

## ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 39

no. 3

pp. 93 - 106

2013



PL ISSN 2083-4772

DOI: 10.2478/aep-2013-0025

© Copyright by Polish Academy of Sciences and Institute of Environmental Engineering of the Polish Academy of Sciences,  
Zabrze, Poland 2013

PILOT PLANT STUDIES ON NO<sub>x</sub> REMOVAL VIA NO OZONATION  
AND ABSORPTION

WŁODZIMIERZ KORDYLEWSKI\*, MACIEJ JAKUBIAK, TOMASZ HARDY

Wrocław University of Technology, Faculty of Mechanical and Power Engineering,  
Institute of Power Engineering and Fluid Mechanics  
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

\*Corresponding author e-mail: wlodzimierz.kordylewski@pwr.wroc.pl

**Keywords:** de-NO<sub>x</sub>, nitric oxide, ozonation, absorption.

**Abstract:** The results of experimental investigations on the removal of NO<sub>x</sub> from gases applying ozone as the oxidizing agent and the absorption of higher nitrogen oxides in the sodium hydroxide solutions are presented. The experiment was conducted using a pilot plant installation with the air flow rate 200 m<sup>3</sup>/h, being a prototype of a boiler flue gas duct and a FGD scrubber. It was shown that in the range of [NO<sub>ref</sub>]<sup>1</sup> = 50 ÷ 250 ppm the mechanism of NO ozonation depends on the molar ratio  $X = O_3/NO_{ref}$ : for  $X \leq 1.0$  oxidation of NO to NO<sub>2</sub> predominates and NO<sub>2</sub> is poorly absorbed, for  $X \gg 1.0$  NO<sub>2</sub> undergoes further oxidation to N<sub>2</sub>O<sub>5</sub>, which is efficiently absorbed in the scrubber. The stoichiometric molar ratio of complete conversion of NO into N<sub>2</sub>O<sub>5</sub> is  $X = 1.5$ , in these studies to reach the effectiveness  $\eta \geq 90\%$  the molar ratio  $X$  was much higher (2.75).

## INTRODUCTION

In Poland, the main sources of air pollution are the following sectors: energy production, industry, transport and municipal sector [11]. The Polish energy generating sector will have to fulfil the EU emission limit values for SO<sub>2</sub>, NO<sub>x</sub> and dust from coal-fired boilers after January 1<sup>st</sup> 2016. The new IE Directive [4] has preserved the previous LCP D emission limit values [3], which means that the NO<sub>x</sub> emission must be below 200 mg/m<sup>3</sup> (O<sub>2</sub> content 6%). Up to now almost exclusively the primary methods of NO<sub>x</sub> emission reduction, called low-NO<sub>x</sub> combustion systems, were applied in Poland, because they were appropriate to meet the actual emissions limits at reasonable costs [17]. However, the emission limit value 200 mg NO<sub>2</sub>/m<sup>3</sup> (O<sub>2</sub> content 6%) cannot be executed using only the low-NO<sub>x</sub> combustion systems in hardcoal-fired and old lignite-fired power plants.

Since the 1980s the emission values for NO<sub>x</sub> from coal-fired power plants in the developed EU countries have been controlled by applying the selective catalytic reduction (SCR), which has a status of the Best Available Technology (BAT). The SCR method is very effective in control of the NO<sub>x</sub> emission; however its capital and exploitation costs are considered high [12]. The application of SCR in the pulverised coal-fired boilers procures some troubles; the life-time of catalysts is limited because of fly ash erosion

requiring their regeneration or replacement. When biomass is co-fired the catalysts could be poisoned by alkali metals. The use of ammonia or urea may induce risk of the ammonia-slip.

The problems mentioned caused that new technologies (alternative to SCR) have been updated for the highly-efficient and low-cost denitrification of flue gas. A promising alternative are wet processes for simultaneous removal of  $\text{NO}_x$ ,  $\text{SO}_2$  and Hg, which could be combined with the flue gas desulfurization (FGD) methods. Concerning  $\text{NO}_x$  removal, these methods are based on the preliminary oxidation of low soluble NO and absorption of higher nitrogen oxides in alkaline solutions [6]. Therefore, a lot of effort has been devoted to examine efficient, safe and economic NO oxidizers in recent decades [2]. A considerable amount of works have been done on the ozone injection technology for  $\text{NO}_x$  control. Despite many publications, patents, economic analyses and promising results in bench-scale in this area there are no commercial applications [7, 15]. The main obstacle is of economic nature; ozone generation is energy-consuming and requires an expensive apparatus, such as powerful ozonizers and feed oxygen supply systems. Therefore, to make the method cost-effective the optimisation of NO ozonation is necessary, which requires further studies.

Most of experimental studies performed on NO ozonation were lab-scale ones with use of bubble washers for the absorption. The authors' team conducted several such experimental studies in previous years [5, 9]. However, the lab-scale conditions are far from conditions existing in industrial installation, like in power plants. The reported studies were conducted in the pilot plant scale (rate flow of carrier gas was  $200 \text{ m}^3/\text{h}$ ) in order to examine the influence of such factors, as scale and geometry of the installations and scrubbing of  $\text{NO}_x$ .

The results of experimental investigations on ability of the  $\text{NO}_x$  removal from gases applying ozone as the oxidizing agent and a wet scrubber for washing higher nitrogen oxides from the gas are presented. The experiment was conducted using a pilot plant installation with air flow  $200 \text{ m}^3/\text{h}$ , being a prototype of a boiler duct of flue gas and the wet scrubber. The main aim of the research was to confront the effectiveness of  $\text{NO}_x$  removal obtained in the lab- and pilot- scale and interpretation of the resulted discrepancy.

## MECHANISM OF NO OXIDATION BY OZONE

Ozone plays a significant role in the atmospheric chemistry, due to ultraviolet radiation which enhances formation of the hydroxyl radicals OH being the most important cleaning agents in the atmosphere [16]. It also principally contributes to nitrogen oxide NO oxidation into more reactive nitrogen dioxide  $\text{NO}_2$ , which next undergoes conversion to nitric acid and nitrites removed from the atmosphere with acid rains. Knowledge of the atmospheric chemistry could be helpful in order to understand the mechanism of NO ozonation in the method of  $\text{NO}_x$  abatement which applies preliminary NO oxidation and absorption of the oxidation products in wet scrubbers. The temperature range is approximately like in troposphere, however lack of ultraviolet radiation causes that the number of chemical reactions is smaller. In order to discuss the assessed experimental results the following set of chemical reactions of major importance was considered (Table 1).

The reaction (1) is very fast, which could lead to a hasty conclusion about the possibility of rapid removal of  $\text{NO}_x$  in a small oxidizing reactor. The reaction (2) tends to

Table 1. Values of rate constants [18]

Reactions	Values of $k_f$ and $k_b$ (298 K), dm <sup>3</sup> , mole, s	No.
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$1.08 \cdot 10^7$	(1)
$\text{NO} + \text{NO}_2 = \text{N}_2\text{O}_3$	$4.76 \cdot 10^9 / 3.6 \cdot 10^8$ , [14]	(2)
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$2.39 \pm 0.14 \cdot 10^4$	(3)
$\text{NO}_2 + \text{NO}_3 = \text{N}_2\text{O}_5$	$3.16 \pm 0.61 \cdot 10^4 / 3.51 \pm 0.71 \cdot 10^{-3}$	(4)
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	$2.43 \pm 0.34 \cdot 10^{-3} [\text{H}_2\text{O}]^{-1}$	(5)
$2\text{O}_3 + \text{M} \rightarrow 3\text{O}_2$	depends on specific M	(6)

be often neglected in the chemical mechanisms of NO ozonation since N<sub>2</sub>O<sub>3</sub> is an unstable product. However, N<sub>2</sub>O<sub>3</sub> may play an important role in absorption and was therefore included in Table 1 [8].

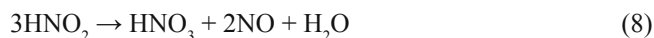
When the molar ratio of ozone to nitrogen oxide  $X$  assumes the sub-stoichiometric values ( $X < 1$ ), nitrogen dioxide is the main product of NO oxidation [13]. When the ozone concentration grows to the over-stoichiometric values ( $X > 1$ ), the reaction (3) of NO<sub>2</sub> and overdosed O<sub>3</sub> becomes important because NO<sub>3</sub> radicals are formed. For more intensive NO ozonation ( $X \gg 1$ ) nitrogen trioxide reacts with NO<sub>2</sub> to form dinitrogen pentoxide N<sub>2</sub>O<sub>5</sub>.

The recombination reaction (6) was included into the Table 1 in order to take into account reactions of ozone with particle matter in gas (dust particles), walls and steam, which may influence the necessary ozone excess to achieve the required degree of NO<sub>x</sub> emission reduction.

The NO oxidation phase is followed by the absorption phase. It is generally accepted that NO has a very low solubility [10]. The nitrogen dioxide was previously considered to be highly soluble in water [5], which was proven to be a mistake. In fact, NO<sub>2</sub> solubility is low ( $0.3 \div 0.5$  g/l for  $p_{\text{NO}_2} = 0.1$  MPa), which is only one order higher than the solubility of NO [10]. The absorbed NO<sub>2</sub> reacts with water producing nitrous and nitric acid [18]:



Unfortunately, nitrous acid HNO<sub>2</sub> is unstable and can decompose with the release of NO, as follows [19]:



Perhaps, low solubility of NO<sub>2</sub> and the disproportionation of nitrous acid are the reasons why the efficiency of NO<sub>x</sub> removal for the molar ratio  $X \leq 1$  is not better than 20% [9, 13]. Hence, an intensive ozonation of NO is required to form dinitrogen pentoxide, which can be considered as highly water soluble due to the hydrolysis reaction (5) producing stable nitric oxide HNO<sub>3</sub> [1].

However, the NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> need a longer reaction time than NO<sub>2</sub>, because the reactions (3) and (4) are much slower than the reaction (1). This indicates that NO ozonation has to be much more intensive, and that the residence time must be much longer.

## EXPERIMENTAL

The investigations were conducted applying the pilot plant installation (Fig. 1). It included the carrier gas channel 4 of the inner diameter  $D_i = 290$  mm and the length approx. 15 m with the fabric filter 5, after which there was the absorption column 20 of the inner diameter  $d_i = 190$  mm and the height 4 m and the container of sorbent at the bottom 13. The absorber column was equipped with four nozzles injecting sorbent under pressure 0.2 MPa at four levels.

The carrier gas was air sucked into the pilot plant under controlled flow rate (200 m<sup>3</sup>/h at the temperature of 20°C) by the fan 16. The carrier air was doped by nitrogen oxide from the steel cylinder 3 (99,5% of NO from Air Liquide Polska Sp. z o.o.) by the electronic mass flow controller 2 of the type GFC37 (delivered by AALBORG). The concentrations of NO and NO<sub>2</sub> in the carrier air were measured after the absorber demister 22 by the gas analyser 23 Gasetmet DX-4000. The reference concentrations NO<sub>ref</sub> and NO<sub>x,ref</sub> denoted the concentrations of NO and NO<sub>x</sub> which were measured in the carrier air after the absorber when ozone was not generated by the ozonizer 7.

Ozone (1÷5% O<sub>3</sub> in oxygen by volume, depending on the required molar ratio  $X$ ) was injected into the carrier air under pressure 0.07 MPa by a lance 11 with five nozzles at the rate of 1.2 m<sup>3</sup>/h. The oxidizing tubular reactor was approximately horizontal duct connected to the container 13 of sorbent (Fig. 1). The residence time in the tubular reactor was approx. 2 s.

In order to produce ozone the ozone generator 7 of the type OZAT CFS-3 2G from Degremont Technologies Ltd (Ozonía) was fed by oxygen from the steel oxygen cylinder 6. The ozone flow rate was controlled by two rotameters: the main one inside the ozone generator 7 for the measurement of oxygen flow rate and the auxiliary one 9 for the measurement of ozone/oxygen mixture flow rate to the ozone analyser 10 (DMT 964 BT model of BMT MESSTECHNIK GMBH).

The absorbent (aqueous solution of sodium hydroxide) was pumped from the container 13 through four rotameters 14 and atomised in the absorption column 20 by the nozzles 12, 18, 19 and 21. The oxidation-absorption processes were conducted at the temperature of approx. 22°C.

The effectiveness of NO oxidation in the gas phase was determined based on the concentrations of NO measured in the carrier air after the absorber 20 by following expression called the oxidation ratio  $OR$  (%):

$$OR = \left( 1 - \frac{[NO_{out}]}{[NO_{ref}]} \right) \cdot 100\% \quad (9)$$

The effectiveness of NO<sub>x</sub> removal  $\eta$  from the carrier air was defined:

$$\eta = \left( 1 - \frac{[NO_{x,out}]}{[NO_{x,ref}]} \right) \cdot 100\% \quad (10)$$



The recorded changes of NO and NO<sub>2</sub> concentrations in the carrier air after the absorber 20 when the mole ratio  $X$  varied from 0 to 2.75 are shown in Fig. 3. Initially the nitrogen oxide concentration decreased almost proportionally to the ozone molar ratio rise and for approximately  $X \cong 1.0$  dropped to 10 ppm. Then, the oxidation rate of the remained NO was slowing down, perhaps because of the competition from much higher concentration of NO<sub>2</sub>.

In the first, sub-stoichiometric stage the nitrogen dioxide concentration quickly increased and after achieving the maximum at  $X = 1.0 \div 1.25$  it was gradually declining,

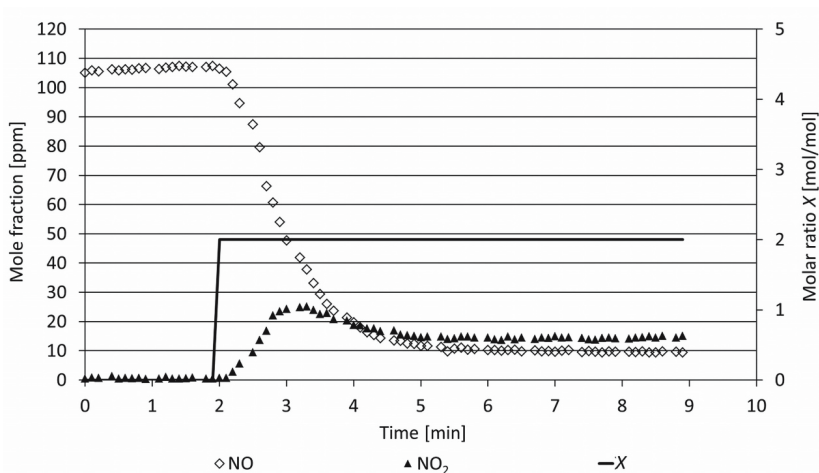


Fig. 2. Changes of NO and NO<sub>2</sub> concentrations after sudden ozone injection into the carrier gas ( $X = 2.0$ ,  $[\text{NO}_{\text{ref}}] = 105 \text{ ppm}$ ,  $L/G = 10 \text{ dm}^3/\text{m}^3$ , 0.1 M solution of NaOH)

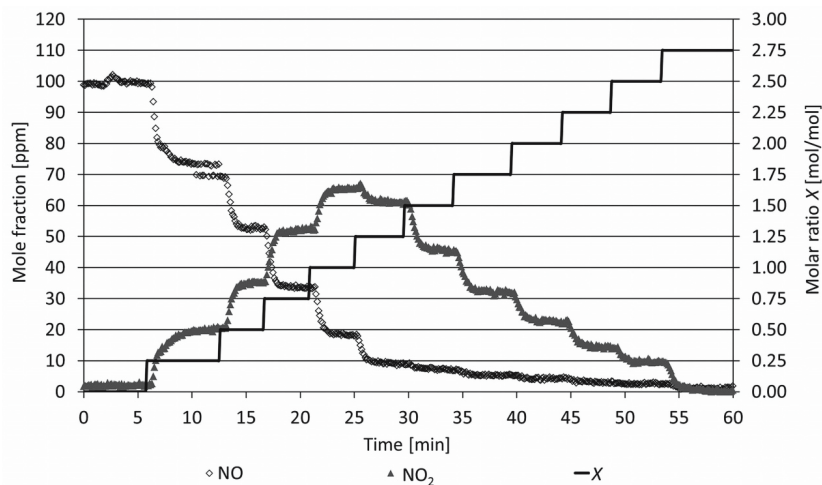


Fig. 3. Time dependence of NO and NO<sub>2</sub> concentrations against the molar ratio  $X = 0 \div 2.75$  ( $[\text{NO}_{\text{ref}}] = 105 \text{ ppm}$ ,  $L/G = 10 \text{ dm}^3/\text{m}^3$ , 0.1 M solution of NaOH)

and it approached zero at  $X \cong 2.75$ . An explanation of this behaviour should be related to the chemical kinetics of the NO ozonation: the ozone excess caused oxidation of NO<sub>2</sub> to NO<sub>3</sub>, which reacted with NO<sub>2</sub> producing N<sub>2</sub>O<sub>5</sub> according to the chemical reaction (4).

### ***Influence of the molar ratio $O_3/NO_{ref}$ on the effectiveness of NO<sub>x</sub> removal***

The ozone demand for NO<sub>x</sub> removal is an important parameter influencing the cost of flue gas denitrification. It depends not only on the chemistry of NO and NO<sub>2</sub> ozonation, but also the mixing pattern of O<sub>3</sub> and NO<sub>x</sub> and the residence time before the absorption process are important. The role of these physical factors is not yet properly understood, but their unfortunate choice can result in a substantial increase of the ozone excess.

The oxidation ratio *OR* and the effectiveness of NO<sub>x</sub> removal were calculated from the formulas (9) and (10) applying the NO and NO<sub>2</sub> concentrations measured in the carrier air after the absorber 20 vs. molar ratio *X* (Fig. 4). Until the molar ratio *X* reached approximately 1.0 the oxidation ratio *OR* was increasing almost proportionally to *X* in accord with the reaction (1). Further growth of the molar ratio flattened the dependence *OR* on *X*, which means that the oxidation rate of the rest of NO declined. The effectiveness of NO<sub>x</sub> removal  $\eta$  was low (< 20%) for the sub-stoichiometric ozone flow rate ( $X \leq 1.0$ ), until the ozone flow rate increased substantially ( $X \gg 1$ ) the rate of NO<sub>x</sub> removal accelerated and achieved 90%. Hence, due to the different chemical reaction rates the NO ozonation process can be divided into two stages: fast oxidation of NO to NO<sub>2</sub> and next much slower reactions (3) and (4) in which N<sub>2</sub>O<sub>5</sub> is finally produced.

### ***Absorption of NO ozonation products: influence of NaOH concentration in aqueous solutions***

The influence of the sodium hydroxide concentration in the aqueous solution serving as sorbent in the absorption column 20 on the dependence of the oxidation ratio *OR* on the molar ratio *X* is shown in Fig. 5. The effect was not significant, however, the oxidation

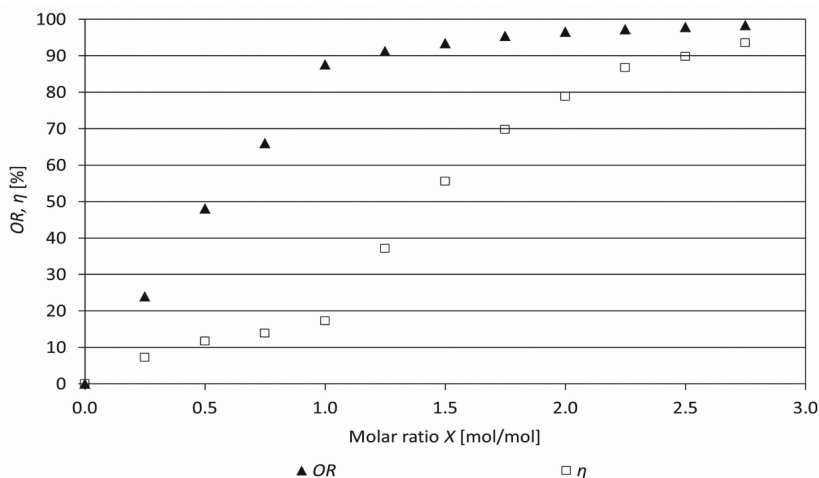


Fig. 4. Oxidation ratio *OR* and the effectiveness of NO<sub>x</sub> removal  $\eta$  vs. molar ratio *X* ( $[NO_{ref}] = 105$  ppm,  $L/G = 10$  dm<sup>3</sup>/m<sup>3</sup>, 0.1M solution of NaOH)

ratio  $OR$  slightly improved when the NaOH concentration increased, especially for the over-stoichiometric conditions ( $X > 1.0$ ). This phenomenon can be explained supposing more efficient absorption of  $NO_2$  in highly alkaline solutions and weaker disproportionate effect [20].

The effect of the NaOH concentration in the solution on the effectiveness of  $NO_x$  removal was more interesting (Fig. 6). Approximately, until  $X \leq 1$  the influence of the NaOH concentration on the dependence of the effectiveness of  $NO_x$  removal  $\eta$  on molar ratio  $X$  was insignificant and weakly diverse. This can be explained by almost complete consumption of ozone in the oxidation process of NO and ineffective  $NO_2$  absorption.

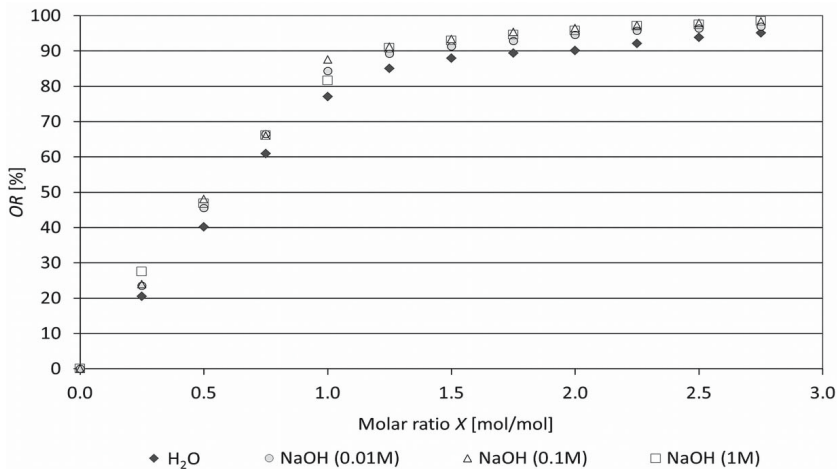


Fig. 5. Oxidation ratio  $OR$  vs. the molar ratio  $X$  depending on the NaOH concentration ( $[NO_{ref}] = 100$  ppm,  $L/G=10$  dm<sup>3</sup>/m<sup>3</sup>)

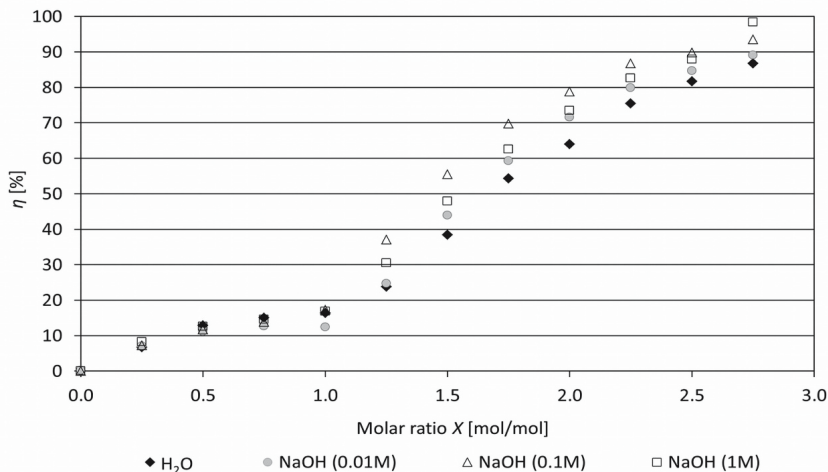


Fig. 6. Effectiveness of  $NO_x$  removal  $\eta$  vs. the molar ratio  $X$  depending on the NaOH concentration ( $[NO_{ref}] = 100$  ppm,  $L/G=10$  dm<sup>3</sup>/m<sup>3</sup>)



Only when  $X > 1.0$  the effectiveness of NO<sub>x</sub> removal improved for higher concentrations of NaOH; the effect was more explicit, however not dramatic. It is not a surprise that also water appeared to be an effective absorbent [9, 20].

### ***The impact of liquid to the gas ratio (L/G)***

The influence of the intensity of sorbent spraying into the carrier air flowing through the absorption column on the oxidation ratio  $OR$  for the concentration of NaOH 0.1 M is presented in Fig. 7. The observed effect was very weak in the studied range of  $L/G = 0 \div 10$ . Because the value  $L/G = 0$  means that sorbent was not flowing through the column [26], Fig. 7 indicates that absorption in NaOH solutions does not influence the process of NO oxidation and that the oxidation ratio  $OR$  values calculated applying NO measured after the absorption column from the formula (9) are correct.

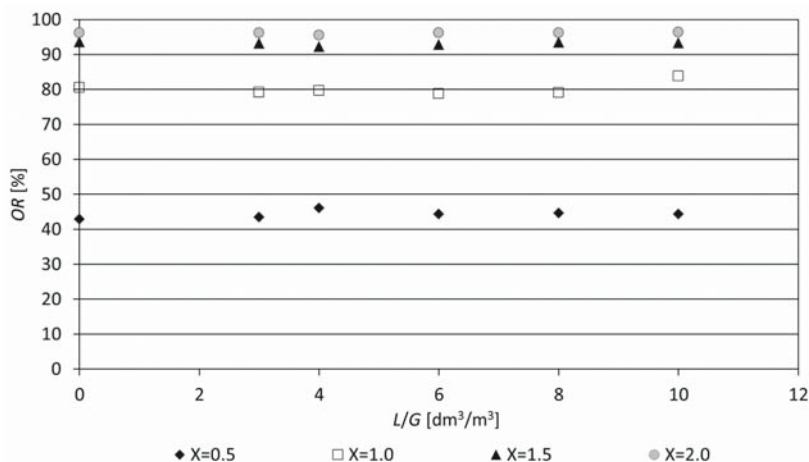


Fig. 7. Oxidation ratio  $OR$  vs. the  $L/G$  ratio depending on the molar ratio  $X$  ( $[NO_{ref}] = 100$  ppm, 0.1 M solution of NaOH)

The influence of the intensity of sorbent spraying into the carrier air on NO<sub>x</sub> removal was more complicated: for  $X = 0.5$  and 1.0 the effectiveness  $\eta$  increased with the  $L/G$  ratio and reached approx. 10% plateau for  $L/G \geq 4$ , whereas for over-stoichiometric  $X$  (1.5 and 2.0) the  $L/G$  ratio did not affect the effectiveness of NO<sub>x</sub> removal (Fig. 8).

The change of the  $\eta = f(L/D)$  profile when the molar ratio  $X$  switched between sub- and over-stoichiometric values can be explained by the consideration of NO oxidation products: for  $X \leq 1.0$  the main oxidation product was NO<sub>2</sub> and the increase of sorbent flow improved the effectiveness for small  $L/G$  ( $< 4$ ). For the over-stoichiometric  $X$  (1.5 and 2.0) perhaps the NO ozonation products were predominated by N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub> disappeared from the carrier air. This also explains high effectiveness of NO<sub>x</sub> removal even without scrubbing ( $L/G = 0$ ) (Fig. 8).

### ***Influence of the initial concentration of NO<sub>ref</sub>***

The effect of the initial concentration of nitrogen oxide NO<sub>ref</sub> on its oxidation rate was investigated by changing NO<sub>ref</sub> in the carrier air and adjusting the ozone concentration in

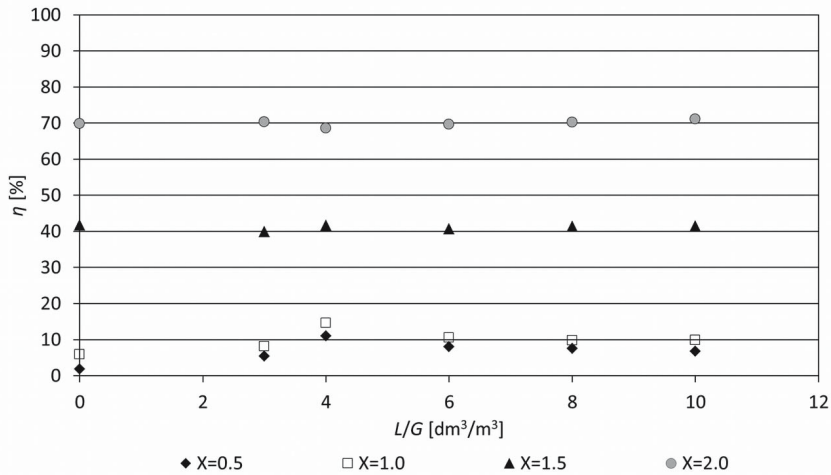


Fig. 8. Effectiveness of NO<sub>x</sub> removal  $\eta$  vs. the  $L/G$  ratio depending on the molar ratio  $X$  ( $[NO_{ref}] = 100$  ppm, 0.1 M solution of NaOH)

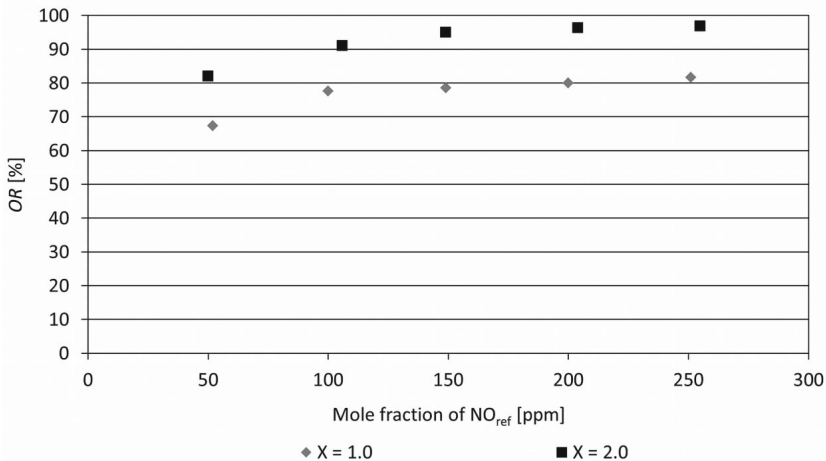


Fig. 9. Oxidation ratio  $OR$  vs. the reference concentration  $NO_{ref}$  at the molar ratios  $X = 1.0$  and  $2.0$  ( $L/G = 10$  dm<sup>3</sup>/m<sup>3</sup>, 0.1 M solution of NaOH)

oxygen supplied by the ozone generator 7 to assure the molar ratio  $X = 1.0$  or  $2.0$ . In such a way the conditions of mixing ozone and nitric oxide remained unchanged.

Fig. 9 shows that the decrease of  $NO_{ref}$  concentration had a similar impact on the oxidation process of NO for the molar ratios  $X = 1.0$  and  $2.0$ ; the oxidation ratio  $OR$  diminished with the decrease of NO concentration.

The same effect was observed for the removal of  $NO_x$ ; the effectiveness  $\eta$  diminished with the decrease of NO concentration below 150 ppm (Fig. 10). In this case the impact appeared to be even stronger.

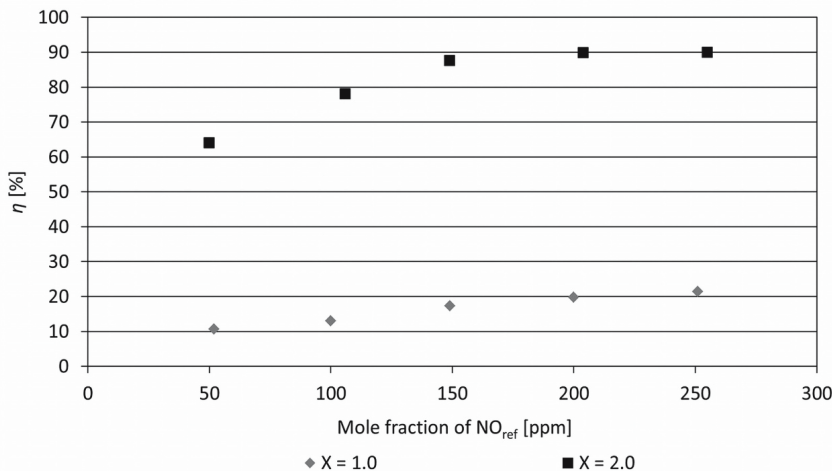


Fig. 10. Effectiveness of NO<sub>x</sub> removal  $\eta$  vs. the reference concentration NO<sub>ref</sub> for the molar ratios  $X = 1.0$  and  $2.0$  ( $L/G = 10 \text{ dm}^3/\text{m}^3$ ,  $0.1 \text{ M}$  solution of NaOH)

The fall of the effectiveness of NO<sub>x</sub> removal can be an effect of diminished rates of the chemical reactions (1), (3), and (4) and abated efficiency of the oxidation products scrubbing for the diminished NO<sub>ref</sub> concentrations below 150 ppm.

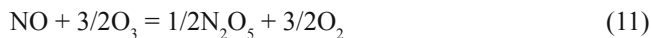
## DISCUSSION

The obtained results are qualitatively similar to the results of the previous lab-scale experimental studies, when the oxidation products of NO were absorbed in bubble washers [5]. This time it was seen even more distinctly that for  $[\text{NO}_{\text{ref}}] \cong 100 \text{ ppm}$  the process of NO ozonation can be divided into two stages depending on the molar ratio  $X$  values. For the sub-stoichiometric values ( $X \leq 1.0$ ) the oxidation of NO to NO<sub>2</sub> was the predominating process and the oxidation ratio  $OR$  reached approx. 90%. The concentration of NO<sub>2</sub> rose, because its absorption was inefficient and the consumption rate by the reaction (3) was small (Fig. 3). The effectiveness of NO<sub>x</sub> removal was below 20%. In the second stage ( $X > 1.0$ ) the overdosed ozone oxidized NO<sub>2</sub> which led to dinitrogen pentoxide formation and improvement of the effectiveness of NO<sub>x</sub> removal above 90%.

There are some quantitative differences between the results obtained in the lab- and pilot scale studies [5]. The scale effect in the NO oxidation process was not substantial; the oxidation ratio  $OR$  achieved 90% in the pilot scale installation, while in lab-scale it was 95% for  $X = 1.0$ . This difference can be explained by more difficult conditions of ozone and NO mixing in the much larger pilot-scale duct.

The scale effect was more evident for the effectiveness of NO<sub>x</sub> removal. In the lab-scale studies the effectiveness  $\eta$  exceeded 90% for the molar ratio  $X = 1.5$ , whereas in the pilot plant studies to reach such value of the effectiveness  $\eta$  the ozone excess had to increase up to  $X = 2.75$  (Fig. 4). This substantial discrepancy can be explained taking into consideration the fact that N<sub>2</sub>O<sub>5</sub> at the room temperature forms aerosol, whose particles were more effectively precipitated in a bubble washer than in the scrubber.

The significance of the molar ratio value  $X = 1.5$  can be explained by assumption that the conversion of  $\text{NO}_2$  into  $\text{N}_2\text{O}_5$  is a necessary condition for the efficient removal of  $\text{NO}_x$ . A combination of the chemical equations (1), (3) and (4) leads to the summary chemical reaction:



It means that the stoichiometric molar ratio  $\text{O}_3/\text{NO}$  should be  $X = 1.5$ , which is 50% more than it results from the model of fast oxidation of  $\text{NO}$  by ozone in the Eq. (1).

## CONCLUSIONS

The results of the conducted experimental studies on the removal of  $\text{NO}_x$  ( $[\text{NO}_{x,\text{ref}}] = 50 \div 250$  ppm) from the carrier air applying  $\text{NO}$  ozonation and the oxidation products scrubbing lead to the following conclusions:

1. The mechanism of  $\text{NO}_x$  removal from gases by the method of  $\text{NO}$  ozonation and absorption depends on the molar ratio  $X = \text{O}_3/\text{NO}_{\text{ref}}$ : for  $X \leq 1.0$  the oxidation of  $\text{NO}$  to  $\text{NO}_2$  is the predominating reaction and  $\text{NO}_2$  is poorly absorbed, for  $X \gg 1.0$   $\text{NO}_2$  undergoes further conversion in reactions (3) and (4) and the absorption of the oxidation products becomes effective.
2. The effectiveness of  $\text{NO}_x$  removal appeared to be sensitive to the installation scale; its increase results in a higher demand of ozone supply.
3. The concentration of  $\text{NaOH}$  in aqueous solutions had a small impact on the effectiveness of  $\text{NO}_x$  removal from gas and lack of sorbent injection only slightly decreases the effectiveness  $\eta$ .
4. The effectiveness of  $\text{NO}_x$  removal was distinctly reduced when the initial concentration of  $\text{NO}_{\text{ref}}$  diminished below 150 ppm.

## SYMBOLS

$d$	absorption column diameter, mm
$D$	carrier gas channel diameter, mm
$k$	reaction rate constant, $\text{dm}^3, \text{mol}, \text{s}$
$L/G$	liquid to gas ratio, $\text{dm}^3/\text{m}^3$
$[\text{NO}_x]$	mole fractions of $\text{NO}_x$ , ppm
$[\text{NO}]$	$\text{NO}$ mole fraction, ppm
$[\text{NO}_2]$	$\text{NO}_2$ mole fraction, ppm
$OR$	oxidation ratio of $\text{NO}$ in the gas phase, %
$X$	molar ratio of $\text{O}_3$ to $\text{NO}$ , mol/mol
$\eta$	effectiveness of $\text{NO}_x$ removal, %

### Subscripts

$b$	backward
$f$	forward
$i$	inner
$out$	output

ref reference  
l in liquid

### ACKNOWLEDGEMENTS

*The results presented in the paper were obtained from research work co-financed by the National Centre of Research and Development in the framework of Contract SP/E/1/67484/10 – Strategic Research Programme – Advanced technologies for obtaining energy: Development of a technology for highly efficient zero-emission coal-fired power units integrated with CO<sub>2</sub> capture.*

### REFERENCES

- [1] Bertram, T.H., & Thornton, J.A. (2009). Towards a general parameterization of N<sub>2</sub>O<sub>3</sub> reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chlorides. *Atmospheric Chemistry and Physics*, 9, 8351–8363.
- [2] Chironna, R.J., & Altshuler, B. (1999). Chemical aspects of NO<sub>x</sub> scrubbing. *Pollution Engineering*, 4, 32–36.
- [3] Directive 2001/80/EC of the European Parliament and of the Council. 2001.
- [4] Directive 2010/75/EU of the European Parliament and of the Council. 2010.
- [5] Dora, J., Gostomczyk, M.A., Jakubiak, M., Kordylewski, W., Mista, W., & Tkaczuk, M. (2009). Parametric studies of the effectiveness of oxidation of NO by ozone. *Chemical and Process Engineering*, 30, 621–634.
- [6] Ellison, W. (2003). *Chemical process design alternatives to gain simultaneous removal in scrubbers*. Las Vegas: POWER-GEN International.
- [7] Fu, Y., & Diwekar, U.M. (2004). Cost effective environmental control technology for utilities. *Advances in Environmental Research*, 8, 173–196.
- [8] Głowiński, J., Biskupski, A., Słonka, T., & Tylus, W. (2009). Absorption of nitrogen oxides at the final stage of ammonium nitrite production. *Chemical and Process Engineering*, 30, 217–229.
- [9] Jakubiak, M., & Kordylewski, W. (2010). Effectiveness of NO<sub>x</sub> removal from gas via preoxidation of NO with ozone and absorption in alkaline solutions. *Chemical and Process Engineering*, 31, 699–709.
- [10] Joshi, J.B., Mahajani, V.V., & Juvekar, V.A. (1985). Absorption of NO<sub>x</sub> gases. *Chemical Engineering Communications*, 33, 1–92.
- [11] Kryza, M., Błaś, M., Dore, A.J., & Sobik, M. (2010). Fine-Resolution Modeling of Concentration and Deposition of Nitrogen and Sulphur Compounds for Poland – Application of the FRAME Model. *Archives of Environmental Protection*, 36, 49–62.
- [12] Krotla, K., Wala, T. & Brudziana, P. (2009). Porównanie nakładów inwestycyjnych i kosztów eksploatacji urządzeń typu SCR w zależności od stopnia redukcji NO<sub>x</sub>, IX Conference Research and Development in Power Engineering – RDPE, Warszawa, 8–11 December (2009).
- [13] Nelo, S.K., Leskela, K.M., & Sohlo, J.J.K. (1997). Simultaneous Oxidation of Nitrogen Oxide and Sulfur Dioxide with Ozone and Hydrogen Peroxide. *Chemical Engineering & Technology*, 20, 40–42.
- [14] Nist database: www.nist.gov, 2012.
- [15] Omar, K. (2008). *Evaluation of BOC's Lotox process for the oxidation of elemental mercury in flue gas from a coal-fired boiler*. Wyoming: Western Research Institute Laramie.
- [16] Prather, M.J., & Logan, J.A. (1994). Combustion's impact on the global atmosphere. 25th Symposium (International) on Combustion, Pittsburgh, USA, 31 July – 5 August 1994, 1513–1527.
- [17] Pronobis, M. (2002). *Modernization of power plants boilers (in Polish)*. Warszawa: Wydawnictwo Naukowo-Techniczne.
- [18] Skalska, K., Miller, J.S., & Ledakowicz, S. (2011). Kinetic model of NO<sub>x</sub> ozonation and its experimental verification. *Chemical Engineering Science*, 66, 3386–3391.
- [19] Thielmann, M., Scheibler, E., & Wiegand, K.W. (2005). *Nitric Acid, Nitrous Acid, and Nitrogen Oxides*. 177–255. Weinheim: Ullmann's Encyclopedia of Industrial Chemistry, Wiley-Vch.
- [20] Thomas D., & Vaderschuren, J. (1999). Analysis and prediction of the liquid phase composition for the absorption of the nitrogen oxides into aqueous solutions. *Separation and Purification Technology*, 18, 37–45.

BADANIA W SKALI PILOTOWEJ DOTYCZĄCE EFEKTYWNOŚCI USUWANIA NO<sub>x</sub>  
PORZEZ UTLENIANIE NO I ABSORPCJĘ

Przedstawiono wyniki badań doświadczalnych dotyczące usuwania NO<sub>x</sub> z gazów z zastosowaniem ozonu jako utleniacza i absorpcji wyższych tlenków azotu w roztworach wodorotlenku sodu. Badania prowadzono na strumieniu powietrza 200 m<sup>3</sup>/h w instalacji pilotowej będącej prototypem instalacji kotłowej odprowadzenia spalin i skrubera IOS. Wykazano, że w zakresie [NO<sub>ref</sub>] = 50÷250 ppm mechanizm ozonizacji NO zależy od stosunku molowego  $X = O_3/NO_{ref}$ : dla  $X \leq 1.0$  przeważa utlenianie NO do NO<sub>2</sub> a NO<sub>2</sub> jest słabo absorbowany, dla  $X \gg 1.0$  NO<sub>2</sub> ulega dalszemu utlenianiu do N<sub>2</sub>O<sub>5</sub>, który jest efektywnie absorbowany w skruberze. Stosunek molowy przy całkowitej konwersji NO do N<sub>2</sub>O<sub>5</sub> wynosi  $X = 1.5$ , w przeprowadzonych badaniach, aby osiągnąć efektywność  $\eta \geq 90\%$  stosunek  $X$  był dużo większy (2,75).