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RESEARCH ON PRODUCTS OF SIMULTANEOUS REMOVAL OF SO₂ AND NO_x FROM FLUE GAS BY OZONATION AND ALKALINE ABSORPTION

The results of laboratory scale research have been presented on the effects of ozonation of carrier gas containing NO_x and SO₂ on by-products trapped in Dreschel washers with solution of sodium hydroxide. The controlling parameter in this process was the ozonation intensity determined by the molar ratio O₃/NO_x. The measured by-products in a scrubber were SO₃²⁻, SO₄²⁻, NO₂⁻, and NO₃⁻ ions. It has been shown that ozonation of flue gas favours oxidation of nitrites to nitrates and sulfites to sulfates in alkaline solution. Some of these results were confirmed in a pilot scale studies. Pilot plant was located in Wrocław CHP (Combined Heat and Power), which provided flue gas for testing at a rate of 200 m³/h from the OP-430 boiler. Exhaust gases were ozonized and captured simultaneously with SO₂. Sodium hydroxide was used in a pilot scale as an absorbent.

1. INTRODUCTION

Because of the risk to the environment, the emissions of NO_x, SO₂ and dust generated during coal combustion in boilers are controlled in all developed countries. According to the EU Directive IED, since 2016 in Poland the emission limits for these pollutants will be in effect [1]. It should also be expected soon restrictions on mercury emissions.

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In EU countries, a specially developed device to remove each of the pollutants from boiler flue gas is used [2]. US and some Asian countries are looking for less expensive methods for aftertreatment systems that will enable the removal of two or even more pollutants simultaneously [3]. In the last decade, significant progress was achieved in this field and some of these methods are close to or have reached a pre-commercial status [4]. Systems of simultaneous removal of pollutants from flue gases typically have a lower capital costs in comparison with the methods used in Europe. Their primary device is a wet scrubber, developed initially for removing SO₂, and then enhanced with additional processes extending its range of applications [4].

The most common methods of simultaneous treatment of exhaust gases from a number of impurities are using oxidizing effects of low temperature plasma that can be generated by electron beam, corona or barrier discharge [4]. Other methods based on oxidation processes use hydrogen peroxide, chlorine and its compounds as oxidants [5]. generally, the next stage after oxidation is absorption in alkaline solutions [4]. Efficiency and economical aspect of simultaneous exhaust gas treatment systems are compared with selective catalytic reduction (SCR) and flue gases desulfurization (FGD).

The SCR is a very effective method in controlling the NO_x emissions and has got the BAT status. However, it has also some disadvantages, especially when using in pulverized coal-fired boilers. Ammonia is a poisonous substance, therefore it usually is delivered in a highly diluted form and has to be evaporated before the injection. There is also risk of the so-called ammonia-slip. The temperature of de-NO_x process in SCR is in the range of 380–450 °C, and therefore additional heat exchangers are required for “low-dust” technology, or the live-time of the catalysts is shortened due to intensive fly ash erosion in “high-dust” technology. When biomass is co-firing the SCR catalysts could be poisoned by potassium.

The use of ozone for controlling of the NO_x emission also has some weak points. Ozone is generated from oxygen, which has to be separated from air. The apparatuses used for oxygen separation and ozone generation are rather sophisticated and expensive. The process of ozone generation is energy-consuming (10–12 kWh per/kg O₃). Ozone is not neutral for environment, therefore its maintenance should be controlled to prevent emission. An important advantage of the ozonation method is oxidation of metallic mercury with ozone, which makes possible to capture this part of mercury in a wet scrubber.

The comparison of total costs of the both methods is not easy because the ozonation method is not entirely commercial. A preliminary estimation favours the ozonation method. The capital costs of the methods are comparable but the exploitation cost of the ozonation method is from 2 to 3 times lower than the SCR exploitation cost [6].

The aim of these studies was to characterize the by-products of simultaneous removal of NO_x and SO₂ from flue gas using ozone for pre-oxidation of NO and alkaline absorber. It has been shown that the intensity of ozonation X_{NO} and residence time have a significant impact on the final composition of by-products trapped in the alkaline solution.

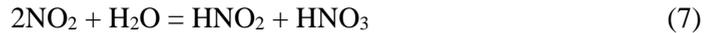
2. THE PRINCIPLE OF THE METHOD

Nitrogen oxides (NO_x) are a mixture of nitrogen oxide (NO) and nitrogen dioxide (NO₂). Compared with sulfur dioxide (SO₂), nitric oxide (NO) is poorly soluble, and the solubility of NO₂ is only one order of magnitude higher [7]. Only further oxidation of NO_x to higher oxides enables their efficient removal with wet methods.

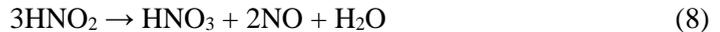
The most effective NO_x oxidizing agent is ozone [8]. Its valuable advantage is allowing the oxidation of NO to dinitrogen pentoxide (N₂O₅), while other oxidants only provide oxidation NO to NO₂. The primary chemical reactions of oxidation of NO to higher oxides by ozone are as follows [9, 10]:



Reaction (1) is very fast, so for a molar ratio $X_{NO} = \text{O}_3/\text{NO} = 1$ almost entire NO is immediately oxidized to NO₂. Simultaneously with the reaction (1) N₂O₃ is formed in the rapid reaction (2). Thus, the exhaust gas containing NO, after passing through sodium hydroxide solution, forms nitrite mainly as a result of absorption of N₂O₃. In turn, nitrate is formed by the parallel course of the reaction (7) and its amount in relation to nitrite depends on the concentration of NO₂ in the gas phase



The problem is the instability of nitrous acid, which undergoes disproportionation with remission of nitrogen oxide NO,



which causes that the NO_x is captured in alkaline solutions with the effectiveness not higher than 60% [11].

However, it is possible to improve the effectiveness of the oxidation products of NO capture owing to oxidation of nitrogen dioxide by ozone, which leads to the formation of N₂O₅. Dinitrogen pentoxide has a high solubility (similar to that of SO₂) and

is converted to stable nitrate ions in solutions. In exhaust gases, N_2O_5 reacts with steam and gaseous HNO_3 is created whose solubility is fivefold higher than that of SO_2 [7].

The oxidation of NO_2 to N_2O_5 requires more time since the reactions (3) and (4) are slower than reaction (1), and further increase the demand for ozone, which in theory is $X_{NO} = 1.5$, but in practice it is always higher. However, thanks to this it is possible to reduce NO_x in the exhaust gas to a dozen mg/m^3 , which was confirmed by the results of removing nitrogen oxides from flue gases in a pilot plant described elsewhere [12].

In gas phase, at temperatures below 60 °C, ozone reacts with almost no sulfur dioxide [10, 13] and, in addition, there are no interactions between NO_x and SO_2 . Otherwise happens in solutions: absorption of SO_2 in alkaline solutions leads to the formation of sulfite ions SO_3^{2-} , which create with the physically dissolved nitric oxide NO complex dinitrosulfite ions $(NO)_2 \cdot SO_3^{2-}$, which significantly increase the concentration of NO in the absorbing solution [14]. At the stage of complexation, there is no change in the oxidation state of nitrogen but in the acidic environment, the complex compound is decomposed to form nitrous oxide N_2O and sulfate ions, whereas in the alkaline solution it can oxidize with oxygen to form nitrous acid and sulfate ions [15]. In the presence of a strong oxidizer such as ozone these reactions are likely to run faster and nitrite ions can be oxidized to nitrates. In this case, it would be a different, additional way of binding nitric oxide NO in the absorbing solution, next to the previously discussed mechanism (1)–(6). In the liquid phase, nitrogen dioxide plays an important role because it is believed that the NO_2 acts as a catalyst for accelerating conversion of sulfite ions to sulfates [16].

Understandably, the removal of nitrogen oxides and sulfur dioxide from the flue gas is only a part of the problem of reduction of NO_x and SO_2 emission. Also important are the end products of flue gas cleaning because they often have a decisive effect on the functionality of methods. For example, in the case of the removal of NO_x , the end products formed in the absorber are nitrates and nitrites. If we assume that they will be discharged in the effluent, it is important to distinguish between them because their permissible concentration is very different (Table 1) [17].

Table 1

Permissible industrial effluent pollution
for nitrites and nitrates

Chemical compound	Amount
Nitrite, $mg NO_2^-/dm^3$	1
Nitrate, $mg NO_3^-/dm^3$	30

Therefore the more oxidized form is preferred because of its higher permissible concentration in the effluent. The same is the case with the current sulfur dioxide in the

exhaust gases. Sulfites are much more harmful to the environment than more oxidized form, i.e. sulfates (Table 2) [17]. In addition, nitrates and sulfates can be recycled as an additive to liquid fertilizers. For this reason, it is important to understand the mechanisms of formation of sulfates and nitrates and to establish conditions allowing the conversion in industrial installations.

Table 2

Permissible industrial effluent pollution
for sulfites and sulfates

Chemical compound	Amount
Sulfite, mg SO ₃ ²⁻ /dm ³	1
Sulfate, mg SO ₄ ²⁻ /dm ³	500

3. EXPERIMENTAL

In the laboratory research, the carrier gas was the dehumidified air from the compressor, with sulfur dioxide and nitrogen oxide added from steel cylinders. Two Dreschel washers containing 100 cm³ of 0.1 molar solution of NaOH (analytical grade POCH S.A.) were applied as an absorber. Ozone was introduced into the carrier gas feed immediately before the scrubbing. The scheme of the laboratory setup is shown in Fig. 1. More details and conditions of NO oxidation with ozone are presented elsewhere [18].

Concentrations of gaseous pollutants were measured using gas analysers TESTO 350 XL and TESTO 350 S. In order to prevent damage to the gas analysers the ozone destructor was used. Ozone was generated in the ozone generator type OZAT CFS-3 2G of Degremont Technologies. Its concentration was measured with the ozone analyser BMT 964 of BMT Messtechnik type. The intensity of ozonation was defined as the molar ratio $X_{NO} = O_3/NO$, also in the case of simultaneous removal of sulfur dioxide and nitrogen oxides, and when the carrier gas contained only sulfur dioxide the molar ratio $X_{SO_2} = O_3/SO_2$ was more appropriate.

The experiment time was 1 hour. After the experiment the samples of absorption solution were tested in terms of content of nitrite, nitrate, sulfite and sulfate. The concentration of nitrite and nitrate in NaOH solution was investigated by spectrophotometric method (NO₃⁻ – 300 nm; NO₂⁻ – 355 nm) using Cary 50 UV/Vis from Varian and SO₃²⁻ (by iodometry method) and SO₄²⁻ by ions chromatography or plasma spectrophotometry.

In case of the pilot plant the same methods and apparatus have been used to pollutants control in flue gas and the products determination in absorption solutions. Absorbent in the spray absorber column was a 0.1 molar solution of NaOH (technical grade

POCH S.A.). In this experiment, the intensity of ozonation was determined using the molar ratio $Y = O_3/(NO + CO)$ since carbon monoxide has been effectively oxidized in the process.

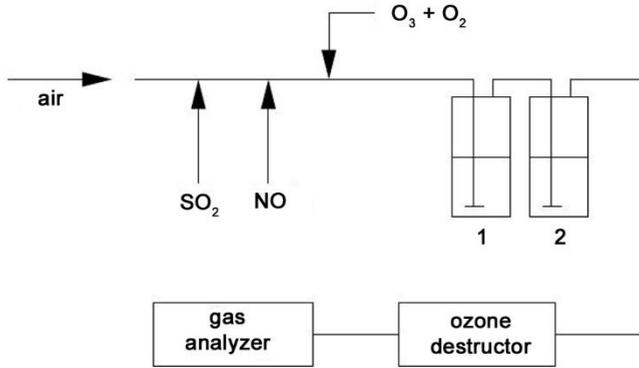


Fig. 1. Scheme of the experimental setup

The pilot plant was located in Wrocław CHP which provided flue gas from the OP-430 boiler for testing at a rate of 200 m³/h. The earlier studies have mainly been devoted to examination of the NO_x removal from flue gas by the ozonation method [12]. The effect of prolonged residence time on the effectiveness of NO_x removal and the characteristic of products were investigated by adding an oxidation reactor 220 dm³ in volume in front of the absorber. It provided the residence time of approx. 6 s (Fig. 2).

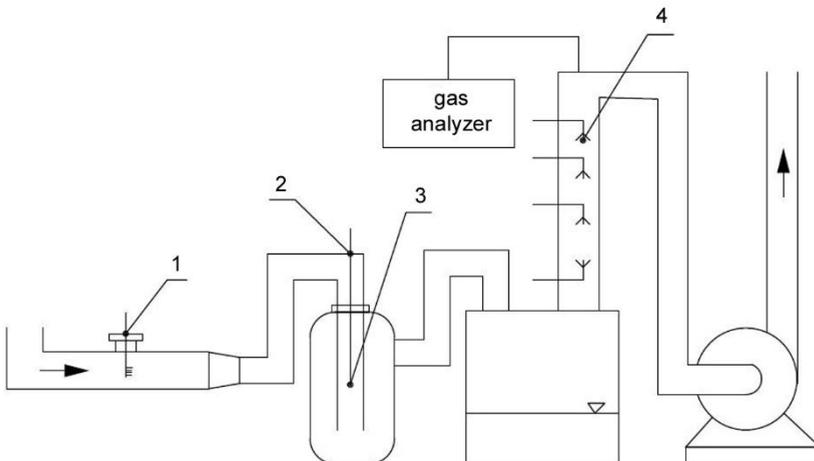


Fig. 2. Ozonation stage in pilot plant studies:
1, 2 – ozone injectors, 3 – oxidising reactor, 4 – spray absorber

The effectiveness of NO_x removal in laboratory and pilot tests was calculated from:

$$\eta_{\text{NO}_x} = \frac{1 - [\text{NO}_x]^{\text{out}}}{[\text{NO}_x]^{\text{int}}} \times 100\%$$

where $[\text{NO}_x]^{\text{int}}$ and $[\text{NO}_x]^{\text{out}}$ denote the initial and outlet NO_x concentrations in ppm.

4. RESULTS

4.1. THE INFLUENCE OF THE OZONATION INTENSITY ON THE FORM OF NITROGEN IN ALKALINE SOLUTIONS

The carrier gas flow of 130 dm³/h was doped with nitric oxide to obtain the content of 400 ppm NO. Ozone introduced into the carrier gas stream (6 to 32 g O₃ per 1 m³ of O₂) was selected so that the molar ratio of X_{NO} was in the range 0 to 2.5. After the absorption completion, the concentration of NO₂⁻ and NO₃⁻ ions in washer solutions were measured.

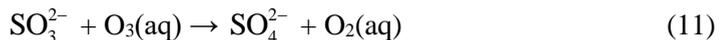
It was found that with increasing intensity of ozonation X_{NO}, the conversion of nitrite to nitrate increased significantly. For molar ratio X_{NO} > 1.5 nitrite ions practically disappeared from the solution (Fig. 3). Nitrogen delivered in the carrier gas as NO and captured in the scrubbers was balanced with the uncertainty of <10%.

4.2. INFLUENCE OF THE OZONATION INTENSITY ON THE OXIDATION STATE OF SULFUR IN ALKALINE SOLUTIONS

There were no changes in concentration of SO₂ due to ozone addition [12], what is consistent with the literature data [19]. However, it is well known, that the oxidation of sulfite ion in aqueous medium with ozone plays an important role in the conversion of SO₂ to sulfate in the atmosphere [13]. The main stages of this mechanism are the transfer of sulfur dioxide into the liquid phase (SO₂(g) → SO₂(aq)), then hydration and dissociation:



and finally oxidation by ozone:



Ozone (10 wt. % in oxygen) was added to the carrier gas (130 dm³/h) containing 1200 to 1500 ppm SO₂. Figure 4 shows the measured concentration of sulfite and sulfate ions as a function of the molar ratio of O₃/SO₂ = X_{SO₂}, which varied in the range of 0–2.

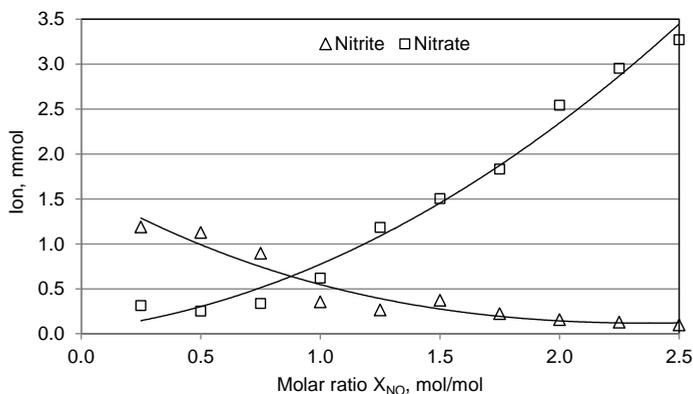


Fig. 3. Amounts of NO₂⁻ and NO₃⁻ ions vs. molar ratio X_{NO}

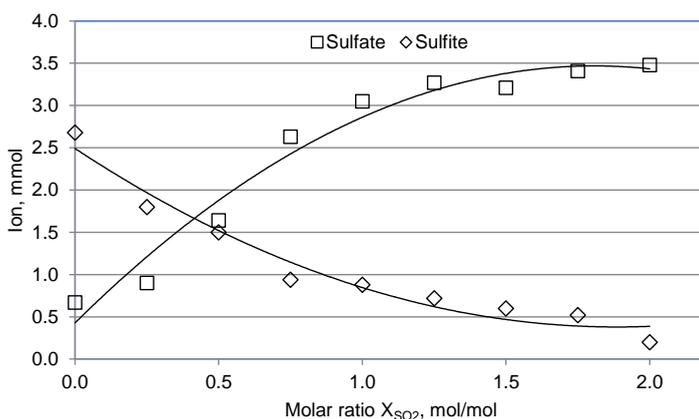


Fig. 4. Amounts of SO₃²⁻ and SO₄²⁻ ions vs. molar ratio X_{SO₂}

With increasing ozonation intensity X_{SO₂} also the conversion of sulfite to sulfate ions increased. Efficiency of conversion of SO₂ to SO₄²⁻ was about 90% for the molar ratio X_{SO₂} > 1.75. Sulfur delivered in the carrier gas and captured in the washers was balanced with the uncertainty in the range of 4–17%.

4.3. IMPACT OF OZONATION ON THE PRODUCTS OF SIMULTANEOUS REMOVAL OF NO AND SO₂

The carrier gas flow (130 dm³/h of air) containing NO and SO₂, 400 ppm each, was fed with ozone at the rate required to reach the molar ratio X_{NO} in the range 0–2.5.

of nitrate ions collected in the washers 1 and 2 and collected from the oxidation reactor was also higher than without the reactor. Furthermore, due to wetting of the oxidation reactor, initial separation of nitrogen compounds from sulfur compounds occurred because half of the nitrate ions were captured in the wet washer. As a result, effectiveness of NO_x capture η_{NO_x} was improved further (Table 3).

Table 3

Efficiency of NO_x removal and the composition of products in the presence and without the oxidation reactor

X_{NO}	Oxidation reactor	Inlet		Outlet			Ions				η_{NO_x}
		SO_2	NO_x	NO	NO_2	NO_x	SO_3^{2-}	SO_4^{2-}	NO_3^-	NO_2^-	
		[ppm]					[mmol]				
1.0	–	427	414	12	158	170	0.1	2.48	1.332	0.09	58.9
1.0	dry	432	454	20	152	172	0	2.42	1.585	0.07	62.1
1.0	wet	410	474	9	73.2	82.2	0	2.38	1.77	0.07	82.7

4.5. PILOT PLANT STUDIES

Based on the results of investigations obtained in the lab scale, the pilot plant was modified by adding an oxidation reactor 220 dm³ in volume in front of the absorber (Fig. 2). It secured the residence time of ca. 6 s.

The effectiveness of aftertreatment for SO_2 , CO and NO_x was very good (cf. [12, 20]). CO and SO_2 were not detected in the exhaust gas from the absorber and the concentration of nitrogen oxides in the treated flue gas was also very low (Table 4). However ozone consumption was higher than in the laboratory tests, among others, due to CO oxidation in flue gas, the molar ratio Y was used in the Table 4, according to the suggestion in the paper [20].

Table 4

Efficiency of NO_x removal with use pre-oxidation reactor [ppm]

$Y = \frac{[\text{O}_3]}{[\text{NO}] + [\text{CO}]}$ [mol/mol]	Time [min]	Concentration (no ozonation)			Concentration (with ozonation)		
		NO	NO_2	CO	NO	NO_2	NO_x
2.2	20				5	6	11
	40	132	0	40	2	10	12
	60				0	6	6

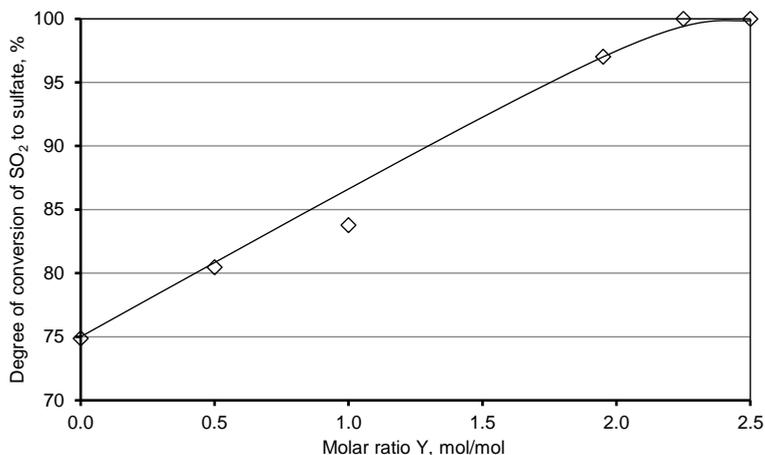


Fig. 6. Degree of conversion of SO₂ to sulfate vs. molar ratio *Y*

Although the concentrations of NO₂⁻ and NO₃⁻ in water used in the absorber were two orders of magnitude smaller than the concentrations in the solutions after the experiment, it was impossible to determine the concentration of NO₃⁻ precisely as an unidentified component in solution raised the absorbance in the range 260–300 nm. Fortunately, the absorbance increase at 350 nm was very small, which made it possible to confirm the absence of nitrite in the solution, as in the case of laboratory tests. It was possible to correctly establish concentrations of SO₃²⁻ and SO₄²⁻ ions. This allowed one to verify that the ozonation has a positive impact on the oxidation of SO₂ to SO₄²⁻ (Fig. 6) and simultaneous oxidation of nitrites to nitrates.

5. SUMMARY

Ozonation of exhaust gas causes oxidation of NO_x to higher oxides which allows one to capture them together with sulfur dioxide in a single absorber.

Ozonation of flue gas favours conversion of nitrites to nitrates and sulfites to sulfates in alkaline solution facilitating their removing.

Application of the oxidation reactor creates the perspective of separating the capture nodes for nitrogen and sulfur compounds and to allow their separation.

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