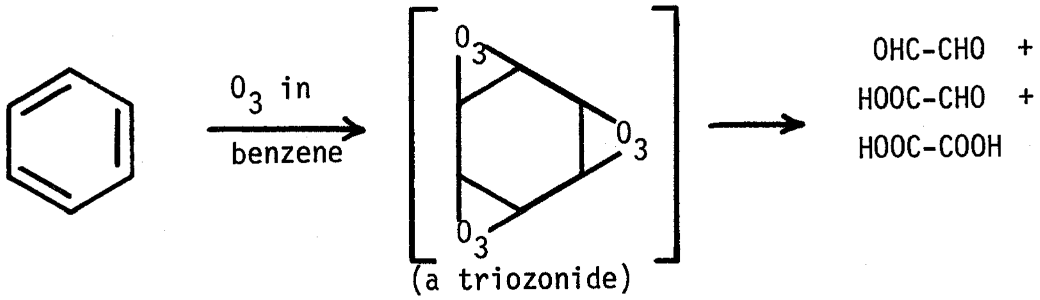
Mallevialle (1975) ozonized 100 to 200 mg/l aqueous solutions of salicylic acid. The TOC remained constant during the first 10 minutes of ozonation (25 mg/l total dosages), but then dropped steadily. Phenol, catechol and three unidentified phenols were isolated from the ozonate. 2,3-Dihydroxybenzoic acid was shown to be absent. Three moles of ozone/mole of salicylic acid were required to destroy all of the starting acid. Infrared analysis showed the products to have strong -OH and -COOH absorptions, indicating that a mixture of carboxylic acids was formed.



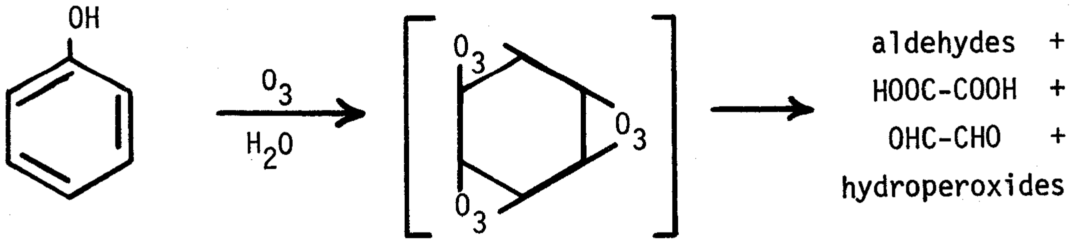
Spanggord & McClurg (1978) ozonized aqueous solutions of N,N-diphenylhydrazine hydrochloride at pH 7 and identified ring- and N-hydroxylated derivatives, plus free uns-diphenylhydrazine:



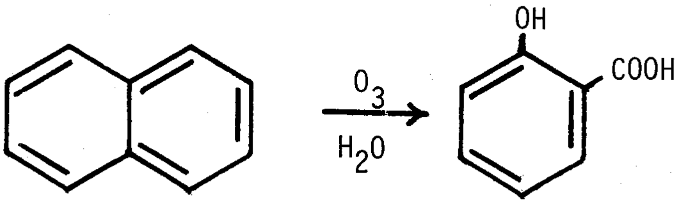
Jürs (1966) reviewed the current literature of the time and concluded that ozonation of benzene (in benzene) produced a triozonide which, when treated with water, rapidly decomposed to form glyoxal, glyoxylic acid and oxalic acid:



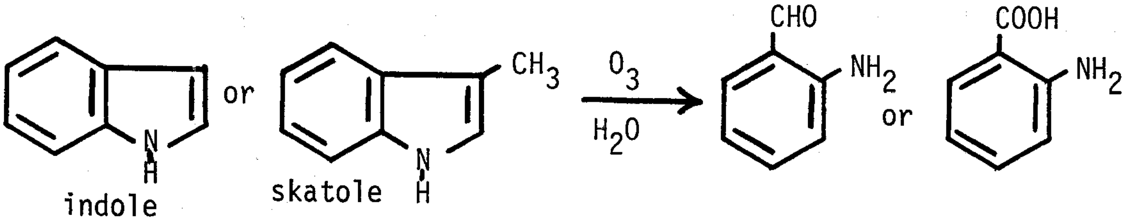
Jürs also concluded that ozonation of phenol, even in water, proceeds through a triozonide, which is transient, decomposing into aldehydes, oxalic acid, glyoxal and hydroperoxides:



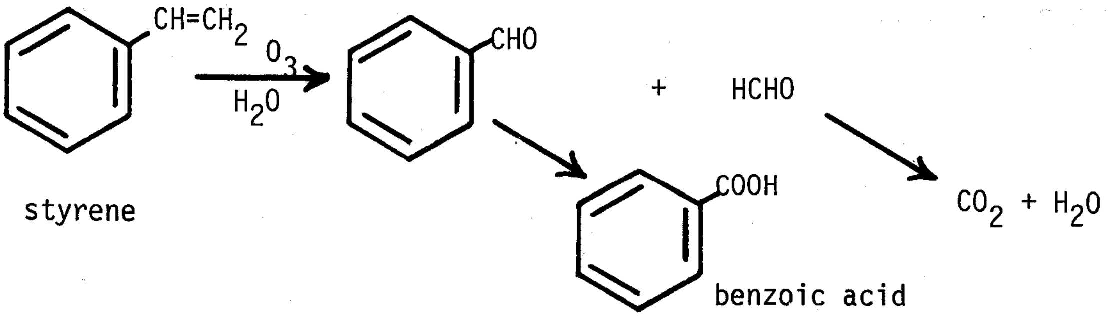
Ozonation of naphthalene in water produced salicylic acid (Jürs, 1966):



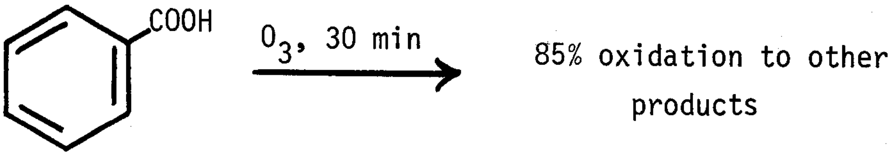
Ozonation of indole and skatole proceeds through ozonides which, when treated with water, form o-aminobenzaldehyde and/or o-aminobenzoic acid (Jürs, 1966):



Yocum (1978) studied the ozonation of styrene under aqueous conditions, but only to the benzoic acid stage of oxidation. He found that initial cleavage of the exocyclic double bond occurred rapidly, producing benzaldehyde and formaldehyde. Further oxidation of formaldehyde to CO_2 and water occurred rapidly, as did the oxidation of benzaldehyde to benzoic acid. This last step (benzaldehyde to benzoic acid) required 1.47 moles of ozone/-mole of aldehyde.

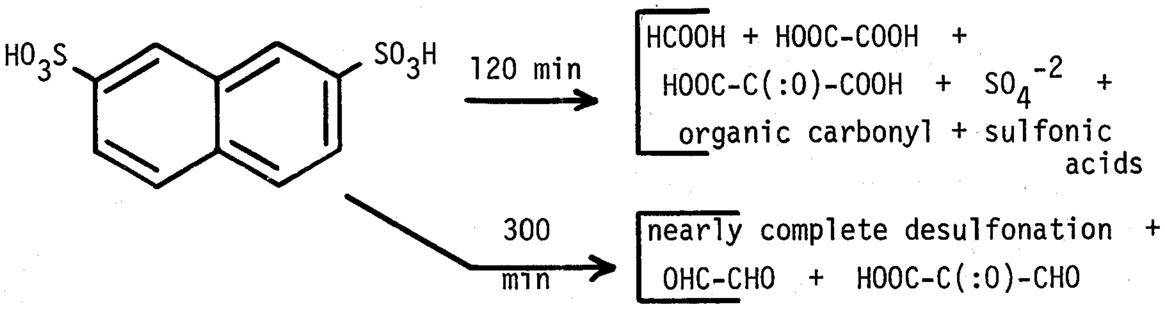


Further ozonation of benzoic acid solutions caused attack at the o-, m- and p- positions on the aromatic ring. After 30 minutes of ozonation of a 300 mg/l solution of acid with 4 moles of ozone/mole of benzoic acid, the benzoic acid was 85% oxidized to other products.

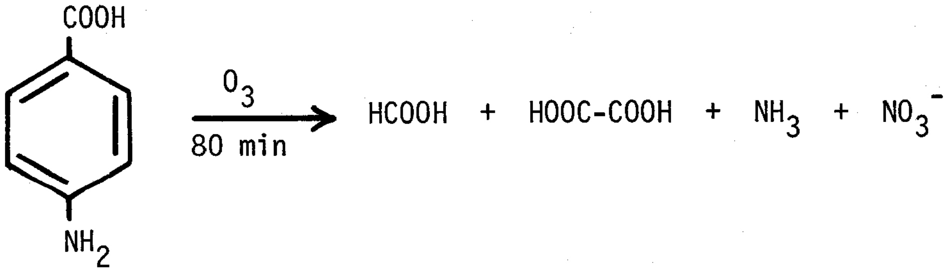


Finally, Yocum (1978) determined that the biodegradability of ozonized styrene is much higher than that of styrene itself. The starting BOD-5/TOC ratio was 0.47, but after 150 minutes of ozonation it had increased to 2.69. This shows that ozonation in aqueous solution can convert relatively non-biodegradable compounds into compounds which are biodegradable.

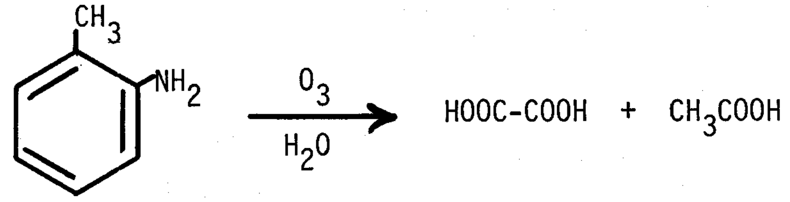
Ozonation of naphthalene-2,7-disulfonic acid (Gilbert, 1978) for 120 minutes produced formic, oxalic and mesoxalic acids, (accounting for 25% of the TOC) sulfate ion, plus organic carbonyl compounds and organic sulfonic acids. After 300 minutes of ozonation, nearly complete desulfonation was achieved (nearly quantitative yield of sulfate ion). Glyoxal and mesoxalic acid semialdehyde also were identified. The BOD-5/COD ratio increased from 0 to 0.8, indicating that the oxidation products are biodegradable.



Ozonation of 4-aminobenzoic acid (Gilbert, 1978) gave formic and oxalic acids, ammonia and nitrate. After 80 minutes of ozonation, only 70% of the organically-bound nitrogen was measured as ammonia and nitrate. This indicates that organic compounds containing nitro or amino groups still were present. The BOD-5/COD ratio increased from 0 to 0.4.

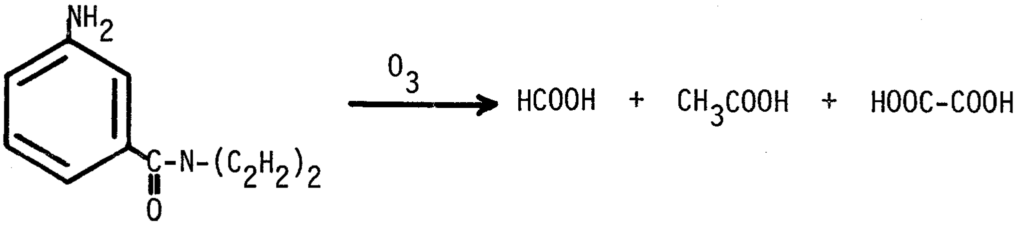


Chian & Kuo (1976) ozonized aqueous solutions of o-toluidine and found acetic and oxalic acids:



o-toluidine

Ozonation of aqueous solutions of N,N-diethyl-m-toluamide produced formic, acetic and oxalic acids (Chian & Kuo, 1976):



Gilbert (1977) found that 3 to 8 kg of ozone are required to remove 1 kg of aromatic sulfonic acids from aqueous solutions. Ozonation of p-toluene sulfonic acid in water formed organic peroxides, the concentrations of which decreased to 0 mg/l in 120 minutes, plus H_2O_2.

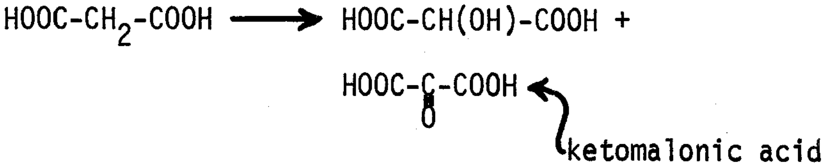
Sato, Yokoyama & Imamura (1974) ozonized aqueous solutions of azobenzene. During the early stages of ozonation, they identified nitrosoazobenzene and nitroazobenzene as initial oxidation products. However, with further ozonation, these products were converted into oxalic acid, glyoxylic acid and nitrate ion. This indicates that nitroso compounds can be formed in aqueous solution from azobenzenes, but that if sufficient oxidant is used, the intermediate nitroso compounds can be converted into innocuous organic materials.

Many papers by Prengle and his co-workers (1976, 1977, 1978) describe the combination of ozone with UV radiation. The combination oxidizes organic compounds at a faster rate than does ozone alone. Prengle et al. (1977) followed the UV/ozonation of pentachlorophenol (PCP) by gas chromatography. After 1 hr of treating a 7 mg/l aqueous solution at pH 9.6 with ozone/UV, the PCP concentration had dropped and the amount of chlorine found in solution as chloride ion was more than 50% of that available. In addition, the TOC value had dropped. This indicates that the aromatic ring had been ruptured, forming CO_2, in addition to chloride ion.

Similarly, a 100 mg/l solution of o-dichlorobenzene treated 30 minutes by UV/ozonation showed 100% destruction of the aromatic compound, but only 50% of the available chlorine was recovered as chloride ion.

Reactions With Aliphatic Compounds

Dobinson (1959) ozonized aqueous solutions of malonic acid and identified hydroxymalonic acid and ketomalonic acid as products:



$$HOOC-CH_2-COOH \longrightarrow HOOC-CH(OH)-COOH + HOOC-\underset{\displaystyle O}{\underset{\|}{C}}-COOH$$

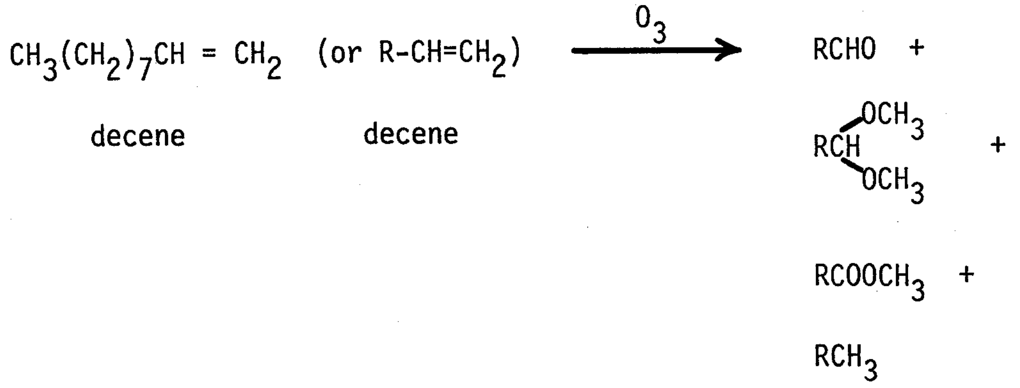
Jürs (1966) in reviewing the literature, concluded that in non-aqueous, non-polar solvents (carbon tetrachloride, hexane, etc.) ozonation of aliphatic double bonds proceeds through polymeric ozonides. In non-aqueous polar solvents (such as acetic acid), monomeric ozonides are favored.

In water, however, Jürs concluded that ozonides hydrolyze to peroxydiesters, which further hydrolyze to dialcohols and aldehydes. Peroxyacids decompose in water to aldehydes or acids and H_2O_2. Acids and aldehydes can recombine to form dialcohols.

Pryde et al. (1968) studied the ozonolysis of aliphatic unsaturated materials in water. Methyl oleate (5 g in 25 g of distilled water) ozonized 20 to 30 minutes with 2 to 3% ozone in oxygen produced an 82% yield of compounds containing new carbonyl groups.

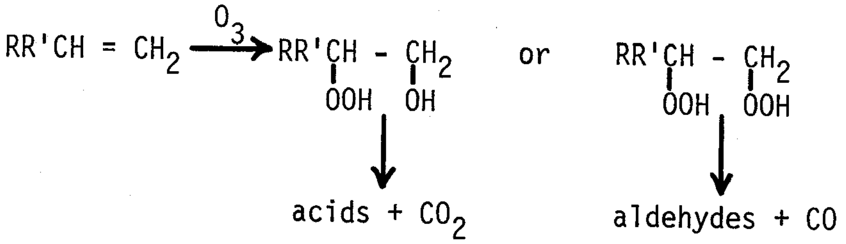
$$\underset{\text{methyl oleate}}{CH_3(CH_2)_7\text{-}CH = CH\text{-}(CH_2)_7COOCH_3} \xrightarrow{O_3} \text{compounds containing } {>}C = O \text{ groups}$$

When 1-decene (0.2 to 0.5 g) was ozonized for 16 hrs in water an aldehyde, a dimethyl acetal, a methyl ester and a hydrocarbon were produced. All of these resulted from cleavage of the double bond:



$$\underset{\text{decene}}{CH_3(CH_2)_7CH = CH_2} \quad \underset{\text{decene}}{(\text{or } R\text{-}CH{=}CH_2)} \xrightarrow{O_3} RCHO + RCH(OCH_3)_2 + RCOOCH_3 + RCH_3$$

Pryde et al. (1968) concluded that ozonolysis of dispersions of slightly soluble (in water) organics in water proceeds through hydroperoxides and/or dihydroxyperoxides, both of which rearrange readily in water to produce acids, hydrocarbons and CO_2 or aldehydes and CO.



$$RR'CH = CH_2 \xrightarrow{O_3} \underset{OOH}{RR'CH} - \underset{OH}{CH_2} \longrightarrow \text{acids} + CO_2 \quad \text{or} \quad \underset{OOH}{RR'CH} - \underset{OOH}{CH_2} \longrightarrow \text{aldehydes} + CO$$

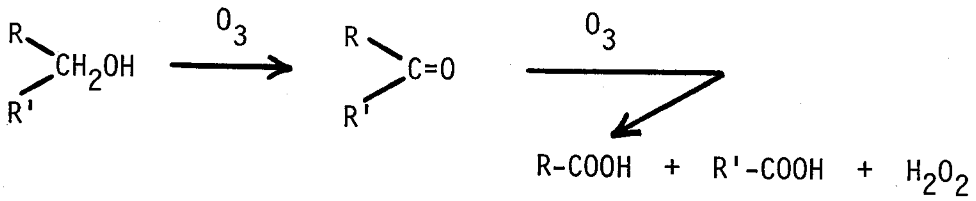
Dorfmann (1973) ozonized cysteine in water and isolated cystine as an initial oxidation product. Cystine then formed unidentified degradation products upon continued ozonation:

$$\underset{\text{cysteine}}{HSCH_2CH(NH_2)COOH} \longrightarrow \underset{\text{cystine}}{-[SCH_2CH(NH_2)COOH]_2} \longrightarrow \text{degradation products}$$

Kraznov et al. (1974) ozonized aqueous solutions of aliphatic alcohols and aldehydes. Ethanol, butanol and octanol in dilute aqueous solution with 33 mg/l ozone dosages produced aldehydes, then acids, but did not produce any CO_2. The rate of oxidation increased with increasing pH:

$$\left.\begin{array}{l} CH_3CH_2OH \\ CH_3CH_2CH_2CH_2OH \\ CH_3(CH_2)_6CH_2OH \end{array}\right] \xrightarrow[33\ mg/l]{O_3} \text{aldehydes} \text{ —— } \text{acids (no } CO_2)$$

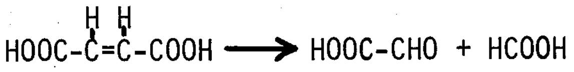
Secondary alcohols readily produced ketones upon ozonation, which oxidized further to organic acids and H_2O (Kraznov et al., 1974). Ketonic intermediates were lower boiling than the alcohols, and were more readily stripped into the gas phase:



Aldehydes formed peroxy acids, which produced organic acids + H_2O_2 on continued ozonation in dilute aqueous media (Kraznov et al., 1974).

$$RCH = O \xrightarrow{O_3} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}H \xrightarrow[H_2O]{O_3} R\text{-}COOH + H_2O_2$$

Gilbert (1977) ozonized 1 liter solutions (0.001 mole/l) of maleic acid at an initial pH of 5. After 50 minutes of ozonation, during which time 195 mg of ozone (39%) was utilized, oxidation of maleic acid was complete. Degradation of maleic acid was rapid, and glyoxylic and formic acids were formed simultaneously as maleic acid disappeared. After complete disappearance of maleic acid, formic acid was ozonized to CO_2 and water, and glyoxylic acid was ozonized to oxalic acid:



$$HOOC\text{-}\overset{H}{C}{=}\overset{H}{C}\text{-}COOH \longrightarrow HOOC\text{-}CHO + HCOOH$$

$$HCOOH \longrightarrow CO_2 + H_2O$$

$$HOOC\text{-}CHO \longrightarrow HOOC\text{-}COOH$$

The total amounts of maleic, glyoxylic, oxalic and formic acids and CO_2 determined on each sample analyzed was equal to the amounts calculated on the basis of this mechanism. Therefore, these specific materials are the only oxidation products of maleic acid. Gilbert also concluded that under his experimental conditions, little oxidation of oxalic acid occurs upon ozonation.

Prengle et al. (1977) studied the UV/ozonation of 1,4-dichlorobutane and of chloroform in water. With ozone alone, 1,4-dichlorobutane was 50% destroyed in 1 hr of ozonation, whereas UV/ozonation destroyed 100% of the material in 1 hr. The stoichiometric amount of chloride ion was found after 1 hr of UV/ozonation.

UV/ozonation for 2 hrs resulted in 80% destruction of chloroform. However, only 25% of the theoretical amount of chloride was recovered, therefore, much of the "destroyed" chloroform must have been stripped out of solution. The rate of decrease of TOC was almost as rapid as the rate of decrease of chloroform concentration, therefore there are few non-volatile, carbon-containing organic oxidation products of chloroform.

Chian & Kuo (1976) studied the oxidation of several refractory aliphatic compounds in aqueous solution with ozone and ozone/UV combinations, and with the pH contolled by addition of HCl or NaOH solutions as needed during the reactions. After 1-propanol (408 mg/l) was ozonized for 1 hr at pH 9 (1,980 mg total ozone dose), a solution having 0 mg/l ozone concentration was produced. Propionaldehyde (85 mg/l) was formed and carbon balance analyses showed that this compound and 1-propanol (145 mg/l remaining) were the only two organic materials present. TOC was reduced from 225 to 210 mg/l, indicating that some CO_2 had been formed.

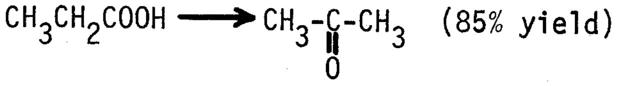
$$CH_3CH_2CH_2OH \longrightarrow CH_3CH_2CHO + CO_2$$

UV/ozonation of 1-propanol (410 mg/l) under the same conditions produced 95 mg/l of propionaldehyde; 120 mg/l of propanol remained, and TOC was reduced to 205 mg/l.

In both cases of ozonation of 1-propanol, TOC levels did not begin to fall significantly until after aldehyde production had peaked (45 minutes with ozone alone, 40 minutes with UV/ozone).

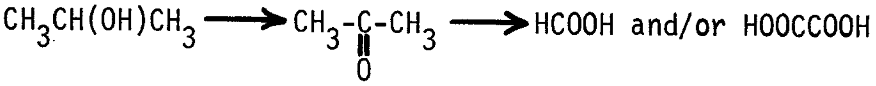
Propionic acid (490 mg/l) was ozonized at pH 9 for 2 hours (2,960 mg total ozone dose). Again, dissolved ozone concentration was 0 mg/l, indicating that the ozone demand had not been satisfied. Unreacted acid concentration was 235 mg/l and TOC had dropped from 235 to 200 mg/l. Oxidation products were not identified.

For the balance of this work of Chian & Kuo (1976) lower concentrations of organic compounds were chosen so that ozone residual concentrations of 4 mg/l or higher were present. Ozonation of propionic acid at pH 7 resulted in 17% TOC reduction and formation of acetone. No monocarboxylic acids were detected and acetone accounted for over 85% of the TOC of the reaction mixture:



$$CH_3CH_2COOH \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \quad \text{(85\% yield)}$$

UV/ozonation of 2-propanol substantially increased the rate of TOC removal. An initial TOC of 110 mg/l was reduced to 20 mg/l (85%) after 135 minutes of UV/ozonation. The compound 2-propanol disappeared after 30 minutes and the concentration of acetone formed reached its maximum value at this time. On continued UV/ozonation, the acetone level decreased to 0 mg/l after 75 minutes. The C_2 to C_6 monocarboxylic acids were not detected in the ozonate, but NaOH addition was required throughout the reaction in order to maintain a constant pH. This indicates that formic and/or oxalic acids were produced from the ozonation of acetone.



$$CH_3CH(OH)CH_3 \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow HCOOH \text{ and/or } HOOCCOOH$$

Ozonation of methyl ethyl ketone (MEK) for 2 hrs at pH 7 produced a small amount of acetate ion. MEK accounted for over 85% of the ozonate TOC. Much of the loss of MEK was attributed to air stripping (40% TOC removed after 2 hrs). By contrast, after 2 hrs of UV/ozonation, MEK was completely eliminated. Acetate ion reached its maximum concentration after 35 minutes, then decreased to 0 mg/l at 105 minutes. Trace amounts of acetone and ethanol were detected.

$$CH_3CH_2C(:O)CH_3 \longrightarrow CH_3COO^-$$

Ozonation of acetic acid for 2 hrs at pH 7 (adjusted at the beginning, but allowed to rise during treatment) resulted in 14% removal of TOC. Glyoxylate anion concentration increased with time, but was always low:

$$CH_3COOH \xrightarrow[UV]{O_3} OHC\text{-}COO^-$$

UV/ozonation of acetic acid was much more rapid. After 75 minutes, no acetate was detected. Glyoxylate ion (at lower concentrations than with ozone alone) remained level in concentration during the first hr, but then decreased to 0 mg/l. No alcohols were found, nor formic acid, but oxalate ion was found in the ozonate:

$$CH_3COOH \xrightarrow[UV]{O_3} OHC\text{-}COO^- \longrightarrow {}^-OOC\text{-}COO^-$$

Ozonation of diethyl ether for 2 hrs at pH 9 produced ethyl acetate and acetate ion as the major oxidation products, but small amounts of acetaldehyde, methyl formate, ethanol, acetone and ethyl formate also were isolated. During the later stages of ozonation, TOC reduction rates became slower, when ethyl acetate and acetate ion were the major constituents. Good agreement between the calculated and experimentally determined TOC indicated that all the oxidation products were accounted for and that CO_2, therefore, is not an oxidation product:

$$CH_3CH_2OCH_2CH_3 \xrightarrow{O_3} CH_3COOC_2H_5 + CH_3COO^- \text{ (major) } +$$

$$CH_3CHO + HCOOCH_3 + CH_3CH_2OH + CH_3C(:O)CH_3 + HCOOC_2H_5$$

UV/ozonation of diethyl ether resulted in 94% removal of TOC under the same conditions, because of further oxidation of ethyl acetate and acetate ion to CO_2. Formation of acetate ion occurs by 2 routes: from the ether and from ethyl acetate. Small amounts of the same other organics as obtained with ozone alone also were isolated after UV/ozonation.

Quantitative determination of oxalate and glyoxylate showed that acetate concentration reached 0 mg/l when oxalate concentration reached its maximum. This indicates that the degradation route of acetate by UV/ozonation is through glyoxylate and oxalate to CO_2. Since the amount of oxalate formed was not equal to the amount of acetate present, it is likely that glyoxylate (the precursor of oxalate) can be oxidized directly to CO_2.

$$CH_3COO^- \longrightarrow OHC\text{-}COO^- + {}^-OOC\text{-}COO^- \longrightarrow CO_2$$

Spanggord & McClurg (1978) ozonized aqueous solutions of oleic acid and isolated 3 organic acids. During ozonation, the pH dropped to 3.8:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + O_3 \rightarrow C_8H_{17}COOH +$$

$$OHC(CH_2)_7COOH +$$

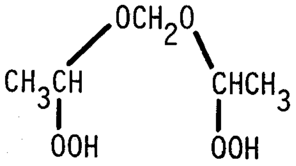
$$HOOC(CH_2)_7COOH$$

Ozonation of diethylamine produced acetaldoxime plus an unidentified nitrogen-containing compound, not a nitrosamine (Spanggord & McClurg, 1978):

$$(C_2H_5)_2NH \xrightarrow{O_3} CH_3CH{=}NOH + \text{unidentified compound}$$

Spanggord & McClurg (1978) ozonized concentrated solutions of ethanol in water (several percent) with very large doses of ozone (several thousand mg/l) for 1 to 2 hrs. Acetaldehyde and acetic acid were identified along with a dihydroperoxide, which was shown to exhibit mutagenic activity:

$$CH_3CH_2OH + O_3 \longrightarrow CH_3CHO + CH_3COOH +$$



These authors do not believe that the dihydroperoxide will form in drinking water or wastewaters containing low concentrations of ethanol and when ozonized under conditions normally employed in water and wastewater treatment (low ozone dosages, short contact times).

Gilbert (1978) ozonized 1 liter samples of 1 mmole/l aqueous solutions of aliphatic compounds with 10 mg of ozone/minute until the initial compound became undetectable. Oxalacetic acid consumed 1.8 mmole of ozone/mmole of acid, and a 60% yield of oxalic acid was isolated along with mesoxalic acid (both formed by oxidation of glyoxylic acid intermediate) and formic acid:

$$HOOCC(:O)CH_2COOH + O_3 \longrightarrow OHCCOOH + HOOC\text{-}COOH\ (60\%) +$$

$$HOOC\text{-}C(:O)\text{-}COOH + HCOOH$$

Dihydroxyfumaric acid consumed 1.4 mmoles of ozone/mmole of acid and rapidly produced oxalic acid as the major product, plus traces of dihydroxytartaric acid, mesoxalic acid and the semialdehyde of this acid:

$$HOOC\text{-}C(OH){=}C(OH)COOH + O_3 \longrightarrow HOOC\text{-}COOH\ (\text{major}) +$$

$$HOOC\text{-}C(OH)_2C(OH)_2COOH +$$

$$HOOC\text{-}C(:O)\text{-}COOH +$$

$$HOOC\text{-}C(:O)\text{-}CHO$$

Malonic acid consumed 4 mmoles of ozone/mmole acid. Oxalic acid and mesoxalic acids were the major oxidation products isolated. The concentration of tartronic acid increased from the start of ozonation, then decreased, forming mesoxalic acid and H_2O_2:

$$HOOCCH_2COOH + O_3 \longrightarrow HOOC\text{-}COOH + HOOCCH(OH)COOH \quad \text{(tartronic acid)}$$

$$\swarrow$$

$$HOOC\text{-}C(:O)\text{-}COOH + H_2O_2$$

Tartronic acid was converted totally to mesoxalic acid and in 40 minutes of ozonation had used 1 mmole of ozone/mmole acid. There was no decrease in TOC nor formation of H_2O_2 during this time:

$$HOOC\text{-}CH(OH)\text{-}COOH + O_3 \longrightarrow HOOC\text{-}C(:O)\text{-}COOH$$

Glyoxal disappeared after 50 minutes of ozonation, producing glyoxylic acid which further oxidized to oxalic acid, then disappeared after 60 minutes of total ozonation. No H_2O_2 was formed:

$$OHC\text{-}CHO + O_3 \longrightarrow HOOC\text{-}CHO \longrightarrow HOOC\text{-}COOH$$

Ozonation of the 6-carbon containing muconic acid, HOOCCH=CHCH=CHCOOH, produced 2-carbon containing fragments and only traces of 3-carbon containing compounds. The 4-carbon containing fumaric acid, HOOCCH=CHCOOH, behaved similarly upon ozonation.

Kuo, Chian & Chang (1978) treated 2-propanol and acetic acid with ozone and UV/ozone. The compound 2-propanol formed acetone, which then formed acetic acid and oxalic acid plus traces of formaldehyde and formic acid upon continued ozonation:

$$CH_3CHOHCH_3 + O_3 \longrightarrow CH_3C(:O)CH_3 \longrightarrow CH_3COOH + HOOC\text{-}COOH + HCHO + HCOOH$$

Acetic acid produced glyoxylic acid initially, which rapidly formed oxalic acid, which slowly formed CO_2 upon continued ozonation or UV/ozonation:

$$CH_3COOH + O_3 \rightarrow HOOC\text{-}CHO \longrightarrow HOOC\text{-}COOH \longrightarrow CO_2$$

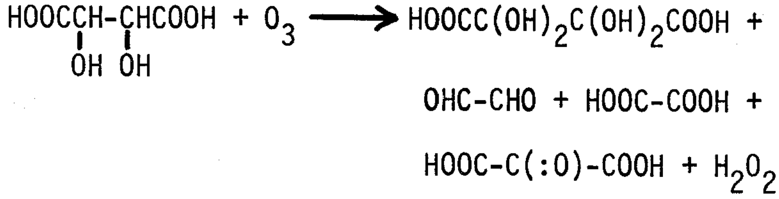
Schalekamp (1977) reported that the Lake of Zürich water contains various organic aldehydes (heptanal through tetradecanal) in concentrations of 8 to 40 nanog/l. After ozonation (1 to 1.5 mg/l dosages) these aldehydes plus hexanal were present in higher concentrations (up to 920 nanog/l). Passage of ozonized Lake Zürich water through activated carbon reduced the concentrations of these aldehydes to below the levels originally present.

Gilbert (1977) ozonized aqueous solutions of several aliphatic compounds. In pure solutions at pH 3 to 7, 1 kg of COD was removed from solution with

1.2 kg of ozone. In wastewaters, 2 to 5 kg of ozone were required to remove 1 kg of COD. Ethanol ozonized for 350 minutes produced acetaldehyde, acetic acid, formic acid, CO_2 and H_2O_2:

$$CH_3CH_2OH + O_3 \rightarrow CH_3CHO + CH_3COOH + HCOOH + CO_2 + H_2O_2$$

Tartaric acid ozonized for 80 minutes at pH 3 and pH 7 produced dihydroxytartaric acid, glyoxal, oxalic acid, mesoxalic acid and H_2O_2:

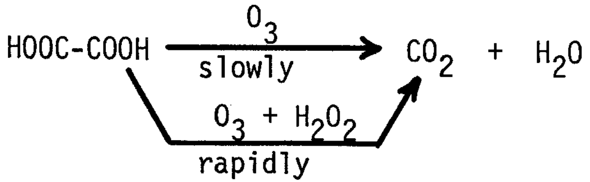


$$\underset{OH}{HOOCCH}\text{-}\underset{OH}{CHCOOH} + O_3 \longrightarrow HOOCC(OH)_2C(OH)_2COOH + OHC\text{-}CHO + HOOC\text{-}COOH + HOOC\text{-}C(:O)\text{-}COOH + H_2O_2$$

Malonic acid ozonized for 90 minutes at pH 4 produced tartronic acid, mesoxalic acid, oxalic acid and CO_2 plus H_2O_2:

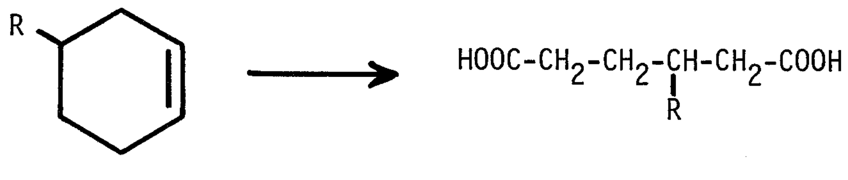
$$HOOCCH_2COOH + O_3 \rightarrow HOOC\text{-}CH(OH)\text{-}COOH + HOOC\text{-}C(:O)\text{-}COOH + HOOC\text{-}COOH + CO_2 + H_2O_2$$

Finally, Gilbert (1977) showed that the presence of H_2O_2 had a remarkable catalytic effect on the oxidative decomposition of oxalic acid. In the absence of peroxide, ozonation of oxalic acid produced CO_2 very slowly, but when small amounts of H_2O_2 were added, oxalic acid produced CO_2 rapidly.

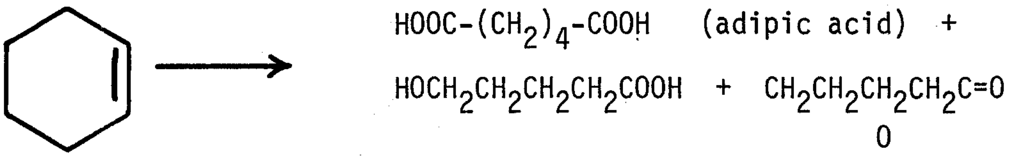


Reactions With Miscellaneous Compounds

Fremery & Fields (1963) studied the reactions of cyclic olefins with ozone in aqueous alkaline emulsions containing hydrogen peroxide. In general, α,ω-dicarboxylic acids were isolated, depending upon the specific cyclic olefin starting material:



Cyclohexene upon treatment with ozone prepared from oxygen gave a mixture of products containing peroxides and peroxypolymers. These were shown to be side products of the main reaction, for when nitrogen was substituted for oxygen as the ozone carrier gas, cyclohexene gave 20 to 28% adipic acid plus small amounts of δ-hydroxyvaleric acid and its lactone:

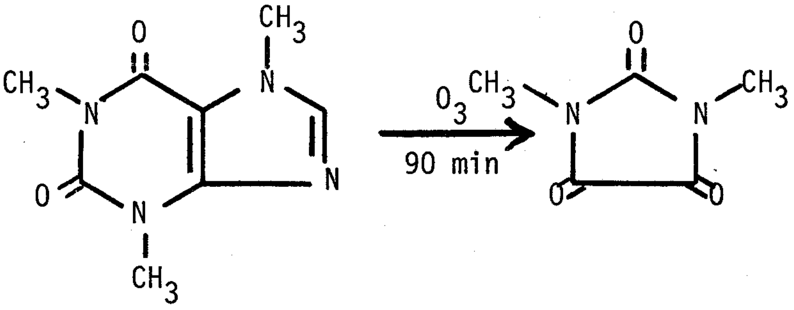


$HOOC-(CH_2)_4-COOH$ (adipic acid) +

$HOCH_2CH_2CH_2CH_2COOH$ + $\underset{O}{CH_2CH_2CH_2CH_2C{=}O}$

Weber & Waters (1972) ozonized aqueous, 0.0005M solutions of dimethyl mercury. After 10 minutes of ozonation, the concentration of alkyl mercury compound became undetectable.

Shapiro et al. (1978) ozonized aqueous solutions of caffeine (660 mg/l) with 1,630 mg of ozone over 90 minutes; 4.2 moles of ozone were consumed/mole of caffeine. Four major products were isolated (above 5% each) plus 4 minor products. One of the major products was shown to be dimethylparabanic acid by independent synthesis. Caffeine has been shown to be a constituent of sewage treatment plant effluents:



caffeine

dimethyl parabanic acid

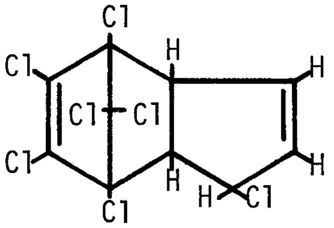
Reactions With Pesticides

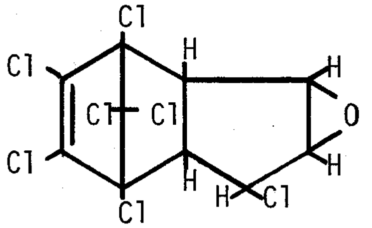
Robeck et al. (1965) ozonized aqueous solutions of lindane, dieldrin, DDT and parathion and found that dosages of 10 to 38 mg/l of ozone were required to destroy these pesticides to acceptable levels. These dosages were considered to be too high to be practical in drinking water treatment plants. These authors also concluded that the more usual drinking water treatment plant ozone dosages of 1 to 2 mg/l probably would oxidize parathion to paraoxon, a compound which is more toxic than is parathion.

Gabovich et al. (1969) ozonized aqueous solutions containing 10 mg/l of malathion. Ozone dosages of 3.5 mg/l (0.5 mg ozone/mg malathion reduced the concentration of malathion to 2 mg/l. Increasing the ozone dosage to 9.8 mg/l (1/1 ozone/malathion) reduced malathion concentration to 1 mg/l. A dosage of 26 mg/l of ozone caused 100% destruction of malathion.

Hoffman & Eichelsdörfer (1971) dissolved various pesticides in hexane or acetone, then diluted the pesticide solutions with water to make aqueous solutions as high in concentration as 2 mg/l of pesticide. These were ozonized over 45 minutes with total ozone dosages up to 240 mg/l. At these dosages, aldrin and heptachlor were "quantitatively" reacted to destruction, but oxidation products were not identified. On the other hand, solutions of dieldrin, heptachlorepoxide, chlordane, lindane, DDT and endosulfan were hardly affected by ozone at all. This raises the question as to whether the ozonation of heptachlor produces heptachlor epoxide. If so, the epoxide will be stable to further ozonation, and itself is a toxic material.

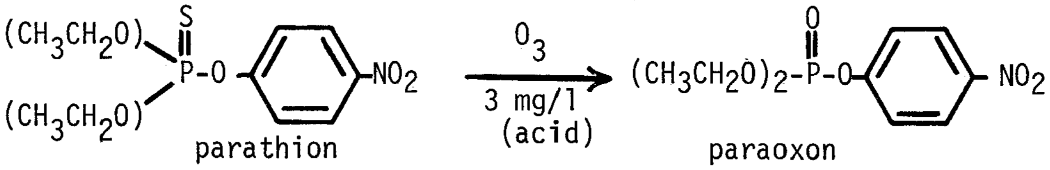
heptachlor

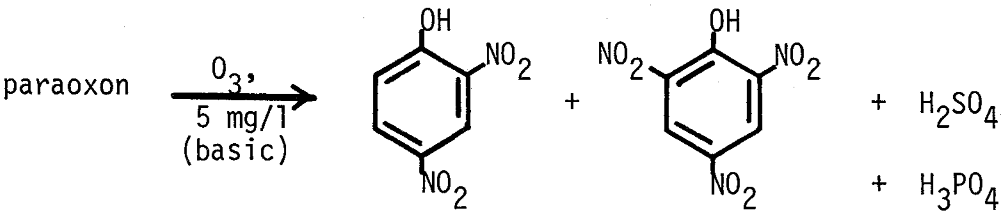




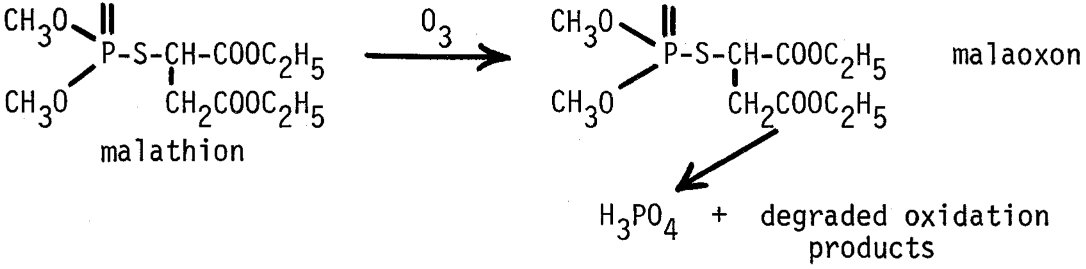
heptachlor-epoxide

Richard & Brener (1978) showed that ozonation of parathion with 3 mg/l ozone dosage forms paraoxon, a more toxic material than parathion itself. The reaction proceeds fastest in acid medium. Continued ozonation of paraoxon (5 mg/l ozone dosage) proceeds slower, with destruction of paraoxon and formation of 2,4-dinitrophenol, picric acid, H_2SO_4 and H_3PO_4:

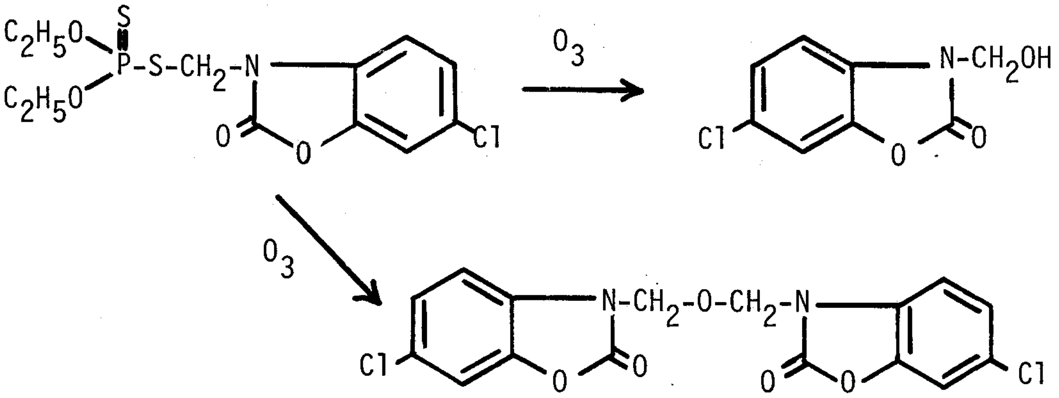




Similarly, Richard & Brener (1978) ozonized malathion and isolated malaoxon as the first step intermediate. Continued ozonation destroyed the malathion, producing H_3PO_4 and unidentified, degraded organic compounds.



Phosalone upon ozonation did not produce an oxon intermediate. Instead the benzoxalone moiety was cleaved to produce the parent alcohol. This alcohol also underwent self-condensation to produce an ether. Both the alcohol and the ether were isolated and identified by Richard & Brener (1978):

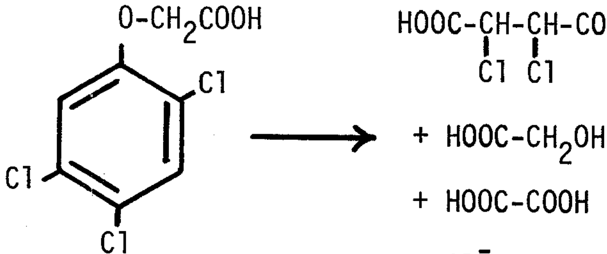


Richard & Brener (1978) concluded that under-ozonation of an organic material can produce other organic materials that are toxic, and that it is essential to know the chemical content of waters to be treated with ozone (or any oxidant).

Mallevialle et al. (1978) ozonized aqueous solutions of aldrin and found this compound to be easily degraded by ozone. On the other hand, when aldrin was added to aqueous solutions containing humic acids, 0.45 µg/l of aldrin was detected even after 10 minutes of ozonation. These researchers concluded that ozonation studies on organic compounds conducted in pure solutions can be misleading. It is necessary to know the humics or soils content of water to be ozonized, since these materials can adsorb dissolved organics and thereby "protect" them from the oxidizing action of ozone.

Prengle and Mauk (1978) showed that ozonation of DDT in water proceeds very slowly, but the oxidation rate is accelerated by combining UV radiation with ozonation.

Weil et al. (1977) ozonized 0.001M solutions of 2,4,5-T with 0.048 mole/hour of ozone and identified oxalic acid, glycolic acid, dichloromaleic acid, chloride ion and CO_2 as oxidation products. No ozonides or polymeric peroxides could be found. The concentration of dichloromaleic acid peaked after 8 to 9 minutes, that of glycolic acid peaked after 12 minutes and that of oxalic acid peaked after 20 minutes of ozonation, after which the concentration of all three intermediate products decreased with increasing time of ozonation. The concentration of dichloromaleic acid became zero in 25 minutes:



2,4,5-T

peaked in 8 to 9 min

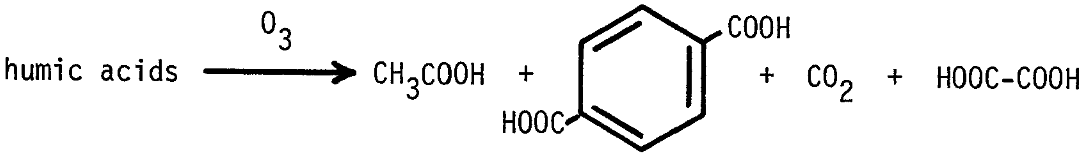
peaked in 12 min

peaked in 20 min

Reactions With Humic Materials

Ahmed & Kinney (1950) ozonized KOH solutions containing 2 g of humic materials. Water soluble, ozone-resistant acids were isolated, and 65% of the original carbon was isolated as CO_2.

Kinney & Friedman (1952) ozonized aqueous alkaline solutions of humic acids and isolated and identified small amounts of acetic acid, terephthalic acid, CO_2 and traces of oxalic acid:



Dobinson & Lawson (1959) ozonized solutions of humic acids isolated from coal and identified small amounts of acetic acid and CO_2 as reaction products.

Kinney & Leonard (1961) ozonized aqueous solutions of kerogen and isolated water soluble acids having molecular weights of 200 to 400. The equivalent weight of these acids was 120, and they were shown to be polyfunctional.

Shevchenko & Taran (1966) ozonized aqueous solutions containing 1 g/l of humic acids for 80 minutes and identified formic, acetic and oxalic (2.23%) acids.

Buydens (1970) ozonized samples of raw water from the River Meuse and found higher SS, higher phenol and higher COD contents after using 0.87 to 1.58 mg/l ozone doses. The author concluded that ozonation decomplexes iron and manganese from organic ligands, thereby liberating more phenolic and COD constituents. In addition, ozone decomposes high molecular weight polymeric humic materials into shorter, phenolic fragments.

Mallevialle (1975) ozonized neutral waters containing 100 to 200 mg/l of humic acids to attain 90% reduction in color levels in 10 minutes. After

20 minutes of ozonation the solution turned violet, which was ascribed to the decomplexing of manganese, followed by oxidation to permanganate. Chromatography of this solution showed the presence of phenolic compounds and formic acid. The author concludes that insufficient ozonation will increase the concentrations of these materials, but for most water supplies, maintaining a residual of 0.4 mg/l of ozone over 6 minutes will be a sufficient dosage.

Waters containing 525 mg of humic acids required 100 mg of ozone to destroy 95% of the color and 320 mg of ozone to destroy 95% of the polyhydroxyaromatics (Malleviallé, 1975).

Rook (1976) coagulated and filtered Meuse River water, then ozonized it 8 minutes with 2 mg/l doses, then chlorinated the ozonized waters. After 8 minutes of ozonation, haloform formation was reduced by 65%. However, after the ozonized water had stood for 24 hours, then was chlorinated, the amount of haloforms produced was about the same as without chlorination.

SUMMARY OF OZONATION REACTIONS

With Aromatic Compounds

- Phenol reacts readily with ozone in aqueous solution to produce the dihydroxybenzenes catechol, hydroquinone and resorcinol. The first 2 compounds are further oxidized to o- and p-benzoquinone, respectively.
- All of the above oxidized aromatic compounds, upon further oxidation with ozone, undergo ring cleavage to produce aliphatic unsaturated diacids: muconic, fumaric and maleic, plus the hydroxylated saturated diacids: tartaric and mesotartaric. In addition, glyoxal, glyoxylic acid, glycolic acid and oxalic acid are formed, along with CO_2.
- Oxalic and acetic acids are relatively stable to ozonation in the absence of a catalyst such as UV light or H_2O_2, and thus can be considered to be relatively stable oxidation products from the ozonation of phenol in water.
- Ozonation just to the point of destruction of phenol requires 2 to 3 mg of ozone/mg of phenol, but COD levels are reduced only 50%. To destroy phenol <u>and</u> lower COD levels to zero requires 8 to 12 mg of ozone/mg of phenol.
- Ozonation of chloro-substituted phenols ultimately cleaves the aromatic C-Cl linkages, forming chloride ion plus the same types of ring-ruptured aliphatic compounds as does phenol.
- Cresols and xylenols undergo oxidation with ozone at faster rates than does phenol. Before ring cleavage occurs, o-cresol forms salicylic acid.

- Upon ring rupture, ozonized cresols produce the same types of aliphatic products as does phenol, plus mesotartaric, propionic and acetic acids.

- Xylenols produce all these aliphatic products plus hydroxyphthalic acid (before ring-rupture) and diacetyl and glyoxal (after ring-rupture).

- Nitro, amino and sulfonic acid groups on aromatic rings are split off by ozonation, but at much slower rates than is chlorine. Amino groups are converted to ammonia and nitrate ion. Sulfonic acid groups are converted to sulfate.

- Azobenzene in water gave nitrosoazobenzene and nitroazobenzene as initial oxidation products. However, continued ozonation converted these intermediate compounds into oxalic acid, glyoxylic acid and nitrate ions. Thus, nitroso compounds can form during the early stages of ozonation; these will continue to oxidize to innocuous organic materials provided that sufficient amounts of ozone and/or oxidation times are supplied.

- Aromatic hydrocarbons such as pyrene, phenanthrene and naphthalene oxidize by ring rupture. Only 1 ring in phenanthrene opens readily, however. When aliphatic hydrocarbon groups are present on the aromatic rings, these oxidize first, before the ring ruptures.

- Chlorobenzene reacts with ozone slower than does phenol, but gives the same ring-ruptured, aliphatic oxidation products as does phenol. Intermediate oxidation products include o-, m- and p-chlorophenols plus chlorotartaric acid. Chlorocresols, chlorophenols and thiophenols give ozonation products similar to those from phenol.

With Aliphatic Compounds

- There is no evidence that ozone reacts with saturated aliphatic hydrocarbons under water or wastewater treatment conditions.

- There is also no evidence that ozone oxidizes trihalomethanes. Reduction in concentration of THMs upon ozonation appears to occur by air stripping of aqueous solutions. Ozone combined with UV radiation does oxidize chloroform to produce chloride ion, but no identified organic oxidation product.

- Unsaturated aliphatic or alicyclic compounds react with ozone, usually at the unsaturated bond, cleaving the molecule into 2 oxidized fragments (aliphatics) or into diacids or carbonyl acids (alicyclics). The 2 aliphatic fragments normally are an acid plus an aldehyde or ketone.

- Primary aliphatic alcohols generally are oxidized to aldehydes, then to acids, but at slower rates than phenol oxidation with ozone.

- Secondary aliphatic alcohols produce ketones, then acids plus H_2O_2 upon ozonation.

- Formic acid readily produces CO_2 and water upon ozonation, but oxalic acid is relatively stable to ozonation in the absence of UV radiation or H_2O_2. Acetic acid and propionic acid also are relatively stable to ozonation.

- Oxalic acid oxidizes directly to CO_2 without producing formic acid. Reaction with ozone alone is very slow, but proceeds rapidly in the presence of UV radiation or H_2O_2.

- Maleic acid produces glyoxylic and formic acids initially. Glyoxylic acid then produces oxalic acid, CO_2 and water. These are the sole products of ozonation of maleic acid.

- Propionic acid and 2-propanol produce acetone upon ozonation. Acetone can undergo the haloform reaction and produce chloroform if present during post-chlorination of ozonized water.

- Ozonation of acetate ion and acetic acid ultimately produces glyoxylate ion or glyoxylic acid, respectively, which then form oxalic acid.

- Diethylamine produces acetaldoxime upon ozonation, plus an unidentified nitrogen-containing compound, not a nitrosoamine.

- Prolonged ozonation of a concentrated ethyl alcohol solution in water produces a stable dihydroperoxide which exhibits mutagenic activity.

- Ozonation of Lake of Zürich raw water increased the aldehyde concentrations. Ozonation followed by activated carbon adsorption reduced the aldehyde concentrations below their original concentrations.

- UV/ozonation of refractory organic materials increases the rate at which they are oxidized by ozone, but not the nature of the oxidation products.

With Pesticides

- Ozonation of parathion and malathion produces paraoxon and malaoxon, respectively, as intermediates, which are more toxic than are the starting materials. Continued ozonation degrades the oxons, but requires more ozone than does the initial thion oxidation. Phosalone oxidizes without forming an oxon intermediate. Thus, under-ozonation can produce intermediates which are more toxic than are the starting materials.

- Ozonation of heptachlor produces a stable product, not yet identified. Heptachlorepoxide is known to be stable to ozonation. This suggests that ozonation of heptachlor may produce the epoxide, which then would be unaffected by further ozonation.

- Aldrin and 2,4,5-T are readily oxidized by ozone, but dieldrin, chlordane, lindane, DDT and endosulfan are only slightly affected by ozone.
- UV/ozonation destroys DDT, PCBs, malathion and many other pesticides, but requires more extended contact times and ozone doses.
- Ozonation of aldrin in pure water solutions proceeds rapidly, but at a much slower rate in the presence of humic acids. Similar oxidation rates were observed with solutions of benzopyrene in pure water (rapid) versus water containing colloidal soil particles (slow). This indicates that dissolved organic materials can be adsorbed by humics or soil particles and be "protected" from oxidation, at least partially. This would also indicate that oxidation of water supplies or of wastewaters with ozone should follow a filtration step.

With Humic Materials

- Humic materials are resistant to ozone, requiring lengthy times of ozonation to produce small amounts of acetic, oxalic, formic and terephthalic acids, CO_2 and phenolic compounds.
- Ozonation of humic materials in water followed by immediate chlorination (within 8 minutes) reduced trihalomethane formation by 65%. However, when ozonized waters containing humics were allowed to stand 24 hours and then chlorinated, there was no change in the amounts of trihalomethanes formed. This indicates that although ozone changes the chemical nature of trihalomethane precursors, there is continued reaction upon standing, not entirely with residual ozone, to form materials equally capable of producing trihalomethanes upon chlorination.
- Ozonized organic materials generally are more biodegradable than the starting, unoxidized, compounds.

A comparative summary of the reactions of organic materials with ozone, chlorine dioxide and chlorine is given in Table 71, which is taken from Miller et al. (1978), who conducted a detailed assessment of the state-of-the-art of the treatment of water supplies with ozone and with chlorine dioxide for EPA's Water Supply Research Laboratory.

CONCLUSIONS

- Complete oxidation of dissolved organic materials to CO_2 and water in aqueous solutions is rare by means of any oxidant.
- In general, if an organic material is resistant to oxidation by ozone (the most powerful oxidant used in water and wastewater treatment), it will also be resistant to oxidation by other (weaker) oxidants.

TABLE 71. COMPARISON OF OXIDATION OF ORGANIC COMPOUNDS WITH OZONE, CHLORINE DIOXIDE AND CHLORINE

Type of Organic	Oxidation Products Isolated Upon Treatment With		
	ozone	chlorine dioxide	chlorine
Phenol	intermediates: polyhydroxyaromatics and quinones. Then ring ruptured, nonhalogenated difunctional products (alcohol-aldehyde; aldehyde-acid; alcohol-acid). End Products: oxalic acid, CO_2+H_2O	Same as for ozone plus chlorinated phenols and chloroquinones. Upon ring rupture, the same non-chlorinated products as for ozone are obtained, plus some chlorinated aliphatics	chlorophenols plus ring-ruptured products (presumably chlorinated); also non-chlorinated products (aromatic and ring-ruptured)
Cresols and xylenols	Same products as from phenol, plus methyl-substituted compounds (salicyclic acid as aromatic intermediate, propionic and acetic acids after ring rupture). Acetic acid, oxalic acid, CO_2+H_2O end products		probably chlorinated aromatics, then ring rupture.
Chlorinated phenols	Chloride ion plus same products as from phenol. Oxalic acid + CO_2 end products.	Chloroquinones plus ring-ruptured, halogenated and non-halogenated aliphatics	probably more highly chlorinated phenols, then ring rupture.

(continued)

TABLE 71. (continued)

	ozone	chlorine dioxide	chlorine
Chlorinated benzenes	Chlorophenols, then chloride ion and non-chlorinated, ring-ruptured products, as with chlorophenols, plus some chlorotartaric acid.		probably more highly chlorinated products.
miscellaneous aromatics	nitro, amino and sulfonic acid groups are cleaved, but more slowly than chlorine. Oxalic acid + CO_2 are end products.	benzoic, phenysulfonic and cinnamic acids are not reactive to ClO_2. Nitro groups are split off during ring oxidation.	
polycyclic aromatics	undergo ring rupture producing polycarboxylic aromatics, which become increasingly resistant to further oxidation.	produces polycyclic non-halogenated quinones plus chlorinated polycyclic aromatics. Eventual ring rupture likely, but at slower rate than with ozone.	Probably same products as with chlorine dioxide.
diphenylhydrazine or diphenylamine	hydroxylamines and ring hydroxylated diphenylamine.	ring-chlorinated, ring-hydroxylated and ring-chlorinated + hydroxylated diphenylamine.	
nitrogen heterocycles	ring rupture to amino acids, then further degradation to aliphatic end products	thianine stable. Pyrimidine and indole rings apparently stable. Substituents oxidize, but do not chlorinate	

(continued)

TABLE 71. (continued)

	ozone	chlorine dioxide	chlorine
unsaturated aliphatics	cleavage of double bond to aldehydes, ketones and acids. Possible formation of epoxides.	dichloro compounds, chloroketones, chlorohydrins, then epoxides	dichloro compounds, chlorohydrins, then epoxides under alkaline conditions.
primary aliphatic alcohols	yield aldehydes, then acids, then CO_2. Ethanol forms a dihydroperoxide with mutagenic properties under stringent conditions.	yield acids which are stable to further oxidation. Unsaturated acids (crotonic, maleic and fumaric) are stable to ClO_2.	
secondary alcohols	yield ketones, then fragmented acids, then CO_2.	yield ketones, then acetic acid, which is stable.	
primary aliphatic amines		no reaction.	
secondary aliphatic amines	aldoximes + other N-containing compounds, not nitrosamines	very slow reaction	
tertiary aliphatic amines		secondary amine + aldehyde	
chloroform	no reaction except in presence of UV	probably no reaction	no reaction

(continued)

TABLE 71. (continued)

	ozone	chlorine dioxide	chlorine
humic materials	slowly reactive, producing phenols, ozone - resistant acids (increasing COD) and CO_2.	slowly reactive, producing phenols and increasing COD	trihalomethanes
sugars, carbohydrates		ring substituents oxidize without ring rupture until excess ClO_2 employed.	
trihalomethane precursors	1) O_3 + rapid chlorination 65% lowering of THM 2) O_3 + chlorination after 24 hrs has no effect on THM yield.	no THMs produced from pure ClO_2 (containing no free chlorine)	trihalomethanes
phosalone, aldrin	readily oxidized to destruction.		
2,4,5-T	ring rupture to oxalic acid + CO_2 + chloride ion.		
parathion, malathion	produces oxons, then degradation products.		
dieldrin, chlordane, lindane, DDT, PCBs, PCP, endosulfan	only slightly reactive with ozone, but will oxidize with ozone/UV.		

- Conversely, ozone will oxidize some organic materials that other oxidants will not oxidize (such as primary and secondary amines, amino acids, double bonds conjugated with carbonyl groups, etc.), and at faster rates.

- Oxidation products formed by ozonation do not contain halogen atoms, unless bromide ion is present. In this case, bromide is oxidized to bromine, which then may react with organic materials present.

- Oxidation of phenols with ozone or chlorine dioxide produces oxidized aromatic compounds as intermediates, which undergo ring rupture upon treatment with more oxidant and/or longer reaction times. In many cases, the same, non-chlorinated, ring-ruptured aliphatic products are produced using ozone or chlorine dioxide.

- Oxidation of phenols with chlorine dioxide or chlorine produces chlorinated aromatic intermediates before ring rupture.

- Ozonation of chlorinated aromatic compounds ruptures the rings and cleaves carbon-chlorine bonds, forming chloride ion, non-chlorinated aliphatic oxidation products and CO_2.

- Oxidation products formed upon ozonation, and non-chlorinated oxidation products from chlorine dioxide are more biodegradable than are the starting organic materials.

- Oxalic and acetic acids are only slowly reactive with ozone, and are the most stable organic end products of oxidation of organic materials with ozone.

- Combination of ozone with UV light increases the rate of oxidation of ozone-resistant organic materials, but the same organic oxidation products are obtained as with ozone alone.

- Epoxide compounds have been isolated from reactions of compounds containing double bonds with chlorine <u>or</u> chlorine dioxide. Heptachlorepoxide is stable to ozonation, indicating that it <u>may</u> form upon ozonation of heptachlor.

- Oxidation of aldrin or 3,4-benzopyrene with ozone in clean water proceeds rapidly, but proceeds significantly slower when humic materials or soil particles are present. Thus dissolved organics can be adsorbed onto humic or soil materials and be resistant to oxidation.

- Oxidation of parathion and malathion with ozone proceeds through the more toxic oxon intermediates (paraoxon and malaoxon, respectively). These same intermediates <u>may</u> form with other oxidants, but no literature has been found to confirm this.

- Bromide and iodide ions are readily oxidized to the free halogens by chlorine or by ozone. The free halogens then can undergo the haloform reaction to produce trihalomethanes, if the proper organic compounds are present. Formation of bromine-containing trihalomethanes upon treating humic materials with chlorine dioxide (even containing a slight excess of free chlorine) has not been observed.

- Ozonation of humic materials followed by immediate chlorination shows a significant reduction in trihalomethane formation. However, ozonation followed by chlorination 24 hrs later shows no reduction of trihalomethane formation.

- Regardless of the oxidant employed, many (possibly all) of the same organic oxidation products will be present in the water or wastewater at the same treatment point. More significantly, in the case of chlorine, these same (non-chlorinated) oxidation products probably have been present all along. A detailed review of the organic oxidation products of chlorine should be made for comparison with this survey of oxidation products of organic compounds with ozone.

- Trihalomethane formation in drinking waters can be eliminated by changing the disinfecting oxidant, but this will have no effect upon formation of the other, non-chlorinated organics.

- Similarly, formation of chlorinated organics in wastewaters can be eliminated by substituting another oxidant for chlorine, but this will have no effect upon the formation of the other, non-chlorinated organics.

- These last three conclusions indicate that rather than considering an "alternative oxidant to chlorine" for treating water or wastewater, it is more meaningful to consider "alternative treatment schemes for removing organic materials" before the oxidant is added. Depending on the source of organic pollution and its nature, little may be gained by simply changing the oxidant.

- There are 3 basic approaches to minimize the amount of oxidized organic materials remaining in wastewaters treated with oxidants:

  -- Add sufficient oxidant (with oxidation catalyst, if appropriate) to convert all organic materials to CO_2 and water. This may be the most costly approach, in terms of oxidant, and may not even be possible, depending upon the specific organic materials present.

  -- Eliminate or significantly reduce the amount of organic materials present before oxidant is added. This would involve better pretreatment, filtration, use of more or improved flocculants, etc.

  -- Oxidation with a non-halogenating reagent (ozone, chlorine dioxide in some cases, permanganate, H_2O_2, etc.) usually will produce oxidized organic materials which are more biodegradable. Following oxidation with a biological filtration step (such as Biological Activated Carbon--see next section) will allow significant reduction of dissolved organics and ammonia concentration using smaller amounts of oxidant than in the first two approaches.

- Since halogenated organic materials are both more difficult to oxidize and are less biodegradable, their formation during the early stages of water or wastewater treatment processes should be avoided, if at all possible. If early stage emphasis is placed on removal of organics to the maximum degree practicable under specific plant conditions, the following benefits can accrue:

    1) chlorine demand will be reduced.

    2) amounts of oxidized organics formed later in the process will be reduced.

    3) amounts of formed trihalomethanes and other halogenated organics will be reduced.

    4) Detrimental effects on finished wastewater caused by high organic and high chlorine levels will be reduced.

- If the presence of halogenated organic compounds cannot be avoided (for example, if they are present in high concentration in the raw wastewater), pretreatment with the combination of ozone with UV radiation should be considered, especially as a pretreatment step before BAC media.

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SECTION 7

BIOLOGICAL ACTIVATED CARBON

INTRODUCTION

Biological Activated Carbon (BAC) is a terminology applied to the sequential combination of water or wastewater treatment process steps involving:

(1) oxygenation or chemical oxidation (usually with ozone) followed by
(2) sand or anthracite filtration, followed by
(3) GAC adsorption.

This processing sequence promotes the growth of aerobic bacteria on both the inert media and GAC filters. These aerobic bacteria simultaneously reduce levels of Dissolved Organic Carbon (DOC) and ammonia (by conversion to nitrate). The functions of ozonation are to:

(1) partially oxidize the dissolved organic materials, promoting further oxidation by the aerobic bacteria,
(2) lower the molecular weights of the non-carbon adsorbable organic materials and
(3) raise the level of DO.

BAC processes were discovered and developed in European drinking water treatment plants, and now are in full scale operation in some 23 plants in Germany, France, Switzerland and Holland. The process also is being developed at the Cleveland, Ohio Westerly Sewage Treatment Plant in the United States. BAC processes have never been designed specifically for treating industrial wastewaters, and the potentials for this type of processing are discussed in this section.

BACKGROUND

In a recent article which discusses the use of GAC in water treatment, McCreary & Snoeyink (1977) state that "beds of GAC are a convenient place for microorganisms to grow because bacteria attach themselves to the irregular external surfaces of the carbon particles and are very difficult to dislodge via backwashing procedures." In the presence of soluble carbonaceous matter, which serves as food for these organisms, and in the absence of oxygen, anaerobic bacteria can develop. There are numerous instances in which sulfidic odors have been reported emanating from GAC columns used for the removal of dissolved organic materials contained in sewage treatment plant effluents (Guirguis, Melnyk & Harris, 1976d; Directo, Chen & Kugelman, 1977) and drinking water supplies (Monsitz & Ainesworth, 1970).

On the other hand, given sufficient DO and carbonaceous matter, the bacteria which develop in carbon beds will be aerobic. These do not produce sulfidic odors.

Many of the advantages of BAC (ozonization, followed by filtration through inert media, then GAC adsorption) were first recognized by German water treatment scientists in the 1960s in drinking water plants along the Rhine River in the Düsseldorf area. Subsequently, BAC processes also have been installed in Swiss, French and Dutch drinking water treatment plants, and are subjects of active pilot studies in Belgium. In the United States, the U.S. Environmental Protection Agency's Water Supply Research Laboratory in Cincinnati, Ohio has been testing a pilot BAC unit since late in 1976 (Carswell, 1977).

Independently of this research on BAC for drinking water treatment, research workers in the United States at the Cleveland Regional Sewer District have successfully adapted BAC for the processing of physical/-chemical treated sewage (Guirguis *et al.* 1976a,b,c,d; 1978, Prober *et al.*, 1977; Hanna, Slough & Guirguis, 1977). The process also is being studied for treating sewage treatment plant effluents in Israel (Wachs *et al.*, 1977).

FUNDAMENTAL PRINCIPLES

The terminology, BAC, has been applied by Rice, Miller, Robson & Kühn (1977, 1978) to the combination of treatment processes consisting of (1) ozonation followed by (2) filtration through an inert medium, such as sand or anthracite, followed by (3) passage through GAC columns or beds. A reoxygenation step may be desirable before passage of the water through GAC. Figure 27 shows a schematic of the BAC subsystem.

GAC is made biologically active by the deliberate introduction of sufficient DO to aqueous streams just before they are passed through GAC columns or beds. As long as the water contains sufficient DO to maintain aerobicity of the bacteria and sufficient dissolved carbon to provide food, the aerobic bacteria will thrive in this environment. Eberhardt (1975) has likened bacterial activity in such an ideal environment to a "herd of cows grazing in a luscious meadow".

At our present stage of understanding, there are 2 mechanisms by which biological activity is utilized in the BAC media. Microorganisms are present both on the surface of the carbon and in the large macropores. Dissolved organics will be adsorbed both at the surface and in the large and small pores of the GAC, but can be biodegraded directly only when adsorbed in the macropores. However, those surface- and macropore-adsorbed organics do not have to be well adsorbed, provided that they are biodegradable. Preozonation converts larger, less biodegradable organic molecules into smaller, more biodegradable organics, for example, into acetic and oxalic acids.

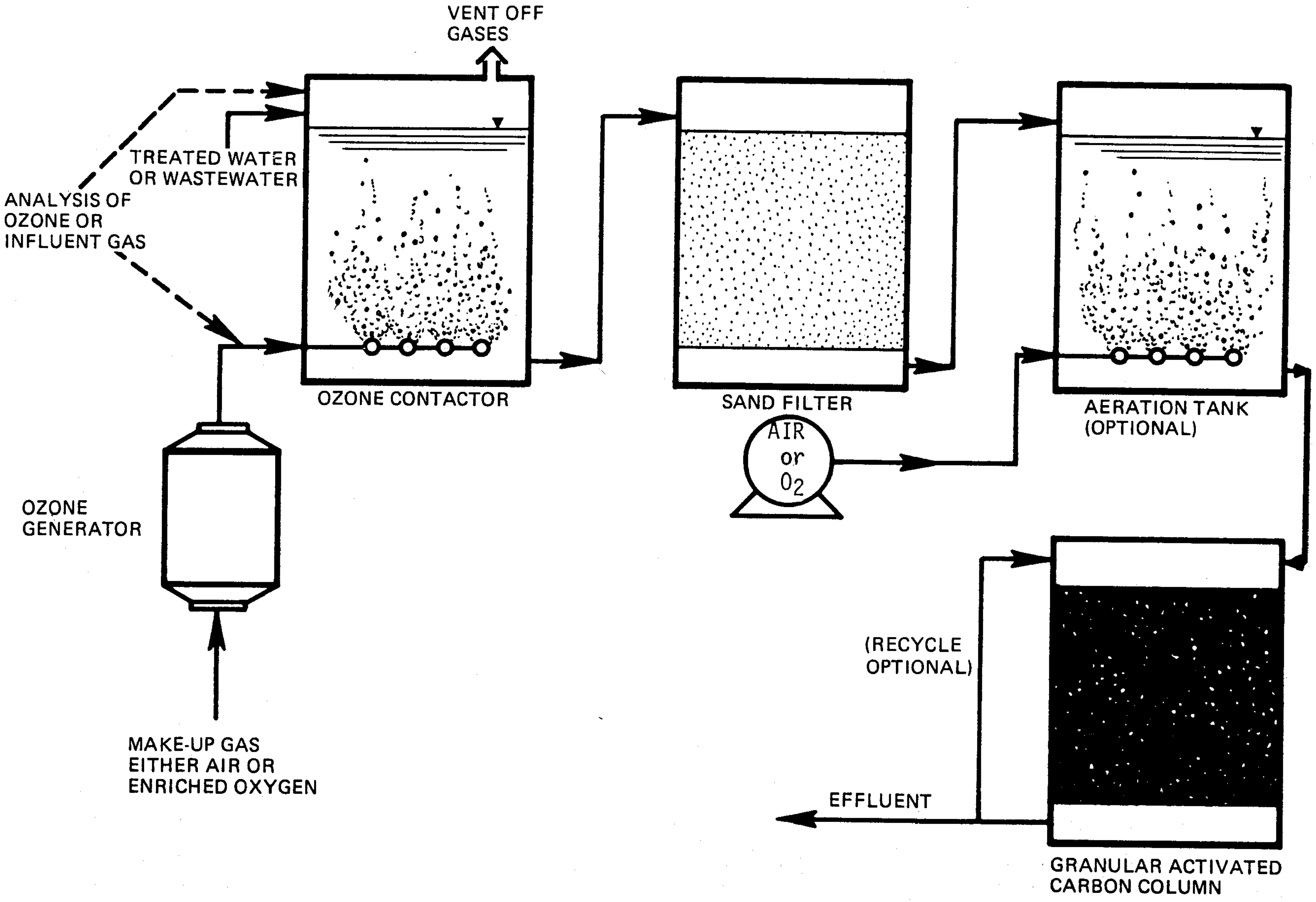


Figure 27. Biological activated carbon system.

The larger, less biodegradable organic molecules can be captured and adsorbed in the carbon pores. When these are present in the macropores, the bacteria can degrade the adsorbed organics and reactivate the loaded GAC.

According to the second mechanism (Rice et al., 1979) organic materials which are adsorbed in the micropores of the GAC where bacteria cannot penetrate, can be desorbed either by enzymes generated by the bacteria present, or by more tightly adsorbed organics. Enzymatic action itself will convert non-polar, tightly adsorbed organic compounds into more polar compounds, which are less tightly adsorbed, thus assisting the desorption process.

Both proposed mechanisms result in extended operating lives of the GAC media before it has to be physically removed from the columns or beds and regenerated.

Sontheimer (1977b) has summarized the German findings to date which have led to the current theories of operation of BAC.

Although aerobic bacteria are necessary to obtain the benefits from BAC, so also is the adsorptive capacity of the GAC for the dissolved organic materials which will serve as food for these bacteria. This means that the macropore surface area and internal pore volume of the carbon both should be high. Stated another way, it is important that the less readily biodegraded organic materials present in solution be adsorbable onto the activated carbon column, since the empty bed contact times of solutions with the carbon particles in the columns or beds in water and wastewater treatment plants are relatively short (15 to 30 minutes). This does not necessarily give the bacteria sufficient time to degrade larger organic carbon molecules, ideally to CO_2 and water. Therefore, it is important to be able to retain the dissolved organic molecules in the activated carbon medium so that the bacteria then will have sufficient time to degrade them, even though the actual contact times involved are relatively short.

Many organic materials are readily adsorbed by GAC, but many others are not. It is well known, for example, that high molecular weight natural humic acids, so prevalent in drinking water supplies, are not readily adsorbed by activated carbon (Kühn, Sontheimer & Kurz, 1978).

If solutions of these high molecular weight, non-sorbable organic materials are ozonized before passage through the GAC columns, they are converted to lower molecular weight, more readily biodegradable organic materials (Kühn, Sontheimer & Kurz, 1978; Guirguis et al., 1976a, 1976c). At the same time, ozonation introduces a large quantity of oxygen into the water which promotes aerobic bacterial growth.

ADVANTAGES OF BIOLOGICAL ACTIVATED CARBON IN DRINKING WATER TREATMENT

In European pilot studies and in drinking water treatment plants it has been shown by many workers (Scheidtmann, 1975; Schalekamp, 1975; Van Lier et al., 1975; Sontheimer, 1975; Eberhardt, 1975; Van der Kooij, 1975; Kühn, Sontheimer & Kurz, 1978; Gomella & Versanne, 1977; Sontheimer et al., 1978) that pre-ozonation followed by activated carbon adsorption results in:

- Increased capacity of the carbon to remove organics (by a factor of about 10),
- Increased operating life of the carbon columns before having to be regenerated (up to 3 yrs), especially if the GAC can be kept free of halogenated organics,
- Biological conversion of ammonia to nitrate in the GAC columns, which occurs simultaneously with removal of dissolved organics,
- Use of less ozone and less GAC for removing a given amount of organics than using either process alone,

Independent studies on physical/chemical treated sewage at Cleveland Regional Sewer District (Guirguis et al., 1976a,b,c,d; 1978) and in Israel (Wachs et al., 1977), have confirmed these advantages with respect to removing organic materials.

EUROPEAN BACKGROUND

Introduction of GAC into European drinking water treatment practices occurred shortly after World War II. Its initial application was for dechlorination, then for tastes and odors (Hopf, 1960). Many surface waters containing ammonia undergo breakpoint chlorination at the beginning of the treatment process. This technique effectively removes ammonia, but produces considerable amounts of residual chlorine and chlorinated products in the water (Sontheimer et al., 1978). German water treatment objectives are to process surface waters to the same quality as that of natural groundwater (which does not have to be treated in many cases). Therefore, waters treated by breakpoint chlorination have to be dechlorinated before they are treated further or distributed (Sontheimer, 1977a).

The City of Düsseldorf originally installed ozone for oxidation of iron and manganese in its sand bank filtered Rhine River raw water in the mid-1950s (Miller et al., 1978; Hopf, 1960). GAC was installed in 1961 for removing organics. Today, ozonation is followed by storage for 20 to 30 minutes in a holding tank, then by filtration through an inert medium, then GAC adsorption, then treatment with a small quantity (up to 0.3 mg/l) of chlorine dioxide for residual.

Over the years which followed installation of "the Düsseldorf Process", it was noted that more dissolved organic carbon was being removed than could be expected on the basis of the simple summation of the known effects of ozonation and of GAC treatments. When it was also discovered that ammonia levels were much lower after GAC treatment than before ozonation (at pH below 9.0, ozone does not oxidize ammonia), the biological activity within the carbon columns was examined in closer detail.

The Rhine River in the Düsseldorf area contains considerable amounts of chlorinated organic materials which are not removed during river sand bank filtration. These halogenated organics also are more resistant to oxidation by ozone than are non-halogenated organics and thus are less likely to be converted into readily biodegradable materials. In addition, halogenated organics are more tightly adsorbed by the GAC (Kühn & Fuchs, 1975; Kölle, Sontheimer & Steiglitz, 1975).

Combining the stronger adsorptivity of halogenated organics onto GAC with their lesser reactivity upon ozonation and their lower biodegradability, simply means that breakthrough of halogenated organics can occur more rapidly than does breakthrough of non-halogenated organic compounds from GAC columns, even though the GAC columns may contain optimal biological activity. Thus German water works along the Rhine in the Düsseldorf area monitor their carbon column capacities for Total Organic Chlorine (TOCl) (Kühn & Sontheimer, 1973a,b; Kühn, 1974; Kühn & Sontheimer, 1974), as well as for DOC (Wölfel & Sontheimer, 1974), and/or UV absorption. Carbon columns at three Düsseldorf plants along the Rhein (Flehe, Am Staad, Holthausen) are backwashed every 4 to 6 weeks and regenerated every 5 to 6 months (Miller _et al._, 1978). GAC regeneration is paced by TOCl levels, and biological activity is maximized so as to prevent breakthrough of biodegradable materials before TOCl.

When activated carbon columns at Düsseldorf are regenerated, however, only 80% of the carbon charge is taken out of the columns. This leaves 20% of biologically active GAC in the column so that the level of bioactivity will not drop significantly when fresh or regenerated carbon is added. With fresh carbon columns, about 15 days of operation usually are required for biological activity to build up to an effective "steady state", particularly for ammonia removal (Poggenburg, 1977).

EUROPEAN DRINKING WATER TREATMENT EXPERIENCES WITH BAC

Switzerland

Activated carbon was installed at Zürich initially to protect against oil spillage, later for protection against phenol spills, and for dechlorination (Schalekamp, 1975). Zürich's Lengg and Moos plants take raw water from the Lake of Zürich, which contains very low concentrations of chlorinated organics and is otherwise a very clean raw water supply. There is no need for breakpoint chlorination (because of very low ammonia content), but a small dose of chlorine (1 mg/l maximum) _is_ added at the intake to prevent growth of mussels. GAC treatment insures dechlorination of this amount of chlorine. Before passage through activated carbon, however, the water is ozonized with dosages of 1 to 1.5 mg/l.

In actual plant studies (Schalekamp, 1975), both the top and bottom layers of the carbon beds showed equal loadings of organics at the end of 7 months. This indicates that the GAC should be regenerated. However, regeneration of this carbon was _not_ required because the continued efficient removal of DOC from the aqueous medium by this carbon remained nearly the same as that of the new carbon (Figure 28). This behavior was attributed by Schalekamp to biological activity within the carbon bed.

At the Zürich Moos plant, the slow sand filter was fitted with a 5 cm layer of GAC. The efficiency of DOC removal from the aqueous solution remained essentially constant over the 3 year period (about 2.8 mg/l residual COD in the filtrate) (Figure 29). This performance, again attributed to bacterial degradation of the adsorbed organics, was obtained without reactivation of the carbon, although twice weekly backwashes were required.

Operational costs for the carbon beds at the Zürich Lengg plant are $0.016/cu m (6.05¢/1,000 gal) which is 12.5% of the total plant operating costs. Since treated Swiss surface waters must not be inferior to unobjectionable well or groundwater, BAC filtration is a necessary and also economically feasible component in the treatment process (Schalekamp, 1977).

Holland

Van Lier _et al_. (1975) describe experiences with activated carbon filters in Dutch pilot plant studies at Amsterdam. Three carbon pilot units were studied side by side, using 2 meter column heights and 8 cu m/sq m/hr flow rates for 3 months. The water was treated by iron coagulation, rapid sand filtration, chlorination, then:

Process #1: Ozonation, rapid sand filtration, BAC, slow sand filtra tion,

Process #2: Rapid sand filtration, slow sand filtration,

Process #3: Activated carbon, slow sand filtration.

These researchers concluded that:

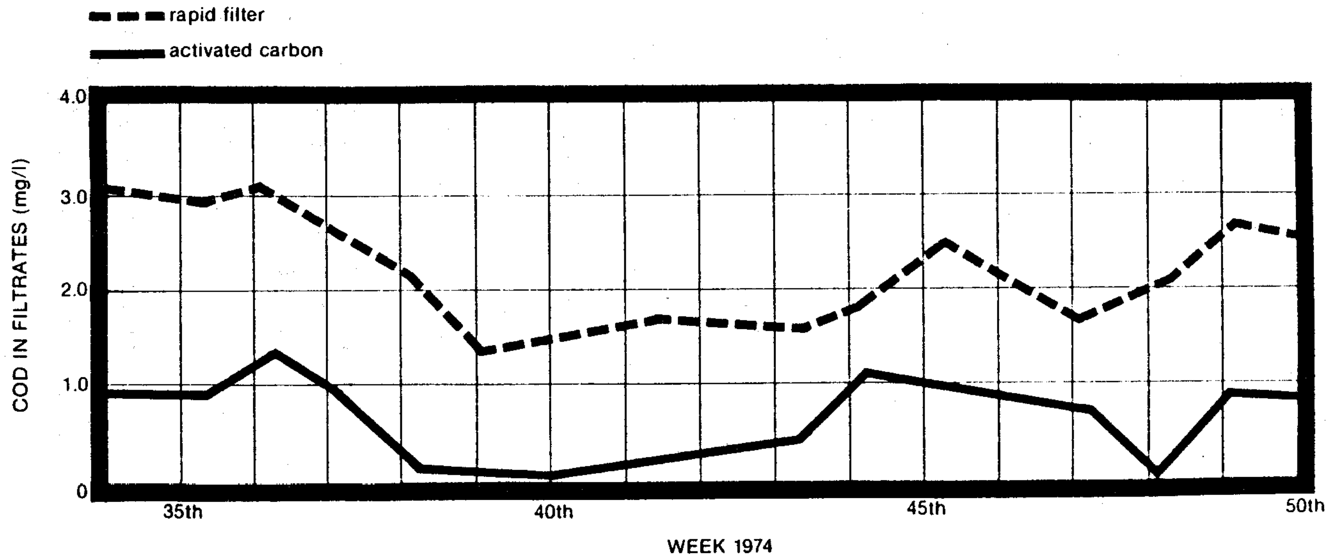
1) Ozonation increases bacterial counts considerably after rapid and slow sand filtration,

2) Water treated by Process #1 (with ozone) produces water with reduced levels of color, UV absorption and $KMnO_4$ consumption than waters treated by Processes #2 or #3 without ozone,

3) Slow sand filtration in all 3 systems reduces bacterial counts, color and $KMnO_4$ consumption,

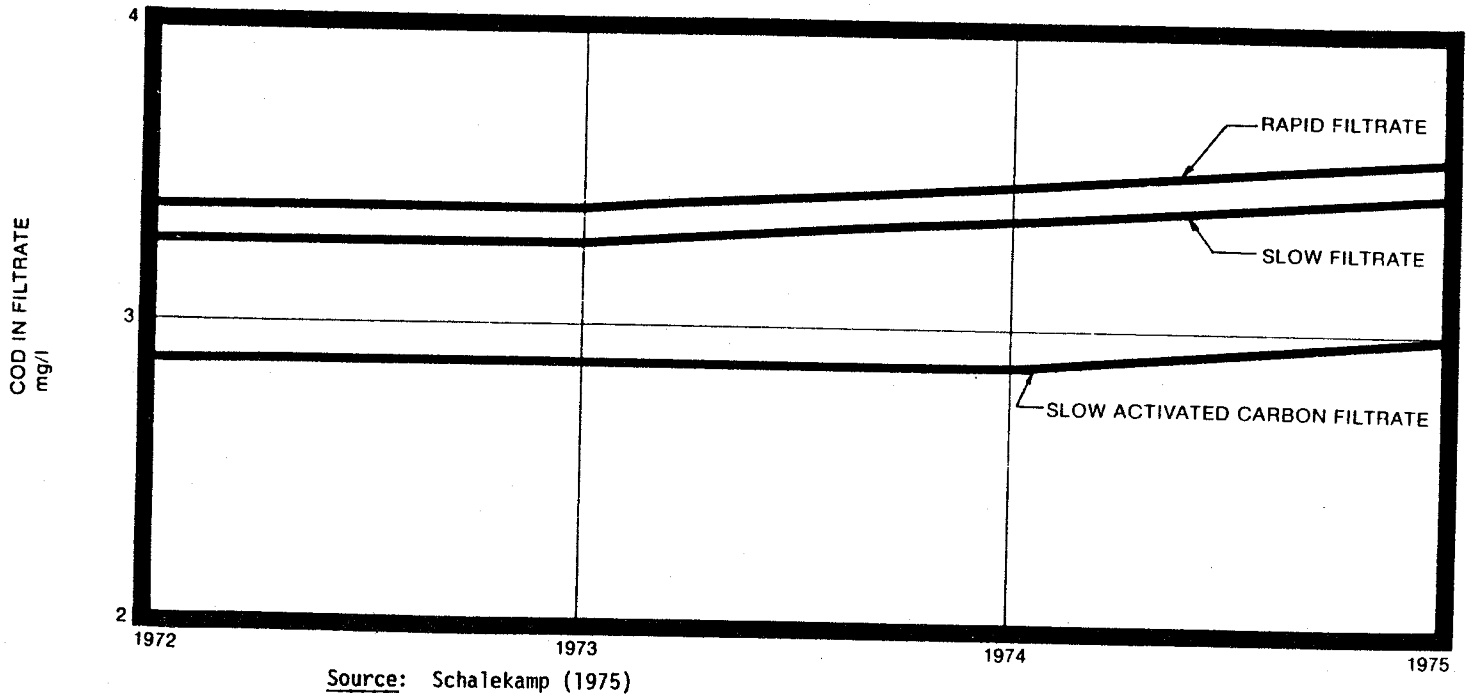
4) Water qualities by Processes #2 and #3 are about the same, but the frequency of backwashing of the slow sand filters is more frequent in these processes, which do not include ozonation,

5) Service time of the GAC column with ozone was much longer (300 days) than those without ozone (175 days) as measured by UV absorption of the filtrates.



Source: Schalekamp (1975)

Figure 28. Efficiency of removal of COD from rapid filter and activated carbon at Lengg plant, Zürich, Switzerland.



Source: Schalekamp (1975)

Figure 29. Efficiency of COD removal of BAC over 3 years at Moos Water Works, Zürich, Switzerland.

For the same concentration of DOC in the influent, the amount of DOC removed by the carbon in the summer is much greater than in the winter. This is explained on the basis of increased biological activity in the carbon columns at the higher summer temperatures. Oxygen consumption in the winter was found to be 0.006 g/hr/kg of carbon and 0.024 to 0.030 g/hr/kg of carbon in summer.

Longer service times were observed for BAC columns which had optimum contact times of 20 to 25 minutes (empty bed).

Costs of operating carbon filters decreased with increasing retention times. Costs of 0.06 guilder/cu m (2.55 ¢) were estimated for 25 to 30 minute retention times. Reactivation costs were estimated at 0.03 guilder/cu m (1.23 ¢).

Also in Holland, Van der Kooij (1975) investigated the presence and behavior of bacteria on activated carbon filters. Tests were conducted on 3 experimental filters: GAC, granular non-activated carbon and sand.

Each filter was fed with tap water at 13 to 17°C and 3.5 m/hr (3 minutes contact time) flow-through rates over a 10 month period (side-by-side experiments). Bacterial counts were made at regular intervals by the colony count technique on diluted agar (0.35 g/l beef extract, 0.65 g/l peptone, 10 g/l agar) after incubation for 10 days at 25°C. The number of bacteria in the activated carbon column was always 10 times higher than the number found on sand or on non-activated carbon.

From these experiments, Van der Kooij (1975) calculated the average surface area occupied by a single bacterial cell to be 40 sq microns when the colony count is 10^8/cu cm. Since the surface area of the activated carbon used for these tests was greater than 40 sq cm/cu cm, it was concluded that the density of bacteria on the carbon surface is very low. This was confirmed by electron microscopy. It was also concluded that normal adsorption processes on activated carbon are not hindered by the presence of the bacteria on the carbon.

GERMANY

Wiesbaden

Klotz, Werner & Schweisfurth (1975) studied the microbiology in GAC filters at the Schierstein water treatment plant in Wiesbaden. At this plant, Rhine River water is aerated, settled, chlorinated to the breakpoint, flocculated, filtered through sand, then passed through activated carbon and sent to ground infiltration. There is no pre-ozonation of the activated carbon column.

Studies of the performances of and the activities of bacteria in activated carbon columns at Wiesbaden over a period of 3 years have shown that seasonal influences are only slight. There is a tendency for decreased microbial activity in winter, as indicated by oxygen consumption and CO_2 production values. However, changes in raw water quality also can cause substantial and distinct changes in the colony numbers.

Adsorption isotherms were determined for bacteria loaded on the carbon. At high colony numbers (above 10^{10}/ml) the system tended to saturation. At 10^7 to 10^8/ml, up to 90% of the bacteria were adsorbed onto the carbon (Figure 30). After 20 to 30 hrs of operation, adsorption and desorption were nearing the steady state (Figure 31) of about 10^8 colonies/g of carbon. Electron scan microscopic analysis of GACs treated differently showed that the bacteria are always present in the form of a single bacterial layer. Thus the carbon surface is only fractionally utilized (about 1%) by the adsorbed bacteria, leaving 99% of the surface area of the carbon free for adsorption of dissolved organic materials.

Bremen

Extensive pilot plant studies on the BAC process have been conducted by Eberhardt, Madsen & Sontheimer (1974). The original Bremen plant treats Weser River water by flocculation, rapid sand filtration, slow sand filtration and chlorination. A semi-works size pilot facility employing GAC with preozonation was constructed in 1969, and research reported in this article was conducted on BAC over a 3 yr period. DOC of the raw water was 5 to 10 mg/l, and the permanganate numbers varied from 10 to 22 mg/l.

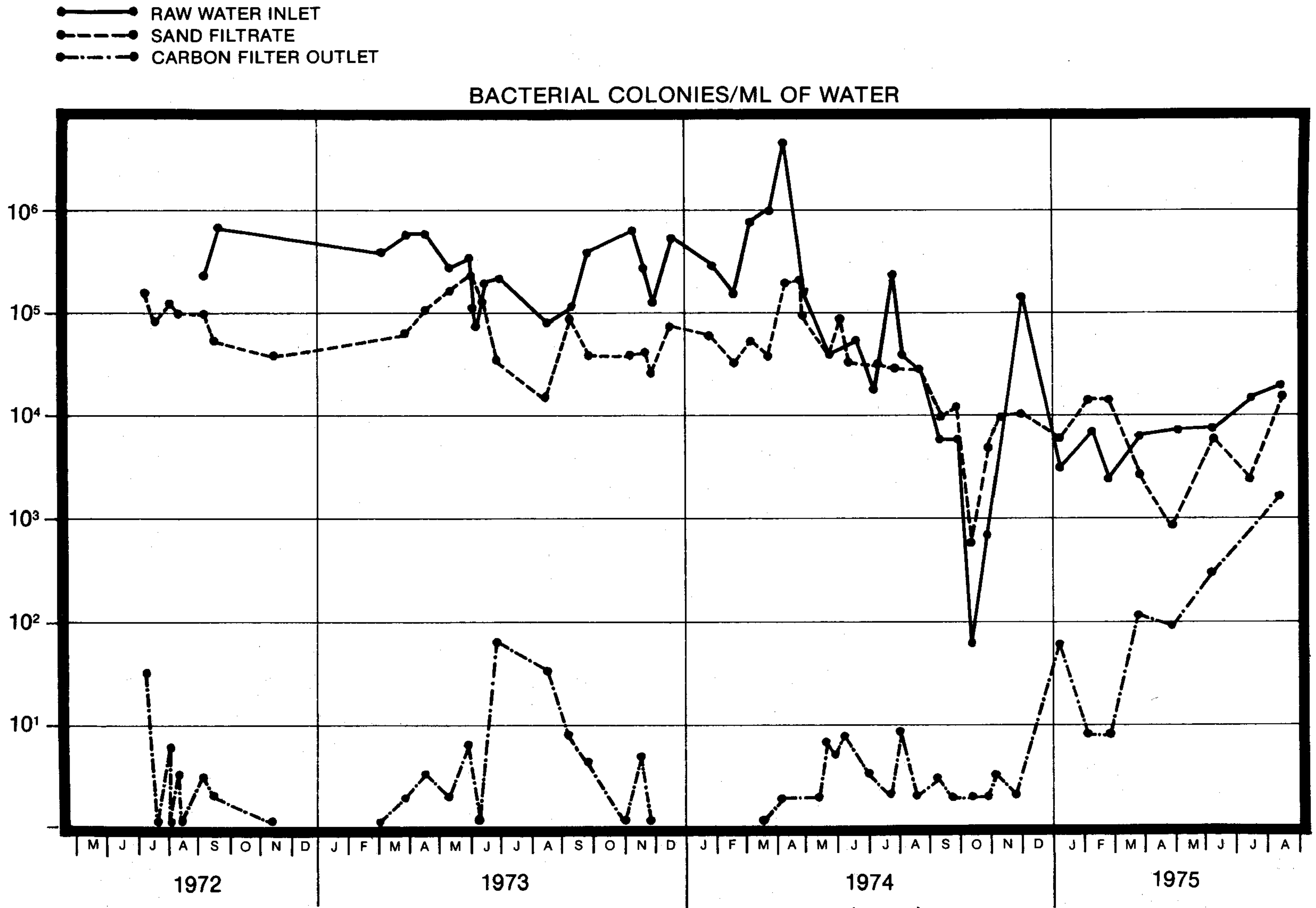
The test facility (Figure 32) consisted of an ozone contact chamber (0.7 m diameter, 3 m high), 2 holding tanks (each 2.5 cu m), a slow sand filter (0.7 m diameter, 3 m height) and an activated carbon filter (0.8 m diameter, 3 m height). Provision also was made to periodically close off the flow of water through the carbon column. At these times, the water in the carbon columns was recycled back through the carbon beds, and analytical parameters were measured. These included DO, DOC, CO_2, ammonia, nitrate, etc. In this manner, material balances were determined.

Eberhardt, Madsen & Sontheimer (1974) concluded that BAC provides the following performance advantages in producing drinking water from the River Weser:

1) 100 to 140 g of DOC is bacterially oxidized/cu m of activated carbon per day. Consumption of oxygen during the summer averaged 360 g/cu m of activated carbon/day and 240 g/cu m/day during winter.

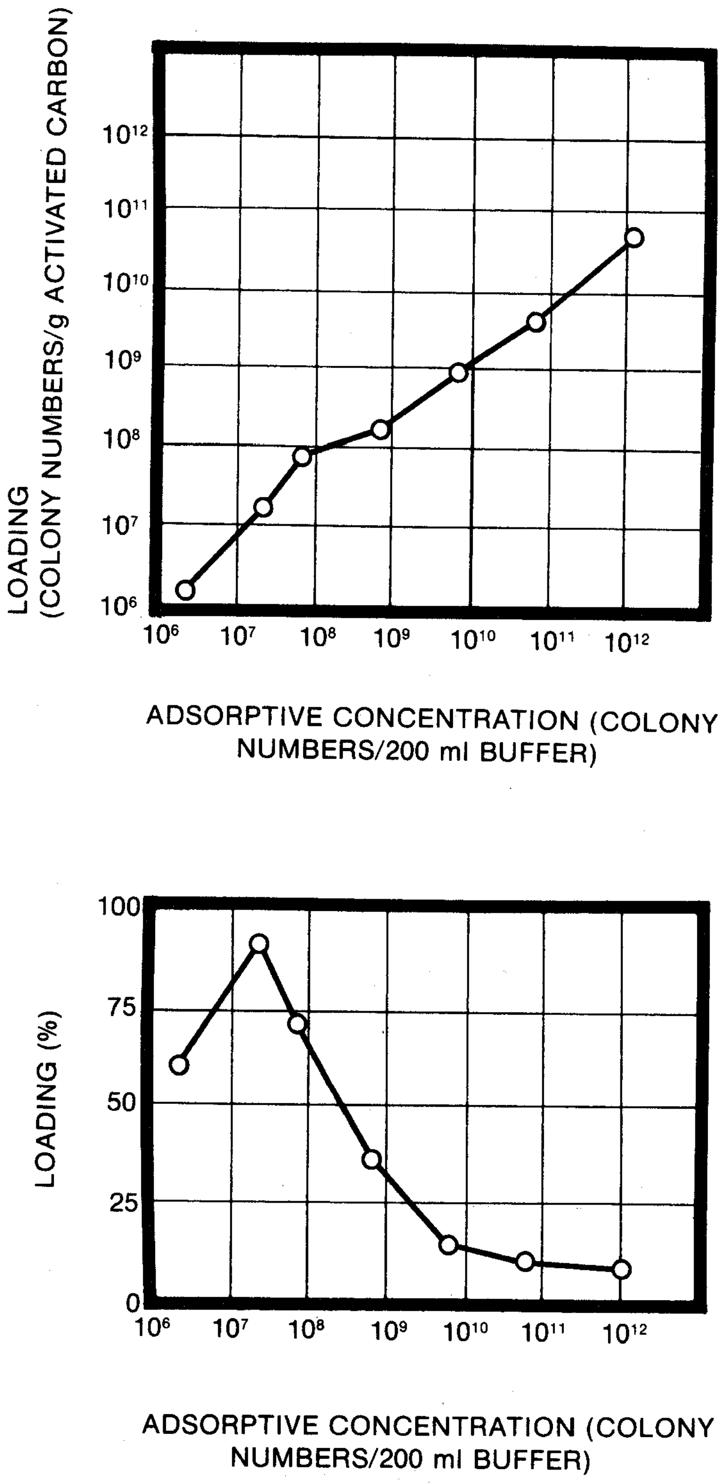
2) After 3 years of operation without regeneration, the total bacterial count reductions averaged 97% and the E. coli reductions averaged 96%.

3) The amount of organic substances removed is dependent upon the concentration in the influent and the residence time in the filter. Theoretical empty-bed residence times of 30 minutes are sufficient for optimum organics removal.



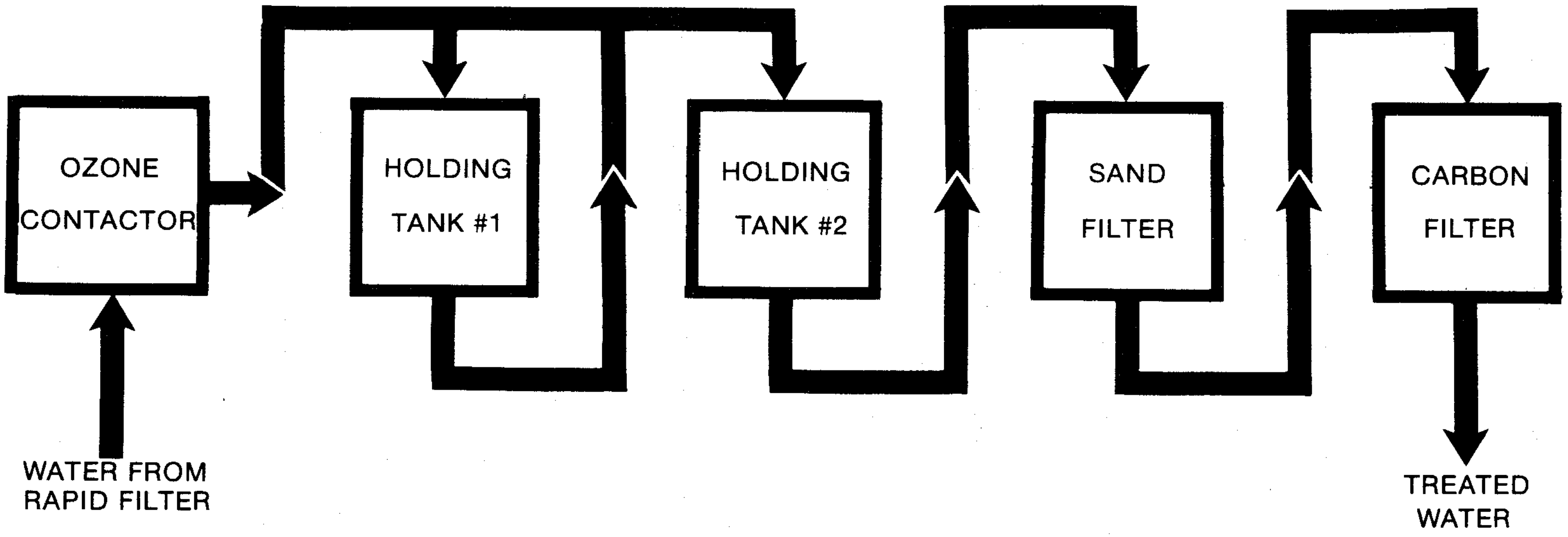
Source: Klotz, Werner & Schweisfurth (1975)

Figure 30. Behavior of microbial populations on activated carbon over 3 years at Wiesbaden, Federal Republic of Germany.



Source: Klotz, Werner & Schweisfurth (1975)

Figure 31. Microbiological loading of activated carbon - dependence on adsorptive concentration.



<u>Source</u>: Eberhardt, Madsen & Sontheimer (1974)

Figure 32. Bremen, Federal Republic of Germany, water works pilot plant.

4) Higher efficiencies of organics removal are obtained at lower filtration rates.

5) Increased efficiencies of organics removal are obtained with smaller grain sizes of GAC.

6) Best results are obtained from activated carbons which have high adsorptive capacities (for organics) and high pore volumes.

7) BAC columns are 10 to 100 times more biologically active per unit volume of carbon than are slow sand filters, probably because of the high concentrations of organic materials in the carbon pores.

Once the bacterial activity in the activated carbon column has been fully established, the organics removal process starts with adsorption of organics, biological mineralization (degradation) of the adsorbed organics and biological regeneration of the activated carbon. The process kinetics at Bremen were found to follow a zero order reaction.

The operative process is adsorption from water containing only organic substances with fresh GAC. However after 2 to 3 months of operation, biochemical processes have reached a steady state and are in full operation. After biological equilibrium has been attained, then adsorption and biochemical degradation (mineralization) of the organic substances both occur in parallel, and either adsorption or mineralization processes may predominate. At constant temperature and bed loading, the mineralization rate was found to be constant and independent of the concentration of organics in the feed water during the Bremen studies.

In other tests conducted at Bremen (Eberhardt, 1975), prechlorination of the water was found to have an adverse effect on the operation and the effectiveness of BAC columns, even with preozonation. Prechlorination reduced both the growth of bacteria and efficiency of removal of the organics by the carbon. In addition, chlorinated organics are less biodegradable. Detrimental prechlorination effects are not related to the oxidative powers of chlorine, since pretreatment with $KMnO_4$ did not reduce the biochemical degradation effectiveness.

Nitrification of Ammonia

Under aerobic conditions, ammonia nitrogen is converted biologically to nitrate ion in two discrete steps:

$$NH_4^+ + 1.5O_2 \longrightarrow NO_2^- + 2H^+ + H_2O \qquad \text{(step 1)}$$

$$NO_2^- + 0.5O_2 \longrightarrow NO_3^- \qquad \text{(step 2)}$$

Step 1 is accomplished by means of Nitrosomonas bacteria; step 2 is accomplished by Nitrobacter. During nitrification, some ammonia-nitrogen becomes part of the cell tissues of the bacteria.

The nitrification process is known to occur in rapid sand filters if the temperature is above 5°C (Eberhardt, 1975). It is only necessary to assure that there is sufficient oxygen in the water and sufficient retention time for the bacteria to work.

Nitrification of ammonia takes place in activated carbon at the same rate as in sand filters, which is not surprising since ammonia is not adsorbed by the carbon. There is some indication, however, that activated carbon may be somewhat more efficient at temperatures below 5°C (Eberhardt, 1975), possibly because of the large surface area and increased pore volumes of carbon as compared with sand. These may provide more space or volume for the nitrifying bacteria.

Ammonia nitrification in carbon columns usually requires 3 months to attain steady state conditions, and during this time there may be problems caused by sudden surges of ammonia in surface waters. However, if fresh activated carbon columns are dosed with small amounts of ammonium salts, nitrification is attained more rapidly, sudden surges in ammonia concentrations can be handled better, and the efficiency below 5°C will also improve (Eberhardt, 1975).

Total nitrification of 1 gram of ammoniacal nitrogen requires 3.56 g of oxygen, according to the stoichiometry (Jekel, 1978):

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O$$

However, Gomella & Versanne (1977) found that only 3.2 g of oxygen is required for nitrification at the drinking water treatment plant at Rouen-la-Chapelle, France. Since aerobic bacteria on activated carbon columns and nitrification processes both consume DO, it is therefore necessary to provide oxygen to the water before it enters the carbon columns. This can be done by simple aeration, by addition of oxygen, or by pre-ozonizing the water.

Aeration will provide DO levels of 6 to 10 mg/l in water, depending upon the temperature of the water. Therefore, if more than 3 mg/l of ammonia is present originally, more DO will be required for nitrification than can be supplied by aeration. In such cases, pure oxygen should be added, which can increase DO levels to as high as 40 to 50 mg/l. These higher levels of DO can be obtained using pure oxygen because the solubility of pure oxygen is not reduced by the presence of large quantities of nitrogen present in air.

It is equally necessary to prevent the presence of bacterial growth inhibitors, such as toxic heavy metals and halogenated organic micropollutants, from entering the BAC media and interfering with the growth of bacteria and/or the progress of biological oxidation.

CASE HISTORIES

Mülheim, Germany

The "Rheinisch-Westfälische Wasserwerksgesellschaft mbH" has taken advantage of BAC to radically change the drinking water treatment process at the 48,000 cu m/day (12.7 mgd) Dohne plant in Mülheim, Germany (Sontheimer *et al.*, 1978). Raw water for this plant is the River Ruhr, which until mid-April, 1977 was treated by breakpoint chlorination for ammonia removal, flocculation, sedimentation then GAC dechlorination and ground filtration. Over the years, ammonia concentrations have increased, requiring prechlorination doses of 10 to 50 mg/l. In turn, these high chlorine doses produced large amounts of chlorinated organics (Table 72) which not only were incompletely adsorbed by the carbon columns and passed through the plant into the distribution system, but also caused frequent regeneration of activated carbon columns (every 4 to 6 weeks).

TABLE 72. ORGANOCHLORO COMPOUNDS AFTER BREAKPOINT CHLORINATION TREATMENT (DOHNE PLANT, MÜLHEIM, FEDERAL REPUBLIC OF GERMANY)

Sampling Point	DOCl* ppb	DOClN** ppb	Sum of Haloforms ppb	$CHCl_3$ ppb
Raw water (Ruhr River)	17	5	9	<1
After flocculation + sedimentation			15	6
After sand filtration	203	30	23	7
After GAC adsorbers	151	17	21	7
After ground passage + chlorination	92	18	23	9

* DOCl = Dissolved Organic Chlorine

** DOClN = Dissolved Organic Chlorine, Non-polar

Source: Sontheimer, *et al.*, 1978

During a 2 year pilot study on the use of pre-ozonation of activated carbon for removal of chlorinated organics, it was found that breakpoint chlorination could be eliminated completely and the BAC operation could be relied upon totally for removal of ammonia. At the same time the DOC was reduced to the desired levels.

This process, involving pre-ozonation of activated carbon, was installed and began operating in mid-April, 1977. After the first 3 months of operation, the performance of the full scale plant process was as effective as was the pilot process at the same stage of development (Sontheimer, 1978).

As the new process at Dohne was installed and operated for the first 90 days (Table 73), the first step was pre-oxidation with about 1 mg/l of ozone with addition of poly-aluminum chloride and lime as flocculants. Pre-ozonation oxidizes manganese and aids in flocculating the organics. After flocculation and sedimentation, 2 mg/l of ozone is added to oxidize dissolved organics. After a retention time of 15 to 30 minutes, the ozonized water is preflocculated using 0.2 mg/l aluminum chloride and 0.1 mg/l polyelectrolyte, filtered (rapid sand), then passed through BAC where the bulk of DOC and ammonia are removed. Filter rates during the first 90 days of plant operations were 18 m/hr (18 cu m/sq m/hr = 18 m/hr) through 2 m carbon bed depths. The GAC used during this period was the old GAC, exhausted during use under the old process.

In November, 1977, the carbon bed depths were increased to 4 m to increase the empty bed retention time to 15 minutes, and the GAC columns were charged with fresh GAC. This has further improved process efficiencies and protects against possible surges in organic pollution or ammonia in the raw water. After more than 1 yr of operation since November, 1977, the GAC columns are performing as predicted from the earlier pilot plant studies and have not yet required regeneration (Jekel, 1978).

After activated carbon filtration, the treated water is sent to ground infiltration (12 to 50 hrs retention time), after which it is chlorinated (0.2 to 0.3 mg/l) and sent to the Mülheim distribution system.

A comparison of the performance of the new process (first 90 days of operation using 2 m deep GAC columns and old GAC) versus the older one is given in Table 74. The DOC of treated water today is less than one-half that of water treated by the old process. Even lower DOC values are expected since the carbon column depths have been increased.

Table 75 shows the bacterial content of waters at the various points in the new treatment process. E. coli counts/100 ml are essentially 0 mg/l after filtration and remain essentially 0 mg/l after BAC filtration as well.

Pilot plant data are presented in Table 76 which show the effects of variation of activated carbons on removal of DOC, inorganic carbon, ammonia and DO. In addition, this table also compares the removal of these same parameters with carbon column depths of 2.5 m and 5.0 m for two different activated carbons.

Removal of ammonia and DO are fairly independent of carbon type or column depth. On the other hand, removals of DOC and inorganic carbon are affected by the carbon type. Most significant, the amount of DOC removed with 5.0 m columns is about 50% higher than with 2.5 m columns, although the amount of inorganic carbon measured increases only slightly.

TABLE 73. PROCESS PARAMETERS AT THE DOHNE WATERWORKS, MÜLHEIM, FEDERAL REPUBLIC OF GERMANY, BEFORE AND AFTER CHANGE OF TREATMENT

Old process	Treatment step	New process
10-50 mg/l Cl_2	Preoxidation	1 mg/l O_3
4-6 mg/l Al^{+3}	Chemical dosing	4-6 mg/l Al^{+3}
0.1 kw/cu m	Power input	2.5 kw/cu m
ca. 0.5 min	Retention time	ca. 0.5 min
5-15 mg/l $Ca(OH)_2$	Flocculation	5-15 mg/l $Ca(OH)_2$
ca. 1.5 hr ret. time	Sedimentation	ca. 1.5 hr ret. time
------	Ozonation	2 mg/l O_3 ca. 5 min ret. time
v* = 22 m/hr h** = 2 m	Activated carbon adsorber	v* = 18 m/hr h** = 2 m
12-50 hr ret. time	Ground passage	12-50 hr ret. time
0.4-0.8 mg/l Cl_2	Safety chlorination	0.2-0.3 mg/l Cl_2

v* = filter velocity = cu m/sq m/hr = m/hr
h** = bed height

Source: Sontheimer *et al.* (1978)

TABLE 74. MEAN DOC AND UV EXTINCTION VALUES FOR THE DIFFERENT TREATMENT STEPS AT THE DOHNE PLANT, MÜLHEIM, FEDERAL REPUBLIC OF GERMANY

Measurement point	1975			1976			April-July 1977		
	DOC mg/l	UV** m^{-1}	UV/DOC	DOC mg/l	UV** m^{-1}	UV/DOC	DOC mg/l	UV** m^{-1}	UV/DOC
Raw water (Ruhr River)	3.9	6.8	1.7	5.0	9.1	1.8	3.6	6.1	1.7
After flocculation + sedimentation	3.2	4.5	1.4	4.0	5.5	1.4	2.9	3.2	1.1
After filtration	3.2	4.4	1.4	3.8	5.4	1.4	2.6	1.8	0.7
After GAC adsorption	3.0	4.0	1.3	3.7	5.3	1.4	2.3*	1.6*	0.7*
After ground passage	1.8	3.1	1.7	2.1	4.0	1.9	0.9	1.6	1.6

** UV extinction measured at 254 nm and extrapolated to a 1 meter long cell

* GAC adsorbers filled with fully loaded GAC used in the old process

Source: Sontheimer *et al.* (1978)

TABLE 75. GEOMETRIC MEAN VALUES OF BACTERIAL COUNTS AT THE DOHNE PLANT, MÜLHEIM, FEDERAL REPUBLIC OF GERMANY, USING OZONE

Sampling point	Bacterial counts/ml		E. coli/100 ml	
	Total M_g*	σ_g**	M_g*	σ_g**
Raw water (Ruhr River)	14,490	2.0	1,620	1.7
After floccn + sedimtn	2,340	4.2	6.7	3.2
After filtration	6,010	4.9	<<1	---
After GAC adsorption	3,700	4.0	<<1	---
After ground passage	27	2.3	<<1	---

* M_g = geometric mean ** σ = geometric standard deviation

Source: Sontheimer *et al* (1978)

TABLE 76. PERFORMANCE OF BIOLOGICAL ACTIVATED CARBON ADSORBERS. MEAN VALUES FOR 6-MONTH OPERATION AFTER A 3-MONTH STARTING PERIOD (DOHNE PILOT PLANT, MÜLHEIM, FEDERAL REPUBLIC OF GERMANY)

GAC		ΔDOC mg/l	ΔInorg C mg/l	ΔNH_4^+ mg/l	ΔO_2 mg/l
type	bed depth m				
LSS	2.5	0.92	0.83	1.31	6.32
LSS	5.0	1.69	0.96	1.34	6.67
ROW	2.5	1.09	0.97	1.31	6.49
ROW	5.0	1.59	1.05	1.34	6.71
NK-12	2.5	0.99	1.36	1.28	6.03
F-400	2.5	1.26	1.11	1.32	6.95
BKA	2.5	1.00	0.97	1.28	5.99

Source: Sontheimer *et al*. (1978)

During pilot plant studies at the Dohne plant with the BAC process, activated carbon columns were found to have operational lives of at least 1 yr, and in some cases 2 yrs, without requiring regeneration. Life of the full scale carbon columns at Dohne is now estimated to be at least 2 yrs (Sontheimer, 1978). No signs of loss in performance of the activated carbon have been noted during the first 12 months of operation, and the carbon columns have not yet had to be regenerated (Jekel, 1978).

Elimination of breakpoint chlorination at the beginning of the Mülheim process eliminates formation of chlorinated organics which caused the activated carbon columns to have to be regenerated every 2 months under the old process. The 10 to 50 mg/l of chlorine previously required for this step now has been replaced with 3 mg/l of ozone. Additional cost-savings associated with this change include the labor which was required with breakpoint chlorination. Formerly, a technician was required to sample water every two hours and to analyze for chlorine and for ammonia. This labor requirement has been eliminated (Sontheimer, 1977a,b). In all, annual cost savings at Mülheim are on the order of $200,000 to $400,000, allowing for depreciation of ozonation equipment and the doubled-size GAC columns (Rice *et al*., 1979).

Rouen-la-Chapelle, France

At the 50,000 cu m/day (13.2 mgd) plant at la Chapelle St. Etienne de Rouvray in Seine Maritime (west of Paris near the Atlantic Ocean), well waters drawn from near the Seine contain 2 to 3 mg/l ammonium ion, 0 to 0.2 mg/l manganese, various micropollutants [detergents, phenols, substances extractable with chloroform (SEC), etc.] and are practically devoid of DO. Since 1968, the ammonia content of the raw water has risen from an average of 0.3 mg/l to an average of 2.6 mg/l. This increase required that the treatment process be improved. Breakpoint chlorination was discarded because it would have required very large contact chambers (close to 7,000 cu m) and would have produced chlorinated organics which then would have to be removed.

After 3 yrs of pilot plant studies, the following process was developed, was installed and began operating in February 1976 (Gomella & Versanne, 1977):

- Pre-ozonation (0.7 mg/l) for Mn, organics and adding DO to the water
- Filtration through quartz sand
- Filtration through BAC
- Ozonation for disinfection (1.4 mg/l)
- Post-chlorination (0.4 to 0.5 mg/l)

Any residual ozone remaining from the preozonation step will be decomposed to oxygen when it enters the carbon column, providing further quantities of DO for the bacteria. This single operation of preozonation assures the following:

- oxygen demands of the materials in water are satisfied,
- water is oxygenated,
- complex, biorefractory molecules are broken down and become biodegradable,
- the content of various micropollutants is lowered,
- manganese is oxidized and precipitates, to be retained on the sand filter so that it does not block adsorption sites on the BAC.

Most of the nitrification occurs in the sand filters. Periodic backwashing of these sand filters to remove oxides of manganese does not upset the action of these bacteria. Similarly, bacterial activity in the activated carbon beds (75 cm deep) is not displaced during backwashing. The BAC beds are backwashed once each month, but have not yet had to be regenerated after more than 2 yrs of operation (Gomella, 1978).

This plant began operating in February, 1976 and showed the performances listed in Table 77 for the first year of operation. The average performance for the first several months of 1977 are stated to be superior to those for the same period of 1976 (Gomella & Versanne, 1977). A case history of the Rouen plant has been published recently by Rice, Gomella & Miller (1978).

BAC IN SEWAGE TREATMENT

In the United States

Independently of results obtained in European drinking water treatment plants, researchers at the Cleveland Regional Sewer District, Cleveland, Ohio, have discovered the same advantages of preozonizing GAC columns (Guirguis *et al.*, 1976, 1978; Prober *et al.*, 1977; Hanna, 1977; Hanna, Slough & Guirguis, 1977).

The Westerly sewage treatment plant (50 mgd) treats 50/50 industrial/-municipal sewage. In order to assure meeting EPA discharge standards for BOD, SS, phosphorus and fecal coliforms, Cleveland Regional Sewer District chose to install a physical/chemical treatment process involving lime addition, flocculation, precipitation, filtration, pH reduction, then GAC for removal of organics, and finally, disinfection with ozone.

During early operation of the 30 gpm pilot plant at Cleveland's Westerly plant, however, it was quickly found that the performance of the GAC columns was unsatisfactory. The amount of BOD and COD being passed through to disinfection was quite erratic, requiring different amounts of disinfectant from day to day, and even from hour to hour. Upon attempted disinfection of the carbon column effluent with ozone, significant reductions in COD values were obtained, indicating that some dissolved organic materials (which were quite reactive with ozone) were not being adsorbed by the activated carbon.

TABLE 77. ROUEN-LA-CHAPELLE (FRANCE) PLANT OPERATIONAL DATA (1976)

Parameter	Raw water	Pre-ozonized	Filtered (sand & GAC)	Post-ozonized	% Elimination
Turbidity	4	--	--	2	50%
Ammonia mg/l NH_4^+	1.80	1.80	0.40	0.26	86%
Mn mg/l	0.15	0.07	0.04	0.02	87%
Detergents mg/l DBS	0.12	0.09	0.06	0.03	75%
Phenols μg/l	6.5	4.0	1.5	0	100%
SEC* μg/l	590	470	250	150	75%
Substances extbl w/-cyclohexane μg/l	1,335	740	535	410	69%

* SEC = substances extractable with chloroform

av. NH_3 content of raw water: 0.3 mg/l in 1968
2.6 mg/l in 1975

Source: Miller *et al.* (1978)

In addition, intolerable sulfidic odors were being generated in large quantities by the anaerobic bacteria which had developed in the activated carbon columns. It was also anticipated that the carbon would have to be regenerated every 30 to 40 days. The original Westerly process and a summation of its major problems is shown in Figure 33.

Provision then was made to add ozone prior to the GAC column of the pilot plant. This caused growth of aerobic bacteria in the column, and the production of sulfidic odors quickly ceased. Soon after, the capacity of the column for dissolved organics was found to have increased dramatically (by a factor of 10). The organic removal performance became steady and the pilot plant column (30 gpm pilot process) was operated for 11 months without the need for regeneration.

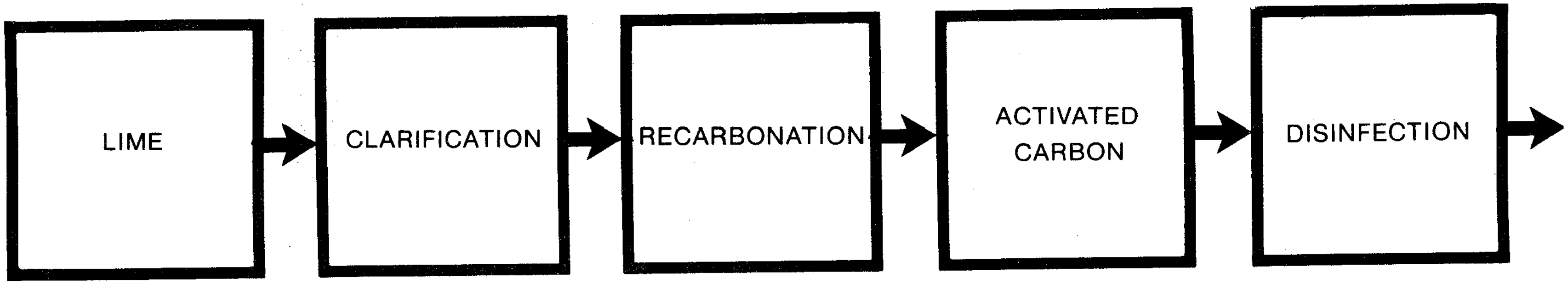
Carbon column effluents after preozonation consistently contained less than 20 mg/l BOD and 40 to 70 mg/l COD (influent to carbon column contained 150 to 200 mg/l COD). During the 11 month initial operating period without carbon regeneration, the cumulative COD loading on the carbon increased to about 1.05 lbs (476 g) of COD/kg of activated carbon. This remarkable behavior is shown in Figure 34. The disinfectant demand of the carbon column effluent became steady, and no further reductions in COD values were observed upon ozonation of the carbon column effluent.

Figure 35 summarizes the total performance of the Cleveland pilot plant BAC column through mid-September, 1977. After a total of 17 months of operation with preozonation, there was still no indication that regeneration was necessary, and the cumulative COD loading had reached 1.6 lbs/lb of GAC by mid-September, 1977 (Hanna, 1977).

Other pertinent data relative to the Cleveland Westerly plant research have been reported by Prober, Hanna & Guirguis (1977). A fresh activated carbon column without preozonation or preoxygenation reached a steady state within 1 week after being placed in operation. Soluble COD concentration in the effluent quickly increased until it was within about 20 mg/l of the influent concentration (about 90 mg/l). Over a long term average, the column was steadily removing about 20 mg/l of COD, regardless of the influent COD concentration, which varied between 80 and 110 mg/l.

Optimum performance of the Cleveland preozonized activated carbon columns occurs when the influent DO content is about 20 mg/l and when the preozonation dose is 5 mg/l. At steady state operation, the BAC columns remove 0.005 lb of COD/lb of activated carbon/day. DO uptake of the BAC columns averages 14 mg/l (Prober et al., 1977).

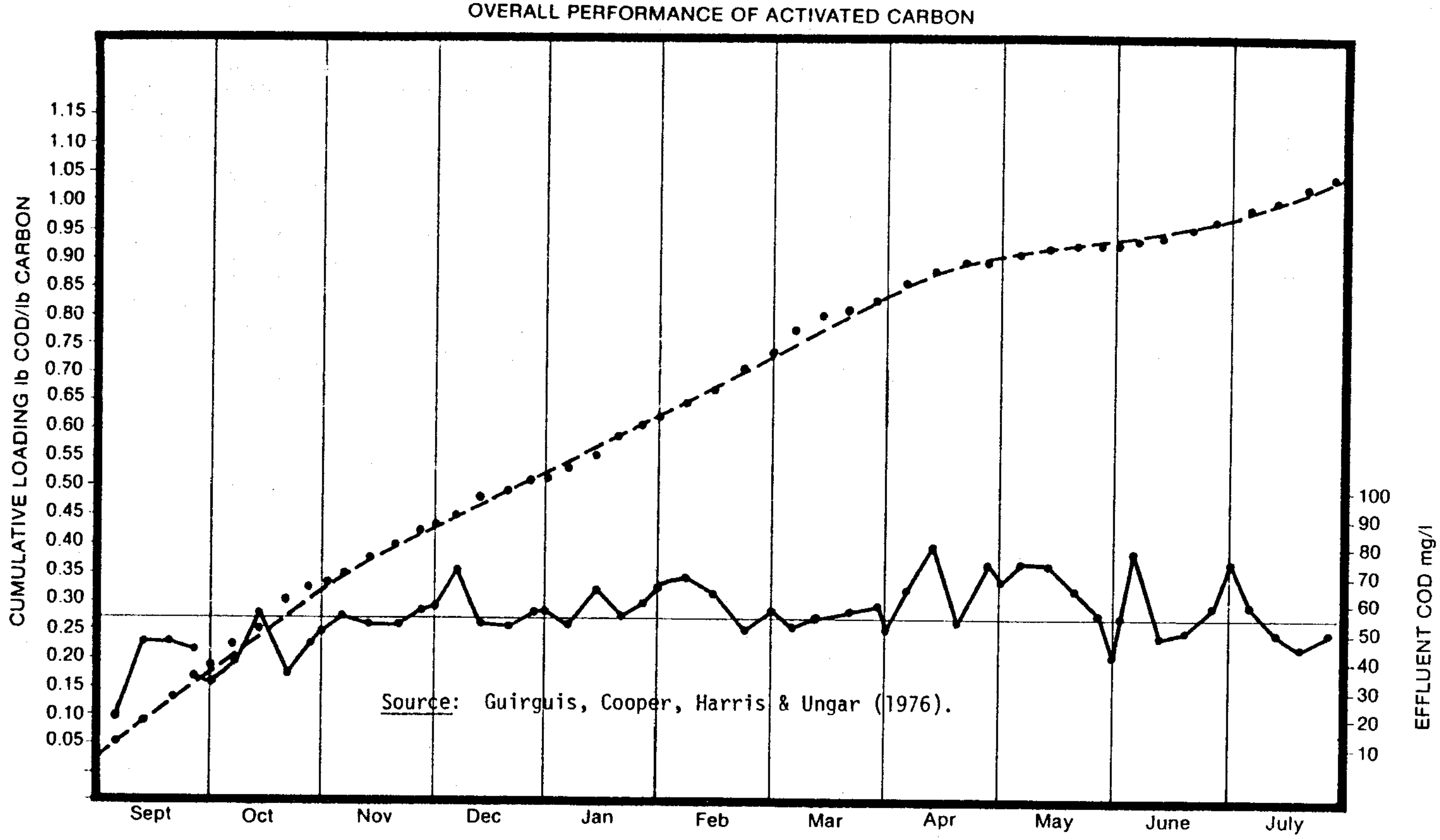
At present, Cleveland Regional Sewer District is designing a modification to the 50 mgd Westerly plant which will incorporate 6,700 lbs/day of ozone generation capacity for preozonizing the activated carbon at a dosage of 5 mg/l.



Problems:

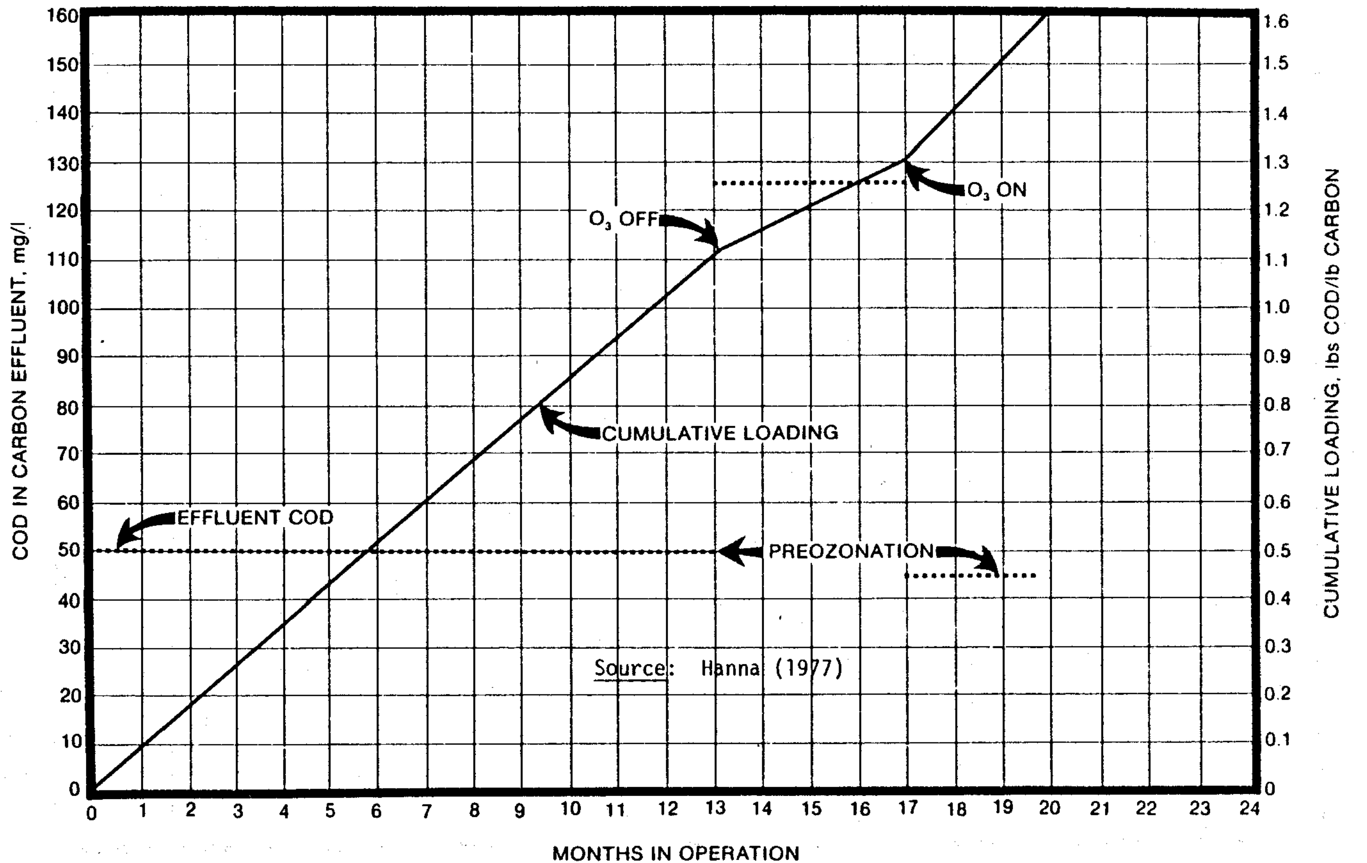
- Regenerate Carbon Every 30-40 Days
- Sulfidic Odors
- Erratic TOC Reductions
- Erratic Disinfection Demands

Figure 33. Westerly plant, Cleveland, Ohio -- original design.



Source: Guirguis, Cooper, Harris & Ungar (1976).

Figure 34. Performance of preozonized activated carbon at Westerly plant, Cleveland, Ohio.



Source: Hanna (1977)

Figure 35. BAC performance at Cleveland Regional Sewer District.

In Israel

Preliminary studies reported by Wachs et al. (1977) on treatment of domestic sewage with ozone, then BAC, also appear striking. These researchers presented results showing that effluents with TOC contents of less than 2 mg/l can be obtained by this technique, albeit with rather large ozone dosages (100 to 120 mg/l).

Ozone-containing air (19 g of ozone/l of air) was passed through lime treated sewage at the rate of 10 l/hr. Using ozone contacting times of 30 minutes, COD removal efficiencies were found to be only as high as 50% at pH 8 to 9 (Table 78, Figure 36). Even at pH 11, more than 170 mg/l of ozone dosages were required to lower the COD by 50%.

Filtrasorb 300 activated carbon columns 2.5 cm in diameter and 70 cm high were prepared and used to filter the ozonized lime treated effluents at flow rates of 3 bed volumes/hr. Ozonized effluents were stored "a number of hours" before being introduced into the activated carbon columns.

Figure 37 shows that ozonized, lime treated effluent having an average COD of 33.7 mg/l upon filtration through BAC produced effluent having an average COD of 3.4 mg/l. The carbon column was operated 12 days, during which time the effluent COD concentration ranged from 0 mg/l to 10 mg/l. Backwashing was performed on the eighth day of operation.

POTENTIALS OF BAC FOR TREATING INDUSTRIAL WASTEWATERS

During this survey of the state-of-the-art of Ozone for Industrial Water and Wastewater Treatment, only 3 of the technical articles reviewed described the conjunctive use of ozonation followed by GAC. Enhancement of the biological activity in the carbon media was not considered in these articles.

In Vienna, Austria, a car wash built in 1970 recycles 19,915 gpd of wash water, ending with ozonation followed by GAC (Baer, 1970). However, this article was written as the water treatment system was installed, and the biological aspects of the carbon medium were not considered in the description of the process.

In Japan, the Kanebo Company installed an ozone/GAC treatment system at its Nagahama factory in 1974 (Anonymous, 1974). This system handles 3,300 cu m/day (0.87 million gal) of dyeing wastewaters. The "synergistic effect" of the sequential combination of ozonation followed by GAC is noted in this article, which also states that "the combined use of ozone and activated carbon, as compared with the separate use of each, will often produce a doubled effect and result in low investment costs". This statement is not explained further, however.

At the Nagahama factory, dyeing wastewaters are sent to a 600 cu m holding tank from whence it is passed, consecutively, through 2 ozonation

TABLE 78. OZONATION OF LIME-TREATED EFFLUENTS IN ISRAEL (1). REACTION RATES, COD REMOVAL AND pH CHANGES

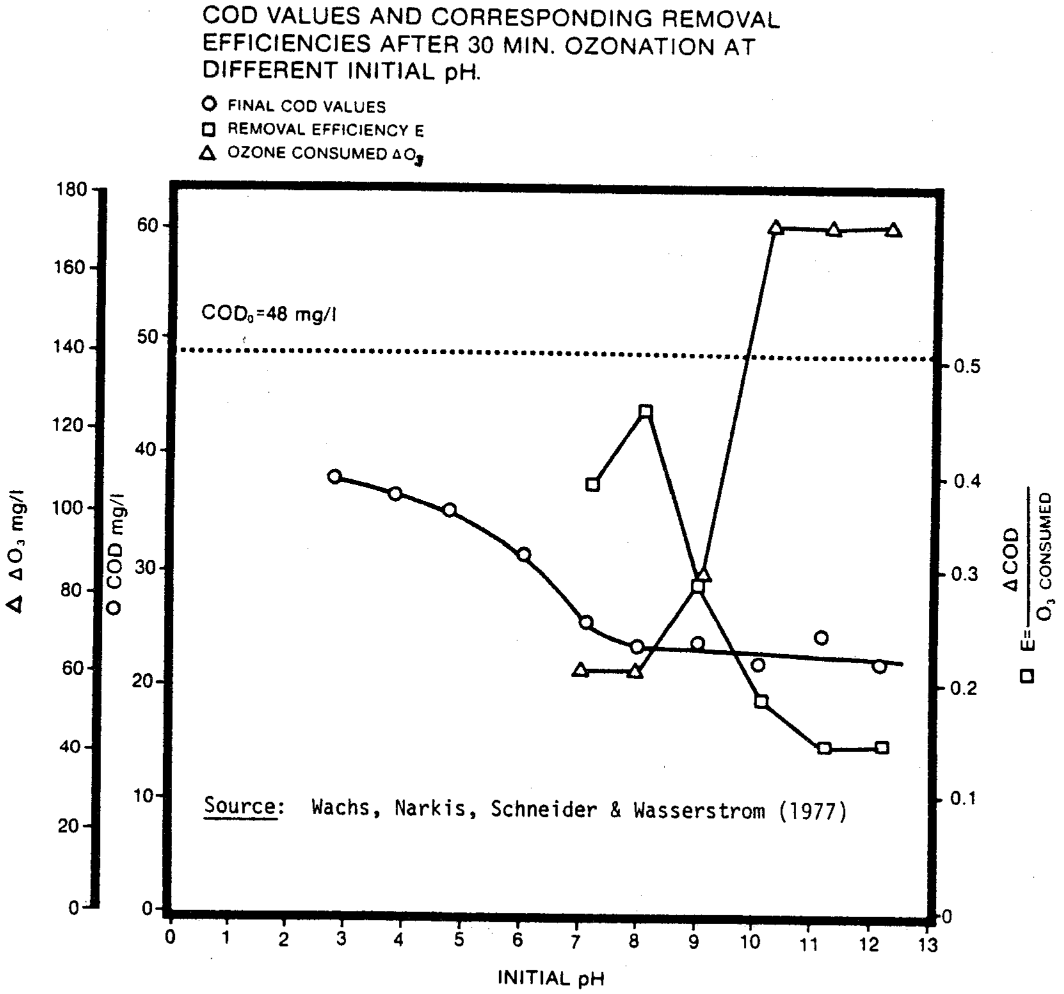
COD mg/l	pH		K x 10^3 min^{-1}	COD_{60} mg/l	% COD removed in 60 min
	initial	final (2)			
37	11.6	11.2 (60)	4.7	19	48%
33	11.2	11.2 (90)	5.6	15	54%
33	8.3	5.5 (90)	3.2	21	36%
40	11.2	11.1 (70)	4.9	20	49%
40	7.2	6.2 (70)	2.6	28	30%
(3) 26	8.3	7.7 (90)	2.4	19	28%

(1) Flow rate of gas stream into reactor was 0.4 l/min. Concentration of ozone in gas stream varied between 18 and 19 ppm.

(2) In brackets: length of ozonation time, in minutes.

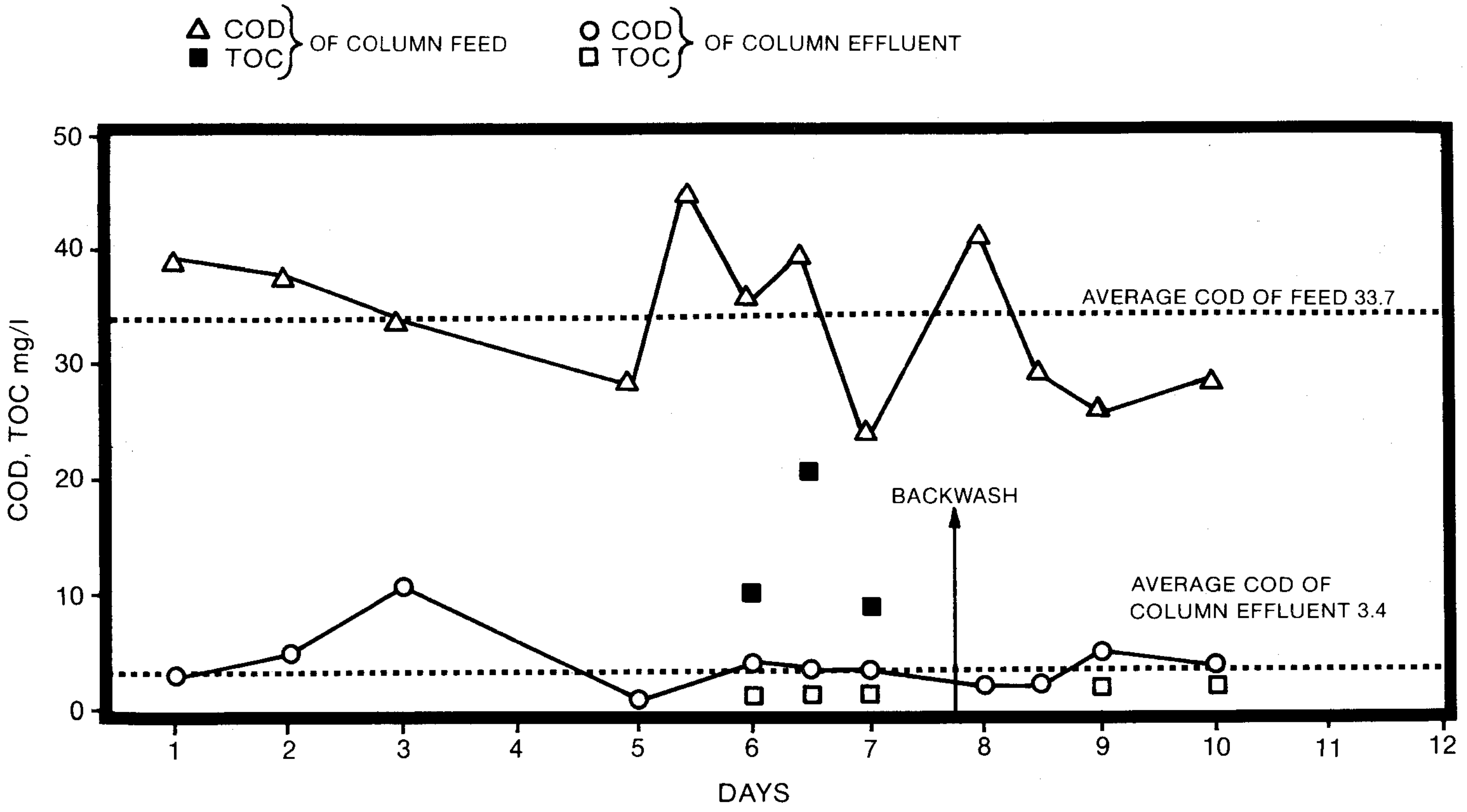
(3) Ammonia desorption practiced priot to ozonation.

Source: Wachs, Narkis, Schneider & Wasserstrom (1977)



Source: Wachs, Narkis, Schneider & Wasserstrom (1977)

Figure 36. Ozonation of Israel lime treated sewage effluents without BAC.



Source: Wachs et al. (1977)

Figure 37. Biologically extended activated carbon treatment of ozonated effluent.

reaction towers, each 2,800 mm in diameter and 5,000 mm in height. The specifics of ozone contacting in this installation are not described, but ozone is supplied by means of 3 generators, each capable of generating 2.4 kg/hr of ozone from air (7.2 kg/hr total ozone generation capacity). At its maximum addition rate, ozone is dosed at 50 mg/l, and dye colors and dissolved organic substances are decomposed at this point.

Ozonized wastewater passes through an intermediate tank, then is sent upflow at 17 m/hr through a pulse head type carbon adsorption tower packed with Pittsburgh GAC. The carbon adsorption tower is 3,200 mm in diameter, 7,500 mm in height and contains about 38 tons of GAC. After carbon adsorption, the pH of the treated wastewater is adjusted and the water is discharged.

Spent GAC is regenerated on-site at the rate of 3.3 tons/day, using a Nicols-Herreshoff vertical type gas furnace. Exhaust gases from the ozone contacting tower are heated and passed through a 500-liter tower packed with activated carbon. This treatment destroys residual ozone remaining in the off-gases.

Pertinent wastewater parameters obtained on these dyeing wastewaters using the ozone/GAC process are listed in Table 79, and a schematic drawing of the plant is shown in Figure 25 in Section 5, under Textiles. Major points to be noted are that the BOD values of ozonized wastewaters are about the same as those of the raw wastewater, and that COD values are lowered by 10 to 15% by ozonation. After GAC adsorption, both BOD and COD values have been reduced 60 to 80% from those of the raw wastewater. There is no recognition in this article of biological activity in the carbon tower.

TABLE 79. RESULTS OF OZONE/GAC TREATMENT OF DYEING WASTEWATERS

Parameter	Initial	After Ozone	After GAC
Color*	0.2-0.35	0.05-0.1	0.02-0.05
pH	6.0-8.0	6.0-7.0	6.5-7.5
SS (mg/l)	8-15	5-10	0.6-2
BOD (mg/l)	110-160	100-140	20-50
COD (mg/l)	120-170	100-150	20-50
Phenol (mg/l)	1-2	0.1-0.2	0

* color determined by average of absorbance at 430, 530, 550, 610 & 660 nm

Source: Anonymous, 1974

It should be noted that the COD values of the raw and finished wastewaters are similar in magnitude to those of the Cleveland Westerly sewage treatment plant, where the pilot plant activated carbon column has operated biologically for 20 months without requiring regeneration. Although Cleveland's influent contains 60/40 municipal/industrial wastes, whereas Nagahama's influent is specifically dyeing wastewater, Cleveland obtains extended performance of its BAC column using a preozonation dosage of only 5 mg/l, whereas Nagahama employs a maximum of 50 mg/l dosage of ozone.

The Nagahama factory ozone/GAC installation is claimed to be completely free of sludges (normally produced by coagulative precipitation methods or activated sludge), only a small plant area is required for the installation (about 500 sq m) and the costs of operation of the process are 34¢/1,000 gal of wastewater treated.

The synergistic effect of following ozonation with GAC adsorption during treatment of textile wastewaters also was noted by Mizumoto and Horie (1974). They concluded that the overall cost of a wastewater treatment plant using both ozone and GAC in sequence would be less than a plant using either process alone, to attain the same level of treatment. Ozone treatment removed only about 10% of the BOD, while activated carbon removed 60% to 80%. Ozonation removed most of the color and GAC adsorbed that which remained.

Kawazaki (1965) studied the ozonation of surface active agents. Greater than 90% decomposition was obtained using a 5-fold excess of ozone. On the other hand, these surface active agents also were adsorbed onto activated carbon, after which Kawazaki "regenerated" the activated carbon with ozone. Details of this "ozone regeneration" of activated carbon are not given in the English abstract of this article.

In principal, any industrial wastewater which contains biodegradable dissolved organic materials and/or ammonia and which does not contain components which are detrimental to biological activity (such as heavy metals or toxic substances) can be processed by the BAC technique. Feed waters which do contain materials toxic to biological proliferation should be suitably pretreated to remove those contaminants.

Heavy metals can be removed by oxidation or chemical coagulation, flocculation and filtration. Many biologically toxic materials can be removed in the same manners. Oxidation can be combined with the preozonation step of the BAC process. For example, ferrous and manganous ions are readily oxidized by ozone to ferric and manganic ions, respectively, which rapidly hydrolyze, then coagulate, settle, and are readily removed from solution by filtration. Additionally, Netzer & Bowers (1975) have shown that aluminum, cadmium, chromium, copper, lead, mercury, nickel, silver and zinc also can be removed by ozonation of lime treated waters, followed by pH adjustment.

For organic materials which are toxic to bacterial activity, an understanding of the nature of specific organic materials present is necessary to determine the specific oxidative type of pretreatment which should be utilized.

For example, if the toxic organic materials do not contain halogens and contain carbon-carbon unsaturation, they can be converted to oxygenated carbonaceous materials during preozonation by attack at the unsaturation. Oxidation with ozone during the pretreatment step will occur with unsaturated aliphatic organics as well as aromatics (phenols) and even many polycyclics, such as phenanthrene and benzpyrenes.

Organic compounds which contain halogens are not as rapidly biodegradable as are organics which do not contain halogens, nor are they as reactive with strong oxidizing agents, including ozone. On the other hand, the combination of UV radiation with ozone (Prengle et al., 1978, 1977, 1976, and references cited therein) or of ultrasound with ozone (Sierka, 1977) has shown remarkable ability to degrade these refractory organic compounds in a much shorter time than can ozone alone. If such materials are present in industrial wastewaters to be treated, consideration should be given to these synergistic oxidation techniques.

In addition, it has been shown (Gilbert, 1978, 1977) that small amounts of hydrogen peroxide also enhance the oxidative powers of ozone toward organic materials normally resistant to ozonation.

Finally, the ozone/UV or ozone/ultrasound combination is capable of breaking carbon-chlorine bonds in many organic compounds normally refractory to ozone. Arsovic & Burchard (1977) showed the degradative effects of ozone/ultrasound on the formation of chloride ion when chlorobenzenes and chlorophenols are oxidized. Since it is generally accepted that the carbon-halogen bond is the moiety in the organic molecule which renders it more resistant to biodegradation, if this bond can be destroyed in pretreatment, the oxidized organic fragments, without covalently bonded halogen, will be more rapidly biodegraded in the subsequent biologically active sand and GAC filters.

DESIGN PARAMETERS

In designing BAC systems for removal of dissolved organics and conversion of ammonia, it is important to consider parameters such as column or bed size, wastewater flow rates, empty bed contact time of water with GAC, temperature of operation, preozonation dosage, the need for sand filtration prior to GAC adsorption and the need for supplemental oxygen prior to the BAC medium. If the GAC medium is too small, and the water contaminants are of high concentration and the flow rates are high, obviously the wastewater contaminants will break through the carbon rapidly. Even though the bacterial activity may be in full operation, the rate of pollutant charge will be greater than the rate of pollutant removal, by means of biological processes.

Biological degradation of dissolved organic materials will be faster the more oxygen the compounds contain. Therefore, the amount of preozonation required will be determined by the elemental composition of the dissolved organics as well as their structures (which will affect their reactivity with ozone). It is possible that some organic pollutants are sufficiently oxygenated that preoxidation with ozone will not be required. In such events, it should be acceptable merely to apply sufficient DO before the sand filter (by aeration or by oxygenation) to promote the aerobic bacterial growths in the prefilter and in the GAC media.

In operating BAC columns or beds, it is important to monitor the influent and effluent to the BAC medium for DOC, ammonia (if present), CO_2 (formed by biological conversion of DOC) and DO, in order to determine the rate at which biological decomposition is occurring under the specific conditions at hand. Similar analyses of the influent to the prefilter also will be useful to determine the degrees of pollutant removals obtained in this step.

COSTS

Because BAC systems have not yet been defined, optimized and installed for treating industrial wastewaters, it is not possible to offer accurate cost estimates of specific systems for specific wastewaters. In addition, costs of specific systems will be affected considerably by the amount of preozonation required, the volume of carbon media to be employed, as well as the wastewater components and their concentrations. Nevertheless, the following projections are applicable from the drinking water treatment field where both ozone and GAC have been employed for a number of years.

Miller et al. (1978) surveyed the costs for ozone treatment of European drinking water supplies. With average ozonation doses ranging from 1.5 to 3.0 mg/l and with ozone generation capacities of 1,000 to 3,000 lbs/day, the ozonation costs range from 1.75 to 4.0¢/1,000 gal of water treated. These figures include the capital costs for air preparation equipment (normally used in drinking water treatment plants), ozone generation, ozone contacting, treatment of off-gases from ozone contacting, instrumentation and automation for the ozonation subsystem, and installation and housing for the ozonation system, operation, maintenance and amortization (usually over 20 yrs at 8% interest).

The rather broad range of European ozonation system costs is affected mainly by the cost of housing for the ozonation system and the local cost of electrical energy. If the ozonation system is housed in a separate building, as opposed to being retrofitted into an existing building, then the costs will be about 25% higher (Miller, 1978).

In many industrial situations, it may be advantageous to utilize oxygen for the generation of ozone. In such cases the electrical cost for ozone generation will be effectively halved, since double the concentration of ozone is generated per unit time and per unit of electrical energy input to the generator. However, contactor off-gases will have to be recycled in this instance, in order not to lose the large amounts of oxygen which will be present in the contactor off-gases. This will be an added cost, which may or may not balance the savings in energy obtained by using oxygen as the ozone generating feed gas instead of air.

Recent estimates by the U.S. Environmental Protection Agency Water Supply Research Laboratory (Clark & Stevie, 1978) have been made for GAC installations to satisfy the requirements of EPA's newly proposed regulations for the control of organics in drinking water (U.S. EPA, 1978). For a plant treating 12 to 13 mgd of water, the estimated cost of activated carbon adsorption will be about 22¢/1,000 gal of water treated. This estimate is based upon the following considerations:

- the cost of installed capital (GAC columns plus reactivation facilities) is equal to the cost of operation and maintenance
- GAC columns are 13 ft deep and 12 ft in diameter
- empty bed contact time is 18 minutes
- on-site regeneration of GAC will be required, and capital costs for regeneration are equal to the capital costs of the GAC installation
- GAC regeneration will be conducted every 2.4 months

Assuming that a properly designed and operating BAC facility would reduce the regeneration requirements for GAC, to allow the wastewater treatment to send spent carbon out for regeneration on a contract basis, then the 22¢/1,000 gal figure would be lowered by about one-third, to the 14 to 15¢/1,000 gal range (Table 80). To this should be added the costs for ozonation treatment, which EPA estimates (Clark & Stevie, 1978) to be 1.8¢/1,000 gal per mg/l dosage of ozone in the 12 to 13 mgd treatment plant size.

TABLE 80. ESTIMATED COSTS FOR GAC TREATMENT*

EPA estimate (Clark & Stevie, 1978)	:	22¢/1,000 gal
● plant size	:	12 to 13 mgd
● GAC column size (1 unit)	:	13 ft deep x 12 ft wide
● empty bed contact time	:	18 minutes
● GAC regeneration	:	on-site, every 2.4 months
● cost of capital	:	11¢/1,000 gal
● operation & maintenance cost	:	11¢/1,000 gal
if off-site regeneration	:	14 to 15¢/1,000 gal

* These estimates are made for treating drinking water

This would mean that for a plant treating 12 to 13 mgd of wastewaters requiring a 5 mg/l preozonation dosage, GAC costs would be about 15¢/1,000 gal, plus 5 x 1.8 = 9¢/1,000 gal ozonation costs, or 24¢/1,000 gal (Table 81). This figure should be compared with the costs at:

(1) the Nagahama dye waste treatment plant in Japan, of 34¢/1,000 gal for treating 0.87 mgd using a maximum ozone dosage of 50 mg/l (Anonymous, 1974) and

(2) the Rouen-la-Chapelle water treatment plant in France, of 46¢/1,000 gal, which produces 12 mgd of drinking water using a 2-stage ozonation process (total ozone dosage = 2 mg/l) and BAC (Rice, Gomella & Miller, 1978).

TABLE 81. PROJECTED COSTS FOR BAC TREATMENT

BASES

- plant size : 12 to 14 mgd
- preozonation dosage : 5 mg/l
- GAC column size : 13 ft deep x 12 ft diameter
- empty bed contact time : 18 minutes

ESTIMATED COSTS

- ozonation : 1.8¢/1,000 gal/mg/l dosage x 5 = 9¢/1,000 gal
- GAC : = 15¢/1,000 gal

TOTAL 24¢/1,000 gal

SUMMARY

In European drinking water treatment plants, BAC media, properly designed and operated, greatly extend the period of activated carbon performance before regeneration is required. In the absence of chlorinated organics, properly designed and operated BAC columns in drinking water treatment plants are expected to operate effectively for periods of at least 2 to 3 yrs without requiring regeneration. In the presence of chlorinated organics, however, breakthrough of these halogenated materials will occur sooner, and require the carbon to be renegerated at that time.

A pilot plant BAC column has been operating efficiently at Cleveland's Westerly sewage treatment plant using a 5 mg/l preozonation dosage for 60/40 municipal/industrial wastewater. This column has not required regeneration for over 21 months, and its performance in removing COD and BOD still is as good as it was in the virgin state (Hannah, Slough & Guirguis, 1977).

Extension of the BAC concept to industrial wastewater holds promise for being able to provide a cost-effective treatment for those wastewaters containing ammonia and dissolved organic materials which can be converted to rapidly biodegradable materials upon ozonation. Materials toxic to aerobic biogrowths in the activated carbon media must be removed by a pretreatment step. Halogenated organics, which are known to be only slowly biodegradable, might be oxidized in pretreatment by a combination of ozone with UV radiation or ultrasonics. Demonstrations of the BAC process are needed with specific industrial wastewaters before its potentials can be determined.

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-80-060	2.	3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE Ozone for Industrial Water and Wastewater Treatment, A Literature Survey	5. REPORT DATE April 1980 issuing date
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) and Myron E. Browning Rip G. Rice Allied Chemical Co., Jacobs Engrg. Group, Wash.,D.C. 20005 /Syracuse, NY 13209	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Jacobs Engrg. Group and Allied Chemical Company Wash., D.C. 20005 Syracuse, NY 13209	10. PROGRAM ELEMENT NO. C33B1B
	11. CONTRACT/GRANT NO. Grant No. R-803357
12. SPONSORING AGENCY NAME AND ADDRESS Robert S. Kerr Environmental Research Laboratory Office Of Research And Development U.S. Environmental Protection Agency Ada, Oklahoma 74820	13. TYPE OF REPORT AND PERIOD COVERED Final Report/7-1974 to 7-1977
	14. SPONSORING AGENCY CODE EPA/600/15
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

The project explored the technology of ozonation applicable to industrial water and wastewater treatment. The final report documents existing equipment, extent of application and practical usage, contract systems, monitoring and detection devices, general and specific economics, and most recent acceptable procedures.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ozonation, oxidation, industrial wastes, industrial waste treatment, activated carbon treatment	Ozone wastewater treatment, biological activated carbon treatment	68.d.

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 394
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1980-657-146/5656

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