DE GRUYTER OPEN
Chemical and Process Engineering 2017, 38 (1), 177-191
DOI: 10.1515/cpe-2017-0014

INFLUENCE OF OXIDIZING REACTOR ON FLUE GAS DENITRIFICATION BY OZONATION AND POSSIBILITY OF BY-PRODUCT SEPARATION

Włodzimierz Kordylewski*[1], Adam Hałat[2], Dariusz Łuszkiewicz[1]

[1]Wroclaw University of Science and Technology, Faculty of Mechanical and Power Engineering, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

[2]Wrocław University of Science and Technology, Faculty of Chemistry, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Results of laboratory scale research have been presented on the effects of an oxidizing reactor on ozone consumption and by-producs composition and separation of simultaneous NO_x and SO_2 removal from a carrier gas by ozonation method and absorption in an alkaline solution. The additional Dreschel washer added before two washers containing 100 ml of 0.1 molar NaOH solution played the role of an oxidation reactor. Its effect was investigated using an empty (dry or wetted) or filled with packing elements washer. The measured by-products in a scrubber and in the oxidizing reactor were SO_3^{2-}, SO_4^{2-}, NO_2^- and NO_3^- ions, respectively. It has been shown that use of oxidizing reactor improves NO_x removal efficiency reducing ozone consumption. Wetting of the oxidation reactor with water enables a preliminary separation of sulphur and nitrogen species between the oxidizing reactor and an alkaline absorber. Application of packing elements in the oxidizing reactor allows to retain 90% of nitrogen compounds in it. Some results were confirmed by tests in pilot scale.

Keywords: ozone, simulated flue gas, denitrification, desulphuration, by-products

1. INTRODUCTION

Oxidative methods for removing nitrogen oxides from flue gas, which consist of pre-oxidation of NO_x and absorption of oxidized components in alkaline solutions, are a promising alternative to the method of NO_x reduction, like SCR. Much research work has been carried out in many countries, such as U.S.A. (Carpenter, 2013), in Asia (Japan (Yamamoto et al., 2001), China (Zhang et al., 2014) and Korea (Mok, 2006)) and also in Europe (Poland (Krzyżyńska and Hutson, 2012) and Denmark (Stamate et al., 2006)). Much effort was devoted to the selection of an appropriate oxidant (Nelo et al., 1997), of which the most effective proved to be ozone (Jaroszyńska-Wolińska, 2009; Nelo et al., 1997).

In the U.S.A., LoTOx (Low Temperature Oxidation for NO_x Control) a method for cleaning exhaust gases from nitrogen oxides has been developed, which went through a commercial implementation. It involves the addition of ozone into exhaust gas duct, and then absorbing NO_x oxidation products in an alkaline absorber (Carpenter, 2013). In Denmark research on ozonation of the exhaust gas from a boiler powered by biomass and oil was conducted, oxidation products being captured in the water scrubber (Stamate et al., 2006). In Japan successful tests were conducted on exhaust gas from a Diesel engine. Moreover, ozone has proven to be helpful in regeneration of the ceramic particulate filter (Okubo et al.,

---

*Corresponding author, e-mail: wlodzimierz.kordylewski@pwr.edu.pl

2006). Fujishima et al. (2008) used the ozonation method to clean exhaust gas from oil combustion. Thanks to special design of an ozone probe they were able to inject ozone to the exhaust gas at the temperature of about 250 °C. Actually, there are about 30 industrial installations using the ozonation method for exhaust gas treatment in the world (Modern Power Systems, 2015).

The main object of further research is optimization of the ozonation method in order to improve its efficiency and reduce ozone consumption (Głomba and Kordylewski, 2014; Jędrusik et al., 2015). It was established that increasing the contact time between ozone and exhaust gas, improves efficiency of NO_x and Hg^0 removal (Dora et al., 2009). Interesting studies were performed by combining ozonation with addition of ethanol (Jie et al., 2016) and pyrolusite (Sun et al., 2011), and applying catalysts (cerium-titanium) (Jie et al., 2014). Results are promising, but the methods are still at the stage of laboratory tests. Different types of gas reactors were used to improve the effects. In case of experimental research of the $LoTO_x$ method an additional reactor to increase the residence time from 0.5 to 6 s was used (Omar, 2008). Zhang at al. (2014) used a stainless steel reactor to provide sufficient reaction time in gas phase and maintain constant temperature of the process.

Important elements of any emission control are its by-products (Carpenter, 2013). As a result of exhaust gas ozonation nitrates and nitrites and sulphites and sulphates are retained in the alkaline absorbent (Kuropka, 2012). Lower oxidized forms, i.e. nitrites and sulphites, are more dangerous for the environment, therefore more attention has to be paid to improve the organization of ozonation for obtaining more friendly by-products (Regulation of the Minister of Environment, 2009).

The aim of this study was to find the best solution for the oxidation reactor by improving its efficiency of the exhaust gas ozonation and subsequent by-product composition optimization. There was also another noteworthy effect of the oxidation reactor relies on the separation of nitrogen and sulfur species. This effect was significant only when the oxidation reactor was wetted. The possibility of separation of sulfur and nitrogen compounds is important from the point of view of their utilization. An attempt to explain the mechanisms of chemical reactions associated with the use of an oxidizing reactor was made. Tests were performed in a lab-scale, but some solutions developed in the lab were tested in a pilot plant.

2. THE MECHANISMS OF CHEMICAL REACTIONS OF NO_X AND SO_2 WITH OZONE

Because the main topic are by-products of nitrogen oxide removal from flue gas by ozonation and absorption in alkaline solutions, a discussion about mechanisms of chemical reactions will be helpful. The basic reaction scheme of NO_x oxidation by ozone in gaseous phase is as follows (Skalska et al., 2011):

$$NO+O_3 \rightarrow NO_2+O_2 \tag{1}$$

$$NO+NO_2=N_2O_3 \tag{2}$$

$$NO_2+O_3 \rightarrow NO_3+O_2 \tag{3}$$

$$NO+NO_3=2NO_2 \tag{4}$$

$$NO_2+NO_3=N_2O_5 \tag{5}$$

$$N_2O_5+H_2O \rightarrow 2HNO_3 \tag{6}$$

$$2O_3+M \rightarrow 3O_2 \tag{7}$$

The products of NO_x oxidation in gaseous phase are determined by the molar ratio O_3/NO in the temperature range of 20−100 °C. For $O_3/NO \approx 1$ the main nitrogenous component of flue gas after ozonation remains NO_2, because the reaction (1) is fast (Skalska et al., 2011) and the product of reaction (2) N_2O_3 is unstable. However, the role of N_2O_3 in the absorber cannot be overestimated, because N_2O_3 is well-soluble, while NO and NO_2 are only weakly-soluble (Sander, 1999). Dissolved N_2O_3 and NO_2 react with water to form nitrous and nitric acid according to:

$$N_2O_{3,aq}+H_2O_{,aq}=2HNO_{2,aq} \tag{8}$$

$$2NO_{2,aq}+H_2O_{,aq}=HNO_{2,aq}+HNO_{3,aq} \tag{9}$$

However, the efficiency NO_x capture in this way (8, 9) from flue gas is limited to about 60% due to the reactions of disproportionation of nitrous acid with release of NO (Joshi et al., 1985):

$$3HNO_{2,aq}=HNO_{3,aq} + 2NO_{aq}+H_2O_{aq} \tag{10}$$

$$2HNO_{2,aq}=NO_{aq}+NO_{2,aq}+H_2O_{aq} \tag{11}$$

Further increasing the molar ratio $O_3/NO > 1$ results in oxidation of NO_2 to NO_3 in reaction (3), which combined with NO_2 gives a very well-soluble dinitrogen pentoxide (N_2O_5) (Wang et al., 2015). In a solution N_2O_5 is converted into stable nitrate ions NO_3^-. In the exhaust gas N_2O_5 reacts with steam and gaseous HNO_3 is formed whose solubility is fivefold higher than that of NO_2 (Sander, 1999). In order to obtain more complete oxidation of NO_x to N_2O_5 longer residence time before the absorber is necessary, therefore an oxidizing reactor was applied in the experiment. The presence of SO_2 in flue gas has no visible impact on the mechanism of NO ozonation, since ozone practically reacts with SO_2 at temperature above 100 °C (Sun et al., 2014):

$$SO_2+O_3\rightarrow SO_3+O_2 \tag{12}$$

Moreover, at temperature > 100 °C thermal decomposition of ozone (7) begins to be of significance (Fridman, 2008). Theoretically, SO_2 could react with nitrogen dioxide:

$$SO_2+NO_2\rightarrow NO+SO_3 \tag{13}$$

However, due to high energy of activation (113 kJ/mol) this reaction could also be neglected (Zhang et al., 2014).

Chemistry of interaction between dissolved nitrogen oxides and sulphur dioxide is much more complicated and important for the by-products of ozonation. There is an old idea, that interaction between nitrogen dioxide and sulphur ions enhances simultaneous capture of these pollutants (Chen et al., 2002). The summary reactions in an alkaline solution are well known, for example for sodium hydroxide solution:

$$HNO_2+NaOH\rightarrow NaNO_2+H_2O \tag{14}$$

$$HNO_3+NaOH\rightarrow NaNO_3+H_2O \tag{15}$$

$$SO_2+2NaOH\rightarrow Na_2SO_3+H_2O \tag{16}$$

In an alkaline solution the absorption of NO_2 is similar to that of water (9), except that decomposition is prevented according to the reaction (14) (Thomas and Vanderschuren, 2000). Nitric acid instantaneously dissociates and leads to the formation of stable nitrate (15). The mechanism of SO_2 absorption in aqueous alkaline solutions could be represented by the following two equations (17, 18) (Hikita H. et al., 1977)

$$SO_2+OH^-=HSO_3^- \tag{17}$$

$$HSO_3^-+OH^-=SO_3^{2-}+H_2O \tag{18}$$

The rate and stoichiometry of SO_3^{2-} and NO_2 reaction have been studied by a number of researchers. Littlejohn et al., (1993) believe that nitrogen dioxide accelerates the catalytic conversion of sulphite ions to sulphate. Chen et al., (2002) suggested that the effectiveness of sodium sulphite (Na_2SO_3) aqueous solution for NO_2 absorption can be explained by the interactions between $NO_{2,aq}$ and SO_3^{2-} expressed by the overall reaction:

$$2NO_2 + SO_3^{2-} + H_2O = 2NO_2^{-} + 2H^{+} + SO_4^{2-} \tag{19}$$

The presence of ozone in solution is an additional factor supporting the oxidation of sulphite ions according to the reaction:

$$SO_3^{2-} + O_{3,aq} \rightarrow SO_4^{2-} + O_{2,aq} \tag{20}$$

3. EXPERIMENTAL

3.1. Lab-scale investigations

Studies on a laboratory scale involved examining the impact of the use of an oxidation reactor on the efficiency of removing pollutants from a carrier gas by the method of ozonation and reaction products obtained in the absorber. A general scheme of the bench scale laboratory is demonstrated in Fig. 1.

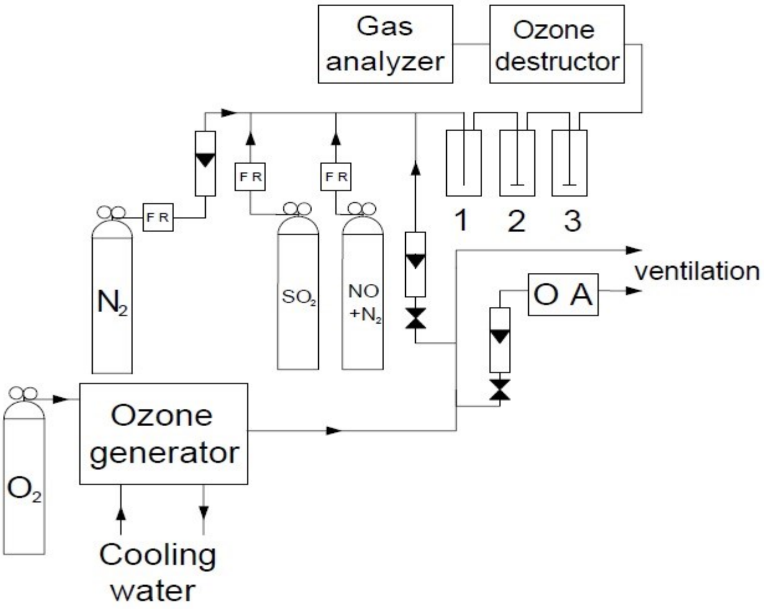

Fig. 1. Scheme of test stand, FR– flow controller, OA – ozone analyser,
1– oxidizing reactor (*OR*), 2, 3 – washers with 0.1 M NaOH solution

The carrier gas was technical nitrogen discharged from a steel cylinder (PN-EN ISO 14175 – N1, 99.5N_2, Air Products), whose flow rate was controlled by a flow controller ALBORG GFC 17. To the carrier gas sulphur dioxide (99.98% SO_2, Linde) and nitrogen oxide (10% NO in N_2, Linde) from a steel cylinder were added and controlled by flow regulators (NO - ERG 1000N_2; SO_2- ERG 100N_2). Ozone was generated in an ozone generator (OZAT CFS-2G) of DEGREMONT TECHNOLOGIES, which was fed by technical oxygen from a steel cylinder (PN-EN ISO 14175 - O1, 99.5% O_2, Air Products). The concentration of ozone was measured by an ozone meter BMT 964 of BMT Messtechnik GmbH.

The carrier gas was flowing through two Dreschel's washers 2, 3, each containing 100 ml of 0.1 M sodium hydroxide solution (POCH S.A.). Before the washers 2, 3 an additional washer 1 served as an oxidizing reactor (*OR*). The effect of oxidizing reactor was tested by the use of: "dry" (empty) and "wet" washer 1 (whose walls were wetted with about 30 ml of distilled water or filled with wet packing elements). Concentrations of contaminations in the carrier gas were measured by exhaust gas analysers (TESTO 350XL, TESTO 350S or Gasmet DX-4000). Due to sensitivity of the electrochemical sensors to ozone, prior to the gas analyser an ozone destructor was placed (Fig. 1). Basic installation test parameters were shown in Table 1. The governing parameter in these studies was the intensity of ozonation defined as the molar ratio X_{NO}:

$$X_{NO}=\frac{O_3}{NO}, \quad \frac{\text{mol } O_3}{\text{mol NO}} \tag{21}$$

Table 1. Basic parameters

Parameter	Unit	Amount
Carrier gas volume flow rate	dm^3/h	130
Ozone concentration	g/Nm^3	7 - 50
NO_x concentration	ppm	400 - 500
SO_2 concentration	ppm	700 - 800
Measurement time	h	0.5
Residence time of the oxidizing reactor	s	6

3.2. Pilot-scale investigations

The stand for pilot research for NO_x removal by ozonation method was shown in our earlier works (Głomba et al., 2016; Głomba and Kordylewski, 2014). The pilot plant was located in the Wrocław CHP (Combined Heat and Power), which provided the exhaust gas with volumetric flow rate of 200 m^3/h from OP 430 boiler. The same methods and equipment were used for measuring the concentration of contaminants. Before the absorber a "wet" oxidizing reactor (*OR*) was added, 200 dm^3 in volume, which provided a residence time of about 6 s (Fig. 2). The exhaust gas temperature at the installation inlet was controlled by the cooler and it was in the range from 60 to 80 °C.

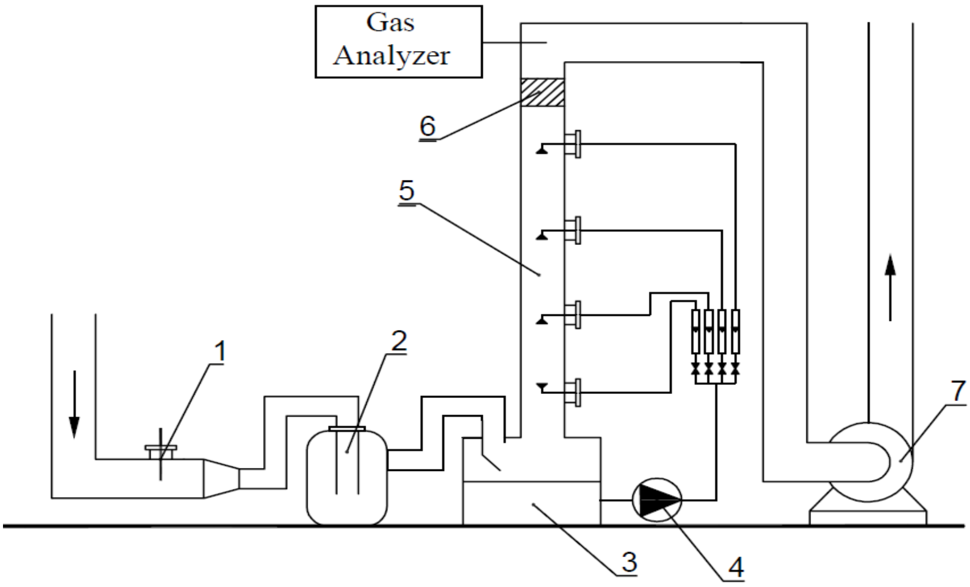

Fig. 2. Fragment of pilot installation for simultaneous NO_x and SO_2 removal from flue gas, 1 – ozone injector, 2 – oxidizing reactor (*OR*), 3 – absorbent tank, 4 – absorbent pump, 5 – spray tower, 6 – demister, 7 – fan

3.3. Research methodology

Efficiency of nitrogen oxides removal from flue gas η_{NOx} was determined by measuring NO_x concentration after ozone destructor C^{out}_{NOx} referring these values to NO_x concentration on installation inlet C^{int}_{NOx}.

$$\eta_{NOx} = \left(1 - \frac{C^{out}_{NOx}}{C^{int}_{NOx}}\right)100\% \tag{22}$$

Samples of the sorption liquid collected from the absorber tank were analysed for the presence of nitrite, nitrate, sulphite and sulphate ions. Concentrations of nitrite and nitrate ions in NaOH solution were determined by adsorption spectrophotometry in UV range using spectrophotometer UV/Vis Cary 50 from Varian. Concentrations of sulphite ions were measured by iodometric method, while sulphate ions were measured by ion chromatography or plasma spectroscopy (ICP).

Based on the obtained results of concentration measurements of nitrate and nitrite ions the number of moles of nitrogen compounds in absorption liquid in the washers 2 and 3 $\left(n^A_{NO_{(2,3)}}\right)$ and those collected from the oxidizing reactor $\left(n^R_{NO_{(2,3)}}\right)$ were calculated. The fraction of nitrogen compounds captured in the oxidizing reactor δ was determined from the following relationship:

$$\delta = \frac{n^R_{NO_{(2,3)}}}{n^R_{NO_{(2,3)}} + n^A_{NO_{(2,3)}}} \tag{23}$$

The degree of conversion of sulphite to sulphate ions (η_{SO4}) was determined by referring the number of Na_2SO_4 moles (n_{SO4}) to the sum of sulphite (n_{SO3}) and sulphate moles in the absorption liquid:

$$\eta_{SO4} = \frac{n_{SO4}}{n_{SO3} + n_{SO4}} \cdot 100\% \tag{24}$$

4. INFLUENCE OF OXIDIZING REACTOR ON EFFECTIVENESS OF NO REMOVAL AND BY-PRODUCT COMPOSITION

4.1. Oxidation reactor without filling

The investigations were conducted in the lab-scale setup (Fig. 1), wherein the carrier gas (N_2) was doped only with NO, so that its concentration was about C^{int}_{NOx} = 500 ppm. The duration of a single measurement was 30 minutes. The molar ratio X_{NO} was varied from 0 to 2.0.

Dynamics of the process of NO ozonation was illustrated by measuring changes of NO, NO_2 and NO_x concentrations with time for $X_{NO} = 1.0$ after the ozone destructor (Fig. 3). The values of nitrogen oxide concentration were stabilized within approx. 10 minutes after the injection of ozone to the carrier gas. The use of the oxidizing reactor did not change the character of NO_x response to ozonation compared to the situation without oxidizing reactor (Kordylewski et al., 2013).

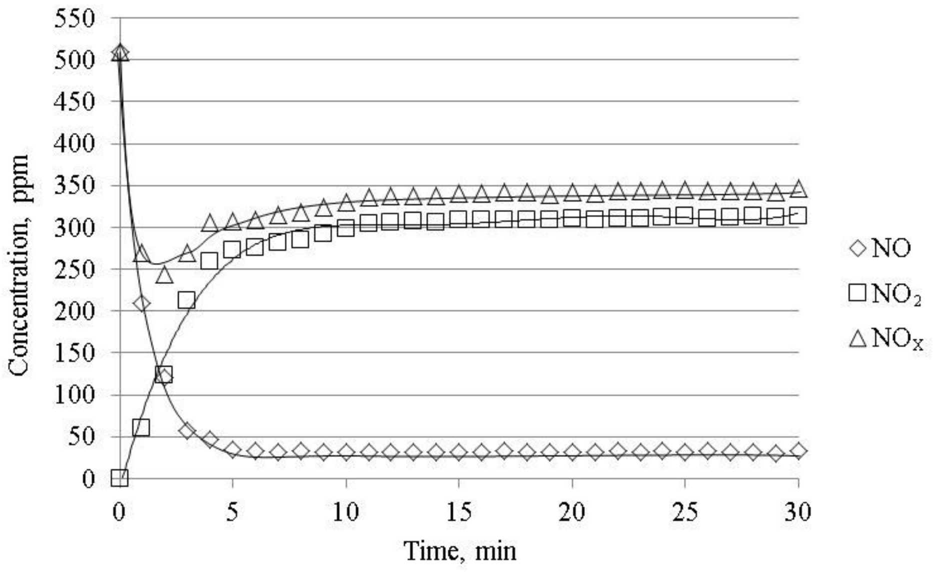

Fig. 3. Changes in NO, NO_2 and NO_x concentrations with time in the carrier gas after start of the ozone feed for $X_{NO} = 1.0$ ("dry" *OR*)

The impact of the oxidizing reactor (*OR*) on the efficiency of NO removal from the carrier gas for the molar ratio X_{NO} in the range of 1.0–2.1 is shown in Fig. 4. The oxidizing reactor improves the efficiency of NO_x removal. The best results were achieved for the "wet" oxidizing reactor, e.g. for $X_{NO} = 1.4$, NO removal efficiency was about 93%.

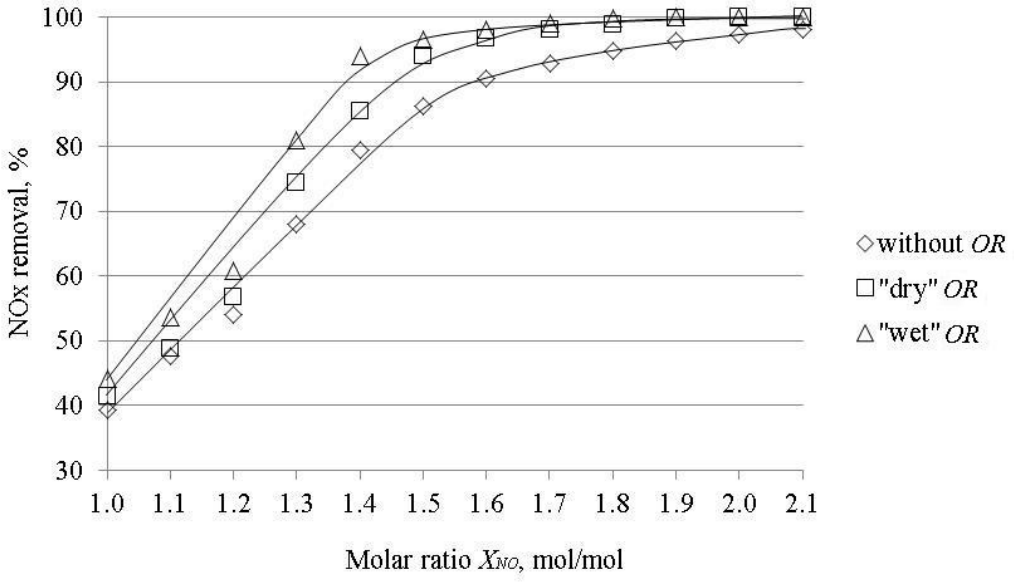

Fig. 4. The influence of the oxidizing reactor (*OR*) on the efficiency of NO_x removal from the carrier gas, (C_{NOx}^{int} = 500 ppm)

Solutions from the washers 2 and 3 and washings from the "wet" oxidizing reactor (*OR*) were analysed for the presence of nitrite and nitrate ions. Figure 5 shows how the number of moles of nitrate and nitrites ions varied vs. the molar ratio X_{NO}.

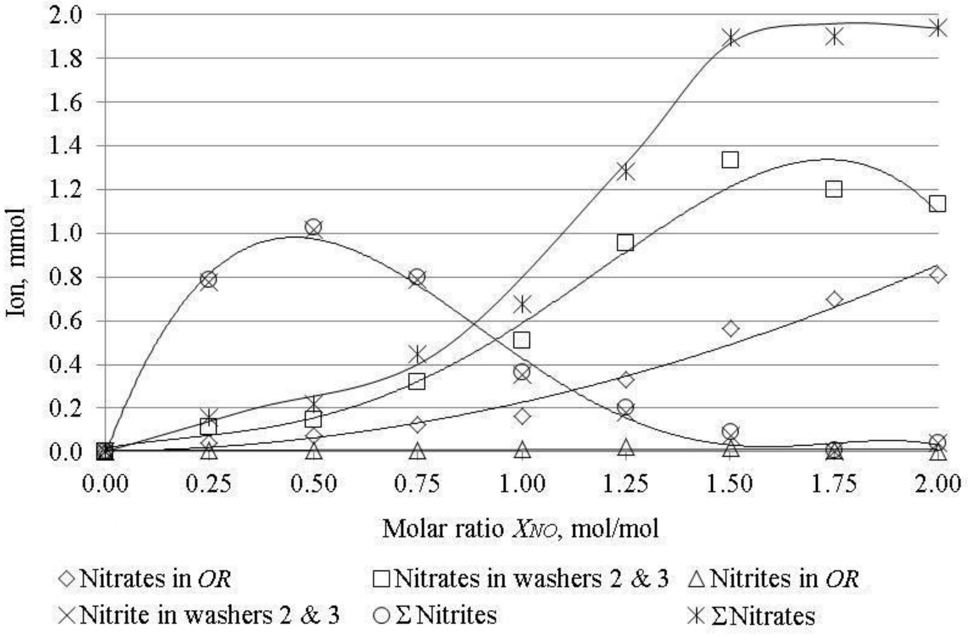

Fig. 5. The influence of intensity of ozonation (X_{NO}) on the composition of by-products in the liquids collected from washers 2&3 and "wet" *OR*

With increasing intensity of ozonation X_{NO}, the number of nitrate ions was increasing and the number of nitrite ions was decreasing in absorbent from the oxidizing reactor and the washers 2 and 3, respectively. Nitrogen in the inlet carrier gas and in the products (NO_x in the outlet carrier gas, nitrates and nitrites in the solutions) was balanced with error not exceeding 10%. The fractions of nitrogen compounds captured in the washers 2 and 3 and in the "wet" oxidizing reactor (*OR*) depending on the molar ratio X_{NO} are shown in Fig. 6.

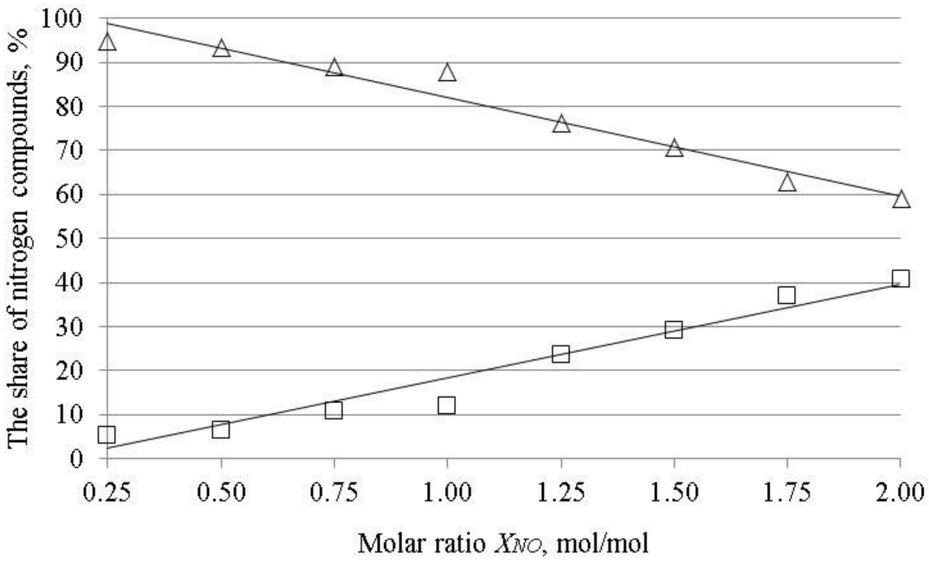

Fig. 6. The fractions of nitrogen compounds δ captured in (ΔΔΔ) washers 2&3 and (□□□) "wet" *OR* vs. the molar ratio X_{NO}

A part of the nitrogen compounds was retained in the "wet" oxidation reactor, and its share grew up with the ozone increasing intensity. For example, at $X_{\mathrm{NO}} = 2.0$ the amount of nitrate and nitrite ions measured in the "wet" oxidizing reactor constituted 40% of their total quantity retained in all washers 1, 2 and 3.

4.2. Oxidizing reactor with packing elements

In order to increase the fraction of captured nitrogen compounds in the oxidizing reactor, different packing elements of the oxidizing reactor were applied, which should enlarge the contact surface of N_2O_5 with water. As packing elements the Białecki's rings made of stainless steel (440 m^2/m^3) and the Rashig rings made of ceramic (243 m^2/m^3) and glass (253 m^2/m^3) were used (Wallas, 1988). The packing elements before measurements were wetted by about 30 ml of distilled water. The results of measurements are shown in Table 2.

The use of packing rings made of stainless steel resulted in retention of approx. 92% of nitrogen species in the oxidation reactor, which means a prominent improvement in relation to the reactor without packing elements. Moreover, the use of packing elements resulted in an increase in the efficiency of denitrification for $X_{NO} = 1.0$.

Table 2. Nitrate and nitrites ions in the washers 2 and 3 and in the oxidizing reactor (*OR*)

Packing elements/material	X_{NO}	NO_x inlet	NO_x outlet	Washers 2&3		*OR*		η_{NOx}	δ
				NO_2^-	NO_3^-	NO_2^-	NO_3^-		
		ppm	ppm	mmol	mmol	mmol	mmol	%	%
No	1.0	482	160	0.024	0.888	0.006	0.221	66.8	19.9
No	1.5	523	9	0.040	0.980	0.005	0.400	98.3	32.7
Yes/stainless steel	1.0	550	40	0.048	0.224	0.130	2.180	92.7	82.9
Yes/stainless steel	1.5	550	0	0.016	0.118	0.100	1.990	100	91.6
Yes/ceramic	1.0	450	78	0.044	0.230	0.050	0.770	82.7	79.0
Yes/ceramic	1.5	450	0	0.014	0.270	0.020	0.950	100	78.2
Yes/glass	1.0	508	72	0.182	0.306	0.020	0.722	85.8	66.9
Yes/glass	1.5	500	0	0.012	0.164	0.015	0.944	100	87.9

δ- fraction of nitrogen compounds captured in oxidizing reactor (see formula 22)

5. INFLUENCE OF OXIDIZING REACTOR ON EFFECTIVENESS OF SIMULTANEOUS REMOVAL OF NO AND SO_2 AND BY-PRODUCTS

5.1. Oxidizing reactor without packing elements

The investigations were conducted in the lab-scale setup (Fig. 1), but the carrier gas (N_2) was doped with NO and SO_2, to reach their initial concentrations of about 400 ppm and 800 ppm, respectively. The duration of a single measurement time was 30 minutes. The molar ratio X_{NO} was varied from 0 to 2.0.

The influence of the oxidizing reactor on the efficiency of NO removal depends on the molar ratio X_{NO} and is shown in Fig. 7. No remark is made on sulphur dioxide, because it was completely removed from the carrier gas in all measurements.

Dynamics of the process was very similar to that of NO removal, wherein absorption of sulphur dioxide in the NaOH solution took place immediately, while stabilization of nitrogen oxide concentrations followed by about 10 minutes. Comparison of the efficiency η_{NO} revealed a substantial difference between the experiments with and without the oxidizing reactor, again the highest efficiency was achieved for the "wet" oxidizing reactor.

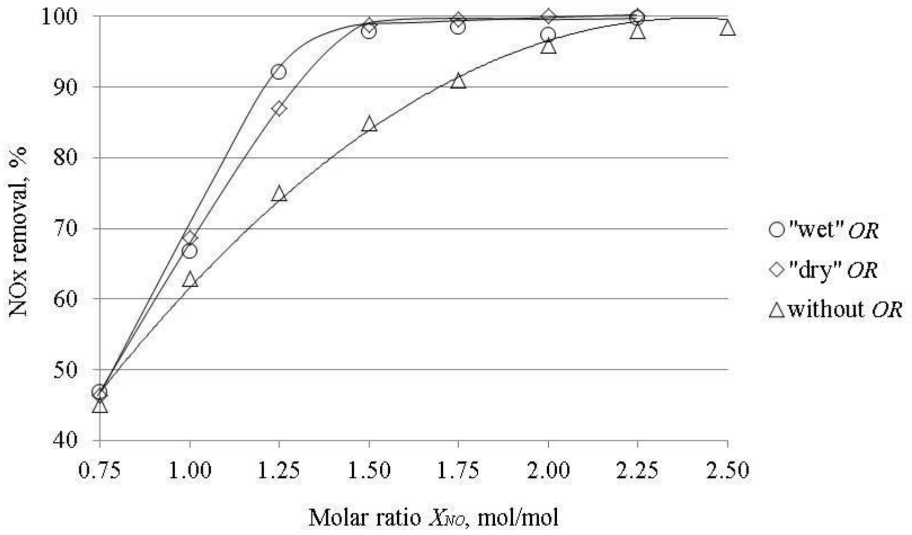

Fig. 7. The influence of oxidizing reactor on NO_x removal efficiency vs. molar ratio X_{NO} for initial concentration of approx. 400 ppm NO and 800 ppm SO_2

Figure 8 shows by-product composition (amount of ions measured in the washers 2 and 3, and the *OR*) vs. molar ratio X_{NO} when "wet" oxidizing reactor was used. With an increase of the ozonation intensity X_{NO} grew nitrates, while decreasing the amount of nitrites in the solution. The by-product composition for "dry" oxidizing reactor had the same character, only in this case nitrates were formed more slowly.

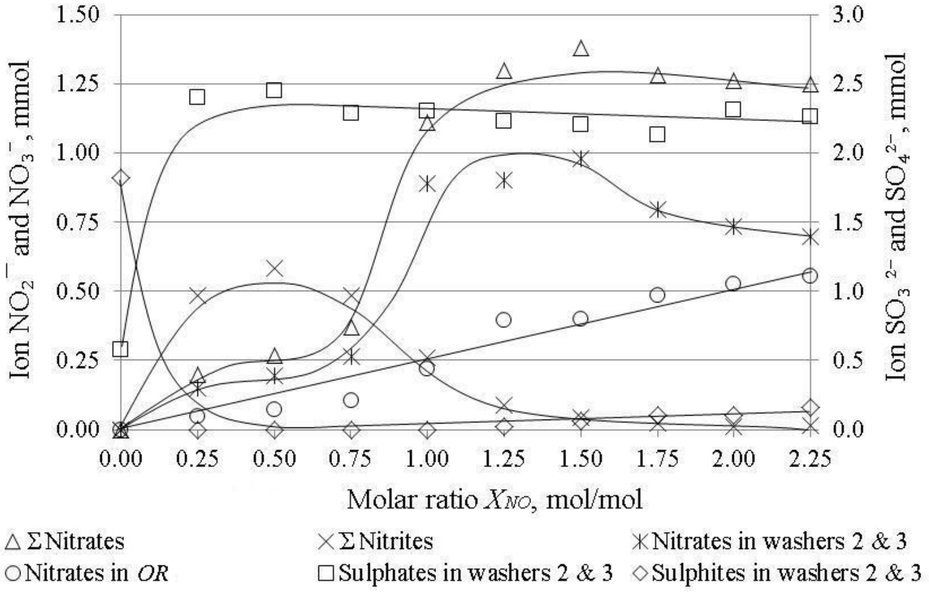

Fig. 8. Composition of by-products of simultaneous removal of NO and SO_2 vs. molar ratio X_{NO} when "wet" oxidizing reactor was used

In the earlier work (Głomba et al., 2016) it was demonstrated that ozonation of gas containing sulphur dioxide, promotes the conversion of sulphite to sulphate being absorbed in the alkaline solution although complete oxidation of sulphite required the ratio $\frac{O_3}{SO_2}$ of at least 2.0. In the case of ozonation of gas containing NO and SO_2 complete oxidation of sulphite occurred at much lower values, i.e. $\frac{O_3}{NO+SO_2} \approx 0.1$ for $\frac{NO}{SO_2} = 0.5$, which indicates there was another agent which stimulated this process.

The agent is nitrogen dioxide, which accelerates oxidation of SO_3^{2-} ions. Littlejohn et al. (1993) suggest that NO_2 acts catalytically in this process.

The fraction of nitrogen compounds captured in the washers 2 and 3 and in the "wet" oxidizing reactor *OR* is shown in Fig. 9. The obtained results also indicate that sulphur dioxide was not removed from the carrier gas in the oxidation reactor, the washings from the oxidizing reactor contained only nitrites and nitrates.

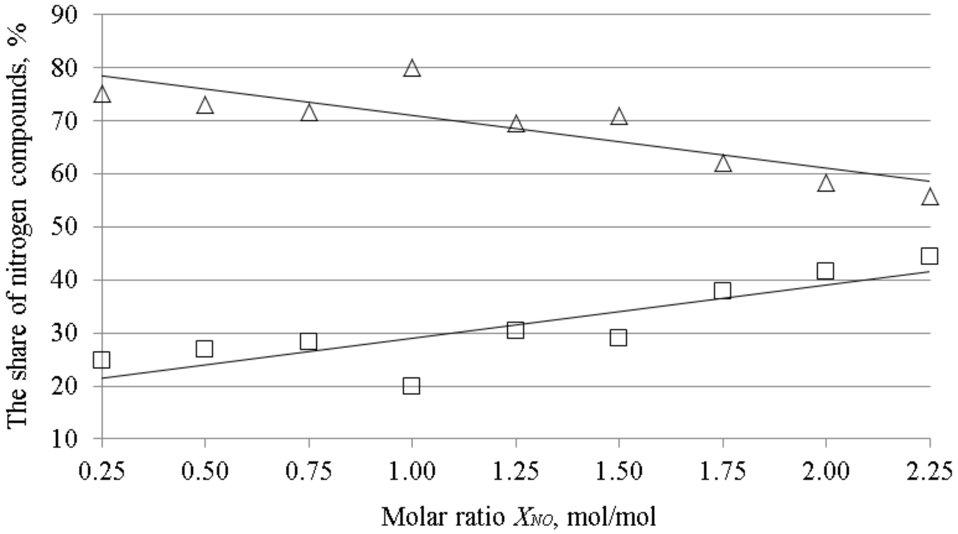

Fig. 9. The fractions of nitrogen compounds δ captured in (ΔΔΔ) washers 2&3 and (□□□) "wet" *OR* vs. the molar ratio X_{NO}

5.2. „Wet"oxidizing reactor with packing elements

The "wet" packed bed in the oxidizing reactor was used to maximize the fraction of contaminates captured in the reactor. The same packing elements were as those of NO_x removal from the carrier gas in Section 4.2. The results of measurements are summarized in Table 3.

Table 3. Results of analysis of absorbents from washers 2 and 3 and the oxidizing reactor (*OR*) for different filling materials

Packing elements /material	X_{NO}	Washers 2&3				*OR*			η_{NOx}	δ
		NO_2^-	NO_3^-	SO_3^{2-}	SO_4^{2-}	NO_2^-	NO_3^-	SO_4^{2-}		
		mmol	mmol	mmol	mmol	mmol	mmol	mmol	%	%
No	1.0	0.240	0.890	0.02	2.30	0.006	0.22	0.022	66.8	20
No	1.5	0.040	0.980	0.06	2.20	0.005	0.40	0.024	98.3	29
Yes/stainless steel	1.0	0.202	0.126	0.08	2.22	0.05	1.29	0.07	91.7	80
Yes/stainless steel	1.5	0.040	0.164	0.12	2.18	0.03	1.36	0.08	99.5	87
Yes/ceramic	1.0	0.256	0.192	0.09	1.99	0.04	1.12	0.06	88.9	72
Yes/ceramic	1.5	0.050	0.284	0.10	1.97	0.05	1.33	0.07	99.8	81
Yes/glass	1.0	0.244	0.170	0.10	2.10	0.023	0.72	0.10	89.6	64
Yes/glass	1.5	0.060	0.244	0.18	2.07	0.033	0.97	0.11	99.0	77

δ- fraction of nitrogen compounds captured in oxidizing reactor (see formula 22)

Also in this case increased effectiveness of NO_x removal from the carrier gas was noticed, especially significantly for $X_{NO} = 1.0$. In addition, approx. 80% of nitrogen compounds was retained in the oxidation reactor regardless of the packing material. The positive effect of packing elements was probably due to an increase in contact surface of N_2O_5 with the solution.

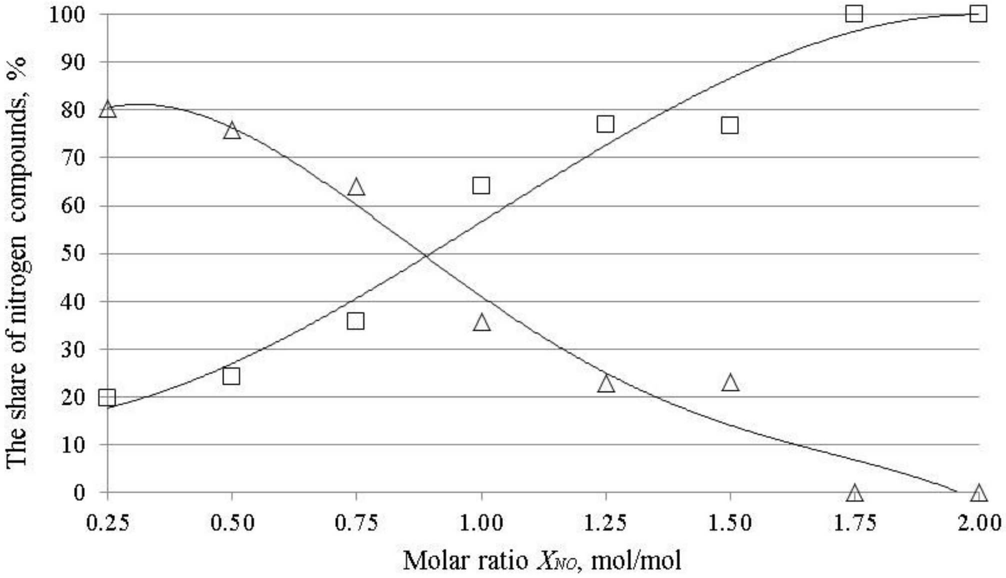

Fig. 10. Separation of the fraction of nitrogen compounds (NO_2^- and NO_3^-) δ between the (ΔΔΔ) washers2&3 and the (□□□) oxidizing reactor (*OR*) with glass packing elements vs. the molar ratio X_{NO}

More specifically, separation of nitrogen ions between the washers 2 and 3 and the oxidation reactor packed with Rasching rings are presented as a function of X_{NO} in Fig. 10. Starting from $X_{NO} > 1.75$ virtually almost all nitrogen (as nitrate) was retained in the oxidizing reactor. As for sulphur dioxide, a little was retained in the oxidation reactor; only 1 and 4% of initial content of SO_2 in the reactor without packing elements and with packing elements, respectively. These results should be considered as promising because they confirm the possiblity of nitrogen and sulphur compound separation.

5.3. Use of oxidizing reactor in pilot plant studies

Also in the pilot-scale investigations positive effects of the "wet" oxidizing reactor were found. For each molar ratio X_{NO} the efficiency of NO_x removal was higher from about 20 to 40% than that without the reactor. For example, for the molar ratio $X_{NO} \approx 1.7$ the efficiency of NO_x removal from flue gas reached practically 100% when the oxidizing reactor was in use (Fig. 11).

Unfortunately, not many results concerning by-products captured in the absorber were obtained, because difficulties were encountered in the analysis of nitrogen compounds by the spectrophotometric method. The difficulties were caused by the fact that the absorber was fed with water from Odra river containing some impurities (Głomba et al., 2016). This did not prevent analysis of sulphites and sulphates in the absorber. As in the laboratory in this case it has also been found that the ozone treatment of flue gas significantly improves the conversion efficiency of SO_3^{2-} to SO_4^{2-} (Table 4).

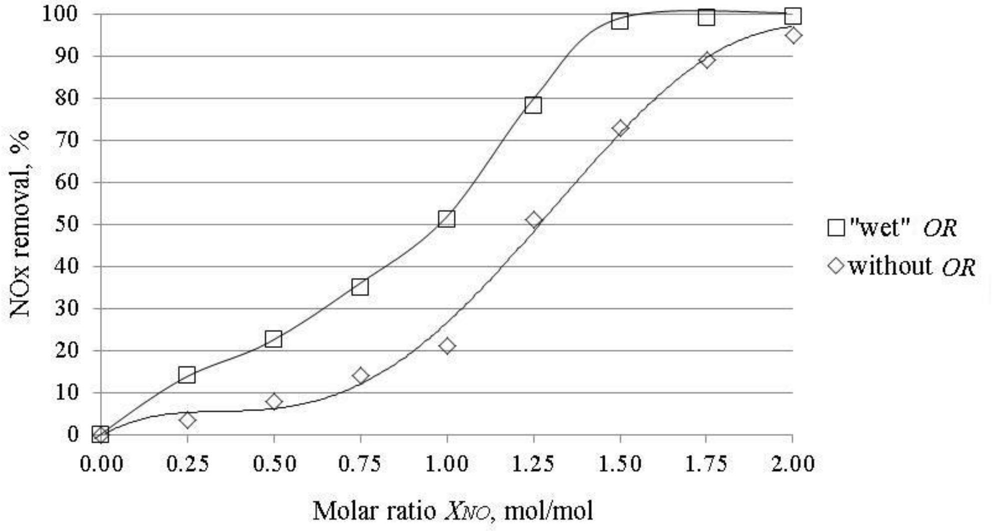

Fig. 11. Efficiency of NOx removal vs. the molar ratio X_{NOx} in the pilot-plant

Table 4. Influence of flue gas ozonation on the conversion efficiency (η_{SO4}) of SO_3^{2-} to SO_4^{2-}

X_{NO}	Initial SO_2 concentration	Scrubber			η_{SO4}
		SO_3^{2-}	SO_4^{2-}	$SO_3^{2-} + SO_4^{2-}$	
	ppm	mmol	mmol	mmol	%
1.0	136	99.3	512.4	611.7	83.8
2.0	207	80	2599	2679	97.0
2.25	203	0	2452	2452	100.0

6. SUMMARY

Investigations carried out in the lab- and pilot-scale enabled to draw the following conclusions:

- The oxidizing reactor improves the efficiency of denitrification, which reduces consumption of ozone.
- Denitrification is much more efficient in humid gas phase with packing elements than in an aqueous absorption solution.
- Wetting of the oxidation reactor with water enables a preliminary separation of sulphur and nitrogen compounds.
- Application of packing elements in the oxidizing reactor allows to retain 90% of nitrogen compounds in the reactor.

The results presented in this paper were obtained in the study financed by the National Centre for Research and Development under the Contract SP/E/1/67484/10- Strategic project- Advanced technologies energy generation: Development of technology for highly efficient "zero-emission" coal-fired units with integrated CO_2 *capture from flue gas.*

SYMBOLS

C	concentration, ppm
M	stable particle for energy carrying
n	number of moles

OR	oxidizing reactor
X_{NO}	molar ratio O_3/NO, mol O_3/mol NO

Greek symbols

δ	fraction of nitrogen compounds captured in oxidizing reactor, %
η_{NOx}	efficiency of NO_x removal, %
η_{SO4}	degree of conversion of SO_3^{2-} to SO_4^{2-}, %

Superscripts

A	amounts related to solution in washers
int	related to parameters at inlet
out	related to parameters at outlet
R	amounts related to oxidizing reactor

Subscripts

aq	liquid state
NO_x	sum of NO and NO_2
$NO_{(2,3)}$	sum of nitrites and nitrates,
SO3	sulphites
SO4	sulphates

REFERENCES

Carpenter A. M., 2013. Advances in multi-pollutant control. *IEA CLEAN COAL CENTRE*, CCC/227.

Chen L., Lin J.-W., Yang Ch.-L., 2002. Absorption of NO_2 in a packed tower with Na_2SO_3 aqueous solution. *Environ. Prog.,* 21, No.4, 225-230. DOI: 10.1002/ep.670210411.

Chirona R.J., Alshuter B., 1999. Chemical aspects of NO_x scrubbing. *Pollution Engineering*, 32, 33-36.

Dora J., Gostomczyk M.A., Jakubiak M., Kordylewski W., Mista W., Tkaczuk M., 2009. Parametric studies of the effectiveness of NO oxidation process by ozone. *Chem. Process Eng*., 30, 621–634.

Fridman A., 2008. *Plasma Chemistry*. Cambridge University Press, Cambridge.

Fujishima H., Kuroki T., Tatsumi A., Okubo M., Otsuka K., Yamamoto T., Yoshida K., 2008. Performance characteristics of pilot-scale NO_x removal from boiler emissions using plasma-chemical process. *11th International Conference on Electrostatic Precipitation*, Hangzhou, 644-648. DOI: 10.1109/08IAS.2008.120.

Głomba M., Hałat A., Kordylewski W., Łuszkiewicz D., 2016. Research on products of simultaneous removal of SO_2 and NO_x from flue gas by ozonation and alkaline absorption. *Environ. Prot. Eng.*, 42, 125-136. DOI: 10.5277/epe160208.

Hikita H, Asai S., Tsuji T., 1977. Absorption of sulfur dioxide into aqueous sodium hydroxide and sodium sulfite solutions. *AIChE J.*, 23, 538–544. DOI: 10.1002/aic.690230419.

Jaroszyńska-Wolińska J., 2009. *Investigations of the chemical reactions of nitrogen oxides with ozone generated in low-temperature plasma*. Instytut Chemii i Technologii Jądrowej, Warszawa.

Jędrusik M., Kordylewski W., Łuszkiewicz D., 2015. Removal of nitrogen oxides from flue gas by ozonation method. *Rynek Energii*, 6, 119-124.

Jie D., Heruijing C., Qin Z., Jiandong L., Junjun X., Shule Z., 2016. Selective denitrification of flue gas by O_3 and ethanol mixtures in a duct: Investigation of processes and mechanisms. *J. Hazard. Mater.*, 311, 218–229. DOI: 10.1016/j.jhazmat.2016.02.063.

Jie D., Qin Z., Shule Z., 2014. Simultaneous desulfurization and denitrification of flue gas by catalytic ozonation over Ce–Ti catalyst. *Fuel Process. Technol.,* 128, 449–455. DOI: 10.1016/j.fuproc.2014.08.003.

Joshi J.B., Mahajani V.V., Juvekar V.A., 1985. Absorption of NOx gases. *Chem. Eng. Com.*, 33, 1-92. DOI: 10.1080/00986448508911161.

Kordylewski W., Jakubiak M., Hardy T., 2013. Pilot plant studies on NOx removal via NO ozonation and absorption. *Arch. Environ. Prot.*, 39, 93-106. DOI: 10.2478/aep-2013-0025.

Krzyżyńska R., Hutson N.D., 2012. Effect of solution pH on SO_2, NO_x, and Hg removal from simulated coal combustion flue gas in an oxidant-enhanced wet scrubber. *J. Air Waste Manage. Assoc.*, 62, 2, 212-220. DOI: 10.1080/10473289.2011.642951.

Kuropka J., 2012. *Technologie oczyszczania gazów z dwutlenku siarki i tlenków azotu*. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław.

Littlejohn D., Wang Y., Chang S-G., 1993. Oxidation of aqueous sulfite ion by nitrogen dioxide. *Environ.* ***.*** *Sci. Technol.,* 27, 2162-2167. DOI: 10.1021/es00047a024.

Modern Power Systems, 2015. A pioneering NOx removal technology for the power industry. *Modern Power Systems*, 35(5), 32-33.

Mok S.Y., 2006. Absorption-reduction technique assisted by ozone injection and sodium sulfide for NO_x removal from exhaust gas. *Chem. Eng. J.*, 118, 63-67. DOI: 10.1016/j.cej.2006.01.011.

Nelo S.K., Leskela K.M., Sohlo J.J.K., 1997. Simultaneous oxidation of nitrogen oxide and sulfur dioxide with ozone and hydrogen peroxide. *Chem. Eng. Technol.*, 20, 40-42. DOI: 10.1002/ceat.270200108.

Okubo M., Kuroki T., Kitaura K. and Yamamoto T., 2006. Diesel engine emission control using pulsed corona plasma-chemical hybrid process. *J. Environ. Eng.,* 1, 29-38. DOI: 10.1299/jee.1.29.

Omar K., 2008. Evaluation of BOC's LotOx process for the oxidation of elemental mercury in flue gas from a coal-fired boiler. *Topical report for Linde Group and U.S. Department of Energy by Western Research Institute (WRI-08-RO10)*.

Regulation of the Minister of Environment on conditions to be met when introducing sewage into the water or soil and on substances particularly harmful to the aquatic environment (*Dz. U. 2009, nr 27, poz. 169*), (in Polish).

Sander R., 1999. *Compilation of Henry's Law constants for inorganic and organic species of potential importance in environmental chemistry*. Air Chemistry Department Max-Planck Institute of Chemistry, Germany.

Skalska K., Miller J.S. , Ledakowicz S., 2011. Kinetic model of NOx ozonation and its experimental verification. *Chem. Eng. Sci.*, 66, 3386-3391. DOI: 10.1016/j.ces.2011.01.028.

Stamate E., Jorgensen L., Jensen T. K., Chen W., Kristensen P. G., Tobiasen L., Simonsen P., Michelsen P. K., 2009. Pilot test and optimization of plasma based DeNOx. *Final Report PSO project No. 2006-1-6365*.

Sun W.Y., Ding S.L., Zeng S.S., Su S., Jiang W., 2011. Simultaneous absorption of NOx and SO_2 from flue gas with pyrolusite slurry combined with gas-phase oxidation of NO using ozone. *J. Hazard. Mater.*, 192, 124–130. DOI: 10.1016/j.jhazmat.2011.04.104.

Sun C., Zhao N., Zhuang Z.K., Wang H., Liu Y., Weng X., Wu Z., 2014. Mechanisms and reaction pathways for simultaneous oxidation of NO_x and SO_2 by ozone determined by in situ IR measurements. *J. Hazard. Mater.*, 274, 376–383. DOI: 10.1016/j.jhazmat.2014.04.027.

Thomas D., Vaderschuren J., 2000. Analysis and prediction of the liquid phase composition for the absorption of nitrogen oxides into aqueous solutions. *Sep. Purif. Technol.*, 18, 37-45. DOI: 10.1016/S1383-5866(99)00049-0.

Wallas S.M., 1988. *Chemical processes: Equipment selection and design.* Butterworth, Wobum, MA.

Wang H., Zhuang Z., Sun C., Zhao N., Liu Y., Wu Z., 2016. Numerical evaluation of the effectiveness of NO_2 and N_2O_5 generation during the NO ozonation process. *J. Environ. Sci.* (*China*). 41, 51-58. DOI: 10.1016/j.jes.2015.05.015.

Yamamoto T., Okubo M., Hayakawa K., Kitaura K., 2001. Towards ideal NOx control technology using a plasma-chemical hybrid process. *IEEE Trans. Ind. Appl.*, 37, 1492-1498. DOI: 10.1109/28.952526.

Zhang J., Zhang R., Chen X., Tong M., Kang W., Guo S., Zhou Y., Lu J., 2014. Simultanoeus removal of NO and SO_2 from flue gas by ozone oxidation and NaOH absorption. *Ind. Eng. Chem. Res.,* 53, 6450-6456. DOI: 10.1021/ie403423p.

Received 08 September 2016
Received in revised form 01 March 2017
Accepted 03 March 2017