APARATURA
BADAWCZA I DYDAKTYCZNA

Condition of the ambient air of Georgia and methods of its protection against nitrogen oxides

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ABSTRACT

In order to achieve a planned objective, the following aspects are considered in the work: the basic sources of ambient air pollution in Georgia; dynamics of the emissions of harmful substances in the air from various economic sectors; ambient air quality monitoring system in Georgia; qualitative condition of ambient air of Georgia; characteristic of some natural zeolites of sedimentary origins of Georgia and a possibility of their application for the purification of industrial emissions.

Stan powietrza w Gruzji i metody jego ochrony przed tlenkami azotu

STRESZCZENIE

W pracy uwzględniono następujące problemy i główne źródła zanieczyszczenia powietrza w Gruzji. Są to: dynamika emisji szkodliwych substancji do powietrza z różnych sektorów gospodarki, system monitoringu jakości powietrza, stan jakości powietrza, charakterystyka naturalnych zeolitów gruzińskich i możliwości ich wykorzystania do pochłaniania zanieczyszczeń emitowanych z przemysłu.

1. INTRODUCTION

At present, the attention of all mankind is fairly turned to a global process of environmental pollution state; a question of sanitary position of the ambient air of large cities and industrial centers is especially sharp. Technical progress continuously increases emission of ambient air pollutants and the concentrations of the certain components greatly exceed their maximum permissible levels. To solve this problem, nations take complex administrative measures on national, regional and local levels by using market mechanisms of impact including establishment of the strict emission norms and creation of effective legislative system [1, 2].

According to the Georgian legislation, at planning and realization of any activity, it is necessary to take appropriate measures to prevent or reduce the risks of impacts of harmful substances on the environment and health of the population. Georgian legislative regulations of the environmental protection include the laws acts, and the international normative acts as well.

At present, Georgia is a participant of about 50 multilateral and bilateral international agreements for the environmental protection which assign the certain obligations to the country. By associating to these international documents, the country has fixed its political will to the international community – to contribute to the decision of the global problem [3, 4].

Because of the absence of an appropriate analytical base and a perfect monitoring system in the country, the basic and the most labor-consuming elements of the given research were gathering and studying of the data and assessment of the ambient air quality of Georgia. Therefore, it was impossible to assess an actual ambient air condition all over the country and to receive the information about the emissions from the stationary sources, as the instrumental measuring of the emissions (even from the large industrial enterprises) was not conducted in Georgia.

Proceeding from the above, the assessment of the ambient air condition in the territory of Georgia has been done by a rated method of emissions based on the features of technological processes of manufactures (capacity of the manufacture, the used raw material, used fuel, efficiency of gas trap installations, etc.) and widely used all over the world.

2. EXPERIMENTATION

Quantitative prognostication of the existence of harmful substances which indirectly get into the air is possible by the rated method. To calculate the individual and total quantities of emissions of «the main pollutants» from the various sectors of the economics, the mean specific emission factors of the industrial production have been used. Calculation of these factors is based on the recommendations and procedures of IPCC and EMEP/EEA approved in the world, though modified in certain degree for the specific characters of Georgia [5, 6]. Based on the rated model, quantities of the emitted harmful substances have been determined, and dynamics of their variations has been analyzed for the period of 2000-2010. It has been revealed that motor vehicles are the basic sources of the ambient air pollution in the country and a fraction of emission (SO_2, CO_2, N_xO_y) from them is higher than that from the stationary sources of pollution. The fraction of emission from motor vehicles makes 71 % of the total emission in the whole country and its dynamics quickly increases. This tendency is clearly noticed in large, overcrowded by transport cities. For example, 38.7 % of all vehicles is concentrated in Tbilisi, where about one third of the country's population lives. The ambient air pollution of Tbilisi by vehicles is caused by the following physical and chemical factors: intensity and volume of emissions of the harmful substances; a type and quality of the used fuel; a technical condition of vehicles; a proper organization of traffic; natural ventilation (a micro-relief of city, feature of its building up, meteorological parameters, seasonal prevalence), etc. A strong negative impact of pollutants on the health of the population is observed in case of the bad ventilation conditions. Rapid increase of SO_2 emissions that corresponds to the increase of diesel fuel consumption is especially dangerous.

2.1 Fractions of emissions of air pollutants

In the 70-80s of the last century, the stationary sources of pollution played a significant role in the country's ambient air pollution; but at present, the fraction of industrial sector makes 4%, and that of energy sector – 25%. Mostly solid particles (dust) are emitted into the atmosphere from the industrial sector; especially greater amount of dust emission is characteristic for ce-
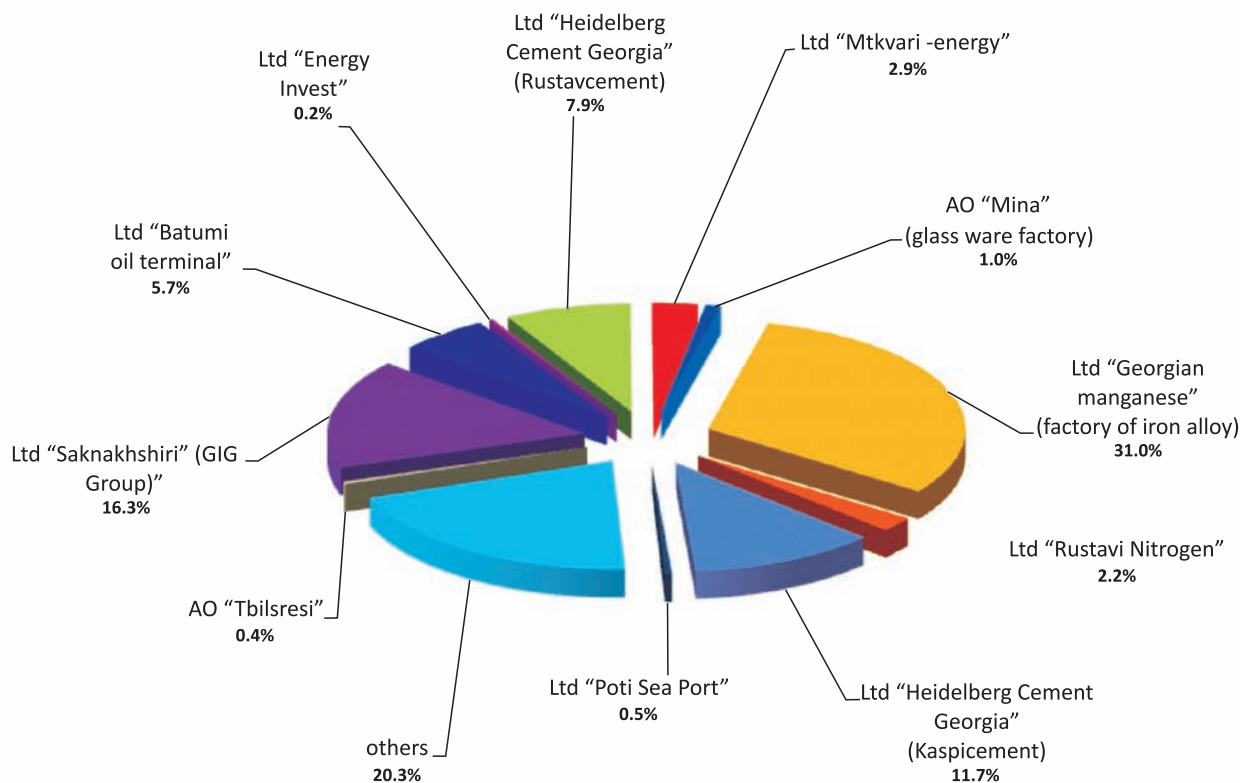
Figure 1 Fractions of emissions of air pollutants from the main stationary sources
Rysunek 1 Udział w emisji zanieczyszczeń powietrza głównych źródeł stacjonarnych

ment plants, plasterboard, concrete-asphalt producing industries. Combustion products such as carbon dioxide, nitrogen and sulfur oxides, and volatile organic compounds (VOC) are emitted into the atmosphere from the energy sector. Qualitative and quantitative variations of atmospheric emissions from these sectors depend on the various energy sources (coal, oil, black oil, natural and liquefied gas etc.). For example, more pollutants (SO_2, CO_2, N_xO_y, solid particles, etc.) are emitted into the air at combustion of black oil and coal than at combustion of natural or liquefied gases. Absence of effective gas and dust cleaning systems or poor quality of the existing ones is a major problem of the industrial and energy sectors. In respect to the ambient air pollution, several large stationary sources may by identified from these sectors and their emission fractions are represented on Figure 1.

Ambient air pollution from the agricultural sector of Georgia has a local character after establishment of smaller scale farms instead of large scale cattle-breeding and poultry-farming complexes. Compared to the other sectors, they have less impact on the country's ambient air quality. On the basis of the monitoring results, the tendency of

the ambient air quality variation is given for the last seven years (2005-2011) (Fig. 2).

The state monitoring of the air condition has been carried out by the National Environmental Agency under the Ministry of Environment Protection. At present, monitoring of the ambient air pollution is conducted only in five cities of Georgia: Tbilisi, Kutaisi, Batumi, Zestafoni and Rustavi where seven measurement stations are located. Three of these stations were installed only in 2009 (two in Tbilisi and one in Rustavi) (Tab. 1).

It has been revealed that in almost all the cities where the observations were conducted (in the period of 2005-2011), concentrations of dust (solid particles), carbon dioxide, nitrogen and sulfur oxides exceeded their maximum permissible levels. It is necessary to note that this tendency was not noticed in 2008-2010. In spite of this, concentrations of the pollutants increased in some cities in 2011 compared to that of the above period.

Concentrations of dust, nitrogen and sulfur oxides in the ambient air of Tbilisi, Kutaisi and Batumi are above the maximum permissible levels. The basic sources of the pollution in these cities are motor transport and construction works.
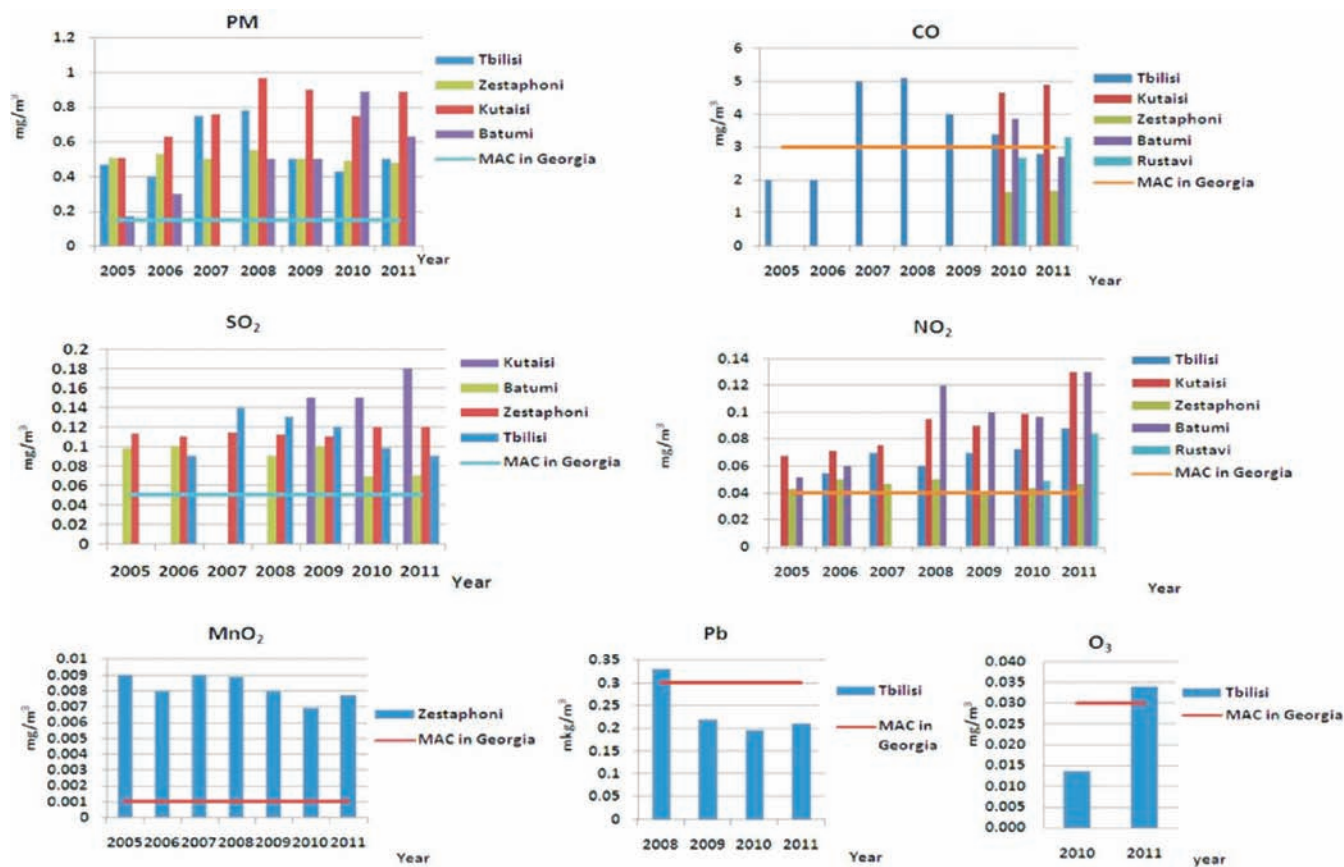
Figure 2 The diagrams, reflecting variations of mean annual concentrations of the basic ambient air pollutants for the period of 2005-2011

Rysunek 2 Diagramy obrazujące zmiany średnich stężeń głównych zanieczyszczeń powietrza w latach 2005-2011

Table 1 Location of the ambient air quality control stations in cities

Tabela 1 Rozmieszczenie stacji kontroli zanieczyszczeń powietrza

Pollutants	Number of control stations						
	Tbilisi			Batumi	Rustavi	Kutaisi	Zestafoni
	3 stations			1 station	1 Station	1 Station	1 Station
	I	II	III				
Dust	●			●		●	●
SO$_2$	●			●		●	●
NO$_2$	●	●		●	●	●	●
CO	●	●	●	●	●	●	●
O$_3$	●						
Pb	●						
MnO$_2$							●
NO						●	

Regular monitoring of the ambient air pollutants has revealed that in Zestafoni, where the ferro-alloy plant of «Georgian Marganese» Ltd is located, the mean annual concentration of manganese dioxide exceeds its permissible level. In Tbilisi, concentration of lead in emissions has decreased since 2008 and at present, it does not exceed the national standard. Determination of ground level ozone in the country has begun since 2010 and its concentration slightly exceeded a maximum permissible level in 2011.

Thus, it has been shown that in Georgia, the existing ambient air quality monitoring system does not correspond to the international requirements. The quantity of the measurement stations, their arrangement, selection of data, processing and conservation of the information do not allow us to really estimate the country's ambient air condition.

2.2 Natural zeolites as purifying agents of the ambient air

In spite of the existing numerous methods of de-activation of harmful components in the atmospheric emissions, search for the rational and effective methods of purification is becoming more actual. At present, among the methods of gas purification systems, special attention is given to the adsorption methods, as only adsorbents allow to catch practically all the components of gaseous emissions in the atmosphere. In this aspect, natural adsorbents – zeolites, characterized by their high adsorption capacity and selectivity against these ambient air pollutants are poorly studied. It is necessary to note, that Georgia is rich in sedimentary natural zeolite deposits [7, 8] by the help of which the degree of purification meeting the modern sanitary requirements is achieved. The expediency of application of natural zeolites is proved by the economic calculations as well. Treatment of poor zeolitic deposits and the subsequent separation of zeolite fractions is 20 times as cheap as the manufacture of synthetic zeolites; but their extraction from mono-mineral beds is 100 times cheaper.

Zeolites, as an independent group of minerals, were identified by the Swedish scientist A. Kronstedt in 1756, after discovery of Stilbite. A. Kronstedt named this mineral zeolite, that means «a boiling stone» in Greek. The 7th International Conference devoted to the 250 anniversary of the introduction of the term – zeolite [9] and concerned

to the deposits of natural zeolites, their properties and the practical implementation took place in Sokoro (New Mexico, USA) in 2006. According to the monography «Natural zeolites» by G. Gotardi and E. Galli [10], types of zeolites in nature are total about 46; from them chabazite was the first (1792) and Vilxenderzonite the last (1984) to be discovered. For the last decade of the second millennium, three more new types of natural zeolites have been discovered; the last one known in the literature as Mutinaite [11], was found in basalt rocks of Antarctica.

At present, huge deposits of zeolite bearing rocks with a high content of the basic mineral and having an industrial application have been discovered on all the continents of our planet. From twenty types of zeolites found in rocks, only eight of them (analcime, chabasite, clinoptilolite, erionite, heulandite, laumontite, mordenite and phillipsite) are more widely represented [12].

2.3 Application of natural zeolites for purification of ambient air from N_xO_y oxides

Information about the application of various types of natural zeolites and their modified forms in the processes of cleaning of the industrial wastes, polluting ambient air, have been considered and generalized. The results of the separation and purification of gaseous emissions from carbon, sulfur and nitrogen oxides, ammonia and other ambient air pollutants [13-15] are widely represented in the given researches.

Characteristics of some Georgian sedimentary natural zeolites (analcite, clinoptilolite, mordenite and phillipsite) and their absorptive properties against the main pollutants have been investigated and the results are given in Table 2.

In the presented work, adsorption-separation properties of natural zeolites in relation to CO_2, CO, N_xO_y have been investigated by a method of gas-adsorption chromatography. By the example of the separation of the prepared calibrated mixtures (air, CO_2, CO, N_xO_y), influence of the gas-carrier rate and the temperature of a chromatographic columns on the quality of the separation of the model mixture have been studied. During the investigation, optimal conditions and the sorbents (clinoptilolite and mordenite) with the best adsorption properties against the components under investigation have been determined. The nature and a degree of the replacement of cations in zeolites have an essential impact on

Table 2 Some physical-chemical and structural features of the investigated zeolites [7]
Tabela 2 Niektóre fizykochemiczne i strukturalne właściwości badanych zeolitów

№	Structural type, code	Name of zeolite	Crystalline structure	Volume of an elementary cell, nm³	Free volume, cm³/cm³	Size of the windows, nm,	Density of the framework, g/cm³
1	MOR	mordenite	rhombic	2.794	0.28	0.67 x 0.7 and 12-members 0.29 x 0.57 and 8-members in rings	1.70
2	ANA	analcime	cubic	2.60	0.18	0.26 and 6- members in rings	1.85
3	HEU	clinoptilolite	monoclinic	2.10	0.34	0.40 x 0.55 and 8-members 0.44 x 0.72 and 10 members in rings	1.71
4	PHI	phillipsite	rhombic	2.022	0.31	0.42 x 0.44 and 8-members 0.28 x 0.48 and 8-members 0.33 – and 8-members in rings	1.58
System of channels	MOR	Two-dimensional, channels ‖ To axes B and C					
	ANA	one-dimensional, channels ‖ To directions [111]					
	HEU	Two-dimensional, channels ‖ axes A; ‖ axes C; ⊥ axes A, B and C					
	PHI	three-dimensional, channels ‖ To directions [001]					

the nature of the interactions between sorbates and adsorbents, on their retentions as well. Therefore, some cation-modified forms (Na, K, Ca, Cu, NH_4) of clinoptilolite and mordenite were prepared. Investigation of adsorption-separation properties of these samples have shown their modification by NH_4^+ cations and hydrogen forms obtained after decrepitation essentially differ by their sorption properties. Hydrogen form of mordenite has been distinguished by the best adsorption properties against the air pollutants. During the investigation, the most attention was given to nitrogen oxides (N_xO_y), as they help to form acid rain, contribute to global warming, hamper the growth of plants, and form toxic chemicals with other pollutants [16]. At high concentrations in ambient air, nitrogen dioxide can irritate the lower airways of the respiratory tract, especially the lung tissues.

To control the concentration of the aggressive gases in the air, the procedure of quantitative chromatographic analysis has been developed.

Polymeric sorbent Poropak Q characterized by its high separation efficiency, even at low temperature, has been chosen as a chromatographic column packing material. In the process of the work, calibrated mixtures (air, N_2O, NO_2, NO) of different concentrations have been prepared. The experiment was carried out on the chromatograph «Tsvet 500»; the detector – catharometer, temperature – 20-25°C. Separation has been reached for all the concentrations of the calibrated mixtures at the determined optimum conditions. Chromatographic peak heights were used for the determination of the individual component concentrations (Fig. 3, 4, 5) [17].

Adsorption dynamics is the basis for the gas purification process by solids. To study the dynamics of the adsorption process of gas mixtures purification by the hydrogen form of mordenite, a flowing type laboratory device has been designed. Nitrogen oxide concentrations were determined from the chromatograms by calibration curves.
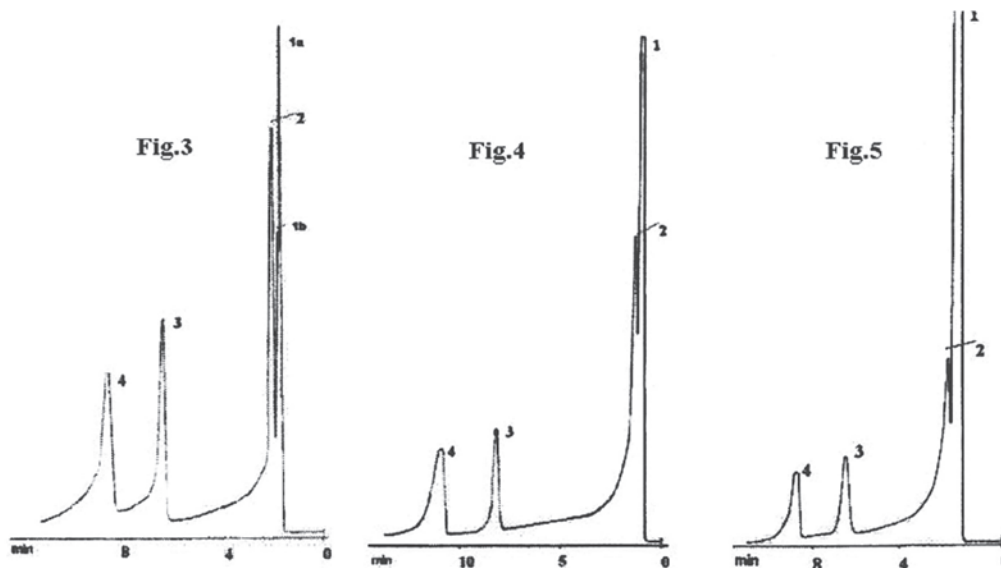
Figure 3, 4, 5 Chromatograms of the calibrated mixtures of various concentrations:
Figure 3 air - 25%; NO – 25%; NO_2 – 25%; N_2O – 25%: 1 - air (1a-N_2, 1b-O_2); 2- NO; 3- NO_2; 4- N_2O
Figure 4 air - 50%; NO – 16.5%; NO_2 – 16.5%; N_2O – 16.5%: 1 - air; 2- NO; 3- NO_2; 4- N_2O
Figure 5 air - 75%; NO – 8.5%; NO_2 – 8.5%; N_2O – 8.5%: 1 - air; 2- NO; 3- NO_2; 4- N_2O
Rysunek 3, 4, 5 Chromatogramy mieszanin kalibracyjnych o różnych stężeniach

The principal information about the work of sorbent layer – output curves (isoplanes) were plotted in C/C_o – τ coordinates; where C is the concentration of the polluting components, τ is the breakthrough moment (working time of the sorbent layer till its complete saturation) [18].

The experiments were carried out till the complete tryout of zeolite layer (till the pollutant concentration was equal to its concentration in the initial mixture C_o). Dynamic (a_d) and equilibrium (a_p) adsorption activities, time of the protective action of a sorbent layer (τ), length of a mass exchange zone (Lo), and share of the used sorbent layer (η) were calculated from the graphic data. By empirical selection, the optimum size of the sorbent grains (which fluctuated within the limits of 0.25-0.315 mm) has been established for the 24 cm long adsorption column at 25°C temperature [19].

Output curves (isoplanes) N_2O adsorption dynamics from the air on differently granulated (0.25-0.315; 0.5-1.0 mm) H-mordenite and at different temperatures of the adsorption column are represented in Figure 6.
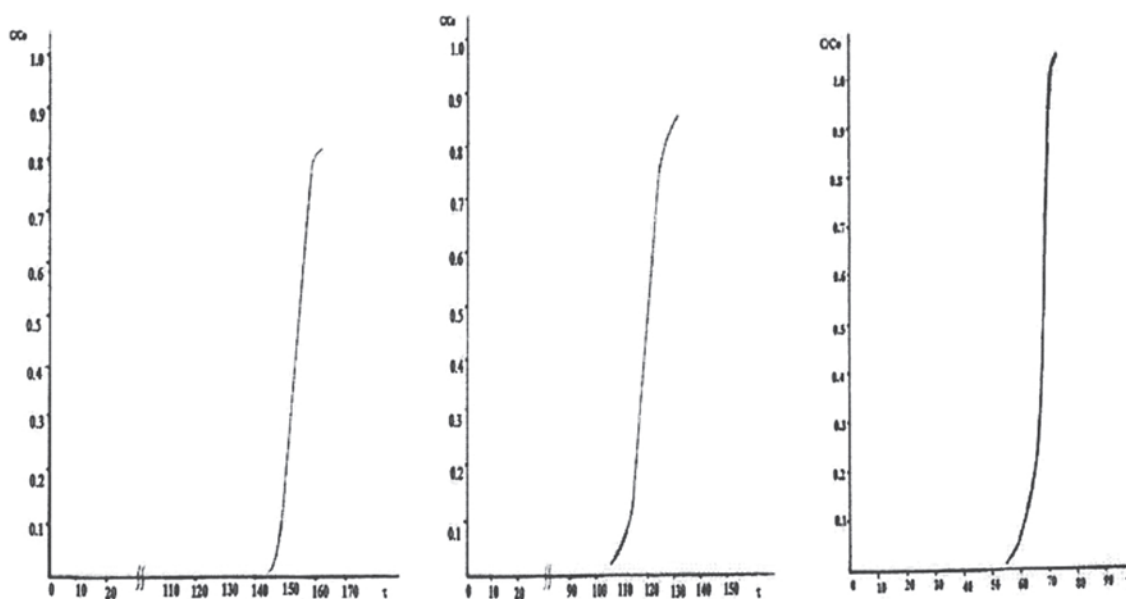
Figure 6 Output curves (isoplanes) of N_2O adsorption dynamics from the air
Rysunek 6 Krzywe wyjściowe dynamiki sorpcji N_2O z powietrza

According to obtained data, equilibrium and dynamic adsorption activity of the layer were determined with respect to N_2O (correspondingly a_{eq} and a_d, g/100g). The value of L_o, mass-transfer zone length (height of working layer) was calculated according to the Michaels-Treybal equation [20]. The degree of using of the adsorption volume of the layer η (%) was determined from the formula:

$$\eta = {a_d}/{a_{eq}}.$$

Adsorption characteristics were calculated according to N_2O peak, as it was the last peak on the chromatogram (Fig. 3-5).

As it is seen in Fig. 6, decrease in the size of the sorbent granules has a considerable impact on the time of the protective action (increased by 1.5 times). Application of the sorbent of this size is acceptable for the laboratory conditions, but in industry, bigger-size granules are needed for large-tonnage adsorption. In liquid phase process, increase in adsorption column temperature highly promotes increase in diffusion coefficient, decrease in mass transfer zone and correspondingly, increase in dynamic activity of sorbent; but in gas phase, dynamic activity of sorbent decreases at 50°C of an adsorption column and correspondingly decreases the breakthrough moment. The results of the adsorptive purification on H-mordenite at different temperatures (25°C; 50°C) and granulation (0.25-0.315 mm) are given in Table 3.

For the regeneration of the adsorbent (to remove the accumulated pollutants), the combined method (combination of displacement and thermal methods) of sorbent regeneration was used; supposedly, the products formed after regeneration can be used as fertilizers in agriculture. Aqueous solution of ammonium hydroxide (NH_4OH) was used as a displacing substance. Essentially, adsorbent regeneration temperature has an influence on the adsorptive activity, time of a sorbent layer protective action, and on other dynamic characteristics of purification process, which were calculated from the output curves (isoplanes).

The offered method of regeneration of the hydrogen form of mordenite is very profitable and optimal, that allows application of adsorbent in the subsequent cycles of purification without losing its adsorptive activity.
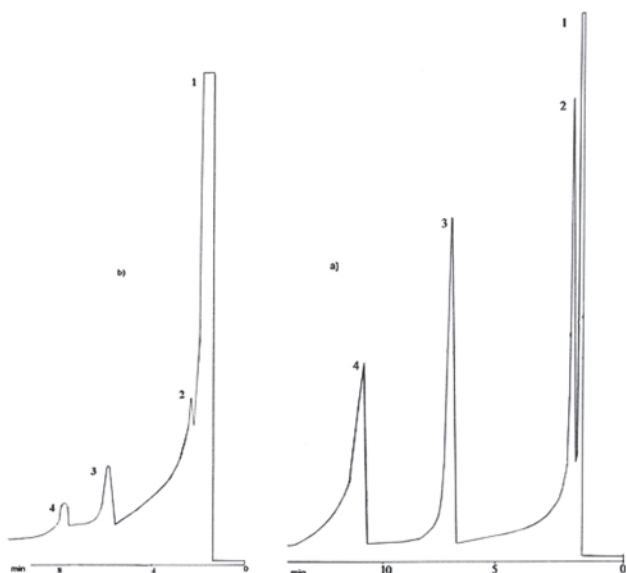
The investigated sample (the hydrogen form of mordenite) has been approved by the example of purification of the industrial emission (taken from a discharged pipe of the contact device) of the «Rustavi Nitrogen» plant producing nitric acid by oxidation of ammonia. In the adsorption column (24 cm x 1 cm) of the laboratory device, the sample moved at the rate of 100 ml/min. For three hours, about 18 liters of a gas mixture were passed through the adsorption column. After the specified time, a control sample was taken for the chromatographic analysis and for the comparison to the initial data at the output of the column (Fig. 7).

From the chromatographic data, percentage compositions of the investigated mixtures were determined by the planimetric method. The initial sample contained: air − 19.57%; NO − 31.55%; NO_2 − 22.14%; N_2O − 26.75%; but the sample taken at the output of the adsorption column contained: air − 53.39%; NO − 21.96%; NO_2 − 13.05%; N_2O − 11.61%.

Table 3 Adsorptive purification on H-mordenite at different temperatures and granulation.
Tabela 3 Adsorpcyjne oczyszczanie na mordenicie-H o różnej granulacji, w różnych temperaturach

Indices of adsorption dynamics	Temperature of the adsorption column, °C		
	25°C		50°C
	Different granulation of the samples under investigation		
	0.25-0.315 mm	0.5-1.0 mm	0.25-0.315 mm
Length of a mass exchange zone -L_o, mm	3.45	3.96	3.85
a_d Dynamic activity of sorbent against gas, g/100g	25.8	23.70	9.12
a_w equilibrium activity of sorbent against gas, g/100g	27.5	26.40	10.2
η - share of the used sorbent %	93.82	89.77	89.4

As the obtained data have shown, concentrations of nitrogen oxides in the sample decreased approximately twice; it should be taken into consideration that the adsorption column of the laboratory device is quite small, but the flow rate is rather high. At selection of the optimal experimental conditions, compete adsorption of nitrogen oxides is probably possible.

3. CONCLUSION

Thus, the obtained data testify that the investigated sorbent efficiently works as an adsorbent, especially for the retention of nitrogen oxides.

Figure 7 Chromatograms of the analyzed sample mixtures: a) sample of the initial gas mixture; b) sample at the output of the adsorption column 1. Air ; 2. NO; 3. NO_2; 4. N_2O
Rysunek 7 Chromatogramy analizowanych mieszanin: a) mieszanina pierwotna; b) mieszanina na wyjściu z kolumny adsorpcyjnej

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