

# **Study on By-Products of Ozonation during Ammonia Removal under the Existence of Bromide: Factors Affecting Formation and Removal of the By-Products**

Min Yang, Kazuya Uesugi, and Haruki Myoga  
Central Research Laboratories, Organo Corporation, Toda City, Japan

Received for Review: 20 July 1998  
Accepted for Publication: 22 January 1999

## **Abstract**

Factors affecting the formation of by-products of ozonation during ammonia removal under the existence of bromide were investigated. The presence of reducible N compounds could significantly reduce the formation of bromate and brominated organics; however, it was difficult to completely prevent formation of the by-products. It was therefore concluded that while the method used in this study was an effective process to decompose ammonia, it should be applied to the treatment of wastewaters containing low concentration of TOC. For power plant condensate demineralization wastewater containing TOC of 3 to 4 mg L<sup>-1</sup>, TOX formed during ammonia removal ranged from 0.20 to 0.30 mgBr L<sup>-1</sup>. The only halogenated organic substance of the power plant wastewater detected on GC spectrum was bromoform, whose concentration varied from 0.11 to 0.14 mg L<sup>-1</sup>. Column test results indicated that bromate could almost completely be decomposed to bromide by activated carbon under proper space velocity and pH. Activated carbon was also very effective in adsorption of CHBr<sub>3</sub>: 1 g activated carbon adsorbed ca. 20.3 mg of CHBr<sub>3</sub>.

## **Introduction**

It has been known that ammonia could be decomposed to nitrogen gas by ozonation under the existence of bromide (Haag et al., 1984, Somiya et al., 1995). In this process, Br<sup>-</sup> is rapidly oxidized to HBrO by O<sub>3</sub>, and then the bromine-ammonia breakpoint reactions lead to decomposition of NH<sub>4</sub><sup>+</sup>. Br<sup>-</sup> released by the decomposition of NH<sub>4</sub><sup>+</sup> will be oxidized again by O<sub>3</sub>, and could therefore be utilized repeatedly. Unlike biological denitrification processes which normally include a series of biological reactions in three different reactors, i.e., nitrification tank, denitrification tank, and BOD decomposition tank, and require solid-liquid separation, this process can decompose ammonia in a single ozonation reactor. In order to develop a new ammonia treatment method, we have studied the characteristics of decomposition of NH<sub>4</sub><sup>+</sup> by ozonation under the existence of Br<sup>-</sup> (Yang et al., 1997). It was found that NH<sub>4</sub><sup>+</sup> could be decomposed to N<sub>2</sub> at a reaction rate higher than biological nitrification.

However, it is necessary to evaluate the effects of the possible by-products before this process is applied to NH<sub>4</sub><sup>+</sup> decomposition since the active species, HBrO and O<sub>3</sub> are involved in the reactions. Many studies have recently been carried out on the formation and minimization of disinfection by-products (DBPs) of ozonation of natural water containing Br<sup>-</sup>, and the mechanisms of formation of DBPs have become relatively clear (Luong et al., 1982, Haag et al., 1983, Siddiqui et al., 1993, Glaze et al., 1993, Shukairy et al., 1994). It appears that ozonation of natural waters in the presence of Br<sup>-</sup> invariably leads to the formation of brominated organics and BrO<sub>3</sub><sup>-</sup>. Although the results obtained from ozonation of natural water are very helpful in understanding the formation of ozonation by-products during NH<sub>4</sub><sup>+</sup> decomposition, further study is needed for better understanding the formation, minimization, and removal of the by-products involved in wastewater treatment since both the O<sub>3</sub> dose and Br<sup>-</sup> concentration used for NH<sub>4</sub><sup>+</sup> removal in wastewater treatment would be 2 to 3 orders higher than those involved in disinfection.

In this study, factors affecting the formation of by-products of ozonation during NH<sub>4</sub><sup>+</sup> removal under the existence of Br<sup>-</sup> were investigated. Evaluation of TOX (total organic halide) formation was carried out by using humic acids as model TOC source. The methods for removal of TOX and BrO<sub>3</sub><sup>-</sup> were also investigated by using activated carbon as both an adsorbent and catalyst.

## Material and Methods

### Verifying Formation of Bromate and TOX

Formation of bromate: Synthetic wastewater was prepared by adding  $\text{NH}_4\text{HCO}_3$  ( $\text{NH}_4^+\text{-N}$ ,  $15 \text{ mg L}^{-1}$ ) and  $\text{NaBr}$  ( $\text{Br}^-$ ,  $30 \text{ mg L}^{-1}$ ) into deionized pure water. A polyacrylate container with an effective volume of 1 L was used as the reactor. Ozone was continuously introduced through a recirculation pump at a  $\text{O}_3$  feeding rate of  $21 \text{ mg min}^{-1}$  after synthetic wastewater was filled into the reactor. The reaction pH was kept at 7.0 with a pH controller. Samples were taken at a proper interval, and excessive  $\text{Na}_2\text{SO}_3$  was added into the sample to prevent further reaction.

Formation of TOX: Humic acids were extracted with 1 N  $\text{NaOH}$  solution, and the extract was used as TOC source stock. Synthetic wastewater prepared by dissolving  $(\text{NH}_4)_2\text{SO}_4$  ( $270 \text{ mgN L}^{-1}$ ),  $\text{NaBr}$  ( $90 \text{ mgBr L}^{-1}$ ), and humic acids extract ( $0\text{--}20 \text{ mgTOC L}^{-1}$ ) into deionized water was fed continuously into a polyacrylate column ( $d=18\text{cm}$ , water level= $2.2\text{m}$ ) from the top, and  $\text{O}_3$  gas produced from PSA (pressure swing adsorption)  $\text{O}_2$  was introduced from the bottom through 4 sintered glass filters ( $d=2\text{cm}$ ) at a flow rate of  $4 \text{ L min}^{-1}$ . The  $\text{NH}_4^+\text{-N}$  loading rate and  $\text{Br/N}$  weight ratio were kept at  $1 \text{ kgN m}^{-3}\text{d}^{-1}$  and 0.33, respectively. The pH in the lower part of the reactor was automatically controlled in the range of 6.5 to 7.0, and the  $\text{O}_3$  feeding rate was adjusted manually according to ORP (oxidation-reduction potential) values which were measured by an ORP electrode inserted just over the filters (Yang et al., 1997).

### Activated Carbon Experiment

Two polyacrylate columns ( $d=2.7 \text{ cm}$ ), each packed with 92 g of activated carbon (Diahope 006, Mitsubishi Chemicals Co. Ltd, Japan) was used to remove  $\text{CHBr}_3$  and  $\text{BrO}_3^-$ , respectively. Synthetic wastewaters containing  $\text{CHBr}_3$  and  $\text{BrO}_3^-$ , respectively were fed from the bottom of the columns. The concentration of  $\text{CHBr}_3$  was initially  $142 \text{ mg L}^{-1}$  (average value), and the space velocity (SV) of wastewater was  $11 \text{ h}^{-1}$ . After 500 h, the concentration of  $\text{CHBr}_3$  was increased to  $623 \text{ mg L}^{-1}$  (average value). The effects of SV and pH on the decomposition of  $\text{BrO}_3^-$  were investigated at a  $\text{BrO}_3^-$ -Br concentration of  $5 \text{ mg L}^{-1}$ .

### Analytical Methods

$\text{Br}^-$ ,  $\text{NO}_3^-\text{-N}$ , and  $\text{BrO}_3^-$ -Br were measured on ion-chromatograph (IC-200 or IC-7000, Yokogawa Instruments Co. Ltd., Japan).  $\text{NH}_4^+\text{-N}$  was measured by an ion-selective electrode meter. The oxidizing Br was determined by a thiosulfate-iodide titration with pH adjusted to ca. 4.5 by 50% acetic acid solution. TOC and TOX were measured on a TOC meter (TOC-5000, Shimadzu Co. Ltd., Japan) and a TOX meter (TOX-I0, Mitsubishi Chemicals Co. Ltd., Japan). The identification and determination of brominated organics were conducted on a GC with an ECD detector (G-3000, Hitachi Co. Ltd, Japan).

## Results and Discussion

### Formation of Bromate and Brominated Organics

Fig. 1 shows the variations of  $\text{NH}_4^+\text{-N}$ ,  $\text{BrO}_3^-$ -Br, and  $\text{Br}^-$  during a batch experiment. It was found that  $\text{NH}_4^+\text{-N}$  decreased almost linearly with time and  $\text{Br}^-$  was constant at ca.  $30 \text{ mg L}^{-1}$  until  $\text{NH}_4^+\text{-N}$  was near zero.  $\text{HBrO}$ -Br was reduced to  $\text{Br}^-$  by  $\text{Na}_2\text{SO}_3$  added during sampling, and so the measured  $\text{Br}^-$  was the sum of free  $\text{Br}^-$  and  $\text{HBrO}$ -Br. The constant value of the sum of free  $\text{Br}^-$  and  $\text{HBrO}$ -Br indicated that  $\text{BrO}_3^-$ -Br formation was negligible when there existed  $\text{NH}_4^+\text{-N}$ , which was verified by the measurement of  $\text{BrO}_3^-$ -Br. After 18 min of ozonation,  $\text{NH}_4^+\text{-N}$  decreased to  $0.3 \text{ mg L}^{-1}$  and  $\text{BrO}_3^-$ -Br increased to a detectable level ( $0.11 \text{ mg L}^{-1}$ ). It was possible that the measured  $\text{NH}_4^+\text{-N}$  concentration was actually the sum of N concentrations of  $\text{NH}_4^+$  and bromamines, i.e., the sum of reducible N compounds, since the rate constant of reaction between  $\text{HBrO}$  and  $\text{NH}_3$  was as high as  $8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  (Haag et al., 1984). The fact that  $\text{BrO}_3^-$ -Br had not been detected for the first 14 min indicated that  $\text{BrO}_3^-$ -Br could not be produced by ozonation of bromamines. However, when the measured  $\text{NH}_4^+\text{-N}$  concentration became as low as  $0.3 \text{ mg L}^{-1}$ ,  $\text{HBrO}$ -Br, which

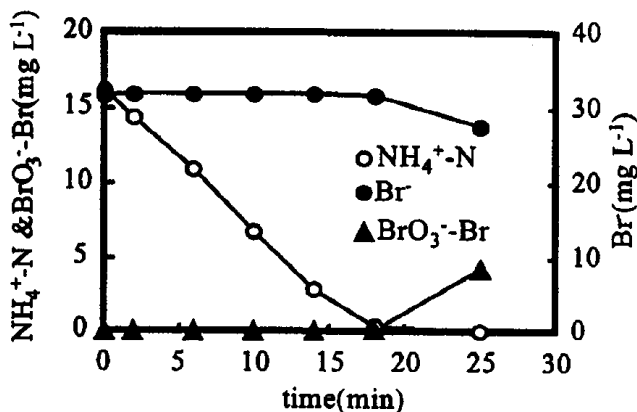


Fig. 1 Variations of  $\text{NH}_4^+\text{-N}$ ,  $\text{BrO}_3^-$ -Br, and  $\text{Br}^-$ .

could be oxidized to  $\text{BrO}_3^-$ -Br by  $\text{O}_3$ , existed as well as the combined Br, i.e., Br in the form of bromamines. That is why  $\text{BrO}_3^-$ -Br formed even under the existence of the reducible N compounds. When the reducible N compounds were completely decomposed, formation of  $\text{BrO}_3^-$ -Br proceeded at a very high reaction rate. From the viewpoint of restraining  $\text{BrO}_3^-$ -Br formation, it is therefore desirable that ozone supply is properly controlled.

In order to investigate the effects of TOC concentration on TOX formation, continuous  $\text{NH}_4^+$  decomposition was carried out at TOC concentrations ranging from 0 to  $20 \text{ mg C L}^{-1}$ . The results are shown in Fig. 2. It was found that TOX formation increased with the increase of TOC concentration, even when the effluent  $\text{NH}_4^+$ -N was kept in the range of 1 to  $10 \text{ mg L}^{-1}$ . The high yields of TOX indicated that bromamines were sufficiently active to attack organics and form brominated organics. The oxidizing Br concentration, which was the sum of free  $\text{HBrO}$ -Br and Br in the form of bromamines, slightly increased from  $32 \text{ mg L}^{-1}$  at TOC of 0 to  $38 \text{ mg L}^{-1}$  at TOC of  $20 \text{ mg L}^{-1}$ . It seemed that with the increase of TOC, higher oxidizing Br concentration was needed to support the reactions of  $\text{NH}_4^+$  decomposition as well as bromination of organics. TOX formation was found to increase significantly when the effluent  $\text{NH}_4^+$ -N concentration was reduced to 0 (Fig. 3). It has been reported (Somiya, et al, 1995) that  $\text{NH}_4^+$  decomposition occurred after the decomposition of organics. The results in this study indicated that the bromination reactions were much more like competitive reactions of  $\text{NH}_4^+$  decomposition. On the other hand,  $0.5$  to  $1.0 \text{ mg L}^{-1}$  of  $\text{BrO}_3^-$ -Br was detected under the existence of effluent  $\text{NH}_4^+$ -N. When the effluent  $\text{NH}_4^+$ -N was reduced to 0, as high as  $10 \text{ mg L}^{-1}$  of  $\text{BrO}_3^-$ -Br was detected. Therefore, keeping the effluent  $\text{NH}_4^+$ -N concentration over 0 is an efficient method to restrain the formation of TOX and  $\text{BrO}_3^-$ -Br. However, since significant TOX formed even at an effluent  $\text{NH}_4^+$ -N concentration of 1 to  $10 \text{ mg N L}^{-1}$ , it should be reasonable to restrict this  $\text{NH}_4^+$ -removal process to the treatment of wastewaters with a low TOC concentration.

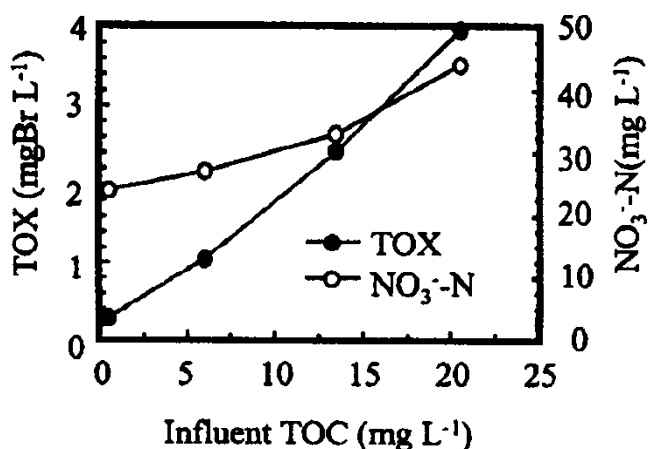


Fig.2 Effect of TOC on formation of TOX and  $\text{NO}_3^-$ -N.

when the effluent  $\text{NH}_4^+$ -N concentration was reduced to 0 (Fig.

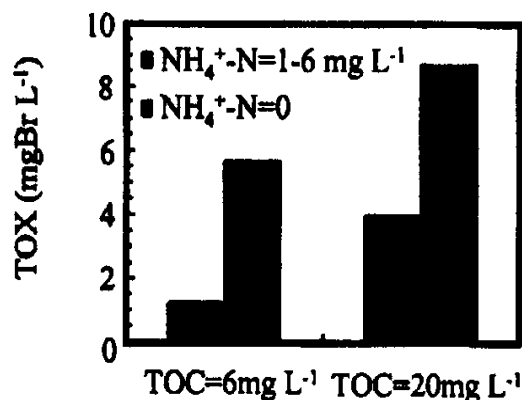


Fig.3 Effects of effluent  $\text{NH}_4^+$ -N on TOX formation.

A pilot plant test was carried out to treat power plant condensate demineralization wastewater which contained TOC of 3 to  $4 \text{ mg L}^{-1}$ .  $\text{NH}_4^+$ -N ratio in raw water was adjusted to ca.  $600 \text{ mg L}^{-1}$ , and the HRT was 16 h. Under the conditions of Br/N ratio of 0.33 and pH of 6.9, the concentration of TOX ranged from 0.20 to  $0.32 \text{ mg Br L}^{-1}$  (see Table I). The only halogenated organic substance from the effluent detected on GC-MS spectrum was  $\text{CHBr}_3$ , whose concentration varied from 0.11 to  $0.14 \text{ mg L}^{-1}$ . Both TOX and  $\text{CHBr}_3$  were reduced to undetectable level after the treated wastewater was passed through a granular activated carbon (GAC) column ( $\text{SV}=0.3 \text{ h}^{-1}$ ).

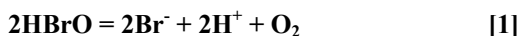
Table I. Results of CD wastewater treatment

	$\text{NH}_4^+$ -N $\text{mg L}^{-1}$	TOC $\text{mg L}^{-1}$	TOX $\text{Mg Br L}^{-1}$	$\text{CHBr}_3$ $\text{mg L}^{-1}$
raw water	600	3-4	ND	ND
reactor effl.	1.5	3-4	0.20-0.32	0.11-0.14
GAC effl.	1.2	3-4	ND	ND

### Activated Carbon Experiment

It has been reported that  $\text{BrO}_3^-$ -Br could be removed by activated carbon (Yamada, 1993, Siddiqui et al., 1995). In this case, reduction of  $\text{BrO}_3^-$ -Br was found to follow adsorption. In this study,  $\text{BrO}_3^-$ -Br produced during decomposition of  $\text{NH}_4^+$  was found to be in the range of ppm order, which was 1 or 2 orders higher than those produced during disinfection. Therefore, it was necessary to remove  $\text{BrO}_3^-$ -Br at a very high removal rate. Although powdered activated carbon (PAC) was able to completely remove  $\text{BrO}_3^-$ -Br, it would require an extremely high PAC dose and produce sludge originated mainly from PAC. In comparison, granular activated carbon (GAC) was favorable because it could be kept in the system without solid-liquid separation processes.

Fig. 4 shows the effects of SV on  $\text{BrO}_3^-$ -Br removal rate. The  $\text{BrO}_3^-$ -Br removal rate increased from 18% to 38% when the SV (space velocity) was lowered from  $17 \text{ h}^{-1}$  to  $5 \text{ h}^{-1}$ . Fig. 5 shows that  $\text{BrO}_3^-$ -Br removal rate and SV were in a log-log relationship. It could be estimated from Fig. 5 that near complete decomposition of  $\text{BrO}_3^-$ -Br would be obtained at a SV lower than  $1 \text{ h}^{-1}$ . The effect of pH was evaluated in Fig. 6. It was found that  $\text{BrO}_3^-$ -Br removal rate increased with lowering pH, which agreed with other studies (Siddiqui, et al., 1995). Almost 100 % removal of  $\text{BrO}_3^-$ -Br was obtained at pH of 3.0. When  $\text{NH}_4^+$  decomposition was controlled at the optimum pH (pH 6.0 to 7.0), the effluent pH was in the range of 3 to 4, perhaps due to the decomposition of  $\text{HBrO}$  out of the reactor [eq. 1]. Therefore, it is relatively easy to obtain complete removal of  $\text{BrO}_3^-$ -Br by keeping a proper SV and pH.



For the removal of  $\text{CHBr}_3$ , activated carbon adsorption is the main option. A column test was conducted to obtain the amounts of  $\text{CHBr}_3$  adsorbed on activated carbon. Fig. 7 shows the results of activated carbon adsorption. It was found that even at a SV as high as  $11 \text{ h}^{-1}$ , effluent  $\text{CHBr}_3$  concentration was kept at less than  $0.01 \text{ mg L}^{-1}$  for ca. 1000 h. From Fig. 7, it was calculated that 1 g activated carbon adsorbed ca. 20.3 mg of  $\text{CHBr}_3$  before the effluent  $\text{CHBr}_3$  reached  $0.05 \text{ mg L}^{-1}$ . That is, if activated carbon was used for the removal of  $\text{CHBr}_3$  produced during treatment of power plant condensate demineralization wastewater, the activated carbon column could be operated at SV  $10 \text{ h}^{-1}$  for ca. 6 month before regeneration was needed.

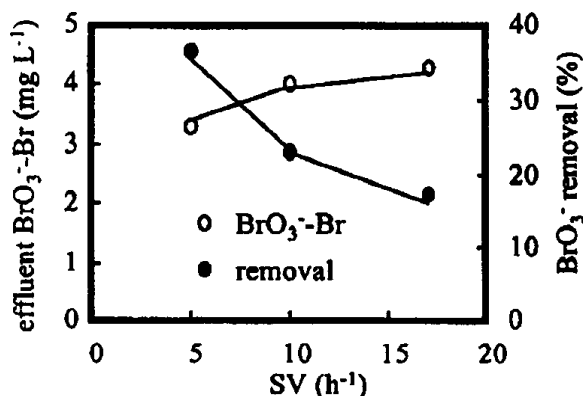


Fig. 4 Effects of SV on  $\text{BrO}_3^-$  decomposition.

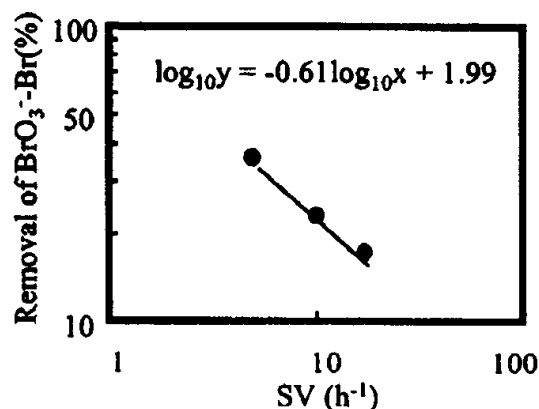


Fig. 5 Relation between  $\text{BrO}_3^-$  removal and SV.

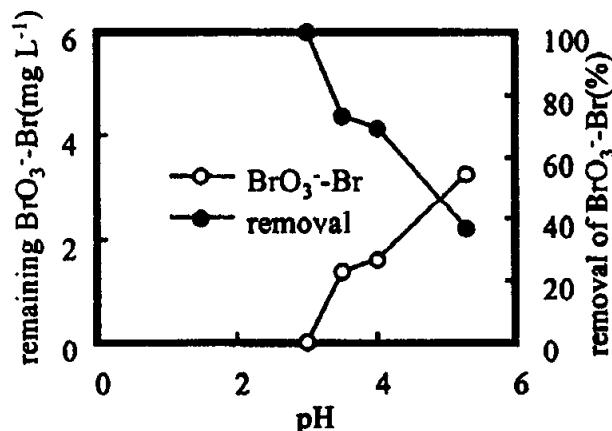


Fig. 6 Effects of pH on  $\text{BrO}_3^-$  removal.

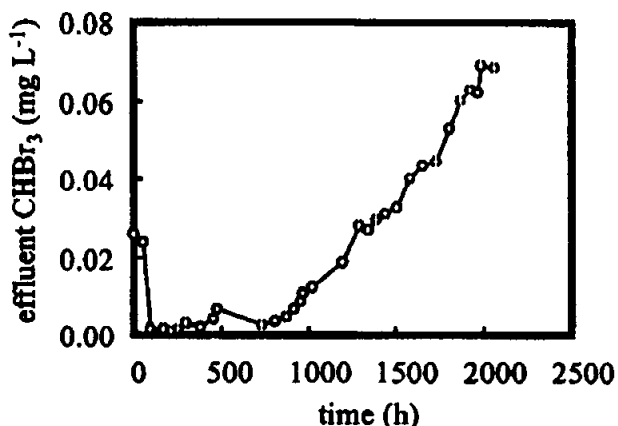


Fig. 7 Results of GAC adsorption test of  $\text{CHBr}_3$ .

## References

- Glaze W. H.; Weinberg H. S. and Cavanaugh J. E., Evaluating the formation of brominated DBPs during ozonation, *J. AWWA*, 85:1,96-103(1993).
- Haag W. R. and Hoigne J., Ozonation of bromide-containing waters: Kinetics of formation of hypobromous acid and bromate, *Environ. Sci. Technol.*, 17: 5, 261- 267(1983).
- Haag W. R., Hoigne J. and Bader H., Improved ammonia oxidation by ozone in the presence of bromide ion, *Water Research*, 18: 9, 1125-1128(1984).
- Luong T. V., Peters C. J. and Perry R., Influence of bromide and ammonia upon the formation of trihalomethanes under water-treatment conditions, *Environ. Sci. Technol.*, 16:8,473-479(1982).
- Shukairy H., Miltner R.J. and Summers R.S., Bromide's effect on DBP formation, Speciation, and Control: Part 1, Ozonation, *J. AWWA*, 86:6,72-87(1994).
- Siddiqui M. S. and Amy L. G., Factors affecting DBP formation during ozone- bromide reactions, *J. AWWA*, 85:1,63-72(1993).
- Siddiqui M. S., Amy L. G. and Zhai W., Removal of bromate after ozonation by activated carbon, *Proceedings of 12th World Congress of IOA*, Lille, France, 1, 263-276 (1995).
- Somiya I., Lee H. D. and Fujinaga A., Ozonation of ammonia nitrogen under the coexistence of organic compounds, *Proceedings of 12th World Congress of IOA*, Line, France, 1,65-73 (1995).
- Yamada H., By-products of ozonation of low bromide waters and reduction of the by- products by activated carbon, *Proceedings of 11th World Congress of IOA*, San Francisco, CA, S-9-58-67 (1993).
- Yang M., Uesugi K., and Myoga H. Study on environmental factors affecting ammonia removal by ozone under the existence of bromide, *J. Japan Society on Water Environment*, 20:7(in press, 1997).

## Key Words

Ozone; Ozonation; Ammonia Removal; By-product Formation; Bromate Formation; Power Plant Demineralization Wastewater; Power Plant Wastewater; Wastewater; Nitrogen Compounds;