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EVALUATION OF THE INFLUENCE OF THE CATALYSTS APPLICATION ON THE LEVEL OF EMISSIONS OF CARBON MONOXIDE IN THE MANUFACTURE OF ELECTRODES

The object of research is emissions harmful to the environment by the example of emissions from the manufacturer of electrodes of Ukrgrafit JSC (Zaporizhzhia, Ukraine). As well as carbon material, during the heat treatment of which the formation of carbon monoxide occurs, taking into account the use of the catalyst directly in the technological process of heat treatment of carbon material. Based on the simulation of dispersion of emissions of Ukrgrafit JSC in the air, taking into account the size of the sanitary protection zone, it is shown that the CO surface concentration, taking into account background pollution, exceeds the maximum permissible concentration (MPC) at control points. It is determined that in order to achieve the established standards at the border of residential development, it is necessary to modernize production by introducing scientific and technical solutions to protect the atmosphere from pollution by carbon monoxide. Physical modeling of the processes of heat treatment of carbon materials for the production of electrodes, such as bedding, granular pitch, charge for billets, in a laboratory setup is carried out. The thermal regime is evaluated for the level of carbon monoxide emissions during firing of carbon material. The results are compared with the data obtained by examining the parameters of the furnaces in the enterprise.

The efficiency of using the catalyst directly in the technological process of heat treatment of carbon material to the efficiency of the oxidation of carbon monoxide is determined. It is established that a successful solution to the problem of exceeding the standard of carbon monoxide emissions in the technology for the production of electrodes is possible by using overfill modified with manganese dioxide with a MnO_2 content of 1.5 %.

It is shown that after the catalytic neutralization of carbon monoxide, the maximum CO surface concentration on the boundaries of housing taking into account background pollution does not exceed the maximum permissible concentration. This ensures that 0.576638 MPC is obtained from the value of the maximum one-time maximum permissible concentration of carbon monoxide, minimizes the environmental risks from the company's emissions for the population. Modernization of production by introducing a system of catalytic neutralization of carbon monoxide does not require special equipment, compared with well-known analogues it does not require significant investment.

Keywords: *carbon monoxide, flue gases, carbon material, manganese dioxide, atmospheric air, neutralization, production modernization, reduction of emissions.*

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1. Introduction

Protecting the air basin from pollution by toxic emissions is extremely important for all countries of the world, but the air mass is equally polluted throughout the planet. The greatest shortage of clean air is observed in economically developed countries and large cities, where metallurgical, chemical, energy, petrochemical and construction enterprises are intensively working. These objects during operation emit harmful substances into the atmosphere, among which carbon monoxide is considered to be the single most common cause of poisoning in industrial and domestic conditions [1].

Despite the fact that CO is highly toxic and has large atmospheric emissions, until recently, no country has introduced methods for the sanitary cleaning of exhaust gases from this hazardous component. An exception is only emissions of automobile gases, the purification of which is carried out by the method of catalytic oxidation of CO. However, such equipment is very expensive, has low throughput and can't satisfy the needs of large enterprises. The development of catalysts for the oxidation of CO to CO_2 in production is an important scientific and applied task, since it is of great practical importance for solving the problems of technogenic environmental pollution.

Therefore, the solution to the problem of the negative environmental impact of emissions of carbon monoxide by enterprises is very relevant and requires the introduction of effective and low-cost tools without significant re-equipment of production.

2. The object of research and its technological audit

The object of research is emissions harmful to the environment by the example of emissions from the manufacturer of electrodes of Ukrgrafit JSC (Zaporizhzhia, Ukraine). As well as carbon material, during the heat treatment of which the formation of carbon monoxide occurs, taking into account the use of the catalyst directly in the technological process of heat treatment of carbon material.

On the example of Ukraine, because, despite a marked reduction in industrial production, a significant part of powerful metallurgical plants, thermal power plants, coal coking enterprises, including the production of graphite electrodes, oil refineries and chemical enterprises, significantly pollute the air. Particularly difficult is the situation in industrial regions where powerful industries are concentrated, often with outdated environmentally hazardous technologies, the use of which significantly worsens the environmental situation in Ukraine. For example, in the Zaporizhzhia region, sources of 60–70 % of pollutant emissions from the total gross volume are Zaporizhstal PJSC, Dniprospetsstal PJSC, Zaporizhzhia Ferroalloys Plant JSC, Ukrgrafit JSC, Zaporizhzhia Abrasive Plant PJSC, Zaporizhkoks JSC, Zaporizhzhia Titanium and Magnesium Combine LLC, Zaporizhogneupor JSC, Zaporizhzhia Factory of Welding Fluxes and Glassware OJSC and a number of other enterprises [2]. These objects during operation and the intensive use of various modes of transport emit carbon monoxide into the atmosphere. In particular, in the emissions of Ukrainian Graphite CJSC, carbon monoxide is present in an amount of about 42 % [2]. Today, with a standard maximum permissible emission of CO of 250 mg/m^3 in furnaces No. 9, sources 326, the actual emissions reached 998.3 mg/m^3, in furnaces No. 10 of source 347–1750 mg/m^3. Therefore, the calculations were carried out precisely taking into account the emissions of sources 326 and 347.

Despite the fact that the emission standards approved by order of the Ministry of Environmental Protection of Ukraine dated June 27, 2006 No. 309 «On the approval of the standards for maximum permissible emissions of pollutants from stationary sources» are essentially regulatory standards for emissions into the air, the ecological situation in Ukraine not only has not improved, but in some regions has worsened significantly [3]. The situation can be improved only by optimizing production processes, modernizing technologies and introducing technological innovations.

3. The aim and objectives of research

The aim of research is to develop scientific and technical solutions to protect the atmosphere from pollution by carbon monoxide.

To achieve this aim in the work it is planned to solve the following scientific and technical problems:

1. To calculate the dispersion of pollutants in the atmospheric air contained in the emissions of the company Ukrgrafit JSC and justify the need for production modernization to reduce carbon monoxide emissions into the atmosphere.
2. To carry out physical modeling of the processes of heat treatment of carbon materials in a laboratory setup, to compare the results with the data obtained by examining the operation parameters of furnaces in the enterprise.
3. To determine the effectiveness of the use of catalysts for the oxidation of carbon monoxide in the process of heat treatment of carbon material.
4. To develop recommendations for reducing carbon monoxide emissions in the production process.
5. To calculate the dispersion of carbon monoxide in the air, taking into account the reduction of its emissions in the production process.

4. Research of existing solutions of the problem

The enterprises producing electrode products emit about 4–5 million m^3 of gas per hour into the environment. Mostly flue gas contains carbon monoxide and tarry substances, which are a mixture of aromatic polycyclic hydrocarbons [4].

Adsorption, thermal and catalytic methods are most often used to reduce emissions of carbon monoxide and polycyclic aromatic hydrocarbons.

Adsorption methods that are widely used in industry for gas purification, in this case, are not suitable for use directly in the technological process of roasting electrodes. The complexity of their use is due to:

- large volumes of gases that must be cleaned;
- need for preliminary removal of dust and other impurities and the disposal of regeneration gases;
- loss of adsorbent as a result of its mechanical destruction;
- decrease in activity during operation, in turn, requires significant capital costs.

The main disadvantage of gas purification from carbon monoxide is its insufficient efficiency at a high CO initial concentration [5].

When using thermal oxidation of carbon monoxide by burning it to carbon dioxide, it is necessary to reach a temperature of 850–900 °C, which involves the burning of large volumes of natural gas [2, 6]. Moreover, the thermal method does not always allow reducing the CO content to the level of maximum permissible emissions.

One of the effective methods for cleaning gas emissions from carbon monoxide and polycyclic aromatic hydrocarbons is a method based on the use of catalysts [2, 7]. The catalytic oxidation of impurities in combustion products is effective, as a rule, at temperatures above 300 °C [8]. The post-oxidation process occurs at a short contact time with the catalysts, which is associated with high flow rates of industrial emissions. The main advantages of the catalytic method compared with the thermal method of afterburning are to simplify the process, lower the temperature and significantly increase the speed and increase the cleaning efficiency.

As catalysts for the purification of gas emissions from carbon monoxide and aromatic polycyclic hydrocarbons, metal and oxide catalysts based on noble and transition metals, as well as natural minerals, chamotte, dump metallurgical slag, intermetallic compounds, mullite-siliceous fibrous refractory are used. The advantage of using metallurgical slag as technogenic raw materials is its low cost and availability [8, 9]. The use of nickel-aluminum intermetallic compounds is more expedient from an economic point of view in comparison with a palladium catalyst, however, the production of alloys from pure metal powders also involves significant capital costs [10, 11]. Mullite-siliceous fibrous refractory, unlike previous catalysts, can be installed stationary at the flue outlet of a furnace [12, 13]. However, mullite-siliceous material, like bauxite is available, has a common drawback – a low catalyst life due to coking [13, 14]. The use of ferrite sludge formed in the processes of wastewater treatment from heavy metal ions as catalysts can be considered the most promising [15, 16]. In other words, the use of ferrite as an oxidizing agent with low sensitivity to catalytic poisons as a valuable raw material for CO oxidation catalysts has good potential for environmental use. Since in the case of its use there will be no problems with its disposal, since ferrite is non-toxic and biodegradable. Another advantage of these catalysts is the presence of magnetic properties, which make it easy to remove them from the reaction medium with a magnet and reuse several runs with almost no loss of catalytic activity [2, 17]. According to the results of the study [16], a copper-ferrite catalyst can completely convert CO to CO_2 at 140 °C, and its catalytic properties do not decrease even at low oxygen concentrations of about 1 %.

However, for the production of graphite electrodes, a more promising direction is the modernization of the electrode firing regulations [18], the advantage of which is economic feasibility. At the same time, the costs for the construction of gas after-treatment plants are sharply reduced, as proposed in [19, 20]. In addition, during the construction of plants for catalytic gas oxidation, it is necessary to spend a large amount of natural gas on heating the gas emissions necessary for the neutralization of carbon monoxide and aromatic hydrocarbons. A possible option for the modernization of the burning procedure is also the inclusion of catalysts in the carbon sprinkling of «green electrodes», which will significantly reduce the concentration of carbon monoxide in the gas emissions of the electrode burning furnaces.

5. Methods of research

Calculation of dispersion of pollutants in atmospheric air using an electronic computer (computer) using the automated air pollution calculation system «EOL Plus (version 5.3.8)» developed by Topaz LLC (Kyiv, Ukraine) and agreed by the Ministry of environmental protection and natural resources of Ukraine (3141/10/2-10 of March 27, 2007).

The location of the source of pollutant emissions into the atmosphere is defined in the «*X–Y*» coordinate grid, which is oriented to the cardinal directions: the «0Y» axis – to the «South-North» direction, here «0X» – «West-East». The calculations were performed at a weighted average hazardous wind speed of 1 U_h, 0.5 U_h, 1.5 U_h, 0.5 m/s, 1 m/s, 1.5 m/s, 2.0 m/s, 2.5 m/s. The settlement site is represented by a square with a side of 6.0 km. The calculations are performed with a grid spacing of 250 m.

Background concentrations of the pollutant were taken according to data provided by the Zaporizhzhia Regional Center for Hydrometeorology (Ukraine).

The average annual wind rose, which is characterized by P values for various points, is taken according to data provided by the Zaporizhzhia Regional Center for Hydrometeorology.

The size of the regulatory sanitary protection zone (SPZ) is 1000 m. The standard size of the SPZ is maintained.

In order to assess the maximum possible impact of emissions on the state of atmospheric air, the maximum power of carbon monoxide emission of stationary sources of emissions of 326, 347 – furnaces is used to calculate the dispersion.

The processes of gas generation during the heat treatment of carbon material in the heat chamber of the installation are described in [21]. In this case, air or a mixture of air and carbon dioxide was blown through the chamber in which the sample of carbon material was heated when the chamber was heated by an electric heater from room temperature to a temperature of ~850 °C. As a carbon material, powders, granulated pitch, and a charge for the production of blanks green electrodes are used. In this case, the gas analyzer at the outlet measured the concentrations of CO, CO_2, O_2 in the gas stream.

6. Research results

6.1. The results of calculations of the dispersion of carbon monoxide to the implementation of the developed measures. To justify the feasibility of reducing CO emissions, let's calculate the dispersion of pollutants in the air contained in the emissions of Ukrgrafit JSC.

The calculation results of the dispersion of carbon monoxide are given in Table 1.

According to the results of the calculations, it is found that the calculated concentrations, taking into account the background levels, exceed the maximum single maximum carbon monoxide concentration of 5 mg/m^3 at three control points (Table 2). This indicates the need to modernize production to reduce carbon monoxide emissions.

Table 1

Dependence of carbon monoxide concentrations on point coordinates for given directions and values of wind speed

X coordinate, m	*Y* coordinate, m	Concentration at a point, mg/m^3	Concentration at a point, MPC grades	Wind direction, deg.	Wind speed, m/s	Source code	Contribution, %	Source code	Contribution, %
12514	15220	5.005290	1.001058	320.00	3.69	326	62.85	347	37.15
12020	15480	4.547040	0.909408	340.00	2.50	326	66.82	347	33.18
12098	16430	4.272675	0.854535	30.00	3.69	326	99.97	347	0.03
12156	16496	4.292175	0.858435	30.00	3.69	326	99.88	347	0.12
12478	16768	4.420265	0.884053	20.00	3.69	347	100.00	326	0.00
13480	16820	5.203105	1.040621	70.00	2.50	347	100.00	326	0.00
12800	16906	4.498690	0.899738	30.00	2.50	347	100.00	326	0.00
14202	17174	4.920315	0.984063	120.00	2.50	347	74.24	326	25.76
14112	17224	5.010380	1.002076	120.00	2.50	347	68.26	326	31.74
14008	17230	4.900765	0.980153	110.00	2.50	347	81.83	326	18.17
13934	17232	4.956135	0.991227	110.00	2.50	347	75.28	326	24.72

Table 2

The coordinates of the points where the concentration of CO exceeds the maximum permissible concentration (MPC)

X coordinate, m	*Y* coordinate, m	Concentration at a point, mg/m^3	Concentration at a point, MPC grades	Control point
12514	15220	5.005290	1.001058	SPZ (1000 m)
13480	16820	5.203105	1.040621	SPZ (1000 m)
14112	17224	5.010380	1.002076	Living sector, Dosiahnen str., 2, Kyiv, Ukraine

6.2. Development of technical solutions to reduce the concentration of carbon monoxide in gas emissions to an acceptable level. In general, the emission rate of gas emissions is about 40,000 m^3/h. The existing emission cleaning system, based on the use of electrostatic precipitators, provides almost complete cleaning of emissions from resinous substances and practically does not affect the change in the concentration of carbon monoxide in emissions. Therefore, the attention to the conversion of carbon monoxide in the heat treatment of carbon materials is largely paid attention to. From the results obtained earlier [22], it is known that the release of carbon monoxide is largely associated with the burning and temperature of the green electrode blanks (Table 3).

The above data show that the maximum increase in the concentration of carbon monoxide in flue gases increases at temperatures of 300–400 °C with a heat treatment time of 100–200 hours from ~ 400 hours of the total processing time. It should be borne in mind that in multi-chamber Riedhammer furnaces, flue gas moves from the previous hot to the subsequent colder firing chamber.

Table 3

Change in the temperature of green electrode blanks and the concentration of carbon monoxide in the flue gases of Riedhammer furnaces [22]

t, h	50	100	150	200	250	300	350	400
T, °C	125	200	280	350	405	480	580	730
C_{CO}, mg/m^3	2900	3700	3500	3000	1000	245	20	20

At the same time, in the flue gases supplied to preheat the electrode blanks, the oxygen content reaches 13.7–14.5 %, the water vapor content is 8 %, and the concentration of carbon dioxide is ~3.12 %. Under these conditions, carbon monoxide can almost completely oxidize to carbon dioxide. Nevertheless, at the outlet of the furnace, the concentration of carbon monoxide in some cases reaches 3500–3700 mg/m^3. Therefore, the processes of gas formation during heat treatment of carbon material in a heat chamber from room temperature to a temperature of ~850 °C are studied. In this case, a slightly different picture was observed by the change in carbon monoxide concentration depending on the heating time and temperature (Fig. 1–3).

Before analyzing the data on the concentrations of CO in the gas mixture, it should be noted that the gas volumetric velocity under production conditions is 0.004–0.006 h^{-1}, and in the laboratory chamber heat chamber it is 0.0007–0.006 h^{-1}. Although there is a significant difference in the processes implemented. As for the heat chamber, the gas stream after it almost immediately enters the gas analyzer with a temperature drop of 100–200 °C. In production, the gas stream for analysis is taken directly from the heating chamber without significant cooling.

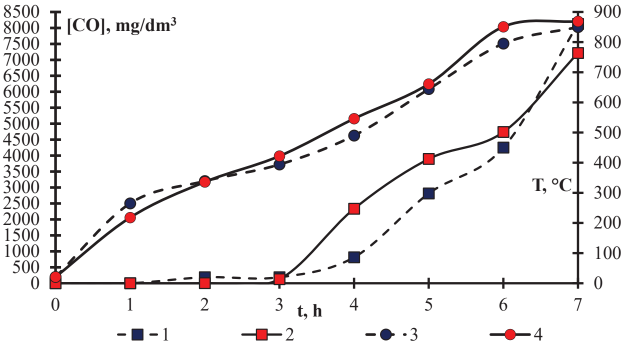

Fig. 1. Change in the concentration of carbon monoxide in a mixture of gases (air and CO$_2$) (1, 2) after passing it through a heat chamber, loaded overfill, and the temperature of the carbon charge (*m*=382–445 g) (3, 4) from the heating time at a concentration oxygen (CO$_2$), %: ~14.5 (35.0) (1, 3); 20.95–16.7 (0.0–2.65) (2, 4) at a gas-air mixture flow rate, dm^3/h: 376 (1, 3), 588 (2, 4)

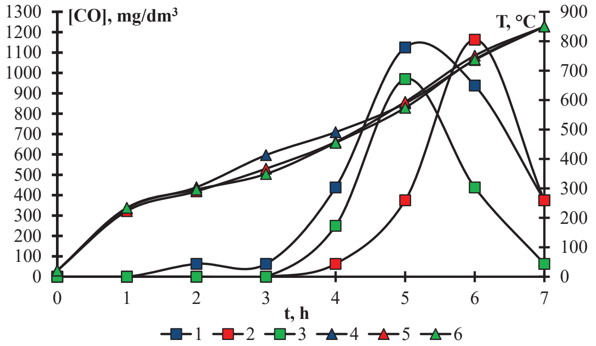

Fig. 2. Change in the average concentration of carbon monoxide in a mixture of gases (air and CO$_2$) (1, 2, 3) after passing it through a heat chamber loaded with granular pitch, and the temperature of the carbon charge (*m*=5 g) (4, 5, 6) from heating time at oxygen concentration, %: 13–15 (1, 4); 15–16 (2, 5); 17–18 (3, 6) at a gas-air mixture flow rate, dm^3/h: 131.4 (1, 4); 98.4 (2, 5), 60.0 (3, 6)

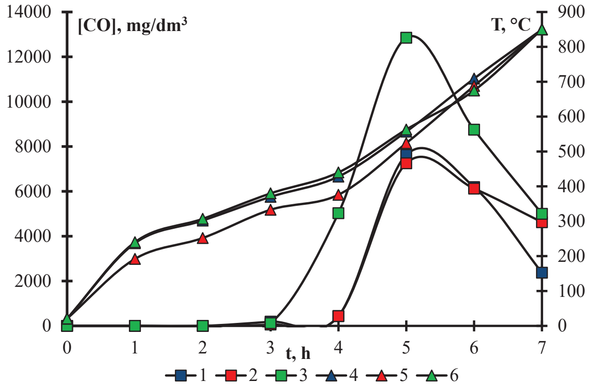

Fig. 3. Change in the average concentration of carbon monoxide in a mixture of gases (air and CO$_2$) (1, 2, 3) after passing it through a heat chamber loaded with a charge, and the temperature of the carbon charge (*m*=450 g) (4, 5, 6) over time heating at oxygen concentration, %: 13–15 (1, 4); 15–16 (2, 5); 17–18 (3, 6) at a gas-air mixture flow rate, dm^3/h: 135.2 (1, 4); 131.4 (2, 5), 98.4 (3, 6)

As can be seen from Fig. 1, 2, at temperatures up to 450 °C there is no noticeable emission of carbon monoxide when heating the powder and granular pitch. With further heating of the filling (Fig. 1) to 850 °C, the concentration of carbon monoxide increases significantly. In the case of heating the pitch, the maximum concentration of CO, depending on the gas flow rate, is reached at temperatures of 570–650 °C. When using a mixture for the manufacture of electrodes, intense emission of carbon monoxide occurs at temperatures above 400 °C. The maximum is reached at temperatures of 520–570 °C. At a further increase in temperature, the concentration of carbon monoxide in the gas mixture decreases.

The temperature shift of the intensive formation of carbon monoxide in the production environment towards lower temperatures compared with the laboratory setup is explained much more slowly by heating the carbon material in the production environment. So, in production, the temperature of electrodes from overfilling increases on average by 2.75 °C per hour, in the temperature range 350–580 °C, the temperature increases by 1.15 °C per hour. Under the conditions of using the laboratory setup, the temperature from 20 to 850–870 °C rises at 7 hours, i. e. ~120 °C per hour. It is obvious that under production conditions fragments of a carbon material, volatile polycyclic resins, capable of easy oxidation, oxidize upon prolonged heating at lower temperatures than in a laboratory setup. When simulating the firing process as a result of rapid temperature changes, the maximum of carbon monoxide formation shifts to higher temperatures. At the same time, for overfilling, the loading of which is 431.4–445 g, the maximum is reached at a temperature of 600–800 °C (Fig. 4). Moreover, at high temperatures, a significant part of the overburden is oxidized to carbon dioxide (Table 4). At 600–850 °C, the amount of CO_2 formed reaches ~4.5 % at an oxygen concentration of 14 %, ~2 % at an oxygen content in the gas-air mixture of 15.5 %, and ~1.5 % at an oxygen concentration of 17.5 %. The maximum concentration of carbon monoxide in this concentration range is $61.71 \cdot 10^{-2}$ % at an oxygen concentration of 14 %, $138.43 \cdot 10^{-2}$ % and $96.05 \cdot 10^{-2}$ % at an oxygen content of 15.5 % and 17.5 % In this case, an increase in the amount of oxidized CO at an oxygen concentration of 14 % is associated with a significant increase in the consumption of the gas-air mixture.

For granular pitch, which is used in an amount of 5 g, the maximum concentration of carbon monoxide is reached at a temperature of 570–670 °C, for a charge the maximum concentration of CO is formed at 400–650 °C. In this case, the mass of the mixture is 450 g. Obviously the achievements maximum emission of CO at oxygen concentrations of 13–18 % (Fig. 3) is due to the stability of the pressed billet to oxidation.

To assess the effect of time on the oxidation processes of the overburden in a heat chamber of a laboratory setup, a test was conducted under isothermal conditions (Tables 5, 6). In this case, a constant concentration of carbon monoxide was observed at temperatures of 500 °C at an oxygen concentration of ~21 % and 400 and 500 °C at an oxygen concentration of 13.8 %. Moreover, under these conditions, the concentration of CO did not exceed 270 mg/m^3. At temperatures of 600–800 °C and an oxygen concentration of 21 % per hour of heating, the CO concentration was 1667 mg/m^3 at 600 °C, 5958 mg/m^3 at 700 °C, 8125 mg/m^3 at 800 °C. For four hours, the CO concentration falls at 600, 700 and 800 °C (Table 5).

A similar trend was observed at 600 and 700 °C with an oxygen concentration of 14.28 %. But at the same time, the maximum concentration of CO did not exceed 3375 mg/m^3, and at 4:00 it decreased to 2421 mg/m^3 (Table 6).

Obviously, with a decrease in the rate of rise in the temperature of the preforms at an oxygen concentration of 13.8–14.4 %, degassing of the preforms can be achieved with a CO concentration in the gas mixture of 125–270 mg/m^3.

The solution to the problem was more successful when using overfill modified with manganese dioxide with a MnO_2 content of 1.5 %. In this case, even when purging through cleaners placed in a heat chamber, clean air, the CO concentration in the gas mixture was below 70 mg/m^3 at temperatures up to 520 °C (Fig. 5, 6). This is a significantly lower figure than when using modified overfill.

Given that a significant increase in the formation of CO occurs at a workpiece temperature of 300–400 °C, the use of modified overfilling is a simple and convenient method for preventing the release of carbon monoxide into the atmosphere in the processes of electrode firing.

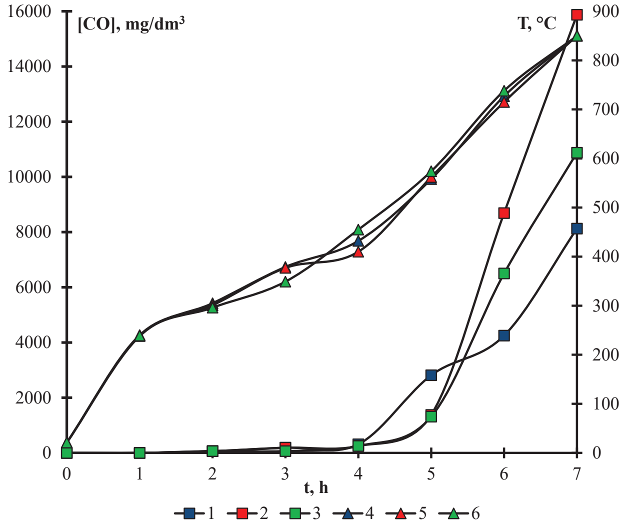

Fig. 4. Change in the average concentration of carbon monoxide in a mixture of gases (air and CO_2) (1, 2, 3) after passing it through a heat chamber, loaded overfill, and the temperature of the carbon charge (m=431.4–445 g) (4, 5, 6) from the heating time at oxygen concentration, %: 13–15 (1, 4); 15–16 (2, 5); 17–18 (3, 6) at a gas-air mixture flow rate, dm^3/h: 131.4 (1, 4); 98.4 (2, 5), 60.0 (3, 6)

Table 4

The dependence of the temperature in the heat chamber, the concentration of CO, CO_2 on the heating time of the carbon material (filling) at an oxygen concentration in the gas mixture, %: 14.06 (1), 15.50 (2), 17.50 (3) with the flow of the gas mixture dm^3/h: 376 (1); 350 (2) 323 (3)

t, h	*T*, °C			[CO], mg/m^3/[CO·10^2], %			[CO_2], %		
	1	2	3	1	2	3	1	2	3
0	21	20	20	0/0	0/0	0/0	34.92	28.09	18.57
1	265	270	258	63/0.54	0/0	0/0	34.92	28.09	18.57
2	339	335	320	187/1.61	125/1.07	63/0.54	34.89	28.11	18.58
3	394	393	396	250/2.15	188/1.61	250/2.15	35.31	28.18	18.59
4	490	476	513	1125/9.66	438/3.76	313/2.69	35.52	28.41	18.85
5	644	634	653	5125/43.99	3000/25.75	5312/45.60	35.61	28.50	19.07
6	795	785	731	7188/61.71	16125/138.43	11188/96.05	36.26	29.12	19.77
7	850	850	850	4875/41.85	13125/112.67	9875/84.77	39.48	30.22	21.00

Table 5

Dependence of the concentration of oxygen, carbon dioxide, carbon monoxide in a gas mixture on the time of air purging through a carbon-loaded heat chamber (fillings) (m=393–400 g) at an air flow rate of 650 dm^3/h at an average temperature in the heat chamber, °C: 495 (1); 615 (2); 700 (3); 800 (4)

t, h	[O_2], %/[CO_2], %				[CO], mg/m^3/[CO·10^2], %			
	1	2	3	4	1	2	3	4
0.5	19.05/0.91	18.53/1.10	17.86/1.30	17.40/1.74	1011/8.68	1667/14.31	5958/51.15	8125/69.75
1	19.11/0.93	18.64/1.12	17.80/1.31	17.39/1.75	1014/8.71	1396/11.98	5117/43.93	7094/60.90
1.5	19.07/0.95	18.71/1.14	17.83/1.32	17.38/1.76	1012/8.69	1286/11.04	4659/39.99	6474/55.58
2	19.08/0.96	18.65/1.15	17.82/1.31	17.41/1.77	1010/8.67	1135/9.74	4200/36.06	5854/50.26
2.5	19.06/0.97	18.60/1.16	17.85/1.33	17.45/1.76	1015/8.71	1089/9.35	4034/34.63	5328/45.74
3	19.04/0.98	18.59/1.15	17.88/1.34	17.46/1.74	1020/8.76	1042/8.95	3867/33.20	4802/41.22
3.5	19.03/0.97	18.63/1.17	17.87/1.35	17.44/1.75	1050/9.01	1011/8.68	3800/32.62	4354/37.38
4	19.05/0.96	18.64/1.16	17.86/1.33	17.43/1.76	1081/9.28	979/8.40	3790/32.54	3906/33.53

Table 6

Dependence of the concentration of oxygen, carbon dioxide, carbon monoxide in the gas mixture on the time of air purging through a carbon-loaded heat chamber (overfill) (m=393–400 g) at temperature, °C; 400 (1); 500 (2); 600 (3); 700 (4) at a gas mixture flow rate; dm^3/h: 470 (1); 609 (2); 389 (3); 383 (4)

t, h	[O_2], %/[CO_2], %				[CO], mg/m^3/[CO·10^2], %			
	1	2	3	4	1	2	3	4
0.5	13.80/34.41	13.80/34.11	14.28/31.83	14.28/30.84	125/1.07	191/1.64	2750/23.61	3375/28.97
1	13.81/34.81	13.82/34.04	14.27/31.92	14.20/30.59	125/1.07	220/1.89	2720/23.35	3277/28.13
1.5	13.82/33.05	13.81/34.22	14.20/31.51	14.10/29.85	125/1.07	250/2.15	2240/19.23	3121/26.79
2	13.80/33.40	13.78/34.60	14.15/31.90	13.95/29.58	125/1.07	270/2.32	1764/15.14	2966/25.46
2.5	13.78/33.86	13.77/34.65	14.10/30.93	13.97/29.60	125/1.07	270/2.32	1642/14.10	2798/24.02
3	13.75/34.76	13.74/34.71	14.11/30.41	13.90/29.69	125/1.07	169/1.45	1525/13.09	2629/22.60
3.5	13.76/34.82	13.75/34.80	14.12/30.42	13.88/29.59	125/1.07	265/2.28	1321/11.34	2525/21.68
4	13.74/34.91	13.74/34.92	14.15/30.58	13.85/29.50	78/0.67	257/2.21	1113/9.56	2421/20.78

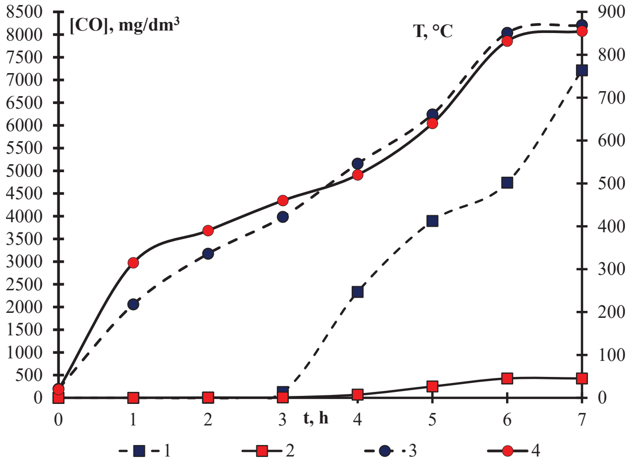

Fig. 5. Change in the concentration of carbon monoxide (1, 2) in the gas mixture after passing it through a heat chamber loaded with unmodified (1, 3) and modified MnO_2 carbon charge (2, 4) (overfill) and the temperature of the carbon charge (3, 4) from heating time at an oxygen concentration of 20.95 % with a gas-air mixture flow rate of 588 dm^3/h

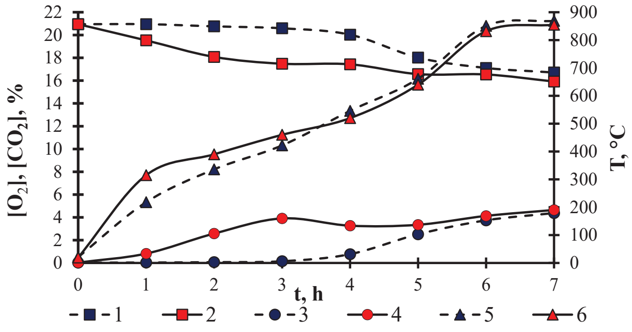

Fig. 6. Change in the concentration of oxygen (1, 2), carbon dioxide (3, 4) in the gas mixture after passing it through a heat chamber loaded with unmodified (1, 3, 5) and modified MnO_2 carbon charge (2, 4, 6) (overfill) and the temperature of the carbon charge (5, 6) of the heating time at an oxygen concentration of 20.95 % at a gas-air mixture flow rate of 588 dm^3/h

6.3. The results of calculations of the dispersion of carbon monoxide to the implementation of the developed measures. When calculating the dispersion of carbon monoxide in atmospheric air using a concentration of 70 mg/m^3 as maximum, the results are shown in Table 7.

Table 7

The dependence of carbon monoxide concentrations after the implementation of the developed measures to reduce CO emissions from the coordinates of the point for given directions and values of wind speed

X coordinate, m	*Y* coordinate, m	Concentration at a point, mg/m^3	Concentration at a point, MPC grades	Wind direction, deg.	Wind speed, m/s	Source code	Contribution, %	Source code	Contribution, %
12514	15220	2.883192	0.576638	320.00	3.78	326	73.98	347	26.02
12020	15480	2.877041	0.575408	340.00	2.52	326	77.21	347	22.79
12098	16430	2.874588	0.574918	30.00	3.78	326	99.98	347	0.02
12156	16496	2.874911	0.574982	30.00	3.78	326	99.94	347	0.06
12478	16768	2.875518	0.575104	50.00	3.78	326	100.00	347	0.00
13480	16820	2.879185	0.575837	70.00	2.52	347	100.00	326	0.00
12800	16906	2.876196	0.575239	70.00	3.78	326	100.00	347	0.00
14202	17174	2.878713	0.575743	120.00	2.52	347	63.21	326	36.79
14112	17224	2.880358	0.576072	120.00	2.52	347	56.14	326	43.86
14008	17230	2.877798	0.575560	110.00	2.50	347	72.84	326	27.16
13934	17232	2.879029	0.575806	110.00	2.52	347	64.50	326	35.50

As can be seen from the Table 7, after the implementation of the developed measures to reduce CO emissions, the maximum surface concentration at control points, taking into account background pollution, does not exceed the MPC and amounts to 2.883192 mg/m^3 or 0.576638 of the maximum single MPC of carbon monoxide (5 mg/m^3).

7. SWOT analysis of research results

Strengths. Compared with analogues, the positive effect of the object of research in the form of building blocks for introducing into the production of the system of catalytic neutralization of carbon monoxide consists in minimizing the environmental risks of carbon monoxide emissions for the population. As for the enterprise, the modernization of production does not require special equipment and increases the environmental safety of the enterprise.

Weaknesses. The weaknesses of the proposed effective measures include the need to obtain a license when using potassium permanganate as a precursor, as well as the organization of circulation of strict reporting documents on the acquisition, transportation, storage and use of this precursor.

Opportunities. Due to the fact that the processes of heat treatment of carbon materials are accompanied by the formation of high concentrations of carbon monoxide and are environmentally hazardous, developed countries refuse to use such industrial technologies. On the other hand, there is a need to conduct heat treatment processes to obtain scarce, valuable, and expensive materials, in particular, next to the production of graphite electrodes, it relates to the production of graphite, etc. Improving their manufacturing technology will allow the manufacturer to provide the market with scarce expensive products while reliably protecting the environment from carbon monoxide poisoning.

Threats. The disadvantage of this process is an increase in the loss of carbon material in 1.6–2.0 times due to the acceleration of the oxidation processes of the bulk to CO and CO_2. Therefore, in the case where carbon oxidation is an undesirable process, manganese dioxide must be applied to an inert material, for example, zeolite. However, this approach will require the installation in the production of additional equipment for the catalytic neutralization of carbon monoxide.

8. Conclusions

1. As a result of the assessment of the impact of the enterprise on production of electrode products of Ukrgrafit JSC on the level of pollution on the environment, taking into account the size of the sanitary protection zone, it is found that the maximum concentration of carbon monoxide at the control points is 5.2 mg/m^3, which exceeds the value of the maximum single maximum permissible concentration.
2. A significant increase in the production of CO in carbon material kilns under production conditions occurs at a workpiece temperature of 300–400 °C. Physical modeling of the heat treatment of carbon materials in a laboratory setup shows that, as a result of a rapid change in temperature, the maximum of carbon monoxide formation shifts to a region of more high temperatures.
3. As a result of the studies, it is found that when using an overfill modified with manganese dioxide with a MnO_2 content of 1.5 %, the concentration of CO in the gas mixture is below 70 mg/m^3 at temperatures up to 520 °C.
4. Recommendations are developed to reduce carbon monoxide emissions in the production process. According to these recommendations, the advantage of using modified MnO_2 refilling is the low material cost of processing carbon material compared with the significant investment in the construction of catalytic reactors for the CO disposal.
5. It is shown that after the catalytic neutralization of carbon monoxide, the maximum surface concentration of CO on the boundary of housing, taking into account background pollution, does not exceed the maximum permissible concentration. This provides a successful solution to the problem of exceeding the carbon monoxide emission standard. The use of modified overfilling is a simple and convenient method for preventing the release of carbon monoxide into the atmosphere during electrode firing processes.

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