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## REMOVAL OF NITROGEN OXIDES FROM FLUE GASES IN A PACKED COLUMN

The state of technology and the possibilities of removal of nitrogen oxides from flue gases in alkaline solutions with oxidants have been presented. The results of the research on the absorption of nitrogen oxides in alkaline solution of sodium hypochlorite in a packed column showed high efficiencies of removal of nitrogen oxides in a wide range of the following parameters: gas velocity, spraying density, concentration of nitrogen oxides in gas and concentration of spraying solution.

### 1. INTRODUCTION

Nitrogen oxides belong to the most troublesome gaseous components polluting atmospheric air. Among several nitrogen oxides ( $N_2O$ ,  $NO$ ,  $N_2O_3$ ,  $NO_2$ ,  $N_2O_4$ ,  $N_2O_5$ ), the most common in atmospheric air are nitrogen oxide ( $NO$ ) and nitrogen dioxide ( $NO_2$ ). In chemical engineering and combustion techniques, their total content ( $NO + NO_2$  converted to  $NO_2$ ) is marked with a common symbol  $NO_x$  [1]. Those pollutions are heavily toxic for human environment taking parts in forming photochemical smog.

Nitrogen oxides accompany all combustion processes of solid, liquid and gas fuels, therefore power industry, heat engineering and transport are the main and most serious source of those pollutions (Table).

The sources of emissions of  $NO_x$  to atmospheric air are also industrial technologies which emit nitrogen oxides as a result of certain chemical reactions. This includes mostly chemical plants producing nitric acid and fertilizers, sulfuric acid by the nitric method, and nitric acid derivatives in organic syntheses. Moreover, the sources of emissions of nitrogen oxides are all reactions of surface pulping of metals in nitric acid. Those sources pose a major threat for natural environment because of their sometimes substantial local concentration.

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Table

Emission of nitrogen oxides in Poland as NO<sub>2</sub> [2]

Emission sources	1990	1995	2000	2007	
	[Gg·year <sup>-1</sup> ]				[%]
Commercial power industry	370	377	237	249	28.1
Industrial power industry	130	111	81	101	11.7
Industrial technologies	200	103	109	73	8.2
Stationary sources <sup>a</sup>	100	115	97	113	12.7
Mobile sources	480	414	314	349	39.3
Total	1280	1120	838	885	100.0

<sup>a</sup>Local boiler houses, domestic hearths, craft workshops etc.

The majority of more important sources emit to atmospheric air gases of low degree of oxidation, which highly complicates removal of nitrogen oxides from exhaust gases and from industrial flue gases [1].

## 2. METHODS OF REMOVAL OF NITROGEN OXIDES FROM GASES. STATE OF TECHNOLOGY

Methods of removal of nitrogen oxides from flue gases applied in recent years belong to the following groups [1]:

- catalytic reduction (non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR)),
- adsorption,
- absorption (acid and alkaline).

Catalytic reduction is an efficient but very expensive method of gas treatment. It is used mainly in highly industrialized countries to neutralise nitrogen oxides from energetic exhaust fumes and from industrial flue gases, which are formed during production of nitric acid. This method requires using catalysts and, as reducing gases: hydrogen, carbon oxide, methane and other hydrocarbons, as well as ammonia reacting selectively with nitrogen oxides in the presence of oxygen. This method is currently not commonly applied in Poland, mainly due to substantial investment and exploitation costs. The cost of reactor results mainly from the demand for catalyst mass (depending on concentration of nitrogen oxides in gases), it depends on the catalyst vitality and on consumption of reducing gases and on the annual number of working hours at full load [1].

Despite high efficiency, adsorption methods exploiting traditional adsorbents have not been commonly used in installations for removing nitrogen oxides from industrial flue gases, mainly for economical reasons and because of difficulties connected with

regeneration of adsorbent or its utilization. Technology of cleaning flue gases from nitrogen oxides on anion exchangers [1] elaborated by the author is advised for neutralising nitrogen oxides from small emitters characterised by variable emission. Typical of this technology is a powerful tolerance for nitrogen oxides in the gas treated with maintaining high efficiency of treatment, as well as its simplicity and user-friendliness of the apparatus.

Methods of absorption of nitrogen oxides in solutions belong to the earliest ones in technology of industrial flue gases treatment. Those methods are based on fundamental properties of nitrogen oxides present in gases: their solubility in water [3, 4] or in solutions of nitric acid [5, 6] and sulfuric acid [7–9] as well as their ability to form appropriate salts, nitrates and nitrites in reactions with substrate of alkaline character [10–17].

Absorption of nitrogen oxides in acids leads to producing of nitric acid or concentrated nitrogen oxides, thus application of such methods does not lead to formation of side-products but only to increase of the amount of the basic product. In most cases, the methods are not complicated in terms of chemical and processes engineering. Their shared defect is too slow mass transfer, which demands big capacities of apparatuses in industrial conditions. Many other corrosion problems are linked to these methods, which is usually omitted in the works on laboratory scale.

On the other hand, methods of absorption of nitrogen oxides in alkaline solutions are generally rated higher in terms of efficiency. They are usually more expensive because the products require further technological proceedings. Absorption methods, however, provide decrease of content of nitrogen oxides in industrial flue gases to the extent defined by sanitary norms.

Generally, absorption methods are characterised by a simplified technological outlines and simple, typical apparatuses. Running of the process does not also cause substantial problems with their exploitation. Specialised sources, however, do not provide essential information on designing installations for purification of flue gas from nitrogen oxides.

### 3. ALKALINE ABSORPTION OF NITROGEN OXIDES

Application of the alkaline absorption to protect environment is determined by physicochemical properties of nitrogen oxides. Nitrogen dioxide has sufficiently high solubility and reactivity with water and with aqueous alkaline solutions, and as such it can be absorbed in solutions [1, 10–17]. Nitrogen oxide is poorly soluble in water and its reactivity with alkaline solutions is low. To remove nitrogen oxide from gases by the absorption method in solutions, it should be oxidized to nitrogen dioxide in accordance with the following reaction:



If the volume of NO in the mixture of NO and NO<sub>2</sub> will be equal to or smaller than the volume of NO<sub>2</sub>, in consequence of contact with alkaline solution such as NaOH, the outcome will be total absorption of both oxides in accordance with the following reaction:

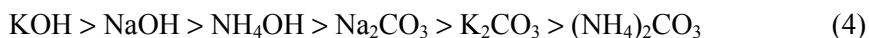


At the excess of nitrogen dioxide, apart from the processes described by Eq. (2), nitrogen dioxide will react with NaOH as follows:



At the excess of nitrogen oxide, only the number of molecules of nitrogen oxide equivalent to nitrogen dioxide will react (2), whereas the remaining NO will not react with NaOH and will remain in the gas phase.

Atroščenko [10] found that the mixture of nitrogen oxides of the volume ratio of NO<sub>2</sub> to NO higher than or equal to unity, is absorbed with the highest rate in alkaline solutions. It was confirmed by Głowiński et al. [17]. The role of concentration and type of absorption liquid on the absorption rate of nitrogen oxides was studied by Kuznecov [11]. He stated that the change of the initial concentration of the studied solutions from 10 into 100 g/dm<sup>3</sup> increases the rate of absorption by 4–5 times. Kuropka established a sequence of activities of alkaline solutions used for the absorption of nitrogen oxides, which diminishes in the following order [1, 15]:



The influence of concentration of absorbing solution on the absorption of nitrogen oxides was different for the examined solutions. For the solution of NaOH, violent impact of the solution's concentration on the absorption efficiency reached the value of 2 wt. %, and for the solution of sodium carbonate it reached the value of 10 wt. %.

The mechanism of the absorption process of nitrogen oxides in alkaline solutions was examined also by Aoki [13] and Carta [14]. They determined the speed of nitrogen oxides absorption in NaOH solutions and the influence of nitrite ions on the process of absorption.

### 3.1. ALKALINE ABSORPTION OF NITROGEN OXIDES WITH OXIDANTS

Attempts were made to solve the problem of raising the level of oxidation of nitrogen oxides by absorption with simultaneous oxidizing of nitrogen oxides with compounds which easily release oxygen in the liquid phase. Useful for these purposes proved to be compounds with strongly oxidizing properties, such as sodium hypochlorite [1, 15], sodium chlorite [18–20], calcium hypochlorite [21], potassium permanga-

nate, and potassium dichromate [1, 15, 22], salts of iron, copper, nickel and cobalt [1, 15, 23, 24] and hydrogen peroxide [1, 15, 25].

The research on absorption of nitrogen oxides in alkaline solutions of sodium hypochlorite (NaOCl) have been presented elsewhere [1, 15]. It was determined that the level of absorption of nitrogen oxides is over 90%, and the process itself runs almost with the stoichiometric ratio in terms of the sorption capacity of the solution.

Mechanism and kinetics of the  $\text{NO}_x$  absorption in alkaline solutions of sodium chlorite was studied by Sada [18, 19]. He stated that the reaction rate decreases exponentially upon increasing NaOH concentration. Too low concentration of  $\text{OH}^-$  ions causes degradation of sodium chlorite to gaseous chlorine dioxide, which next in the gaseous phase oxidizes nitrogen oxide. Sada claims that to stop degradation of  $\text{NaClO}_2$  and provide absorptive liquid with constant oxidizing property, concentration of  $\text{OH}^-$  ions must be maintained at a constant level. He suggests, then, to use sparingly soluble alkaline hydroxides:  $\text{Ca}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$ .

Furuta removed nitrogen oxides from flue gases using solutions of calcium hypochlorite of the concentrations of 3–15  $\text{g/dm}^3$  [21] with 95–100% efficiency. Using hydrogen peroxide in a packed column in a laboratory scale [25] lead to the conclusion that the efficiency of  $\text{NO}_x$  absorption is low (4.5–9%), allowing, however, to treat gases which contain 0.5–1.0 vol. % of nitrogen oxides with 85–95% efficiency.

Great interest was evoked by the possibility of removing  $\text{NO}_x$  from flue gases in alkaline solutions ( $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Ca}(\text{OH})_2$ ) with the use of ozone as an oxidants in gaseous phase. Dimov [26] states that high efficiency of absorption is possible to be obtained at relatively slight ozone consumption. Pronounced effect is reached by using ozone in the absorption of nitrogen oxides of low concentration. The appropriate apparatus for this process is a packed column. Because of very high rate of oxidation, ozone is added to gases immediately before the absorption column. The efficiency of absorption at the gas velocity of ca. 4 m/s exceeds 95% [26].

In the paper, substantial parameters have been determined of the process of removing nitrogen oxides from gases in a packed column sprayed with alkaline solution with the addition of sodium hypochlorite were presented.

#### 4. CONDITIONS OF EXPERIMENTS AND RESULTS OF THE RESEARCH

In the experiments, a packed column 1.0 m high and 0.025 m in diameter was used. Details concerning the installation have been described elsewhere [1]. Variable parameters were as follows:

- gas volume stream  $(4.9\text{--}49.0)\cdot 10^{-5} \text{ m}^3/\text{s}$ ,
- gas velocity 0.1–1.0 m/s,
- initial concentration of  $\text{NO}_x$  (converted to  $\text{NO}_2$ ) in gas 1.0–10.0  $\text{g/m}^3$ ,

- volume stream of spraying solution  $(6.8\text{--}54.4)\cdot 10^{-7}\text{ m}^3/\text{s}$ ,
- spraying density  $5\text{--}40\text{ m}^3/(\text{m}^2\cdot\text{h})$ .

Various types of packings were used as well as and various spraying solution differing also in concentrations. During a single experiment with a given type of a packing and a given type and concentration of the spraying solution, the gas volume stream was maintained at a constant level, whereas the initial  $\text{NO}_x$  concentration (converted to  $\text{NO}_2$ ) in the gas and the volume stream of the spraying solution were changed. In the examined range of variable parameters, the averages from 3 measurements were taken into account.

The possibility of increasing the efficiency of  $\text{NO}_x$  absorption in 5 wt. % solutions of NaOH [1] was tested by adding NaOCl,  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$  as oxidants to the spraying solution. The influence of basic process parameters such as gas velocity, concentration of nitrogen oxides in gas, concentration of oxidants in spraying solution and spraying density on the absorption efficiency has also been tested.

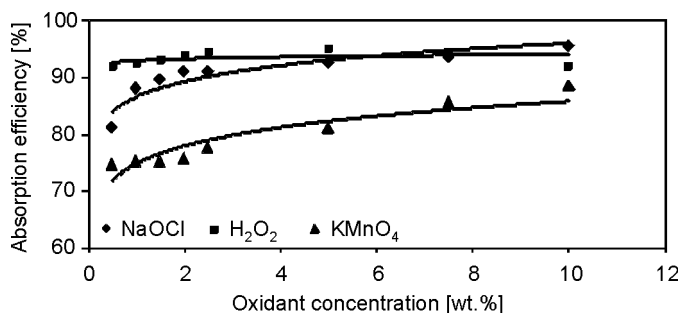


Fig. 1. Effect of the addition of oxidant into 5 wt. % solution of NaOH on the absorption of nitrogen oxides at constant initial concentration of  $\text{NO}_x$  of  $3.5\text{ g}/\text{m}^3$  gas, gas velocity of  $0.2\text{ m}/\text{s}$  and spraying density of  $20\text{ m}^3/(\text{m}^2\cdot\text{h})$

In Figure 1, the effect of addition of an oxidant into NaOH solution on the efficiency of absorption of nitrogen oxides was shown. The concentration of the oxidant in 5 wt. % solution of NaOH was changed in the range from 0.5 to 10 wt. %. During an experiment for a given type of spraying solution, the gas velocity of  $0.2\text{ m}/\text{s}$ , spraying density of  $20\text{ m}^3/(\text{m}^2\cdot\text{h})$  and initial  $\text{NO}_x$  concentration of  $3.5\text{ g}/\text{m}^3$  in the gas cleaned were maintained. In the examined range, the efficiency of the absorption of nitrogen oxides was increasing upon the increase of the oxidant concentration. This is most evident for hydrogen peroxide, then for sodium hypochlorite and potassium permanganate. The effect of NaOCl concentration is mainly visible up to 2 wt. %, the dependence is linear above this value (similarly as for hydrogen peroxide and potassium permanganate), and further increase of NaOCl concentration causes slight increase of the process efficiency.

Exemplary dependence of the efficiency of absorption of nitrogen oxides on the gas velocity for NaOCl oxidizing solutions with various contents of the oxidant is shown in Fig. 2.

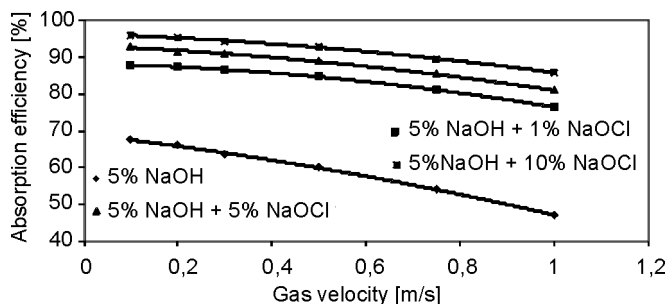


Fig. 2. Dependences of the absorption efficiency of nitrogen oxides on the gas velocity for solutions with various contents of NaOCl at constant initial concentration of  $\text{NO}_x$  of  $3.5 \text{ g/m}^3$  of gas, gas velocity of  $0.2 \text{ m/s}$  and spraying density of  $20 \text{ m}^3/(\text{m}^2 \cdot \text{h})$

The efficiency of the process decreases upon increasing the gas velocity; the shape of the curves is similar for all types of spraying solutions. The effect of addition of NaOCl to the basic NaOH solution is evident from Fig. 2. For example, using of 1 wt. % of NaOCl at the gas velocity of  $0.2 \text{ m/s}$ , increases the efficiency of the absorption by 21.4%, whereas at the gas velocity of  $0.8 \text{ m/s}$ , it increases by 27%. From the dependences shown in Fig. 3, it can be observed that increasing the spraying density improves the efficiency of absorption of nitrogen oxides in alkaline solution of NaOCl by 4–6%.

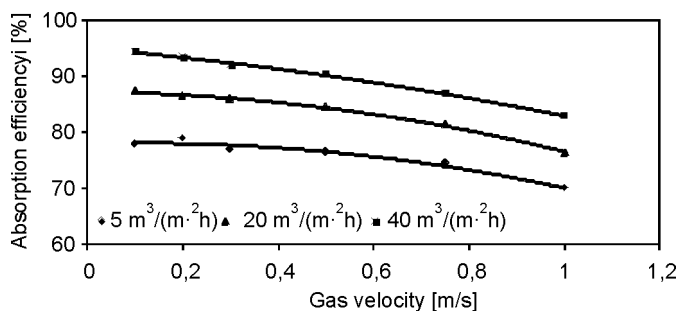


Fig. 3. Dependences of the absorption efficiency of nitrogen oxides on the gas velocity for various spraying densities with 5 wt. % solution of NaOH with the addition of 1 wt. % NaOCl at constant initial concentration of  $\text{NO}_x$  of  $3.5 \text{ g/m}^3$  of gas)

Upon the increase of  $\text{NO}_x$  concentration in the gas treated, the efficiency of the process increases linearly, while the increase of the efficiency of treatment is not known (Fig. 4). Using various heights and kind of packings in a column confirmed [1] that the efficiency of the absorption increases upon the increase of the contact time of the gas with the absorption solution. Using spraying between the layers of the packing and applying packing of an increased specific surface area improves the efficiency of the process by a few percent [1, 8, 15]. Applying packings with an increased specific surface area limits resistances of the gas flow influencing the economics of the installation.

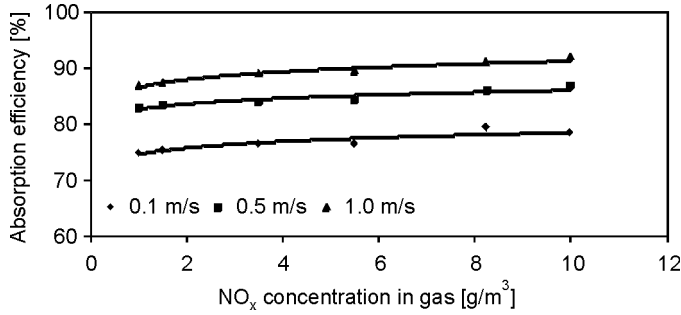


Fig. 4. Dependences of absorption efficiency of nitrogen oxides on their concentration in gas for various gas velocities, at the spraying density of  $20 \text{ m}^3/(\text{m}^2 \cdot \text{h})$  with 5 wt. % solution of NaOH with the addition of 1 wt. % of NaOCl

Technological experiments under industrial conditions [1] confirm that the efficiency of the absorption of nitrogen oxides does not depend on NaOH concentration in the absorptive solution, whereas NaOCl concentration greatly influences the efficiency of the absorption. Consumption of absorptive solution to absorb 1 kg NO<sub>x</sub> (converted to NO<sub>2</sub>) was 1.645 kg of NaOCl and 0.891 kg of NaOH.

Quantitative description of the process of mass transfer with incorporating the so-called efficiency of absorption was used. The efficiency of absorption allows one to estimate in a very simple and clear way the influence of basic parameters of the process on the efficiency of gas treatment. It was assumed that the efficiency of the absorption is the function of the following variables:

$$\eta = f(w_{og}, L, c_{og}, c_r) \quad (5)$$

where:  $\eta$  – efficiency of absorption, %,  $w_{og}$  – gas velocity calculated for the diameter of the empty column, m/s,  $L$  – density of spraying,  $\text{m}^3/(\text{m}^2 \cdot \text{h})$ ,  $c_{og}$  – initial concentration of NO<sub>x</sub> (converted to NO<sub>2</sub>) in gas,  $\text{g}/\text{m}^3$ ,  $c_r$  – concentration of the absorptive solution,  $\text{kg}/\text{m}^3$  or wt. %.

For the examined range of variable parameters, the determined values of the efficiency of absorption  $\eta$  were plotted as the following functions:

$$\eta = f(w_{og}), \quad \eta = f(L), \quad \eta = f(c_{og}), \quad \eta = f(c_r) \quad (6)$$

After analysing the plots, the effectiveness of mass transfer was shown as the following function:

$$\eta = 1 - \exp(-f(\text{process variables})) \quad (7)$$

In the examined case, the following dependence was obtained:

$$\eta = 1 - \exp(-f(w_{og}, L, c_{og}, c_r)) \quad (8)$$



and it was used as the function:

$$\eta = 1 - \exp \left( -B_0 (w_{og})^{B_1} (L)^{B_2} (c_{og})^{B_3} (c_r)^{B_4} \right) \quad (9)$$

The coefficients  $B_i$  were assigned by the linear multiple regression method. In the examined range of the variable parameters for the absorption of nitrogen oxides in alkaline solutions of NaOCl, the following relation was defined:

$$\eta = 1 - \exp \left( -0.682 (w_{og})^{-0.152} (L)^{0.229} (c_{og})^{0.068} (c_r)^{0.033} \right) \quad (10)$$

for which the multiple correlation coefficient  $R$  equals 0.88, and the mean error is 4.91%.

## 5. SUMMARY

Research on the absorption of nitrogen oxides in alkaline solutions with oxidants allowed one to examine the influence of basic process parameters such as: gas velocity, concentration of nitrogen oxides in gas, concentration and type of solution and spraying density, on the process of gas treatment.

Experimental data verifies reports from specialised literature and provides essential knowledge on designing installations for removing nitrogen oxides from gases.

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