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ENVIRONMENTAL SCIENCES DIVISION
Publication No. 1219

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ABSTRACT

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A review of the literature on the chemistry and biological effects of ozone was conducted to evaluate the potential of ozone to function as a power plant biocide. Evaluation of this potential is dependent upon determining the ability of ozone to maintain the integrity of both the condenser cooling system and the associated ecosystem. The well-known bactericidal capacity of ozone and the limited biofouling control studies conducted thus far suggest that ozone can control both slime and macroinvertebrate fouling at power plants. However, full-scale demonstrations of the minimum levels of ozone required and of solution of the practical aspects of application have not been performed.

Information relating to environmental effects of ozonation is also insufficient for any but tentative conclusions. Identification of ozonation products in potential power plant effluent waters has not been attempted. By analogy with known products in ozonated waste waters and from theoretical considerations, the most common compounds expected in power plant effluents are residual ozone, aldehydes, ketones, and carboxylic acid molecules. Decomposition of residual ozone is apparently slow enough to allow transport into the external environment. Residual ozone is toxic to some aquatic organisms at concentrations as low as several hundredths of a part per million for

short exposure durations. Most aldehydes, ketones, and carboxylic acids are moderately low in toxicity and probably would not represent an environmental problem at the concentrations likely to be released. However, studies in aqueous media have indicated the possibility of formation of ozonated organics of potential environmental or public health concern. These reaction products include epoxides, peroxides, and stable hydroperoxides. Other studies have indicated the presence of hydroxylated and oxidized PAHs, amine oxides, and nitrosoamines. Potential for an even broader variety of products is indicated by results of laboratory studies and the known complexity of compounds found in natural waters. Some compounds of the above generic types have been found to be highly toxic, mutagenic, or carcinogenic. Existing data thus point to a potential for environmental effects of ozonated effluents, but the extent to which that potential will be realized under conditions of ozone application at power plants is not possible to estimate with assurance. The supposition that this potential is relatively low, however, implies that this is a propitious time for support of a limited research program designed to initiate evaluation of ozone as a power plant biocide.

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INTRODUCTION

Substantial interest has recently surfaced concerning the potential use of ozone (and other alternatives to chlorine) as a biofouling control agent at electric generating stations. About 90% of the power plants in the United States currently use chlorine for control of fouling (McLean 1973, Brungs 1976). This preponderance of use has resulted from the early discovery of its effective biocidal capacity, simplicity of application, and economy. However, increasing awareness of the potential health and environmental impacts of both residual chlorine (Mattice and Zittel 1976, Mattice 1977) and chlorinated organics (Jolley 1973, Alavanja et al. 1978) have stimulated reexamination of alternatives to avoid these problems. Ozone has received much of the emphasis of this search.

This emphasis on ozone has resulted from three characteristics. First, it is an excellent bactericide, rendering it potentially effective in controlling slime communities, which are the major cause of decreased heat exchange across condensers. Second, residual ozone is subject to relatively rapid degradation in natural waters, decreasing potential interactions with biota in the receiving water body. Finally, the major breakdown product is oxygen, which should improve water quality at levels not resulting in supersaturation. These characteristics indicate a good potential for use of ozone as a biocide at power plants.

The prognosis for biofouling control using ozone is not, however, entirely optimistic. Ozone is (1) costly and difficult to use, and (2) potentially capable of reacting with organic materials in natural waters to produce ozonated organics of health and environmental consequence (Cotruvo 1976). These aspects of ozone use suggest that ozone may not be a panacea for the concerns voiced regarding chlorine.

Evaluation of ozone as a power plant biocide is dependent upon capacity to satisfy two criteria: maintenance of condenser function and avoidance of environmental impact. Resolution of the potential conflict between these criteria requires a broad base of information (Fig. 1). Determination of the minimum dosage necessary to maintain condenser function is a key component of the evaluation. It provides a sound basis for identification and quantification of effluent reaction products and sets levels for realistic investigations of effluent toxicity. Once data are available in each of these areas (Fig. 1), comparison of ozone and other biocides, particularly chlorine, is possible. Without these data, comparisons can only be tentative.

The following sections review the available literature concerning ozone to determine whether there are sufficient data on the various aspects discussed above to select ozone as a viable alternative to chlorine in preventing fouling at power plants. The sections report (1) the depth and breadth of the literature search, (2) the chemistry, and (3) the biology of ozone as they apply to this goal.

OZONE LITERATURE SEARCH

The search of the literature for documents concerning ozone represents an expansion of previous efforts. Since 1971 the ORNL Ecological

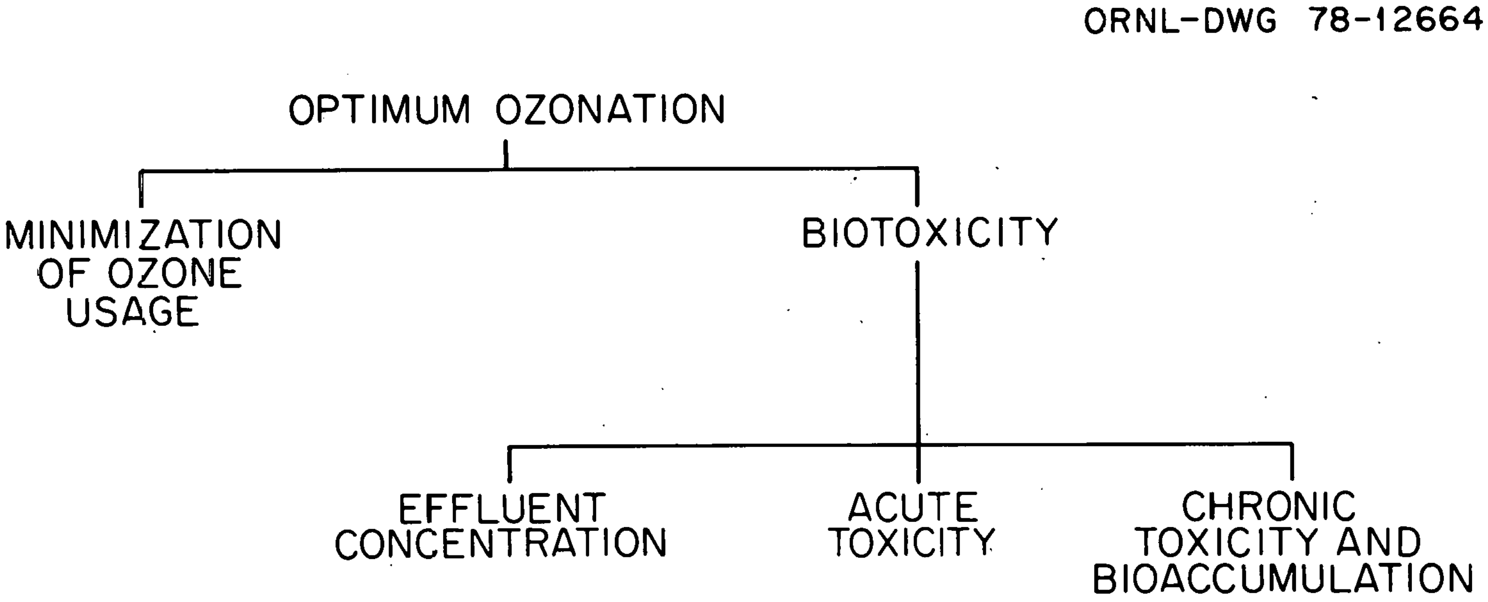

Fig. 1. Categories of information required for evaluation of ozone as a power plant biocide.

Sciences Information Center (ESIC) has been compiling annotated data bases to aid in the assessment of ecological effects of cooling systems of electric generating plants. Existing data bases related to power plant operation include thermal effects, impingement, entrainment, and chlorine. Using seed money allocated in early 1977 by the Exploratory Studies Program, ORNL, Oak Ridge, Tennessee, this effort was expanded to include literature concerning the chemistry of ozone and its degradation products as well as the effects of these compounds on aquatic biota. This literature was systematically collected and abstracted for inclusion into a computerized data base.

Potentially appropriate titles were identified using several methods. The large-scale commercial data bases of the ORSDI (Oak Ridge Selective Dissemination of Information) were searched for pertinent information. The data bases consulted were: Biological Abstracts (BA); Bio-Research Index (BRI); Chemical Abstracts, Even Issues (CAE) and Odd Issues (CAO); National Agricultural Library (CAIN); Chemical-Biological Activities (CBAC); and Government Reports Announcements (GRA). Both current and retrospective searches were carried out. Following review of the abstracts obtained from these data bases, papers which appeared to be within the scope of the project were obtained. The documents, comprising environmental journals, conference proceedings, and books, were acquired by reprint cards, by interlibrary loans, and by personal contacts. Additional documents were then derived from the bibliographies of these studies and from personal contacts with certain of the authors identified. All of the papers are available in the Ecological Sciences Information Center files.

Somewhat less than two hundred papers were considered to contain information pertinent to project goals. More than 1000 citations from the open literature were scanned. A total of 323 documents were acquired. After discussions with project staff members (in ecology and chemistry), 170 of these were selected for input into a computer data base. An annotated bibliography of abstracts of these papers will soon be available. The documents which were acquired but were found not to be in scope at the present time are being held for possible later expansion of the data base.

The literature on the chemistry of ozone deals primarily with the decomposition of ozone in aqueous solution, general ozonation reactions, reactions of ozone and selected organics, and the identification of decomposition products formed by the interactions of ozone with organic compounds. The question of epoxide and ozonide formation is addressed in some papers.

Documents related to biological effects deal predominantly with the bactericidal and virucidal properties of ozone. Most of the toxicity studies concern the lower aquatic organisms although some information is given on higher order animals. Papers on freshwater systems predominate although limited information is available on marine systems. Examples of the types of papers selected are: disinfection of drinking water, disinfection of sewage effluents, and biofouling control; comparative effectiveness of chlorine and ozone as biocides; use of ozone in fish hatcheries, shellfish culture, and seaquaria and aquaria; effects of ozone on the cellular level; bioassay studies;

mutagenic screening of some decomposition products; and acute and chronic effects of residual ozone on fish and invertebrates.

CHEMICAL ASPECTS OF OZONATION OF POWER PLANT COOLING WATERS

Introduction

Relatively little information is available concerning the chemistry of ozone following its use in prevention of biofouling of condenser surfaces in electric power plant cooling systems. A thorough search has been made for studies and information concerning the chemistry of ozone and possible effects on the constituents in natural waters, which may be used for condenser cooling. Although much information is available concerning the use of ozone in nonaqueous chemical reactions, only scant information was found concerning ozonation products in aqueous systems and, in particular, those systems with low concentrations of organic constituents and low concentrations of ozone application. Both conditions would be found at power plants. Investigations into this complex and difficult area have only recently been initiated, following development of instrumentation with sufficient capability and sensitivity to detect and identify organic constituents at part-per-billion concentrations (Sievers et al. 1977).

The chemistry and ozonation reactions of ozone that are applicable to understanding possible effects on the constituents in cooling water are reviewed in this paper. The physical and chemical properties of ozone per se (e.g., thermodynamic properties) will not be reviewed.

Experimental evidence indicates that product formation following ozonation will differ in marine (or estuarine) and fresh waters. Ozone is a very reactive species with an oxidation potential of 2.07 V, second only to fluorine. Consequently, ozone will oxidize chloride and bromide present in cooling waters according to the following equations:

$$O_3 + 2H^+ + 2Cl^- \gtrless O_2 + Cl_2 + H_2O \quad , \tag{1}$$

and

$$O_3 + 2H^+ + 2Br \gtrless O_2 + Br_2 + H_2O \quad . \tag{2}$$

These reactions occur rapidly in acid solutions, but only the bromide reaction may occur at a rate sufficiently rapid to form halogenated organics and then only at the higher concentrations of bromide that occur in estuarine and marine waters (Taube 1942). Free bromine or chlorine would hydrolyze rapidly to hypobromous to hypochlorous acids in aqueous solution. These will react rapidly with organic material present in the natural water to produce haloforms (Rook 1974). Apparently, ozonation of drinking water supplies does not form trihalomethanes (Symons 1976), thus giving presumptive evidence that the chloride in fresh waters is either oxidized slowly to chlorine or that any chlorine formed is rapidly converted to chloramines (Symons 1976). It is believed that the kinetics of the chloride oxidation are not favorable at neutral pH values and at low ozone and chloride concentrations. However, ozonation of estuarine and sea water does result in the production of bromoform (Carpenter and Smith 1978, Helz et al. 1978, Mangum and McLlhenny 1975, Pitchet and Hurtbise 1976, Blogoslawski and Stewart 1976, Blogoslawski et al. 1976). Thus, ozonation of estuarine and marine cooling waters probably also creates other bromo-compounds in addition to bromoform. The formation of halogenated organics during ozonation must, therefore, be considered a possibility in at least some cooling waters.

The actual proportions of the products formed are dependent upon the relative reaction rates under the prevailing conditions, but few data are available from which to draw conclusions. Direct reactions of ozone with materials which may exist in natural waters are given below to illustrate some of the most likely possibilities.

Primary Classes of Ozone Reactions

Decomposition of Ozone

The decomposition mechanism apparently depends on environmental pH. Alder and Hill (1950) determined that the rate of disappearance of ozone was first order with respect to ozone in both water and carbon tetrachloride. The rates in the two media are different and much faster than in the gas phase; essentially a constant concentration of intermediates is present in the water solution. The decomposition rate is consistent with the following mechanisms:

$$O_3 + H_2O \xrightarrow{k_1} HO_3^+ + OH^- \quad , \tag{3}$$

$$HO_3^+ + OH^- \xrightarrow[k_2]{k_1} 2HO_2^{\cdot} \quad , \tag{4}$$

$$O_3 + HO_2^{\cdot} \xrightarrow{k_3} HO^{\cdot} + 2O_2 \quad , \tag{5}$$

and

$$HO^{\cdot} + HO_2^{\cdot} \xrightarrow{k_4} H_2O + O_2 \quad . \tag{6}$$

Alder and Hill (1950) assumed that reactions 3 and 5 are responsible for the ozone disappearance and are presumably slow and rate-determining; reaction 4 is an equilibrium maintained as long as ozone is in the system, and reaction 6 is the rate-breaking step. The decay of ozone at pH 10 to 13 and 25 C with ozone at 10^{-4} to 10^{-5} $\underline{M}$ concentrations was also determined by Czapski et al. (1968) to be first order:

$$-\frac{d[O_3]}{dt} = k_{obs}\ [O_3] \quad , \tag{7}$$

where $k_{obs} = 700\ \underline{M}^{-1}\ sec^{-1}$. Apparently, however, in more acidic solutions (pH values of 2 and 4), the reaction of ozone in aqueous solution is second order. At pH 6 the reaction rate is between first and second order, and at pH 8 the decomposition rate becomes first order. At pH values greater than 6 the decomposition rate increases rapidly with pH (Hewes and Davison 1971, Stumm 1954).

There is some disagreement about the half-lives of residual ozone in aqueous solutions, but many of the predictions indicate a need for environmental concern. Table 1 compares estimates derived in two studies. Those calculated by Czapski et al. (1968) are generally larger than those of Sennewald (1933), but in most cases the times are long enough for transport into the environment. Thus, ozone itself appears

Table 1. Ozone decomposition rates under several experimental conditions

pH	Media	1933 data[a]	1968 data[b]
6	phosphate	63 min	26.7 hr
7	phosphate	42 min	2.6 hr
8	phosphate	12 min	16.0 min
8	borate	25 min	16.0 min

[a] Sennewald 1933.

[b] Czapski et al. 1968.

sufficiently stable to present some toxicity problems to downstream aquatic species.

Ozonation Reactions in Aqueous Media

Ozonation conditions can be selected to produce either direct oxidation of the organic substrate or hydroxyl radical oxidation of the organic substrate (Fig. 2). The pathway of primary importance in the acidic region, or when solutes are present that react extremely rapidly with the ozone, leads to highly selective oxidation reactions directly with organic compounds. In these oxidations, reactive groups in the organic compounds (e.g., amino groups) will be the principal focus of attack (Hoigne and Bader 1976). In more alkaline solutions favoring the decomposition of ozone to the hydroxyl radical, this radical becomes the principal oxidizing agent. The knowledge accumulated by radiation chemists and biologists concerning the hydroxylation reactions may be used to predict the products of oxidation by the hydroxyl radical (Hoigne and Bader 1976).

Direct ozonation reactions

These highly selective reactions have been the subject of much study, for example, the ozonation of the carbon-carbon double bond. The mechanism of ozonation and the reaction products do not vary significantly with type of solvent (solvent polarity) (Bailey 1972, 1975; Hoigne and Bader 1976; Oehlschlaeger 1978). Historically, the difference between these reaction types and the less selective types to be discussed later has not been recognized; however, in general, studies

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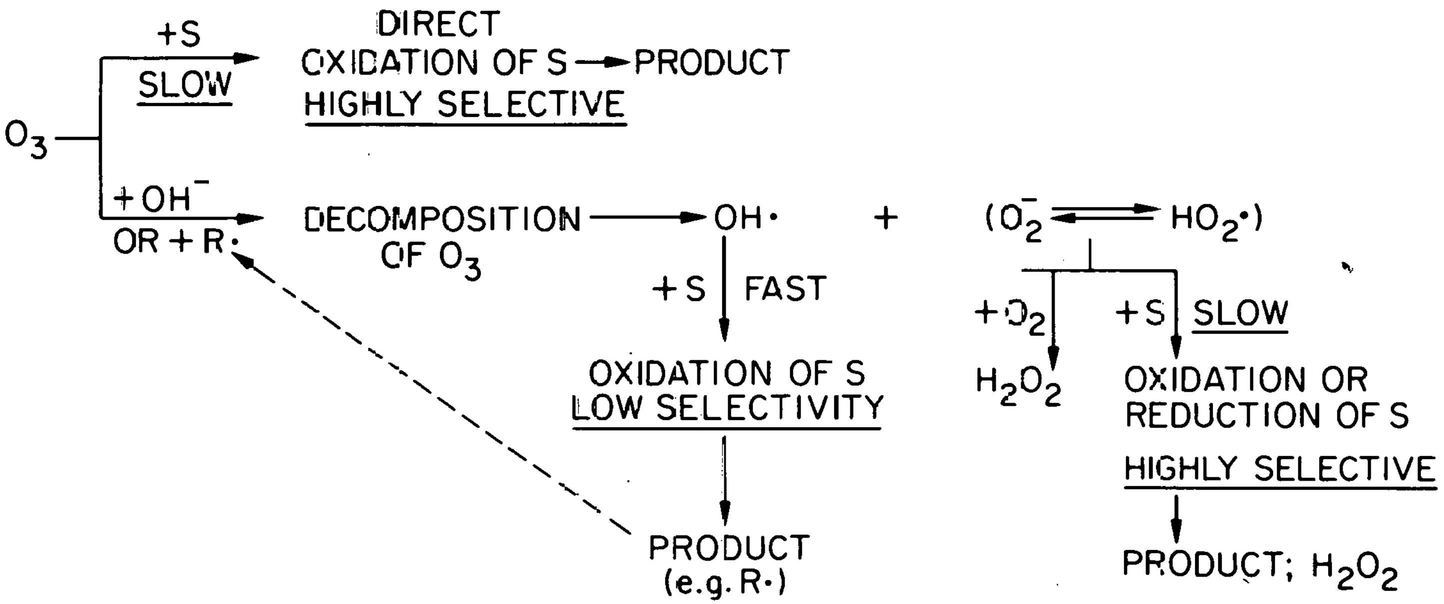

Fig. 2. Reactions of substrates (S) with O_3 and the O_3-decomposition reaction compete for O_3 consumption (from Hoigne and Bader 1976).

in nonaqueous solvents have been of the highly selective direct ozonation type. The ozonation of the olefinic double bond, and the Criegee mechanism for explaining the experimental results, is probably the best-known example of the highly selective reaction. A more complete treatment of these reactions is given below (Ozone Reactions with Organics).

Hydroxyl radical oxidation

Under reaction conditions usually prevalent in drinking-water or wastewater-treatment (and thus cooling-water treatment), reaction conditions (alkaline pH) favor the decomposition of ozone into hydroxyl radicals that react less selectively with organic solutes.
Experimental results confirm that $OH^{\cdot}$ radicals are the principal oxidizing intermediates formed from ozone decomposition (Hoigne and Bader 1975). Apparently, ozone decomposes in aqueous solutions by a catalyzed chain reaction involving the hydroxyl ion (Eqs. 3-6). Free radicals (e.g., O_2^-, $HO_2^{\cdot}$ and $OH^{\cdot}$) could thus be formed.
Because of the free radicals, the selectivity of the ozone oxidation reactions might correspond with the selectivity found in irradiated systems. At pH 10.5, good agreement was found between irradiated and ozonated systems for oxidation of selected solutes, indicating a similar mechanism operating for both agents (Hoigne and Bader 1975, Hewes and Davison 1971). The main oxidizing decomposition product of ozone in water is the $OH^{\cdot}$ radical. Thus, radiation chemistry of the $OH^{\cdot}$ radical can be used to predict some products of ozonation. (See:

Anbar and Neta 1967, Dorfman and Adams 1973, Chutny and Kucera 1974a, 1974b, and Hoigne and Bader 1975, 1976).

Ozone Reactions with Organics

In this discussion, as noted earlier, ozonation reactions with organics have not been differentiated into the two major classes, i.e., direct reactions and free radical oxidations. Organic groups which can be oxidized by ozone are: olefinic carbon-carbon double bonds, acetylenic carbon-carbon triple bonds, aromatic molecules, carbocyclic molecules, heterocyclic molecules, carbon-nitrogen bonds, amines, sulfides, sulfoxides, phosphines, phosphites, arsines, selenides, alcohols, aldehydes, hydrocarbons, silicon-carbon bonds, and carbon-metal bonds (Bailey 1975). Data which exist concerning interaction of ozone with these potential reactants are summarized below.

Carbon-Carbon Double Bond

The classical reaction of ozone with organic constituents is the ozonolysis reaction with the carbon-carbon double bond (e.g., olefinic bond) (Bailey 1958; Bailey et al. 1959, 1972). The Criegee mechanism for ozonolysis of the double bond has been elegantly detailed and explains well the reaction products (Bailey 1975) (Fig. 3). The initial attack is a 1,3-dipolar cycloaddition to give an ozonide, a 1,2,3-trioxolane which breaks down to a carbonyl oxide zwitterion. The high energy, unstable zwitterion intermediate stabilizes itself by polymerization or dimerization, reacts with either the aldehyde or ketone which has formed with it, or reacts with the solvent to give

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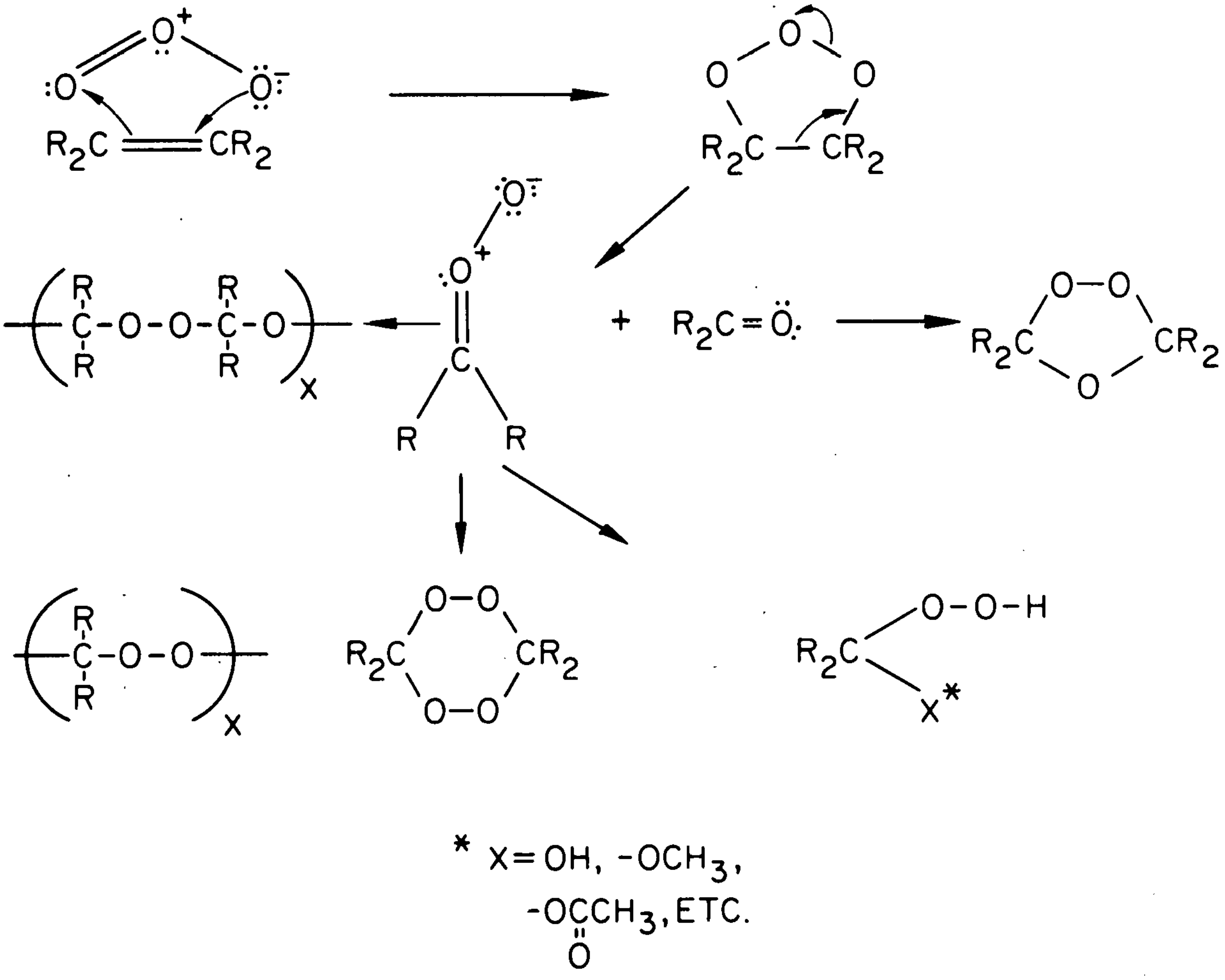

Fig. 3. Revised Criegee ozonolysis mechanism (adapted from Carlson and Caple 1977).

peroxidic ozonolysis products. In aqueous solution the peroxidic ozonolysis products should be a hydroxy hydroperoxide. Apparently this is easily decomposed to an aldehyde (or ketone) or to a carboxylic acid (Bailey 1975). Experimental results corroborate the formation of aldehydes, ketones, and carboxylic acids (Bailey et al. 1959, 1972; Carlson and Caple 1977; Pryde et al. 1968; Criegee 1953; Fremery and Fields 1963; Fields 1965; Yocum 1978; Sturrock et al. 1963).

Olefins

Ozonation of olefins can result in a wide variety of products. Most common products are esters, lactones, or anhydrides when ozonation is carried out in the presence of methyl alcohol. The formation of epoxides during ozonation is limited to olefins with strong steric hindrance at one of the carbon atoms. For example, ozonation of diphenylethylene gives a liquid ozonide and ozonation of p-Methoxystyrene yields only the ozonide. Unsymmetrical olefins with two strong electron-donating groups yield the epoxides instead of ozonides (Criegee 1959). Polynuclear aromatic hydrocarbons (e.g., anthracene, naphthalene, and phenanthrene) are more reactive than benzene derivatives and less reactive toward ozone than olefins. Stable hydroperoxide derivatives also can be formed during ozonation. For example, stable hyperoxides were produced following ozonation of both a cyclic olefin and a cyclic sulfone.

Ozonation of oleic acid is of particular interest because of its environmental occurrence in natural waters. Spanggord and McClurg (1978) obtained the classic ozonation products from the ozonation of oleic acid, namely, nonanoic acid, 9-nonanal carboxylic acid, and nonanedioic acid. They indicated the intermediate ozonides and epoxides probably did not survive the final pH (3.8) of their experimental reaction conditions. Similarly, Carlson and Caple (1977) ozonated oleic acid at pH 3.9 and obtained the following compounds: n-nonyl aldehyde, caprylic acid, suberic acid, n-nonyl methyl ketone, azelaldehydic acid, and azelaic acid resulting from the cleavage of the olefinic bond. All the cleavage products are predicted by the Criegee mechanism. However, in addition, oleic acid epoxide and 9,10-dihyroxystearic acid were identified. The identification of the epoxide product from an aqueous ozonation is highly significant. The noncleavage products, the oleic epoxide and the dihydroxy-substituated oleic acid, are probably not formed by the direct epoxidation of oleic acid by ozone. Instead they are likely formed by a peracid epoxidation of oleic acid; the peracids were formed by autooxidation of aldehydic products.

Aromatic compounds

Ozonation of aromatic compounds apparently involves ozonolysis at the most reactive aromatic bond and electrophilic ozone attack at individual carbon atoms. The unsubstituted benzene ring is much less reactive toward ozone than the olefinic bond. The effects of substituents on the benzene ring are similar to those of electrophilic additions in that alkyl, aryl, oxygen, etc., substituents facilitate ozonolysis, whereas nitro, carboxyl, halogen, and sulfonic acid substituents undergo slow ozonolysis reactions. The cleavage products of the benzene ring systems are glyoxals (R-CO-COH) and glyoxalic acids (R-CO-COOH)

(Carlson and Caple 1977). The following compounds are listed in the order of decreasing reactivity toward ozone: olefins, phenanthrene, anthracene, naphthalene, and benzene (Oehschlaeger 1978). Styrene is oxidized 10^5 times faster than benzene, and xylene is oxidized 25 times faster than benzene (Hoigne and Bader 1976). Yocum (1978) indicated that the ozonation of styrene produces benzaldehyde and formaldehyde intermediates and benzoic acid.

Phenol and its homologs are the only aromatic compounds studied extensively in aqueous solutions with respect to ozonation. Carlson and Caple (1977) determined the intermediates in the ozonation of phenol to be catechol, o-quinone, and muconic acid. However, Spanggord and McClurg (1978) indicated that resorcinol was also a product. This had not been previously reported. Initial electrophilic attack by the ozone and subsequent nucleophilic substitution on the ring to form an intermediate (Fig. 4) permits two modes of elimination and the formation of either catechol or resorcinol. Eisenhauer (1968) reported that ozonation of phenol proceeds through catechol and hydroquinone to the o- and p-quinones, and through muconic acids to maleic, fumaric, and oxalic acids. Gould and Weber (1976) recently determined the kinetics of phenol ozonation in addition to the kinetics of the ozonation of chemical oxygen demand (C.O.D.) and total organic carbon (T.O.C.).

Miscellaneous double bonds

Carlson and Caple (1977) determined that ozonation of alpha-terpineol at either pH 3 or 10 produced a keto-lactone. This product is consistent with the Criegee mechanism via initial alkene cleavage

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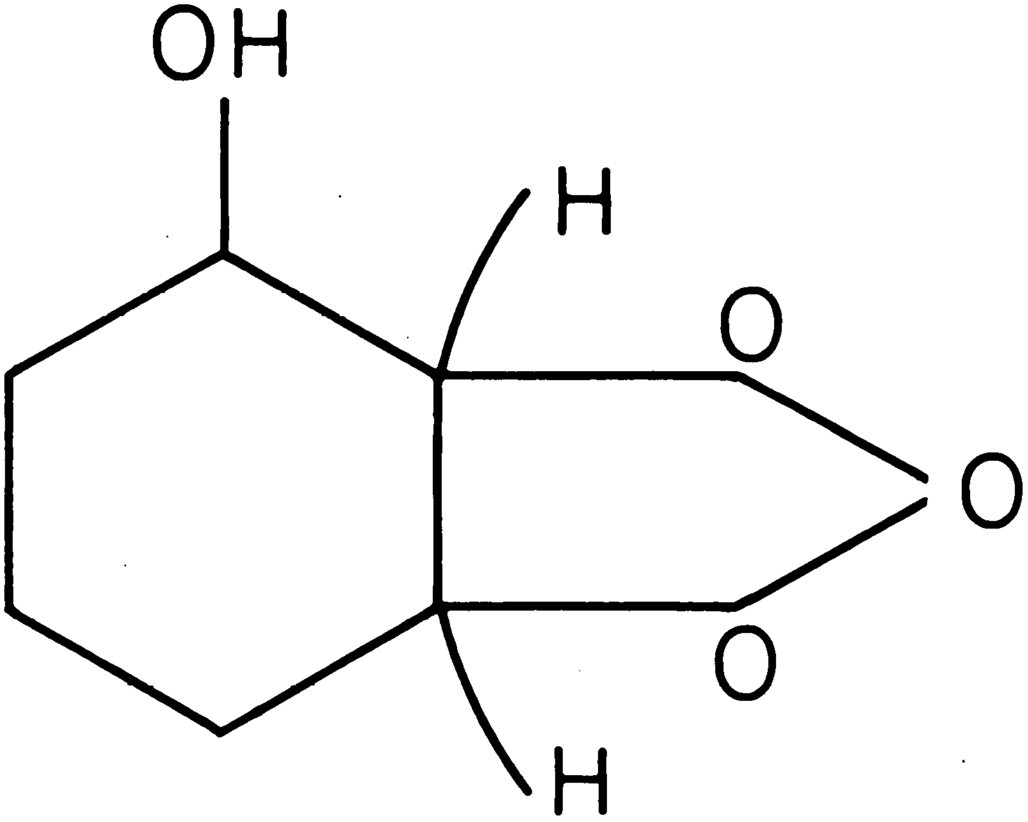

Fig. 4. Intermediate formed following ozonation of phenol.

and the hydroxy-hydroperoxide intermediate. Other minor oxidation products were separated from the reaction media but have not been identified.

The products of ozonation of linoleic acid (with conjugated double bonds) may also be predicted by the Criegee mechanism. Some of the identified products were: n-hexanal, 2-heptanone, hexanoic acid, 9-oxopelargonic acid, azelaic acid, and 3-nonenal (Carlson and Caple 1977).

Anethole ozonates to form anisaldehyde with little ring rupture (Mosher 1959). Cinnamyl alcohol yielded normal ozonation products, glycolic aldehyde, and benzaldehyde. Benzofuran on ozonation gave salicyclaldehyde (Milas and Nolan 1959). The aromatic compounds, *p*-toluenesulfonic acid, naphthalene 2,7-disulfonic acid, nonylbenzenesulfonic acid, 4-chloro-*o*-cresol, 2-nitro-*p*-cresol, and *p*-aminobenzoic acid, were ozonated. Reaction products included methyl glyoxal, acetic acid, pyruvic acid, oxalic acid, and mesoxalic acid. In general, simple 1-carbon, 2-carbon, 3-carbon, and 4-carbon oxidation products were formed (e.g., formic, acetic, and oxalic acids) (Gilbert 1978).

Carbon-Nitrogen Bonds

Carbon-nitrogen double bonds may be as reactive toward ozone as carbon-carbon double bonds depending upon substituents. Ozone can electrophilically attack the carbon atom of the carbon-nitrogen double bond. Oximes and hydrazones produced corresponding ketones and sometimes the N-nitrosoamine (Erickson et al. 1969). Ozone can also act as a nucleophilic reagent in its initial attack on some carbon-nitrogen double bonds. Electrophilic attack appears to be the established method involved in the ozonation of the carbon-carbon double bond, the ozonation of amines, and the ozonation of sulfides. Apparently in the initial attack of ozone on Schiff bases and nitrones, it reacts as an nucleophilic agent. Ozonation of N-benzylidine-t-butylamine yielded the corresponding amide and benzaldehyde or benzoic acid. For N-benzylideneneaniline and N-cyclohexylideneisobutylamine cleavage was the major reaction. Ozonation of the oximes, N-phenylbenzaldoxime and N-t-butylbenzaldoxime, produced benzaldehyde and the corresponding nitroso compound, which was further oxidized by ozone to the nitro compound (Riebel et al. 1960).

Amines

Spanggord and McClurg (1978) determined that two new products were produced by the ozonation of diethylamine, acetaldoxime, and a hydroxylamine or nitrosoamine. The ozonation reaction common to tertiary amines results in formation of an amine oxide,

$$R_3N + O_3 = R_3N^+\text{-}O^- \quad . \qquad (8)$$

Ozonation of diphenylhydrazine hydrochloride at pH 7 produces diphenylamine, an aromatic ring-hydroxylated derivative, and a nitrogen-hydroxylated derivative (Spanggord and McClurg 1978).

Purines and pyrimidines (and nucleic acids)

Products of ozonation of purines and pyrimidines have not been identified, but are probably similar to those produced by free radical attack following irradiation, and include additions of OH and H across the double bonds (or opening of the rings) or perhaps formation of thymine dimers. Ozone breaks the C-N bonds of the sugars to the bases in nucleosides and nucleic acids and apparently also degrades the sugars. In addition to the chemical effects on the bases and sugars, ozone may also affect the double-stranded DNA helix, as occurs during irradiation (Scott 1975). Ozonation of caffeine produces dimethylparabanic acid as the principal product (Shapiro et al. 1978).

Sulfur-Containing Compounds

Ozone rapidly oxidizes thioglycolic acid, cysteine, and glutathione in aqueous solutions. Sulfhydryl enzymes, papain and glyceraldehyde 3-phosphate dehydrogenase, are also inactivated by ozone but may partially be reactivated by cysteine (Menzel 1971).

Carbon-Hydrogen-Oxygen Compounds

Glyoxylic, oxalic, formic, and acetic acids are common end-products of the ozonation of alcohols, phenols, malonic acid, chlorophenols, maleic acid, humic acids, and many aliphatic and aromatic compounds. It is significant that the principal component of natural waters (i.e., humic acids) are ultimately degraded to such simple products. Reaction stoichiometries were not specified (Kuo et al. 1977).

Conversely, Spanggord and McClurg (1978) reported the formation of a mutagenic product from the ozonation of ethanol. The major products were an aldehyde and acetic acid. However, apparently a trimer acid peroxide (Fig. 5) is formed which is mutagenic according to the Ames test.

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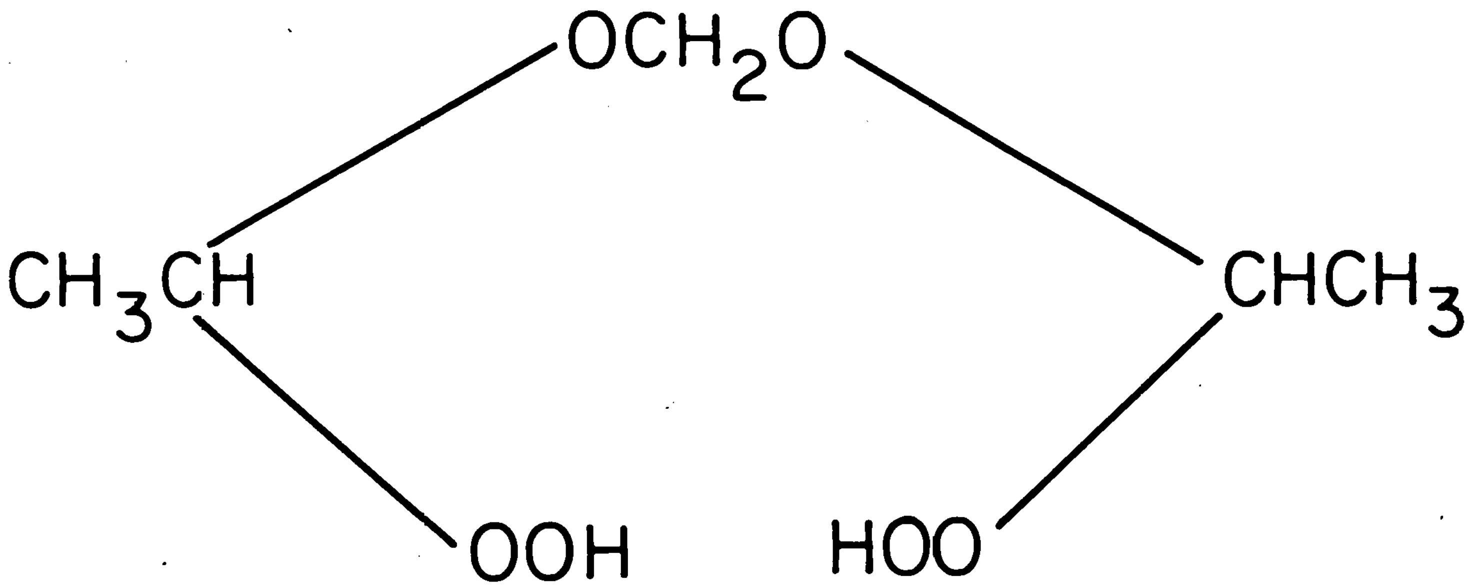

Fig. 5. Mutagenic compound formed following ozonation of ethanol.

Ozonation of Organics in Natural Waters

The complex array of organic chemicals present in natural waters indicates that aqueous ozonation should produce myriad reaction products. Although the most prominent organic materials present in cooling waters are humic acids, almost every other known family or group of organic chemicals has also been detected in natural waters. Analysis of the U.S. Environmental Protection Agency report (Shackleford and Keith 1976) on organic constituents identified in waters of all types indicates that 55 different groups or families of organic chemicals have been identified in rivers and in effluents emptying into the rivers. Many of these, if not most, should potentially react with ozone. The concentrations and nature of ozonation products would be dictated by water quality and composition before ozonation, ozone concentrations, reaction time, and temperature.

Relatively little information concerning analyses of ozonated natural or polluted waters exist in the literature. Analysis of ozonated wastewaters has revealed that the principal volatile ozonation products are n-heptane, n-octane, n-hexanal, n-heptanal, n-octanal, and n-nananal in the low and sub part-per-billion ranges (Sievers et al. 1977, 1978a, 1978b). These products are expected following ozonation of olefinic double bonds if the ozone molecule were the selective oxidizing agent (see Carbon-Carbon Double Bonds). However, the large number of potential reactions indicates the inadequacy of this single study to delineate the limits of product formation in natural waters.

Summary

Although the ozonation of cooling waters has been studied relatively little, experimental results from laboratory tests indicate that a large variety of products may be anticipated following ozonation of natural waters. These products are expected to be principally aldehydic and carboxylic acid molecules. However, the list of potential products as derived from laboratory studies of ozonation of specific compounds and generic compound types is very extensive. The few studies of aqueous systems have indeed identified various aldehydes as the principal ozonation reaction products in wastewater, but at least one epoxide has been detected and identified, and a mutagenic peroxide has been isolated and identified. Stable hydroperoxides have also been formed following ozonation. Several studies have also indicated the presence of hydroxylated and oxidized PAHs, amine oxides, and nitrosoamines. These studies indicate the need for extensive attempts to determine ozonated products formed in a variety of qualities of cooling waters.

BIOLOGICAL ASPECTS OF OZONATION OF POWER PLANT COOLING WATERS

Introduction

The literature available on biological aspects of ozone includes a diversity of subjects, but there exists, however, a paucity of data concerning biological effects. Much of this literature relates to use of ozone for disinfection of wastewaters, with particular orientation toward sewage treatment. The remaining studies concern (1) other practical applications of ozone, (2) delineation of the effects of both residual ozone and ozonation products on mesozoan species, and (3) comparison of the relative efficiencies of ozone and chlorine as biocides with respect to both utilitarian and environmental impact considerations. All of these studies are relevant to evaluating the efficacy of ozone to function as an alternative to chlorine for biofouling control at electric generating stations.

In the following review of the ozone literature, some of the more pertinent papers and studies related to power plant usage will be summarized and evaluated. The data of concern relate to optimum use of ozone at power plants and have two foci: (1) minimization of the use of ozone, and (2) determination of the toxicity of ozone and ozonated products formed under conditions expected in the effluent, when conditions defining minimal effective levels are met. Specific objectives of this review are to determine if available information is sufficient to define (1) the effective dose-times of ozone required for biofouling control at power plants, and (2) the toxicity of residual ozone or ozonated products to aquatic organisms. Comparison of ozone and chlorine as biocides at power plants is dependent upon the capacity of the literature pertaining to ozone to satisfy these objectives.

The literature review which follows is organized into three sections to facilitate this comparison. The first two sections present evidence concerning the applications and toxicological effects of ozone and/or its reaction products. The third section presents data derived from studies designed specifically to compare the relative usefulness and environmental effects of ozone and chlorine.

Applications of Ozone

The central theme of many of these papers focused on specific applications of ozone such as biofouling control, maintenance of water quality in aquaria or seaquaria, and disinfection of hatchery and waste water effluents. Although less quantitative experimental data have generally been presented in these papers, information presented is pertinent background data consistent with the objectives presented in the introduction. Separation of marine and freshwater data has not been attempted in this review because of the paucity of information related to identification of reaction products and understanding of ozone reaction mechanisms in marine systems.

Blogoslawski and Stewart (1976) reviewed the multiple applications of ozone in marine systems and suggested that ozone, under certain conditions, can produce long-lived bromo-compounds which may be harmful to aquatic life. The principal marine applications of ozone were microbial control for shellfish depuration and red tide detoxification.

Biofouling Control

The effectiveness of ozone in preventing marine fouling in seawater intake systems was examined by Mangum and McIlhenny (1975). A continuous residual ozone concentration varying from 0.5 to 1.5 ppm prevented the growth of barnacles, algae, and slime on test pipes. The predominant toxic species was believed to be the hypobromite ion. Exposure to 1 ppm ozone for 85% of the 168-hr test period was required to completely control fouling. Exposure for 30% of the test period did not control fouling.

Garey (1976) investigated the effectiveness of ozone in reducing slime growth within the condensers of a marine power plant. Communities were exposed to 0.1, 0.3, and 0.6 ppm residual ozone for time periods of 1, 10, and 100 min. Ozone appeared to reduce growth; however, residual ozone in seawater was found to be essentially nonexistent and the effective agents were hypothesized to be hypobromous acid and hypobromite ion resulting from oxidation of bromide. Results of studies where freshwater slime communities were exposed to 0.1, 0.3, and 0.6 ppm residual ozone for time periods of 1, 10, and 100 min indicated that ozone was very effective in controlling these communities (Marine Research Inc., 1977).

Studies by Toner and Brooks (1977) indicated that ozone could inhibit settling of <u>Mytilus edulis</u> larvae on intake tunnels but that prohibition of this settling would require constant ozonation of the intake water. This marine mollusc is primarily responsible for biofouling in the intake pipes of marine and estuarine power plants. Larvae were exposed for 5 min to 0.5 to 1.5 ppm residual ozone, depending on larval size and water temperature. Juveniles were treated for 1 hr at 0.8 to 0.9 ppm. Smaller larvae displayed increasing susceptibility to ozone as temperatures increased, but juveniles were not affected by ozone.

After summarizing the known advantages and disadvantages (based on environmental and economic considerations) of ozone as an alternative biocide, Sengupta et al. (1974) concluded that ozone can be expected to prevent biofouling in both fresh and salt water systems, but that ozonation cannot be considered a viable technology until (1) all engineering problems have been solved, and (2) the expected environmental benefits exceed the additional cost of converting from present practices to ozonation. Lebourveau (1974) also expressed the concerns of the electric power industry with respect to ozone, stating that test data are needed to balance biocide effectiveness against the impact on valuable marine species. The power industry expressed hopes that a system can be found which will be selective to the fouling communities without causing harm to organisms in the receiving aquatic ecosystem. This seems unlikely.

Aquaria and Oceanaria

Application of these data to power plant situations is of questionable value because of filtration procedures which probably remove most, if not all, of the toxic materials prior to organism exposure. Ozone has been utilized in several public seawater aquaria and no harmful effects to fish have been detected as long as ozone concentrations are maintained below 0.5 ppm for less than 6 hr/day (Sander and Rosenthal 1974). Residual ozone can rarely be detected in these aquaria, however, because it is usually destroyed by passing the treated water through activated charcoal filters before it is returned to the fish tanks. Seaworld of Ohio ozonates 450,000 gal (1.7×10^6 liters) of artificial seawater before passing it through a rapid sand filter. Only sodium chloride is used to make up the seawater, and at the ozone concentration employed, no residual ozone has been detected. Sea World of Orlando adds 1.0 to 1.5 lb/day (0.68 kg/day) of ozone (from air) to 167,000 gal (0.6×10^6 liters) seawater containing fish and sharks with no apparent harm to the organisms (Blogoslawski and Stewart 1976). Murphy (1974) indicated that even though relatively stable residual substances, currently thought to be peroxy-radicals or hypobromites, are formed when seawater is ozonized, their effects on oceanaria populations have not been observed to be detrimental. He recommended that these compounds be identified and their properties and effects on aquatic life be assessed.

Hatchery Disinfection

Results of investigations concerning the use of ozone in controlling harmful microorganisms in fish hatchery and shellfish cultures have identified ranges of residual ozone that are toxic to some selected organisms. For example, Rosenlund (1974) found that ozone residuals of 0.01 to 0.06 ppm had to be continuously maintained in a trout hatchery effluent to kill all bacteria, but that trout exposed to these concentrations experienced 100% mortality in 4 hr. In order to reduce effects of ozonated effluents on fish it was recommended that the ozonated water be retained until the residual decomposed and gas supersaturation was eliminated.

Straub (1975) found that improved breeding and hatching yields of trout and pike in a fish hatchery could be achieved by ozonation of effluent water. Ozonated effluent was first passed through a quartz sand filter and then aerated to remove residual ozone; no residual ozone could be detected in the effluent supplied to the fish tanks. Moffet and Shleser (1974) investigated the potential use of ozone as a disinfectant for lobster culture by exposing larvae of the American lobster to 0.4 ppm ozone for 30 min. One-third of the larvae died within six days, but no controls were run to validate these results. Reduction of harmful microflora by ozonation is believed to increase larval survival, and, according to the authors, there appears to be a potential for the use of ozone in rearing-facilities for lobster larvae.

Wastewater Disinfection

The disinfection properties of ozone have been recognized for at least a century, and treatment of water by ozonation has been adopted in many European countries, with recent interest being developed in the United States. A mass of literature exists concerning the disinfection properties of ozone and the effectiveness of ozone in water treatment. Many of the studies on this subject report dose-time relationships that kill microorganisms such as bacteria, viruses, and fungi in wastewater effluent. Some studies report the basic physical and chemical properties of the effluent, but the products of ozonation that may be the causative toxic agents have not been identified or quantified.

An excellent synthesis and summary of the existing literature related to wastewater disinfection with ozone has been given by Venosa (1975). A majority of his literature review dealt with inactivation of bacteria (*E. coli*) viruses or whole sewage effluents. In general, residual ozone concentrations maintained for 5 min or less at 1 to 2 ppm are adequate to kill most bacteria and viruses. Spores and cysts are more resistant and generally require higher doses and longer contact times (up to 4 hr). The conclusions states that, "there exists much controversy, contradiction, confusion, and nonfactual subjective judgment concerning the use of ozone for disinfection of water and wastewater." For example, he stated that it is often difficult to discern whether authors of papers he reviewed were discussing ozone residual or applied ozone when reporting data on concentrations necessary for a certain microbiocidal effects. Some of the questions that need to be answered concern the effects of ozonated effluents on fish and aquatic life, the effect of ozone on wastes, and the disinfection pattern of ozone (e.g., all-or-none effects, etc.).

Recognizing some of the unanswered questions discussed by Venosa (1975) in his review, Cronholm et al. (1976) conducted investigations to determine the feasibility of using ozone to reduce microorganisms and nonbiological pollutants in sewage effluents. Studies using 1 to 2 ppm ozone resulted in such rapid bacterial and viral inactivation that it was not possible to present survival data as a function of exposure time. The most significant result of this study, however, indicated that the nature of the water is an essential variable in determining effective ozone doses to inactivate bacteria and viruses. According to the authors, ozone in wastewater may have to be increased by a magnitude of 25 to 50 over those required to achieve equivalent virucidal effects in drinking water. The study did not indicate the specific compounds which inhibit ozone disinfection. In general, they found that ozone was less effective than chlorine in reducing biological and nonbiological pollutants in effluents and recommended that ozone not replace chlorine for the particular system they studied.

A comprehensive review of the literature related to ozonation of organics and identified reaction products of these organics is presented by Chian and Kuo (1976). The major ozonation products of various organics have been identified as formic, glyoxylic, oxalic, and acetic acids along with other aldehydes, ketones, and carboxylic acids. These compounds are known to be of low to moderate toxicity (Carlson and Caple 1977). The ozonation of these first three acids is believed to be primarily responsible for the removal of organic substances from water. Carlson and Caple (1977) ozonated various organic compounds, such as fatty acids which are common in wastewaters, and found, for example, that some oxides and epoxides were produced when oleic acid was ozonated at an O_3 flow rate of 30 ml/min for 20 to 215 min. Epoxides and peroxides are known to be highly toxic as well as mutagenic and carcinogenic under certain conditions (see section on Mutagenic Effects below).

Effects on Aquatic Organisms

Studies on the acute and chronic effects of residual ozone and its reaction products on aquatic organisms are important for indicating (1) ranges and levels of dose-time exposures effective for killing organisms or disrupting normal biotic functions, (2) relative effectiveness of ozone and other biocides for controlling organisms under various water types and, (3) possible modes of biotic-abiotic interactions occurring during biocide applications in various types of aquatic systems. These studies have generally been directed toward determination of direct effects on mortality and mutagenic effects.

Direct Effects on Mortality

Hubbs (1930), conducting one of the first bioassays with residual ozone, reported that residual ozone concentrations as low as 0.09 ppm were lethal to fish; crayfish died after exposure to 1.16 ppm ozone; and "minute planktonic and bottom invertebrates" were "all more or less quickly killed" in a residual ozone concentration of 1.25 ppm. Exposure of fish generated a wide range of responses from altered locomotory and respiratory movements at the lower concentrations (< 0.05 ppm), through loss of equilibrium and wild swimming, followed by quiescent periods terminating in death. Hubbs hypothesized that the effect of ozone was cumulative and irreversible beyond the stage of first equilibrium loss.

When unicellular algae, zooplankton, and various "worms" which are commonly found in aquarium and pond water were exposed to concentrations of residual ozone ranging from 0.3 to 0.5 ppm for 5 to 10 min, Bringman (1954) found that 50% of the chlorophyll was destroyed in the algae after a 10-min treatment; all zooplankton were killed after 5 to 6 min, and all "worms" were killed after a 10-min exposure.

The acute effects of residual ozone on four species of marine phytoplankton, crab zoea and megalops, and a small fish, the Atlantic Silversides were determined by Toner and Brooks (1974). Residual ozone concentrations of 0.08 to 0.2 ppm killed all crab magalops and fish within 30 min; 1-min exposure to 0.08 ppm residual ozone killed 30 to 40% of the crab zoea within 48 hr, and populations of marine phytoplankton decreased within 24 to 48 hr after exposure to 0.1 to 1.0 ppm residual ozone. The authors concluded that small residual concentrations of ozone adversely affect a diverse range of marine organisms and that ozone may not be a suitable biocide for antifouling because it appears to be just as toxic as chlorine to organisms exposed to power plant effluents.

Results of acute and chronic bioassays on seven species of fish, six species of invertebrates, and Daphnia magna with ozone led Arthur et al. (1975) to conclude that ozone had a potential for use in sewage treatment. No measurable toxicity to these organisms was found from either short- or long-term exposure to ozonated effluents (no residual ozone was measurable). Acute toxicity due to residual ozone was only observed when continuous levels of residual ozone were maintained in the effluents. Residual ozone concentrations of 0.2 to 0.3 ppm killed fathead minnows after 1- to 3-hr exposures.

Ward (1976) reviewed several studies related to the effects of residual ozone on aquatic organisms. Residual ozone concentrations ranging from 0.05 to 0.23 ppm killed five species of fish within a time range of 45 min (trout) to 72 hr (goldfish). Barnacles exposed to residual ozone concentrations of 0.4 to 1.0 ppm died within several days to a week and unknown "low" (no doses given) concentrations of ozone caused death (no times given) of seven genera of freshwater protozoa and rotifers. The conclusion of this review was that since ozone dissipates so rapidly in most natural waters, any residual ozone discharge is likely to be too little to exert adverse effects upon biotic populations of the receiving aquatic system.

The specific ozone reaction products which affect aquatic organisms have not been identified; however, some reaction products such as organic peroxides and hydroperoxides have been observed to have a deleterious effect on nonaquatic organisms. Peroxides have been observed to produce mutations in Drosophila (Altenburg 1954, Sobels 1956), Neurospora (Dickey et al. 1949), and in other organisms, and to induce mortality in mice (Horgan et al. 1957).

It appears, therefore, that the toxicity of ozonated organics to aquatic organisms is a justified concern that warrants investigation because: (1) ozonation of wastewater is known to produce some toxic reaction products (see sections on Wastewater Disinfection and Ozone Chemistry), and (2) some reaction products such as hydroperoxides and organic peroxides have been demonstrated to be highly toxic to various nonaquatic organisms.

Mutagenic Effects

The mutagenic effects of residual ozone on aquatic organisms are not well documented. Cotruvo et al. (1976) ozonated 28 organic compounds and investigated the mutagenic effects of the products on bacteria. Only seven of these compounds produced mutagenic activity, and then only after prolonged (up to 6 hr) exposure to ozone. Mutagenic activity was not related to dose, and results of many of the bioassays could not be replicated. The effects of ozone-treated seawater on the development of oyster eggs indicated that fertilization, meiosis, and cleavage were abnormal in ozone-treated water in which eggs were held at 0.18 to 0.4 ppm for up to 2 hr (McLean et al. 1973). Following exposure of root meristem cells of Vicia faba to ozone, Fetner (1958) found a high incidence of abnormal mitotic activity compared to the controls.

The specific ozone reaction products which produced the mutagenic effects in the above studies have not been identified. In nonaquatic organisms, however, organic peroxides and hydroperoxides have been shown to be capable of inducing lethal mutations in Drosophila (Altenburg 1954, Sobels 1956), Neurospora (Dickey et al. 1949), and Escherichia coli (Davis 1959). The LD_{50} of linoleic acid peroxide (0.26 μmol/g) was comparable to the level of organic peroxide previously found in mice after receiving an LD_{50} dose of X-rays (0.22 μmol/g) (Horgan et al. 1957). Thus, organic peroxides and hydroperoxides produced in water are extremely toxic to a wide variety of organisms.

Ozone and Chlorine Comparisons

Results of acute and chronic bioassays using seven species of fish and six species of invertebrates, including Daphnia magna, led Arthur et al. (1975) to conclude that chlorinated sewage effluents were lethal to these test animals at appreciably lower concentrations than ozonated effluents. The respective 7-day TL_{50} values of total residual chlorine to fish and invertebrates ranged from 0.08 to 0.26 and 0.21 to 0.81 ppm, respectively. No measurable toxicity to these organisms was found from either short- or long-term exposure to ozonated effluents. Acute toxicity in ozonated effluents was observed only when continuous levels of residual ozone were maintained in the effluents. Residual ozone concentrations of 0.2 to 0.3 ppm killed fathead minnows after 1-

to 3-hr exposures compared to 12-hr exposure with 0.19 to 0.34 ppm residual chlorine.

Ward et al. (1976) conducted extensive bioassays using ozone, chlorine, and bromine chloride to determine the comparative effectiveness of these biocides as wastewater disinfectants. Acute toxicity tests were performed at various effluent concentrations on several species of fish and Daphnia magna and life-cycle toxicity studies were conducted using the fathead minnow, Pimephales promelas. Residual ozone concentrations of 0.005 ppm or less had no effect on the survival or reproductive capacity of fathead minnows, while total residual chlorine concentrations of 0.045 ppm or more caused growth retardation and mortality of the continuously exposed minnows. Chlorine was found to be the most toxic of the biocides tested. However, examination of the disinfection capability of ozone was often limited by inadequate dosages resulting from design limitations, mechanical failures, and operator inexperience.

Ward (1976) also presented some data on the 96-TL_{50} concentrations of ozone, chlorine, and bromine chloride for three species of fish. Although the 96-hr-TL_{50} values varied according to species, they generally were in the range of 0.1 to 0.2 ppm for all three biocides. The conclusion reached was that similar concentrations of ozone and chlorine appear to produce similar short-term adverse effects on aquatic organisms.

In a study conducted at the Connecticut River Vermont Yankee Power Plant by Marine Research, Inc. (1977), ozone was shown to be a more effective biocide than chlorine in controlling freshwater slime communities. Freshwater slime communities were exposed to residual ozone and chlorine concentrations of 0.1, 0.3, and 0.6 ppm for time periods of 1, 10, and 100 min. Time of exposure was found to be more important than treatment level, and it was recommended that ozone be considered a viable alternative to chlorine in freshwater systems.

Summary

Most of the available literature pertaining to aqueous applications relates to the use of ozone for disinfection of waste water and drinking water. A very limited number of papers discussed the use of ozone for treating effluents in fish hatchery and shellfish culture systems and the potential beneficial uses of ozone for power plant biofouling control and seawater aquarium treatment. Although a significant volume of chemical papers is available, scant information on the ozonation of organic constituents in cooling waters has been found. The products of ozonation of these waters are hypothetical at this juncture, but several potential products are known to be highly toxic. For example, ozonation of oleic acid, a known constituent of wastewaters, results in formation of oleic acid oxides or epoxides. Peroxides and epoxides are known to be highly toxic as well as mutagenic and carcinogenic under certain conditions. Peroxides have been observed to produce mutations in *E. coli* and *Drosophila*, and certain peroxides have been shown to be extremely toxic to mice. Toxicity of epoxides and peroxides to aquatic organisms, however, has not been determined. It appears, therefore, that the toxicity of ozonated organics to aquatic organisms is a justified concern that warrants investigation.

It appears that residual ozone levels of 0.01 to 1.5 are toxic to most aquatic organisms. Some of the more important nonbiological factors that determine the sensitivity of organisms to residual ozone are nature of the water (wastewater effluent, treated effluent, etc.) and salinity. Microorganisms are sensitive to lower concentrations than macroinvertebrates and fish. Identification of the ozone residuals that are toxic to organisms has not been accomplished. Characterization of the initial, intermediate, and residual toxic species and the identification of the fate of ozone must be made before a judgment about the efficiency of ozone and accurate establishment of standards for the control of biofouling can be made.

It also appears that ozone is more effective than chlorine in controlling biofouling organisms in freshwater systems, but somewhat less effective in marine systems. The residual oxidant species of ozone and chlorine appear to be similar in seawater; however, these compounds need to be investigated, identified, and their properties and effects on aquatic life assessed.

CONCLUSIONS AND RECOMMENDATIONS

Definitive evaluation of ozone as a power plant biocide is presently impossible. Available information is insufficient to determine the degree to which ozone application at power plants can satisfy the criteria of maintenance of condenser integrity and avoidance of environmental impacts. Field studies have indicated that ozone can reduce fouling at marine power plants, and laboratory studies have suggested that concentrations of 0.5 to 1.5 ppm are sufficient to control fouling. However, information is lacking on minimum required dosage and the variation of this dosage with geographical location and water quality. Potential reaction products in natural waters include a broad spectrum of compounds, but identification and quantification of ozonated materials in effluents remain virtually unstudied. Because the reaction products will undoubtedly vary with water quality, as well as ozone application level and temperature, it is not possible to assess the relevance of the toxicity studies which have been completed. The narrow range of both ozonated compounds and biotic species studied lends credence to the assumption that toxicological data are insufficient to assess the potential impacts of power plant ozonation. The questions raised previously (see Introduction) remain valid, given present knowledge of the various aspects of the potential interaction of ozone with power plant cooling waters.

A research program designed to provide information to evaluate biocidal ozonation of power plant cooling waters is both timely and justifiable. Information to allay or substantiate the concerns expressed by environmentalists and regulatory personnel regarding the health and environmental impacts of chlorination is not expected to be available prior to the early 1980s. If these potential impacts are substantial and are not ameliorable via simple measures (e.g., dechlorination), alternate biocides will be required for on-line use with as short a conversion time as possible. Information does not currently exist to define an appropriate alternate. Research now might provide that information in time to facilitate selection of an alternate biocide, should one be required. Justification of research specifically designed to assess ozone as an alternate is based on the studies presented in previous sections: (1) it appears to be effective in biofouling control; (2) a back-log of technical experience with application procedures already exists in the field of drinking water treatment; and (3) the major products (oxygen and aldehydic and carboxylic acid molecules) are not likely to be toxic at the concentrations expected in power plant effluents. Although a potential does exist for formation of toxic ozonated organics in cooling water effluents, this potential appears low enough to warrant further investigation.

We recommend a limited research program designed to proceed in a logical sequence of stages to evaluation of ozone as a power plant biocide. Completion of each stage should generate sufficient information to direct further studies or to discontinue research. Initial studies should focus on minimum levels required for biofouling control and acute screening bioassays of ozonated organics formed in a wide variety of natural waters. The screening bioassays should be initiated at effluent concentration levels.

Any demonstration of toxicity would then justify steps to identify the causative agent(s) via liquid chromatographic isolation and GC/MS analysis, and to shift the scope of the project to emphasize studies of partitioning, persistence, degradation, etc. Results indicating that the causative agent(s) are moderately toxic, highly persistent, and of high bioaccumulation potential would lead to the conclusion that ozone is not a viable alternative biocide, and research could be concluded.

If acute toxicity is not demonstrable, results from a greater diversity of bioassay regimes, including expansion of tests to include long-term chronic-exposure studies on aquatic vertebrates, must be obtained before final acceptance of ozone as an alternative biocide.

A sequential procedure, such as outlined above, could prevent funding of research yielding information of little value for practical application and facilitate a reasoned evaluation of the potential of ozone for use at power plants.

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