Bromate Formation and its Control in Advanced Water Treatment System

高度浄水処理における臭素酸の生成と制御

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1 Introduction

We have many experiences of musty odor in tap water caused by microbes of lakes and rivers in Japan. As a measure for these cases, some waterworks have introduced advanced water treatment systems composed of ozone and granular activated carbon. The Tokyo waterworks has also installed an advanced treatment system of ozonation and biological activated carbon treatment in the plants of Tone River system one after another, whose water is often affected by musty odor.

But during the ozonation, bromate, which is detected a little in raw water, is formed from bromide ion by way of hypobromite. In April of 2004, bromate was included in Japanese drinking water quality standard. The value is 0.01 mg/L. Bromate needs to be reduced in case of high concentration of bromide ion in raw water.

This report shows the effectiveness of advanced oxidation process (AOP) for reducing bromate formed by ozonation in case of high bromide concentration of raw water and the result of a bromate formation control study in Misato purification plant, which has ozonation treatment system.

2 Occurrence of musty odor and countermeasures in Japan

In recent years, while the number of waterworks, which had experiences of musty odor in raw water, has stopped increasing, the number of supplied people suffering from the musty odor and taste has been decreasing dramatically (Fig. 1).

The decrease is considered to be attributed to installation of advanced water treatment systems such as ozonation-BAC filtration in the Metropolitan purification plant that has much supplied population. And nine million m3/day of ozonation facility is in operation from 2000.

In Tokyo, musty odor and taste has occurred in waters of the Tone River System. The Edo River, the branch of the Tone, has some inflowing small rivers. Since 1970's, these rivers have been seriously contaminated by domestic wastewater and bred many musty odor-producing microbes. The Kanamachi purification plant, which takes from the Edo River, tried to remove it by powdered activated carbon, but couldn't enough.

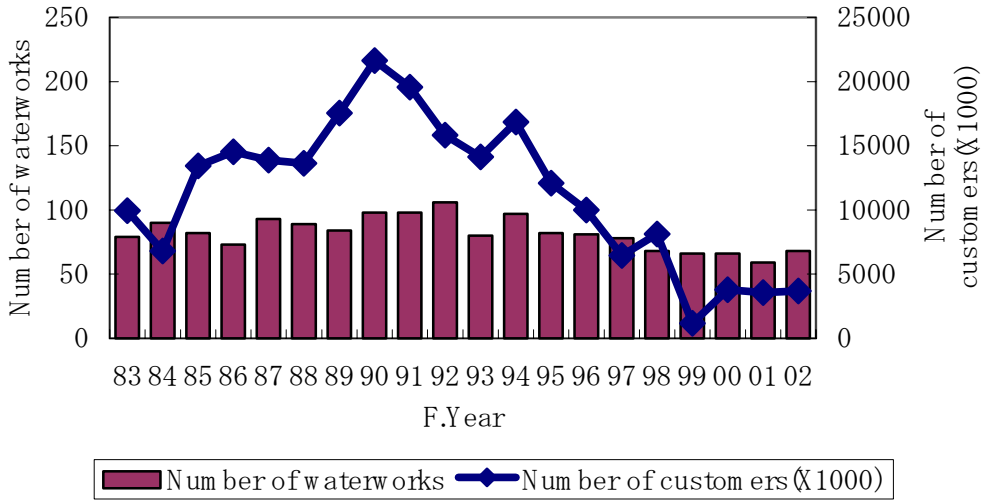

Fig.1 Trend of the number of waterworks and customers suffering from odor of tap water

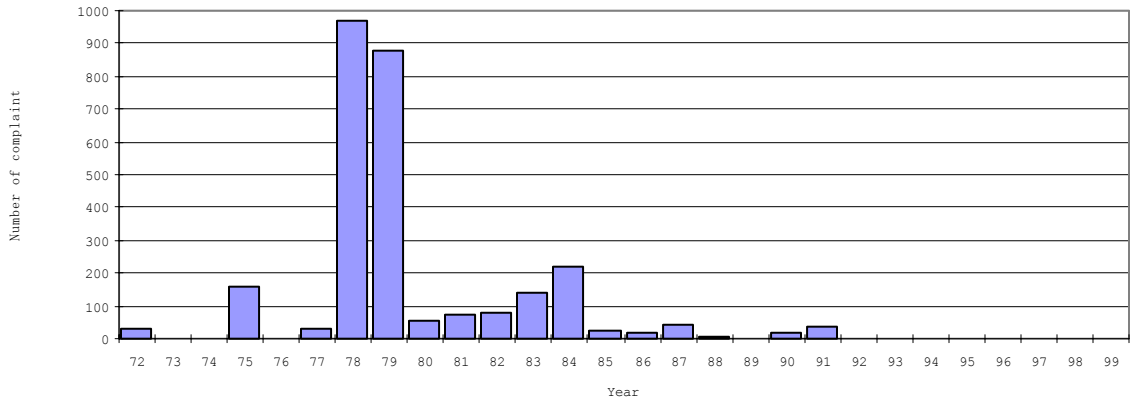

Fig. 2 Trend of the number of complaints in Kanamachi plant

The Tokyo waterworks requested the government and relevant jurisdiction to improve water sources such as promotion of constructing sewerage system. But as it would have taken much time, we installed the advanced treatment system with ozonation and biological activated carbon expecting more effective and stable treatment in 1992.

Table 1 shows the effect of treatment on each subject.

Since installing the advanced treatment system, no complaint about odor and taste has been received (Fig. 2).

In order to remove trihalomethane precursors as well as musty odor, the Tokyo waterworks will sequentially install the advanced water treatment system in purification plants taken from The Tone River.

Table 1 Removal efficiency at each stage of treatment

(%)

	Coagulation sedimentation	Ozone	BAC	Total
2-MIB	20	70	10	100
MBAS	10	35	35	80
NH_3-N	10	0	90	100
THM-FP	30	10	20	60

3 Bromate formation by ozonation and its control

In Japan, bromide concentrations in raw waters are usually less than 0.05 mg/L and if the residual ozone concentration is controlled appropriately, bromate formation probably makes no matter. But under the influence of soil, seawater, and industrial wastewater, bromide level in raw waters become high. It is necessary to take some measures in these area. If using sodium hypochlorite for disinfection, addition from the disinfectant is also considered.

In Tokyo, we can usually satisfy a bromate standard of 0.01 mg/L by controlling the dissolved ozone concentration. But we studied the effect of reduction in bromate formation by advanced oxidation processes, preparing for high level of bromide in raw water in the future.

4 The study on reduction of bromate formation by advanced oxidation processes

1) Objective and Background

The Tamagawa water treatment plant has been halted treating for drinking water because the raw water got deteriorated. Toward resumption of treatment for drinking water, a large scale of ozonation experimental plant was equipped and various water treatment experiments have been conducted.

We have studied utility of advanced oxidation processes (AOPs) by combination of ozone and another oxidizing agent. This process generates higher reactive OH radicals, which directly oxidize organic substances in water, than ozonation only.

Compared the effects on oxidizing dissolved organic substances using various oxidizing agent, hydrogen peroxide or EDTA or ultraviolet radiation, titanium oxide, hydrogen peroxide was adopted as the oxidizing agent.

Next, we compared process performances of simultaneous treatment method with that of sequential treatment method. The simultaneous treatment method was injecting hydrogen peroxide and ozone simultaneously and sequential treatment method was injecting hydrogen peroxide after ozonation. In reduction of organic substances, there was little difference between the two methods. In contrast, bromate formation was much lower in the simultaneous treatment method. In sequential treatment method, bromate ion was formed before the injection of oxidizing agent because ozone was fed previously. On the other hand in the simultaneous method bromate was formed just a little. It was estimated that the simultaneous method was able to reduce bromate formation by disappearance of dissolved ozone before the formation.

In the raw water taken from lower reaches of the Tama River, bromide ion concentration is very high, as well as organic matter. That is why ozonation for removing organic matter produces much bromate.

On this report, we show results of bromate formation depending on the method of ozone injection adopting hydroxyl peroxide as the oxidizing agent.

2） Experimental plants outline

The water used in this study was sampled after coagulation and sand filtration applied to raw water from downstream of the Tama River. Fig. 3 shows the ozone contacting system outline.

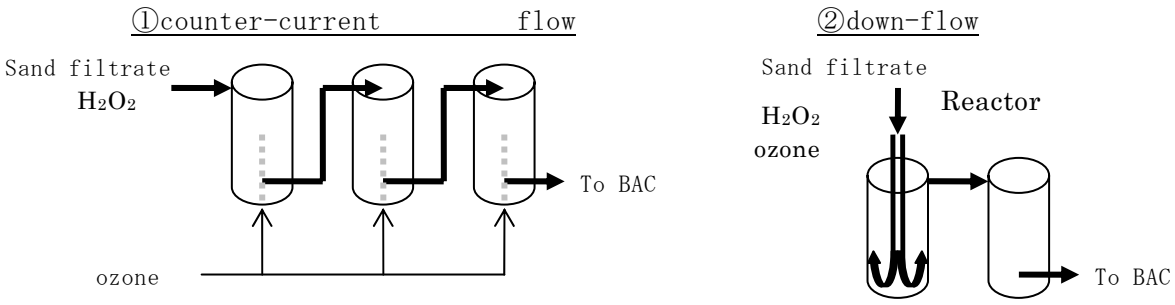

Fig. 3 Ozone contacting system

Table 2 Experimental condition

	Ozonation		AOP	
Injection	C.C	D.F	C.C	D.F
Depth of contactor	6,8,10	6,10	6,8,10	6,10
Water volume (m3/d)	60,80,100	60,80,100	60,80,100	60,80,100
Retention time (min)	4×3	5	4×3	5
Ozone concentration (mg/L)	injection=3 disol.O3=0.2	injection=3 disol.O3=0.2	disol.O3=0.2	disol.O3=0.2
H2O2/O3 ratio	-	-	0.2 0.5 2 5	

C.C: counter current flow injection method

D.F: down-flow injection method

One was a three-stage countercurrent flow system. Ozone gas was continuously diffused at the bottom of each column in countercurrent flow with the water. Hydrogen peroxide was injected at an influent point in the first reactor. The other was a Down-flow injection system. Both of ozone and hydrogen peroxide were simultaneously injected at the top of a water column. Ozonation water, effluent from ozone reactor, was filtered with BAC and sand filter to appreciate the effect of this system totally. Table 2 shows the condition of the experiments and Table 3 shows the water quality of studied water.

Table 3. studied water quality

		Max	Min	Average
Water temp.	℃	28.6	8.0	18.0
PH		7.7	7.0	7.4
DOC	mg/L	2.0	0.6	1.4
Bromide ion	μg/L	260	24	150

3) Result and discussion

Fig. 4 shows the seasonal change of bromate concentration in ozonation comparing down-flow injection with counter-current flow injection. During ozonation, competition occurs between organic substances decomposition and bromate formation for dissolved ozone. Previous works reported that the ozone consumption by decomposition of organic substances preceded bromate formation and the ozone consumption for bromate occurred after the decrease of decomposable organic substances. [1)]

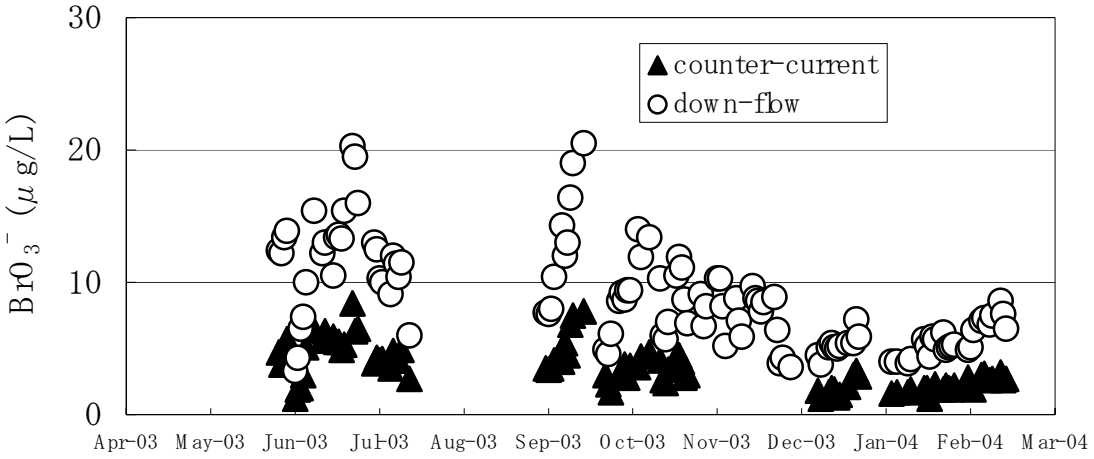

Fig. 4 Seasonal change of bromate concentration in the counter current flow injection and down-flow injection methods

From the result of our experiment, it was estimated that bromate formation was inhibited in the counter-current flow injection method because ozone consumption by organic substances decomposition preceded until the latter half of ozonation times. In contrast, in the down flow injection method, it was estimated that bromate formation by high concentration of ozone occurred from the initial period of reaction because decomposition of organic substances ended in very short time.

Bromate amount produced by ozone consumption on the down-flow injection method is more than by the other method. The organic substances decomposition abilities of the two injection methods were nearly same. As the down-flow injection treats substances in short time, the self-decomposition rate of ozone is relatively small in it. This leads to much consumption of ozone for bromate formation.

Multi-linear regression was performed in order to select some parameters controlling the bromate formation. The bromate formation is considered to depend on water temperature, pH, ammonium-nitrogen, bromide level, organic substances, and Ct value. From the characteristic of studied water (the Tama River), parameters were

limited to water temperature, bromide ion, and Ct value. The result showed that the strongest parameter was raw water temperature, bromide concentration in raw water and Ct value were followed (Table 4).

Table 4 multi-linear regression analysis on bromate formation

Contact method		counter current injection		down-flow injection	
O3 control method		Dissolved O3 conc.	O3 injection rate	Dissolved O3 conc.	O3 injection rate
Multiple correlation coefficient		0.89	0.74	0.95	0.72
Regression coefficient	Water temp.	0.74	0.88	1.1	0.92
	Bromide	0.49	0.63	0.67	0.91
	Ct	0.23	0.55	0.44	0.33

On the other hand, in the advanced oxidation process adding hydrogen peroxide, bromate production was suppressed remarkably, as the H_2O_2/O_3 ratio was raised. In the down flow method, bromate concentration was less than water quality standard (10 μ g/L) at the injected H_2O_2/O_3 ratio over 2 (Fig. 5). The reduction rate of trihalomethane forming potential value with AOP was smaller than that with ozonation only.

And DOC reduction rate did not change. We estimated that strong oxidation by AOP proceeded decomposition of persistent organic substances and produced trihalomethane precursor which was smaller molecule and highly reactive to chlorine. We plan to research dynamics of organic substances with molecular weight fractionation etc (Fig. 6).

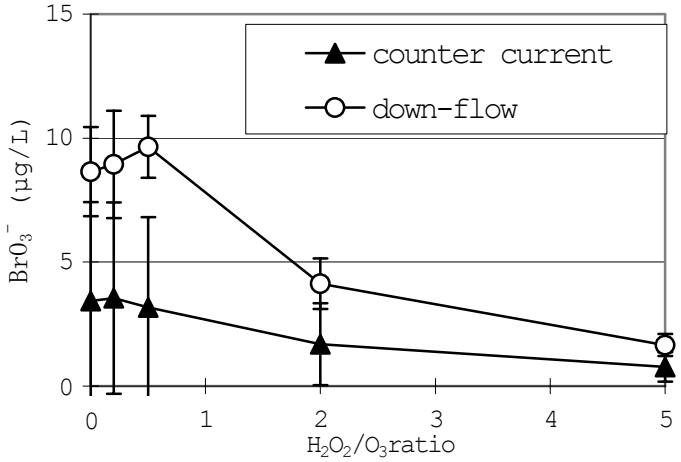

Fig.5 H_2O_2/O_3 ratio and amount of $BrO3^-$
(controlled O3 concentration)

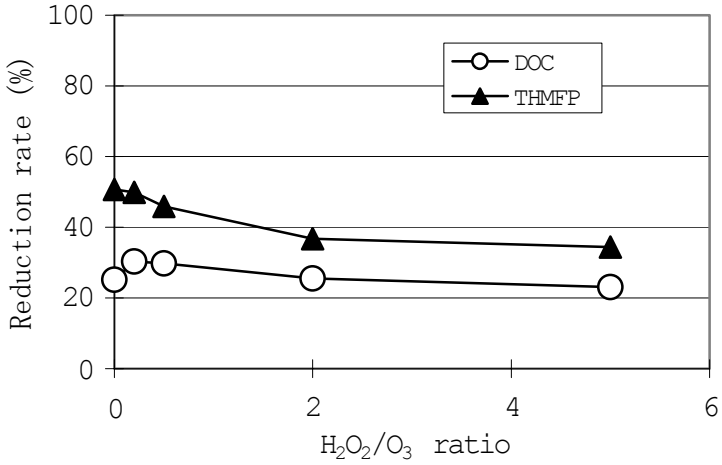

Fig. 6 Relation between H_2O_2/O_3
ratio and DOC, THMFP reduction rate

5 Survey on bromate concentration and measures to reduce at the Misato purification plant

The Misato purification plant has introduced advanced water treatment system and on-site producing facility of sodium hypochlorite. As bromate concentration of treated water sometimes rises to a higher level in summer, many researches on the reduction

have been conducted. This section is a report on the survey of bromate concentration in the water of each purification process and a method of controlling bromate formation.

The Misato purification plant is at Misato city in Saitama Prefecture, which is 20 km away from Tokyo. The plant is the newest plant in the Tokyo waterworks. The operation started in 1985. The total capacity of water purification facility is 1,100,000m^3/day. It takes raw water from the Edo River and supplies treated water about 1.8 million in Tokyo. Since 1999, advanced water treatment facilities, combined with ozonation and biological activated carbon, have been operated. At present half volume of the capacity, 550,000 m^3/day is treated in the system. Ozone injection method is three step counter-flow type.

The result of the survey shows bromate was higher in summer than in winter. In the raw water bromate was rarely detected and the concentration was about 0.5 μg／L. Lower bromate concentration in a conventional treatment process in 2003 than 2002 was observed. The reason was considered to be the change of raw material to the salt that had bromide fewer.

Table 5 bromate concentration at each stage of the treatment process

	Bromate (μg/L)		
	Maximum	Minimum	Average
Raw water	0.7	DI	DI
Settled water	1.1	DI	0.7
Ozone contactor 1st	0.8	0.7	0.8
Ozone contactor 2nd	2.1	0.5	1.0
Ozone contactor 3rd	6.3	0.5	1.8
Reactor	6.4	0.8	2.0
BAC outlet	6.7	1.0	2.1
Filtrate (conventional)	10.7	0.7	2.3
Filtrate (advanced water treatment)	12.1	0.6	3.2
Examination from Jun. 2002 to Feb. 2004			
DI: limit of determination			

During the ozonation process bromate concentration gradually increased as flowing through each reactor (Table 5). Bromate formation reaction was estimated to come to equilibrium before reaching the third reactor. Bromate concentration in the ozonated water and BAC filtered water were the same levels. This meant BAC treatment couldn't remove bromate formed by ozonation.

Next, bromate concentrations were measured in water at the output of contacting reactor as the target value of dissolved ozone changed. Table 6 presents the results.

The results confirmed bromate formation by ozonation was proportional to the dissolved ozone concentration in water at the output of ozone reactor. And it was considered to depend on pH, water temperature, organic matters, ammonium-nitrogen. And then previous various bromate formation models were considered.

Table 6 Bromate concentration of ozonated water

Bromate (μg/L)					
Date	Target0.04mg/L	Date	Target0.09mg/L	Date	Target0.18mg/L
7/9	Dl	7/23	1.4	7/16	1.2
8/13	0.7	8/27	3.6	8/20	3.1
9/3	1.6	9/17	6.4	9/10	12.1
10/29	1.3	11/19	1.7	11/5	7.0
11/12	1.4	12/16	2.1	11/26	2.9
dl: limit of determination (less than 0.5 μ g /L)					

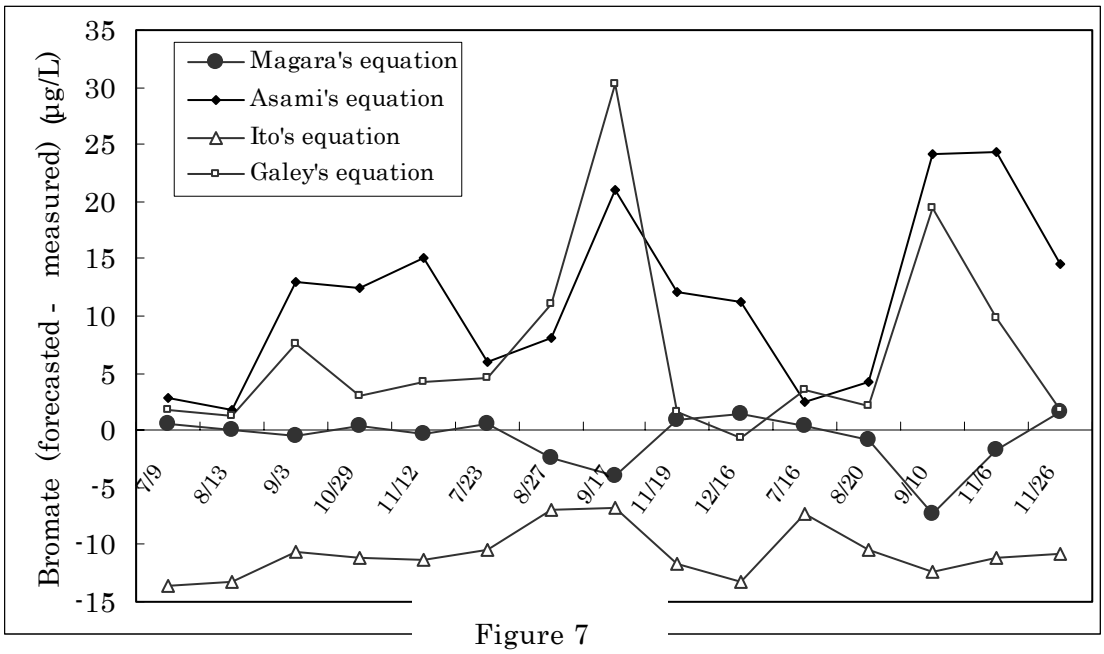

Figure 7

Figure 7 shows the difference between the measured values and the forecasted values of bromate formation. This shows that bromate formation on the Misato purification plant was satisfied the forecast by Magara *et al.* [2] But at the period of high water temperature, the model was sometimes unsatisfied.

Therefore we are now developing bromate formation prediction model taking water temperature into account as an essential parameter. On the Misato purification plant, by controlling pH and the target value of dissolved ozone concentration at the output of ozone reactor, bromate formation can be controlled under 50% of bromate standard 10μg/L.

Table 5 shows that in a conventional treatment process, bromate increases in the sand filtrate added from on-site producing sodium hypochlorite as a disinfectant. And lower bromate concentration in 2003 than in2002 was observed. The reason is considered to be the change of raw material to the salt that has bromide fewer.

6 conclusion

In the purification plant that has advanced water treatment facilities, severe control of injection rate of ozone and pH control are needed to reduce the bromate concentration formed by ozonation. In certain circumstances, advanced oxidation process should be taken into consideration. On the other hand for the reduction of bromate in sodium hypochlorite, the bureau changed the material salt of the disinfectant to that of low bromide concentration.

Moreover, the Tokyo waterworks requests the government to reduce bromide ion in river water because bromate formation depends on bromide concentrations in raw water. And data of bromide concentration in river water are necessary to appreciate the actual circumstances. With these measures the Tokyo waterworks aims to meet the drinking water standard.

In these days the run of sales on water purifiers for homes and bottled waters seems to show the tendency of customers that they would not want to drink tap water. But according to a survey of customers, they hope improvement of the quality of tap water.

To fulfill the expectation of the customers the Tokyo waterworks is trying to improve the water quality of all parts that is from sources to taps. We consider that sense of security and confidence of customers on water quality is the most important matter. We are going to improve the water quality and publicize now.

References

1) Asami M, Aizawa T, Magara Y., J.Japan Society on Water Environment 19(11), 930-936, (1996)

2) Asami M, Aizawa T. J.Health Science, 45, 344-355, (1996)

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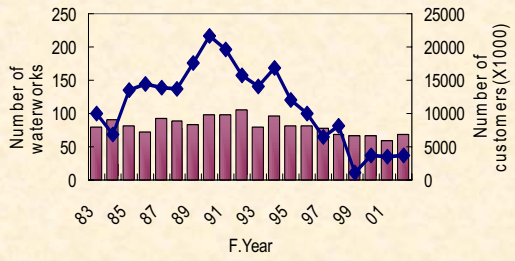
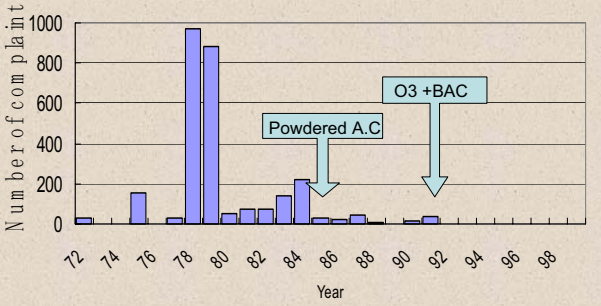
Contents

Influence of Odor



Presented by Ministry of health, labour and welfare

Number of Complaints in Kanamachi P.P.area



At the Tasting stand of Advanced Treated Water

Kanamachi purification plant

Bromate formation in plants

Bromide

Industrial wastewater

Soil

Seawater

Contaminant of sodium hypochlorite

Measures

<0.01mg/L

Control of dissolved O3

Advanced oxidation process

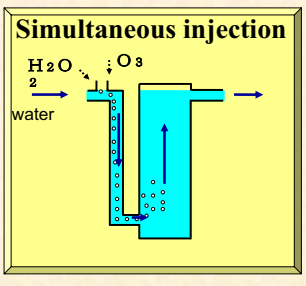
Change of the salt

Advanced Oxidation Process Experiment

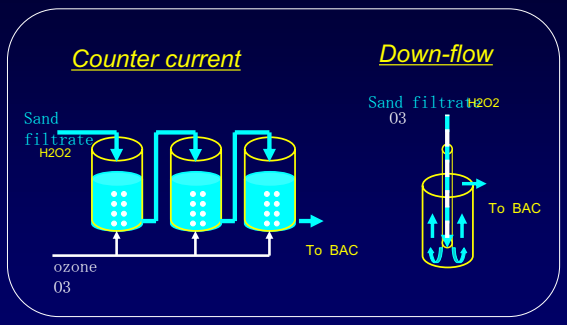
Advanced Oxidation Process study in Tokyo

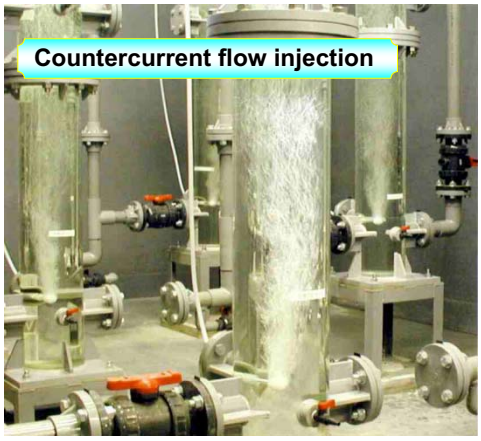
Suitable Oxidizing Agent

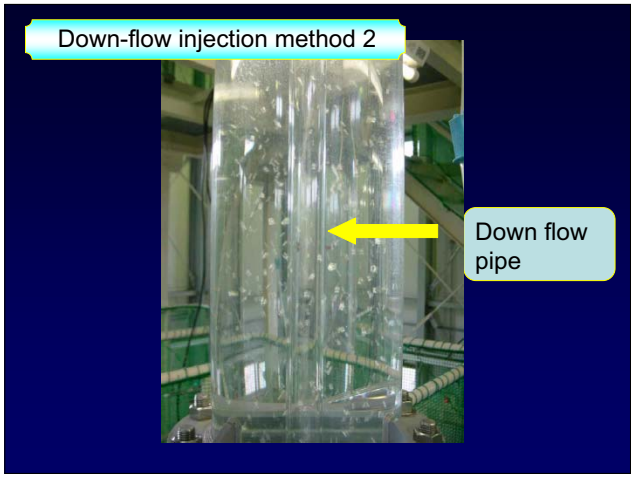
H_2O_2 UV TiO_2 EDTA



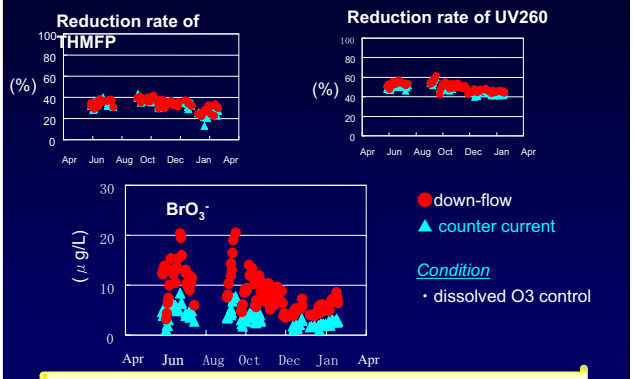
Does Contact method change amount of BrO_3^- ?





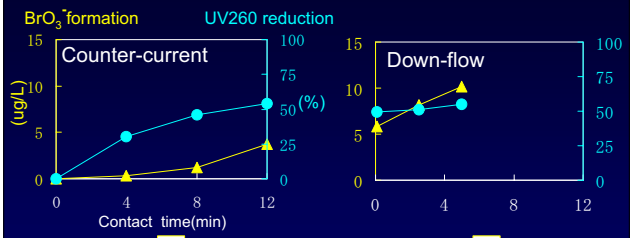


Injection method and Treated water quality



Amount of BrO_3^- Down-flow >Countercurrent

BrO_3^- formation

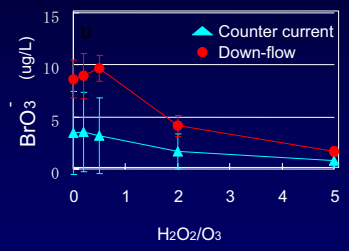


Org. = decomposed gradually
BrO_3^- = from the late stage

Org. = decomposed instantl
BrO_3^- = from the initial stage

experiment condition
・dissolved ozone

BrO_3^- reduction by H_2O_2



Expt.cond.
・dis O3 controlled

Multiple -linear regression

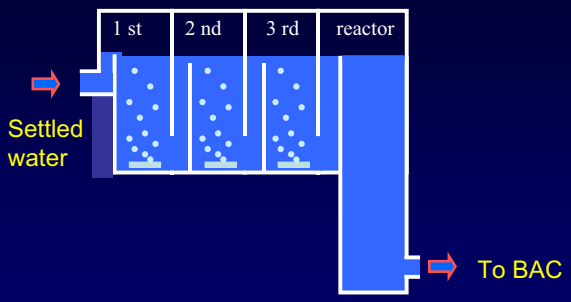
03 flow		Counter current		Down-flow	
03 control		Constant dissol.O3	Constant injection	Constant dissol.O3	Constant injection
Multiple correlation coefficient		0.89	0.74	0.95	0.72
Regression coefficient	W.T.	0.74	0.88	1.1	0.92
	Br^-	0.49	0.63	0.67	0.91
	Ct	0.23	0.55	0.44	0.33

BrO_3^- formation parameters
WT > Br^- > Ct

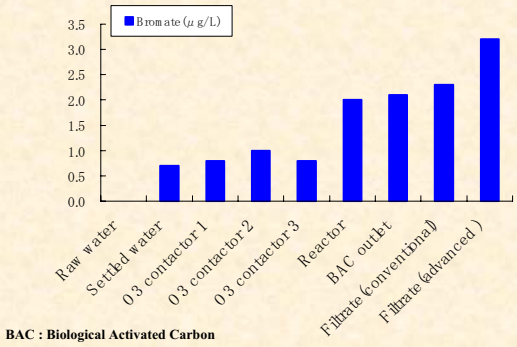
Misato purification plant

O3 & on-site NaOCl

O3 Reactor in Misato plant

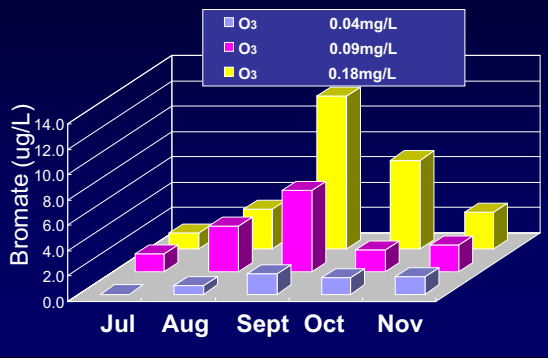


Bromate in Each Treatment Process (MISATO)



BAC : Biological Activated Carbon

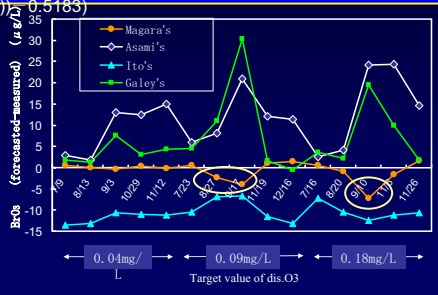
O3 conc. and Bromate formation



Bromate formation models

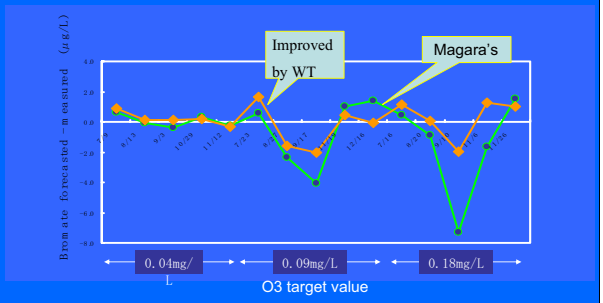
Magara's

【BrO_3^-】
=10＾(0.6354×log(【Br^-】【dis.O_3】【TIME】(【pH】－6.91))－0.5183)



Improvement of the formula

forecasted and measured



Countermeasure for Bromate

- Severe control of O3 injection rate, pH
- Advanced Oxidation Process
- Change of material salt for disinfectant
- Request of reducing Br^- in river waters

Improvement of tap water quality

Thank You Very Much for Your Attention