Advanced Ozone Water-Treatment Technology

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Mitsubishi Electric has developed commercial ozone water-treatment technologies that can provide safe, odor-free drinking water, establish environmentally sound sewage-treatment processes and implement high-quality water reclamation systems. This article introduces advanced ozonization systems the corporation has delivered for treating drinking water and sewage, and a combined process employing ozone and hydrogen peroxide that is currently under development.

Advanced Ozonization Technology for Treatment of Drinking Water

BENEFITS. Ozone treatment of drinking water benefits water quality in several ways.

It prevents formation of trihalomethanes and other organochlorine compounds by decomposing humic acids. Humic acids react with chlorine to produce this class of substances.

It deodorizes drinking water by breaking down two major compounds that contribute to musty smell, geosmine and 2-methylisoborneol, which other processes do not remove.

Combined with activated carbon filtration, it serves to remove agricultural chemicals, wastes from high-tech industrial processes and other substances listed in water-quality regulations.

Japanese water-quality regulations require that trihalomethane, formed by the reaction of chlorine disinfectants and humic substances, be present in tap water at concentrations no higher than 100μg/l. Ozone has long been used as a decolorizing agent to decompose humic acids and other pigmented compounds, and therefore ozone removal of humic substances reduces the potential for trihalomethane formation.

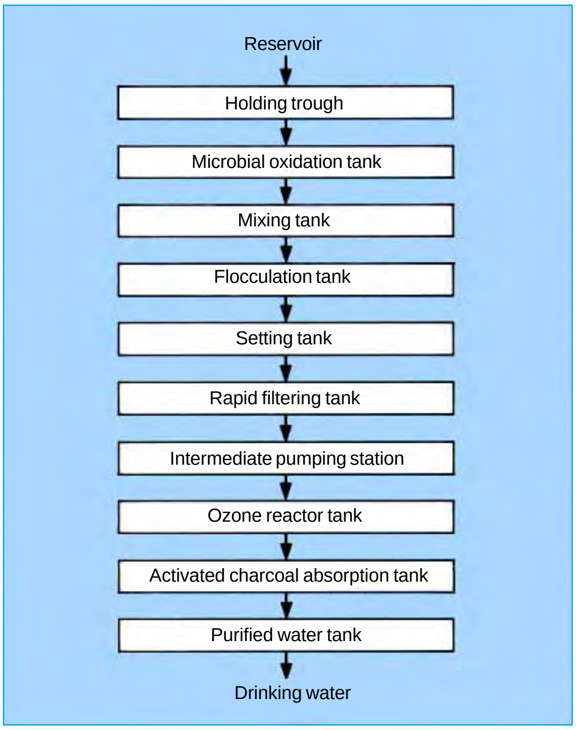

Fig. 1 The water-treatment process at the Chatan Water-Treatment Plant.

Table 1 Main Specifications of Ozone Treatment Facility at Chatan Water-Treatment Plant

Ozone reactor tank	
Construction	Reinforced concrete
No. of tanks	4 (2-stage x 2)
Capacity	194,000m³/day
Tank dimensions	3.85 x 8.8 x 5m (W x L x D*)
Contact time	10 min. (5 min./stage)
Treatment	Diffusion with simultaneous air and water flow
Ozone generator capacities	8.1kg/h x 4
Ozone injection rate	0~4mg/l
Additional equipment	Catalytic ozone breakdown unit

*Effective depth

Activated charcoal absorption tank	
Construction	Reinforced concrete
No. of tanks	17 tanks (4 systems with 1 spare)
Capacity	219,800m³/day
Tank dimensions	5.05 x 10.85m (W x L)
Contact time	12min
Treatment	Fixed-layer, downward-flow activated charcoal
Activated charcoal thickness	2m
Cleaning method	Blowback with air and water
Lower water collector	Porous concrete
Additional equipment	Activated charcoal supply

A WATER-TREATMENT PLANT IN OKINAWA. The corporation has already delivered 18 commercial ozone and activated carbon water-treatment systems. Here we introduce an

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ozonization facility delivered to the Chatan Water-Treatment Plant of the Okinawa Prefecture Enterprise Bureau.

The plant processes up to 194,000m^3 of water per day, concluding with ozonization and active charcoal filtration. Conventional treatment was judged incapable of satisfying water quality requirements because the rivers used as a water source were polluted with domestic wastewater, and the required chlorination would have resulted in excessive trihalomethane formation.

We designed the ozonization system to limit trihalomethanes at the consumers' faucet to 60µg/l and chloroform to 30µg/l, based on Japanese Ministry of Health and Welfare regulations, which limits trihalomethane-forming potential to less than 100µg/l, and WHO water-quality guidelines.

Table 1 lists the facility specifications. Four air-fed glass-tube silent-discharge ozone generators are used, each with an ozone production capacity of 8.1kg/hr. The water is ozonated by mixing ozonated air and water from opposite directions in a large tank, and repeating the process in a second tank. The tanks are 3.85 x 8.8m, with a 5m water depth. The water retention time is 10min.

PERFORMANCE. Table 2 lists the water quality at each stage of treatment in the facility. The ozone treatment and activated charcoal filtering accomplish the greatest reduction in trihalomethane formation potential. These processes both contribute to lower levels of total organic carbon (TOC) and methylene blue active substances (MBAS), and reduce requirements for chlorine and potassium permanganate. The facility met the original design objectives, and has contributed to a safer and better-tasting water supply.

Ozone Processing in Sewage Treatment

BENEFITS. Ozone processing is used in sewage treatment for deodorizing, decolorizing and microbicidal effects. A portion of the treated wastewater can be reclaimed through ozone processing to feed streams and fountains, supplement rivers, and for other recreational purposes, as well as applications in the treatment facility itself.

Ozone processing can also be adopted on a larger scale to decolorize the entire outflow of sewage-treatment plants where pigmented compounds—which the activated sludge process does not remove—are present in high concentrations. Ozone is an effective decolorizing agent because it selectively attacks the double-bonds that give pigments their characteristic colors.

Chlorination byproducts such as trihalomethanes and other hazardous organochlorine compounds in treated-sewage outflows affect ecosystems and can have a negative impact on water quality if they enter water sources. Ozone is more lethal to microorganisms than chlorine without forming these substances.

Many sewage-treatment plants are expected to install ozonization facilities due to these environmental benefits.

A SEWAGE TREATMENT PLANT IN OSAKA. The corporation has delivered 16 ozonization systems for sewage treatment. Here we will introduce an installation at the Chubu Treatment Plant of the South Osaka Central Coast Sewage District.

Industrial wastewater comprises most of the plant's inflow, however it also receives highly colored fiber and food-processing plant wastes that result in discolored waters where the plant discharges its outflow to Osaka Bay—which happens to be a highly visible location near a popular beach area and the New Kansai International Airport.

The plant had used sodium hypochlorite and polyaluminum chloride decolorizing agents; however, residual chlorine from these compounds caused a variety of problems, including breakup of the activated sludge floc, equipment

Table 2 Operation Results of Chatan Water-Treatment Plant

Stage of treatment	THM-FP (µg/l)	TOC (mg/l)	MBAS (mg/l)	Chlorination requirement (mg/l)	$KMnO_4$ requirement (mg/l)
Reservoir	59	1.9	0.08	2.2	7.6
After microbial treatment	57 (3)	1.75 (8)	0.05 (38)	1.0 (55)	6.8 (11)
After settling tank	44 (25)	1.43 (25)	0.05 (38)	0.5 (77)	4.5 (41)
After filtering	41 (31)	1.28 (33)	0.04 (50)	0.4 (82)	3.7 (51)
After ozonation	24 (59)	1.25 (34)	0.01 (88)	0.1 (95)	2.6 (66)
After activated charcoal filtering	15 (75)	0.72 (62)	0.01 (88)	0.0 (100)	1.5 (80)

Note: Figures in parentheses list the cumulative removal of the substance in percent.

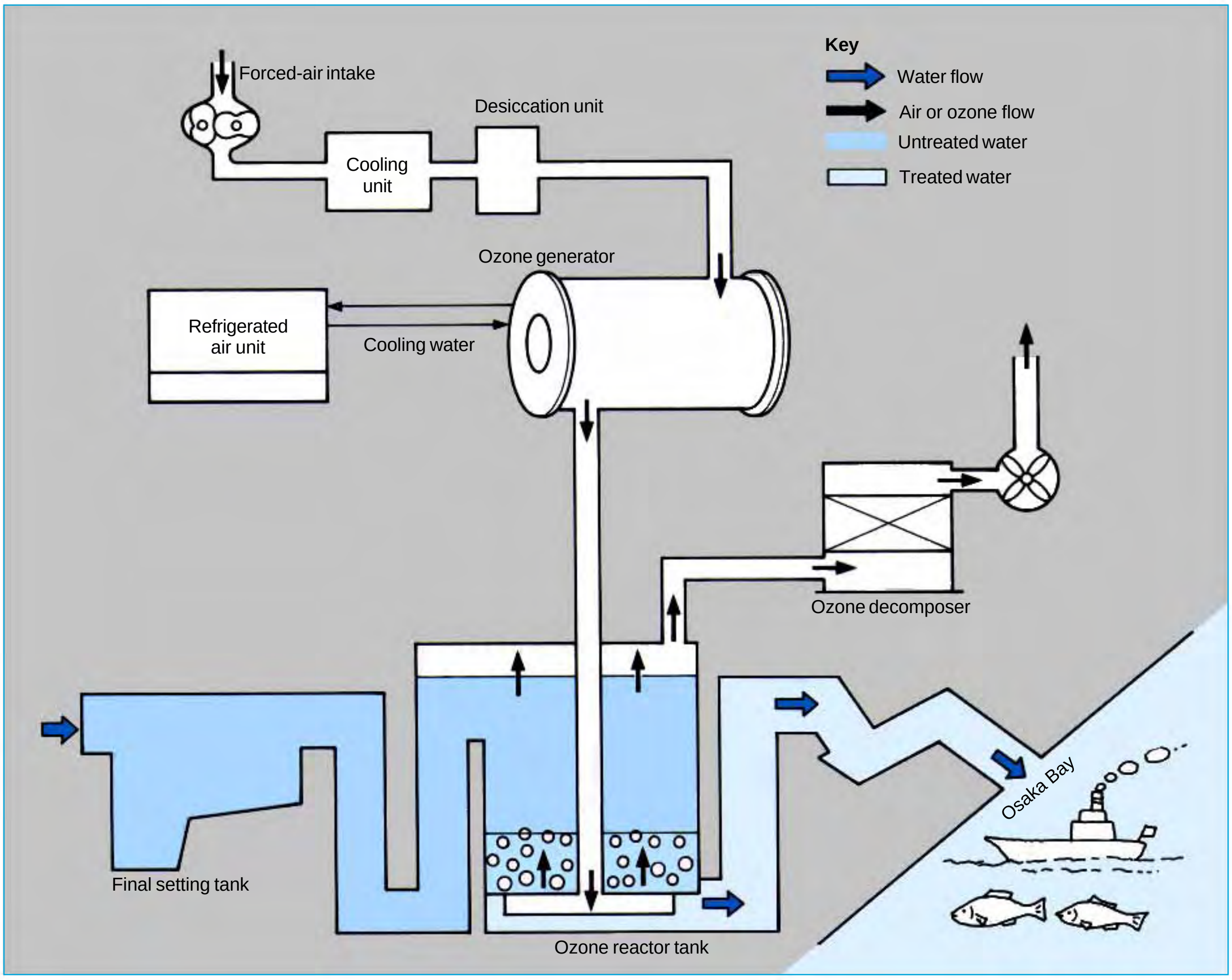


Fig. 2 The ozonation process at the Chubu Treatment Plant.

Table 3 Main Specifications of Ozone Treatment Facility at Chubu Treatment Plant

Item	Type	Number
Air blower	Roots compressor, 9.81N/cm³ (1kgf/cm³), 4.94m³/min, 22kW	6
Ozone generator	Air-fed glass-tube silent-discharge, 4kg/h (1), 5kg/h (2)	3
Ozone injector	Diffusion pipe	2
Ozone reaction tank	Reinforced concrete 2.55 x 4.5 x 4.5m (W x L x D)	2
Ozone decomposer	Activated charcoal decomposer, 200m³/h (standard state)	3

corrosion and high operating costs.

We planned an ozone decolorizing facility for the plant to alleviate these problems. The production system came online in August 1992 following extensive testing.

The ozone facility consists of an ozone generator, ozone reaction tank and catalyzer to break down residual ozone in the vented gas (Fig. 2). The facility employs one 4kg/hr ozone generator and two 5kg/hr generators, all of the air-fed glass-tube silent-discharge type. The water and ozone are mixed in two single-stage diffuser-type reactor tanks that are 2.55 x 4.5m with a 4.5m water depth. The retention time is 14.9 minutes (Table 3).

PERFORMANCE. Table 4 shows the results of the ozone decolorization treatment. Spectrophotometry was used to measure the decolorizing performance. In general the degree of coloring was measured at under 10% (practically colorless), indicating that the facility functioned as planned, although the changing composition and color degree of the effluent from the final settling tank results in some variations.

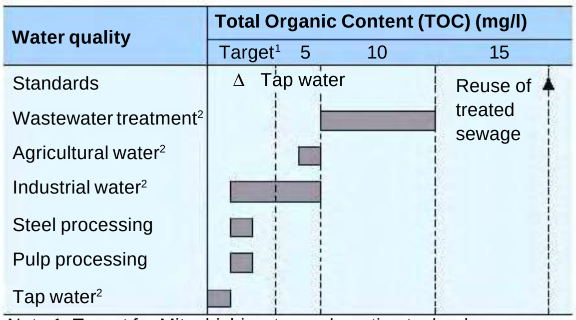
Runs 1~4 in the table show that even when the retention time (the period of contact between the water and ozone) was shortened due to large throughput, constant decolorizing performance could be achieved by boosting the ozone-injection rate. A side benefit of the process is that the chemical oxygen demand (COD) of the effluent dropped by 20~30%.

Table 4 Operation Results of Ozone Treatment Facility at Chubu Treatment Plant

Run No.	Inflow rate (m^3/h)	Reaction time (min.)	Injection rate (mg/l)	Initial water purity(%)	Final water purity(%)	Impurities reduction%	Initial COD(mg/l)	Final COD(mg/l)	COD reduction%
1	274	13.9	30.9	21.9	6.0	73	26.4	19.1	28
2	248	15.4	39.0	15.3	7.1	54	22.8	17.4	24
3	219	17.4	27.0	9.6	2.4	75	16.3	11.5	29
4	234	16.3	17.4	4.3	1.6	63	13.0	11.0	15
Avg. (1~4)	244	15.6	28.6	12.8	4.3	66	19.6	14.8	24
5	138	27.6	29.1	23.7	7.6	68	21.3	15.7	26
6	164	23.2	23.9	20.4	6.6	68	20.9	14.5	31
7	165	23.1	22.2	20.1	6.9	66	21.6	17.4	19
8	162	23.5	20.2	14.7	3.7	75	17.9	14.1	21
Avg. (5~8)	157	24.2	23.9	19.7	6.2	69	20.4	15.4	25

Note: Runs 1~4 employed two ozone generators, and runs 5~8 one ozone generator.

Table 5 Water Quality Levels and Application Requirements



Note 1: Target for Mitsubishi water-reclamation technology
Note 2: Measured values

Combined Ozone and Hydrogen Peroxide Water Reclamation Technology

BACKGROUND. Advanced wastewater treatments hold the potential to increase the water supply and reduce water pollution through extensive water reclamation. Use of reclaimed water is already on the rise, and further growth is expected.

Reclaimed wastewater needs to be sufficiently pure to serve as a source for water-supply systems or to use directly in agriculture and industry. The maximum total TOC for these applications is 2~3mg/l, which requires removal of refractory substances, such as the products of biological metabolism, and residual organic substances that remain in wastewater even after ozone treatment.

Several new processes with high oxidative potential have been studied for this purpose: high-pH ozonization, UV ozonization, and combined ozone and hydrogen peroxide treatment. At Mitsubishi Electric, we investigated combined ozone and hydrogen peroxide treatment, with the goal of achieving TOC levels of 3mg/l or lower.

The combined process is relatively simple to implement. All it requires is that we supplement a conventional ozone injection process with a small amount of hydrogen peroxide.

REACTION MECHANISM. The hydrogen peroxide reacts with ozone to produce hydroxy free radical ·OH (Eq. 1). Even more highly oxidizing than ozone, this species is capable of breaking down refractory compounds and oxidizing almost all residual organics into carbon dioxide and water.

$$
\begin{aligned}
&O_3 + H_2O_2 \rightarrow \cdot OH + \cdot O_2H + O_2 \\
&\cdot OH + O_3 \rightarrow \cdot O_2H + O_2 \qquad \text{........(Eq. 1)} \\
&\cdot O_2H + O_3 \rightarrow \cdot OH + O_2
\end{aligned}
$$

Although the hydroxy free radical easily decomposes alcohol and other organic compounds in laboratory tests, we anticipate that inorganic ions, such as carbonate ions, present in wastewater would react with and consume much of the species. Numerous other compounds in wastewater complicate the issue, requiring further investigation.

RESEARCH AND DEVELOPMENT. Engineers in Europe and the United States are studying the varieties of wastewater, preprocessing steps to limit the ineffective consumption of hydroxy free radical, and suitable reactor vessel designs for the radical reaction. Treatment facilities using the combined process have already been set up at several water-treatment plants. Japan lags the west in the research and development of this technology, with no commercial systems implemented to date, but promising results from initial studies at Mitsubishi Electric sug-

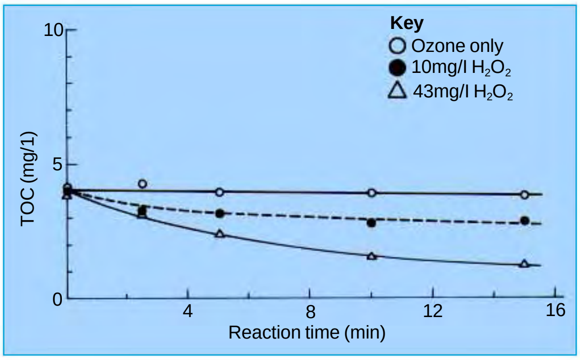


Fig. 3 TOC removal by H_2O_2/O_3 treatment after pretreatment by PAC coagulation and filtration.

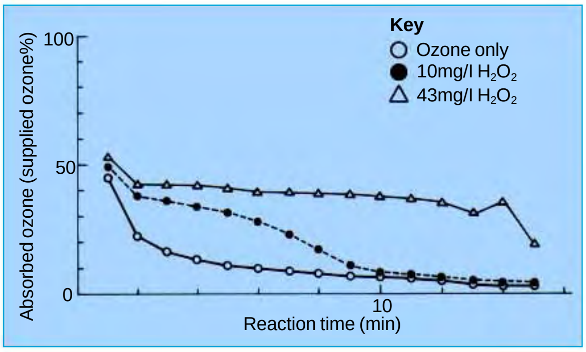


Fig. 4 Ozone absorption characteristics.

gest that this process will be suitable for future water reclamation projects.

EXPERIMENTAL RESULTS. Fig. 3 shows the results of a batch processing experiment where we subjected treated wastewater to PAC coagulation and filtration, and then used a combined ozone and hydrogen peroxide process. While ozone alone does not significantly reduce the TOC, the addition of hydrogen peroxide causes the TOC to decline to as low as 1.5mg/l.

The combined process is also more efficient: the amount of ozone consumed per TOC removed is less than that required for conventional ozonization, and the ozone absorption efficiency is higher than that with conventional ozonization.

Fig. 4 shows the results of batch experiments in water 30cm deep: absorption efficiency is 10% under conventional ozonization, while it rises to 40% with the addition of hydrogen peroxide. The absorption continues to remain high even after the reaction time has elapsed and the hydrogen peroxide has been consumed. The high absorption occurs because the dissolved ozone is quickly utilized in reactions with hydrogen peroxide and hydroxy free radical.

By supplementing existing ozonization facilities with hydrogen peroxide, we can expect to raise the absorption efficiency to 20~25% in tanks 4~5m deep, or convert processes to using compact, contact-type tanks without loss of efficiency.

In summary, the combined ozone and hydrogen peroxide treatment effectively lowers the TOC, allows construction of more compact equipment and is well suited to water-reclamation schemes.

WORK IN PROGRESS. Our current R&D is aimed at determining the best pretreatment processes and conditions, determining the optimum amount of hydrogen peroxide and its best method of introduction, and finally, the optimum ozone injection conditions.

We are also conducting design studies on a practical water reclamation system. A pilot plant will enter operation by March 1996 to help determine the technology's performance under real-world conditions, and we are designing future systems that will be simple, economical to run and easy to maintain.

This R&D project was conducted in affiliation with the Public Utility System Research Project of the Engineering Advancement Association of Japan.

Water purification technology is increasingly important as we face increasing water pollution, growing urban populations and greater water demand. Mitsubishi Electric believes that its work in the field of ozonization technology for water-supply purification and sewage treatment will contribute to the health and environmental quality of future generations. ❑