



OVERALL CHEMICAL REACTION MODEL OF AN OZONE CONTACTOR FOR A WATER PURIFICATION MODEL

K. Kageyama*, S. Watanabe*, K. Baba*, N. Komatsu**
and N. Yamakoshi***

* Hitachi Research Laboratory, Hitachi Ltd, Omika-cho 7-1-1, Hitachi-shi, Ibaraki, 319-12, Japan

** Kokubu Works, Hitachi Ltd, Kokubu-cho 1-1-1, Hitachi-shi, Ibaraki, 319-12, Japan

*** Omika Works, Hitachi Ltd, Omika-cho 5-2-1, Hitachi-shi, Ibaraki, 319-12, Japan

ABSTRACT

For the removal of odorous compounds such as dimethylisoborneol (2-MIB) and trihalomethanes (THMs) in supplied water, advanced water treatment plants using ozonation and activated carbon absorption processes have been built in Japan. This paper describes an over-all chemical reaction model for the ozone contactor of the ozonation process. In this model, the Potassium Permanganate Consumed (PPC) is assumed as an index of typical ozone consuming substances. The experimental data and calculated results for the ozone consuming substances are compared with Total Trihalomethanes Formation Potential (TTHMFP). Furthermore, the promotive or inhibitive reaction of 2-MIB is introduced in the model. This allows the mathematical model to be applied to actual raw water containing many kinds of co-exist substances.

The model appropriateness is discussed using pilot plant data for a year's operation.

Copyright © 1996 IAWQ. Published by Elsevier Science Ltd.

KEYWORDS

dimethylisoborneol; mathematical model; odorous compounds; ozone contactor; Potassium Permanganate Consumed; pilot plant data; simulation; Total Trihalomethanes Formation Potential.

INTRODUCTION

In Japan, many people have made complaints to government agencies about bad odors in the drinking water and this is now a big social problem. In 1994, over 16.8million people were affected by bad odors in the drinking water, and this represents about 14% of the people who use supplied drinking water. The main cause of bad odors is odorous compounds from plant plankton, such as geosmin or dimethylisoborneol, but the problem of THMs (trihalomethanes) is also growing. The raw water includes many kinds of dissolved organic carbon expressed as THMFP (THM formation potential). In ordinary water purification plants, mainly using flocculation and filtration processes, odorous compounds and THMFP are difficult to remove. To remove these substances, the Ministry of Welfare is promoting introduction of an advanced water treatment plant, using ozonation and activated carbon absorption processes. Since the advanced water treatment plant needs more space than a conventional plant, and electricity charges to generate ozone are rather high, the most effective design and the most effective control system for the ozone contactor should be implemented. Development of a simulation method that can evaluate the treatment capacity of the plant would help to meet these requirements.

OZONE CONTACTOR MATHEMATICAL MODEL

Many kinds of ozone consuming substances are included in the water, such as dissolved and undissolved organic carbon, metal ions, etc. With so much variety, it is not easy to detect and measure concentration of each substance, so, Potassium Permanganate Consumed (PPC) is assumed as an index of typical ozone consuming substances. This means that the total concentration of the ozone consuming substances is represented by one PPC value. As a typical odorous compound, 2-MIB is focused on in this study.

Fig.1 shows the ozone reaction scheme dealt with the developed model. Table 1 shows fundamental rate equations of each reaction. The reactions are assumed to consist of:

- (1) Solution of ozone in the gas phase
- (2) Self-decomposition of ozone in the liquid phase
- (3) Oxidation of 2-MIB
- (4) Oxidation of PPC

Self-decomposition of ozone in the liquid phase is assumed to be a first-order reaction. Oxidations of 2-MIB or PPC also are assumed to be first-order reactions with respect to the concentration of ozone in the liquid phase and the concentration of 2-MIB or PPC.

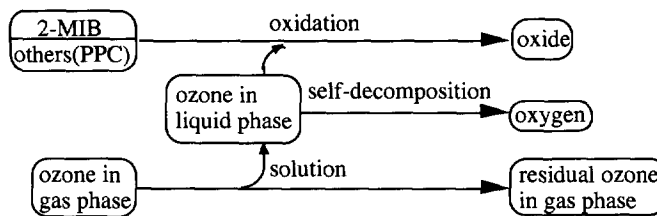


Fig 1. Assumed reaction scheme

Table 1. Rate equations of each reaction

reaction	differential equations
solution	$dCl/dt = KLa \cdot (Cl^* - Cl)$
self-decomposition	$dCl/dt = -Kde \cdot Cl$
oxidation of 2-MIB	$dCs/dt = -R \cdot Kox \cdot Cs \cdot Cl$
	$dCl/dt = -R \cdot Kox \cdot Kr \cdot Cs \cdot Cl$
	$R = 1 + r \cdot Cs2$
oxidation of the Potassium Permanganate Consumed	$dCs2/dt = -Kox2 \cdot Cs2 \cdot Cl$
	$dCl/dt = -Kox2 \cdot Kr2 \cdot Cs2 \cdot Cl$

Cl : concentration of ozone in liquid phase Cg : concentration of ozone in gas phase

Cs : concentration of 2-MIB Cs2 : the Potassium Permanganate Consumed

Cl* : equilibrium concentration of ozone Kde : rate constant of self-decomposition

KL : liquid mass-transfer constant a : interfacial area Kr : ozone consumption by a unit of 2-MIB

KLa : overall volumetric mass transfer coefficient Kox : decomposition rate constant of 2-MIB

Kox2 : decomposition rate constant of the Potassium Permanganate Consumed

Kr2 : ozone consumption by a unit of Potassium Permanganate Consumed R : relative rate constant of 2-MIB

r : inclination of relative rate constant of 2-MIB with the Potassium Permanganate Consumed

It has been reported that oxidation of 2-MIB is promoted or inhibited by co-existing substances (Morioka et al., 1991a,b). For example, humic substances are promoters, while carbonate and chlorine ions are inhibitors. Therefore, a promotive and a inhibitive reaction for the oxidation of 2-MIB are also considered. Figs.2 and .3 show experimental data (Morioka et al., 1991a,b) on the promotive and inhibitive reactions of these substances, where the relative rate constant R is defined by eq.(1).

$$R = \frac{\text{The decomposition rate constant of 2-MIB with co-existing substances}}{\text{The decomposition rate constant of 2-MIB without co-existing substances}} \quad (1)$$

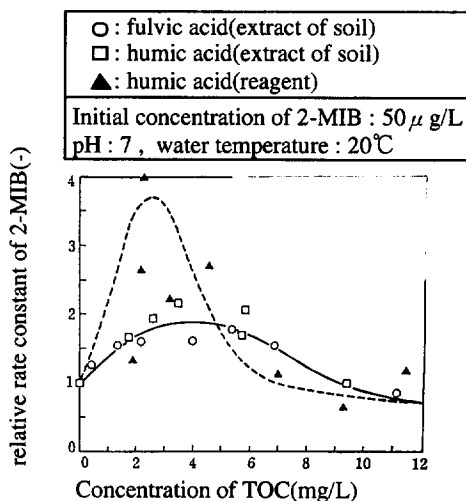


Fig 2. Promotive reaction by humic substances (Morioka et al., 1991b)

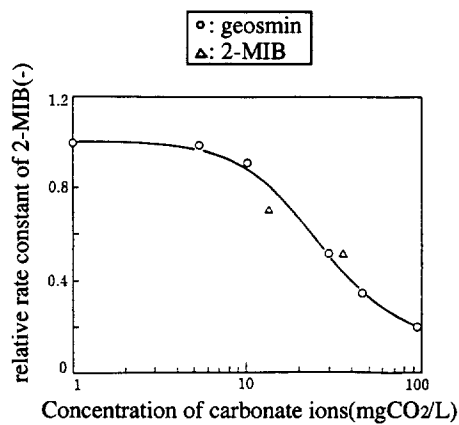


Fig 3. Inhibitive reaction by carbonate ions (Morioka et al., 1991a)

Making a model for this relationship is not easy, for the following reasons;

- (1) R is not linear to the concentration of co-existing substances.
- (2) The rate of promotion is very different according to origin or components of the humic substances.
- (3) In raw water, these substances, promoters and the inhibitors, are co-existing, but their mutual effects have not been reported.

For these reasons, a simplification of the reactions is needed. Four assumptions are introduced.

- (1) PPC is an index of co-existing substances.
- (2) When the concentration of PPC is zero, there is no promotive or inhibitive reaction ($R = 0$).
- (3) The relation between the concentration of PPC and R is linear. The parameter r represents the increasing rate of R to the concentration of PPC.
- (4) A value of r is determined by experimental data, but the value is not constant, because of changing water qualities.

$$R = 1 + r \cdot (\text{Conc. of PPC}) \quad (2)$$

Fig. 4 illustrates the basic idea of this model. Parameters in the model equations, except for the four parameters shown below, are calculated by the experimental equations in Table 2.

- (1) Multiplication of mean bubble diameter and rising velocity of mean bubble (dBVB).
- (2) Decomposition rate constant of PPC (K_{ox2})
- (3) Ozone consumption by a unit amount of PPC (K_{r2})
- (4) Increasing rate of relative rate constant of 2-MIB with PPC (r)

dBVB is a parameter which is closely related to the design of the ozone contactor and diffuser, and K_{ox2} , K_{r2} , and r are parameters related to the water qualities. Therefore, dBVB differs for the design and K_{ox2} , K_{r2} , and r differ for the raw water qualities.

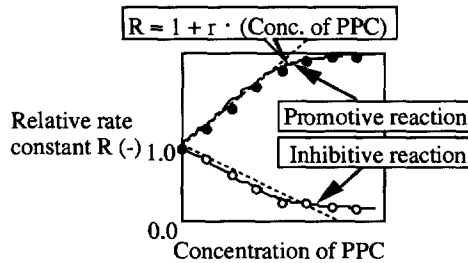


Fig. 4. Basic idea of promotion and inhibition model

Table 2. Experimental equations to fix the value of parameters

parameter	experimental equation	reference
liquid mass-transfer constant	$K_L = (0.038 \cdot T + 1.22) \cdot 10^{-4}$	Muraki, 1970
interfacial area	$a = \frac{1}{V} \cdot \frac{6}{dB \cdot VB} \cdot Q_g \cdot H^{0.77}$	Eckenfelder et al., 1965
partition coefficient	$S = 0.604 \cdot \frac{1 + \frac{T}{273}}{1 + 0.063 \cdot T}$	Muraki, 1970
rate constant of self-decomposition	$K_{de} = 7.41 \cdot 10^9 \cdot \exp(-13.4 \cdot \frac{10^3}{R \cdot T}) [\text{OH}]^{0.5}$	Morioka et al., 1991c
decomposition rate constant of 2-MIB	$K_{ox} = \exp(45.0 + 0.9 \cdot \text{pH}) \cdot \exp(-\frac{11100}{273 + T})$	Moniwa et al., 1991

T: water temperature V: volume of contactor dB: mean bubble diameter VB: rising velocity of mean bubble Q_g: gas flow rate H: water depth R: gas constant [OH]: concentration of OH

As a hydrodynamics model in the contactor, a mixed flow model is applied to the diffuser stage, and a plug flow model to the decay stage. Table 3 shows the mixed flow model. The main ozone contactor mathematical model is constructed by combining these models and assumptions, including four differential equations on concentration of ozone in gas phase, concentration of ozone in liquid phase, concentration of PPC, and concentration of 2-MIB.

TTHMFP is calculated from concentration of PPC. Fig. 5 shows experimental results indicating that the concentration of PPC after ozonation has a correlation with TTHMFP. The correlative equation is:

$$\text{TTHMFP} = 0.010 \cdot (\text{conc. of PPC}) + 0.017 \quad (3)$$

Table 3. Mixed flow model for the diffuser stage

Volume of ozone in gas phase	$V_g \frac{dC_g[\text{out}]}{dt} = Q_g \cdot C_g[\text{in}] - Q_g \cdot C_g[\text{out}] - KLa \cdot V_l \cdot (S \cdot C_g[\text{in}] - Cl[\text{out}])$
Volume of ozone in liquid phase	$V_l \frac{dCl[\text{out}]}{dt} = Q_l \cdot Cl[\text{in}] - Q_l \cdot Cl[\text{out}] + KLa \cdot V_l \cdot (S \cdot C_g[\text{in}] - Cl[\text{out}]) - Kde \cdot V_l \cdot Cl[\text{out}] - R \cdot Kox \cdot Kr \cdot V_l \cdot Cl[\text{out}] \cdot Cs[\text{out}] - Kox2 \cdot Kr2 \cdot V_l \cdot Cl[\text{out}] \cdot Cs2[\text{out}]$
Volume of PPC	$V_l \frac{dCs2[\text{out}]}{dt} = Q_l \cdot Cs2[\text{in}] - Q_l \cdot Cs2[\text{out}] - Kox2 \cdot V_l \cdot Cl[\text{out}] \cdot Cs2[\text{out}]$
Volume of 2-MIB	$V_l \frac{dCs[\text{out}]}{dt} = Q_l \cdot Cs[\text{in}] - Q_l \cdot Cs[\text{out}] - R \cdot Kox \cdot V_l \cdot Cl[\text{out}] \cdot Cs[\text{out}]$
Cl : concentration of ozone in liquid phase Ql : liquid flow rate Cg : concentration of ozone in gas phase Qg : gas flow rate Cs2 : concentration of PPC Vl : volume of liquid phase Cs : concentration of 2-MIB Vg : volume of gas phase [in] : inflow [out] : outflow	

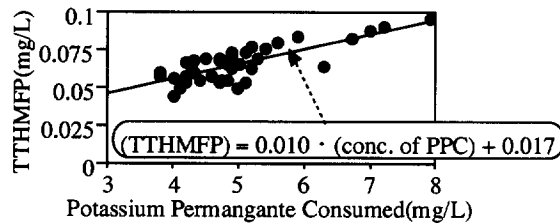


Fig 5. Correlation of Potassium Permanganate Consumed and TTHMFP

OZONE CONTACTOR OF THE PILOT PLANT

The ozone contactor of the pilot plant is shown in Fig.6. It is composed of two diffuser stages and three decay stages. The water inflow is the river water treated by flocculation and sedimentation processes. Water qualities, considered in the ozone contactor mathematical model, are water temperature, pH, concentration of PPC, and concentration of 2-MIB. Fig.7 shows time series data of the main items selected from the liquid flow rate, operation conditions, and water qualities at the inlet of the ozone contactor. Those data were measured about once a week through a year.

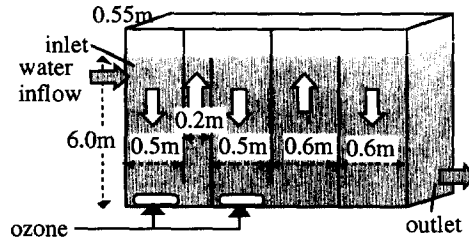


Fig 6. Ozone contactor of the pilot plant

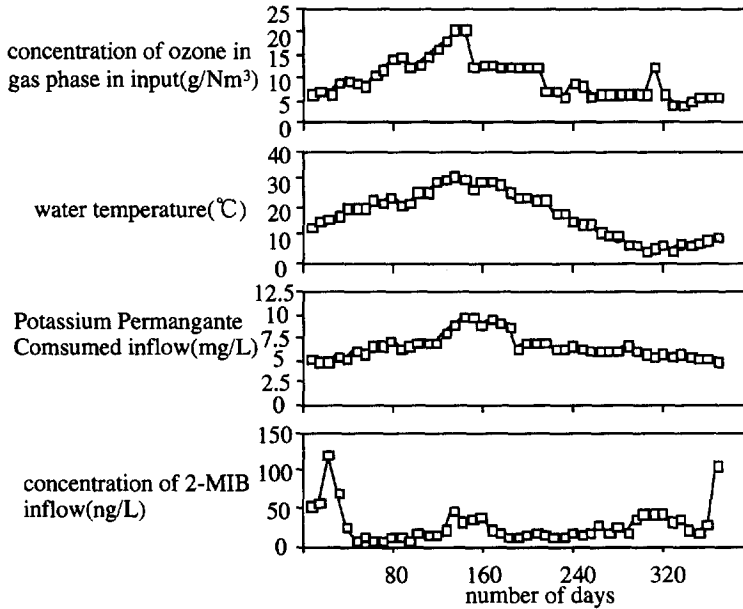


Fig 7. Data of main factors over a year period

RESULTS AND DISCUSSION

In the first step of the simulation, the four parameters shown above unknown were determined from experimental data. The experimental data consists of concentration of residual ozone in the gas phase, concentration of residual ozone in the liquid phase, concentration of residual PPC, and concentration of residual 2-MIB. Three unknown parameters ($dBVB$, $Kox2$, $Kr2$) are related to concentration of residual ozone in the gas phase, concentration of residual ozone in the liquid phase, concentration of residual PPC, and concentration of residual 2-MIB, while the parameter r is related to only the concentration of residual 2-MIB. The determination procedures of each parameter are given below.

- (1) First, three parameters ($dBVB$, $Kox2$, $Kr2$) are determined by the data for concentration of residual ozone in the gas phase, concentration of residual ozone in the liquid phase, and concentration of residual PPC.
- (2) Then, the parameter r is determined by the data for concentration of residual 2-MIB.

The values of the three parameters ($dBVB$, K_{ox2} , Kr_2) are assumed to be constant through the year, and the value of a parameter r is assumed to be different.

From analysis with water qualities such as pH, water temperature, concentration of PPC and some other items, the value of r is found to have a correlation with water temperature. The determined value and correlative equation of each parameter is summarized as follows;

- (1) $dBVB = 0.066(m \cdot m/min)$ (2) $K_{ox2} = 0.02(1/min / mg/L-O_3)$ (3) $Kr_2 = 1.4(g-O_3/g-PPC)$
 (4) $r = 1.926/T - 0.171(1/mg-PPC/L)$ where T is water temperature($^{\circ}C$)

The structural parameter $dBVB$ is thought to be within a reasonable range. By eye observations, dB is within 3-5mm, and VB is about 25cm/s. The multiplication of dB and VB must be within 0.045-0.075 $m \cdot m/min$. Therefore, the determined value, 0.066 $m \cdot m/min$, is thought to be appropriate. The three other parameters (K_{ox2} , Kr_2 , r) must be measured by laboratory experiments.

Results of the simulation using the determined parameters are shown in Fig. 8. The calculated results have good agreement with the experimental data. For an evaluation of the results, a mean error is used. The mean error of the calculated results are as follows;

Concentration of residual ozone in gas phase: 0.28(g/Nm^3) Concentration of residual ozone in liquid phase: 0.07(mg/L) Concentration of residual PPC: 0.27(mg/L) Concentration of residual 2-MIB: 2.59(ng/L) Concentration of residual TTHMFP: 0.0075(mg/L)

It is considered that these error levels are within the allowed range in operating the ozone contactor.

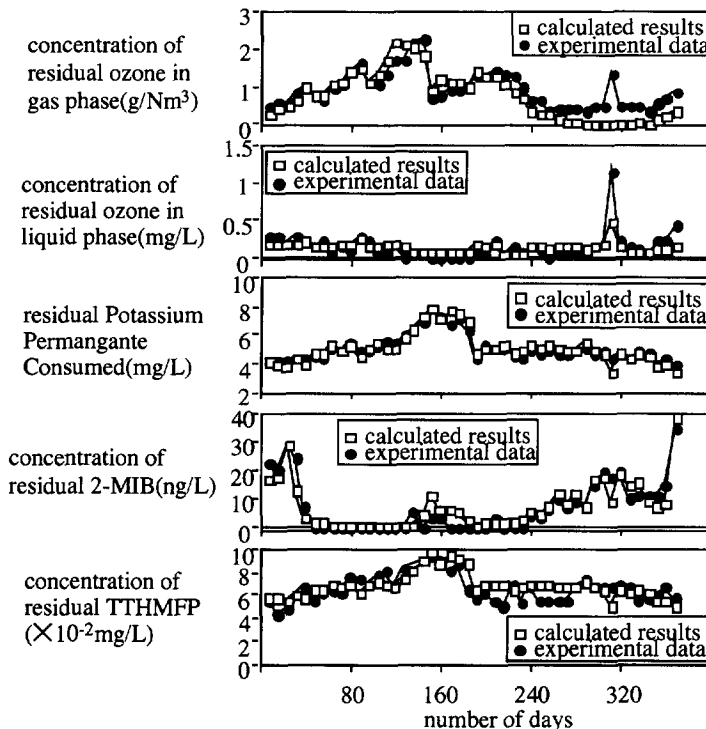


Fig 8. Comparison between calculated results and experimental data

As shown above, even in the cases of fluctuations of water flow rate, water qualities, and operation

conditions, the actual treatment behavior of the pilot plant is simulated through one year's operation with high accuracy by using the ozone contactor mathematical model. This suggests that it would be possible to estimate the efficiency of the ozone contactor, to design a more effective ozone contactor, and to control the ozone dose more appropriately according to the inflow water qualities by further simulation study.

CONCLUSIONS

An ozone contactor mathematical model was developed, which includes the Potassium Permanganate Consumed as an index of the typical ozone consuming substances and by which residual TTHMFP can also be estimated. It was demonstrated that the results of the simulation agreed well with the experimental data of pilot plant data during a one year operation.

This mathematical model includes factors fixed by the design of the ozone contactor such as water depth, cross sectional area, or diameter of mean bubble. Since these structural factors were constant in this study, further study using experimental data of another plant, and a different contactor design should be undertaken to continue verifications of the model.

REFERENCES

- Eckenfelder, Jr. W. & O' Conner, D.J.(1965). Biological Waste Treatment
- Moniwa, T., Okada, M., Motoyama, N., Morioka, T., Hoshikawa, H.(1991). Study on Rate Constant of Odorous Compounds Reaction with Ozone. *Proceedings of 42nd Conference of Japan Waterworks Association* ., 145-147.
- Morioka, T., Motoyama, N., Hoshikawa, H., Okada, M., Moniwa, T.(1991). Effects of Dissolved Inorganic and Organic Substances in Raw Water on the Ozonation of the Musty Odor Substances. *J. Japan Waterworks Association* ., **676**, 16-22.
- Morioka, T., Motoyama, N., Hoshikawa, H., Okada, M., Moniwa, T.(1991). Promotive Effect of Humic Substances on the Decomposition of Musty Odor Substances by Ozonation. *J. Japan Waterworks Association* ., **681**, 21-25.
- Morioka, T., Motoyama, N., Hoshikawa, H., Okada, M., Moniwa, T.(1991). Ozone Absorption Model for Horizontal Flow Contactor. *J. Japan Waterworks Association* ., **682**, 7-17.
- Muraki, Y.(1970). Absorption of ozone in water. *J. Japan Waterworks Association* ., **434**, 30-38.