

JÓZEF KUROPKA*, MIECZYŚLAW A. GOSTOMCZYK*

ABSORPTION OF NITROGEN OXIDES ACIDIC ABSORBENTS

The potentiality for the absorption of nitrogen oxides in acidic solutions when applied for the treatment of flue gases from nitric acid plants, from the manufacture of sulphuric acid by the mixed acid method, and from some small emitters (e.g., electroplating plants) was investigated. The effect of some major parameters (gas velocity, initial concentration of nitrogen oxides in the flue gas, concentration and type of the spraying solution, spraying density) on the kinetics of absorption in acidic solutions was determined. Contribution of oxidizing or catalyzing additives in the acidic solutions to the efficiency of the absorption process was also considered.

1. INTRODUCTION

Apart from some major emission sources, like power generation, heat engineering or traffic, there are a number of technologies that produce nitrogen oxides as a result of the chemical reactions involved. Such technologies are used in the manufacture of sulphuric acid by the mixed acid method. Another portion of airborne nitrogen oxides comes from the reactions that occur during final etching of metals in nitric acid. In rough estimates, the annual industrial emission of these primary pollutants ranges from 4 to 7 million Mg [1]. In some instances, the environmental hazards resulting from such emissions are particularly high because of the increased local concentrations.

Two major methods are available for abating the concentration of nitrogen oxides in industrial gases to the admissible levels. Such an abatement can be achieved by the separation of toxic compounds from the flue gas stream (and recirculation to the manufacture) or by converting them into useful substances. Both approaches are low-cost procedures which can be performed during treatment

* Institute of Environment Protection Engineering, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

of flue gases by absorption of nitrogen oxides into acidic or alkaline solutions. In these methods use is made of the following properties of nitrogen oxides: their solubility in water [2]–[9], their solubility in nitric acid solutions [10]–[13] and sulphuric acid solutions [14]–[17], as well as their ability to form relevant salts, nitrates and nitrites, in reaction with an alkaline substrate [18]–[22]. As a rule, treatment methods based on absorption involve flow diagrams and apparatus, and are easy to handle. Unfortunately, little information and insufficient design data for the removal of nitrogen oxides from industrial gases are reported in specialized literature (if at all).

At the Institute of Environment Protection Engineering, Technical University of Wrocław, research has been carried out for many years with the aim to determine the basic process parameters for nitrogen oxides removal from flue gases by absorption into various solutions [23]–[30].

2. EXPERIMENTAL APPARATUS AND METHODS

The experimental system is shown in fig. 1. Atmospheric air passes through a rotameter (1) to a flask (2) to produce an air– nitrogen dioxide mixture. To achieve the nitrogen dioxide concentration desired, appropriate amounts of sodium nitrite (4) and sulphuric acid (5) (at a constant mix (6) of the reagents) are supplied to

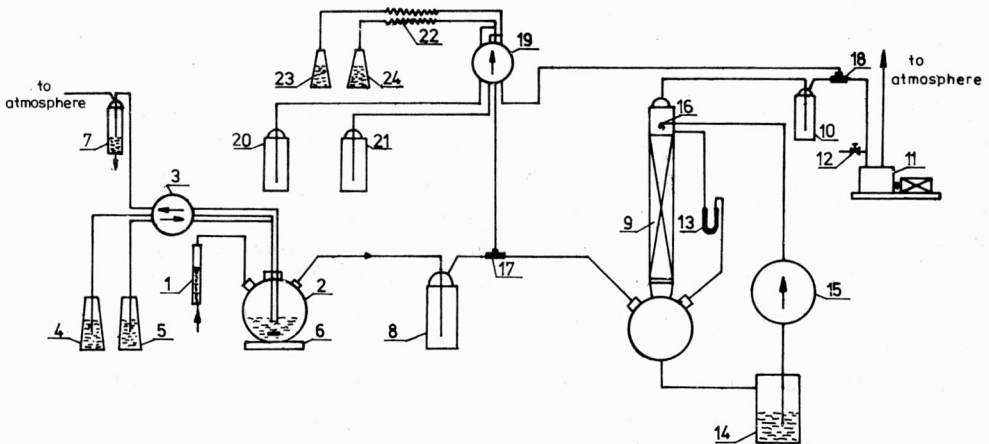


Fig. 1. Experimental system

the flask (2) through a pump (3). The quantity of the reagents in the flask (2) is kept constant by continuous pumping (3) of excess amounts to the tank (7). The air–nitrogen dioxide mixture enters a packed column of 0.025 m diameter (9) via a demister (8). Following treatment, the stream is sent by a vacuum pump (11)

through the demister (10) to enter the atmosphere. Gas flow rate is controlled with an appropriate valve (13), and readings are taken from a liquid-column gauge (13). The spraying solution is supplied from the tank (14) by a pump (15) and an atomizing nozzle (16). Nitrogen dioxide concentration before and after passage through the packed column (17, 18) is determined colorimetrically (Specol). Gas samples for analysis are collected through a suction pump (19). The same pump also serves for the supply of the absorbing solution (20, 21), which changes its colour when reacting with nitrogen dioxide in the coils (22). The gas samples (obtained in appropriate time intervals) are analyzed for nitrogen dioxide content.

The experiments were run in a 0.025 m diameter column with a packing depth of 1 m, at the following values of parameters:

gas flow rate — 4.9 to $49.0 \cdot 10^{-5} \text{ m}^3/\text{s}$,

linear gas velocity — 0.1 to 1.0 m/s,

initial NO_2 concentration in gas — 1.0 to 10.0 g/m³, 0.05 to 0.5 vol. %,

flow rate of spraying solution — 6.8 to $54.4 \cdot 10^{-7} \text{ m}^3/\text{s}$,

spraying density — 5.0 to 40 m³/m² h,

process temperature — 298 K.

The following acidic solutions were used for investigating the absorption of nitrogen oxides [30]:

H_2O , HNO_3 , H_2SO_4 ,

H_2O , HNO_3 , H_2SO_4 with addition of oxidizing or catalyzing agents (e.g., FeSO_4 , $\text{Fe}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, KMnO_4 , CoSO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$).

To provide comparable time of contact between liquid and gaseous phase in the course of the absorption process, the column was packed with $0.025 \times 0.025 \times 0.0006$ m Pall rings.

The objectives of this experimental series can be itemized as follows:

1. To verify the potentiality for acidic absorption (water, nitric acid solution, sulphuric acid solution) in the treatment of flue gases from nitric acid plants, from the manufacture of sulphuric acid by the mixed acid method, or from small emitters (acid etching of metals).

2. To determine the effect of some major parameters (gas velocity; initial concentration of nitrogen oxides in the flue gas stream; concentration and type of the spraying solution; spraying density) on the kinetics of acidic absorption.

3. To establish the contribution of oxidizing (or catalyzing) additives to the kinetics of the absorption process.

The experiments were run in series which consisted of a dozen or more measuring procedures. In each series the concentrations of nitrogen oxides in the flue gas ($\text{NO}_2:\text{NO} = 1$), the concentration of the spraying solution and spraying density were kept constant (gas velocity being a variable parameter). Curves were plotted basing on the results of three experiments for a given gas velocity.

3. RESULTS AND DISCUSSION

3.1. ABSORPTION OF NITROGEN OXIDES IN WATER AND IN INORGANIC ACID SOLUTIONS

The experimental series with the objective itemized as (2) has shown that the curves relating the efficiency of absorption to gas velocity, spraying density, and initial NO_2 concentration are similar in shape for all of the spraying solutions

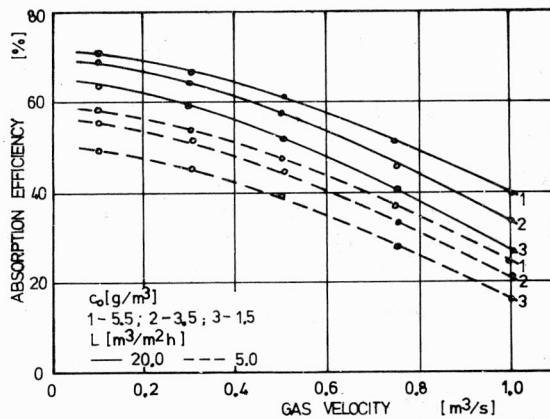


Fig. 2. Effect of nitrogen oxides concentration in flue gas on absorption efficiency for spraying densities (water) of $20 \text{ m}^3/\text{m}^2\text{h}$ and $5 \text{ m}^3/\text{m}^2\text{h}$, and for varying initial NO_2 concentration in the gas

1 - $c_0 = 5.5 \text{ g}/\text{m}^3$, 2 - $c_0 = 3.5 \text{ g}/\text{m}^3$, 3 - $c_0 = 1.5 \text{ g}/\text{m}^3$

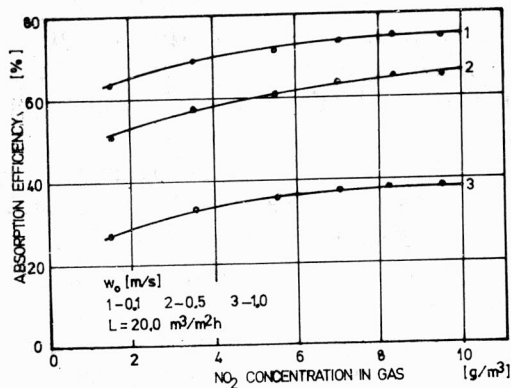


Fig. 3. Absorption efficiency versus concentration of nitrogen oxides in the gas for various velocities and a constant spraying density (water, $20 \text{ m}^3/\text{m}^2\text{h}$)

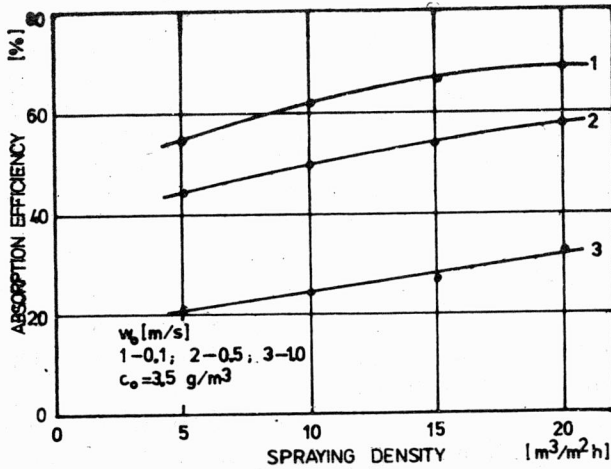


Fig. 4. Absorption efficiency versus spraying density (water) at a constant initial NO_2 concentration and varying gas velocity

applied. In the investigated range of the variable parameters, there are only differences in the absorption efficiency values. Examples characterizing the absorption of nitrogen oxides in water are given in figs. 2, 3 and 4.

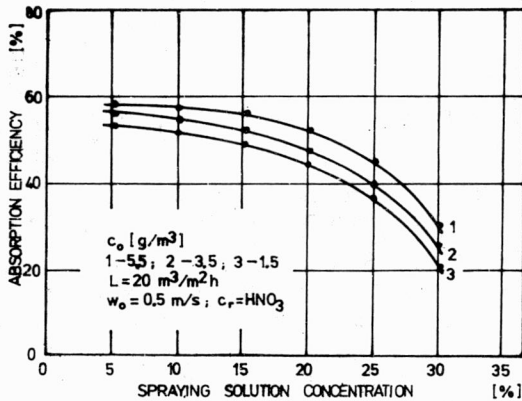


Fig. 5. Absorption efficiency versus concentration of nitric acid solution for spraying density of $20 \text{ m}^3/\text{m}^2\text{h}$, gas velocity of 0.5 m/s , and varying initial NO_2 concentration:
1 - $c_0 = 5.5 \text{ g/m}^3$, 2 - $c_0 = 3.5 \text{ g/m}^3$, 3 - $c_0 = 1.5 \text{ g/m}^3$

As shown by these data, maintaining a spraying density of $20 \text{ m}^3/\text{m}^2\text{h}$ in the absorption column for each of the solutions studied provides a maximum coverage of the packing surface by the spraying solution and, consequently, a maximum removal efficiency. The effect of spraying density on the efficiency of the process is

more pronounced at lower gas velocities (i.e., at a longer time of contact between gas and spraying solution). The efficiency of absorption decreases with the increasing gas velocity. In the investigated range of variable parameters, the contribution of initial NO_2 concentration to the absorption effect increases up to the limit value of about 6.5 g/m^3 (0.31 vol. %). Once this limit value is exceeded, initial NO_2 concentration accounts only for a slight improvement in the absorption efficiency.

Figures 5 and 6 give examples of nitrogen oxides absorption in nitric acid and sulphuric acid, respectively. Thus, for nitric acid, the relationship between the concentration of the spraying solution and the efficiency of the absorption process is particularly distinct in the range of 5 to 20 wt. % to diminish rapidly beyond this range. Here are more details to visualize this behaviour. At an initial NO_2 concentration of 5.5 g/m^3 , a gas velocity of 0.5 m/s and a spraying density of $20 \text{ m}^3/\text{m}^2\text{h}$, absorption efficiency amounts to 58.7%, 52.9% and (only) 30.0% for 5 wt.% nitric acid solution, for 20 wt.% nitric acid solution and for 30 wt.% nitric acid solution, respectively. No significant variations are observed in the shape of the curves for initial NO_2 concentrations different from 5.5 g/m^3 .

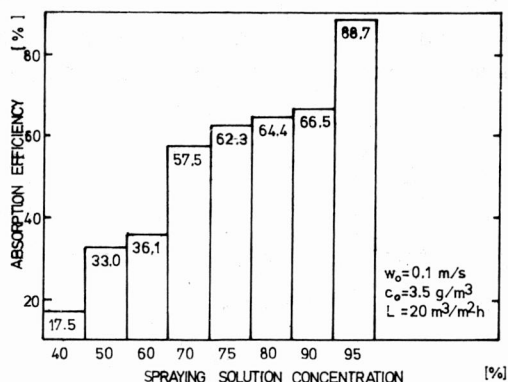


Fig. 6. Absorption efficiency versus concentration of sulphuric acid solution at constant initial NO_2 concentration ($c_0 = 3.5 \text{ g/m}^3$) and constant gas velocity (0.1 m/s)

For sulphuric acid solutions (fig. 6), the relationship between concentration of the absorbent and process efficiency is particularly distinct at 95 wt.% H_2SO_4 , to decrease in the concentration range of 70 to 90 wt.% H_2SO_4 . In solutions of sulphuric acid concentrations below 60 wt.% the relationship is insignificant.

3.2. ABSORPTION OF NITROGEN OXIDES IN ACIDIC SOLUTIONS WITH OXIDIZING (OR CATALYZING) ADDITIVES

In this experimental series attempts were made to improve the kinetics of absorption (in water, in sulphuric acid solution or in nitric acid solution) by the

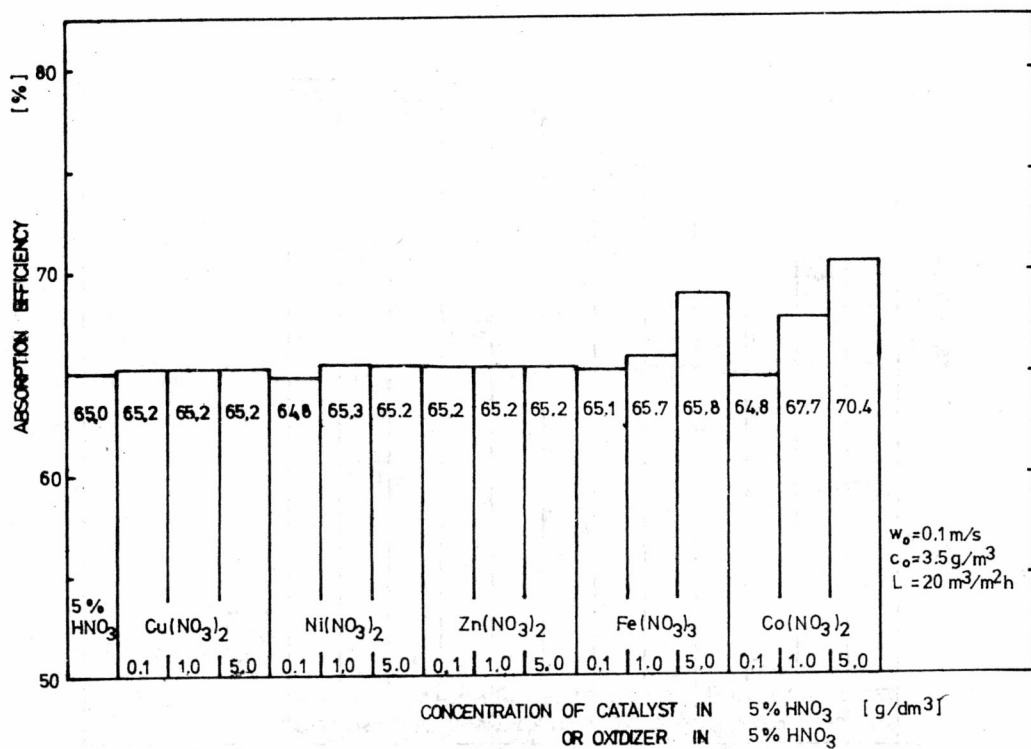


Fig. 7. Effect of oxidizing (or catalyzing) substance addition on the absorption of nitrogen oxides in 5 wt.% nitric acid solution

addition of oxidizing or catalyzing agents into the spraying solution. These were copper, nickel, zinc, iron, manganese, chromium and cobalt salts. For the most active substances, the influence of some major process parameters on the efficiency of absorption was measured under experimental conditions. As shown by the plots of figs. 7 and 8, the best removal of nitrogen oxides from the flue gas stream has been obtained in water and in 5 wt.% nitric acid solution additionally treated with cobalt nitrate (fig. 7). Equally good removal efficiency can be achieved in 60 wt.% sulphuric acid solution treated with potassium dichromate (fig. 8).

The data sets obtained in this study have confirmed the contribution of the oxidizing (or catalyzing) additives on the absorption efficiency. The curves relating the efficiency of the process to gas velocity, spraying density, and initial NO₂ concentration are similar in shape for all of the spraying solutions applied.

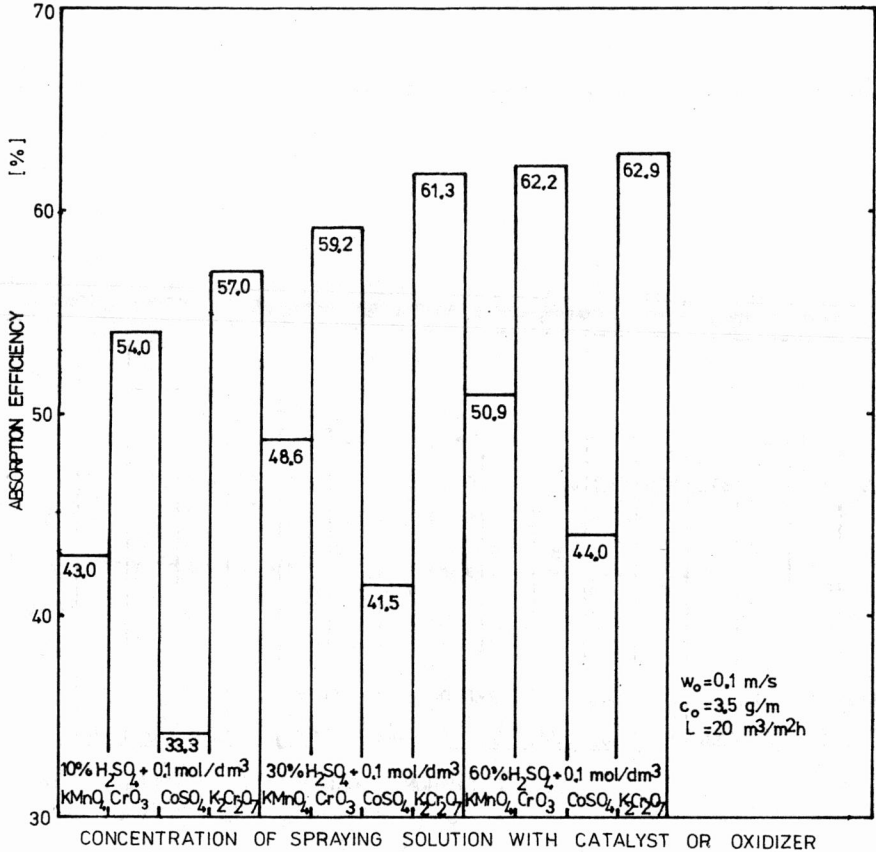


Fig. 8. Effect of oxidizing (or catalyzing) substance addition on the absorption of nitrogen oxides in sulphuric acid solutions

4. SUMMARY

Absorption of nitrogen oxides in acidic solutions runs with a good efficiency at low gas velocities. The process can be carried out

a) in water or 5 wt.% nitric acid solution for the treatment of flue gases from metal etching with recovery of acid (which is to be reused in the etching bath);

b) in diluted solutions of nitric acid at a maximum concentration of 25 wt.% for the treatment of flue gases from nitric acid manufacture;

c) in concentrated sulphuric acid solutions (95 wt.%) for the treatment of flue gases from the manufacture of sulphuric acid by the mixed acid method;

d) in sulphuric acid solution with addition of chromates for the treatment of flue gases from chromium electroplating; the wastewater generated via this route can be reused for the treatment of flue gases at the source of origin.

REFERENCES

- [1] NOWICKI M., *Główne źródła emisji zanieczyszczeń atmosfery na obszarze Polski*, Mat. konf. *Strategia i technika ochrony powietrza atmosferycznego*, Zabrze-Kraków 1985, pp. 1-10.
- [2] BILLET R., *Beitrag zur Absorption von Stickstoffoxiden*, Verfahrenstechnik, 1971, 8, 333-339.
- [3] WEISWEILER W. et al., *Messung der Absorptionsgeschwindigkeit von Stickstoffdioxid in Wasser mit einem Fallfilm Absorber*, Chem. Ing. Tech., 1980, 52(8), 670-671.
- [4] WEISWEILER W. et al., *Einsatz eines Strahldüsenreaktors für die Absorption von Stickoxiden in Wasser*, Chem. Ing. Tech., 1981, 53(2), 124-125.
- [5] KOMIYAMA H., INOUE H., *Absorption of nitrogen oxides into water*, Chem. Eng. Sci., 1980, 35, 154-161.
- [6] LEFERS J., BERG P., *Absorption of NO_2/N_2O_4 into diluted and concentrated nitric acid*, Chem. Engng. J., 1982, 23, 211-221.
- [7] COUNCE R., PERONA J., *Scrubbing of gaseous nitrogen oxides in packed towers*, AIChE J., 1983, 29(1), 26-32.
- [8] WEISWEILER W., BLUMHOFER R., *Absorptionsgeschwindigkeit von Stickstoffdioxid in Wasser, gemessen mit einer Labor-Doppelrührzelle*, Chem. Ing. Tech., 1983, 55(5), 400-401.
- [9] KARLSSON H., *Exact solution to NO_2 absorption*, J. Chem. Eng. of Japan, 1984, 17(2), 214-215.
- [10] KRYSDEV I. et al., *Absorbciya azotnykh okislov iz vykhlopnykh gazov pri proizvodstve azotnoi kisloty*, Inf. Zashchita Atmosfery, 1975, 5, 8-13.
- [11] ATROSHCHENKO V. et al., *Method rescheta processov vzaimodeistviya okislov azota s rastvorami azotnoi kisloty*, Zhurn. Prikl. Khim., 1970, 43(11), 2379-2385.
- [12] TERESHCHENKO L. et al., *O vliyanií sostava gaza na okislenie okisi azota azotnoi kisloty*, Zhurn. Prikl. Khim., 1972, 45(2), 241-245.
- [13] LEFERS J. et al., *The oxidation and absorption of nitrogen oxides in nitric acid in relation to the tail gas problem of nitric acid plants*, Chem. Engng. Sci., 1980, 35, 145-153.
- [14] SWINIARSKI A., *Mechanizm absorpcji tlenków azotu przez kwas siarkowy*, Przem. Chem., 1955, 11, 471-485.
- [15] BYLOV V., *Raschet processa absorbcii okislov azota sernoi kisloty*, Zhurn. Prikl. Khim., 1962, 35, 1503-1505.
- [16] EPIFANOV V. et al., *Vliyanie sernokislotnogo tumana na absorbciiyu okislov azota v proizvodstvie sernoi kisloty nitroznym sposobom*, Khim. Prom., 1976, 52(3), 39-40.
- [17] MALIN K. et al., *Vliyanie izbytká dnuokisi azota na absorbciiyu okislov azota sernoi kislotoi*, Khim. Prom., 1978, 2, 124-125.
- [18] KUZNETSOV I., LUNYAKA K., *Kinetika absorbcii okislov azota vodnymi shchelochnymi rastvorami*, IVUZ Khim. i Khim. Tekhnologiya, 1973, 16(7), 1069-1074.
- [19] OZASA M. et al., *Removal of nitrogen oxide using an alkaline absorption method*, Natl. Tech. Rep., 1974, 20(5), 580-591.
- [20] AOKI M. et al., *Simultaneous absorption of NO and NO_2 into alkaline solutions*, J. Chem. Eng. Jpn., 1982, 15(5), 362-367.
- [21] CARTA G., *Role of HNO_2 in the absorption of nitrogen oxides in alkaline solutions*, Ind. Eng. Chem. Fundam., 1984, 23, 260-264.
- [22] NEWMAN B., CARTA G., *Mass transfer in the absorption of nitrogen oxides in alkaline solutions*, AIChE J., 1988, 34(7), 1190-1199.
- [23] GOSTOMCZYK M. A., KUROPKA J., *Metody absorpcyjne oczyszczania gazów odlotowych z tlenków azotu*, Ochr. Pow., 1978, 5, 113-116.
- [24] KUROPKA J., GOSTOMCZYK M. A., ZADURA W., *Absorpcja tlenków azotu w roztworach utleniających, Gaz, Woda i Technika Sanitarna*, 1980, 9-10, 272-273.
- [25] KUROPKA J., GOSTOMCZYK M. A., *Redukcja tlenków azotu alkalicznymi roztworami siarczków i siarczynów*, Ochr. Pow., 1981, 1, 6-8.

- [26] GOSTOMCZYK M. A. et al., *Badania technologiczne oczyszczania gazów po produkcji kwasu azotowego*, Ochr. Pow., 1981, 3, 63–67.
- [27] GOSTOMCZYK M. A., KUROPKA J., SOSNOWSKI M., *On the removal and reuse of nitric oxides from process gases of sulphuric acid production*, Env. Prot. Engng., 1986, 12(2), 91–98.
- [28] KUROPKA J., GOSTOMCZYK M. A., *Technologia usuwania i utylizacji tlenków azotu z gazów z odlotowych*, Raport Inst. Ochr. Środ. PWr. Nr 33, 1987.
- [29] KUROPKA J., GOSTOMCZYK M. A., *A new technology for the removal and reuse of nitrogen oxides contained in industrial gases*, Env. Prot. Engng., 1988, 14(1), 39–45.
- [30] KUROPKA J., *Oczyszczanie gazów odlotowych z tlenków azotu*, Prace Nauk. Inst. Inż. Ochr. Środ. PWr. Nr 62, seria Monografie Nr 30, Wrocław 1988.

ABSORPCJA TLENKÓW AZOTU BADANIA ABSORPCJI TLENKÓW AZOTU W ROZTWORACH KWAŚNYCH

Zbadano możliwości zastosowania absorpcji tlenków azotu w roztworach kwaśnych do oczyszczania gazów odlotowych z wytwórni kwasu azotowego, z wytwórni kwasu siarkowego metodą nitrozową oraz z małych emitorów, np. z galwanizerni.

Określono wpływ zmian podstawowych parametrów, takich jak prędkość gazu, stężenie tlenków azotu w gazach oczyszczanych, stężenie i rodzaj roztworu oraz gęstość zraszania, na kinetykę procesu absorpcji tlenków azotu w roztworach kwaśnych. Określono również wpływ dodatku substancji utleniających lub katalizujących w roztworach kwaśnych na kinetykę procesu absorpcji tlenków azotu.

АБСОРБЦИЯ ОКИСЕЙ АЗОТА ИССЛЕДОВАНИЯ АБСОРБЦИИ ОКИСЕЙ АЗОТА В КИСЛЫХ РАСТВОРАХ

Исследования возможности применения абсорбции окисей азота в кислых растворах для очистки отходящих газов на азотнокислом заводе, на заводе, производящем серную кислоту нитрозным методом, а также на малых заводах, эмитирующих отходящие газы, напр. в гальваническом цеху.

Определено влияние изменений основных параметров, таких как: скорость течения газа, концентрация окисей азота в очищаемых газах, концентрация и род раствора, а также плотность орошения, на кинетику процесса абсорбции окисей азота в кислых растворах. Определено также влияние добавления окисляющих или катализирующих веществ в кислых растворах на кинетику абсорбции окисей азота.