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I N S T Y T U T M A S Z Y N P R Z E P Ł Y W O W Y C H

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exist for the publication of theoretical and experimental investigations of all aspects of the mechanics and thermodynamics of fluid-flow with special reference to fluid-flow machines

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poświęcone są publikacjom naukowym z zakresu teorii i badań doświadczalnych w dziedzinie mechaniki i termodynamiki przepływów, ze szczególnym uwzględnieniem problematyki maszyn przepływowych

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Nonthermal plasma desorption for NO_x control

The gas flow rate for hazardous air pollutants (HAPs) emission is generally high and their concentrations are low (in ppm levels). When the high flow-rate and low concentration gases are treated, the size of the equipment and the operating cost become large. The new concept – plasma desorption – was investigated, which is able to convert the high flow-rate and low concentration to the low flow-rate and high-concentration emission using the nonthermal plasma. The fundamental characteristics of plasma desorption and regeneration for NO was investigated to achieve the new way of controlling NO_x emissions. The experimental study showed that the higher adsorption was achieved with repeated adsorption due to the redistribution towards the surface. In addition, the gas concentration increased 15 times and the flow rate was reduced to 1/167. Further improvement can be attained using the intermittent plasma desorption with the high flow rate.

1. Introduction

In general, the gas flow rate for hazardous air pollutants (HAPs) emission is high and their concentrations are in ppm levels. When these high flow-rate and low concentration HAPs are treated, the total system cost becomes excessively high regardless of the selection of the control device because both the control device and the operating cost increase with increasing gas flow rate. Applying a more economically sound technology, the high flow-rate and low concentration HAPs are initially adsorbed without using the power and then, desorbed (detached) using the nonthermal plasma from the adsorbed pellets so that we are able to convert from the high flow-rate and low concentration to the low flow-rate and high-concentration HAPs emission and this concentrated HAPs can be treated at a later stage.

Conventional methods for gas phase adsorption are to employ activated carbon, activated alumina or molecular sieve. HAPs being adsorbed on materials are usually incinerated or disposed. Some adsorption materials can be desorbed

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and regenerated by using heat or steam ($>300^{\circ}\text{C}$) or by the pressure and temperature swing adsorption (PTSA) method, but this entails the additional costs of generation of high temperature gas or steam, the apparatus and energy.

The process developed here is to use the nonthermal plasma to desorb from the absorption material and at the same time the adsorption material can be regenerated with a modest power. The system can be operated at the ambient temperature and pressure without using heat. Plasma desorption and regeneration was successfully demonstrated for Methyl Ethyl Ketone (MEK, $\text{CH}_3\text{CH}_2\text{COCH}_3$) using the barrier-type packed-bed plasma reactor [1]. The gas-phase contaminant removal from the material surfaces has been investigated using the low pressure glow discharge plasma [2, 3]. The plasma desorption from the surface may use reactive compounds as dopants to generate reactive species that would react with contaminants on surface. On the other hand, the gaseous compounds were captured inside adsorption materials (pores of adsorption materials). The desorption mechanisms between surface and pores were different. In the present study, we focused on one of the most difficult nitrogen oxide to control to demonstrate the methods and apparatus using this unique nonthermal plasma desorption technology.

2. Experiments

The barrier-type packed-bed plasma reactor consists of a 1.6 mm diameter stainless wire and a cylindrical glass (20 mm inner diameter Pyrex and 26 cm effective length) as dielectric barrier around which the copper screen was wrapped as a ground electrode. The pellets used were 2.0 mm molecular sieve (MS) spheres with various diameter of pores: 3A, 4A, 5A and 13X (pore size of 3\AA , 4\AA , 5\AA and 10\AA respectively). The reactor contains 15.7 mL (5 cm high) of MS pellets. The reactor was energized by the 60 Hz and 20 kHz AC power supply (15 kV and 30 mA, and 9 kV and 28 mA).

A schematic diagram of the experimental setup is shown in Fig. 1. Two percent NO balanced with N_2 in a cylinder was mixed with dry air to obtain the desired concentration and flow rate using the mass flow control valve on each line. The NO concentration was maintained at 1,000~4,000 ppm in order to reduce our experimental time because typical concentrations from industrial emissions are approximately one order of magnitude lower. The NO concentration and reaction by-products such as NO_x ($\text{NO} + \text{NO}_2$), CO, CO_2 and N_2O were measured by the gas analyzer (Horiba, PG-235, Chemiluminescence NO- NO_2 - NO_x , VIA-510, Infrared adsorption for N_2O and CO_2). The applied voltage and the voltage and current waveforms were measured by an oscilloscope (Tektronix TDS380P) through the voltage divider (Tektronix, P6015A). The pressure drop of the reactor was measured using the strain gauge type pressure transducer (Kyowa Electronic Instruments, PDV-25GA). The reactor surface temperature was measured by the infrared thermometer (TASCO, THI-440).

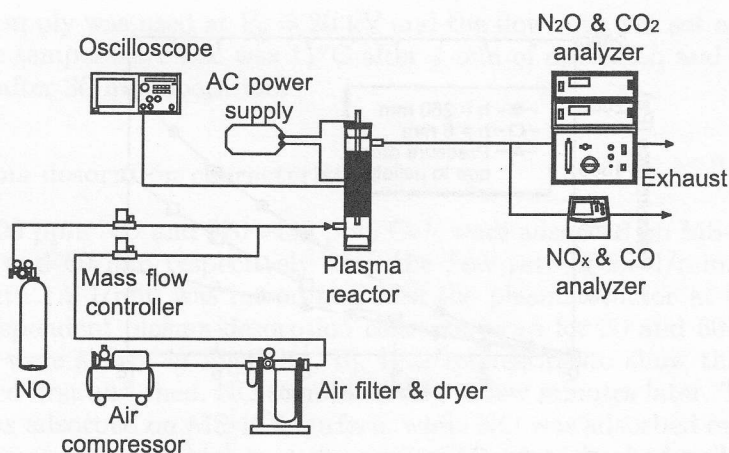


Fig. 1. Schematic diagram of the experimental setup.

3. Results and discussion

3.1. Pressure drop of the plasma reactor

The pellets were filled with an entire 260 mm high reactor and the flow rate was varied up to 10 l/min. Then, the pressure drop was measured without pellets. The difference between those two measurements was the pressure drop of pellets alone. The results were shown in Fig. 2. When the pellets were 5 cm high and the flow rate was 2.0 l/min, the pressure drop became 19 Pa.

3.2. Adsorption characteristics

Adsorption consists of physical and chemical adsorption. The physical adsorption is based on van der Waals attraction of surfaces, while chemical adsorption is related to the transfer of electrons and ions between the surface and a molecule. Initially, the γ -alumina and porous BaTiO_3 pellets were used as an adsorption material which was successfully used in previous Methyl Ethyl Keton (MEK) plasma adsorption experiments [1]. However, NO adsorption was extremely poor. This was primarily related to the pore size of adsorption materials, which were too large compared with the molecular size of NO and CO_2 ($3\sim 4$ Å) for collisions to occur. Then, we used MS-3A, 4A, 5A and 13X for determination of the adsorption characteristics.

The NO and CO_2 concentrations were set at 1,000 ppm and 370~430 ppm respectively. The results were shown in Fig. 3. Because the pore size of the internal MS structure was smaller than the molecular diameter of NO and CO_2 ($3\sim 4$ Å) very little adsorption takes place for MS-3A and MS-4A (pore size of 3 Å and 4 Å respectively). The modest adsorption for MS-5A (pore size of 5 Å) and

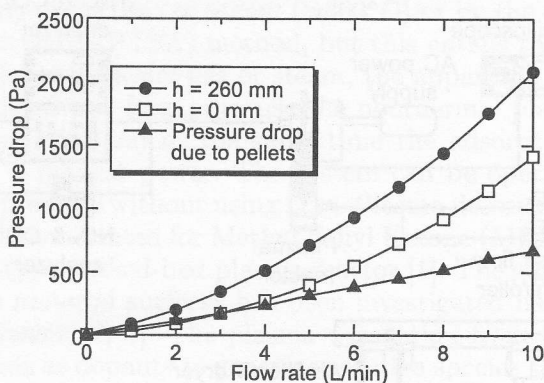


Fig. 2. Pressure drop through the plasma reactor.

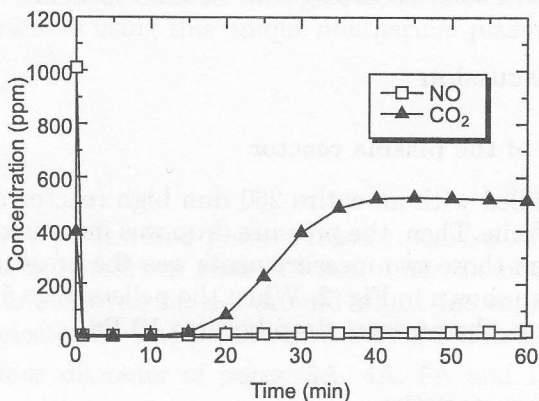


Fig. 3. Adsorption characteristics of MS-13X for NO and CO₂.

the maximum adsorption were achieved for MS-13X (pore size of 10 \AA).

The adsorption characteristics between NO and CO₂ were somewhat different. The CO₂ achieved the saturation state quickly in the case of MS-13X pellets, while NO adsorption was sustained for a long period time (>60 min). This is primarily due to different adsorption characteristics: surface adsorption in the case of CO₂ as oppose to the internal pore adsorption for NO [4]. Both NO and CO₂ start to adsorb on MS surface and then NO penetrates towards the center of the pores, resulting in superior adsorption characteristics. When 400 ppm NO was used, it was totally adsorbed in the pellets after 6 h. When 4,000 ppm NO was used with the flow rate of 2.0 l/min., approximately 500 ppm of NO was leaked through the reactor after 30 min of adsorption although it has not been shown.

The time-dependent reactor surface temperature was measured when 60 Hz

AC power supply was used at $V_p = 20$ kV and the flow rate was set at 1.2 l/min. The surface temperature rise was 11°C after 4 min of operation and never exceeded 20°C after 30 min operation.

3.3. Plasma desorption characteristics

The 4,000 ppm NO and 370~430 ppm CO_2 were adsorbed on MS-13X pellets for 30 min and 60 min respectively with the flow rate of 2.0 l/min. Then, the fresh air with 1.2 l/min was introduced into the plasma reactor at $V_p = 9$ kV. The time-dependent plasma desorption characteristics for 30 and 60 min adsorbed pellets were shown in Figs. 4(a, b). It is interesting to show that the CO_2 was desorbed first and then, NO started to desorb few minutes later. This implies that CO was adsorbed on MS-13X surface, while NO was adsorbed on MS pores. The NO_x desorption was higher in the case of 60 min adsorbed pellets than 30 min adsorbed pellets. This implies that the plasma desorption is related to the distribution of NO adsorption on pellets.

When the applied voltage was increased from 9 kV to 10 kV while other

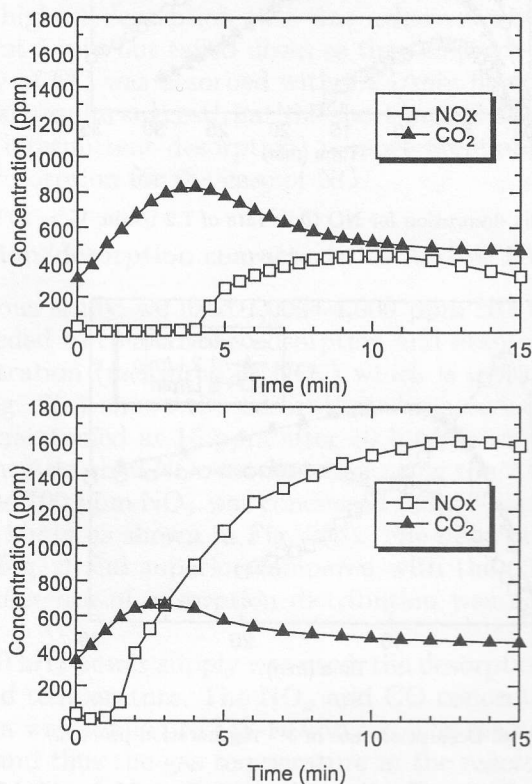


Fig. 4. Plasma desorption for NO (flow rate of 1.2 l/min, $V_p = 9$ kV), a) for 30 min adsorbed MS-13X, b) for 60 min adsorbed MS-13X.

experimental conditions remained the same as in the previous experiment, the amount of NO desorption increased further. It implied that the excited by the plasma species were further influenced towards the center of MS-13 pellets. At the same time, the time required for desorption becomes shorter for $V_p = 10$ kV. In our experiments we measured NO as NO_x ($\text{NO} + \text{NO}_2$). The reactor contained only the height of 5 cm MS-13X pellets at the bottom of the reactor and the upper portion of the reactor was empty so that the reactor behaves like a silent discharge, because the outer screen was extended to 26 cm. Therefore, the part of NO was oxidized to NO_2 by the upper portion of the reactor.

Next, the 4,000 ppm NO was adsorbed on MS-13X for 30 min with the flow

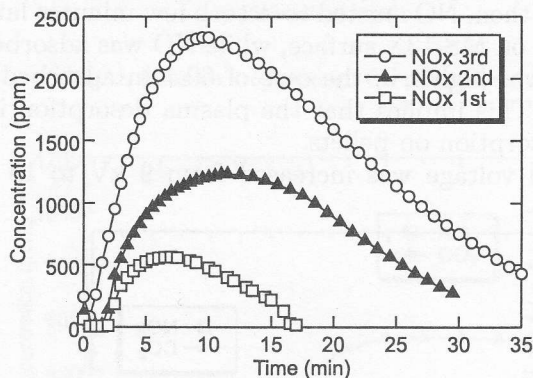


Fig. 5. Plasma desorption for NO (flow rate of 1.2 l/min, $V_p = 10$ kV).

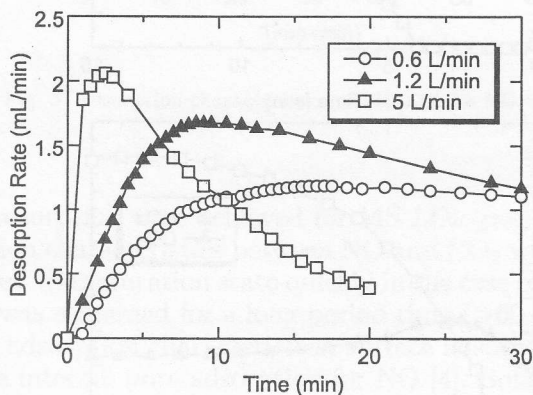


Fig. 6. Desorption rate in 3rd regeneration process.

rate of 2.0 l/min. Then, the plasma was applied at $V_p = 10$ kV to desorb NO while the fresh air was set at 1.2 l/min. After confirming that NO concentration became zero after 17 min; 4,000 ppm NO was adsorbed for another 30 min. The

2nd plasma desorption took place at $V_p = 10$ kV for 30 min. This process was repeated three times to characterize the plasma desorption and regeneration for MS-13X which was shown in Fig. 5. It is clear that the quantity of NO desorption increases with the repeating adsorption. The amount of NO desorption can be estimated by the ratio of the area of the desorption curve to the total adsorption. The amount of NO desorption by the first plasma desorption was approximately 7.5% of the total NO adsorbed.

The second desorption was 13% if first adsorption was taken into account or 20% when only second adsorption was considered. The third adsorption was 15%, if three adsorptions were considered or 38% when only third adsorption was considered. Speculation for the superior desorption characteristics for the repeated adsorption is as follows: freshly adsorbed NO laid on top of previously adsorbed NO, which results in previously adsorbed NO, penetrates further towards the central pores of MS-13X pellets. The NO after third adsorption was accumulated near the surface. Therefore, when the plasma was applied, NO can be easily desorbed into the gas stream [5].

The desorption rate can be expressed as the product of concentration and flow rate. The desorption rate after 2nd adsorption and desorption process was plotted in Fig. 6. The highest desorption rate was achieved when the flow rate was 5 l/min for the first 5 min but tailed down as time elapsed. It is also clear that the highest quantity of NO was desorbed with 1.2 l/min flow rate if it was expressed for 30 min. These results suggest that the short period of plasma desorption with high flow rate (intermittent desorption) is most preferable operation to achieve the maximum desorption for the case of NO.

3.4. Adsorption/desorption characteristics for low NO concentration

In the previous study, we used 1,000~4,000 ppm NO to accelerate the experiments. We needed to confirm the adsorption and desorption characteristics for low NO concentration (measured as NO_x) which is more realistic for industrial applications. Fig. 7(a) shows the adsorption characteristics for 100 ppm NO_x. The NO_x was maintained at 15 ppm after 10 h of operation when the flow rate was at 1.0 l/min. Adsorbed NO was desorbed using the 20 kHz AC power supply ($V_p = 5$ kV). The 100 ppm NO_x was condensed to 2,500 ppm after 3 min with the flow rate of 1.2 l/min as shown in Fig. 7(b). The desorption characteristics was comparable to Fig. 3 and superior compared with the 60 Hz AC power supply although the difference of adsorption distribution was not clear at the present stage.

When the 20 kHz power supply was used, the desorption may be attributed to both plasma and temperature. The NO_x and CO concentrations were measured when the plasma was applied to MS-13X in air. The reactor surface temperature reached 170°C and thus the gas temperature in the reactor may be in the range of 250°C after 3 min of operation as shown in Fig. 8. On the other hand, NO_x and CO generations were as high as 65 ppm and 29 ppm, respectively which was not reflected during the desorption measurements.

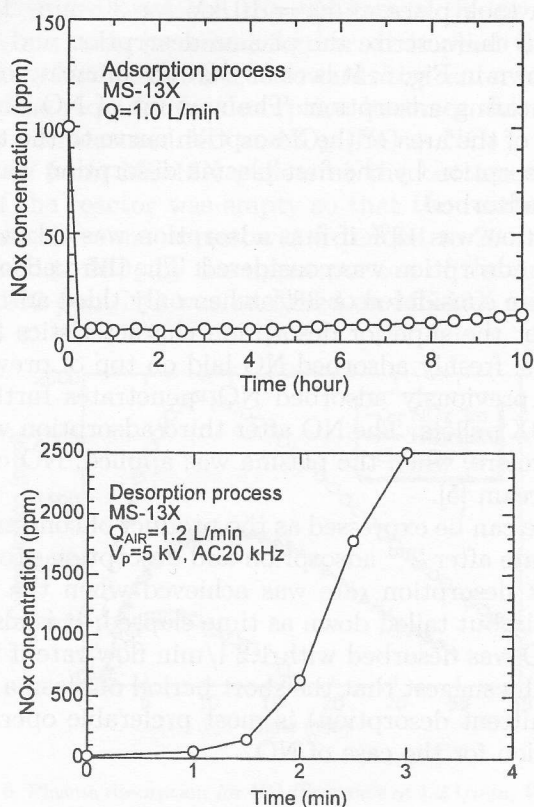


Fig. 7. Adsorption/desorption characteristics on low NO concentration: (a) adsorption for 100 ppm NO_x, (b) desorption with 20 kHz power supply ($V_p = 5$ kV)

The total amount of NO_x adsorbed for 10 h can be calculated from Fig. 7(a) which is (100 ppm) (10 h) (60 min/h) (0.9) = 54,000 ppm · min assuming 90% adsorption and the amount of gas volume treated was calculated using the flow rate and the treatment time, which is (1 l/min) (60 min/h) (10 h) = 600 l. On the other hand, the amount of NO_x desorbed was approximately (1,500 ppm) (1.5 min) = 2,250 ppm · min and the flow volume was reduced to (1.2 l/min) (3 min) = 3.6 L after 3 min of desorption. Therefore, the reduction of the flow rate was (3.6)/(600) = 1/167 and the concentration ratio increased 15 times, respectively. In this particular experiment, only 4.2% of NO_x was desorbed from MS-13X pellets. Desorbed NO_x can be completely and economically removed, for example, by the plasma-chemical hybrid system [6]. The higher desorption can be achieved using the intermittent plasma desorption with the high flow rate, combined with the use of appropriate power supply. This plasma desorption concept is able to reduce the gas volume two orders of magnitude and to increase the concentration 2.5 times. Therefore, the plasma desorption concept leads to

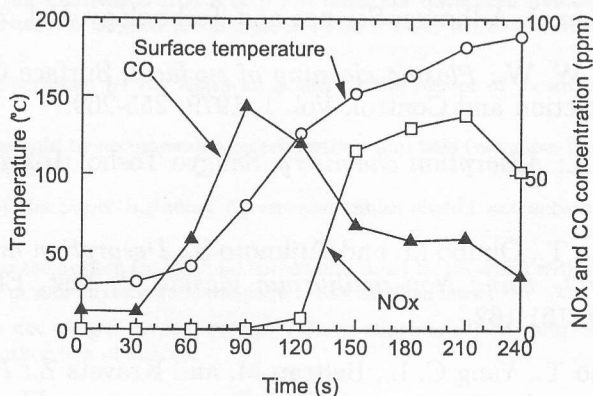


Fig. 8. Time-dependent surface temperature of the plasma reactor, NO_x and CO concentration in air when the plasma was applied to MS-13X.

achieve more attractive control methods for treating various industrial emissions.

3.5. Reaction by-product

The concentration of NO , NO_x , CO , CO_2 and N_2O were measured as the reaction by-products for plasma desorption. Less than 20 ppm of CO and 1 ppm of N_2O were produced when the 60 Hz power supply was used. When the 20 kHz power supply was used, CO concentration reached as high as 72 ppm.

4. Conclusion

The new concept for plasma desorption and regeneration using NO was successfully demonstrated. The higher adsorption was achieved with repeated adsorption, primarily due to NO redistribution towards the surface. The case study showed that the gas concentration increased 15 times and the flow rate was reduced to 1/167. The maximum desorption can be attained using the intermittent plasma desorption with the high flow rate.

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Kontrola stężeń NO_x metodą desorpcji z zastosowaniem plazmy nietermicznej

Streszczenie

Natężenia przepływów gazów zawierających toksyczne związki gazowe są na ogół duże, a stężenia tych związków małe, na poziomie ppm. Instalacje oczyszczające są wówczas znacznie rozbudowane i drogie. Zbadano możliwość zastosowania plazmy nietermicznej do przekształcenia emisji o dużym natężeniu przepływu i małym stężeniu substancji toksycznych w emisję o małym natężeniu przepływu i dużym stężeniu toksyn. Przeprowadzono pomiary adsorpcji i desorpcji NO pod wpływem plazmy wyładowania elektrycznego. Wyniki badań wykazały, że zastosowanie wyładowania dielektrycznego umożliwia pełne wykorzystanie powierzchni materiału do adsorpcji badanych związków gazowych. Natomiast działanie wyładowaniem jarzeniowym na powierzchnię materiału powoduje desorpcję gazów, przy czym uzyskuje się 15-krotne zwiększenie stężenia danego związku gazowego i zmniejszenie natężenia przepływu do 1/167 wartości początkowej. Zastosowanie przerywanej desorpcji plazmowej i dużego natężenia przepływu może zwiększyć ilość uwalnianej substancji gazowej.