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LARGE CAPACITY OZONE GENERATOR AND APPLICATION OF OZONE

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I. INTRODUCTION

Environmental pollution has become a major social problem and laws and regulations are being enacted concerning various types of public hazards such as water pollution, air pollution and noise. Various measures are being undertaken to measure and remove such pollution but a higher level of anti-pollution technology is required because of more severe regulations in keeping with higher standards, the introduction of total amount regulations by some local governments, etc.

Ozone is a strong oxidizing agent which is widely used in the anti-pollution and environmental conservation fields but recently, the applications requiring ozone including water supply treatment, tertiary treatment of sewage, deodorization and wet-type smoke denitration have greatly expanded and there are strong demands for more compact and higher performance ozone generation equipment.

The ozone method not only makes possible the oxidative decomposition of components which can not be oxidized by conventional oxidizing agents, but even if it is used in excess, it breaks down to become oxygen and there is no need to worry about secondary pollution. Plant construction is simple and comparatively cheap and these advantages have long drawn interest. Ozone treatment of water supplies is widely used in Europe and its applications are expanding in such water treatment fields as deodorization, decoloration and removal of organic compounds as water quality deteriorates, as well as in the tertiary treatment of sewage. The application of ozone in gas treatment is common in fields where it is necessary to perform deodorization because ozone is effective in removing components with bad odors. Recently, ozone has been found to be an effective oxidizing agent in the denitration of smoke. Research is underway on application techniques and it is being widely utilized for environmental conservation.

This article gives an outline of ozone generation equipment which is more compact or has a higher performance level because of direct liquid cooling and was developed for large scale ozone generation for denitration. Ozone application techniques for tertiary treatment (decoloration) of excreta and deodorization are also discussed.

II. RECENT OZONE GENERATORS

The amount of ozone required in smoke denitration plants is several hundred kilograms per hour, which is more than 10 times that needed for conventional applications such as usual water treatment. The maximum unit capacity of a raw air ozonizer used mainly in water purification plants is 10kg O_3/h, while denitration requires a unit capacity of 40-50kg O_3/h.

Therefore, there are strong demands for more compactness, a wide drop in equipment costs and improved power consumption to make large capacity ozone generators practical.

As a result of research and development carried out by Fuji Electric for about three years to meet the above demands, it has been possible to (1) suppress temperature rises, the weakest point of ozone generating tubes, by means of a newly developed high performance generating tube with forced cooling, as well as improvement in internal losses due to input power; and (2) vastly improve performance by increasing the discharge power per unit surface of the generating tube by means of a high frequency power supply using a thyristor inverter.

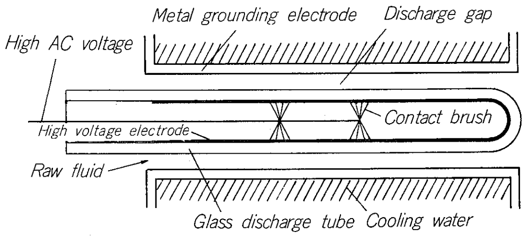
The following sections give an outline of the large capacity ozone generators including basic ozone generating mechanisms.

1. Basic Characteristics and Increased Capacities of Ozone Generators

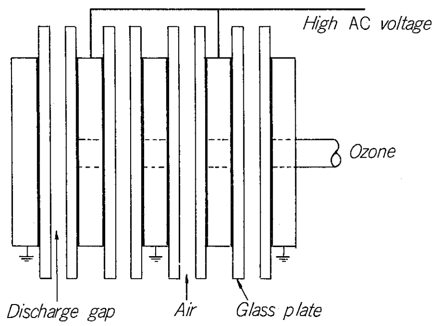
1) Basic construction of the ozone generator and ozone formation reactions

The formation of ozone by means of a silent discharge has been known for many years and the Siemens tube for the generation of ozone was already being produced by W.V. Siemens in 1857. Various improvements were made on ozone generator, with the Siemens tube as the prototype, mainly in Europe. Currently, the most widely used constructions are the concentric cylindrical type and flat type shown in *Fig. 1* (a) and (b) respectively.

As can be seen in *Fig. 1*, the basic structure is an electrode construction with inorganic dielectrics attached to one or both of two metal electrodes facing each other. When there is an AC voltage applied between these two electrodes, a discharge occurs in the gap. This discharge



(a) Cylindrical type



(b) Flat type

Fig. 1 Construction of the discharger

does not become an arc discharge because of the presence of the dielectric and a stable pulse-type discharge occurs. When air or oxygen flows through this discharge gap, ozone is formed with a comparatively high efficiency. The main reaction in the discharge gap is most often shown by the following equations. The concentration of the ozone is determined at the point of equilibrium between the ozone formation and decomposition reactions:

$$\left.\begin{array}{ll} O_2 + e \xrightarrow{k_1} 2O + e \ldots\ldots\ldots & (1) \\ O + O_2 + (M) \xrightarrow{k_2} O_3 + (M) \ldots & (2) \end{array}\right\} \text{Ozone formation reaction}$$

$$\left.\begin{array}{ll} O_3 + O \xrightarrow{k_3} 2O_2 \ldots\ldots\ldots & (3) \\ O_3 + e \xrightarrow{k_4} O_2 + O + e \ldots\ldots & (4) \end{array}\right\} \text{Ozone decomposition reaction}$$

Equations (1) and (2) show the reactions in which O_2 is broken down by electron bombardment and ozone is formed by binding between the decomposed O and O_2. In these equations, (M) signifies a third object such as O_2, N_2 or the container walls. Equations (3) and (4) show the reactions in which ozone and O bind to again form O_2 and ozone is decomposed by electron bombardment. $k_1 - k_4$ are the reaction speed constants. It is known that $k_2 \simeq 1.655 \times 10^{-34}$ exp (600/RT) and $k_3 = 4.91 \times 10^{-11}$ exp (−600/RT) (cm^3/sec)[2] but k_1 and k_4 are values decided by the dissociation sectional area of oxygen and ozone molecules corresponding to the electron energy during the silent discharge, and they are now in the experimental stage.[3] Equation (2) shows an exothermic reaction and (3) is an endothermic reaction. Therefore, the desired conditions for ozone generation are only a high electron temperature and a low molecule temperature for the thermally unbalanced discharge.

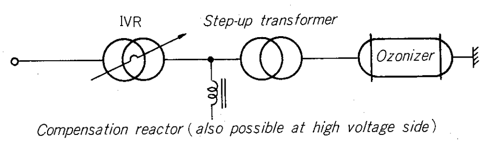
2) Ozone generating tube electrical characteristics and power supply equipment

The electrical characteristics of the silent discharge have been investigated in detail by concentrating void discharges in solid insulation material and the discharge power (W) into the ozone generating tube can be expressed by the following equation:[4]

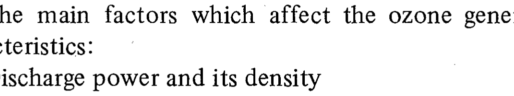
$$W = f \cdot c_g \cdot s\,(V_s + V_e)\left\{2\sqrt{2}\,E_{eff} - (1 + c_a/c_g)(V_s + V_e)\right\} \quad \ldots\ldots\ldots\ldots (5)$$

where
f: frequency
c_a, c_g: static capacities per unit area of gap and dielectric
S: total discharge area
V_s, V_e: discharge starting and extinction voltages
E_{eff}: applied voltage

The discharge power form equation (5) can be controlled by the applied voltage and frequency. When the power variation range is wide or there is high power input, the frequency control system is extremely beneficial with respect to equipment design. In equation (5), the applied voltage is in the form of a sinusoidal wave but if $2\sqrt{2}\,E_{eff}$ in the equation is $2E_{peak}$, the discharge power can be obtained no matter what the waveform. By setting a suitable discharge circuit constant, the power source system can be designed according to various types. *Fig. 2* shows a typical power supply system.



(a) IVR type



(b) Inverter type (both voltage and current types possible)

Fig. 2 Electric block diagram of ozone generator

3) Ozone generation characteristics

The main factors which affect the ozone generation characteristics:

(1) Discharge power and its density
(2) Dielectric material and thickness, gap length and gas pressure
(3) Electrode cooling temperature and temperature in gap
(4) Raw gas properties and water content

Fig. 3 shows the relation between the ozone production of the ozone generator cooled only by the grounded electrode and the ozone absorption in accordance with the ratio (W/Q) of the raw air flow and discharge power. If the discharge power is small, i.e. W/Q is about 0.15, there is a linear increase in ozone concentration but as the discharge power (W/Q) increases, there are gradual deviations from

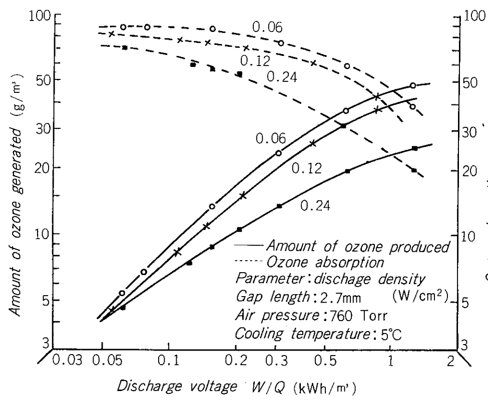


Fig. 3 Relationship between discharge power and ozone production

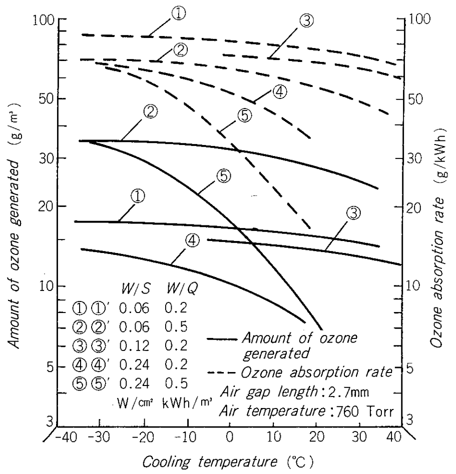


Fig. 5 Relationship between cooling temperature and ozone production

the linear relation and the rate of increase of ozone production drops. This line shows the absorption limit, and the deviations from the straight line when the W/Q ratio becomes large are caused by high level ozone decomposition due to ozone concentration breakdown, as well as electron bombardment and thermal decomposition. As the discharge density (W/S) increases, the W/Q value which can maintain the limit absorption decreases. This is shown in *Fig. 4*. This is because of the high increase in the temperature of the uncooled high voltage electrode due to the increased discharge density.

Fig. 4 shows a case of parallel flow for the cooling water and raw air with both Fuji Electric experimental values and calculated values. The calculated values are based on the exothermic characteristics due to the discharge, and the high voltage electrode and average air temperature distribution are shown. When the cooling water temperature is changed with a constant discharge density, the electrode and average air temperatures alter only in accordance with changing components of the cooling water temperature. The amount of ozone production and ozone absorption change with respect to these temperature changes as shown in *Fig. 5*. In cases of small W/Q and W/S, there is no special effect on the cooling water temperature but when W/Q is large and W/S increases, there is a clear effect on the cooling water temperature.

As can be seen from equation (5), the characteristics of the dielectric used on ozone generators are directly connected to the discharge power. The dielectric constant is large and the dielectric loss is small and both change little with respect to the temperature. The voltage withstand at high temperatures must also be excellent.

As in the case of the dielectric characteristics, the gap length (d) and gap internal pressure (p) not only have a direct relation to the discharge power but also cause considerable changes in the ozone production and ozone absorption. According to Fuji Electric research, the ozone absorption reaches a maximum at about $p \times d \simeq$ 200 Torr·cm. This $p \times d$ value matches the $p \times d$ value for which the total number of O_2 decompositions calculated from the electric field strength and current value is a maximum. This indicates that non-uniformity must be avoided in the manufacture of ozone generators. *Fig. 6* shows that the discharge power and ozone production drop according to the bend of the tube.

When raw gas is used as oxygen, ozone production is about double that when raw air is used. *Fig. 7* shows the changes in the ozone production in accordance with changes in oxygen concentration but, except when O_2 is

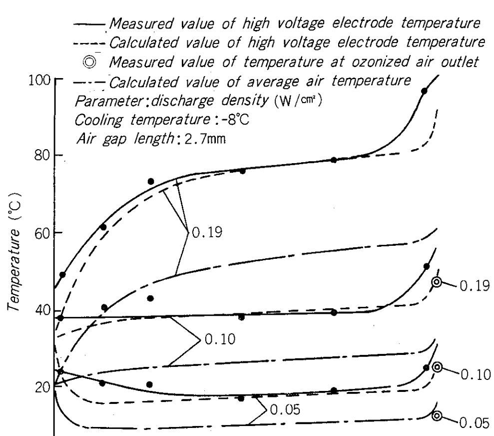


Fig. 4 Temperature distribution of ozone generating tube

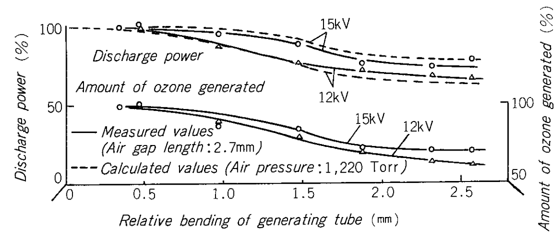


Fig. 6 Relationship between discharge power and tube bending

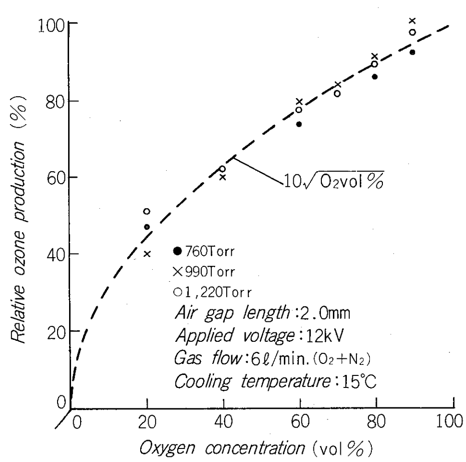


Fig. 7 Relationship between ozone production and oxygen

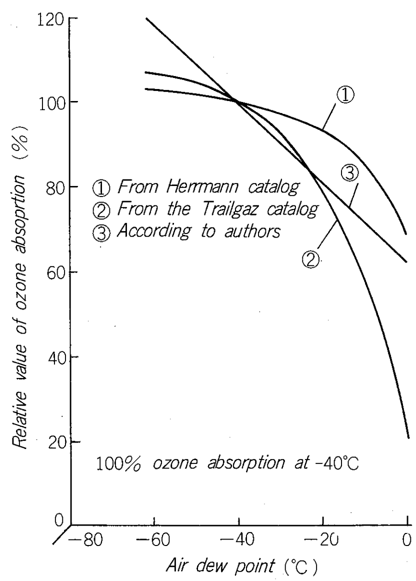


Fig. 8 Relationship between dew point of raw air and ozone yield

near a maximum of 90–95%, ozone production increases in proportion to the 1/2 multiple of the oxygen concentration. This lack of a direct relation between ozone production and the oxygen concentration is due to decomposition of O_2 by N_2 excited by the discharge.

In the case of raw air, increases in the water content must be strictly avoided. When the water content increases, not only is there a drop in the ozone absorption, but it also causes an increase in nitrogen compounds and a breakdown of the dielectric. *Fig. 8* shows the changes in water content and ozone absorption.

4) Large capacity ozone generators

As is evident from the ozone production characteristics described above, it is essential to have a large *W/S* to make the capacity of the ozone generator large (more compact, higher performance). However, when only the *W/S* is increased, this leads to a dielectric temperature increase and can cause a decrease in the ozone absorption, heat brakedown of the dielectric, etc. This makes a capacity increase impossible. One method is to decrease the cooling temperature on the grounding side but, for example, if there is cooling at −30°C, the high voltage terminal is cooled indirectly and large increase in *W/S* can not be expected. The limit is several times that of the conventional ozone generator. Therefore, the only method to reliably increase the capacity of the silent discharge type generator is to directly cool the high voltage electrode and cause a temperature increase in the dielectric.

2. Construction of a Large-capacity Ozone Generator and Ozone Production Characteristics

1) Construction

The high voltage electrode of conventional ozone generators (commercial frequency type) consists of a thin membrane of carbon or aluminum coated or stuck on the dielectric (glass tube) as shown in *Fig. 1*. If there should be a dielectric breakdown when the there is direct liquid cooling by the ozone generating tube in such a construction, this could result in a major accident involving a complete shutdown of the equipment because of leaking water. Fuji Electric uses a generating tube with a dielectric lining on the outer surface of a metal tube as shown in *Fig. 9*. With this construction, there is no need to worry about water leaks even when there is a dielectric breakdown, continuous operation is possible just by means of electrical breaking and a highly reliable direct liquid cooling system is possible. To prevent streamer discharges from the end of the generating tube which is one practical problem, the end of the grounding electrode has a special shape. To keep the electric power loss due to cooling water down to 0.5% or less, measures are taken to maintain cooling water purity, prevent corrosion of the electrode, etc.

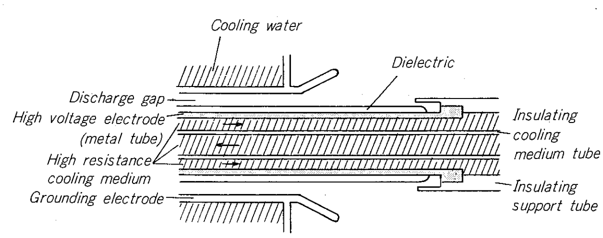


Fig. 9 Construction of large capacity ozone generator

2) Ozone generation characteristics

Fig. 10 shows the ozone generating characteristics when there is direct liquid cooling of both the grounding and high voltage electrodes (both-side cooling system). Because of the direct liquid cooling of both electrodes, the electrodes can easily be maintained at a low temperature is no decrease in ozone absorption even when the *W/S* is more than 10 times greater than that of the commercial frequency ozone generator. *Fig. 11* shows the relation between ozone production and ozone absorption.

As can be seen from *Figs. 10* and *11*, *W/S* must be increased within the range where the ozone absorption is

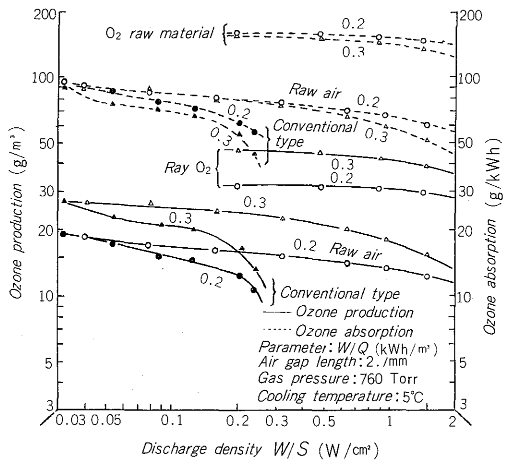


Fig. 10 Characteristics of both-side cooling ozone generator

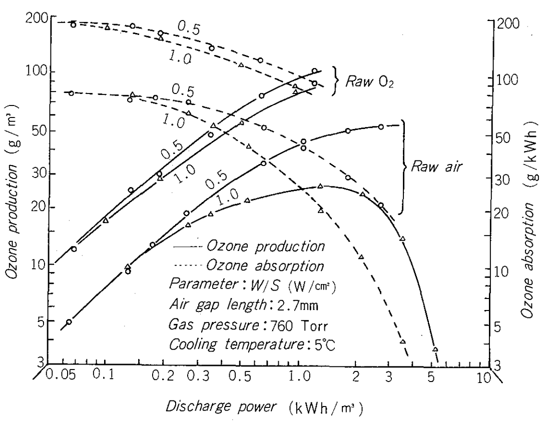


Fig. 11 Relationship between discharge power and ozone production (both-side cooling)

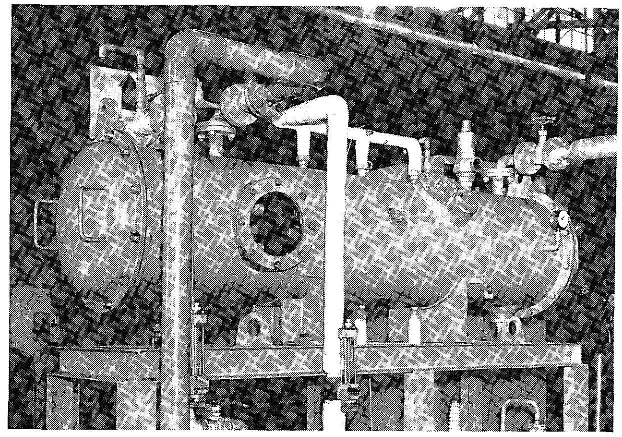


Fig. 12 Model ozone generator

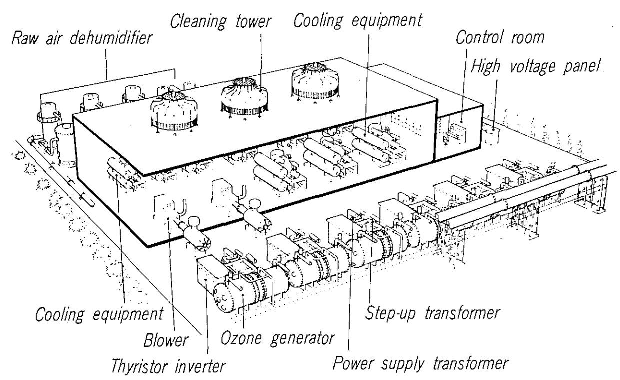


Fig. 13 Bird's eye view of large capacity ozone generating plant

not decreased and to achieve this, it is desirable to have a ozone concentration of 13mg/N1 or less in the case of raw air or 30mg/N1 or less in the case of raw oxygen. The discharge power is about 0.2kWh/m^3

3) Performance of large-capacity ozone generator

Table 1 shows a comparison of the characteristics of the conventional and both-side cooling types. *Fig. 12* shows an outer view of model ozone generator of the both-side cooling type (ozone production: 1kg/h). *Fig. 13* is an immaginary view of large-capacity ozone generating plant.

As can be seen in *Table 1*, the ozone production of the both-side cooling type is about nine times that of the medium frequency type and the ozone absorption is improved by about 13%. It has been possible to make the generator more compact and lower costs compared to conventional generators by means of the improved ozone generating tube cooling tube.

The electrical power required for ozone production has a characteristic limit (about 13kWh/kg O_3) when raw air is

Table 1 Comparison of characteristics of ozone generators

Item \ type	Commercial frequency type	Medium frequency type	Both-side cooling type
Generating tube dimensions (mm)	40φ x 1,000L	40φx1,000L	40φx800L
Cooling water temperature (°C)	Normal temperature	Normal temperature	10°C or less
Frequency (Hz)	50/60	150	2,000
Ozone concentration (mg/N*l*)	16	16	12.5
Ozone generated (g/h)	5/6	9	80
Ozone absorption *(2) (kWh/kgO_3)	14.7/15.4	15.5	13.5

Note: *(1) : Raw air
*(2) : Ozone absorption at net discharge power

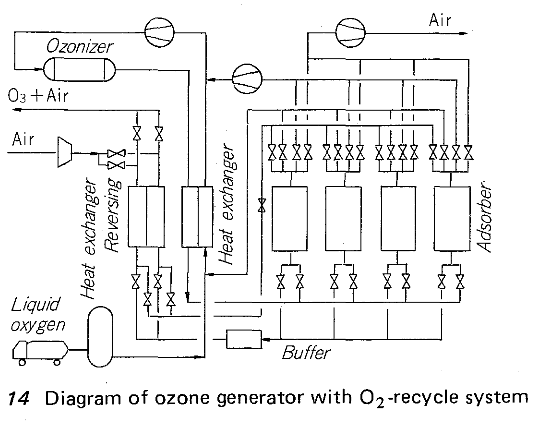


Fig. 14 Diagram of ozone generator with O_2-recycle system

used, and a large decrease in power consumption due to the improvement is ozone generation can not be expected. Therefore, to decrease the power consumption of the ozone generating plant, it is important to improve the efficiency of the auxiliary equipment which account for about 30% of the total power consumption. This involves the use of a low loss thyristor inverter, the utilization of waste heat in the cooling equipment, the use of cooling type dehumidifying equipment, etc. The development of the oxygen recycle system shown in *Fig. 14* suggests one direction for the future with respect to the effective utilization of energy.

III. OZONE APPLICATION TECHNIQUES

Fuji Electric has supplied many ozone treatment systems for such fields as decoloration of dying effluents, cyanide decomposition, phenol decomposition and COD removal. Here, technology for the application of ozone to tertiary treatment of excreta (decoloration) and deordorization will be outlined.

1. Application for the Tertiary Treatment of Excreta (Decoloration)

1) Necessity of tertiary treatment of excreta

Currently, excreta from ordinary residences is treated to achieve values within the effluent regulations in the Water Turbidity Prevention Law by a combination of primary and secondary treatment, and then discharged into rivers of the sea. However, the unpleasant sensation caused by bad odors from the facilities and the color of the effluent is a common problem for such sewage treatment facilities. With respect to odor, the regulations limit seven basic components but there are no restrictions concerning color. However, the actual complaints of local citizens are centered on odor and color, i.e. pollution of the senses, and this has become a major problem. In particular, excreta treatment water normally has a yellowish-brown color and imparts the feeling of urine flowing away. Urgent measures are needed in keeping with the feelings of local residents.

2) Colors of excreta treated water

A normal healthy adult excretes an average of 1–2mg of bile pigment in urine and 250mg in feces daily. The main components of these bile pigments are biliverdin and bilirubin but in the body, they are reduced by intestinal flora to form urobilinogen and stercobilinogen which are excreted in the urine or the feces. However, urobilinogen and stercobilinogen are easily oxidized in the treatment process in the plant (also oxidized during aeration) to form urobilin ($C_{33}H_{42}N_4O_6$) and stercobilin ($C_{33}H_{46}N_4O_6$), and these compounds color the effluent from yellow to yellowish-brown.

3) Effects of pretreatment

The coloring components in excreta treatment water can easily be oxidized and decomposed by the strong oxidizing power of ozone, making the water colorless. However, since ozone is also used in the decomposition of SS, COD components, etc. in the secondary treatment water, the dosage of ozone required for decoloration is affected to some extrent by the properties of the second treatment water. However, since the treatment systems in excreta treatment facilities are diverse and operation control conditions also differ greatly, there are great variations in the properties of the secondary treatment water. Therefore, for effective ozone treatment, it is desirable to employ some type of pretreatment such as coagulation.

Table 2 shows an example of the water quality of an effluent from an excreta treatment plant. *Figs. 15* and *16* show typical decoloration results by means of coagulation.

Table 2 Example of waste water qualities

	A (Total oxidation)	B (Total oxidation)	C (Digestion)	D (Digestion)	E (Digestion)
Coloration	200	110	130	170	100
COD	56	26	58	46	28
BOD	18	–	–	13	8.5
TOD	150	45	130	290	370
TOC	29	29	49	24	28
K-N	42	16	52	70	160
NH_4-N	28	14	52	70	120
NO_2-N	19	37	13	–	4
NO_3-N	14	22	16	4	14
All P	4	3	45	21	–
pH	7.4	7.1	7.0	8.1	8.5

Note: Unit is ppm except for color and pH

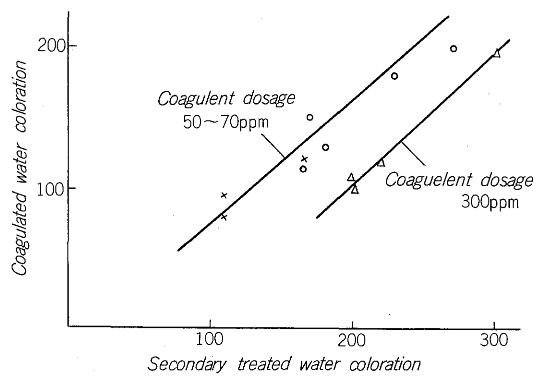


Fig. 15 Decolorization by coagulation

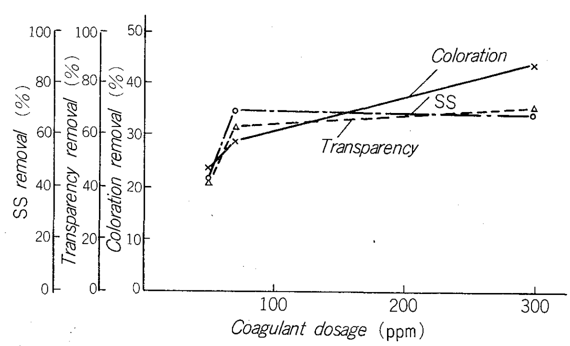


Fig. 16 Coagulent dosage vs. pollutamt removal

A certain degree of decoloration is possible (removal rate of 30–40%) by means of coagulation. Simultaneously, about 70% of the SS is removed and these results improve the transparency.

Fig. 17 shows the effects of ozone treatment after SS removal. The effects are much better when using coagulation and ozone treatment than in the case of SS removal by means of a filter. This appears to be because part of the pigments are also removed together with the SS in the coagulation.

Fig. 18 shows the relation between the coagulant and ozone dosages required for decoloration of secondary treatment water up to a coloration of about 20° in an excreta treatment plant. Up to a certain fixed amount, there is a tendency fo the ozone dosage to drop as the coagulant dosage is increased. However, it appears that there is no meaning in adding more coagulant than is necessary. Therefore, the appropriate coagulant dosage must be decided after careful consideration of the following:

(1) Properties of secondary treatment water
(2) Cost of coagulant
(3) Sludge treatment costs
(4) Ozone generation costs

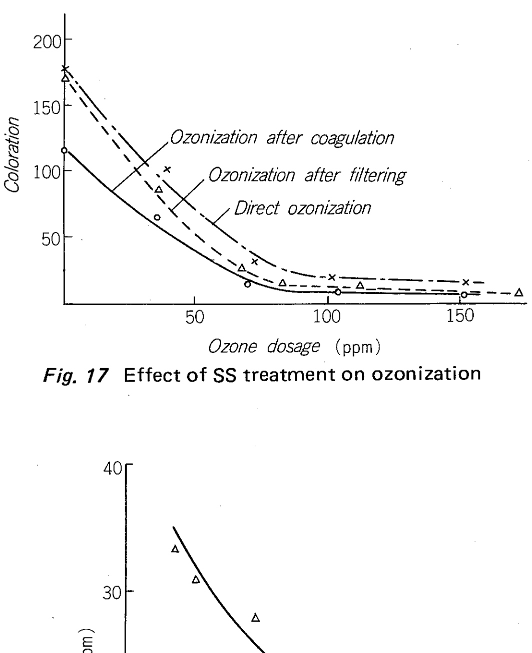


Fig. 17 Effect of SS treatment on ozonization

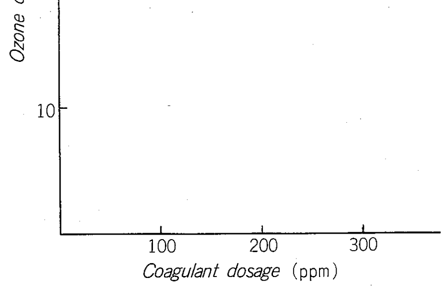


Fig. 18 Relationship between ozone dosage and coagulant dosage

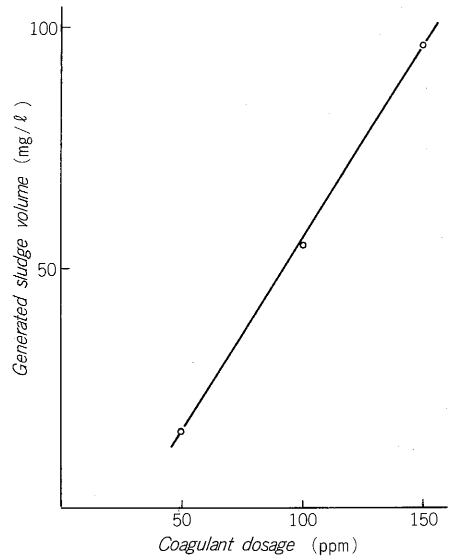


Fig. 19 Coagulant dosage vs. sludge volume

Fig. 19 is example for reference of the relation between coagulant dosage and the sludge volume.

4) Ozone treatment results

As described priviously, the effects of decoloration by ozone treatment differ greatly in accordance with the properties of the secondary treatment water but the amount of ozone required when coagulation is also used is 20–50 ppm.

Fig. 20 shows typical ozone treatment effects when coagulation is also used. The required amount of ozone was less than 30ppm. It is said that when the ozone dosage is increased, the COD also decreases and part of the ozone dosage is consumed by the COD components. For reference, *Fig. 21* shows the relation between ozone dosage and COD reduction in another treatment plant.

Fig. 22 shows the effects of the initial coloration on the amount of ozone required. When the initial coloration is high, the decoloration efficiency per unit of ozone is also high. Therefore, a set amount of ozone is required no matter what the initial coloration. In other words, sufficient

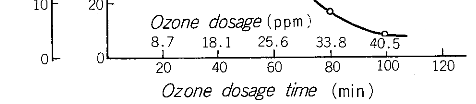


Fig. 20 Effects of decolorization by ozonization

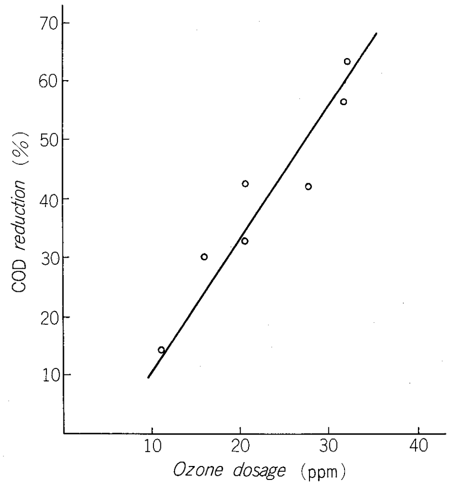


Fig. 21 Relationship between ozone dosage and COD reduction

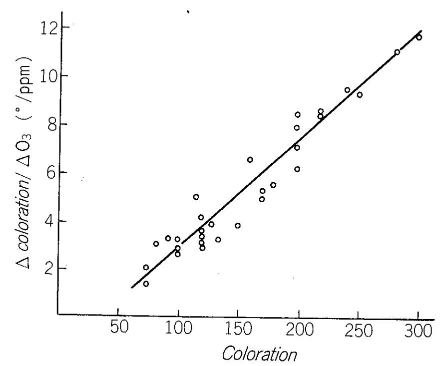


Fig. 22 Colorization of waste water vs. Δ coloration/ΔO_3

decoloration can be expected by the dosing of a fixed amount of ozone (23-24 ppm in this case) no matter what the variation in initial coloration (in cases where coagulation is also used).

5) Fuji Electric ozone decoloration flow

Fuji Electric has developed a basic excreta decoloration system through many pilot plant tests in model plants and partial treatment facilities. Coagulation is used as pretreatment. The standard coagulation employs the common coagulation flotation system but there are also cases where the coagulation and precipitation method is used or rapid filtering equipment is also provided depending on conditions in the facilities concerned. *Fig. 23* shows a standard flowsheet and *Fig. 24* shows the model equipment.

2. Application for Deodorization

1) Necessity of deodorization treatment

Even though the effluent standards restrict the seven basic components in accordance with the Odor Prevention Law, about 25% of the claims related to the typical seven forms of pollution are conerned with odor pollution (According to the 1976 Environmental White Paper, odor is second among pollution complaints after noise and vibrations). Compared with other forms of pollution, odor pollution has a strong connection with the senses and the relation between the damage and the odor is difficult to evaluate quantitatively or objectively. In addition, there is room for the domination of subjective factors with respect to the damage and at the same time, the multiplying and cancelling effects among the odor components are extremely complex. Under such conditions, the people's demands for deodorization treatment technology are increasing and this is one of the most important problems currently being faced.

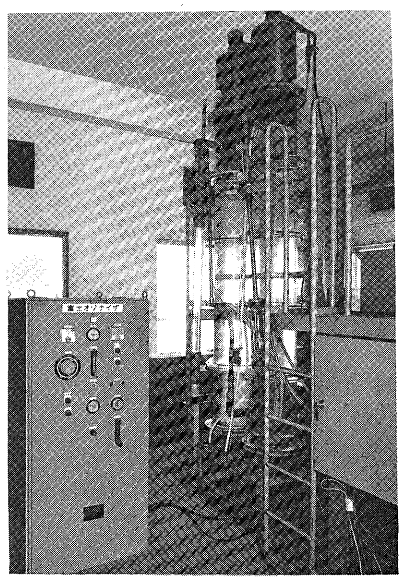


Fig. 24 Decoloration test palnt for excreta

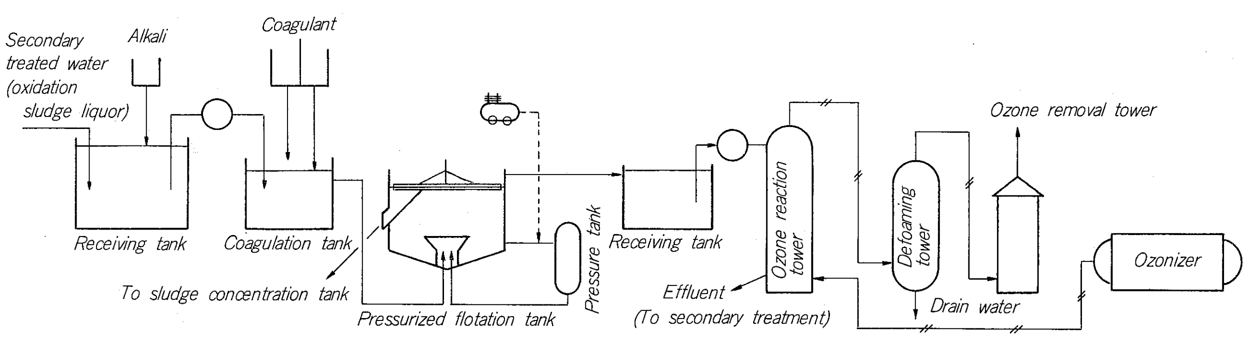


Fig. 23 Flowsheet of ozone decoloization process of excreta

2) Reaction between ozone and odorants

Deodorization by ozone is a type of oxidation. The odors are removed when the odorants are oxidized and decomposed by the strong oxidizing power of ozone. According the the authors' research, the reactions between ozone and the common odorants and the amounts of ozone required are as shown in *Table 3*. *Fig. 25* shows a relative comparison of the decomposition reaction speeds when ozone and these odorants come into contact. Amont the odorants, hydrogen sulfide (H_2S) is decomposed comparatively slowly by ozone, while methyl sulfide [$(CH_3)_2S$] is decomposed mainly into soluble 2-methylsulfone [$(CH_3)_2SO_2$]. Generally when odorants including sulfur are decomposed to form SO_2. *Fig. 26* shows the SO_2 formation conditions in the decomposition of methyl sulfide as a typical example.

3) Combined use of ozone and chemical washing treatment

As described above, typical odorants are decomposed comparatively fast by ozone but in cases where components which do not react with ozone (ammonia), components with a relatively slow decomposition speed (hydrogen sulfide), components for which the main decomposition products are soluble, etc. are included, satisfactory deodorization can not be achieved with ozone treatment alone. Therefore, there are may cases where ordinary water or chemical washing processes are used simultaneously. The following are considered to be the reactions within the system when ozone and chemical washing treatment (using sodium hydroxide and sodium hypochlorite as the chemicals) are employed together to treat gas containing hydrogen sulfide (H_2S), methyl sulfide [$(CH_3)_2S$], methyl disulfide [$(CH_3)_2S_2$] and methyl mercaptan (CH_3SH).

(1) H_2S

$$H_2S \xrightarrow{O_3} H_2O + SO_2 \xrightarrow{NaOH} Na_2SO_3 \xrightarrow{NaClO} Na_2SO_4 + NaCl$$

$$H_2S \xrightarrow{NaOH} H_2O + Na_2S$$

(2) $(CH_3)_2S$

$$(CH_3)_2S \xrightarrow{O_3} (CH_3)_2SO \xrightarrow{O_3} (CH_3)_2SO_2$$

(3) $(CH_3)_2S_2$

$$(CH_3)_2S_2 \xrightarrow{O_3} H_2O + CO_2 + SO_2 \xrightarrow{NaOH} Na_2CO_3 + Na_2SO_3 \xrightarrow{NaClO} Na_2CO_3 + Na_2SO_4 + NaCl$$

$$(CH_3)_2S_2 \xrightarrow{NaClO} H_2O + CO_2 + SO_2 + NaCl \xrightarrow{NaOH} Na_2CO_3 + Na_2SO_3 + NaCl \xrightarrow{NaClO} Na_2CO_3 + Na_2SO_4 + NaCl$$

(4) CH_3SH

$$CH_3SH \xrightarrow{O_3} H_2O + CO_2 + SO_2 \xrightarrow{NaOH} Na_2CO_3 + Na_2SO_3 \xrightarrow{NaClO} Na_2CO_3 + Na_2SO_4 + NaCl$$

4) Features of ozone deodorization

The features of ozone deodorization are as follows:

(1) Except for ammonia, the method is effective against almost all types of odorants and also gainst organic compounds.

(2) Results are also excellent with low concentrations of ordorants.

(3) The ozone dosage is comparatively small and the cost is comparatively low when compared with the combustion.

(4) Treatment is possible in combination with other me-

Table 3 Decomposition of major odorants with ozone

Component	Reaction formula (assumed)	Amount of ozone required (test value)
H_2S	$H_2S \xrightarrow{O_2} SO_2 + H_2O$	O_3/H_2S=4.0mole ratio
CH_3SH	$CH_3SH \xrightarrow{O_2} SO_2 + CO_2 + H_2O$	O_3/CH_3SH=2.5
$(CH_3)_2S$	$(CH_3)_2S \xrightarrow{O_3} (CH_3)_2SO_2$	$O_3/(CH_3)_2S$=1.0
$(CH_3)_2S_2$	$(CH_3)_2S_2 \xrightarrow{O_3} SO_2 + CO_2 + H_2O$	$O_3/(CH_3)_2S_2$=5.0
$(CH_3)_3N$	$(CH_3)_3N \xrightarrow{O_3} NO_2 + CO_2 + H_2O$	$O_3/(CH_3)_3N$=1.0

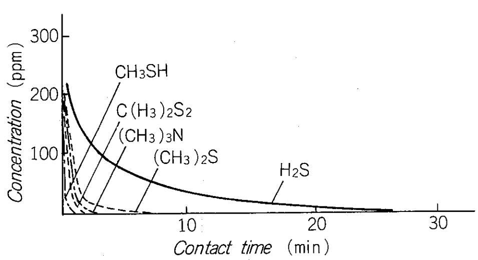


Fig. 25 Contact time and decomposition reaction

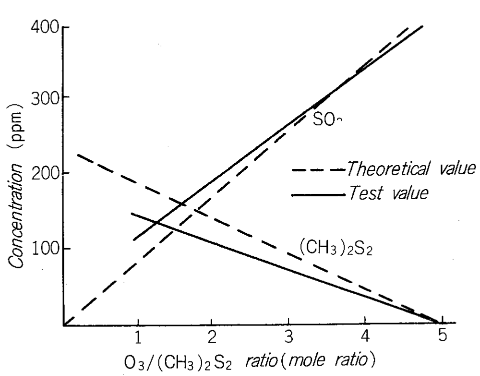


Fig. 26 Converted SO_2 vs. reduced $(CH_3)_2S_2$

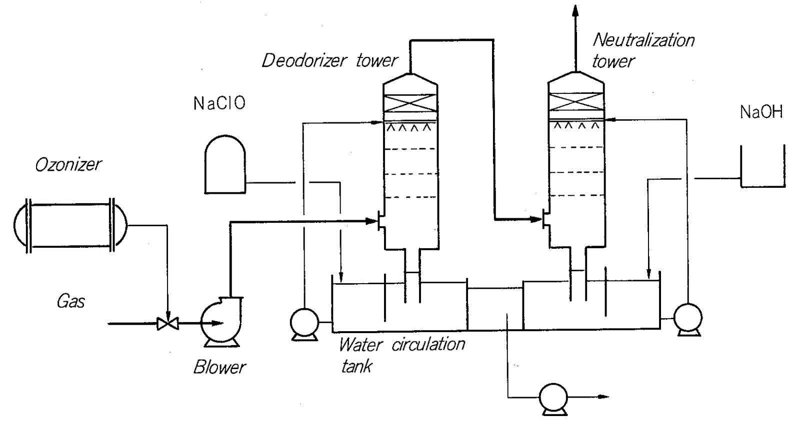


Fig. 27 Flowsheet of ozone-deodorization process

thods (water or chemical washing, etc.) and in this way almost all odorants can be removed.

5) Fuji Electric ozone deodorization equipment

As was mentioned previously, the odorant gas often contains components such as NH_3, H_2S, $(CH_3)_2S$, $(CH_3)_2S_2$ and CH_3CH. Therefore, the deodorization equipment combines the techniques of ozone treatment, water washing and chemical washing. *Fig. 27* shows a flowsheet for exhaust air deodorization equipment of a craft pulp plant with a comparatively high composition of odorants.

IV. CONCLUSION

This article has described the construction of the both-sides cooling type ozone generating tube and the ozone generation characteristics of large-scale ozone generating equipment, as well as excreta tertiary treatment (decoloration) and deodorization among the ozone application techniques. There are still many problems for research and development. In particular, equipment costs of ozone generation equipment for denitration, power consumption, etc. are considered to be on the extended line of conventional ozone generation equipment for water treatment but lower costs and greater energy savings can be expected. Since ozone treatment has excellent features as a new water treatment method, it will become more economical than other treatment methods in keeping with preformance improvements and development of ozone generators, reactors and other equipment. The development of highly safe ozone treatment techniques is also expected.

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