Effect of Exhaust Gas Flow Velocity on the Chemisorption of Nitrogen Oxides

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This study investigates wet scrubbing of diesel exhaust gases for NO_x removal, as NO_x is one of the major pollutants associated with diesel engine operation. Chemical absorption of NO_x was achieved through the interaction of exhaust gases with aqueous absorbent solutions ($KMnO_4$ + HNO_3, $KMnO_4$ + H_2SO_3, $CO(NH_2)_2$ + $SnCl_2$, and water) under bubbling conditions. The dependence of NO_x neutralization efficiency on the flow velocity of treated exhaust gases was established. The proposed relationship, along with the methodology developed on its basis, enables the evaluation of the performance of chemical absorbents in the wet neutralization of NO_x from diesel exhaust gases, taking into account hydrodynamic and gas–liquid interaction effects.

Introduction

Internal combustion engines are a significant source of air pollution. In areas with a high concentration of transport and equipment powered by internal combustion engines operating in confined spaces (such as open pits, ore quarries, and mines), this problem becomes particularly critical. The widespread use of diesel power units, especially as components of distributed generation systems, necessitates addressing the problem of exhaust gas (EG) neutralization for diesel engines operating under stationary conditions. In this context, the development of EG neutralization systems for stationary diesel power plants is of considerable relevance.

Among the main toxic pollutants in diesel EG are nitrogen oxides (NO_x) and particulate matter [1–4]. The operation of diesel power units under stationary conditions significantly broadens the range of applicable NO_x abatement methods. A variety of techniques for NO_x removal from gases have been reported in [5–16], including oxidative–sorption methods, non-catalytic reduction, catalytic reduction, and gas denitrification using radiation.

Reducing NO_x emissions from diesel EG is also an important environmental objective [17–23]. Wet scrubbing of exhaust gases can significantly decrease NO_x emissions into the atmosphere. In this regard, particular attention should be paid to studies aimed at identifying the factors influencing the process of wet NO_x neutralization.

Purposes and research tasking

Based on the analysis of existing methods for removal of nitrogen oxides from gases

[15, 16, 24–28], the application of chemisorption for the treatment of diesel exhaust gases operating under stationary conditions is well justified. In [29, 30], the application area of liquid-phase neutralization of diesel exhaust gases (EG) and the prospects for improving the efficiency of NO_x liquid neutralization were demonstrated. The specific features of the physicochemical interaction with diesel exhaust gases during liquid neutralization determine the field of its application, where the advantages of this method are most effectively realized.

Water is one of the most accessible and simplest absorbents for harmful impurities. Nitrogen dioxide is readily soluble in water, forming nitric acid. Aqueous solutions of various chemical absorbents are also widely used, with their chemical mechanisms of action presented in [30].

The main objective of this study is to determine the dependence of the NO_x neutralization efficiency during chemisorption on the flow velocity of the treated gases.

Experimental methods

The experiments were carried out using both laboratory-scale and full-scale setups. Chemical absorption of NO_x was carried out through the interaction between exhaust gases and aqueous absorbent solutions under bubbling conditions. The laboratory-scale experimental setup (**Figure 1**) consisted of a glass reactor filled with a solution of the investigated chemical absorbent for NO_x, through which a portion of the exhaust gases from a D21A diesel engine was bubbled.

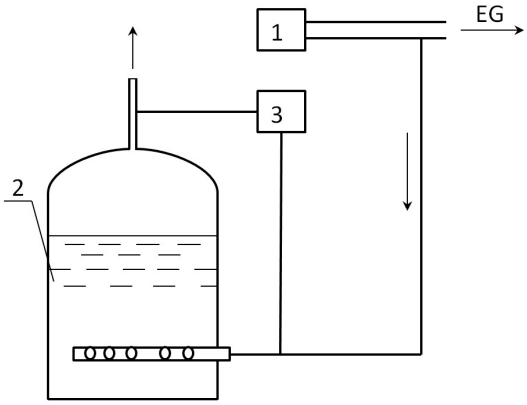

Figure 1. Schematic diagram of the laboratory-scale experimental setup: 1 – D21A diesel engine; 2 – glass reactor (bubbler); 3 – gas analyzer.

In full-scale stationary experimental setups equipped with D21A and KamAZ-740 diesel engines, the exhaust gases were completely passed through a layer of aqueous absorbent solutions in reactors of appropriate dimensions. In all experiments, gas samples for NO content analysis were taken upstream and downstream of the reactors.

Wet neutralization of EG was carried out based on oxidative–sorption and non-catalytic reduction methods.

During the development of a wet exhaust gas (EG) neutralization system for diesel engines at the A.M. Pidgorny Institute of Mechanical Engineering Problems of the National Academy of Sciences of Ukraine (IPMash NAS of Ukraine, currently the A.N. Podgorny Institute of Power Machines and Systems of NAS of Ukraine), it was experimentally established that NO_x neutralization efficiency during wet neutralization using various chemical absorbents is significantly influenced by the

flow velocity of the treated gases (**Figure 2** [30]).

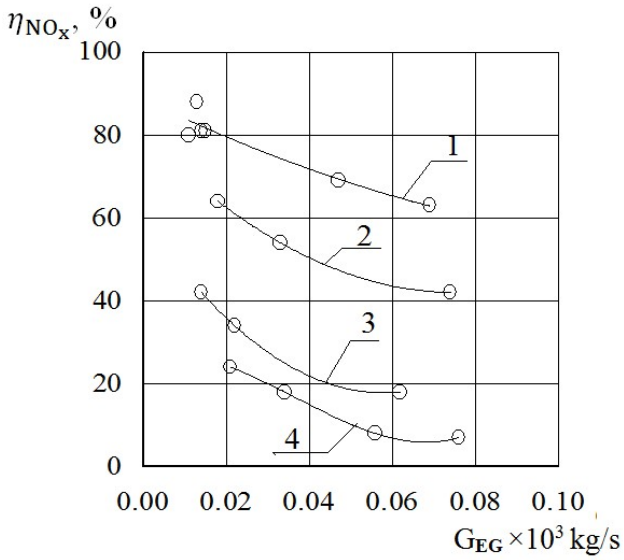

Figure 2. Dependence of NO_x neutralization efficiency on EG flow rate for various chemical absorbents: 1 – aqueous solution of $KMnO_4 + HNO_3$; 2 – aqueous solution of $KMnO_4 + H_2SO_3$; 3 – aqueous solution of $CO(NH_2)_2 + SnCl_2 + HNO_3$; 4 – water.

The flow velocity of the purified gases and the mass flow rate of diesel exhaust gases (EG) are related by the following equation:

$$W_{EG} = \frac{V_{EG}}{S_b} = \frac{G_{EG}}{S_b \cdot \rho_{EG}} \quad (1)$$

where W_{EG} is the flow velocity of diesel exhaust gases; $V_{EG} = G_{EG}/\rho_{EG}$ is the volumetric flow rate of diesel exhaust gases; S_b is the cross-sectional area of the reactor (bubbler); G_{EG} is the mass flow rate of diesel exhaust gases; ρ_{EG} is the density of diesel exhaust gases, which depends on the EG composition, temperature, and pressure.

At low flow rates of treated exhaust gases EG (**Figure 2**), i.e., at low gas velocities in the reactor, the NO_x neutralization efficiency is higher. As the EG flow rate increases, the NO_x neutralization efficiency gradually decreases for all chemical absorbents. Despite the differing effectiveness of the tested absorbent solutions, the pattern of NO_x neutralization efficiency variation with respect to EG flow rate (specifically, the gas velocity during interaction with the aqueous solutions) remained similar for all chemical absorbents.

According to [31], the behavior of the chemical reaction during absorption is influenced by the reaction kinetics, particularly by the residence time of gas and liquid streams in the reaction zone. Based on this, analysis of the experimental data indicates that, when a set of parameters (EG temperature and density, absorbent chemical composition, and similarity of the bubbler design) is kept constant, the variation in NO_x neutralization efficiency for each chemical absorbent can be described by the following relationship:

$$\eta_0 ln \frac{\eta_0 + \sqrt{\eta_0^2 - \eta_{NO_x}^2}}{\eta_{NO_x}} - \sqrt{\eta_0^2 - \eta_{NO_x}^2} = \bar{W}_{EG} \quad (2)$$

where η_{NO_x} is the NO_x neutralization efficiency of diesel exhaust gases; η_0 is the NO_x neutralization efficiency under quasi-steady-state conditions for a given chemical composition of the solution (i.e., the theoretically maximum achievable NO_x neutralization efficiency for the particular chemical absorbent under the condition of $W_{EG} \to 0$). $\bar{W}_{EG} = W_{EG}/W_{EGmax}$ – the relative flow rate of EG in the reactor, where W_{EG} is the EG flow rate calculated at the reactor's cross-section, and W_{EGmax} is the maximum EG flow rate in the reactor.

It was also established that, for each specific absorbent composition, the theoretical maximum neutralization efficiency η_0 is a

constant value, characterizing the ultimate chemical capacity of the solution to neutralize NO_x under conditions of unlimited interaction time between the reactants.

The value of the constant η_0 for a given absorbent composition can be determined as follows. First, the NO_x neutralization efficiency η_{NO_x} is experimentally measured at any relative EG flow rate $\bar{W}_{EG}$ in the laboratory-scale reactor for that chemical absorbent. These measured values of η_{NO_x} and $\bar{W}_{EG}$ are then substituted into equation (2), and the equation is solved for η_0.

The proposed relationship (2), along with the method used to determine the constant η_0, allows using the laboratory setup, the assessment of the potential capacity of the investigated chemical absorbent for NO_x neutralization. It also enables analysis of the full-scale installation's efficiency across the entire range of relative EG flow rates $\bar{W}_{EG}$, i.e. under all operational conditions.

From **Figure 2**, it can be seen that the highest degree of NO_x neutralization efficiency (80–90 %) was achieved with the aqueous solution of $KMnO_4$ + HNO_3. This chemical absorbent, along with pure water, was tested in full-scale installations with D21A and KamAZ-740 diesel engines.

Figure 3 presents the results of experimental studies conducted on both laboratory-scale and full-scale setups using the aqueous solution of $KMnO_4$ + HNO_3 and water, along with the calculated dependencies for these absorbents.

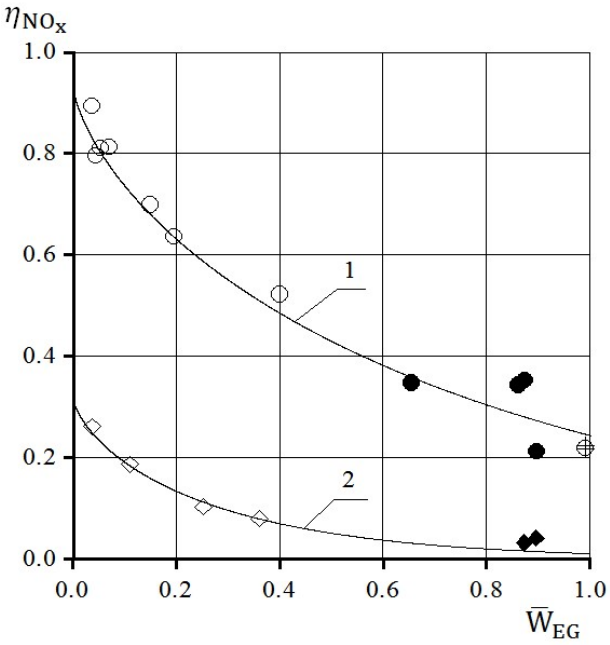

Figure 3. NO_x neutralization efficiency of diesel exhaust gases: 1 – aqueous solution of $KMnO_4$ + HNO_3; 2 – water; ○, ◊ – laboratory-scale setup (D21A diesel engine); ●, ♦ – full-scale setup with D21A diesel engine; ⊕ – full-scale setup with KamAZ-740 diesel engine.

The calculated curves 1 and 2 (**Figure 3**) were constructed using equation (2) and the data from a single point for each (obtained in the laboratory setup with the D21A diesel engine). The calculated constants η_0 for these chemical absorbents were: for the aqueous solution $KMnO_4$ (1 %) + HNO_3 (0.4 %) – $\eta_{0gr1} = 0.91$ (curve 1); and for water – $\eta_{0gr2} = 0.30$ (curve 2). For calculation purposes, W_{EGmax} was taken as the maximum EG flow rate in the reactor of the full-scale installation with the KamAZ-740 diesel engine.

The calculated curves 1 and 2 (**Figure 3**) show good agreement with the experimental results obtained on both laboratory-scale and full-scale setups. In particular, for the full-scale installation with the KamAZ-740 diesel engine, the experimentally measured NO_x neutralization efficiency using the aqueous solution of $KMnO_4$

(1 %) + HNO_3 (0.4 %) was 21.2 %, which is very close to the calculated value (**Figure 3**).

Curves 1 and 2 (**Figure 3**) clearly illustrate the differences in efficiency of the tested absorbents and their capacity to neutralize NO_x across the entire range of operational conditions. The NO_x neutralization efficiency decreases from 91 % to 24 % for an aqueous solution of $KMnO_4$ (1 %) + HNO_3 (0.4 %) and from 30 % to 1 % for water as the relative velocity $\overline{W}_{EG}$ in the reactor increases to its maximum value.

Analysis of the calculated dependencies indicates that, to enhance the efficiency of chemical NO_x absorption from diesel exhaust gases, it is necessary not only to select the optimal chemical composition of the absorbent, but also to consider that, with increasing EG flow rate in the reaction zone, hydrodynamic and gas–liquid interaction processes significantly affect NO_x absorption. At the same time, attempts to increase NO_x neutralization by reducing the EG flow rate in the reactor conflict with the practical limitations on the size of the bubbler and the overall installation. Accordingly, the solution to this problem should represent a compromise that takes into account various operational and design factors: the main operating modes of the diesel engine and the total duration of operation under these modes; the maximum structurally permissible increase in the reactor flow cross-sectional area; and the possibility of ensuring the optimal EG flow velocity in the reactor, considering both the maximum and average EG velocities under the principal operating conditions of the diesel engine.

Thus, the proposed relationship and the methodology developed on its basis provide the following capabilities:

– to investigate the efficiency of chemical absorbents in the wet neutralization of NO_x from diesel exhaust gases, taking into account hydrodynamic and gas–liquid interaction processes;

– to determine the NO_x neutralization efficiency for full-scale installations based on laboratory-scale studies (on the experimental setup);

– to design wet EG neutralization systems with a predetermined calculated of NO_x neutralization efficiency by modifying the installation design (affecting the EG flow rate W_{EG} while considering the permissible mass and size constraints of the bubbler).

In the future, the proposed relationship and the obtained results can be applied in the development of absorption-based chemical-technological processes involving the interaction of two-phase media.

Conclusions

The main advantages of liquid-phase neutralization of diesel exhaust gases (EG) include the possibility of simultaneous trapping of particulate matter and neutralization of toxic gaseous and water-soluble EG components; cooling of EG to temperatures of 40–80 °C, which is important for operation in explosive environments; and effective spark suppression.

Under modern conditions, the advantages of liquid-phase EG neutralization determine the field of its effective application, including diesel

engine testing stations; autonomous stationary diesel power plants; and transport diesel engines operated in areas with limited air exchange and enclosed spaces.

Liquid-phase EG neutralization is also an essential component of exhaust gas treatment systems for special underground diesel-powered installations, diesel load-haul-dump machines, and specialized self-propelled equipment operating in explosive environments (mines, ore pits, etc.). Therefore, under such specific operating conditions, liquid-phase neutralization of diesel exhaust gases will remain in demand in the future.

The efficiency of wet NO_x neutralization depends both on the chemical composition of the absorbent and on the EG flow rate in the reactor. The developed methodology made it possible to determine, both experimentally and theoretically, that when an aqueous solution of $KMnO_4$ (1 %) + HNO_3 (0.4 %) is used as an absorbent, the NO_x neutralization efficiency decreases from 91 % to 24 %. In contrast, when water is used, the efficiency decreases from 30 % to 1 % as the relative velocity $\bar{W}_{EG}$ increases from zero to its maximum value. The calculated dependencies are in good agreement with the experimental data.

It has been established that for each absorbent composition, the theoretical maximum NO_x neutralization efficiency under bubbling conditions with unlimited reactant contact time (i.e., quasi-steady-state conditions at $W_{EG} \rightarrow 0$) is a constant value characterizing the limiting chemical capacity of a given absorbent for NO_x neutralization. For an aqueous solution of $KMnO_4$ (1 %) + HNO_3 (0.4 %), this value is 0.91, whereas for water it is 0.30.

To enhance the efficiency of wet NO_x neutralization from diesel exhaust gases, it is essential to optimize the chemical composition of the absorbent and to consider that, with increasing EG flow rate in the absorption zone, hydrodynamic and gas–liquid interaction processes significantly affect NO_x neutralization. In particular, an increase in the EG flow velocity in the reactor leads to a reduction in the interaction time between the EG flow and the aqueous absorbent solution, thereby decreasing the NO_x neutralization efficiency.

The developed methodology allows for the design of wet EG neutralization systems with a predetermined calculated of NO_x neutralization efficiency by adjusting the flow rate of treated gases while accounting for the permissible mass and dimensional constraints of the equipment.

References

[1] Thakur P. Diesel Exhaust Control. Advanced Mine Ventilation 2019:157-187.

[2] Fan Z, Lin L. Exposure Science: Contaminant Mixtures. Encyclopedia of Environmental Health 2011:645-656.

[3] Reşitoğlu İ, Altinişik K, Keskin A. The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems. Clean Technologies and Environmental Policy 2014;17(1):15-27.

[4] Dobrzyńska E, Szewczyńska M, Pośniak M, Szczotka A, Puchałka B, Woodburn J. Exhaust emissions from diesel engines fueled by different blends with the addition of nanomodifiers and hydrotreated vegetable oil HVO. Environmental Pollution 2020;259:113772.

[5] Sassykova L, Aubakirov Y, Sendilvelan S, Tashmukhambetova Z, Faizullaeva M, Bhaskar K, Batyrbayeva A, Ryskaliyeva R, Tyussyupova B, Zhakupova A, Sarybayev M. The Main Components of Vehicle Exhaust Gases and Their Effective Catalytic Neutralization. Oriental Journal of Chemistry 2019;35(1):110-127.

[6] Shcheklein S, Dubinin A. Analysis of nitrogen oxide emissions from modern vehicles using hydrogen or other natural and synthetic fuels in combustion chamber. International Journal of Hydrogen Energy 2020;45(1):1151-1157.

[7] Sun J, Caton J, Jacobs T. Oxides of nitrogen emissions from biodiesel-fuelled diesel engines. Progress in Energy and Combustion Science 2010;36(6):677-695.

[8] Chong H, Park Y, Kwon S, Hong Y. Analysis of real driving gaseous emissions from light-duty diesel vehicles. Transportation Research Part D: Transport and Environment 2018;65:485-499.

[9] Miller B. Nitrogen oxides formation and control. Fossil Fuel Emissions Control Technologies 2015:243-280.

[10] Reid H, Aherne J. Staggering reductions in atmospheric nitrogen dioxide across Canada in response to legislated transportation emissions reductions. Atmospheric Environment 2016;146:252-260.

[11] Mei X, Xin Y, Zhang Y, Nie W, Zhang Z, Lu P, Zhang Z, Chen G, Zhang J. Electrification-Enhanced Low-Temperature NOx Storage–Reduction on Pt and K Co-Supported Antimony-Doped Tin Oxides. Environmental Science & Technology 2023;57(49):20905-20914.

[12] Shukla M, Chauhan B, Verma S, Dhar A. Catalytic Direct Decomposition of NOx Using Non-Noble Metal Catalysts. Solids 2022;3(4):665-683.

[13] Zhao J, Sun J, Meng X, Li Z. Recent Advances in Vehicle Exhaust Treatment with Photocatalytic Technology. Catalysts 2022;12(9):1051.

[14] Jo H, Ko A, Jang J, Lim O. Study on Rates of NH3 Adsorption and Desorption in SCR on Various Engine Operation Conditions. Sustainability 2023;15(19):14468.

[15] Li X, Ren S, Chen Z, Wang M, Chen L, Chen H, Yin X. A Review of Mn-Based Catalysts for Abating NOx and CO in Low-Temperature Flue Gas: Performance and Mechanisms. Molecules 2023;28(19):6885.

[16] Gan L, Liu Y, Ye P, Niu H, Li K. Reaction Mechanism for the Removal of NOx by Wet Scrubbing Using Urea Solution: Determination of Main and Side Reaction Paths. Molecules 2022;28(1):162.

[17] Goto T, Ohyama R. An experimental study on neutralization of non-thermal plasma oxidized diesel engine combustion exhaust NOx gases with hydrated lime filter. The 17th Annual Meeting of the IEEE Lasers and Electro-Optics Society, 2004. LEOS 2004. 2004:114-117.

[18] Seo H, Jeong R, Boo J, Song J, Boo J. Study on Chemical Removal of Nitric Oxide (NO) as a Main Cause of Fine Dust (Air Pollution) and Acid Rain. Applied Science and Convergence Technology 2017;26(6):218-222.

[19] Pan S, He K, Lin K, Fan C, Chang C. Addressing nitrogenous gases from croplands toward low-emission agriculture. npj Climate and Atmospheric Science 2022;5(1):43.

[20] Guo X, Chen L, Zheng R, Zhang K, Qiu Y, Yue H. Differences in Soil Nitrogen Availability and Transformation in Relation to Land Use in the Napahai Wetland, Southwest China. Journal of Soil Science and Plant Nutrition 2019;19(1):92-97.

[21] Ladan S, Jacinthe P. Nitrogen availability and early corn growth on plowed and no-till soils amended with different types of cover crops. Journal of soil science and plant nutrition 2017;17(1):74–90.

[22] Martínez J, Galantini J, Duval M. Contribution of nitrogen mineralization indices, labile organic matter and soil properties in predicting nitrogen mineralization. Journal of soil science and plant nutrition 2018;18(1):73–89.

[23] Saggar S, Jha N, Deslippe J, Bolan N, Luo J, Giltrap D, Kim D, Zaman M, Tillman R. Denitrification and N2O:N2 production in temperate grasslands: Processes, measurements, modelling and mitigating negative impacts. Science of The Total Environment 2013;465:173-195.

[24] Ali M, Hussain I, Mehmud I, Umair M, Hu S, Sharif H. Recent Breakthroughs and Advancements in NOx and SOx Reduction Using Nanomaterials-Based

Technologies: A State-of-the-Art Review. Nanomaterials 2021;11(12):3301.

[25] Martinovic F, Castoldi L, Deorsola F. Aftertreatment Technologies for Diesel Engines: An Overview of the Combined Systems. Catalysts 2021;11(6):653.

[26] Zhu Z, Xu B. Purification Technologies for NOx Removal from Flue Gas: A Review. Separations 2022;9(10):307.

[27] Gooneh-Farahani S, Anbia M. Strategies to Reduce NOx Emissions from Flue Gas: Trends and Prospects. Water, Air, & Soil Pollution 2025;236(11):718.

[28] Sun Y, Li M, Zhu T, Li X, Gao Y, Fu J. Removal of NOx and PM from Non-Road Mobile Machinery by the Combination of Ozone Oxidation and Venturi Scrubbing. Processes 2025;13(11):3525.

[29] Semykin VM. Analysis of the Application Area of Liquid-Phase Neutralization of Diesel Exhaust Gases. Automobile Transport: Collection of Scientific Papers of Kharkiv National Automobile and Highway University 2008;22:128–130.

[30] Kudryash AP, Kireeva VN, Semykin VM. Neutralization of nitrogen oxides in diesel exhaust gases under steady-state conditions. Bulletin of Kharkiv State Polytechnic University. Internal Combustion Engines 1999;58:139–146.

[31] Ramm VM. Gas Absorption. Moscow: Chemistry 1976;656.