Korean J. Chem. Eng., **26**(6), 1601-1607 (2009)
DOI: 10.2478/s11814-009-0343-z

Microwave effect in removal process of NO by electron beam irradiation and quantitative prediction of the removed NO

Dong Hwa Lee*, Soog Dong Kim*, Byung Nam Kim*, Yang Soo Won, and Do Hung Han*,†**

*School of Chemical Engineering and Technology, Yeungnam University
**School of Civil and Environmental Engineering, Yeungnam University,
214-1 Daedong, Gyeongsan, Gyeongbuk 712-749, Korea
(*Received 17 August 2009 • accepted 25 August 2009*)

Abstract−A flow process with electron beam (EB) irradiation carried out the removal of NO in air by adding microwave (MW) to improve the removal efficiency of NO. The EB irradiation combined with MW irradiation was very effective in the range of NO removal efficiency of 70-80% and reduced required doses up to more than 30%, compared to the flow process without MW. On the other hand, MW irradiation was unlikely to affect the NO removal above 90% of removal efficiency. In addition, MW effect appeared definitely in the dose ranges of 8-24 kGy, whereas the effect became minor below 8 kGy and above 24 kGy. This study found that MW irradiation can play an auxiliary role in NO removal with EB irradiation and the effect of MW on the NO removal is based on an intrinsic kinetic to the exclusion of a thermal effect. The concentrations of removed NO could be linearly correlated as $\Delta C=k[NO]_o+k_o$. Where, k was proportional to dose and k_o could be related to $k_o/D^n=aD+b$, giving n value of 0.7 without MW irradiation and 0.4 with MW irradiation, respectively.

Key words: NO Removal, Electron Beam, Microwave, Flow Process, Correlation of Removed NO

INTRODUCTION

Main sources of air pollution are fine particles, hydrocarbons, sulfur dioxide, nitrogen oxides, etc. Of these pollutants, emissions of SO_2 and NO_x are regulated in many countries because the compounds can cause respiratory ailments. Moreover, SO_2 and NO_x in air can generate sulfuric acid and nitric acid, which cause the formation of acid rain that is eventually damaging to soil, surface waters, plants, etc. The acid rain can cause metals to leach from surrounding soils into the underground water system, ultimately destroying the ecosystem.

Over the last few decades, extensive work has been carried out for utilizing radiation technology for environmental remediation. This includes application of radiation technology for simultaneous removal of sulfur dioxide and nitrogen oxides from flue gases, purification of drinking water and waste water purification and hygienization of sewage sludge for use of agriculture.

Many researchers have studied to remove SO_2 and NO_x in flue gas by means of electron beam (EB) radiation technology. This technology, called electron beam dry scrubbing (EBDS), has been developed due to several merits, such as simultaneous removal of SO_2 and NO_x, dry process, and no discharge of any wastes. It has been well known that NO can be converted into nitric acid by oxidizing it with OH radical, which was produced by a water radiolysis with electron beam irradiation, and the nitric acid reacts with ammonia eventually to produce ammonium nitrate (NH_4NO_3) under electron beam irradiation. The ammonium nitrate is a white colored fine particle that can be used as a fertilizer.

†To whom correspondence should be addressed.
E-mail: dhhan@ynu.ac.kr

The EDBS process was first developed by Tokunaga et al. [1,2] in Japan. The EBDS process has been implemented by commercial scale in China [3], Japan [4] and Poland [5]. However, it isn't yet widely applied in industrial plants compared to conventional processes such as wet gas desulfurization for SO_2 removal and selective catalytic reduction for NO_x removal. The main reason is that EBDS requires high energy consumption for NO_x removal, even though the removal SO_2 with EBDS requires low energy consumption [6-8]. Higher energy consumption in EBDS process needs more units of EB accelerators [9]. A large number of accelerators installed may cause a difficult operation of sequent accelerators as well as an increase of total investment cost.

Several researchers have persevered in their efforts to increase removal efficiencies of both NO_x and SO_2. Of those, it was found that the microwave (MW) irradiation system combined with electron beam was effective to increase NO_x removal efficiency remarkably [10-14]. In these studies, the role of microwaves was to generate non-thermal plasmas that were capable of forming several radicals leading to purification of flue gases. Ighigeanu et al. [10,11] found that a simultaneous irradiation of EB and MW could reduce the required dose of EB at 80% removal efficiency of NO_x more than two times compared to EB irradiation, where the initial concentrations of SO_2 and NO_x were 2,000 ppm and 730 ppm, respectively. Also, according to Radoiu et al. [12,13], the simultaneous treatment with EB and MW irradiations was found to reduce the total required dose with around 30% at the concomitant removal of NO_x (around 80%) and SO_2 (above 95%).

This study tried to investigate what the main role of MW is in the removal process of NO with irradiation of EB and how the effect of MW is dependent on both initial concentration of NO and absorbed dose of EB. In addition, the equation to predict the removal

amount of NO was derived by correlating with dose and initial concentration of NO, in simultaneous irradiation process of EB and MW as well as in EB irradiation process.

EXPERIMENTAL

1. Equipment for NO Removal

A high voltage electron beam accelerator with maximum beam energy of 0.7 MeV and a maximum beam current of 35 mA (ELV-0.5, BINP, Russia) was used to produce an accelerated electron beam as an energy source for removal of NO.

Equipment for NO removal in air mixture (Fig. 1) was composed of consecutive several units: a flow control unit of inlet gases (NO, air, water, and ammonia or ammonium hydroxide), temperature control unit for gas flow streams, reactor with simultaneous irradiation system of both EB and microwave (MW), cooling systems in reactor and microwave generator, collector of fine particles with cotton filter, and analyzer of gaseous components. Inlet gas mixture was synthesized by using 1 vol% of NO in nitrogen, air, 1 vol% of NH_3 in nitrogen, and pure water. The gas compositions were controlled by three mass flow controllers (1179A, MKS Instruments INC). Water content in gas mixture was controlled by 1 to 3 vol% with a syringe pump (KASP005/150T, Keun-A Mechatronics), and the water was evaporated in the evaporator that was positioned just at the front of the reactor. The evaporator was controlled at 120 °C by means of an electrical heating device with PID controller. All gaseous mixtures were electrically preheated by passing inside of 3/8" stainless steel tube with electrical heating device and PID controller, and the inside of the tube was filled with glass beads. Main flow rate of inlet gas was 5 liter/min (0.3 m^3/hr). Fine particles of ammonium nitrate produced were collected by means of a cylindrical cotton filter inside filled with a ball of thread.

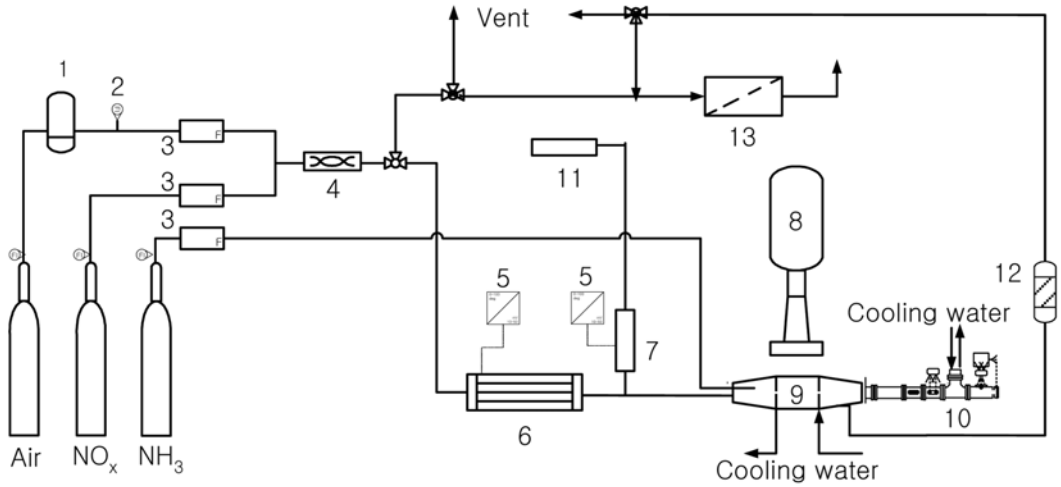

Fig. 1. Schematic diagram of apparatus for NO removal with simultaneous irradiation system of electron beam and microwave.

1. Water absorber
2. Pressure gauge
3. Mass flow controller
4. Gas mixer
5. PID temperature controller
6. Gas preheater
7. Evaporator
8. Electron beam accelerator
9. Reactor
10. Microwave generator
11. Syringe pump
12. Filter
13. Gas analyzer

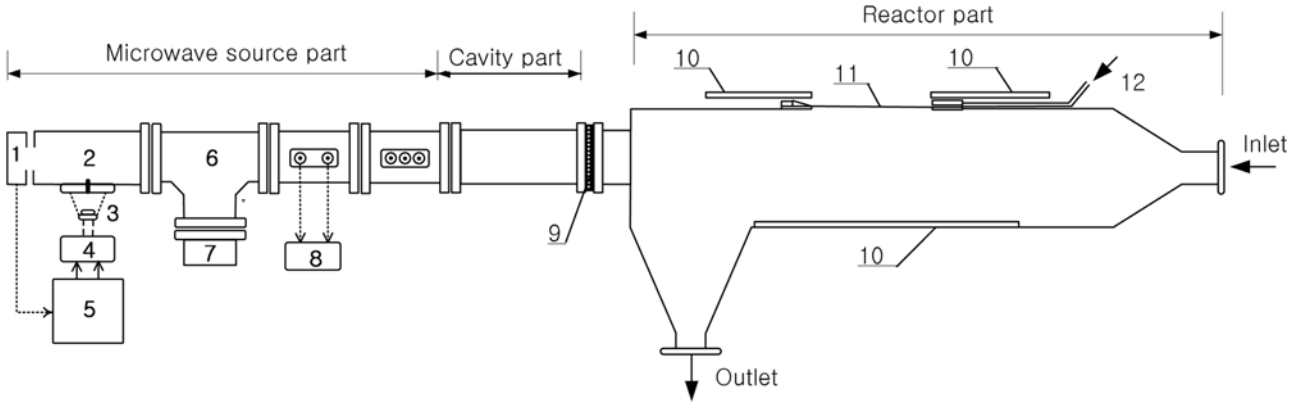

Fig. 2. Drawing of reactor with microwave generation system.

1. AC Detector
2. Wave guide launcher
3. Magnetron
4. Power supplier
5. Controller
6. Circulator
7. Dummy load
8. Power meter
9. Teflon plate
10. Water jacket
11. EB window with titanium foil
12. Air jet stream

Table 1. Specifications of magnetron used for generating microwave

Power rating (W)	700-900
Cathode voltage (V)	4,100
Anode current (mA)	300
Heater voltage (V)	3.3
Current (A)	11
Antenna (mm)	30
Frequency (GHz)	2.465

The EB-absorbed energy of gas mixture, dose, was controlled by changing beam current at a given flow rate of inlet gas. The absorbed dose is proportional to the beam current and inversely proportional to flow rate. Compositions of NO in both influent and effluent streams were monitored by a flue gas analyzing instrument (Ecom®-S^{plus} GA30136, Ecom®-America Ltd.).

2. Microwave Wave Irradiation System

Fig. 2 shows the EB-reaction system combined with microwave generator. Reactor wall was made of stainless steel (SUS 304). Reactor walls were equipped with water jackets to prevent overheating from EB irradiation. Reactor window was covered with 40 μm thick titanium foil, and electron beams irradiated into the reactor through the window. The titanium foil was cooled by a high flow rate of air-jet stream that was supplied from a 10 hp air compressor. The titanium window was surrounded by an aluminum target with water cooling jacket to protect the reactor from overheating by EB irradiation.

Microwaves generated from magnetron were guided into the reactor through a copper waveguide. Teflon plate of 5 mm thickness was positioned at the end of waveguide, to prevent gases from entering into the microwave generator. The waveguide was equipped with a circulator, which was able to suppress possible damage of magnetron due to the reflected microwaves from reactor walls. The circulator with a permanent magnet is capable of turning the reflected microwaves to water absorber (Dummy load) positioned at right-angle for the waveguide. Microwave power was controlled by changing the input voltage of magnetron of 175 to 210 volts. The magnetron could not generate microwave radiation below 175 volts. Table 1 shows the features of the microwave generator.

RESULTS AND DISCUSSION

1. Effect of Microwave on NO Removal

Fig. 3 shows that the microwave irradiation could have a synergistic effect on NO removal in combination with electron beam irradiation. Where, NH_3 was added by a stoichiometric amount based on the initial molar concentration of NO ($[NH_3]_o/[NO]_o=1$), and the water was added by 1 vol% in total flow rate. Additional irradiation of microwave could considerably accelerate the removal efficiency of NO regardless of inlet concentrations of NO: 8 kGy of absorbed energy (dose) without microwave irradiation gave 77%, 70%, and 63% of removal efficiencies for 300 ppm, 600 ppm, and 900 ppm of initial concentration of NO, respectively, whereas the removal efficiencies at the same dose with 210 volts of input microwave were 84%, 77%, and 73% for the corresponding NO concentrations, respectively.

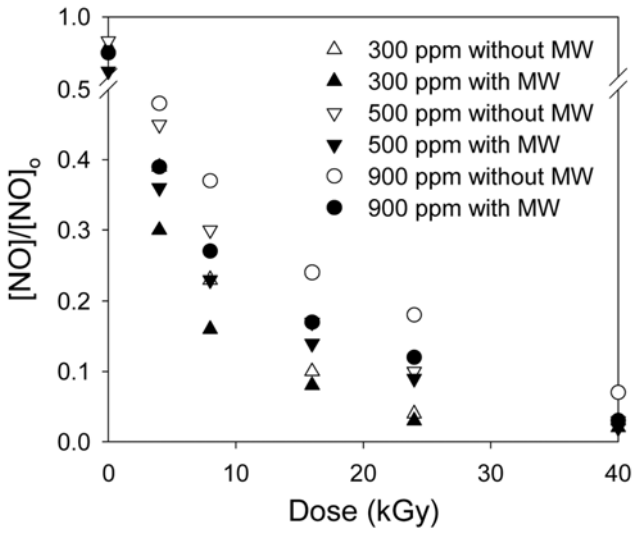

Fig. 3. Effect of microwave on NO removal under electron beam irradiation ($[NH_3]_o/[NO]_o=1$; water=1%; input voltage of microwave=210 V; gas flow rate=5 liter/min, reaction temp. =70 °C).

In Table 2, the required doses at target removal efficiencies were estimated by interpolating the experimental data in Fig. 3. Since the removal rate of NO (F) is inversely proportion to the dose, the percent removal rate (ΔF) is correlated with the dose as in the following equation:

$$F=(F_{with\ MW}-F_{without\ MW})/F_{without\ MW}\times 100$$
$$=(1/D_{with\ MW}-1/D_{without\ MW})/1/D_{without\ MW}\times 100$$
$$=(D_{without\ MW}-D_{with\ MW})/D_{with\ MW}\times 100$$

For example, 80% of removal efficiency at 300 ppm NO required 9.8 kGy without microwave irradiation and 6.7 kGy with microwave irradiation. Therefore, microwave irradiation could set to increase the removal rate by 43.6%. In conclusion, in the NO concentration range of 300-900 ppm, microwave irradiation increased the removal rate by 40.4-154.0% at 70% of removal efficiency and it

Table 2. Predictions of required doses at target removal efficiencies from experimental data in Fig. 3

$[NO]_o$, ppm	70% removal			80% removal			90% removal		
	300	500	900	300	500	900	300	500	900
Without MW	6.3 kGy	8.0 kGy	16.0 kGy	9.8 kGy	14.0 kGy	21.6 kGy	16.0 kGy	24.0 kGy	36.0 kGy
With MW	4.0 kGy	5.7 kGy	6.3 kGy	6.7 kGy	10.5 kGy	13.7 kGy	14.0 kGy	22.9 kGy	36.0 kGy
F* (%)	57.5	40.4	154.0	46.3	33.3	57.7	14.3	4.8	0

*$\Delta F=(D_{without\ MW}-D_{with\ MW})/(D_{with\ MW})\times 100$

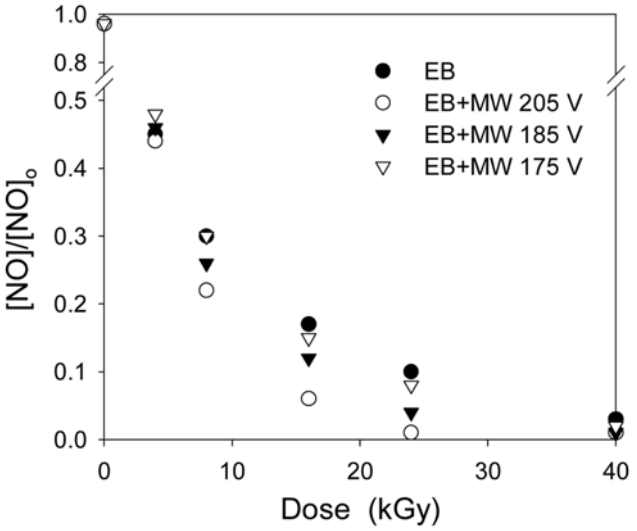

Fig. 4. Effect of microwave input voltage on NO removal under electron beam irradiation ([NO]=500 ppm; [NH_3]=500 ppm; water=2%; gas flow rate=5 liter/min, inlet gas temp.=70 °C).

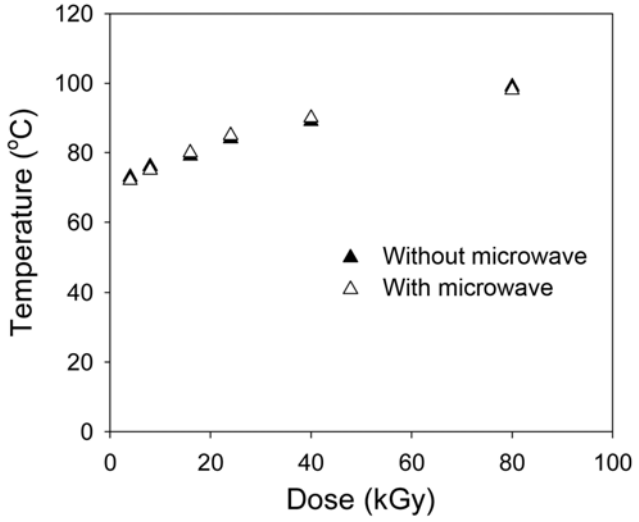

Fig. 5. Changing of gas temperature in reactor with irradiated dosages ([NO]=500 ppm; water=2%; gas flow rate=5 liter/min; input voltage of microwave=205 V, 70 °C).

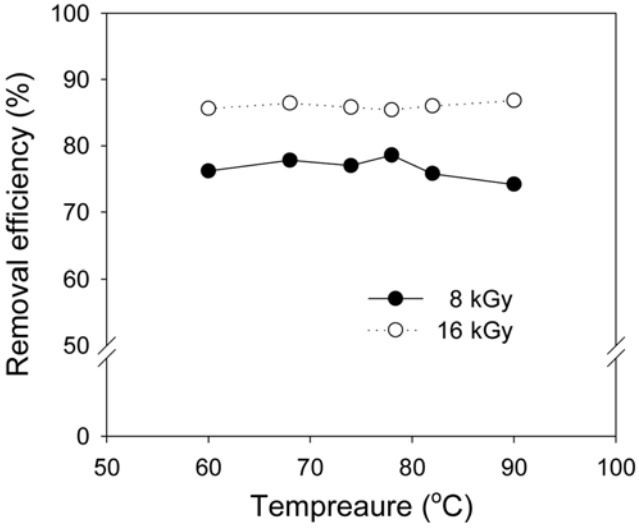

Fig. 6. Effect of inlet gas temperature on NO removal efficiency without irradiation of microwave ([NO]$_o$=500 ppm; [NH_3]$_o$= 500 ppm; water=1%).

did by 33.3-57.7% at 80% of removal efficiency. On the other hand, at 90% of removal efficiency, the microwave could little affect the removal rate of NO.

It has been known that microwave radiation is capable of violently vibrating polar substances, leading to increasing collisions between polar and non-polar substances, and eventually accelerating their reaction rates [15]. Therefore, the removal rate of NO with microwave irradiation might increase considerably at the existence of polar substances such as water and ammonia.

Fig. 4 shows the effect of input voltages of microwave, in range of 175-205 volts, on the removal efficiency of NO under electron beam irradiation. It was seen that the magnetron could not generate microwave at input voltage less than 175 volts. The removal efficiency of NO increased with increasing input voltage of microwave: at 16 kGy and 500 ppm of NO, the removal efficiency was 81% without irradiation of microwave, but it increased to 85%, 88%, and 94% for the input voltages of 175 volts, 185volts, and 205 volts, respectively. In addition, even though the microwave effect definitely appeared at doses of around 8 to 24 kGy, the microwave effect became a little below 8 kGy and above 24 kGy. These results means that, in the removal of NO, the microwave could present a synergistic effect only in combination with electron beam and it does not have removal ability by itself.

2. Effect of Temperature on NO Removal

By microwave irradiation, the temperature of polar substances rises rapidly by vibrating their molecules violently. This study examined whether NO removal efficiency might be affected by such thermal effect. Fig. 5 shows that, at 70 °C of inlet gas temperature, electron beam irradiation increased the gas temperatures in the reactor from 73 °C to 99 °C with increasing doses from 4 kGy to 80 kGy, but microwave irradiation could not bring about additional temperature rise. Fig. 6 shows that inlet gas temperatures that ranged from 60 to 90 °C hardly affected the removal efficiency of NO. The removal efficiency was nearly independent of inlet temperature at 16 kGy but it tended to slightly drop above 80 °C at 8 kGy. From Fig. 5 and Fig. 6, it can be concluded that the high removal efficiency of NO with simultaneous irradiation of both EB and microwave arises from their intrinsic kinetics under the exclusion of thermal effect.

3. Effect of Water Contents on NO Removal

Fig. 7 shows the effect of water content on the NO removal. We could find that, even without water, electron beam irradiation could considerably remove NO to produce white colored fine powders. Other studies [16] found the precursor ion, NO^+, could cluster with NH_3 in NO-NH_3 gas mixture, such as $NO^+(NH_3)_n$. The cluster rapidly increases up to n=13 and then it becomes nearly a stable structure with constant size. An electron beam is also capable of producing NO^+ ions and forming such kind of cluster even without the existence of water.

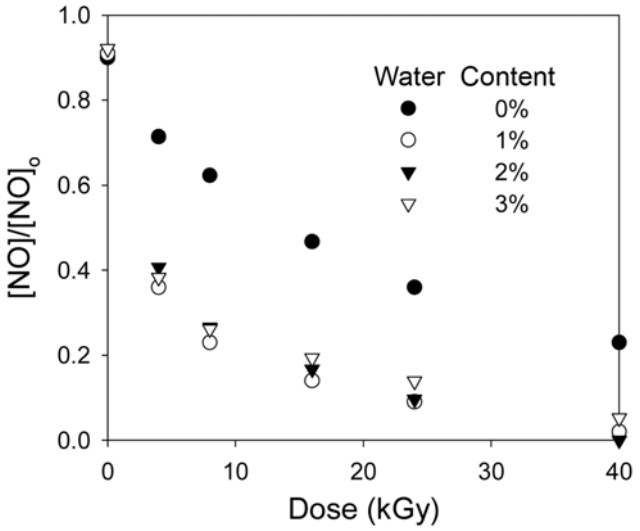

Fig. 7. Effect of water content on NO removal under simultaneous irradiation of electron beam and microwave ([NO]=500 ppm; [NH_3]=500 ppm; gas flow rate=5 liter/min; input voltage of microwave=205 V).

Fig. 7 shows also that the addition of water into NO/NH_3 gas mixture could accelerate the removal of NO in simultaneous irradiation of electron beam and microwave. Addition of 1-3% water almost removed NO near at 40 kGy. However, without addition of water, the removal efficiency at 40 kGy reached near to 80%.

4. Kinetic Considerations for NO Removal Under Simultaneous Irradiation of Electron Beam and Microwave

Many studies have found the removal mechanism of NO with irradiation of electron beam. Water radiolysis, which can be induced by irradiating electron beam into water, can produce several kinds of radicals and ions. The first step in the removal of NO_x by electron beam is to produce the following radicals by a water radiolysis in the existence of air [17]. Microwave radiation can accelerate the water radiolysis since water is a strong polar substance leading to increasing their collisions considerably.

$$O_2, N_2, H_2O \xrightarrow{e^-} OH\cdot, O\cdot, HO_2\cdot, N\cdot$$

Among the radicals, the hydroxyl radical (OH·) is the strongest oxidant. The hydroxyl radical reacts with NO and NO_2 to generate HNO_2 and HNO_3, respectively. Since the OH radical is also a polar substance, the following reactions can be accelerated by microwave irradiation.

$$NO + OH\cdot \rightarrow HNO_2,\ NO_2 + OH\cdot \rightarrow HNO_3$$

On the other hand, O· can produce gaseous ozone to react with oxygen in air. The O· and ozone easily convert NO into NO_2, which is converted to HNO_3 by reacting with hydroxyl radical. Finally, the nitric acid is converted to ammonium nitrate by reacting with gaseous ammonia (or ammonium hydroxide).

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \quad (HNO_3 + NH_4OH \rightarrow NH_4NO_3 + H_2O)$$

It was found that [18], under electron beam irradiation, a part of NH_3 could be oxidized to NH_2 radical, which reacts with NO and NO_2 to produce N_2, N_2O and H_2O. Therefore, it seems that NO_x could be removed apparently, but Fig. 7 indicated that the existence of water could suppress these reverse reactions, leading to complete removal of NO.

Since the consecutive reactions include several kinds of polar substances such as H_2O, OH·, HNO_3, and NH_3, microwave irradiation is likely to accelerate NO removal rate and suppress side and reverse reactions that may cause the removal efficiency of NO to decrease. From these considerations, it is estimated that the microwave effect on NO removal is related to an intrinsic kinetic, which is induced by increasing collisions of polar substances, rather than a thermal effect.

5. Correlation of the Removed NO with Dose

It was found that the amount of removed NO ($\Delta C=[NO]_o-[NO]$) tended to increase linearly with initial concentration of NO, as already indicated by Chemielewski [19]. Fig. 8 plots such correlation with experimental data in Fig. 3, showing that the amounts of removed NO were proportional to influent concentration of NO at each dosage. Table 3 shows that, by using a linear regression in SigmaPlot 7 program, k and k_o in $\Delta C=k[NO]_o+k_o$ could be correlated with irradiated doses. Here, k values were proportional to the dose, giving

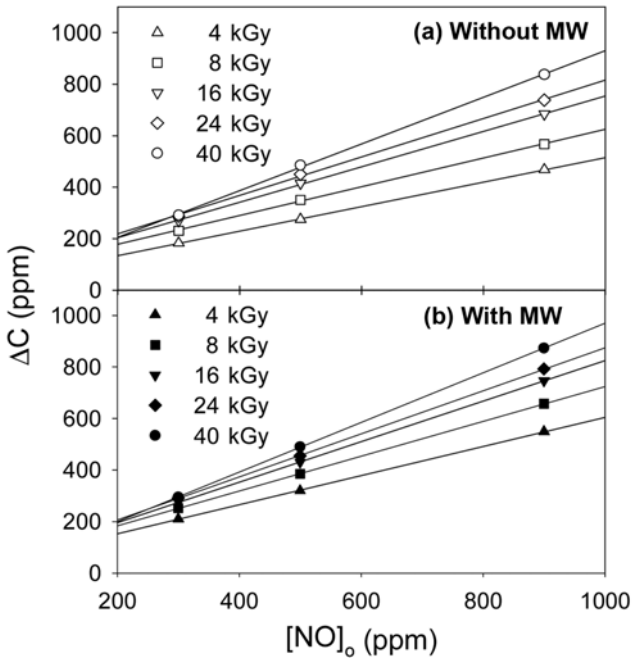

Fig. 8. Linear relationships of the removed NO (ΔC) with influent concentrations of NO ($[NO]_o$) at several doses by using experimental data in Fig. 3.

Table 3. Estimation of k and k_o values with linear correlations in Fig. 8 by using $\Delta C=k[NO]_o+k_o$

Dose, kGy	Without MW		With MW	
	k	k_o	k	k_o
4	0.4761	38.8929	0.5661	38.8929
8	0.5575	66.7500	0.6757	48.4286
16	0.6875	66.7500	0.7861	38.8929
24	0.7457	69.4286	0.8361	38.8929
40	0.9057	24.4286	0.9639	6.1071

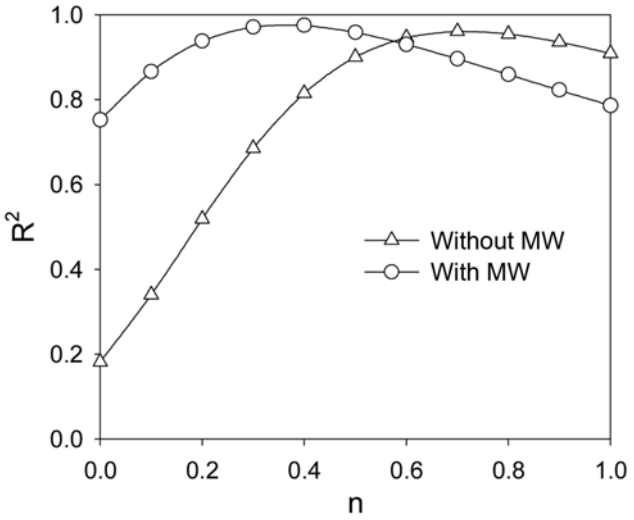

Fig. 9. Testing of linear correlation of k_o/D^n=aD+b.

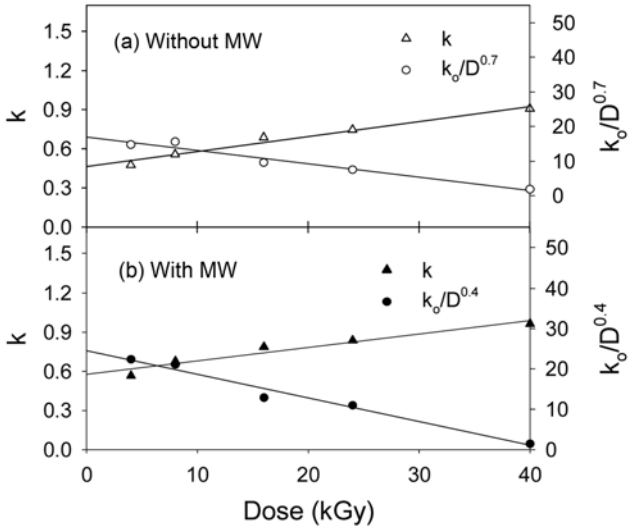

Fig. 10. Testing of linear correlations of both k and k_o/D^n versus doses with microwave irradiation and without microwave one.

larger value in microwave irradiation. However, it seems that k_o values could not have any relevance to dose.

To correlate k_o with the dose, such correlated equation as k_o/D^n= aD+b was tested by changing the n values between 0 and 1 with increment of 0.1. Fig. 9 plots the coefficient of determination (R^2) in the linear correlation with n values. Higher value of R^2 is to better fit the data, in which the best correlation value of r^2 is one. Maximum values of R^2 were around n=0.7 (R^2=0.96099) without microwave irradiation and around n=0.4 (R^2=0.97495) with microwave one, respectively. In Fig. 10, k and k_o/D^n versus doses could be plotted with good linear relationships. Table 4 shows the resultant equations of k and k_o related to the dose.

Fig. 11 compares the calculated ΔC ($\Delta C=k[NO]_o+k_o$) with the experimental ΔC and shows a good consistency between the two values. As a result, when a desired dose is suggested, the removal efficiency of NO can be estimated by means of these equations.

Table 4. Dependence of dose on k and k_o in $\Delta C=k[NO]_o+k_o$, which were estimated from straight lines in Fig. 10

Without MW	$k=1.15186\times10^{-2}\,D+0.46256$
	$k_o=-0.38480\,D^{1.7}+16.92923\,D^{0.7}$
With MW	$k=1.03000\times10^{-2}\,D+0.57606$
	$k_o=-0.58647\,D^{1.4}+24.50170\,D^{0.4}$

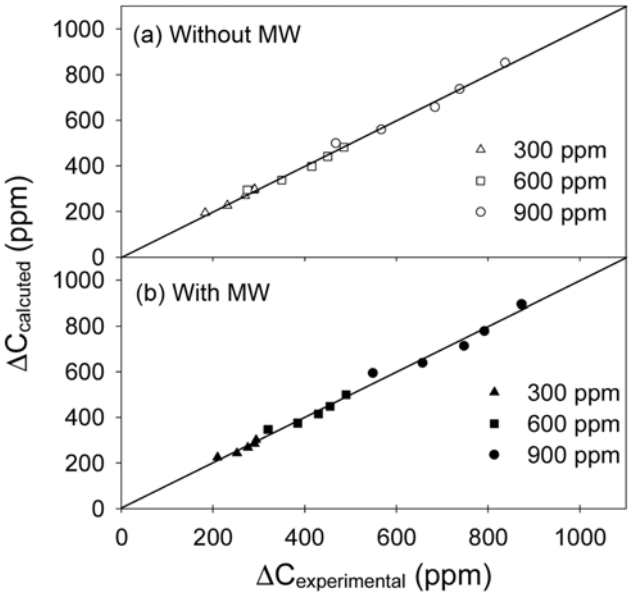

Fig. 11. Comparison of calculated ΔC with experimental ΔC.

CONCLUSIONS

Adding microwave irradiation in the NO removal process under EB irradiation could give a synergistic effect on NO removal. When the required doses at target removal efficiencies were estimated by interpolating the experimental data, the removal efficiencies of 70% and 80% were sensitive to microwave irradiation. On the other hand, at 90% removal efficiency, the microwave hardly affected the removal of NO. In addition, the microwave effect definitely appeared in the dose ranges of 8-24 kGy.

In the course of the NO removal reactions, microwave seems to be capable of violently vibrating several polar substances including water, OH radical, and NH_3 (or NH_4OH), resulting in acceleration of NO removal rate. It can be concluded that MW irradiation plays an auxiliary role in NO removal with EB irradiation and the effect of MW on the NO removal is based on an intrinsic kinetic to the exclusion of a thermal effect.

From the linear correlation for amounts of removed NO ($\Delta C=k[NO]_o+k_o$), it was found that k was proportional to dose, but k_o could be related to k_o/D^n=aD+b (n=0.7 without microwave irradiation, n=0.4 with microwave irradiation), which correlation will be useful for a preliminary estimation for NO removal efficiency at a target dose.

ACKNOWLEDGMENT

This research was supported by the Yeungnam University research

grants in 2007.

REFERENCES

1. O. Tokunaga, N. Nishimura, N. Suzuki and M. Washino, *Radiat. Phys. Chem*., **11**, 117 (1978).
2. O. Tokunaga and N. Suzuki, *Radiat. Phys. Chem*., **24**, 145 (1984).
3. D. Tai, *IAEA workshop on radiation utilization, asia and pacific section* (1966).
4. O. Tokunaga, *Sci. Technol. Jpn*., **16**(65), 47 (1998).
5. A. G. Chmielewski, E. Iller, J. Licki and B. Tymiński, *INCT Annual Report*, 119 (1998).
6. A. G. Chmielewski, B. Tymiński, J. Licki, E. Iller, Z. Zimeck and B. Radzio, *Radiat. Phys. Chem*., **46**, 1067 (1995).
7. O. L. Fainchtein, M. V. Sagaidak and V. V. Morgunov, *Radiat. Phys. Chem*., **65**, 405 (2002).
8. H. R. Paur, W. Baumann, H. Mätzing and W. Linder, *Radiat. Phys. Chem*., **46**, 1119 (1995).
9. E. L. Baranchicov, G. S. Belenky, M. A. Deminsky, V. P. Denisenko, D. D. Maslenicov, B. V. Potapkin, V. D. Rusanov, A. M. Spector, E. V. Shulakov and A. A. Fridman, *Radiat. Phys. Chem*., **45**, 1063 (1995).
10. D. Ighigeanu, D. Martin, E. Zissulescu, R. Macarie, C. Oproiu, E. Cirstea, H. Iovu, I. Calinescu and N. Iacob, *Vacuum*, **77**, 493 (2005).
11. D. I. Martin, D. I. Ighigeanu, E. N. Mateescu, G. D. Craciun, I. I. Calinescu, H. M. Iovu and G. G. Marin, *Industry Applications*, **40**, 41 (2004).
12. M. Radoiu, D. Martin, I. I. Georgescu, I. Calinescu, V. Bestea, I. Indreias and C. Matei, *Nuclear instruments and methods in physics research section B*, Beam Interactions with Materials and Atoms, **139**, 506 (1998).
13. M. T. Radoiu and D. I. Martin, *J. Hazardous Materials*, **97**, 145 (2003).
14. S. D. Kim, in *Ph D. Thesis:* Study on Effect of Desulfurization and Denitrification Processes for Purification of Flue Gas by Electron Beam Irradiation, Major advisor: D.H. Han, Yeungnam University, Korea, December (2005).
15. D. H. Han, S. Y. Cha and H. Y. Yang, *Water Research*, **38**, 2782 (2004).
16. L. Poth, Z. Shi, Q. Zhong and A. W. Castleman, *J. Phys. Chem. A*, **101**, 1099 **(**1997).
17. A. O. Allen, *Radiat. Res*., **1**, 85 (1954).
18. A. G. Chmielewski, Y. Sun, Z. Zimek, S. Bulk and J. Licki, *Radiat. Phys. Chem*., **65**, 397 (2002).
19. A. G. Chmielewski, J. Licki, A. Pawelec, B. Tymiński and Z. Zimek, *Radiat. Phys. Chem*., **71**, 439 (2004).