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LARGE SCALE OZONE GENERATOR FOR WATER TREATMENT (FUJI OZONIZER)

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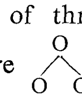
I. INTRODUCTION

Ozone has never been used before in Japan for the large scale purification of water. However, a vast amount of river and lake water has been contaminated by industrial and domestic waste water and attention has been focussed on ozone water treatment.

In the past, ozone generator has not be produced in Japan on an industrial scale. Under these circumstances, Fuji Electric has been engaged in research and development for three years with the cooperation of many parties. As a result on this work, Fuji recently developed a large scale ozone generator for industrial use featuring high reliability, high yield, compactness and low cost; an ozone meter; and a control system for optium ozone supply.

II. PROPERTIES OF OZONE

The physical constants of ozone are shown in *Table 1*. Ozone is a gas with a very high oxidation activity. The molecular structure consists of three oxygen atoms with a symmetrical structure 

. Ozone comes from the Greek word odor which indicates that ozone has its own special odor. Ozone is generally colorless, but at high concentrations of over 15% the color becomes blue.

Ozone can be easily synthesized by an opto-chemical reaction of ultraviolet rays and it is widely known to exist on the surface of the earth. The majority of the ozone exists in a layer 20 to 50 km above the earth's surface. Ozone is relatively unstable and is easily decomposed by heat, light, organic compounds and water molecules in the atmosphere, etc. For example, the half life of a concentration of 1% (wt) of ozone in the atmosphere at normal temperatures is about 16 hours, and for 3 ppm (wt) in water, it is only 30 minutes. Because of this, ozone can not be stored in cylinders, etc.

Table 1 **Physical constant of ozone**

Molecular weight	48.0
Boiling point (760 mm Hg), °C	−111.9
Freezing point (760 mm Hg), °C	−192.7±0.2
Critical temperature °C	− 12.1
Critical pressure, atm	54.6
Gas density (0°C), g/*l*	2.144
Specific heat, cal/mol·deg at 127°C at 25°C	 10.44 9.37

Ozone is a strong oxidizing agent and is second to fluorine in oxidation activity. This is due to oxygen in the nascent state which can be formed in this way: $O_3 \rightarrow O_2 + O$. This nascent oxygen also appears in the case of oxidation with chlorine as follows: $Cl_2 + H_2O \rightleftharpoons HCl + HClO$, $HClO \longrightarrow HCl + O$. However, chlorine's oxidation activity is very weak and it is classified as a medium oxidizing agent.

Ozone dissolves more easily in water than oxygen does. The usual solubility of the 1 to 4% ozone obtained from an ordinary ozonizer is 5 to 20 mg/ℓ (water) (5 to 20 ppm wt). When ozone is used to purify water, many harmful substance are decomposed by the oxidation reaction and since the remaining ozone is rapidly decomposed to form O_2, the odor which remains in chemical water treatment such as chlorination as well as the bad taste of the water are not found with ozone treatment.

Ozone is also an excellent deodorizer. It oxidizes substances with strong odors such as hydrogen sulphide, mercaptans and scatole to improve the odor and also employs a characteristic masking action.

III. OZONE GENERATION METHODS [1]

In addition to an opto-chemical reaction, ozone can be synthesized by various chemical reactions. However, for production of large amounts on an industrial scale, partial discharge (previously known as silent discharge) is the most effective.

1. Principles of Ozone Generation by Partial Discharge

As can be seen in *Fig. 1*, when there are an air gap and a solid insulating material in a series, dielectric breakdown occurs in the air gap if an AC voltage is applied between the electrodes. However, flashover does not occur because of the series in-

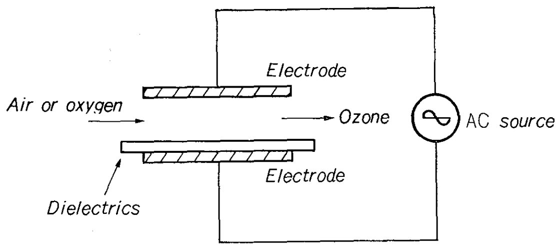


Fig. 1 **Principle of ozone generation tube**

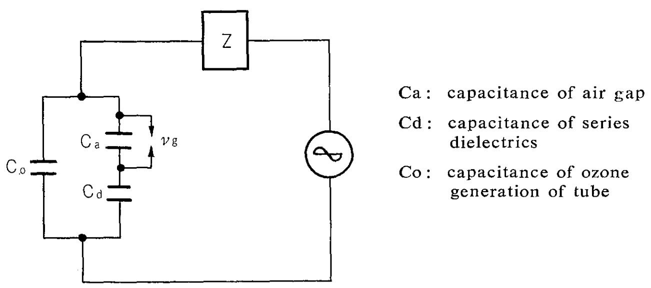


Fig. 2 **Equipment circuit of ozone generation tube**

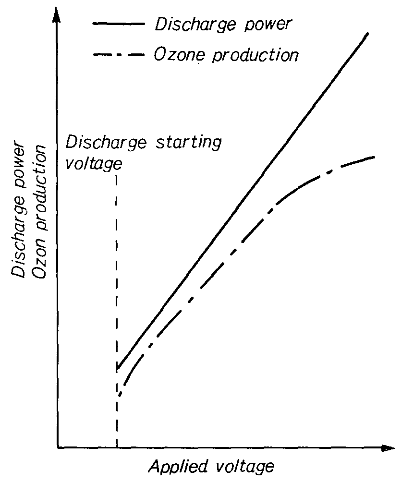


Fig. 3 **Relationship of discharge power and ozone production**

sulating material, but only pulse discharges occur in the region of the air gap.

At this time, the accelerated electron (e) due to the discharge collides with the O_2 molecular and the following reactions occur.

$$O_2 + e \longrightarrow 2O + e \cdots\cdots (1)$$
$$O + O_2 + (M) \longrightarrow O_3 + (M) \cdots\cdots (2)$$

Ozone formation reactions

$$O_3 + O \longrightarrow 2O_2 \cdots\cdots (3)$$
$$O_2 + e \longrightarrow O + O_2 + e \cdots\cdots (4)$$

Ozone decomposition reactions

Ozone is formed in the (2) reaction. At this time a third body M is required; this can be O_2, N_2 or the wall of the vessel. In reactions (3) and (4), the ozone is decomposed. Therefore, the ozone formation and ozone decomposition reactions are competing in the discharge gap. The ozone concentration is determined by the balance between the formation and decomposition reactions. When the discharge intensity is high and the residence time of the oxygen or the crude air in the discharge gap is long, the ozone concentration becomes high but since decomposition easily occurs at the same time for high ozone concentration, the maximum concentration of ozone is generally 3 to 4% (wt) in the case of air and 6 to 8% (wt) in the case of oxygen.

2. Factors in Ozone Formation

Since the ozone is formed through an electrochemical reaction by partial discharge, the main factors in the ozone formation are divided in two kinds; the one is electrical factor, such as discharge intensity and the other is the physical and chemical factor of the reaction atmosphere.

1) Electrical factors

If the physical and chemical conditions are constant and the discharge power is high, the amount of ozone formed increases. The discharge power is determined by the applied voltage, the source frequency, the various conditions in the ozone generating tube, etc. If the applied voltage is high, the discharge power increases almost linearly as shown in *Fig. 3* and the amount of ozone produced increases accordingly. However, there is a tendency for gradual saturation. The upper limit of the applied voltage is determined mainly by the dielectric strength of the dielectrics used in the ozone generating tube. If the source frequency becomes high, the discharge power increases proportionally and ozone production also increases. Therefore, if a high frequency power source is used, the ozone generator can be compact but it becomes necessary to employ a frequency converter and at present it is more economical to use commercial power frequencies. The Fuji ozonizer employs a commercial frequency of 50 to 60 Hz.

2) Physical and chemical conditions

The most important physical and chemical conditions are partial pressure of the oxygen, dryness of the raw gas and temperature.

(1) Partial pressure of the oxygen

There has as yet been no theoretical explanation of the relation between ozone formation, and partial pressure of the oxygen, but from a practical point of view, the production of ozone increases in proportion to approximately the power of 0.5 of the partial pressure of the oxygen. Therefore, if other conditions remain the same, about twice the amount of ozone is obtained when oxygen is the raw material than when air is used (20% oxygen).

If oxygen gas is used as the raw material, the ozone generator becames cheaper but the cost of the oxygen must also be considered.

(2) Temperature

When the temperature is high, the ozone decomposition reaction becomes more active and therefore, it is best to conduct the reaction in as low a temperature as possible. The electrical dischage energy inside the ozone generating tube changes to heat. Therefore sufficient cooling must be provided so that the temperature in the ozone generating tube does not become too high. In a large ozone generator, uniform effective cooling presents a major problem.

(3) Dryness of the raw gas

If there are many water particles in the raw gas, the ozone yield not only decreases but nitrogen oxides (NO, NO_2, etc.) also can be formed as impurities in the ozonized air. The amonunt of water present also influences the life of the ozone generating tube and when there is a lot of water present, it is easy for the discharge to become concetrated locally because of adherence of conductive substances to the glass surface of the ozone generating tube. These substances can cause insulation breakdown of the ozone generating tube.

Therefore, it is necessary to dry the raw gas sufficiently and the dew point should be less than $-40°C$. In the summer, the temperature and humidity in Japan are high and there are also considerable differences throughout the year. Therefore drying of the raw gas presents a major problem.

IV. OZONE GENERATION EQUIPMENT

1. Equipment Construction

As can be seen in *Fig. 4*, the basic components of the ozone generator are (1) the blower to bring in the raw air and the dryer to dry the air, (2) the ozone generating tube, (3) the ozone generator unit, (4) protective fuse and (5) electrical equipment such as the high voltage transformer and the voltage regulator.

1) Blower and dryer

The type of blower differs depending on the conditions used such as the outlet pressure of the ozonized air. The dryer performs pre-drying by a chiller so as to maintain a high level of dryness (dew point of less than $-40°C$) at all time considering the high temperature and humidity conditions in the summer. The main part of the moisture is removed in a drying tower containing a solid dessicant. There are two drying towers which are changed over automatically every 6 to 8 hours so that the used tower can be regenerated. As was described previously,

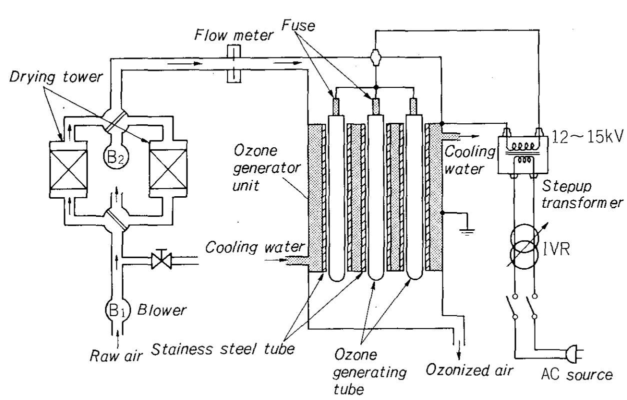


Fig. 4 **Schematic diagram of ozono generator**

the amount of dryness of the crude air has considerable influence on the ozone production and therefore it is important that a high degree of dryness be maintained.

2) Ozone generating tube

The ozone generating tube is arranged in two layers : an outer metal layer and an inner glass tube (inner surface is an electrode), as shown in *Fig. 4*. A spacer is inserted between the metal and glass layers in order to maintain a constant air gap. The ozone is produced when the raw air flows through this gap, a high voltage is applied between the electrode on the inner surface of the glass tube and the metal-tube, and the discharge occurs. The air gap t_a for which a uniform discharge occurs over the entire surface of the ozone generating tube depends on the maintenance of a constant gap over the entire length l of the ozone generating tube and a complete lack of any unevenness on the inner surface of the metal tube and the outer surface of the glass tube.

In former ozone generating tubes, insulation breakdowns sometimes occured during operation and this is one reason which hindered the wide spread use of ozone generation equipment on an industrial scale. As a result of careful studies made on this point by the author, the causes of the insulation breakdown were clarified and it was found that such insulation breakdowns could be prevented by the use of a special glass with a high dielectric strength. Since such glass is used in the ozone generating tube, it features high reliability and long life.

3) Ozone generator unit

As can be seen in the schema shown in *Fig. 4*, the construction is similar to ordinary steel tube type heat exchanger, and a number of stainless steel tubes, in which ozone generating tube is individually inserted, are provided. Cooling water circulates around these tubes so that the raw air and the ozone generating tube are directly or indirectly cooled.

In the ozone formation reaction described previously, the lower the temperature, the higher the ozone production becomes. However, since almost all of the electrical energy in the ozone generating tube due to the discharge is converted into heat, this heat must be effectively removed. In large scale ozone generators, many ozone generating tubes are connected in parallel and the most efficient and uniform cooling must be obtained with as little cooling water as possible. A multi-flow cooling system is employed in order to achieve this requirement The metal materials used for the ozone generator unit and the packing materials are all highly resistant to ozone.

4) Protective fuses

The ozone generating tube has a long life and high reliability but in order to ensure double safety, a protective fuse is attached to each generating tube. In case an ozone generating tube should fail, the

Table 2 **Typical specifications of large scale ozone generator**

Ozone production	Max. 2.1 kg O_3/h (for 10,000 t/d of potable water, 3~5 ppm of dosage)
Ozone concentration	about 2.5 weight %
Raw air	150 m^3/h (below dew point −40°C)
Electric source	7~15 kV, AC 50~60 Hz, 1ϕ
Electric power	about 50 kW
Cooling water	15 t/h

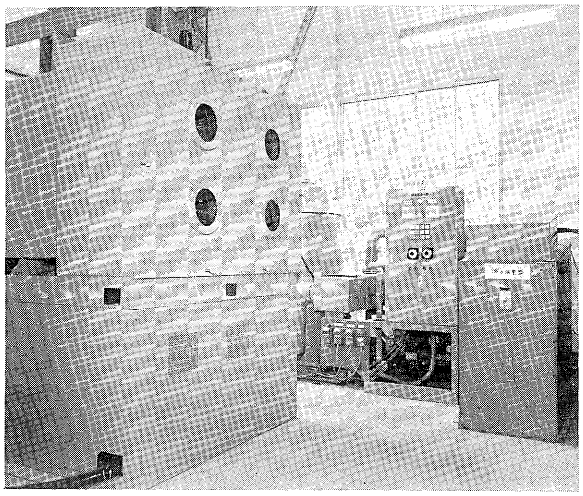


Fig. 5 Outerview of ozone generator

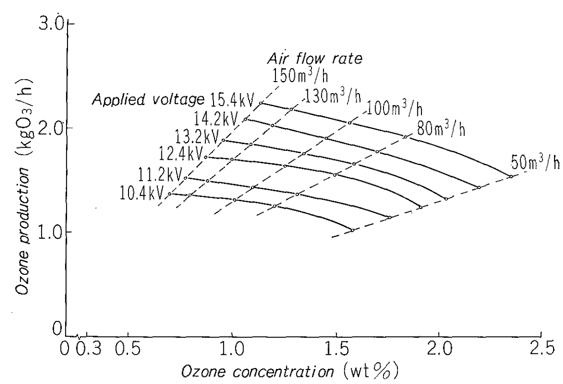


Fig. 6 Characteristics of ozone generation

supply voltage would be cut only to the damaged tube. Therefore, the ozone generating equipment can be operated continuously without any stoppages due to tube breakdowns. The damaged tubes can be replaced during the fixed inspections. The protective fuse used is a high voltage, low current current limiting fuse which was especially developed for use in ozone generating equipment.

5) Electrical parts

The electrical parts consist of the voltage transformer for supply of voltage to the ozone generating tube, the reactor, the voltage regulator and various accessories. The voltage transformer produces a maximum of 15 kV and is located in the bottom part of the ozone generating unit. In this way, the high voltage parts are not exposed. A dry type transformer is used to prevent any combustion. The reactor is used for power factor improvement since the current in the ozone generating tube is a leading current. The voltage regulator is used to regulate the voltage applied to the ozone generating tube and thus controls the amount of ozone produced.

The above has been an outline of the main points concerning the ozone generating equipment. Typical specifications of large scale ozone generators for water treatment are shown in *Table 2*. An outerview of this equipment is shown in *Fig. 5* and the ozone generation characteristics are shown in *Fig. 6*.

2. Features of Fuji Ozonizer

The Fuji ozonizer is large scale industrial equipment which has been produced from both technical and economical standpoints such a reliability, stability and equipment cost.

(1) High reliability

A long life for the ozone generating tube is insured since it employs glass with excellent voltage resistance. In addition, the ozone generation unit has a special multi-flow cooling system and there are protective fuses in each generating tube to provide double and triple safety.

(2) High yield and stability

Since the water is removed sufficiently from the air by means of a high performance dryer, the ozone production is improved and a constant yield is maintained throughout the year.

(3) Compact and low price

Because the applied voltage can be increased by 20 to 30%, the amount of ozone produced per tube is increased so that the unit becomes compact and the equipment costs are low.

(4) Automatic operation

This equipment is automated because the undermentioned ozone concentration meter and automatic ozone injection control equipment are used with the ozone generating equipment.

3. Scale of Ozone Generation Equipment and Amount of Ozone Production

Since a large amount of ozone is required for large scale water treatment stations, the equipment must be divided into several units. Examples of such unit scales are shown in *Table 3*.

Table 3 **Example of various unit scale of ozone generator**

Ozone prodution (kg/h)	Raw air (Nm^3/h)	Cooling water (m^3/h)	Power (kW)	No. of ozone gen. tube
4.0	260	20	100	840
2.0	130	15	50	420
1.0	65	8	25	210
0.4	26	4	10	84
0.2	13	2	5	42

V. OZONE METER AND OPTIMUM OZONE SUPPLY CONTROL SYSTEM

1. Ozone Meter

Iodometric titration is the standard method used for ozone quantitative analysis. This system, however, takes time and it is not used in process control. There are also several simple measuring devices employing thermal conductivity on the market but their stability is not good and the reliability of the mearsured values is low.

In order to measure the ozone concentration in the ozonized air obtained from the ozonizer and cantrol it at a suitable value, and also to detect the minute concentrations of residual ozone remaining in the waste air after the ozone contactor in the water treatment plant and to control the concentration of feed ozone, an ozone meter with rapid response, high sensitivity and high stability is required. A meter utilizing absorption in the ultraviolet region and incorporating all of these features has been developed and will be described here.

Ozone has its absorption band in the ultraviolet region and the molecular absorption coefficient at 2537 Å is extremely high at 3,600 ℓ/mol. cm. Other components (including water vapor) do not have an absorption band near that of ozone. Therefore, ozone can be measured in this way even in this way even in low concentrations.

The basic principle of absorbance measurements is the Lambert-Beer principle: $ln\frac{I_0}{I}=\alpha Cl$ (where I_0 and I are intensity of the incident light and transmitted light respectively, α: molecular absorption coefficient, C: ozone concentration, and l: cell thickness). If the light from the light source is monochromatic, this relation is approximately satisfied and there is a linear relation between $ln\ (I_0/I)$ and C.

The newly developed ozone meter employs a low pressure mercury lamp as the light source. About 90% of the light from this lamp has a wavelength of 2537 Å and it is almost completely monochromatic due to the use of a suitable optical filter.

The optical system consists of two paths and stability is insured by making the two path lengths the same. The light from the source is divided into two parts by a mirror. One of these enters the reference side and the other the sample side of the cell. On the reference side, the light is not absorbed and reaches the receiver directly (I_0). On the sample side, a fixed amount of light is absorbed in accordance with the ozone concentration in the cell and the cell length and the remainder of the light enters the receiver (I). In the receiver, a photomultiplier is employed and the light flux is converted into an electric current. As was described previously, there is a logarithmic relation between the ozone concentration and the absorbance. Therefore, when the changes in the electric current are converted into logarithms, the relation between the concentration and the absorbance becomes linear and reading accuracy can be improved.

Table 4 Specifications of ozone-meter

Optical system	Hg-lamp, two light pathes
Detector	Photo mutiplier
Measuring range	0~50 mg (O_3)/l (air) (4.2 wt%, 20°C)
Sensibility	±2% of F. S.
Circumstance	0~40°C
Measurement cell	Stainless steel or quartz 5~100 mm
Electric source	AC 100 V 50 or 60 Hz

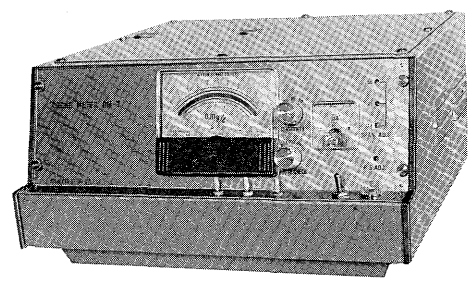


Fig. 7 Outerview of ozone meter

Table 4 showns the main specifications of the ozone meter. The meter is a direct reading portable type in which the zero drift is extremely small even when the meter is used continuously over long periods. The ozone concentration in the ozonized air obtained from the ozone generator is not only completely covered but minute amounts of ozone in the high humidity exhaust gas after water treatment is also measured. Because the cell is long, it is possible to measure the concentration with accuracies to approximately 200 ppm. *Fig. 7* shows an outerview of the ozone meter.

2. Optimum Ozone Supply Control System

Fig. 8 is a sequence diagram of this system. The basic principle of this control system is that when excess ozone is ejected in the water it comes out in the exhuast gas. The minute amount of ozone in the exhaust gas is detected by the ozone meter described above and in this way, the amount of ozone produced by the ozone generator can be controlled.

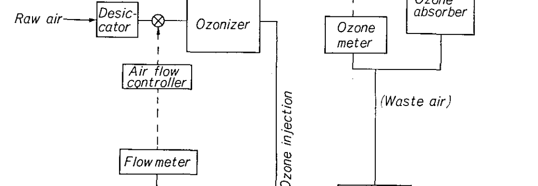


Fig. 8 Optimum ozone supply control system

By means of this system, the optimum, amount of ozone can be supplied in accordance with changes in the quality and quantity of the water. Automatic operation of the system is possible and the ozone can be employed economically.

VI. WATER TREATMENT USING OZONE

1. Effects of ozone Water Treatment

Since ozone has a very strong oxidation activity next to fluorine, it decomposes many of the im purities in water by oxidation. It also acts as a sterilizer, deodorizer, decolorizer and neutralizer of harmful substances. Examples of these effects are shown in *Figs. 9* to *11*[2].

(1) Sterilization

The sterilization action of ozone is 15 to 30 times greater than that of chlorine and it is not infuenced by such thing as pH and temperature. Ozone decomposes rapidly in water to become harmless oxygen so that the unpleasant oders resulting in chlorine treatment are avoided and the water does not taste bad.

(2) Deodorization

The odor of the water is due to many types of things such as artificial pollution, the odor of the soil, odors of molds and odors of algae, but ozone is highly effective in removing most of such odors. Because of fertilization, there has been an abnormal growth of algae in lake water and this has become a problem in many places due to the odor imparted to potable water. It is said that the solution of this problem can not be considered except the application of ozone method.

(3) Decoloration

There are many causes for the coloration of potable water including organic compounds such as humins, but ozone can remove coloring agents in concentrations of 1 to 3 ppm. Ozone has also been tested as a decolorizer for waste water from dye works and has proved effective. A major feature is that it does not give rise to a large amount of sludge like that found in the case of coagulation.

(4) Neutralization of harmful substances

Treatment of surface active agents such as ABS in water is troublesome and they can not be easily decomposed even by biological treatment. At present no good method for treating such agents is available and this presents a major problem. However, ABS can easily be decomposed by ozone oxidation. It is also effective against cyanides, manganese, phenols and iron. Cyanides are oxidized into harmless cyanic acid and phenols into oxalic acid[3].

Since the pH is not influenced in ozoen oxidation like it is by the addition of other chemicals, it is easy to control treatment conditions. However, ozone alone is not effective against BOD, or ammonium compounds, but is highly effective when combined with activated carbon treatment.

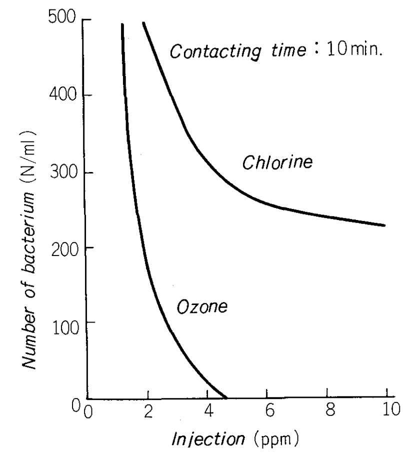


Fig. 9 **Sterilizing effect of ozone**

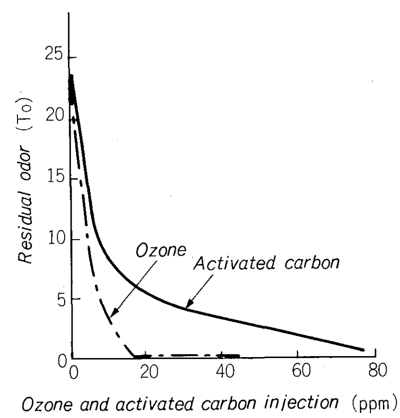


Fig. 10 **Deodorization effect of ozone**

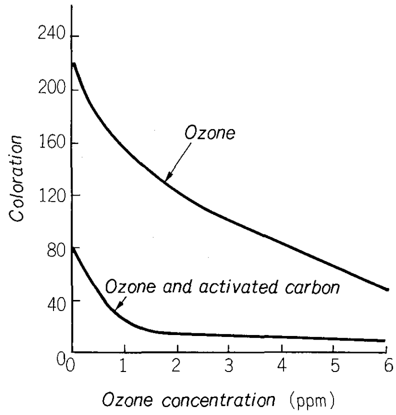


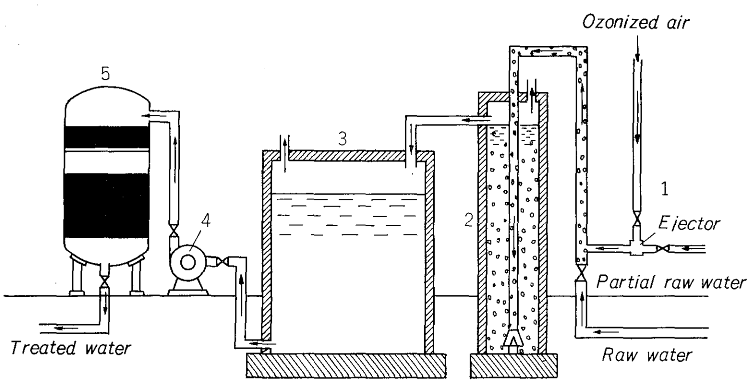
Fig. 11 **Decoloration effect of ozone**

As explained above, ozone has many excellent effects in water treatment and it can sufficiently purify drinking water by the addition of 3 to 5 ppm. It has been used for many years in Europe where the quality of the water is relatively bad and the results have been very good. It is also effective in the treatment of industrial waste water including that from dye works, plating works and phenol plants.

In addition to water treatment, ozone is also applied effectively as an air purifier to remove the odor of excreta, etc., as a food sterilizer and as a common

Table 5 **Water treatment processes using ozone**

Process	Action of ozone
Prechlorination→coagulation→filteration→O_3→filteration and adsorption by activated carbon → sterilization	Treatment of heavily polluted water
O_3 → filteration and adsorption by activated carbon → sterilization	Elimination of Fe, Mn, deodorization, decoloration
Usual process → O_3 → sterilization	Deodorization, decoloration
O_3 → usual process → sterilization	Substitution of prechlorination



1. Ejector system
2. Gas/liquid contactor
3. Reaction tank
4. Pump
5. Activated carbon filteration tank

Fig. 12 An example of water treatment apparatus with ozone

oxidizing agent in the chemical industry.

2. Water Treatment Installations Using Ozone

There are two important point to consider when converting facilities for ozone treatment. One is the problem of where the ozone method should be inserted in the water treatment process. The other is how should the ozone with its high reaction efficiency be added to the water.

The water treatment process can be considered as shown in *Table 5* (for potable water) in accordance with the quality of the raw water used and the purpose of the treatment[4]. The outline of this process is first treatment of ozone and then filtration and absorption treatment of the non-treated impurities with activated carbon.

There are various methods for ozone addition including the ejector type in which the ozonized air is brought in by means of an ejector and the diffuser type in which the ozonized air blown in from the bottom of the water tank in the form of air bubbles. There are many advantages and disadvantages in accordance with such conditions as the ozone dosage and amount of water treated, but ejector method is most widely used because of its good reaction efficiency. However, the diffuser method is very useful in cases when the addition rate is high.

Fig. 12 shows an example of a water treatment device using ozone. One feature of the ozone method is in addition to its excellent water treatment results, advantages can also be obtained in respect to the equipment itself. For example, since ozone reacts rapidly with water, the rate of treatment can be increased, the equipment can be compact and the space occupied is small. Since the raw materials for ozone are only air and electricity, metering and control is easy and related processes can be automated.

It was usually said that the cost ozone treatment is slightly higher than that of usual methods, but in our test[5], the cost required for ozone treatment for drinking water (3 ppm added, 40,000 t/day) was only 1 to 2 yen per m^3 and the total cost including precipitation, filtration and activated carbon treatment was about 8 yen per m^3. The same results were found in European water treatment plants (Düsseldorf, Düisburg, etc.). If the large amounts of activated carbon and chemicals which must be used now to treat heavily polluted water are considered, then ozone treatment can not be said to be expensive. In addition, it is possible to achieve treatment under economical conditions by effectively combining ozone treatment with other treatment systems such as those for industrial waste water and tertiary treatment of municipal waste water depending on the quality of the water and the purpose of the treatment.

References :

(1) Journal of Inst. of Elect. Engr. of Japan, Ozonizer Special Commitee: Ozonizer Hand Book
(2) Kosima: Industrial Water and Waste Water (in Japanese) Vol. 13, No. 1 pp. 25∼36 (1971)
(3) Ikehata: Industrial Pollution (in Japanese) Vol. 5 No. 10 pp. 586∼595 (1969)
(4) Horie: Food Industry (in Japanese) Vol. 13 No. 20 (1970)
(5) Iketi, Mizumoto: Water Tratment Tech. Vol. 12 No. 3 pp. 11∼20.