OZONE AS A DISINFECTANT FOR WATER AND SEWAGE

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Introduction

Most of the conscious efforts in water supply and waste-water disposal have been, and continue to be, directed toward the removal and destruction of pathogenic microorganisms.

Chlorine and some of its compounds meet the general requirements for a disinfectant so well that they have been used almost exclusively. However, we have to reconsider periodically whether other disinfectants could be employed expediently for disinfection purposes.

Ozone has been used in municipal water supplies mainly in Europe. It has, however, never received widespread recognition as a disinfectant in this country. Although information on the properties of ozone is very limited and the few quantitative data available in the literature are scattered and controversial, all recent investigations agree that ozone is capable of efficiently destroying pathogenic organisms borne by water or sewage.

Production of Ozone and Its Transfer into Water

Ozone is relatively safe and easy to handle. It is unstable and must be produced at the point of application. The ozonator is generally made up of a number of elements consisting of flat hollow blocks between which are set pairs of flat glass plates. Each glass plate has an electrode on its exterior surface. A voltage of 8,000 - 20,000 volts is applied across the electrodes and A. C. of 500 cycles is commonly used. The air or oxygen passing to the ozonator must be dried, and normally the refrigerant type of dryer is used. The air or oxygen volume passing through the ozone generater is such that only about 1 - 5 mg ozone per liter of gas is created.

Ozone can conveniently be applied to the water by either one of the following methods: (1) ozonized air is intimately mixed with water in a type of injector; (2) ozone is dispersed under pressure into

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the water through porous media at the bottom of a deep tank; (3) the gas is introduced by means of vortical rotors (cavitators). However, the devices used today let a considerable proportion of the applied ozone escape into the atmosphere. It may therefore be expedient to recover and reuse this ozone.

The rate of ozone transfer into solution is dependent upon the ozone concentration in the gas stream and the applied pressure, according to the laws of Henry and Dalton. If ozone is produced from oxygen instead of air, the yield of ozone (for the same energy uptake) and, therefore, the transfer of ozone into water can be improved considerably. Additional research on mixing and gas transfer in solution is needed to evaluate the dependence of gas-solution transfer on parameters such as bubble size, turbulence, depth of the contact vessel, surface activity of the solution, etc. Such studies should lead to the design of more profitable and efficient ozone-water contacting vessels.

Cost of Ozone

It is a general belief that the use of ozone is limited because of cost. A few data on operational and maintenance cost given by European water supplies indicate, however, that the cost of disinfecting water supplies by ozone is comparable with that of chlorine.[1,2]

Table 1 gives a recent analysis of energy uptake for the produc-

TABLE 1
Energy Uptake for the Production of Ozone and Its Transfer into Solution (*Scheller*[2])
(0.5 mg O_3 is applied per liter water)

	Energy Uptake in watts per gram Ozone
Drying of air	21
Ozone production	23
Ozone transfer into water	20
Auxiliary equipment	2
Total	66

tion of ozone and its transfer into the water by the ozone disinfection plant of the municipal water supply in Berne, Switzerland.[2] This plant disinfects 5.4 mgd of polluted spring water by the application of approximately 0.5 mg of ozone per liter of water. The disinfection of one mgd can be achieved by a total energy uptake of only 120 kilowatt hours.

Chemical and Physical-chemical Properties of Ozone Solutions

An appropriate knowledge of the chemical properties of a disinfectant is a necessary background for the understanding of its disinfecting behavior. The information on chlorination chemistry, for instance, has proved to be of major importance for the intelligent application of chlorine and its compounds for disinfecting purposes. The chemical and physical-chemical properties of ozone, however, are not yet adequately known. This lack of knowledge has obstructed the collection of consistent data on the germicidal properties of ozone.

Ozone Demand

Ozone is next to fluorine in the list of powerful oxidizing agents. It reacts with inorganic and organic reducing substances to produce an "ozone demand." The reaction of organic substances is generally more rapid and more extensive with ozone than with hypochlorous acid. This would indicate a rapid reaction rate of the disinfectant with the vital centers of the microorganisms. The higher oxidation potential of ozone as compared to chlorine is certainly of advantage with respect to removal of color and taste producing constituents in the water. The strong tendency of ozone to combine with reducing substances may, however, also be a disadvantage. Large dosages are required in solutions that contain oxidizable constituents to acquire "free ozone." The "ozone demand" of natural waters is generally larger than the corresponding chlorine demand. The "ozone demand" of a sewage may even be exhorbitant.[3,4]

Ozone Decomposition

Ozone in solution is unstable and decomposes into oxygen. The decomposition is temperature dependent and is strongly catalyzed by trace concentrations of many inorganic and organic constituents of the water. The decomposition rate is especially dependent on the hydroxyl ion concentration (Figure 1).[5] For this reason, ozone does not persist within the treated water. It provides no "residual protection" against recontamination. Attributable to this rapid decomposition, the water disinfected by ozone, on the other hand, is free of odor and the taste of the germicidal agent.

The Intermediates in Ozone Decomposition

The mechanism of ozone decomposition is not fully understood. The strong dependence of the rate of decomposition upon pH and the decomposition catalysis by trace quantities of water constituents can only be explained by assuming that the decomposition occurs in a

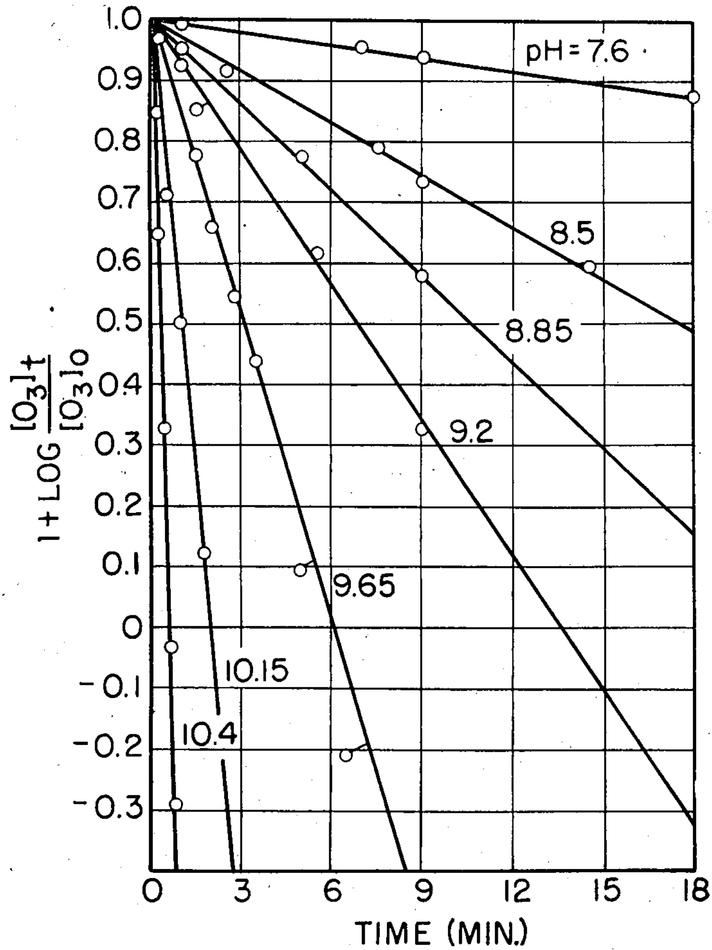

FIG. 1.—DECOMPOSITION OF OZONE IN AQUEOUS SOLUTIONS IN DEPENDENCE OF pH (Stumm[5])

Temperature: 14.6° C; Ionic Strength: $\mu = 0.05$;
Buffer system: $CO_2/NaHCO_3/Na_2CO_3$

stepwise fashion producing, in turn, short lived radicals. Alder and Hill,[6] for example, suggest the following mechanism:

$$O_3 + H_2O \rightarrow HO_3^+ + OH^-$$
$$H_3^+ + OH^- \rightleftharpoons 2HO_2$$
$$O_3 + HO_2 \rightarrow HO + 2O_2$$
$$HO + HO_2 \rightarrow H_2O + O_2$$
$$\overline{\qquad\qquad\qquad\qquad}$$
$$2O_3 \rightarrow 3O_2$$

Despite the considerable controversy on the mechanism of the decomposition reaction, most investigators[5,6,7] agree that the radicals HO_2 and OH are intermediates. We do not know definitely whether these intermediates are of any significance for the interpretation of the chemical and germicidal properties of ozone solutions.

It has been confirmed that the same radicals (OH and HO_2) are produced by irradiation (e.g. x-rays, β-rays) of aerated water.[8,9] The chemical reactions in which these free radicals take part are known to some extent from radiation chemistry. Whether the radicals react with dissolved substances or combine with one another depends on their concentration and on the susceptibility to attack of the dissolved material. The radicals are capable of oxidizing efficiently inorganic[10] and organic[11] constituents and of inactivating enzyme systems.[8] Some investigators assume that OH and HO_2 contribute significantly to the killing of microorganisms by irradiation.[8,12]

These considerations sustain the possible importance of the decomposition intermediates in the reaction behavior of ozone.

Solubility of Ozone and Ozone Uptake by Different Types of Water

Ozone is about 10-12 times more soluble than oxygen, but, because it is at low partial pressure, the maximum concentration that can be obtained in solution is only a few mg/1. Table 2 gives the distribution coefficient in relation to temperature.[3]

Figure 2 represents schematically the ozone uptake by different types of water.[3] Ozonized air is introduced continuously and at a constant rate into different waters under the same mixing conditions. The concentration of "free ozone" is plotted as a function of time, which is representative of the amount of ozone added to the solution. Curve A is obtained with a pure "ozone demand free" water. It is a typical first order gas absorption curve. Curve B is obtained with a

TABLE 2

Solubility Coefficient for Ozone in Water (Stumm[3])

$$g = \frac{O_3\text{ (Water)}}{O_3\text{ (Gas)}} \text{ (at 1 Atm.) Ionic Strength: } \mu = 0.05$$

Temperature, °C	5	10	15	20	25
Solubility coefficient, g	0.45	0.41	0.37	0.34	0.30

The solubility is independent of pH up to pH = 8.5.

water that exerts an ozone demand. A substantially completed oxidation-reduction process takes place before attaining "residual ozone." Thereafter the ozone uptake is the same as with an "ozone demand free" water. Such curves are frequently obtained with the ozonization of ground waters. With some waters (e.g. surface water, sewage)

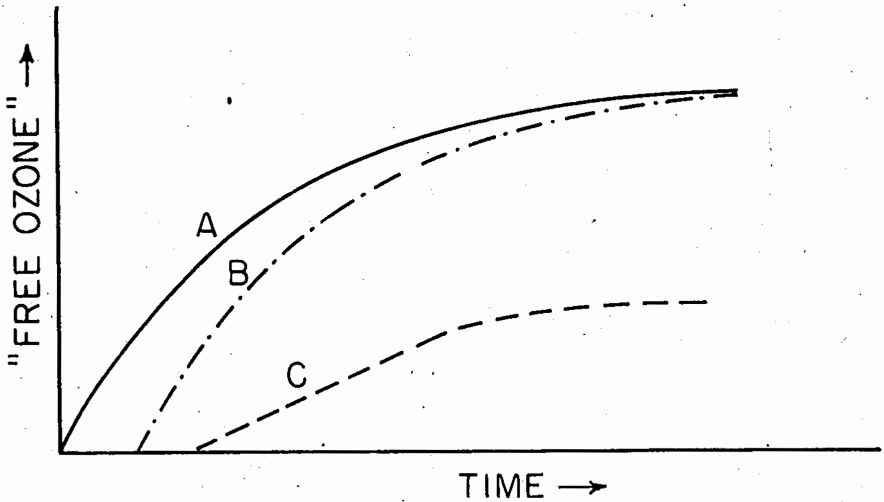

Fig. 2.—Ozone Uptake by Different Types of Water (Schematically, Stumm[3])

curves of type C are customary. In addition to an ozone demand, the rate of uptake of free ozone is decreased due to an additional ozone consumption caused by slow oxidation reactions and by increased catalysis of ozone decomposition.

Ozone Analysis

No analytical technique has yet been developed that permits a sensitive and specific quantitative determination of residual ozone.

The most specific method, the spectrophotometric measurement of absorption of ultraviolet light,[4] is not very sensitive. More sentitive methods reported in the literature (oxidation of o-Tolidin,[4] Mn^{+2},[13] Fe^{+2},[14] Indigo,[15] Iodide[16]) are principally based on the determination of the total oxidizing capacity of the solution rather than the amount of residual ozone only and are not entirely specific. Oxidized inorganic (Iron, Manganese, etc.) and organic constituents and possibly the decomposition intermediates interfere.

Germicidal Properties of Ozone Solutions

The lack of knowledge on the chemistry and kinetics of ozone solutions and the uncertainty of analytical techniques are serious obstacles in all investigations on ozone disinfection. The usual process of bubbling ozone through a bacterial suspension and then measuring the total oxidizable residue may fail to give appropriate estimates of the concentration of bacteriacidal "free ozone." Other investigators have added definite amounts of ozone to a suspension of microorganisms and report values for "lethal ozone dosage." Such values are not necessarily representative, because each particular test solution, even bacterial suspensions in "ozone demand free" water, must be assumed to have a certain ozone consumption. (Minute amounts of nutrients attached to the bacteria exert an ozone demand and catalyze the ozone decomposition strongly.)

A very careful investigation on the kinetics of ozone disinfection has been made by Wuhrmann and Meyrath.[17] Some of their results are summarized in Figures 3 and 4. During each experiment the ozone concentration was kept constant by continuously bubbling air containing small amounts of ozone through the solutions. The results indicate that ozone disinfection is mainly a function of contact time, concentration of ozone, and temperature of the water. The disinfection mechanism, seemingly, is similar to HOCl disinfection. Their investigations reveal that the contact time necessary for 99% destruction of E. Coli is seven times smaller with ozone than with the same amount of hypochlorous acid, while the killing rate for spores (B. megatherium cereus) is about 300 times larger with ozone than with chlorine.

Fetner and Ingols,[18] however, postulate on the basis of their investigations with E. Coli that ozone has a different mode of action than chlorine. They claim that ozone shows an "all-or-none type of effect" within the contact time of one minute. They found no effect of the ozone below a certain critical concentration and above this concentration no detectable survivors.

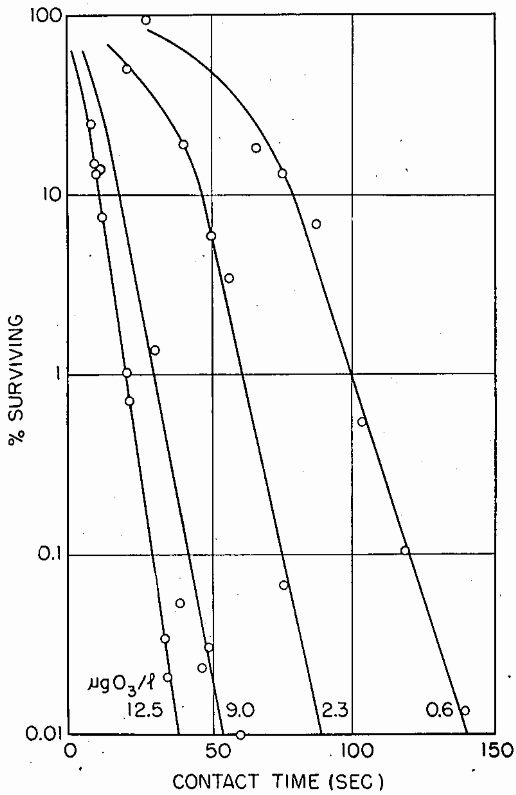

FIG. 3.—BACTERICIDAL ACTION OF OZONE AGAINST *E. Coli* (Wuhrmann and Meyrath[17]) Temperature: 12° C; pH = 7.0; Buffer: $CO_2/NaHCO_3$

Bringmann[19] reports that ozone destroys the following organisms more rapidly than chlorine: E. Coli, spores, different algae, and protozoa. His results indicate that ozone has a considerably higher lethal efficiency than chlorine especially for organisms which exhibit high resistance to disinfection by chlorine.

According to Newton and Jones[20] over 99% of cysts of E. histolytica were killed in water within 1 - 3 minutes after the application of 0.5 - 1 mg/1 of ozone. Hettche and Ehlbeck[21] claim that 0.15 mg/1 ozone inactivates polio virus.

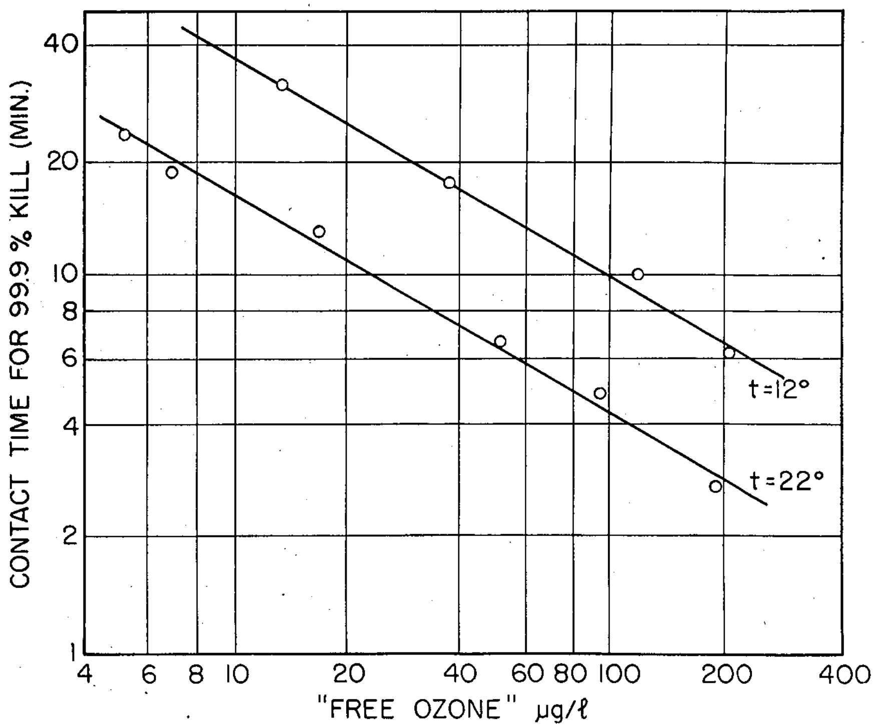

FIG. 4.—BACTERICIDAL ACTION OF OZONE AGAINST SPORES OF *B. megatherium/cereus* (Wuhrmann and Meyrath[17])

Age of the spores: 77-79 days; pH = 7.2; Buffer: $CO_2/NaHCO_3$; Temperature coefficient: 0 = 2.3 per 10° C.

Sewage Disinfection

The constituents of a sewage cause a remarkable ozone consumption. Therefore one would assume that they will heavily interfere in the ozone disinfection and that suspended matter will efficiently shelter embedded organisms against ozone attack.

Some recent reports, however, claim the feasibility of sewage disinfection. A Research Group of the Armour Research Foundation, Chicago, Illinois, and of the Biological Warfare Laboratories, Fort Detrick, Maryland,[22] investigated the possibilities of disinfection and sterilization of sewage by ozone. Their investigations are mainly related to the problem of sterilization of liquid effluents from infectious disease laboratories. These effluents are sterilized today by prolonged heat treatment at 300°F. Their laboratory results indicate that ozone can be successfully used for sterilization of sewage containing Bacillus anthracis, influenza virus, and Bacillus subtilus morphotype globigii (Bg), and for inactivation of toxin of Clostridium botulinum. To obtain sterility the ozone consumption in most experiments was between 50 and 115 mg ozone per liter. The time required to obtain complete sterilization was, with only a few exceptions, below 30 minutes.

Mechanism of Ozone Disinfection

Most investigators agree that the mechanism of disinfection by ozone is similar to that of chlorine. It is assumed that both inactivate essential enzymes of the cells. An important step in the action of the disinfectant seems to be the penetration of the cell wall. Ozone apparently diffuses very well through the cell membrane.

In applying the criterion of free ozone it is assumed that the effectiveness of the bactericidal action is a function of the ozone remaining. In the disinfection of polluted waters or sewage it seems, nevertheless, possible that ozone molecules may achieve the killing of microorganisms while simultaneously satisfying the ozone demand. Leiguardia's[23] investigations support the assumption that the bactericidal action of ozone proceeds parallel with the oxidation of organic matter. It may be inferred that the particles that are produced by the ozonization of water or sewage are, to some extent, also effective in reducing the concentration of microorganisms. Oxidized organic constituents (for example, ozonides which are structurally identical with organic peroxides) may be toxic to microorganisms. (Indications exist that organic peroxides are more bactericidal than hydrogen peroxide.) The possibility that the decomposition intermediates of ozone, the perhydroxyl and hydroxyl radicals, are able to interact with the molecules of cell cytoplasm and contribute to effective disinfection cannot be excluded.

Discussion

The information presented here gives sufficient evidence that ozone has to be considered as a potential disinfectant for water and sewage. It is available at reasonable cost, easy to handle, and can conveniently be applied to the water. Ozone seems to be especially promising with respect to the destruction of those pathogenic organisms that are highly resistant toward the action of chlorine compounds: cysts, some viruses, etc.

Our knowledge, at the present time, of ozone as a disinfectant is not adequate, and more investigations are needed to evaluate the applicability of ozone as a practical tool for the sanitary engineer in water treatment and waste-water disposal.

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