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DEVELOPMENT OF A METHOD FOR CATALYTIC PURIFICATION OF CARBON-CONTAINING COMPONENTS OF GAS EMISSIONS FROM INDUSTRIAL ENTERPRISES*

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Abstract

The aim of the paper is the development of catalytic purification of gas emissions containing carbon monoxide and hydrocarbons from electrode manufacturing enterprises with intermetallic catalysts. In the research work, we carried out comparative tests using the developed and existing catalysts for neutralization of the exhaust gases from the kiln and graphitization furnaces. The results of comparative tests showed that the composition of the developed catalyst has a lifetime of 1.6-1.7 times greater than that of the known nickel catalyst. Application of the developed composition of the catalyst allowed to increase the degree of gases purification to 99.9%.

Keywords: carbon oxide, gas emissions, hydrocarbons, intermetallic catalyst, neutralization

1. Introduction

The annual increase tendency of harmful emissions from industrial enterprises (by an average of 3-7%) is observed in Ukraine recently. Analyses show that about 10 million tons of harmful chemicals are released into the atmosphere annually; moreover, about 70% belong to the waste of stationary sources. This problem is particularly relevant to regions with a significant concentration of industrial enterprises. This fact underlines the urgency of

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solving the problem of health protection of the population, which live in the industrially loaded territories (Belokon', 2011).

Power plants, internal-combustion engines, and industrial plants are the sources of environmental pollution with carbon monoxide (CO) and hydrocarbons (C_mH_n). Chemical and biological properties of CO and C_mH_n and their significant volumes in gaseous emissions increase environmental hazard around the facilities emitting them. The concentration of CO and C_mH_n in the emissions produced by most of these sources does not meet the established standards and is a factor of intensive deterioration of the air quality (Belokon' et al., 2017). Air polluted by carbon monoxide and hydrocarbons has an adverse effect on fauna and flora. The presence of CO and C_mH_n in the air is also harmful to human health, namely, it causes some diseases of the circulatory, respiratory and nervous systems and is especially dangerous for children. Therefore, the development of measures aimed at ensuring the environmental safety of emissions containing carbon monoxide and hydrocarbons is one of the urgent environmental tasks (Belokon', 2015).

Electrode manufacturing enterprises vent about 4-5 million cubic meters of gases per hour. Those gases contain CO and resinous substances consisting of a mixture of polycyclic aromatic hydrocarbons, some of which are carcinogenic. The high environmental hazard of toxic organic substances determines the importance of the introduction of treatment technologies (Denisov, 1991).

The aim of the paper is to develop the method of neutralizing gas emissions containing carbon monoxide and hydrocarbons from the kilns and graphitization furnaces.

To achieve this goal, the following tasks were solved:

- the composition of emissions from kilns and graphitization furnaces was investigated;
- the characteristics of existing catalysts for the neutralization of gas emissions containing carbon monoxide and hydrocarbons were analyzed;
- the intermetallic catalyst was developed and pilot tests were carried out at the electrode manufacturing enterprise.

2. Materials and methods

The catalysts activity tests were conducted in the waste gas flow of the furnace on the laboratory-scale installation at a temperature from 100°C to 500°C and volumetric flow rate (W) ranging from $30 \cdot 10^3$ to $120 \cdot 10^3$ $m^3/m^3 \cdot hr$. The concentration of hydrocarbons in the industrial emissions was measured by gas chromatography using the device "Crystal 2000 M". The concentration of carbon monoxide was measured by means of the gas analysis instrument "Palladium-3".

To reduce the emissions of CO and C_mH_n , an intermetallic catalyst was developed. It consists of nickel and aluminum with additions of copper, cobalt, and manganese. The compound was produced by self-propagating high-temperature synthesis. In the capacity of initial reagents the alumina and nickel powders were used. The powder dispersion makes up to 50-100 mcm. The mix preparing scheme consists of mixing, press-form filling, pressing, thermal treatment and leaching. The pressing power was varied between 2.5-5 tons (Belokon and Belokon, 2018). The thermal treatment was lead in inert atmosphere at atmospheric pressure. The processing temperature was 390-460°C for 0.5-1 hours. The installation presented in Fig. 1 (Belokon et al., 2018) has been developed for studying the catalytic properties of intermetallic catalysts.

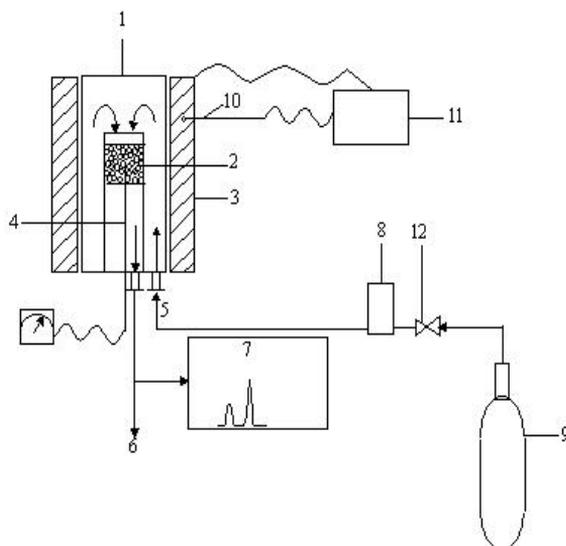


Fig.1. Installation for catalyst testing: 1 - reactor; 2 - catalyst bed; 3 - heating jacket; 4 - thermocouple; 5 - branch pipe for gas supply; 6 - branch pipe for gas removal; 7 - chromatograph; 8 - a rotameter; 9 - a balloon with a model mixture of gases; 10 - control thermocouple; 11 - reactor temperature maintenance unit; 12 - the regulator of the expense of a gas mix

3. Results and discussion

Carbon or graphite electrodes are made of the following materials: low-ash petroleum coke (about 85%); crushed electrodes (about 15%); coal tar pitch (as a binder). The components undergo the stages of crushing, calcination, grinding, fractionation, measuring and mixing. Then the electrode mass is processed in powerful horizontal presses. The received electrodes are dried, fired and they undergo a graphitization process. The content of harmful impurities in the gases generated during the calcination of petroleum coke is, mg/m^3 : 1400 CO; 470 SO_2 ; 107 NO_2 , 0.45 benzene, 0.7 styrene, 0.005 benzopyrene, 1.1 naphthalene, 7.5 acenaphthene, 0.65 phenol.

In the process of baking of extruded electrodes, one section of the kiln vents about 4 thousand m^3/h of gas. In the process of baking of impregnated electrodes, it vents 1.5–2.0 times less (Denisov, 1991). In both cases, a sharp increase in the concentration of harmful components in the gas phase (CO, CH_4 , resinous substances such as benzopyrene) occurs at the beginning of electrode baking. This is caused by the release of low-boiling hydrocarbons from the coal-tar asphalt, for example, benzene, and by the pyrolysis reaction, when they break apart into simpler units, which goes at relatively low temperatures in the oxidizing atmosphere under the arch of the kiln (natural gas burner).

The main toxic components released into the air from electrodes graphitization furnaces are CO, SO_2 , and resinous substances. The concentration of SO_2 in the gas phase reaches 12–33 mg/m^3 ; the concentration of dust in the gases is 17–25 mg/m^3 . From the beginning, the CO content in the gas phase rises progressively as the current capacity increases and reaches a maximum value of 770 mg/m^3 . After 10–13 hours of kiln operation, the temperature of the gases released from the gross mass of carbonaceous materials rises to the CO autoignition temperature. Thus, a considerable part of it is oxidized at the upper levels of filling. Starting from this period, the concentration of CO in the gaseous phase does not correspond to the quantity of CO that is released from the kiln as far as the temperature in the working zone of the kiln continues to increase considerably.

The waste gases contain resinous substances during the whole electrodes graphitization process. Their concentration increases dramatically from 1.5-2.0 to 8-9 mg/m³ during the 37th hour of operation of the furnace when the temperature of the furnace-charge insulation layer rises significantly.

One of the most effective ways of abatement of CO and C_mH_n is the catalytic method. The catalytic process of neutralization of combustion products runs, as a rule, at temperatures above 300°C and under short contact times, due to the high flow rate of industrial emissions. The main advantages of the catalytic process in comparison with thermal afterburning consist of its technological and operational characteristics, namely: high efficiency and economy, the absence of harmful side effects. For the catalytic elimination of CO and C_mH_n metal catalysts are widely used. They have higher activity in the reaction with CO and C_mH_n than oxide catalysts. According to the specific catalytic activity at the temperature of 180°C the metals can be arranged in the increasing order (Borsch et al., 2008): V, Cr, Mn, Cu, Ag, Au, Fe, Co, Ni, Pd, Pt. Among the basic metals, the highest catalytic efficiency values belong to nickel, cobalt, and iron. What is more, by the specific catalytic efficiency nickel is superior to cobalt by 2.1 times and iron by 16 times. Platinum and palladium have the best properties for catalytic oxidation of CO and C_mH_n. However, platinum and palladium are slightly better than nickel by the specific catalytic efficiency: platinum is 6 times more efficient than nickel, and palladium is 5 times more efficient. On the other hand, nickel is much more active than oxide catalysts. The specific catalytic efficiency of nickel at the temperature of 180° C is 3 orders of magnitude higher than that of cobalt oxide, and 6 orders of magnitude higher than that of zinc oxide at 300°C. Thus, as low-temperature catalysts for CO and C_mH_n oxidation, nickel and cobalt catalysts make the most sense. Taking into account the higher activity and lower cost and scarcity of nickel as compared with cobalt, the choice of nickel catalysts for commercial use is the most rational. Thus, among the most effective catalysts are materials containing intermetallic compounds of nickel because of the ability to transfer active oxygen involved in the oxidation process. In this regard, it seems promising to study the properties of the intermetallic compounds of these metals as catalysts.

The pilot tests of the designed intermetallic catalysts were carried out at the electrode manufacturing enterprise for the neutralization of exhaust gases from the kilns and graphitization furnaces. The developed intermetallic catalyst consists of nickel and aluminum with additions of copper, cobalt, and manganese. We tested the catalyst of known composition (52% Al + 48% Ni), the catalyst containing 0.2 %wt of platinum which was spread on alumina and the new catalyst which we have developed previously with optimum composition of 30 % Ni + 10 % Co + 11 % Mn + 2% Cu + 47 % Al (Sereda et al., 2009).

The results of the tests conducted in the flow of exhaust gases showed that the efficiency of the new catalyst proposed and the catalyst containing 0.2 %wt. of platinum differ slightly (Fig. 2, a, b). The highest degree of conversion at a lower temperature was observed in both cases. In the flow with $W = 30 \cdot 10^3 \text{ m}^3/\text{m}^3 \cdot \text{hr}$, under the influence of the catalysts, the degree of CO neutralization reached 99.9 % at the temperature of 200°C. The same degree for C_mH_n was reached under 300°C. Significantly lower activity was the standard catalyst with the 52 % Al + 48% Ni composition. The oxidation of CO and C_mH_n was carried out in the flows with different volumetric flow rates. The results showed that with the increase of the volumetric flow rate from $30 \cdot 10^3$ to $120 \cdot 10^3 \text{ m}^3/\text{m}^3 \cdot \text{hr}$ at the temperature of 300°C the degree of oxidation of CO and C_mH_n decreases from 99.9 to 95% in case of utilization of the new catalyst and the catalyst containing 0.2 %wt of platinum. For the 52 % Al + 48 % Ni catalyst the decrease was from 98 to 75 %.

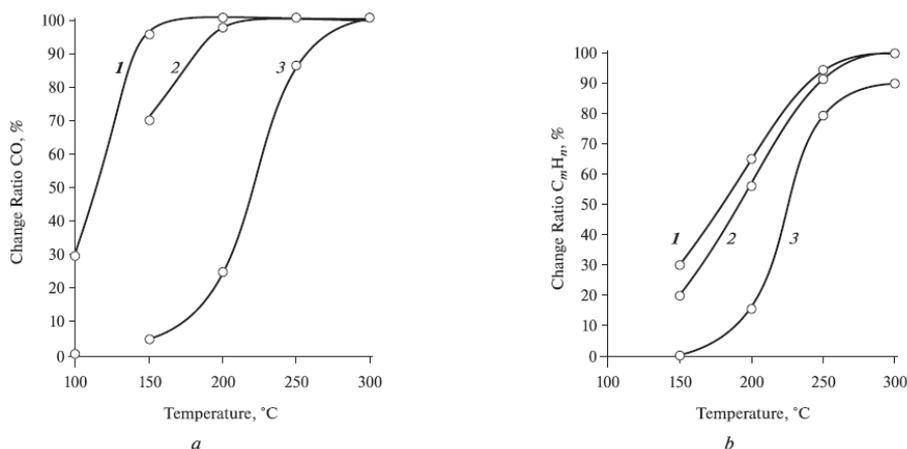


Fig. 2. Catalytic effect of the catalysts under review: a – in the oxidation of CO, %; b – in the oxidation of C_mH_n , %; 1 – Pt-catalyst; 2 – 30 % Ni + 10 % Co + 11 % Mn + 2 % Cu + 47 % Al; 3 – 52 % Al + 48 % Ni

The catalyst with the composition of 52 % Al + 48 % Ni worked stably over 450 hours, after which the degree of gas purification reduced sharply to 85%. The new catalyst worked for 720 hours. Purification completeness is reduced to 99% (Fig. 3). Because the exhaust gases of the graphitization furnace contain SO_2 , the activity of the catalyst with the composition of 52 % Al + 48 % Ni in the oxidation of CO and C_mH_n decreased after 10-20 hours of work due to poisoning; it appeared unstable towards SO_2 . Over the new catalyst and the catalyst promoted with Pt, the presence of SO_2 causes a significant shift (by 200°C) of the curves of oxidation to the higher temperature region.

Complete oxidation of CO and 95 % C_mH_n in the presence of SO_2 was observed at temperatures of 450°C, using a new catalyst, and 400–420°C, using Pt-catalyst at $W = 50 \cdot 10^3 \text{ m}^3/\text{m}^3\cdot\text{hr}$. New catalyst had been working for 600 hours.

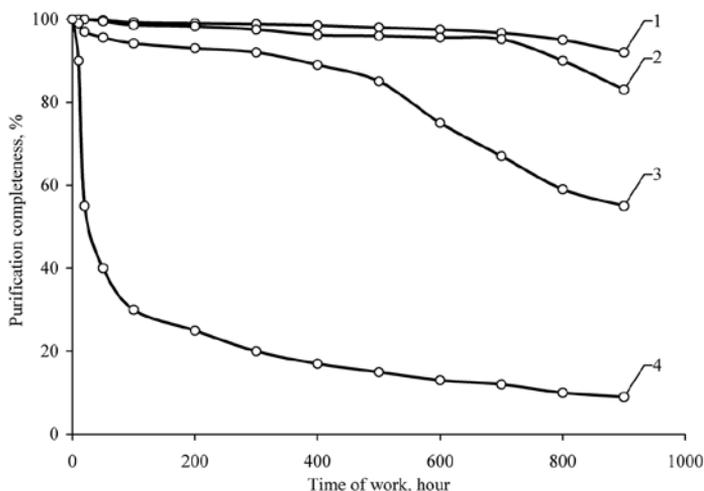


Fig. 3. Dependence of the degree of gas purification from the duration of the catalyst: 1 – Pt-catalyst; 2 – 30 % Ni + 10 % Co + 11 % Mn + 2 % Cu + 47 % Al; 3 – 52 % Al + 48 % Ni, 4 – 52 % Al + 48 % Ni in the presence of SO_2

The comparison of the results showed that new catalyst has substantial advantages with respect to the contacting temperature since it allows for temperatures of the process lower by $\approx 80^{\circ}\text{C}$. It has 1.6-1.7 times longer duration of operation than the catalyst with the composition of 52 % Al + 48 % Ni, its catalytic properties are equal to those of the catalysts containing noble metals and it has a significantly lower cost. Based on the results we recommend the catalyst for industrial use. For the neutralization of exhaust gases from kilns and graphitization furnaces, we can recommend the catalytic neutralization scheme (Fig. 4.)

By means of a ventilation unit, the exhaust gases produced by kilns and graphitization furnaces are sent to the preheater, where they are heated by the heat of flue gases produced by natural gas burning to the temperature of 200°C to start the catalytic reaction and then pass to the catalytic reactor for neutralization. Each kiln and graphitization furnace needs its own reactor. We recommend using the new intermetallic catalyst with the composition of 30%Ni + 10%Co + 11%Mn + 2%Cu + 47%Al (Belokon et al., 2016).

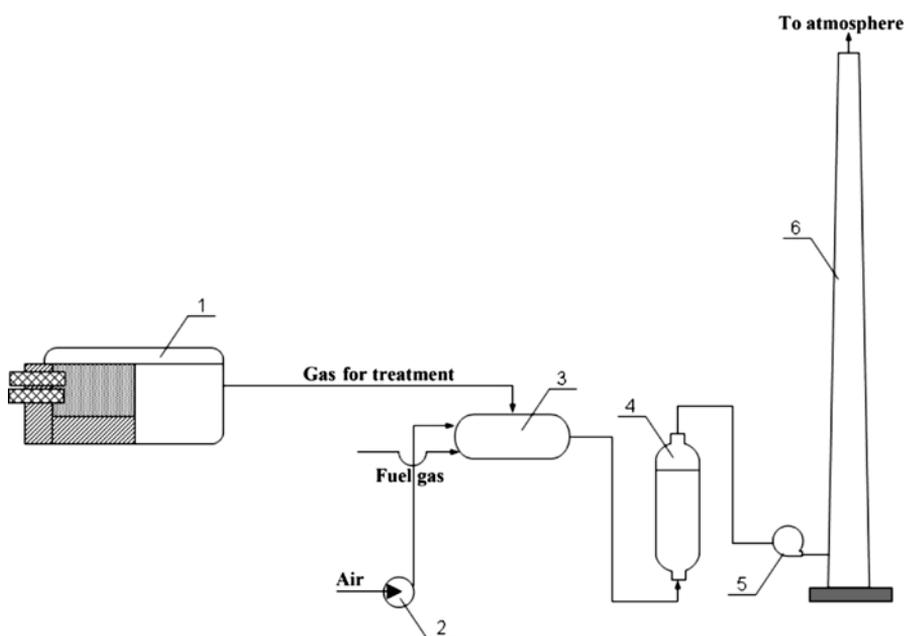


Fig. 4. Installation diagram of catalytic neutralization of waste gases: 1 – furnace; 2 – ventilator; 3 – furnace-preheater; 4 – reactor; 5 – smoke exhauster; 6 – flue gas stack

The exhaust gases from the kilns and furnaces are recommended to be cleaned from resinous substances in an electrostatic precipitator before catalytic reactor. The most compact and economical device is a cyclone-type reactor with a radial gas inlet. The catalyst basket and the adjacent tube-type heat exchanger are inside (Batura, 1991). Between the reactor shell and the outer shell of the catalyst basket, there is an annular channel through which the gas flows. In such a reactor, two processes take place simultaneously: the catalytic oxidation of CO and C_mH_n in the catalyst bed and the heat recovery. First, the exhaust gas flows through the shell side of the recuperator, where it absorbs heat from the partially purified exhaust gas, next, to the header and the mixing chamber, where it is mixed with the hot flue gases fed from the combustion chamber. The exhaust gases heated to the temperature required for the catalytic oxidation are headed to the filling layer of the catalyst basket for oxidizing CO and C_mH_n to carbon dioxide and water. The purified hot exhaust gases flow to

the tube side of the recuperator and the smoke exhauster removes it from the apparatus to the flue gas stack.

The utilization of the new catalyst ensures complete neutralization (99.9%) of CO and C_mH_n in the kiln exhaust gas at the temperature of 300°C with the volumetric flow rate of 32000 h⁻¹, which ensures low energy consumption of the process. A higher temperature is required (450°C) to achieve the same effect in the neutralization of the exhaust gas of graphitization furnaces.

In the process of purification of exhaust gas of the kiln, the new catalyst worked for 720 hours and in the graphitization furnace, it worked for 600 hours. When the activity of the catalyst reduced to 95% because of the carburization with resinous substances, it subjected to regeneration. The catalyst with the new composition can be used at different plants for neutralization of CO and C_mH_n . After neutralization of the waste gases from the kilns and graphitization furnaces over the developed catalyst, the surface concentrations of the pollutants emitted from these sources in residential areas will be reduced to the background level and the risk to public health will be minimal.

4. Conclusions

The method of deactivation of waste gases containing carbon monoxide and hydrocarbons that are emitted by kiln and graphitization furnaces, which is based on intermetallic catalysts, have been developed.

Experimental studies have shown that the application of the new catalyst provides the complete exhaust gas neutralization (99.9%) from CO and C_mH_n in the kilns at the temperature of 300° C with the volumetric flow rate of 32000 h⁻¹, which ensures low energy consumption of the process. A higher temperature is required (450°C) to achieve the same effect in the exhaust gas neutralization in graphitization furnaces.

The results of comparative tests showed that the developed catalyst cycle life is 1.6-1.7 times longer than that of the known nickel catalyst. After neutralization of exhaust gases emitted by kiln and graphitization furnaces by means of the developed catalyst, the surface concentrations of the pollutants in residential areas will be at the background levels and the risk to public health will be minimal.

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References

- Batura P.I., (1991), Catalytic reactors for afterburners flue gas, *Koks i khimiya*, **5**, 32-34.
- Belokon', K.V., (2011), About increasing environmental safety of gas emissions of metallurgical enterprises, *Collection of the Research Papers "Metalurhiya"*, **25**, 164-169.
- Belokon' K.V., (2015), The increasing of enterprises of electrode production ecological safety by catalytic neutralization of gas emissions, *Vestnik Khar'kovskogo natsional'nogo avtomobil'no-dorozhnogo universiteta*, **70**, 42-49.
- Belokon' K.V., Belokon Y.A., Kozhemyakin G.B., Matukhno E.V., (2016), Environmental assessment of the intermetallic catalysts utilization efficiency for deactivation of the pollutants emitted by electrode production enterprises, *Scientific Bulletin of National Mining University*, **3**, 87-94.
- Belokon' Y., Zherebtsov A., Belokon K., Fedchenok A., (2017), The investigation of physical-mechanical properties of intermetallic Ni-Al catalyst with the nanostructure, *IEEE International Young Scientists Forum on Applied Physics and Engineering (YSF-2017)*, 299-302, DOI: 10.1109/YSF.2017.8126638

- Belokon' K., Belokon' Y., Matukhno E., (2018), *Development of Scientific and Technical Decisions for Increasing Environmental Safety of Cleaning Processes from Carbon-Containing Components of Gas Emissions*, XIX International Scientific Conference "New Technologies and Achievements in Metallurgy, Material Engineering and Production Engineering", Collective Monograph, Nr 78, Częstochowa, 44-48.
- Belokon' K., Belokon' Y., (2018), The study of catalysts based on intermetallic NiAl alloys, *Ceramic Transactions*, **262**, 219-225.
- Borsch V.N., Pugacheva E.V., Zhuk S.I., Andreev D.E., Sanin V.N., Yuxhvid V.I., (2008), Multi-metal catalysts of deep oxidation of CO and hydrocarbons, *Dokladi Akademii Nauk (RF)*, **419**, 775-777.
- Denisov S.I. (1991), *Collection and Recycling of Dust and Gases*, Metallurgiya, Moscow, Russia.
- Sereda B.P., Savela K.V., Kozhemyakin G.B., Belokon Yu.A., Ryzhkov V.G., (2009), *The catalyst for the purification of carbon monoxide and hydrocarbons*, State Register of Patents of Ukraine, Kiev, UA, Pat. № 45154.