Abridged version

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Development of Ozone Water Treatment Technology for Industrial Circulating Water*


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1 Introduction

At a steelworks, as much as 120 t of water is required, to produce 1 t of steel products, and as a means of meeting this need, large amounts of circulating water are used. One of the problems with this industrial water is bacterial troubles and the bactericidal chlorine method is usually adopted to solve this problem. Kawasaki Steel has recently developed a bactericidal ozone method that replaces the conventional chlorine method. Ozone has stronger disinfecting power than chlorine. In addition, ozone does not accelerate the corrosion of equipment by water as chlorine does.

Although the disinfection by ozone is a long-standing technique, it has not been spread due to high treatment costs and it has so far been used only for the disinfection of city water in part of Europe.[1] Recently, however, requirements for a complex city water treatment, such as deodorizing and decolorizing, have increased also in Japan and attempts are being made to use ozone in this application.[2]

As for the industrial circulating water, there is a report[3] in the U.S. on a case where a continuous shooting of ozone into cooling towers prevents bactrial troubles. However, there is no water treatment example worldwide in which ozone is used for the whole industrial (circulating) water system.

The ozone method developed recently treats the water of the whole industrial (circulating) water system by continuously shooting ozone into the cooling tower and intermittently shooting it into the water supply system. This method cuts down on the consumption of ozone and proves industrially economical enough.

This technique was developed through joint researches with Mitsubishi Electric Corp. and was put into practical use in the roll cooling water for the 6-stand tandem mill at Kawasaki Steel's Chiba Works.

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This report presents results of fundamental experiments conducted to clarify the disinfecting effects of ozone, and the effect of water quality on the consumption characteristics of ozone. It also describes an example of practical application to the 6-stand tandem mill.

2 Bacterial Troubles in Industrial Water

The greater part of the industrial water used at steelworks is the direct cooling water for hot strip and rolls and the indirect cooling water for heat exchangers and others. As shown in **Table 1**, this cooling water poses the two problems of corrosion and fouling.

Since an increase in corrosiveness of water shortens the life of equipment, the corrosiveness is usually restrained by pH control and corrosion inhibitor addition. Furthermore, troubles caused by foreign materials are serious in attaining stable operation and product quality assurance.

As is apparent from Table 1, fouling is divided into four types; in most cases, fouling is caused by microorganisms and foreign matters in the industrial water are formed by microorganisms and solid materials.

In general, microorganisms concentrate and increase along with organic substances in water at the contact surface between a solid and a liquid, for example, between the pipe wall and the industrial water. In this process, microorganisms secrete hydrocarbonaceous adherent substances and cause suspended solids in the water to coalesce to form a thick soft matter on the pipe wall and others.[4] This matter is called slime.

Chlorine or its compounds have so far been used for disinfecting microorganisms. Several ppm of chlorine is injected into water and remains as chloride ions after disinfection by the oxidation reactions shown below.

Table 1 Cooling water problems

Item	Type of Problem	Remarks
Fouling	1. Spray nozzle clogging 2. Blocking-up at water line 3. Fouling of heat exchanger surface 4. Surface defect of steel product	Cause of fouling 1. Biological matter growth 2. Sedimentation of suspended solids 3. Deposition of corrosion product 4. Crystallization of hardness composition
Corrosion	1. Corrosion at water line 2. Corrosion of heat exchanger 3. Corrosion of machine frame under wet condition by cooling water spraying	Factors affecting corrosion rate pH, chloride, sulphate, total hardness, alkalinity, specific conductivity, residue after evaporation

Therefore, the accumulation of chloride ions occurs in the circulating water system, resulting in an increase in the chloride ion concentration by tens of ppm or, in some cases, hundreds of ppm. In general, halogen ions destroy the passivity of metals and accelerates corrosion.[5-8] Therefore, the use of chlorine in circulating water systems has posed a great problem in controlling the metal corroding nature of water.

Chlorine water:

$$Cl_2 + H_2O \rightleftarrows HClO + H_3O^+ + Cl^-$$

$$HClO + H_2O + 2e^- \rightleftarrows H^+ + Cl^- + 2OH^-$$

Sodium hypochloride:

$$NaClO + H_2O + 2e^- \rightleftarrows Na^+ + Cl^- + 2OH^-$$

3 Microorganism Treatment by Ozone

The disinfecting action of ozone is different from that of chlorine. Ozone has stronger disinfecting power and higher disinfecting rates than chlorine. This is because chlorine attacks the enzyme of cells, while ozone destroys cell walls.[9] Furthermore, ozone oxidizes various organic and inorganic substances in water and has functions such as deodorizing, decolorizing, removal of COD components. Also, ozone does not remain and accumulate because of natural decomposition.

The general characteristics of ozone are shown in **Table 2**.

3.2 Intermittent Ozone Water Treatment System

Usually, ozone is used in city water for the purpose of disinfecting the water itself. In this case, therefore, it is necessary to continuously shoot ozone and this pushes up costs of equipment and operations. In the case of industrial water, however, the purpose of ozonation is to prevent the formation of slime at pipe walls. For this reason, continuous shooting is not always necessary. From the propagation process of microorganisms shown in **Fig. 1**,[10] it is judged that the formation of slime can be prevented if microorganisms are destroyed by intermit-

Table 2 Characteristics of ozone

Item	Value
Molecular formula	O_3
Molecular weight	48.0
Boiling point at 1 atm (°C)	−111.9±0.3
Melting point at 1 atm (°C)	−192.7±0.2
Density of gas at 0°C, 1 atm (g/l)	2.14
Solubility in water at 20°C (g/l)	0.54
Heat of formation at 25°C (kcal/mol)	−34.5±0.2
Half life at dry air (h)	12
Half life at pure water (min)	30
Oxidation-reduction potential (V)	2.07

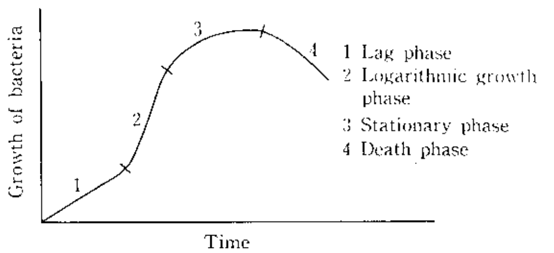


Fig. 1 Growth curve of bacteria (Yoshiharu Eto)[6]

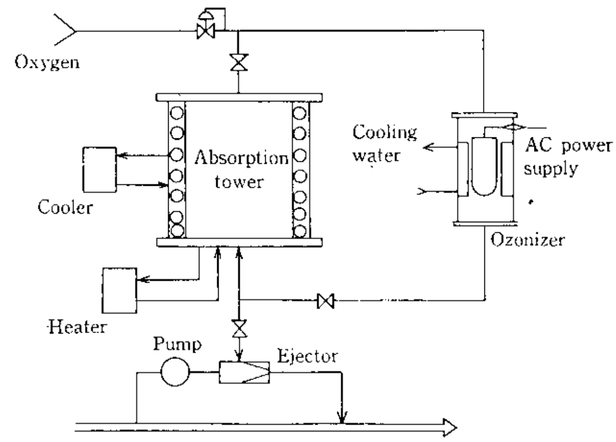
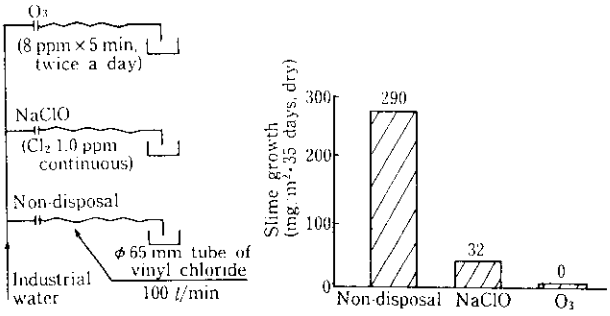


Fig. 2 Schematic diagram of intermittent ozonizer and injector



(a) Diagram of experiment (b) Result of slime growth

Fig. 3 Effect of intermittent ozonation on slime growth

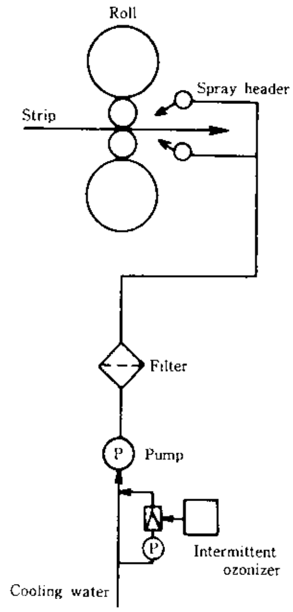


Fig. 4 Ozonation test system

tent shooting within the lag phase before a stage of their logarithmic growth.

Based on the above-mentioned concept, a system for suppressing slime formation was developed by which ozone is intermittently injected into the water supply line. The intermittent ozone shooting equipment (made by Mitsubishi Electric Corp.) is shown in **Fig. 2**. Ozone is generated from oxygen as material by the silent electric discharge method. The generated ozone is caused to be adsorbed by silica gel at −30°C and is stored in it. After the storage of a desired amount of ozone, the silica gel is heated to gasify ozone and the ozone gas is injected into water using an ejector.

3.3 Disinfecting Effect

A test was conducted to compare the disinfecting effect between the intermittent ozone shooting method and the continuous chlorine shooting method. The test circuit used and the results of the test are shown in **Fig. 3**. It was found that slime formation can be inhibited by a 5 min shooting with intervals of 12 h. In the case of chlorine, however, a concentration of injected chlorine of 1.0 ppm is insufficient and the adherence of slime is observed 50 m downstream from the shooting point.

3.4 Optimum Amount of Ozone Shooting

To know shooting conditions, an intermittent ozonization system was installed at a part of the roll cooling water system of a 6-stand tandem mill and an experiment was conducted. The experiment system is shown in **Fig. 4**.

3.4.1 Ozone concentration necessary for disinfection

The relationship between the ozone concentration and the slime growth rate was investigated under a condition of the fixed ozone shooting intervals of 12 h. The

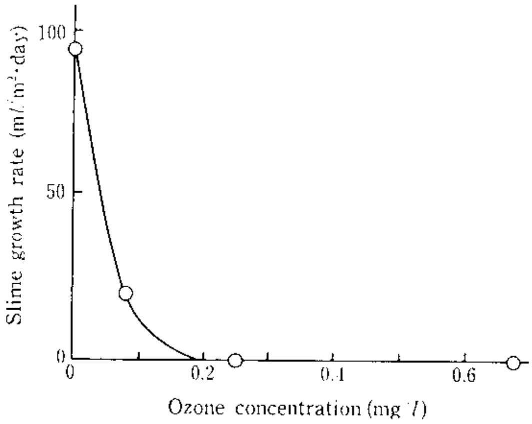


Fig. 5 Relation between ozone concentration and slime growth rate in intermittent ozonation

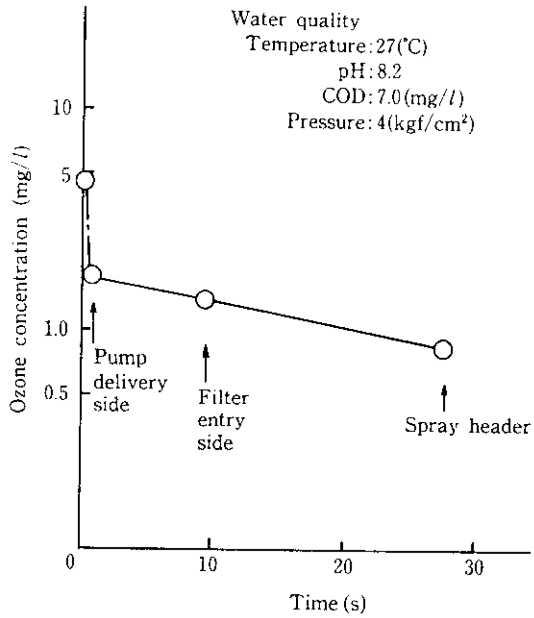


Fig. 6 Example of ozone concentration decreasing

results are shown in **Fig. 5**. It is apparent from this that the ozone concentration necessary for preventing the formation of slime is 0.25 ppm.

3.4.2 Optimum amount of ozone per shot

The ozone concentration in the water decreases because of decomposition by the reaction with organic substances and because of self-decomposition. Decreases in the concentration at each point after ozone shooting are shown in **Fig. 6**. Ozone first rapidly decomposes and decreases in quantity after passing the ejector and then attenuates gradually with a lapse of time.

Since this decreasing rate is proportional to the ozone concentration,[11] a change in the ozone concentration can be given by Eq. (1). Furthermore, the amount of ozone shot to obtain the required ozone concentration can be found form Eq. (2):

$$C_t = C_O e^{-kt} \quad \cdots\cdots (1)$$

$$W_{O_3} = \frac{C_e V T e^{k t_e}}{K} \quad \cdots\cdots (2)$$

$$k = \frac{0.693}{\tau_{1/2}}$$

where t: Time elapsed after ozone shooting (s)

t_e: Time elapsed from the ozone shooting point to the ending point (s)

C_t: Ozone concentration after an elapse of time t (g/m^3)

C_e: Ozone concentration necessary for suppressing slime at the ending point (g/m^3)

C_O: Ozone concentration at the delivery side of ejector (g/m^3)

$\tau_{1/2}$: Half life of the ozone concentration (time elapsed till the concentration decreased to 1/2)

W_{O_3}: Amount of ozone for obtaining a concentration C_O for a time T (f)

V: Amount of water treated (m^3/min)

T: Ozone shooting time (s)

K: Ozone decomposition coefficient at the ejector

The k-value in Eq. (1) is a decomposition constant peculiar to ozone and determined by half life. This is an important value for determining the amount of ozone to be shot. There are studies on the half life of ozone by Morooka[12] and by others. However, there are few studies on the half life of ozone in industrial water. Therefore, a study has been made on the effect of varied water quality, pressures, and temperatures on the half life. The results are shown in **Figs. 7, 8, 9,** and **10**. As a result, it was found that the half life of ozone is affected by COD, pH, pressure, and temperature. The following empirical formula was obtained from this:

$$\tau_{1/2} = 0.693\{K_1[\mathrm{COD}] + K_2\}^{-1} P^{-0.68} \quad \cdots\cdots (3)$$

$$K_1 = 8.32 \times 10^9 [\mathrm{OH}^-]^{0.31} \exp(-7.52 \times 10^3/\theta)$$

$$K_2 = 2.20 \times 10^{10} [\mathrm{OH}^-]^{0.70} \exp(-6.12 \times 10^3/\theta)$$

where [COD]: Chemical demand oxygen (mg/l)

P: Pressure of water (kgf/cm^2)

$[OH^-]$: Hydroxyl ion concentration (mg/l)

θ: Water temperature (K)

The lower any of the three parameters, pH, pressure or temperature, the lower the rate of ozone decrease.

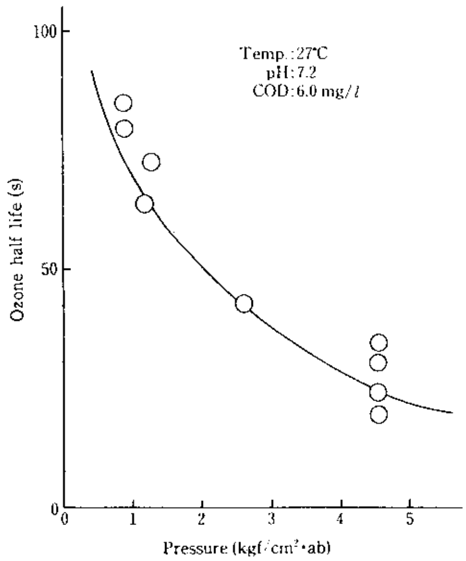


Fig. 7 Influence of pressure on ozone half life

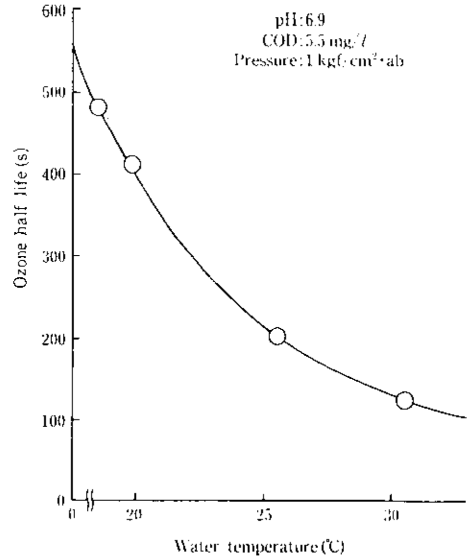


Fig. 8 Influence of water temperature on ozone half life

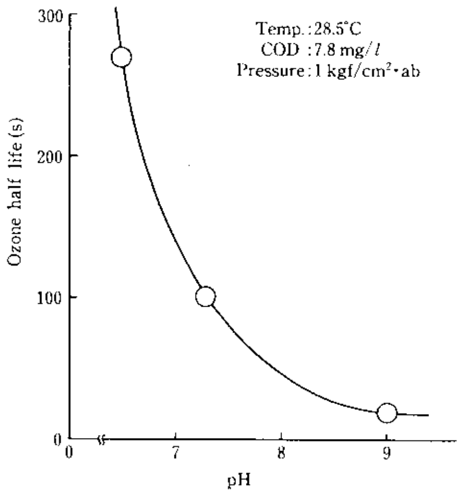


Fig. 9 Influence of pH on ozone half life

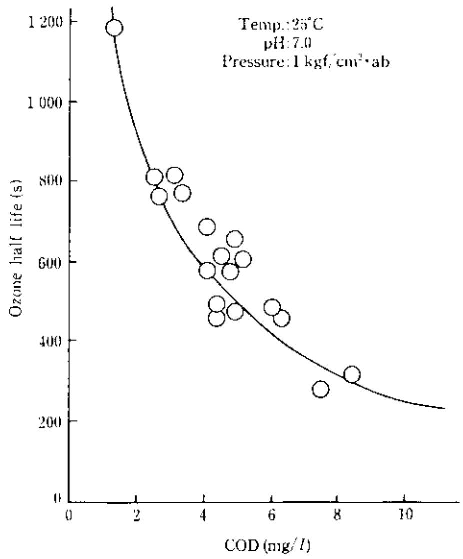


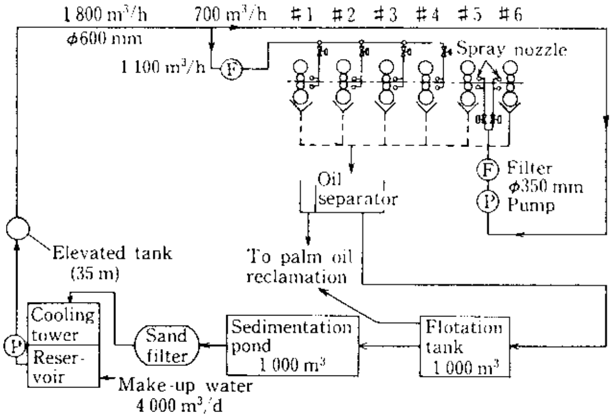
Fig. 10 Influence of COD on ozone half life

4 Application to Roll Cooling Water System of 6-Tandem Mill

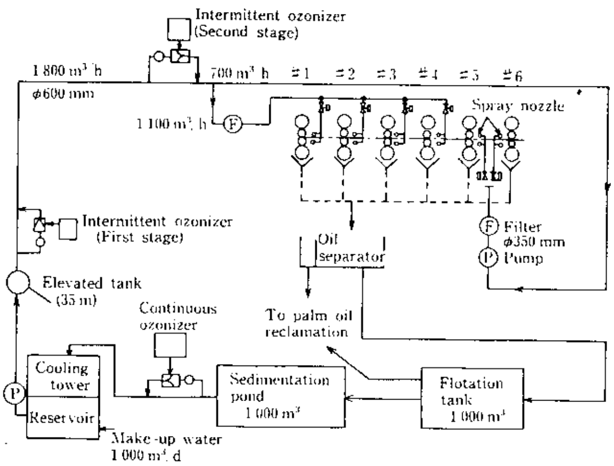
4.1 Bacterial Troubles

The 6-tandem mill is supplied with rolling mill lubricant and roll cooling water by separate systems, so-called the direct system. As shown in **Fig. 11**(a), the roll cooling water is recirculated and used after the floating separation of the rolling mill lubricant that has mixed in the effluent. The water quality after treatment is shown in **Table 3**. The values of *n*-hexane extracted matter and COD are high. Such water tends to promote the growth of microorganisms.

The adherence of slime is shown in **Photo 1**. Microor-



(a) Before ozonation



(b) After ozonation

Fig. 11 Schematic diagram of cooling water in six tandem cold rolling mill

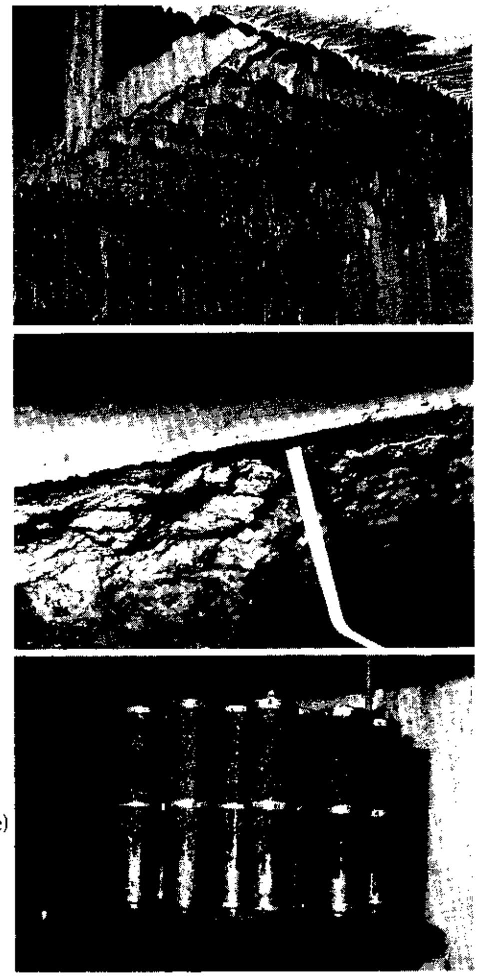


Photo 1 Example of slime adherent

Table 3 Quality of cooling water for six tandem cold rolling mill

Item	Value
pH	8.2
Turbidity (T.U)	6
Suspended solids (mg/*l*)	10
Alkalinity (mg/*l*)	39
Chlorides (mg/*l*)	33
Sulphates (mg/*l*)	255
Total hardness (mg/*l*)	305
Total iron (mg/*l*)	1
Chemical oxygen demand (mg/*l*)	7
Specific conductivity (μs/cm)	636
n-hexane extracted matter (mg/*l*)	8

ganisms that form this slime are shown in **Photo 2**.

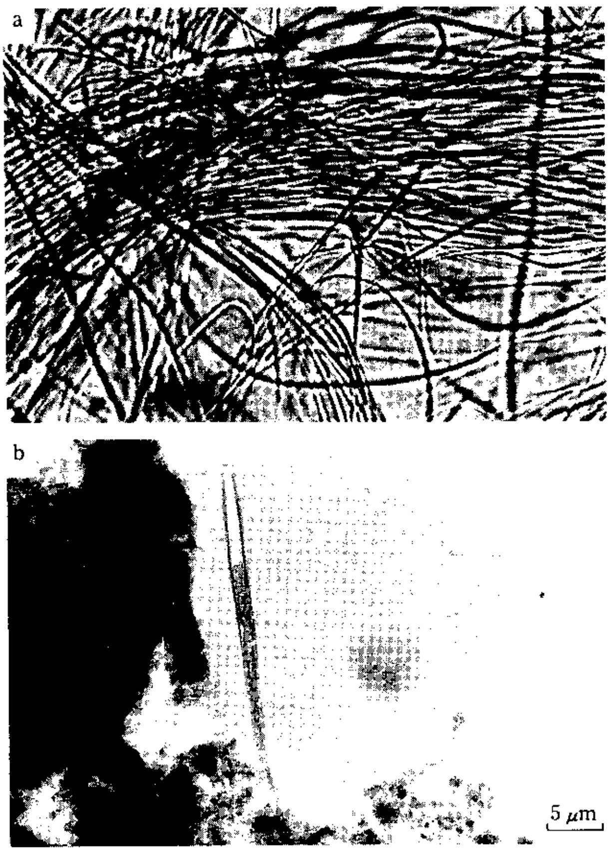
When chlorine is used for slime treatment, the roll cooling water that comes into direct contact with the strip may generate rust because of the accumulation of chloride ions. Therefore, the chlorine method cannot be said desirable. To solve this problem, the circulating water system has so far been used by replenishing more make-up water than usually required.

4.2 Application of Ozone Water Treatment System

Figure 11(b) shows a water treatment system by ozonation and **Table 4** gives the specification of the ozonizer.

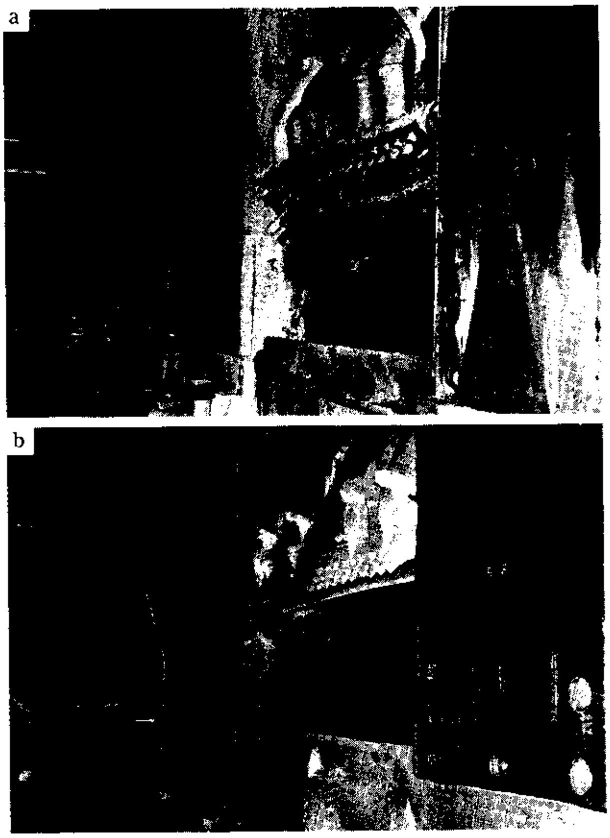
Two intermittent ozonizers are installed; one on the exit side of an elevated tank and the other near the rolling mill, and they are synchronized for shooting. This is because the ozone requirement can be decreased from the attenuation characteristics of ozone, with the result that equipment can be made compact.

Since the cooling tower is open to the air, ozone tends



(a) Sphaerotilus
(b) Nematoda

Photo 2 Examples of microorganism in cooling water



(a) Before ozonation
(b) After ozonation

Photo 3 Effect of ozonation on the prevention of slime fouling

Table 4 Specifications of the ozonizer

Item	Intermittent system		Continuous system
	1st stage	2nd stage	
Capacity of ozonizer (g/h)	25	130	360
Ozone injection at a time (kg)	0.25 max	1.30 max	
Injecting time (min)	5	5	Continuous
Injecting interval (h)	12	12	

to gasify and the disinfecting power decreases. Therefore, ozone is continuously shot at low concentrations.

4.3 Effects of Ozonation

4.3.1 Stabilization of rolling operation

After ozonation was carried out, adherence of slime did not occur in the cooling tower, piping, and devices, and the operation of the equipment became stable. At the same time, it was possible to reduce roll marks on products. **Photo 3** shows examples of the effect. The adherence of slime which has so far occurred is not observed in the least.

The roll change by roll mark troubles and the maintenance of the clogged automatic backwash strainer filters are shown in **Fig. 12**(a) and (b), respectively. It is apparent that both frequencies decrease noticeably after the ozonation.

4.3.2 Decrease in water treatment cost

To prevent the adherence of slime, resupply of a large amount of water to the circulating water system and removal of suspended solids by a sand filter have so far been carried out. These, however, became unnecessary by ozonation, with water treatment costs reduced. The water treatment cost incurred and make-up water ratio are shown in **Table 5** and Fig. 12(c), respectively. It is apparent that the make-up water ratio decreased noticeably after the ozonation.

Table 5 also includes costs of the chlorine method roughly calculated on the assumption that 3.5 ppm of chlorine is shot into the circulating water and that the

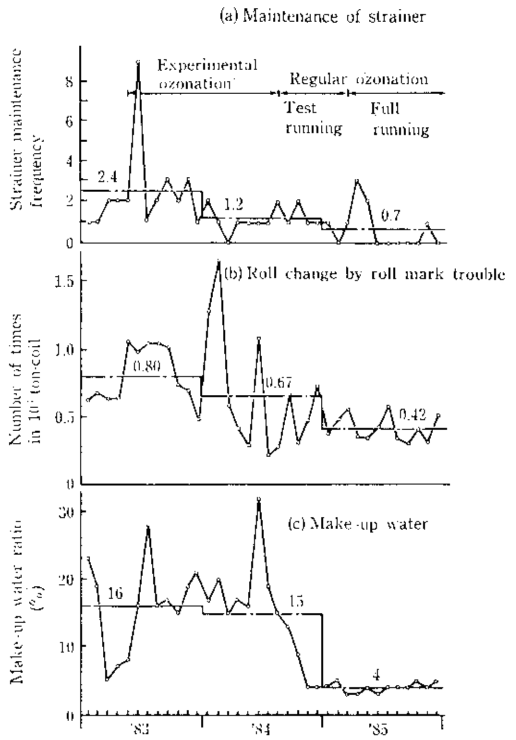


Fig. 12 Effect of ozonation on cold rolling operation

Table 5 Water treating cost for slime control

	Actual data		Case of Chlorination
	Before Ozonation	After Ozonation	
Unit consumption			
Electric power (kWh/m^3-water)	—	0.016	–
Oxygen (kg/m^3-water)	—	0.012	—
Chemicals (kg/m^3-water)	·	– –	0.027 (NaClO containing 12% chlorine)
Fresh water for make-up (m^3/m^3-water)	0.16	0.04	0.120
Pollutional waste water (m^3/m^3-water)	0.15	0.03	0.108
Running cost (¥/m^3-water)			
· Electric power, Oxygen, chemicals	—	0.26	0.54
· Fresh water, waste water	3.70	1.10	2.96
Equipment cost (¥/m^3-water)	1.97 (Sand filter)	0.92	0.04
Total cost (¥/m^3-water)	5.67	2.28	3.54
Water quality			
Choride (mg/*l*)	33	55	(55)
Suspended solid (mg/*l*)	10	15	
n-Hexane extracted matter (mg/*l*)	8	10	
Chemical oxygen demand (ppm)	7	14	

amount of accumulated chloride ion is controlled to 55 ppm or less (chloride ion concentration in the case of ozone process) by supplying make-up water. It is apparent from this that the cost of the ozone method is by far lower than that of the chlorine method in terms of running cost, because the make-up water demand is small in spite of higher equipment cost.

5 Conclusions

Kawasaki Steel has developed a water treatment process by ozonation as a new measure to prevent bacterial troubles in industrial water and has applied it to the roll cooling water system of the 6-stand tandem mill at Chiba Works. As a result, bacterial troubles ceased to occur. The ozone method contributed to stable operation and resulted in a decrease in the water treatment cost.

The authors intend to expand the application of this method to other equipment while reducing the equipment cost of the method.

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