ABSORPTION OF NITROGEN OXIDES AND SULPHUR DIOXIDE UNDER INTENSIVE BARBOTAGE CONDITIONS

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Abstract

This study investigates the efficiency of gas purification from nitrogen oxides (NO_x) and sulfur dioxide (SO_2) using jet-bubbling contact devices under intensified hydrodynamic conditions. The aim is to enhance mass transfer and improve removal efficiency in gas–liquid systems applied in industrial emission control. The research combines theoretical analysis and experimental validation of absorption and oxidation processes. Particular attention is given to the oxidation of nitric oxide (NO) to nitrogen dioxide (NO_2), which significantly increases absorption efficiency. Experimental studies were performed using water and alkaline absorbents, considering the influence of gas concentration, oxidation degree, and physicochemical properties of the liquid phase. Results show that jet-bubbling devices provide high turbulence and interfacial surface development, leading to improved mass transfer compared to conventional equipment. The removal efficiency of nitrogen oxides increases with higher oxidation levels, while sulfur dioxide absorption reaches up to 98.9% under optimal conditions using alkaline solutions. The findings confirm that jet-bubbling contact devices are an effective and compact solution for industrial gas treatment, offering reduced hydraulic resistance, lower energy consumption, and fewer технологических stages. The proposed approach demonstrates strong potential for application in modern environmental protection systems.

Keywords: process intensification, absorption, mass transfer, hydrodynamic parameters, scrubber, contact devices, gas purification, operating parameters, nitrogen monoxide, nitrogen dioxide, absorbent, scrubbing, sulphur dioxide, degree of purification of the gas mixture

Introduction

The problem of environmental pollution caused by chemical toxins remains as acute as ever.

Emissions of nitrogen oxides into the atmosphere remain one of the environmental problems. Nitrogen oxides are formed as a result of the combustion of organic fuels in industries such as power generation, metallurgy, mechanical engineering, the chemical and petrochemical industries, road and rail transport, and others [1-2].

Over the past two decades, it has been established that the NO molecule has a wide range of biological effects, which can broadly be divided into regulatory, protective and harmful effects. Disorders of NO biosynthesis and metabolism are associated with conditions such as essential hypertension, ischaemic heart disease, myocardial infarction, primary pulmonary hypertension, bronchial asthma, neurotic depression, epilepsy, neurodegenerative diseases (Alzheimer's disease, impotence, etc.) [3].

Sulphur dioxide (sulphuric anhydride) also occupies a special place, due to its significant gross emissions and harmful properties [4]. This substance has a negative impact on the human body, flora and fauna, and possesses strong corrosive properties; consequently, it has a detrimental effect on the metal structures of buildings and structures, causing significant damage to property.

Furthermore, when sulphur dioxide combines with moisture, it forms sulphuric acid, which damages the lung tissue of humans and animals. This link is particularly evident when analysing childhood lung conditions and the concentration of sulphur dioxide in the atmosphere of large cities. According to research by American scientists, at SO_2 pollution levels of up to 0.049 mg/m^3, the morbidity rate (in person-days) among the population of Nashville (USA) was 8.1%, at 0.150–0.349 mg/m^3 – 12%, and in areas with air pollution levels above 0.350 mg/m^3 – 43.8%. Sulphur dioxide is particularly dangerous when it settles on dust particles and, in this form, penetrates deep into the respiratory tract [5].

Industrial production mainly emits sulphur dioxide when burning organic fuels containing sulphur. The main sources of SO_2 are the energy sector, metallurgical and engineering enterprises, as well as the petrochemical industry [6-7].

Research into the absorption of nitrogen oxides

To date, there are numerous methods for controlling nitrogen oxides, but they are only suitable for specific production processes and situations. In its own 'niche', the liquid absorption method for NO_x removal is of particular interest. The process of nitrogen oxide absorption has been studied quite thoroughly in both scientific research and industrial practice. The problem lies in the fact that, given the varying characteristics of exhaust gases, a specific technology must be developed for each absorption process.

In many industrial processes, it is not a single nitrogen oxide but a mixture of several that is emitted into the atmosphere – typically NO + NO_2. Moreover,

as is well known, NO_2 is highly soluble in water, whereas NO is poorly soluble in the liquid phase. This raises the question of converting NO to NO_2 in terms of the qualitative absorption of the gas mixture by the absorbent.

For cold nitrous gases, a study was conducted on the absorption of nitrogen oxides in plate-type contact apparatus.

The oxidation of NO to NO_2 mainly takes place in the liquid phase, which accelerates the conversion of nitrogen oxides into HNO_3. Previous studies have shown that in reactors with mesh trays, this process occurs several times more intensively than in packed towers [8, 9]. It can therefore be assumed that in apparatuses with jet-bubbling phase contact, this process will be even more efficient. To evaluate this hypothesis, theoretical calculations were performed, which showed that to achieve high degrees of nitrogen oxide absorption from gases containing approximately 0,5% NO + NO_2, a column with 10–12 jet-bubble contact devices is required. To verify this assumption, the experiments described were carried out.

The experiment used a column with a diameter of 80 mm containing 10 contact devices with perforations ranging from 6 to 17 mm. The live cross-sectional area was 25%.

Nitrogen oxides were absorbed by water, which was fed through a rotameter to the upper part of the contact device. The experiments were conducted at gas flow rates in the column ranging from 0.65 to 0.70 m/s. The temperature of the gas-liquid layer was 15–17°C.

Depending on the initial nitrous oxide content of the gas and the level of NO oxidation, the degree of gas absorption was determined using the following formula:

$$\eta = \frac{C_1 - C_2}{C_1} \cdot 100$$

where C_1 and C_2 - the initial and final concentrations of nitrogen oxides, (vol. %).

To assess the extent to which NO is oxidized to NO_2, the theoretically possible degree of NO_2 absorption by water was also calculated

$$A = \frac{\frac{2}{C} C_{NO_2}}{C_1} \cdot 100,$$

where C_{NO_2} - NO_2 concentration in the exhaust gas (%).

The ratio η / A indicates how much of the nitrogen monoxide oxidized in the column is absorbed by water and converted to HNO_3.

The effect of gas oxidation on the degree of absorption was studied at a spray density L = 2 $m^3/m^2 \cdot h$. The concentration of the initial gas mixture ranged from 0.55 to 0.65% N + NO_2.

The degree of NO oxidation ranged from 0.34 to 0.72, and the absorption level of NO + NO_2 increased as the gas oxidation $\alpha_1 = \frac{NO_2}{NO + NO_2}$ increased. In our experiments, it ranged from 35% to 50%.

As the gas oxidation increases, the theoretical absorption coefficient A also increases, but to a greater extent than η . Therefore, the value of η / A decreases.

If, at an oxidation state of α_1 = 0.34, the ratio η / A averages 140%, then at α_1 = 0.7 it is 106%. This indicates that the less oxidized the gas is, the more NO is converted to NO_2, and the greater the amount converted to nitric acid.

However, not all of the nitrogen dioxide that was present in the gas and has been re-formed is absorbed by water in time. This is indicated by the oxidation state of the gas leaving the column—it remains quite high and depends on the oxidation state of the feed gas α_1. Thus, at α_1 ~ 0.6, the degree of NO oxidation in the gas leaving the column remains approximately constant (α_2 ~ 0.35–0.4). Then α_2 begins to increase. At a degree of oxidation of the feed gas of α_1 ~ 0.7, despite the high degree of NO_2 absorption $\alpha_1 \approx \alpha_2$. Exclusively in the gas phase, the conversion of NO to NO_2 could not occur during the short contact time upstream of the apparatus; therefore, it is achieved on the developed phase contact surface, i.e., up to 90–95% of the total amount of nitrogen monoxide is oxidized in the liquid. The experiments were conducted at a spray density of L = 2 $m^3/m^2 \cdot h$. The gas oxidation level ranged from 0.59 to 0.65, indicating that the degree of nitrogen oxide absorption NO + NO_2 increases from 16% to 42% as the nitrous content of the gases changes from 0.17% to 0.30%.

As the concentration of nitrogen oxides in the gas increases further, absorption increases only slightly. Conversely, as the concentration of NO + NO_2 decreases, the degree of absorption decreases. The following relationship is observed: when the gas contains NO + NO_2 up to 0.3% – (η / A < 100%); if this mixture exceeds 0.3%, the ratio η / A = 100 or higher. In this case, a portion of the NO_2 formed during the oxidation of NO is absorbed as the gas passes through the column. In the column with a jet-bubbling contact device, the gas-liquid system becomes turbulent, which promotes the oxidation of NO to NO_2 - an absorption rate of over 50% was achieved across 10 contact device blocks. Thus, as the concentration of nitrogen oxides in the outlet gas decreases, the efficiency drops sharply.

In addition to the absorption of nitrogen oxides by water, studies were conducted on alkaline absorption (using an aqueous solution of sodium carbonate as the absorbent). The experiments showed that the efficiency of the NO + NO_2 chemisorption process is greatly influenced by the time since the solution was prepared (the so-called “freshness of the solution”). This effect is apparently explained by the fact that in a fresh solution there are no intermediate compounds that inhibit the absorption process.

Analyses were conducted in both the gas and liquid phases, with the balance of gas and liquid absorption falling within the margin of error.

The experimental results are shown in Table 1. The table also includes, for comparison, three sets of experimental data obtained using 15 perforated sieve plates [10].

Table 1.

Absorption of nitrogen oxides in an absorber with a jet-bubble contact device

Gas inlet		Gas outlet		Degree of absorption in the gas phase, η_1, %	Degree of absorption in the liquid phase, η_2, %	Cleansing effect, %	Absorption coefficient, K
$NO + NO_2$	α_1	$NO + NO_2$	α_2				
15 Perforated Plates							
0.64	0.47	0.35	0.35	45.8			
0.61	0.48	0.34	0.34	44.3	-	3.9	68
0.61	0.49	0.34	0.34	44.3			
10 jet-bubble contact devices							
0.53	0.50	0.25	0.52	52.6			
0.46	0.56	0.29	0.38	38.1			
0.30	0.63	0.13	0.67	60.0	44.3	13.4	883
0.46	0.65	0.20	0.35	56.6			
0.54	0.65	0.25	0.50	58.6			
0.61	0.58	0.26	0.42	57.5			
0.59	0.61	0.24	0.37	59.4			
0.68	0.48	0.26	0.46	59.8			
0.26	0.50	0.27	0.48	51.8			
0.57	0.49	0.27	0.48	52.6	56.4	14.2	403
0.54	0.54	0.25	0.50	51.9			
0.58	0.50	0.26	0.54	51.0			

The data presented indicate that jet-bubble contact devices achieved approximately the same degree of nitrogen oxide absorption as 15-pass sieve plates. A comparison of these data shows that the efficiency of the jet-bubble contact devices is approximately 3.5 times higher, and the absorption coefficient is 5.5-6.0 times higher than that of the perforated sieve plates.

Thus, to achieve the same degree of absorption, jet-bubble contact devices will require several times fewer units, which will lead to a reduction in the overall column resistance and a decrease in capital costs.

The following main conclusions can be drawn from the studies conducted.

The degree of absorption depends on the initial nitrogen oxide content of the gas;

When nitrogen oxides in the feed gas are reduced below 0.3% NO + NO_2, the degree of absorption decreases sharply;

Along with the absorption of nitrogen oxides in the column, there is simultaneous intensive oxidation of NO to NO_2, which occurs mainly in the liquid phase.

Sulfur dioxide absorption under conditions of intense bubbling

Methods and techniques for sulfur dioxide purification have been under development by the scientific and industrial communities for quite some time. Among the existing methods, the following should be highlighted: wet (without sulfur recovery, cyclic with sulfur recovery, and with the production of new sulfur-containing chemicals) and dry (with a similar classification of processes for removing sulfur dioxide from gas) [11-13].

However, it should be noted that there is no universal method suitable for every type of production [14]. For instance, wet scrubbing is of particular interest for the purification of sulfur-containing gases at oil refineries, specifically in absorption units operating under enhanced bubbling conditions [15-16].

One of the main objectives in developing technology for the absorption of contaminated gas in an absorption unit is to select a hydrodynamic regime that ensures the greatest possible contact surface area between the gas and liquid phases and, as a result, enables the removal of toxic components from the gas with high efficiency, which is achieved by absorbers operating under intensive hydrodynamic conditions. In addition, such units are compact in size and feature a simple design [17-18].

The scope of application for intensified devices in industry can be very diverse: they can be used for processes such as gas absorption and desorption, dust collection, flue gas cleaning, mist removal, and others.

Absorbers operating under intense hydrodynamic conditions are columns with rectangular or circular cross-sections and horizontally arranged packing elements. The number of packing elements and their configuration depend on the unit's process purpose.

The contact devices in such units are block elements of jet-bubble contact devices with uniformly spaced holes, the total area of which i.e., the free cross-sectional area – typically ranges from 10 to 60% of the total cross-sectional area of the column. The diameters of the contact device's holes are 3-6 mm or more, and the distance between the centers of the holes (pitch) depends on the size of the device's individual cells, as well as the required free cross-sectional area.

By maintaining the velocity of the gas entering the unit through the diffuser within the range of 0.5–3.5 m/s, a fully developed bubbling regime can be achieved through the kinetic effect on the entire gas-liquid system. In this process, the liquid, passing through the distribution device and reaching the contact device in the form of moving foam, and having passed through the contact stages required by the process parameters, is discharged into a drain tank-defoamer, where the

foam is broken down and the liquid is removed from the apparatus via a pipeline.

The height of the moving foam on the contact devices can be adjusted within the range of 30 to 50 mm by varying the inter-contact distance, the gas velocity, and the amount of liquid fed into the unit. The purified gas exits through a fitting at the top of the unit, while the liquid, which has captured harmful impurities in the gas, is drained through a hopper and a fitting at the bottom of the unit.

The aim of the study was to investigate the feasibility of using jet-bubble contact devices in an extended bubbling mode for the capture of sulfur dioxide from process off-gases.

The experiments were conducted on single- and double-block jet-bubble contact devices in an extended bubbling mode.

For the sulfur dioxide experiments, the optimal hydrodynamic operating mode of the apparatus for the air-water system was selected in advance. Experiments showed that the developed bubbling mode and the most stable foam are achieved at a gas-air mixture velocity of 1-3.5 m/s. When using different chemical reagents for sulfur dioxide capture, the gas velocity can be varied within certain limits to optimize the purification process.

The unit operated according to the following scheme: sulfur dioxide from the cylinder flowed through a pressure reducer to the mixer, where air from the compressor was fed. The flow rate of the gas-air mixture was taken to be equal to the air flow rate and was measured using a rotameter. From the mixer, the gas-air mixture was fed into the apparatus from below and, foaming the absorbent, was discharged through the upper part of the apparatus. The absorbent was supplied from a pressure vessel to the upper block of the contact device.

The following were tested as absorbents: triethanolamine, 4% and 8% solutions of caustic soda, and a 3–5% aqueous solution of soda ash.

The absorption capacity of the absorber, or the degree of absorption, was determined as the ratio of the difference between the initial and final concentrations of sulfur dioxide to its initial concentration. Experiments on sulfur dioxide capture were conducted at a normal temperature of 15-35°C, with a gas-air mixture velocity of 0.6-3.5 m/s. The initial concentration of sulfur dioxide in the gas-air mixture ranged from 0.206-1.000%.

The results of the experiments are presented in Table 2. The table shows that triethanolamine proved to be an ineffective absorbent.

The highest degree of purification was achieved using a 5.8% solution of soda ash and an 8% solution of caustic potash, which ensure the capture of sulfur dioxide up to 98.9%.

The tabulated data also indicate that a sulfur dioxide absorption rate of 87.7-90.0% was achieved in the single-block model, and 92.7-98% in the two-block model. Therefore, if a high degree of purification is required, a greater number of block sections must be installed in the apparatus.

When using a two-block contact device in an enhanced bubbling mode with chemical reagents such as a 5.3% aqueous solution of soda ash and 4% and 8% caustic potash, the capture of sulfur dioxide from the gas was 92.3-96%. At the same time, the sulfur dioxide content at the outlet of the bubbling apparatus was 0.0137-0.0150%.

Table 2.

Sulfur dioxide capture efficiency in bubbler columns

Name of the absorbe	Experimental conditions				Concentration SO_2		Degree of absorp-tion
	gas-air mixture ve-locity, m/s	gas-air mixture flow rate, m/s	duration of the experi-ment, s	temperature, °C	at the device's input	at the output of the de-vice	
Single-block contact device							
Trimethylamine	2.6	13.1	13	17	0.9800	0.2400	75.5
-//-	2.6	13.1	10	17	0.5900	0.215	63.5
Sodium carbonate 5.3% aqueous solution	2.0	10.0	30	16	0.2270	0.0217	90.4
Sodium carbonate 5.3% aqueous solution	2.0	10.0	30	16	0.2270	0.0213	90.6
Caustic soda 4% aqueous solution	2.0	10.0	20	17	0.2070	0.0270	86.9
Caustic soda 8% aqueous solution	2.0	10.0	20	15	0.2620	0.0310	88.1
Caustic soda 8% aqueous solution	2.0	10.0	20	15	0.2620	0.0380	85.5
Two-block contact device							
Caustic soda 8% aqueous solution	3.5	17.6	30	16	0.3190	0.0132	95.86
Caustic soda 8% aqueous solution	3.5	17.6	32	16	0.4280	0.017	96
Sodium carbonate 5.3% aqueous solution	3.7	18.7	60	16	0.2100	0.0158	92.5
Sodium carbonate 5.3% aqueous solution	3.7	18.7	60	16	0.2060	0.0150	92.7

Conclusions

Thus, it has been established that sulfur dioxide can be captured by connecting an absorption unit equipped with a jet-bubbling contact device, operating in an enhanced bubbling mode, to the treatment plant. The results demonstrate that the oxidation process predominantly occurs in the liquid phase due to increased turbulence and developed interfacial contact. The findings indicate that jet-bubbling contact devices achieve comparable or higher efficiency than traditional plate columns while requiring fewer stages, thus reducing hydraulic resistance and capital costs.

To achieve the same degree of absorption, jet-bubble contact devices will require several times fewer units, which will lead to a reduction in the overall column resistance and a decrease in capital costs. Jet-bubbling contact devices represent an effective and compact solution for industrial gas purification, providing enhanced mass transfer, high removal efficiency, and reduced operational costs. The proposed approach can be widely applied in modern environmental protection systems.

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