

OZONE IN WATER AND WASTEWATER TREATMENT

Evans

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FOREWORD

The terms "environmental protection" and "ecology" are broadly accepted in our society. They are recognized by every stratum of industrial, commercial, and governmental organizations to be the driving force for an unprecedented unity of effort.

Since the impact of pollution is great, the efforts to reverse the trend must be greater. Much of the pollution of the nation's waterways comes from municipal and industrial sources which, fortunately, can be controlled. Water quality standards are becoming more strict, and the concept of minimal polluttional discharge is being approached.

For these reasons, we reevaluate the technology to satisfy today's needs in terms of current and future requirements for stream standards that preserve water quality, protect public health, and generally improve the environment.

While the "conventional" methods of waste treatment have been improved, standards of quality have surpassed the capabilities of many of these methods. Therefore, some old concepts which are no longer of value should be replaced by an advanced technology designed to meet future needs.

Ozonation is both an old and a new concept. It has been used for sixty-six years for sterilization, for not quite as many years in industrial and commercial applications, and most recently, for wastewater treatment.

In view of resurging interest in ozonation, it seems appropriate to put the subject in sharper focus through a series of articles on ozone applications in water and waste treatment technology. These presentations will show how an old concept can be reevaluated in terms of modern requirements.

The first chapter on the state of the art generally summarizes what the succeeding chapters present in detail. Early application in water disinfection, deodorizing, and decolorizing is reviewed. More recent application in water and wastewater treatment is discussed briefly.

One of the incongruous aspects of this chemical species is the difficulty encountered in the specific analytical determination. The lack of suitable techniques for analysis in low concentrations has been one of the obstacles limiting its study. This is the value of the second chapter which reviews the analytical methods for ozone in water and wastewater. The details of the development of a new analytical procedure as it applies to ozone disinfection are given along with a discussion of the data, a suggestion of the mechanism of reaction, and a description of the effects of interferences most likely to occur in water and wastewater analysis.

Current interest in ozone extends to its use as a powerful oxidant for organic matter in waste streams. Such a use was merely of academic interest until a few years ago, but this is not the case today. The third chapter explores the chemical considerations which held in the evaluation of the potential that ozone as an oxidant could have in wastewater treatment and pollution control applications. It presents a survey of the ozonation chemistry of organic compounds emphasizing functional groupings which react with ozone and the mechanism of these reactions in an aqueous medium.

With this information as a background, chapter four exemplifies how theoretical considerations hold up in the harsh reality of wastewater treatment situations. The current view of ozone treatment for further purification of secondary treatment plant effluents is expanded by the description of a pilot plant study.

Because of the interplay of many circumstances relating to the quality of environment, there has been considerable renewed interest in the use of ozone for disinfection. This potential use is in disinfection of heavily polluted waters used for municipal supplies and of wastewater treatment plant effluents. Although there has been much work done in pure and single-culture systems, chapter five points out that results from such studies are rarely comparable. Chapter six discusses the advantages and disadvantages of ozone as a disinfectant and describes a disinfection study using ozone in both pure-water systems and in a water containing various concentrations of raw domestic sewage.

Based upon promising results of apparent feasibility in proof of theory, the use of ozone and the practice of ozonation has been progressing from an art to a science. The last two chapters present supporting evidence of this fact. These two chapters also present practical aspects

of ozone and ozonation which demonstrate that ozone indeed has advanced beyond the stage of being an academic curiosity.

The editor sincerely appreciates the time and effort each contributor has devoted to this publication. Special thanks is extended to Dr. Nina McClelland, National Sanitation Foundation; for her special interest and help.

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July, 1972

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CHAPTER I

OZONE TECHNOLOGY:

CURRENT STATUS

Francis L. Evans III

The literature is replete with such terms as "resistant," "perdurable," and "refractory" to describe materials that are not removed by waste treatment methods, whether these methods be conventional or "advanced."

The point is that, in view of today's needs and tomorrow's necessarily more stringent requirements, the quantity of materials remaining after treatment must be reduced. Although advances are being made to extend the potential of the conventional treatment methods, their potential has a limited value.

Chemical oxidation has the potential for removing from wastewaters those organic materials which are resistant to other treatment methods whether those methods are biological or the longer trains of processes known as tertiary (or advanced) treatment. Chemical oxidants have not been generally considered for use in domestic wastewater treatment because of the expense of materials and related costs and because of the lack of demand for such vigorous treatment.

However, it is not generally realized and accepted that, since the degree of treatment must be enhanced, there must be an increase in capital expenditure. It is likely, though, that the cost of this treatment will not be beyond the limits of economic acceptability.

The desirable characteristics of a chemical oxidant are that it be easily and economically available and that it not contribute secondary pollutants to the waste stream. The

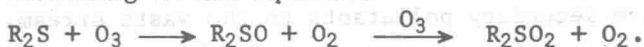
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oxidative destruction of organic compounds—resulting in the formation of carbon dioxide, water, and oxygenated fragments of the original molecule—occurs by bond fission. According to Waters¹ this may be accomplished via two paths: homolytic reactions, in which the electron pairs are disrupted and one of the electrons is transferred to the oxidant; and heterolytic reactions, in which the electron pair is transferred or partially transferred as a unit to the oxidizing substance. As a chemical oxidant, molecular oxygen has no peer and, given sufficient time, will react with any and all organic materials.

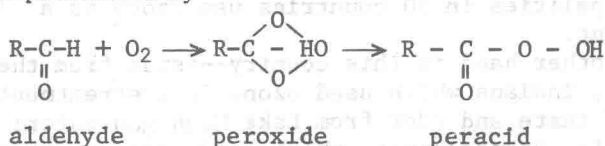
The possible reactions of molecular oxygen can be broadly classified as oxygen insertion or noninsertion reactions.² These are reactions in which oxygen itself combines with the substrate, and reactions in which oxygen merely serves as an oxidizing agent. Since the processes occur more or less spontaneously, they are referred to as "autooxidations."³ However, the rates of reaction are generally too slow to be of any value in waste treatment—biological systems excepted. It is not improbable that autooxidation mechanisms proceed via free radicals including chain mechanisms once the production of the free radical has been initiated. Autooxidation is not, however, necessarily a chain reaction, but the interpretation of some reactions can be made only on that basis.⁴

The oxidative power of ozone has for some time been used in the ozonolysis of olefins: the reaction of ozone with a double bond which leads to cleavage of the bond. The interest in ozonolysis reaction falls into three general areas:⁵ use of ozone to locate unsaturation in structure determinations; use of the reaction synthetically (i.e., to convert unsaturation into ketones, aldehydes, alcohols, or acids; and, finally, study of the mechanism of the reaction.

The reactions of ozone as an oxidant appear to be of at least two distinctive types.⁶ One involves an electrophilic attack by ozone; the other an ozone-initiated oxidation in which ozone serves as the reaction initiator and oxygen is the principal reactant. Examples of electrophilic attack by ozone are the reactions of ozone with tertiary amines, phosphines, arsines, sulfides, and sulfoxides. Decomposition of the substrate sometimes results. As an example, consider the ozone oxidation of a dialkyl sulfide which reacts according to the equation



The well-controlled attack of ozone on the sulfur molecule can best be explained⁷ by the assumption that a terminal oxygen of the ozone molecule executes an electrophilic attack on the sulfur, forming a new bond with the sulfur. The second and third atoms of oxygen are liberated as molecular oxygen. Consideration of ozone oxidation, therefore, should take into account not only oxidation via ozonation mechanisms alone but also autoxidation mechanisms. Examples of ozone-initiated reactions are the oxidative reactions of ozone with aldehydes, ketones, alcohols, ethers, and saturated hydrocarbon groupings. In these reactions, ozone behaves as a radical reagent in an autoxidation process by mobilizing an additional number of oxygen molecules. Consider the oxidation of benzaldehyde to benzoic acid and perbenzoic acid by oxygen containing ozone. Briner, *et al.*,⁸ found a great deal of unreacted ozone, the aldehyde appearing to be only slightly sensitive to the oxidizing action of ozone. However, analysis of the aldehyde solution showed that it had been heavily oxidized and that much more oxygen was taken up in this oxidation than corresponded to the amount of ozone consumed. The reaction steps represented by



constitutes the actual autoxidation. Briner⁹ has suggested that the transformation of aldehyde to peracid proceeds by a chain reaction in which certain short-lived radicals are intermediates. Viewed from an energy standpoint, the reaction chains are energy-induced by ozone transformation into oxygen, the energy released being that which is required for the autoxidation reaction. While Long¹⁰ states that amino acids are not attacked by ozone, Bergel and Bolz¹¹ showed the reaction did occur and that aldehydes, ammonia, and hydrogen peroxide are the major products.¹² The oxidation of coal, carbon black, lampblack, and humic acids by ozone has been reported.¹³⁻¹⁵ The products were mainly carbon dioxide and water-soluble acids.

WATER AND WASTEWATER APPLICATIONS

The events which chronicle the early history of ozone and ozonation can be well described as meager. A duration

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of about 125 years elapsed between the time that the pungent odor of ozone was first noted by Van Marum in 1781, and operation of the first major installation for sterilization at Nice, France, in 1905. About 50 years elapsed (after Van Marum) before ozone was recognized as indeed a unique substance, and an additional 30 years passed before the tri-atomic oxygen formula, O_3 , was established in 1867.

The first use of ozone was for water sterilization when, in 1893, Schneller, Vander Sleen, and Tindal constructed an industrial apparatus at Oudshoorn in Holland for the sterilization of Rhine water after sedimentation and filtration. The city of Paris, at the Saint Maur filtration works, first used ozonation in 1898. Otto-ozone equipment was initially used in 1907 at Nice in the first major installation for the sterilization of a public water supply. Ozonation might have become universal for disinfection in water treatment except for the introduction in this country of cheap chlorine gas, a product of World War I research in poison gases. In Europe and other places, however, ozone for disinfection remained the method of choice, and by 1936 there were more than 100 ozone installations in France and 30 to 40 elsewhere. Today, more than 500 municipalities in 50 countries use ozone as a disinfectant.

On the other hand in this country—aside from the City of Whiting, Indiana which used ozone in pretreatment for removal of taste and odor from Lake Michigan water; and Philadelphia, Pennsylvania, which used ozone to remove taste and odor and manganese from Schuylkill River water—there has been no major ozone installation for municipal water or wastewater treatment, and chlorination remains the principal method of disinfection.

Recently, however, concern has been expressed about possible toxic effects resulting from the discharge of chlorinated municipal and industrial wastes, which could adversely affect aquatic life in a receiving stream. In the search for alternatives to chlorine, ozone is being considered. Although the literature on ozone disinfection is plentiful, the work has generally been done in pure-aqueous and single-culture systems. Despite these simplifications, variations in experimental conditions usually preclude a comparison of results, and such data, having no relation to reality, cannot be extrapolated to a practical situation.

As a result, the literature can be only generalized, and can be done in this way. The use of ozone results in disinfection but not necessarily sterilization. The action

of ozone is rapid. There appears to be a "threshold dose" which must be exceeded, prior to which there is slight bacterial kill and subsequent to which there is rapid kill. This threshold dose is a function of an "ozone demand" of the waste, which, in turn, is an inverse function of the degree of treatment prior to ozone application. Satisfying the ozone demand and disinfection are believed to occur simultaneously. Therefore, a greater degree of pretreatment is advantageous in two ways. One, the ozone demand is reduced by the removal of the more easily oxidizable substrate; and two, clumps or flocs which shield the organisms from the disinfectant are removed. The overall results are that a smaller dose of ozone is required to attain the threshold dose and a greater percent kill is attained with the smaller dose.

Although the disinfection of potable water is the largest application of ozone (aside from industrial uses), other uses of ozone have been made in the treatment of potable water. It is used for taste and odor control and for residual color reduction after conventional water purification by flocculation, sedimentation, and rapid sand filtration. Recently ozone has been applied more fundamentally, following discovery of its extremely effective action on organic colloids, in the "Micellization/Demicellization" process and in the "Microzon" process (an abridgement of the M/D process). These processes result from an attempt to economize on the more "conventional" treatment processes. The intended result was to achieve a higher quality of water at a lower overall cost, and offset the higher capital cost of ozonation equipment when compared to the cost of eliminated processes and chlorination treatment. Laboratory and pilot plant studies have brought about the development of an ozonation/coagulation/filtration process. The M/D Process is particularly suitable for surface waters containing organic matter that is often difficult to coagulate and requires uneconomical doses of electrolyte.

In contemporary uses of ozone, Boucher¹⁶ has summarized the principal applications in sterilization of water, taste and odor control, iron and manganese removal and color reduction. Ozone has been used for odor control in sewage treatment plants in New York¹⁷ and Florida.¹⁸ The Midland (Michigan) Waste Treatment plant initially installed ozone equipment in order to evaluate its effectiveness in deodorizing the exhaust from the vacuum filtration system.¹⁹ The trial was so successful in reducing sulfide odor that ozone is treating the exhaust

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from the sludge storage tank building, and the remaining open facilities (primary settlers, grit chamber and sludge storage areas, and trickling filters) have been covered with Styrofoam domes for exhaust gas ozonation. Similar deodorization is being done at the Mamaroneck Sewage Treatment Plant, Wards Island, and Owl's Head Sewage Treatment facilities in New York.

In the United States, the renewed interest in ozonation has been directed toward using not only the disinfection powers of the chemical but also its oxidation potential. Chemical oxidation as a unit process has not been generally practiced in municipal wastewater treatment. However, increasing demands on the water economy necessitate the reduction of materials remaining after conventional waste treatment. Although advances are being made which extend the effectiveness of conventional treatment methods, the limits of these methods are being approached, and new technology must be devised.

Chemical oxidation may be applicable to many situations; (1) as an alternative to carbon adsorption for use as a tertiary treatment process (and when carbon adsorption and regeneration cannot be economically justified); (2) as a process to supplement carbon or synthetic resin adsorption; (3) to extend the capabilities of intermediate treatment plants; and (4) to enhance effluent quality in high-value reuse situations. For these purposes, the most promising oxidant class appears to be the active-oxygen species—specifically ozone—which offers a vigorous oxidative environment and rapid kinetics.

In evaluating the oxidative potential of ozone, there have been more than a few laboratory studies of its effect on certain specific constituents of wastewaters: anionic, biologically-resistant, surfactants, all other types of surfactants, saturated and unsaturated hydrocarbons, chlorinated hydrocarbon insecticides, humic acids, iron, manganese, cyanides, phenols—even anaerobic sewage micro-organisms to increase their activity. As a result of these laboratory studies, ozonation has been used to treat effluents from specialized industrial activities, and now is being considered for use in the mixed-organics environment of a municipal treatment plant.

Buescher and Ryckman²⁰ used ozone to reduce foaming of ABS; and Evans and Ryckman²¹ reported 97% removal of ABS from secondary sewage treatment plant effluent, accompanied by an 80% reduction in the COD of the effluent. Ozonation of ABS destroyed the biological inertness of the surfactant, probably because the ozonides of the ABS solution served as

the oxidizable substrate for a mixed microbial population. Buescher *et al.* studied the destruction of lindane, aldrin, and dieldrin by various oxidants.²² While ozone readily attacked lindane and aldrin and decreased the concentration of dieldrin, other oxidants as calcium hypochlorite, H_2O_2 , Na_2O_2 , and $KMnO_4$ (each at 40mg/liter dose) either had no measurable effect or only partial removal was achieved. Only aldrin was removed by hypochlorite and permanganate.

At present, there are no known full-scale ozone installations in a treatment plant for wastewater or effluent treatment, although recent studies might alter this. In 1966, a 2700-gallon-per-hour pilot plant was set up at the Eastern Sewage Works, Redbridge, London.^{16,23} The pilot plant provided variable combinations of microstraining, prechlorination, ozonation, coagulation, and rapid sand filtration for the treatment of settled, biologically treated effluents. This M/D process employs the following three stages of treatment:

1. Microstraining for primary filtration,
2. Micellization/Demicellization to produce filterable microflocs, and
3. Rapid sand filtration for elimination of the microflocs.

Ozone is used in the second stage to bring about disruption of the colloidal state by attacking the hydrophillic grouping of organic macromolecular chains for the production of colloidal micelles. The production of "micellization" after ozonation is shown by the development of colloidal turbidity. The negatively-charged micelles require a dose of electrolyte to "demicellize" the water, and the resulting microflocs are subsequently sand-filtered. While the M/D process was in previous operation for water treatment at Roanne, France, and Constance, Germany, the Redbridge installation was the first attempt in waste effluent treatment. The process produced a final effluent low in suspended solids, clear and colorless, and the detergent content was reduced considerably. Concentrations of total solids, ammonia, and nitrate were virtually unaffected, but nitrite was oxidized. Dissolved organic matter was only slightly affected by the 20 mg/liter ozone dose. Ozone killed the vast majority of organisms present, including all the *Salmonella* and viruses. Chlorine produced lower counts than ozone; and chlorine followed by ozone was highly effective, all coliform and *E. Coli* counts being zero.

In a laboratory investigation supporting the Redbridge Pilot project, Gardiner and Montgomery²⁴ studied the effect of ozonation alone on the chemical composition of sewage effluents over a wide range of temperatures and ozone doses. The samples used were laboratory-settled trickling filter effluent; diluted, biologically treated milk waste; and an effluent from the treatment of detergent-free sewage. To some of the samples was added γ -BHC (Lindane) dieldrin, DDT, TDE; 10 mg/liter mixed phenols; 10 mg/liter Dobane JNQ (soft) or 10 mg/liter Dobane PT8 (hard) anionic detergent; and soft and hard non-ionic detergents. Some of the results of the study are as follows:

1. Ten minutes ozonation reduced organic carbon, measured by Beckman carbonaceous Analyzer, only slightly. One hour ozonation, on the other hand, effected a 27% reduction when 94 mg/liter ozone was absorbed. A greater reduction is achieved with a filtered and settled effluent than with a settled effluent.
2. Thirty to sixty minutes ozonation caused a reduction in the carbonaceous BOD; the samples further were likely saturated with dissolved oxygen.
3. The COD reduction in mg/liter was approximately equal to one-half the amount of ozone absorbed (in mg/liter). There was little difference in reduction between filtered and unfiltered settled samples.
4. Nitrite was oxidized rapidly to nitrate; organic nitrogen was slightly reduced; ammonia-N concentrations were unaffected.
5. Removals of phenol, pesticides, and detergents were in agreement with the removals found by other investigators.

While the former Redbridge pilot study demonstrated the usefulness of the M/D process or the Microzon process in the treatment of domestic waste treatment effluents and the associated laboratory study clarified the effect of ozone on some effluent constituents, the specific application of ozonation to the removal of residual organics from wastewaters was investigated by the Air Reduction Company.²⁵ The sample used was trickling filter effluent which was alum-clarified and sand-filtered to produce an influent with a reduced ozone demand. Both clarified and nonclarified secondary effluents were contacted with ozone for periods of time up to one hour. The influence of pH, method of gas dispersion, effluent pretreatment, and ozone concentration in the feed gas were evaluated in terms of ozone reactivity, reduction in the chemical oxygen demand, and reduction in total organic carbon content. This initial

study determined that the operation of a simulated six-stage contactor reduced the COD from 32 to 13 mg/liter and reduced the TOC from 12 to 9 mg/liter at a contact time of one hour. Batch tests determined that the TOC contains a fraction that is refractory to ozone oxidation, a part of which can be removed by pre-clarification. It was demonstrated that ozone efficiency for TOC and COD reduction increased with increasing levels in the sample, indicating that the more readily oxidizable organic compounds in the effluent consume ozone more readily. While the COD showed a primary response to ozonation, no cleavage of organic compounds is needed for a COD reduction. Only on destruction of the organic residue, when oxidation leads to formation of carbon dioxide, is there a reduction in TOC. The fact that a TOC reduction was achieved demonstrates the oxidizing capabilities of ozone in the destruction of organics refractory to biological treatment. Cost estimates, based on the design of six-stage co-current contacting system for 1-, 10-, and 100-mgd plants, assuming 80% ozone utilization, compared favorably with those for activated carbon treatment plants.

Beyond controlled laboratory investigations and industrial waste treatment, pilot-scale ozonation plants have been operated to attack the problem of pollution control from a number of different angles. One plant was designed to treat the combined sanitary and stormwater discharge in Philadelphia (Fairmount Park), Pennsylvania, when storms caused untreated tastes to overflow into the waterways. In this instance, the combination of microstraining and chlorine or ozone were compared. Another plant is operating at the Hanover Park sewage treatment plant of the Greater Chicago MSD. Here, an ozonator is treating sewage effluent at 100 gpm to test ozone's effectiveness in disinfection, color removal, and BOD reduction before releasing the water into Lake Michigan. A two-stage injection system and a five-minute contact time is used. When 0.1 ppm ozone concentration was maintained, it was determined that the effluent was disinfected.

In the industrial waste treatment area, cyanide or phenolic effluents from processes such as blast furnace and open hearth operations, refining, and coke plants are treatable with ozone, as are a variety of waste streams from a synthetic polymer plant. Wastes resulting from glycerol production which contain trace amounts of biologically inert or toxic materials have also been treated with ozone. The Boeing plant at Wichita, Kansas, uses