CHEMICAL OXGEN DEMAND ANALYSIS USING OZONE OXIDATION

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I. INTRODUCTION

Developed mainly for indoor analysis, conventional analysis for water pollution, such as COD and TOD, are not suitable for on-line measurement. Actually, commercial water quality autoanalyzers which automate these conventional methods have major disadvantages: they often require frequent maintenance and they have a high operating cost due to the large amount of chemicals consumed.

We have studied the use of ozone as a new method applicable to on-line water pollution monitoring. As is well known, ozone is a powerful oxidant that can oxidize most organic pollutants in water. Therefore, if the amount of oxygen consumed in the ozone oxidation can be measured, we may use this quantity as an index of water pollution. This may be regarded as a chemical oxygen demand by ozone—COD (O_3). Since ozone can be readily produced by corona discharge, reagents for the analysis are unnecessary. Moreover, the COD(O_3) autoanalyzer can be constructed mainly as a gas analyzing system. This would ensure the reliable and trouble-free measurement.
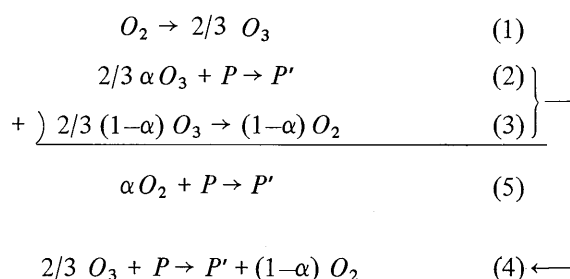
This paper describes a basic study of COD (O_3) and has been presented at Workshop of the Automatic Control of the Sewage Treatment and Water Analysis/Control, Japan(1980).

II. PRINCIPLES

On-line use requires reliable and trouble-free measurement of ozone oxidation. Usually, ozone oxidation has been measured in terms of ozone consumption—the integration of the difference between the ozone injection rate and the ozone discharge rate. This method has the following two problems. First, the ozone consumption includes autodecomposition back to oxygen: accordingly, we cannot measure just the ozone that reacts with the pollutant. Secondly, the reliability of ozone meters has not been adequate.

To solve these problems, we have focussed on oxygen in stead of ozone. Since ozone is produced from oxygen and decomposes to oxygen, we can regard ozone oxidation as the process where oxygen reacts with the pollutants through its high energy allotrope, O_3. This means that the measurement of the ozone consumption can be replaced by the measurement of oxygen consumption. This relationship is shown by a series of reactions (1) - (5). Equation (1) expresses the ozone generation in the ozone generator. Equation (2) and (3) show that $2/3\alpha$ of ozone reacts with pollutants, P, producing P', and the remaining $(2/3)$ $(1-\alpha)$ of ozone decomposes to oxygen. Equation (4), the sum of Eq. (2) and (3), shows that the ozone comsumption consists of the oxidation of P and the autodecomposition. However, summing Eq. (1), (2) and (3), we know that measuring the oxygen material balance including the ozone generation process enables us to measure the ozone oxidation of pollutants. Another advantage of using oxygen is that measurements of oxygen are much more reliable than those of ozone.

$$O_2 \rightarrow 2/3 \ O_3 \qquad (1)$$

$$2/3 \ \alpha O_3 + P \rightarrow P' \qquad (2)$$

$$+ \ ) \ \underline{2/3 \ (1-\alpha) \ O_3 \rightarrow (1-\alpha) \ O_2 \qquad (3)}$$

$$\alpha O_2 + P \rightarrow P' \qquad (5)$$

$$2/3 \ O_3 + P \rightarrow P' + (1-\alpha) \ O_2 \qquad (4)$$

III. METHOD

We used two types of apparatuses denoted by (a) and (b) in *Fig. 1*. In apparatus (a), the ozone-containing gas from the ozone generator is supplied to the reactor, and the effluent gas returns to the ozone generator after being dehydrated through the electric coooler. In this gas-circulating system, since the quantity of oxygen decreases as the reaction proceeds, the pressure decrease in the reactor indicates the oxygen consumption accompanied by the ozone oxidation. Although the pressure is also affected by the temperature, the temperature effect can be compensated for easily. Since the electric cooler cannot reduce the dew
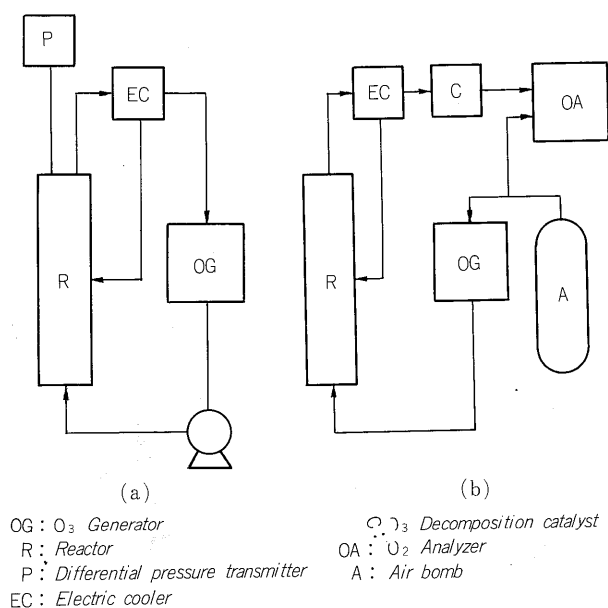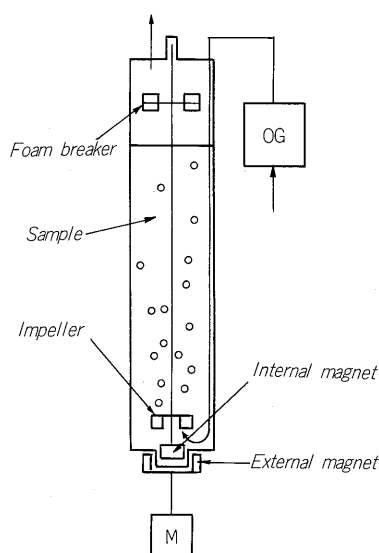
OG : O₃ Generator
R : Reactor
P : Differential pressure transmitter
EC : Electric cooler

O₃ : Decomposition catalyst
OA : O₂ Analyzer
A : Air bomb

Fig. 1 Experimental apparatuses

Fig. 2 Reactor

The reactor, common for both (a) and (b), is shown in *Fig. 2*. An impeller is used to promote the ozone transfer through the gas-liquid interface. Ozone oxidation often produces a large amount of foam. Therefore, the reactor is equipped with a foam breaker rotating with the impeller to prevent the entry of foam into the gas piping. Power is transmitted to the rotating part in the reactor by a magnetic coupling device to maintain air-tightness.

IV. RESULT AND DISCUSSION

4-1. Measurement of the oxygen consumption

Figure 3. shows the typical pressure decrease curve obtained by the use of apparatus (a). The sample is the wastewater from the dining room in our laboratory. For the same sample, COD (Mn) decreases with ozone oxidation as shown in *Fig. 4*. These show that the oxidation of easily decomposable compounds is completed in about an hour and is followed by the gradual oxidation of remaining oxidation-resistant compounds.

On the other hand, using apparatus (b), we can measure the oxygen content difference as shown in *Fig. 5*. This result also shows that easily decomposable compounds can be oxidized in about an hour.
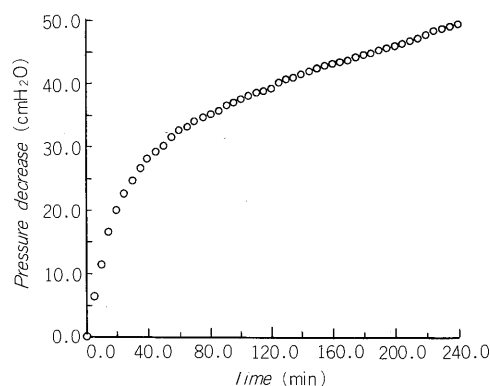

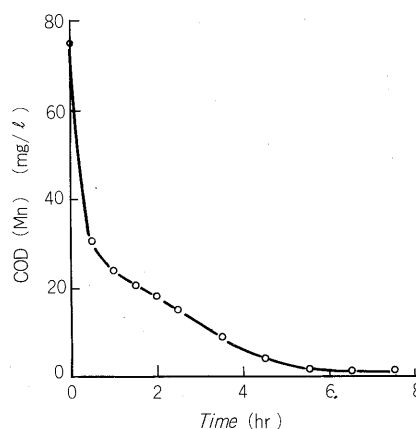**Fig. 3** Pressure decrease with the ozone oxidation

point to a value sufficient for suppressing the production of nitrogen oxides in the ozone generator, we replaced the atmosphere in the reactor with oxygen. To promote the reaction and to prevent the generated CO_2 from being discharged into the gaseous phase, the pH was increased to approximately 12.

In apparatus (b), after passing through the catalyst to decompose the remaining ozone to oxygen, the effluent gas is led to the paramagnetic oxygen analyzer (OXIMAT II, Fuji Electric). The oxygen analyzer measures the oxygen content difference between the effluent gas and the atmosphere. The oxygen consumption can be obtained by integrating the product of the oxygen content difference and the flow rate of the injected air.

Fig. 4 Decrease of COD(Mn) with the ozone oxidation

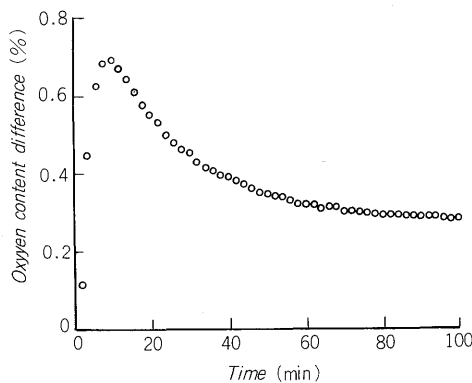**Fig. 5** Variation of the oxygen content difference between the effluent gas and the atmosphere

Fig. 6 Relation between COD(Mn) and the oxygen consumption (wastewater from the dining room)

4-2 The relation between COD(O_3) and COD (Mn)

As described above, we have known that the ozone oxidation rate usually becomes almost constant at a low level after an hour. Therefore, we take the oxygen consumption in an hour as an index of water pollution. In *Fig. 6*, the pressure decrease in an hour measured by apparatus (a) is plotted against COD(Mn) for the wastewater from the dining room. The correlation between them is very high: the correlation coefficient is 0.933. In this figure, symbol ○, □, and △ express the raw wastewater, the supernatant of the activated sludge (the wastewater in the treatment process), and the effluent from the treatment plant, respectively. Note that some COD (Mn) values of the effluent are higher than those of the raw wastewater. This is because the raw wastewater was diluted before the measurement and because data obtained when the effluent quality was extremely poor are included. Similar high correlation can be seen for the effluent from a methane digester (*Fig. 7*): the correlation coefficient is 0.927.

4-3 Evaluation of oxidation ratios

The more the pollutants are oxidized by ozone, the more suitable is COD (O_3) for water pollution index. In *Table 1.* the oxidation ratios of ozone (for 1 and 2 hours at room temperature) are compared with those of potassium permanganate (for 0.5 hour at 100°C) and potassium dichromate (for 2.0 hours at 100°C). The oxidation ratio of ozone is calculated in terms of (T1−T2)/T2, where T1 is the TOD value at the beginning of the ozone oxidation, and T2 is the TOD value after the ozone oxidation. We know from this table that, despite the moderate conditions, the oxidation ratios of ozone are usually higher than those of others. This shows that COD (O_3) is an excellent water pollution index. The high oxidation ratio of ozone also suggests that COD (O_3) will be closely correlated with COD (Cr) rather than with COD (Mn).
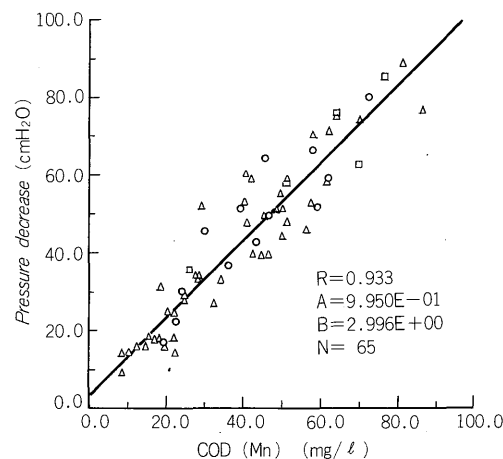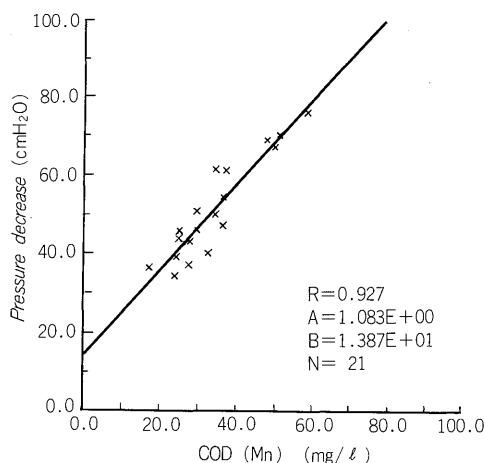

Fig. 7 Relation between COD(Mn) and the oxygen consumption (effluent from a methane digestor)

Table 1 Comparison of the oxidation ratios

Substances	Ratios of Oxidation (%)			
	O_3(1hr)	O_3(2hrs)	KMnO$_4$[1]	K$_2$Cr$_2$O$_7$[1]
Methanol	−	100	27.0	95.3
Ethanol	−	76.9	4.7-19.0	94.7
Acetone	55.1	82.6	0.0	85.1
Acetic acid	20.7	81.2	7.0	94.7
Methylisobutylketone	84.3	100	55.2	−
Oxalic acid	32.3	67.3	−	100
Pyruvic acid	66.7	87.3	37.2	−
Propionic acid	82.3	92.5	8.0	96.7
Malenic acid	83.0	87.5	−	96.0
Glucose	85.4	95.0	46-80	98.1
Tartaric acie	55.9	80.0	93.0	97.4
Dextrin	75.3	85.6	18.0	−
Starch	82.0	93.4	35.0	−
Ethyl acetate	77.7	92.4	4.0	78.0
Citric acid	78.7	93.6	53.0	72.4
Benzene	70.1	98.0	0-35	4-27
Phenol	95.5	96.5	63-80	98.7
Aniline	86.1	90.0	2.1-2.6	3.1
Glutamic acid	85.3	93.8	0.06	1.01
Urea	59.1	59.1	0.613	−
Acetonitrile	41.5	69.9	−	−
Mean	69.3	86.8	28.0	75.1

VI. SUMMARY

We have discussed in this paper COD(O_3), which is the amount of oxygen consumed by ozone oxidation. To measure this oxygen consumption, two types of apparatuses were used: one measures the pressure decrease due to the oxygen decrease in the closed reactor; the other measures the oxygen content difference between the atmosphere and the effluent gas from the reactor. The former is superior to the latter in that pressure measurement devices are very reliable and readily available. However, this method requires compensating for the temperature effect. On the other hand, the latter, free of the temperature effect, is convenient particularly when the temperature is increased to accelerate the reaction. However, a reliable oxygen analyzer must be used because of the small oxygen content differences to be detected. The paramagnetic oxygen analyzer used here meets these demand sufficiently. Using the wastewater from the dining. room, we have known that COD(O_3) can be well correlated with COD(Mn). Moreover ozone can usually oxidize pollutants to a much greater extent than $KMnO_4$ and $K_2Cr_2O_7$. These facts show that COD(O_3) is an excellent index of water pollution. In this study, we have concluded that COD(O_3) is practically applicable to on-line water pollution monitoring.

Reference:

1) H. Yagi, et al : Water and Waste Vol. 18, No. 10, P.79 (1976)