

The object of this study was the value of nitrogen concentration at which the combustion process of anthracite is effectively inhibited. Therefore, the problem of eliminating the sites of self-ignition of coal relates to ventilating the pile with nitrogen, but it is necessary to take into account the required concentration of inert gas. It has been proven that on the basis of experimental studies of the process of inhibition of combustion when washing an anthracite batch with gaseous nitrogen, a sample of heated coal in a normal air atmosphere continues to burn with greater intensity. An increase in temperature by an average of 20 °C was recorded for 40–45 s. Adding nitrogen to the air in an amount of 12.85 % reduces the combustion temperature of anthracite by 2 %, but the cooling time of combustion below the ignition temperature exceeds 120 s. For a nitrogen-air mixture with a nitrogen concentration of 23.81 %, a decrease in the combustion temperature of the sample below its ignition for 120 s was recorded. Further increase in the amount of nitrogen in the nitrogen-air mixture to 28.57 % more effectively cools the combustion of anthracite below the ignition temperature for 70 s. The results showed that with an increase in the concentration of pure nitrogen in the nitrogen-air mixture, the requirements for the purity of nitrogen as a fire extinguishing agent increase. Therefore, it is necessary to introduce it into the *i*-th nitrogen-oxygen composition in such a concentration that the nitrogen content in the formed mixtures with air in both cases is the same. This is due to the fact that the purity of the nitrogen-oxygen mixture and its fire extinguishing concentration reflect the conditions under which there is the use of nitrogen-oxygen mixtures of a certain composition for fire extinguishing. The practical significance is that the results of determining the fire extinguishing concentration of nitrogen make it possible to establish the operating conditions of coal storage facilities during the elimination of fire sites

Keywords: coal, fire site, amount of nitrogen, combustion inhibition, oxygen concentration

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ESTABLISHING PATTERNS IN ELIMINATING COAL FIRE SITES WITH NITROGEN-AIR MIXTURES

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1. Introduction

Fires at coal storage facilities are one of the most complex types of accidents as they are characterized by the duration and complexity of extinguishing and the loss of equipment, which causes significant economic damage.

Such fires occur when coal spontaneously ignites, as well as organic materials used during coal storage, in particular,

wood, lubricants, etc. Signs of a fire include an increase in air or water temperature, an increase in the concentration of harmful gases, a possible increase in the temperature of the embankment, etc. Therefore, there is a growing need to devise measures to prevent and detect spontaneous ignition of coal at storage facilities.

Existing methods for predicting fires at storage facilities are based on determining the surface temperature of the

coal massif, the concentration of carbon dioxide and carbon monoxide in the atmosphere. However, they do not provide an opportunity to unambiguously indicate the coordinates of spontaneous ignition sites, which in turn reduces the effectiveness of detecting and eliminating coal ignition.

Thus, one of the most common techniques of localizing and extinguishing fires at coal storage facilities is inert saturation of the embankment, which is carried out by artificially reducing the oxygen concentration by supplying inert gas. Flue gases and carbon dioxide (CO_2) are mostly used as inert gases.

However, since the late 1980s, nitrogen, which is 1.6 times lighter than carbon dioxide, has been increasingly used for fire extinguishing. As a result, it fills voids in the embankment layers well and moves well, is poorly absorbed by coal and dissolves in water. Nitrogen is supplied to the embankment in an emergency using equipment for storing, transporting, and gasifying nitrogen. Thus, obtaining gaseous nitrogen by gasification of liquid in gasification plants has a number of disadvantages, in particular, low productivity of the plants and significant energy consumption for gasification of liquid nitrogen. However, designing mobile nitrogen compressor stations using membrane air separation technology could eliminate these shortcomings.

Therefore, for the elimination of coal fire sites using nitrogen, research into its fire-extinguishing properties is relevant.

2. Literature review and problem statement

The issue of reducing the risk to the environment and the personnel of the State Emergency Service of Ukraine, which is involved in the localization of the burning process and the elimination of the corresponding consequences, is closely related to the assessment of the risks of the burning process. This is important from the point of view of determining the possibilities for implementing preventive long-term actions to prevent such incidents.

The general strategy for dealing with risks associated with the formation of fire-hazardous situations, as defined in [1], is based on five interrelated stages:

1. Hazard identification (identification of a potential source of ignition, identification of a potential cause of ignition or explosion, identification of the volume and source of an increase in the volume of oxygen).

2. Identification of the object of risk impact (who is in the risk group, degree of involvement).

3. Assessment, localization, elimination, reduction of risks, protection from their negative consequences (reduction of the risk of fire and explosion by eliminating ignition sources, reduction of risk to people by implementing general fire prevention measures).

4. Recording, planning, informing, instructing, and training (recording conclusions, development of an emergency plan, informing and instructing stakeholders, cooperation and coordination of actions).

5. Monitoring (analysis of implemented measures and their effectiveness, modeling and analysis of risks associated with changes in the internal and external context and implementation of corrective actions).

Therefore, the mechanism of hazard formation is associated with the presence of an initiating coincidence of factors, which is implemented in the central hazardous event. This is assumed even in the presence of preventive barriers, if they

do not correspond to the level of threat (risk), are introduced untimely, have technical inconsistencies that form consequences at different levels of impact. However, choosing a strategy for influencing the localization of fire hazard is one of the effective ways to reduce this type of technogenic risks and use environmentally safe substances.

In work [2] it was noted that to effectively suppress the occurrence and development of coal spontaneous ignition (CSC), ammonium polyphosphate was grafted to fly ash (FAC). This was carried out by co-condensation, acid-base modification and amidation to obtain a modified fly ash inhibitor (PMFAC). Then, SEM, TG-FTIR, in-situ FTIR, and molecular dynamics simulation were synthetically used to investigate the inhibition effect and mechanism of PMFAC on CSC. The results showed that nitrogen and phosphorus-containing compounds were successfully attached to the surface of PMFAC, which are effective components for inhibiting CSC. In addition, PMFAC effectively increased the characteristic temperatures in the CSC process, and the addition of 45 % PMFAC increased the ignition temperature by 16 °C. The inhibitors can significantly inhibit the production of CO_2 , CO , CH_4 and H_2O during the CSC process. In addition, PMFAC also had a strong inhibitory effect on the hydroxyl, alkyl, and carbonyl groups involved in the reaction process. The effect progressively increased with the increase of PMFAC concentration, with the highest increase rate reaching 64.4 %. However, the main reaction pathway of $\bullet\text{OH}/\bullet\text{O}/\text{O}_2$ consumption during CSC and under the action of PMFAC was obtained only by molecular dynamics simulations, not their interaction.

Paper [3] states that coal spontaneous ignition has always been a global problem, causing wasteful consumption of coal resources, greenhouse gas emissions, and other air pollution problems. Although coal temperature monitoring is the most direct and accurate means of predicting coal spontaneous ignition, coal temperature is often impossible to measure directly due to various physical limitations. As an alternative, the cited study evaluated the qualitative and quantitative analysis of the CO and C_2H_4 formation rates, as well as various gas ratios, such as the CO/CO_2 ratio and the fire coefficient R_2 ($R_2=100\times\Delta\text{CO}/\Delta\text{O}_2$), to predict spontaneous ignition. This method was established based on temperature-programmed experiments with three different coal grades (including lignite, bituminous coal, and anthracite) and validated using data obtained from on-site monitoring of an actual mine. The results show that the accuracy of the method is 97 % in predicting coal temperature to within 15 °C (the range of the allowable error of the predicted value). This new method is not only accurate and reliable but also has theoretical significance for identifying coal self-ignition in pits and for developing fire prevention and extinguishing technologies. However, it is not stated how much accuracy is sufficient for fire prevention and control.

In the environment of various open coal storages [4], coal seams, workings, etc., some coal masses are often affected by external environmental factors. They are very prone to self-ignition at low moisture content ($\leq 8\%$). In order to investigate the effect of low moisture content on the self-ignition tendency of coals with different degrees of metamorphism, a temperature-programmed oxidation (TPO) experiment and an experiment to study the self-ignition characteristics of coals with different degrees of metamorphism were conducted. The experimental results show that (1) anthracite and oily coal with low moisture content of 1.2 % demonstrate a

stronger tendency to self-ignition. And long-flame coal and brown coal with low moisture content of 3.4 % and 5.6 % are more prone to self-ignition. But it is not said how other types of metamorphic coal with low moisture content are prone to self-ignition.

In [5], it was shown that structural transformations in different coal classes during low-temperature oxidation ($\leq 210^\circ\text{C}$) are crucial for understanding coal autoignition and related environmental problems. In situ Fourier transform infrared (FTIR) was used to isolate variations in aromatic, aliphatic, oxygen functional groups and hydrogen bonds of different coal classes, ranging from brown coal to anthracite. Chemical changes were observed under real-time experimental conditions. Characteristic temperature points were chosen as points where obvious gas changes occurred. Structural parameters were determined by fitting FTIR spectra. The band of highly substituted aromatic rings had a direct correlation with low-rank coal. The degree of substitution (DOS) of aromatic sites by alkyl groups showed a good power function correlation with fixed carbon content. The changes in aliphatic carbon show similar trends with different coal grades. In addition, the increase in coalification reduced the functional oxygen parameter "C". The "C" value of the samples with high oxygen content increased with temperature, which was caused by the oxidation of aliphatic structures. The fitting areas of the $3600\text{--}3000\text{ cm}^{-1}$ region decrease with increasing coal grade. However, the issues related to the change of aromatic structures with temperature change in low-grade coal than in high-grade coal remain unresolved.

In [6], four typical types of hard coal, non-caking coal, low-carbon coal, and anthracite coal were selected as the objects of study. For this purpose, programmed experiments were conducted with the heating of coal samples under different gas concentration conditions to provide a theoretical basis for preventing and combating self-ignition of coal in a gas environment. Experimental results show that with the increase of coal temperature, the oxygen consumption rate and the emission intensity during heating show a slow growth trend followed by a rapid growth. With the increase of the gas concentration in the surrounding environment, the production of CO and CO_2 , the oxygen consumption rate, and the heat release intensity during coal self-ignition tend to decrease. This is mainly because the high gas concentration occupies the adsorption sites on coal molecules, thereby hindering the reaction between coal and oxygen. In addition, by calculating the thermodynamic parameters of coal samples, it was found that the apparent activation energy increases with the increase of gas concentration. Therefore, the increase of the gas concentration in the surrounding environment significantly inhibits the self-ignition process of coal.

In [7], a method for continuous and precise nitrogen injection fire extinguishing was proposed. To implement this method, the study uses FLUENT, FLAC 3D modeling and elasticity principles to determine the process and dynamic parameters of nitrogen injection. This information guides the selection, design, and manufacture of equipment components, which led to the development of a new "rotating tow-type" continuous and precise nitrogen injection fire extinguishing equipment. Taking the Wenzhuang 15,102 working surface as an example, the inertia effect was compared and analyzed using CO, Graham's coefficient R_2 ($\Delta\text{CO}/\Delta\text{O}_2$), R_3 ($\Delta\text{CO}/\Delta\text{CO}_2$) and other quantitative indicators. The conclusions showed the following results: after the deployment

of this equipment, a decrease of about 70 % in CO concentration was observed. In comparison, R_2 in the mining zone decreased by 45 % compared to 0.38 % observed with nitrogen injection into the buried pipe. Similarly, the R_3 values for the cap and the top corner were reduced by approximately 56 % and 60 %, respectively. These significant improvements highlight the high fire suppression efficiency of nitrogen injection in piles. Nothing is said about the extinguishing concentrations.

In [8], it was noted that a new fire-fighting composite gel, made mainly of steel slag (SS) and silica (SF), was developed for the localization of spontaneous ignition in a coal mine. The gelation mechanism of the steel slag-based composite gel (SSG) was investigated using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The obtained data indicate that SSG is formed through hydration and geopolymerization processes involving SS and SF. In an alkaline environment of 1.5 M liquid glass solution, SSG exhibits increased strength and water retention capacity. In addition, the fire prevention and fire extinguishing performance of SSG was analyzed and verified by low-temperature oxidation, thermogravimetry, and low-temperature nitrogen adsorption (LTNA) experiment. SSG proved to be highly effective in suppressing coal self-ignition by suppressing CO formation, increasing the coal oxidation temperature, and reducing the contact area between oxygen and the coal body. However, it is not indicated how these compositions could be used for other materials.

The ignition of lignite, as reported in [9], was evaluated on a heated platform using hydroxyl-planar laser-induced fluorescence (OH-PLIF) in the range of 21–60 % O_2 in both N_2 and CO_2 diluent gases. The results showed that when the O_2 concentration was lower than 40 %, replacing CO_2 with N_2 slowed down the ignition delay time (*tign*). This was evident since no ignition occurred in the 21 % O_2/CO_2 mixture and almost 1.0 s difference in *tign* appeared when replacing CO_2 with N_2 in 30 % and 40 % air atmospheres. In addition, weaker flame brightness and shorter flame duration time (*tvol*) were also observed in O_2/CO_2 compared to O_2/N_2 . Accordingly, a significantly lower OH signal intensity was observed in O_2/CO_2 compared to O_2/N_2 , which was primarily due to the physical and chemical effects of CO_2 . First, the higher heat capacity and lower diffusion rate of O_2 in O_2/CO_2 lead to a lower volatile release rate and a lower flame temperature. The lower flame temperature and volatile release rate will reduce the number of hydrocarbon molecules (RH) and the reaction rate $\text{RH} \rightarrow \text{hydrocarbon radical (R)} + \text{H}$, which will lead to a decrease in the concentration of OH radical as a result of the reaction: $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$. Second, CO_2 directly participates in the three-body reaction $\text{H} + \text{OH} + (\text{M}) \rightarrow \text{H}_2\text{O} + \text{M}$, competing with the primary OH formation pathway, $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, for H radicals, thus suppressing OH radicals. However, when the O_2 concentration exceeded 40 %, *tign* was shorter in O_2/CO_2 by about 1.2–1.4 s than in O_2/N_2 with the same O_2 concentration. At the same time, compared with O_2/N_2 , similar flame brightness and *tvol* were observed in O_2/CO_2 . An obvious increase in OH intensity was also observed in O_2/CO_2 . With higher O_2 concentrations in O_2/CO_2 , the absorption and emission characteristics of CO_2 , increased O_2 diffusion, and reduced specific heat capacity in the O_2/CO_2 gas mixture synergistically contribute to the increase in temperature. And as a consequence, the release of volatiles contributes to the formation of relative humidity, and then increases the concentration of H through the reaction

$RH \rightarrow R+H$. But this leads to an increase in the concentration of OH formed by the reaction $H+O_2 \rightarrow OH+O$.

To prevent spontaneous ignition in coal mines, an environmentally friendly swelling nanogel was developed [10]. Acrylamide (AM) was introduced into the lamellar organic nano montmorillonite (OMMT) with a layered structure, and sodium lignosulfonate was used as the carbon source. Ammonium polyphosphate (APP), which combines the acid source and the gas source, was added to the gel carrier to form a swelling nanogel (CFR). The results showed that the calcined coal treated with CFR was covered with a uniform and dense swelling carbon layer, and the percentage of residual carbon was more than 2.9 times higher than that of the untreated coal. The contents of active carbonyl (CO), hydroxyl (–OH), and alkyl (–CH₃, –CH₂) in the coal samples were effectively reduced by the swelling nanogel (CFR), and the content of the ether bond (C–O–C) was increased. The characteristic temperature points of the coal samples were increased to different degrees. Thus, the intumescent nanogel (CFR) can effectively prevent coal self-ignition. It is not mentioned about its feeding into the coal pile.

In study [11], to examine the approach to prevent coal self-ignition in underground workings, chemical deposits formed by the reaction of two-phase aerosols (CO₂ and hydroxide) were used to prevent the self-ignition of anthracite. A Henan anthracite sample (0.18–0.25 mm) was continuously treated with aerosols. Aerosols Ba(OH)₂-CO₂, Ca(OH)₂-CO₂, Na₂SiO₃-CO₂ and NaAlO₂-CO₂ simultaneously flowed through the surface of the coal sample. After 50–55 s, in addition to Ca(OH)₂-CO₂, white or transparent colloidal deposits appeared and gradually accumulated. After 20 minutes, the weight of the formed deposits (dry mass) reached 0.95–5.10 % of the initial weight of the samples. According to the results of scanning electron microscopy, X-ray diffraction, thermogravimetry, and differential scanning calorimetry, physical experiments, and quantum chemistry modeling, it was concluded that it is two-phase aerosols that form dense ultrathin columnar or flocculent coatings on the coal surface. The main components of the deposits were BaCO₃, CaCO₃, H₂SiO₃, Al(OH)₃, hydrates, etc. The exothermic peak decreased to 69.0–86.2 % of raw coal. Ba²⁺ in the aerosol forms diligand, triligand, and tetraligand complexes with a characteristic structure containing S in coal samples and demonstrate a greater inhibitory effect on re-ignition. But issues related to the extinguishing mechanism remain unresolved.

Coal, especially low-grade coal with a high volatile content, is often spontaneously ignited during storage, which can lead to ignition of the coal composition and loss of thermal energy from the coal [12]. To determine the ignition point, all existing methods use samples of pulverized coal, which are artificially added with a special oxidant and then heated to accelerate the oxidation process. The particle size and test conditions of these methods differed greatly from the actual conditions of coal storage. The presented method used samples of granulated coal, the particle size of which is similar to the storage process, to test its temperature increase under the influence of humidity, pressure, and air flow. The tendency to spontaneously ignite was judged by the rate of increase in the temperature V70 of the sample at 69–71 °C under adiabatic heating conditions. The results show that brown coal had the highest heating rate during low-temperature oxidation, and anthracite had the lowest. The lower the moisture content of the coal, the higher the heating rate during low-temperature oxidation. But the corresponding physical and chemical data of coal are not given.

To investigate the micro mechanism of structural changes in anthracite due to heat accumulation by water and pyrite during oxidation, anthracite samples were selected in [13]. Water was added to coal at 1, 5, 10, 15, and 20 wt. % and pyrite at 1, 2, 4, and 6 wt. % and introduced into experimental samples. The results show that the oxygen-containing functional group of coal increases with the addition of water. It was believed that the content of the aromatic structure of coal is explained by the synergistic effect of water and pyrite. The synergistic effect of water and pyrite accelerates the oxidation process of seven types of active groups in coal samples. The water content was 10–15 wt. %, and the accompanying pyrite was 2–4 wt. %; the contribution to the oxidizing activity of the main active groups of coal was the greatest under oxidizing conditions. But it is not specified to what concentration the oxygen is reduced.

Thus, from our review of the literature [1, 3–10] it was established that spontaneous ignition of coal is a significant problem for the environment. The supply of nitrogen to the fire site is capable of eliminating the ignition of coal but the parameters that enable this process are not defined. Therefore, the establishment of parameters of the use of nitrogen to suppress ignition and the influence of oxygen concentration on this process necessitated the need for research in this area.

3. The aim and objectives of the study

The aim of our work is to establish the regularities of the ignition process of an anthracite sample when nitrogen is supplied to the ignition chamber. This makes it possible to consider the use of nitrogen as one of the elements of fire safety during coal storage.

To achieve the goal, it was necessary to solve the following problems:

- to conduct a study of the ignition inhibition process when washing an anthracite sample with gaseous nitrogen;
- to determine the changes in the nitrogen concentration for a nitrogen-oxygen mixture depending on the oxygen content in it during the inhibition of the ignition process of anthracite.

4. The study materials and methods

4.1. The object and hypothesis of the study

The object of our study is the concentration of nitrogen for inhibiting the ignition process of anthracite. The scientific hypothesis is to comprehensively study the ignition process of anthracite when changing the oxygen concentration and establishing the extinguishing concentration of nitrogen for inhibiting the ignition process of anthracite.

In the process of the study, assumptions and simplifications were adopted that relate to the features of the spontaneous ignition of anthracite on the modeling object. These imply that the features that determine the influence of changes in external conditions and the course of inhibition of the ignition process of anthracite are the same, while temperature, humidity, pressure are not variable.

4.2. Materials under investigation used in the experiment

To study the process of inhibiting the ignition of anthracite, a solid, high-density, shiny type of coal with a minimum

amount of impurities was used; the carbon content in it is over 90 %. The color is black or gray-black, luster: metallic, fracture: shell-like [14]. Density, 1500–1700 kg/m³ (Fig. 1). As a material, a batch of anthracite of the “seed” size class with a size of 6÷8 mm and a mass of 25±0.5 g was used.



Fig. 1. Anthracite sample

To determine the possibility of using nitrogen to inhibit the combustion process of anthracite batch, nitrogen gas was used.

4. 3. Methods of research into the fire-hazardous properties of anthracite and the concentration of nitrogen during the inhibition of the ignition process

To establish the regularities of inhibition of the ignition process of anthracite, nitrogen-air mixtures of a certain concentration were used, which were obtained on a device for determining the minimum fire-extinguishing concentration of gaseous fire extinguishing agents (ISO 14520-1). The required concentration of nitrogen was obtained in module 8 of the preparation of the gas-air mixture and fed to the test chamber, where the ignition chamber 1 was located (Fig. 2).

The essence of the method for determining the efficiency of the inhibition of the ignition process of anthracite is based on the creation of a laminar flow of a gas-air mixture of a given composition under dynamic conditions by mixing the flows of its components, which come from dosing devices with given flows. The ascending flow of the gas-air mixture washes the model ignition chamber. By gradually increasing the flow rate of the gaseous extinguishing agent around the anthracite ignition center, the ignition process of the batch is inhibited, which is recorded by a thermocouple. The volumetric concentration of nitrogen at this moment, calculated from the flow rates of the components of the gas-air mixture, is considered the optimal fire-extinguishing concentration.

The tests are carried out in the following sequence:

1. Through rotameter 9, air is supplied to diffuser 7 of gas duct 6 with a flow rate of 30 dm³/min.
2. A batch of anthracite heated to the ignition temperature in a muffle furnace is placed in model site 1.
3. Nitrogen is supplied to diffuser 7 of gas duct 6 through dispenser 8, increasing its flow rate in each experiment.
4. The value of the coal temperature in the model hearth is recorded at a given nitrogen flow rate.
5. The supply of nitrogen and air is stopped. The combustible substance is removed from the model site, and soot deposits are removed if necessary.

The flame extinguishing criterion was taken as a decrease in the coal temperature below the ignition temperature (~355 °C) for 120 s, which is the standard nitrogen supply time.

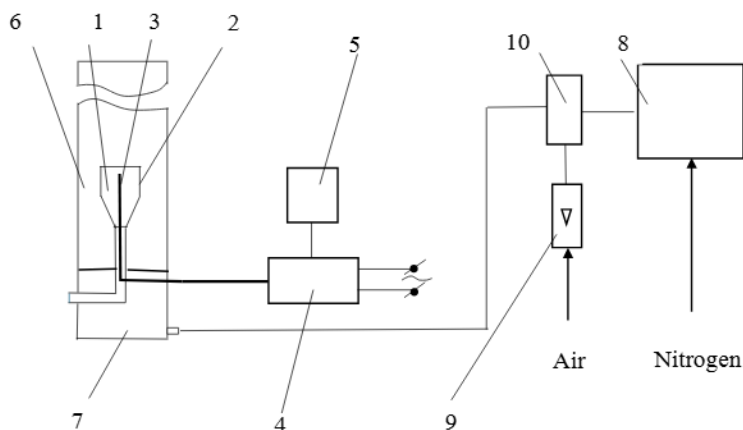


Fig. 2. Diagram of the installation for determining the extinguishing concentration of nitrogen when extinguishing solid combustible substances:

1 – model site; 2 – heater; 3 – thermocouple; 4 – transformer; 5 – thermostat; 6 – (gas pipeline) test chamber; 7 – diffuser; 8 – gas mixture dispenser; 9 – rotameter; 10 – mixing chamber

The concentration of nitrogen C_N (% vol.) is determined from the formula:

$$C_N = \frac{V_N}{V_N + V_O} \cdot 100, \quad (1)$$

where V_N is the nitrogen flow rate (dm³/min);
 V_O is the oxidant flow rate (dm³/min).

5. Results of research on the process of inhibiting the ignition of anthracite when supplying nitrogen to the fire site

5. 1. Determining the process of inhibiting the ignition when washing a batch of anthracite with gaseous nitrogen

The study of the process of inhibiting the ignition of anthracite is illustrated in Fig. 3, 4.



Gas-air mixture unit Test chamber

Fig. 3. The process of supplying a nitrogen-air mixture to the anthracite ignition chamber

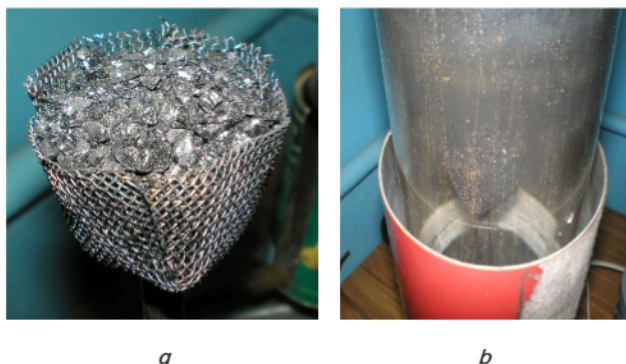


Fig. 4. Structural elements of the installation:
a – model fire site; b – gas duct

Fig. 5 shows the results of the study of the process of inhibition of anthracite ignition in the case of nitrogen supply.

From Fig. 5, it is established that a sample of heated coal in a normal air atmosphere continues to burn with greater intensity since an increase in temperature by an average of 20 °C was recorded for 40–45 s. Adding nitrogen to the air in an amount of 12.85 % reduces the ignition temperature of the anthracite site by 2 % but the cooling time of ignition below the ignition temperature exceeds 120 s. For a nitrogen-air mixture with a nitrogen concentration of 23.81 %, a decrease in the ignition temperature of the sample below its ignition for 120 s was recorded.

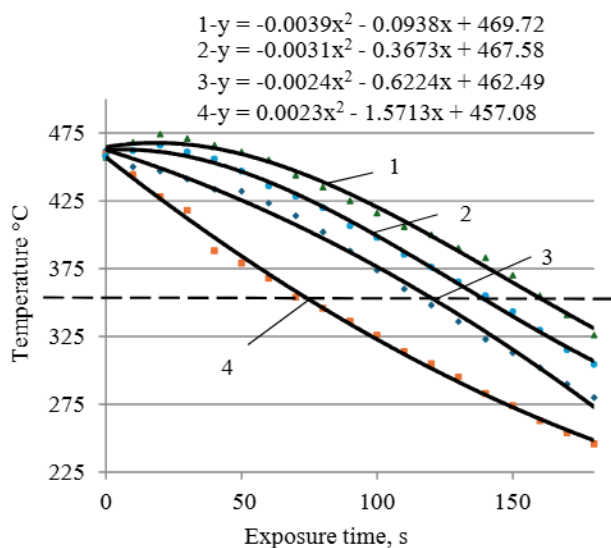


Fig. 5. Dependence of anthracite temperature on holding time in a nitrogen-air environment with nitrogen concentration: 1 – without nitrogen supply, 2 – 12.85 %, 3 – 23.81 %, 4 – 28.57 %

Further increase in the amount of nitrogen in the nitrogen-air mixture to 28.57 % more effectively cools the burning of anthracite below the ignition temperature for 70 s.

To assess the effectiveness of fire protection, the oxygen concentration that can be achieved when nitrogen is supplied was calculated using the equation:

$$C_{O_2} = 20.95 \cdot (1 - 0.01 \cdot C_N), \quad (2)$$

where C_N – nitrogen concentration, %;

C_{O_2} – oxygen concentration in the gas-air environment, %.

The results of the determination of changes in the concentration of oxygen and nitrogen above the coal surface are given in Table 1.

Table 1

Results of determining the changes in oxygen concentration in the gas mixture during quenching of an anthracite batch

Nitrogen concentration, vol. %	Composition of the atmosphere, % vol.	
	Oxygen	Nitrogen
0	21.0	79.0
12.85	18.26	81.74
23.81	15.96	84.04
28.57	14.95	85.05

Thus, the optimal nitrogen concentration in the case of extinguishing anthracite heated to a temperature above the ignition temperature is 23.8 % vol. Taking into account the safety factor of 1.2 (NFPA 1660), the standard extinguishing concentration C_{EN} should be 28.6 % vol., and the oxygen concentration should not exceed 16 %.

5. 2. Results of determining the nitrogen concentration for a nitrogen-oxygen mixture for inhibiting the ignition process of anthracite

According to our analytical data, a dependence plot was constructed of nitrogen concentration on the content of oxygen impurities in the fire extinguishing substance, at which the ignition process of anthracite is effectively inhibited, shown in Fig. 6.

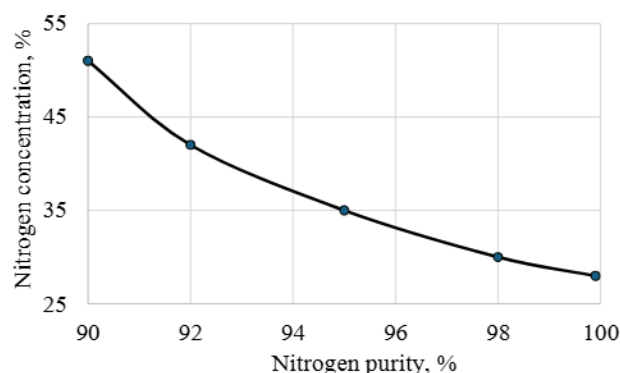


Fig. 6. Dependences of nitrogen concentration of the nitrogen-oxygen mixture on the oxygen content in it

With a decrease in the oxygen content, the curve deviates more intensively from the axis of the compositions and should naturally end at points that correspond to the values $C_N=100$ % and the limiting concentrations of oxygen.

To achieve the same fire-extinguishing effect as in the case of introducing pure nitrogen into the air in a concentration $C_{N_0}^i$ of i -th nitrogen-oxygen composition, it is necessary to introduce it in such a concentration that the nitrogen content in the formed mixtures with air in both cases is the same.

Let us denote the nitrogen content in the i -th nitrogen-oxygen mixture as $C_{N_2}^i$. For convenience, all concentrations will be expressed in volumetric (or molar, which is equivalent for gases) fractions. In particular, for pure nitrogen $C_{N_2}^1=1.00$, and for air of normal composition $C_{N_2}^n=0.79$.

Now let us express the nitrogen content (X) in mixtures prepared by introducing diluents (pure nitrogen and nitrogen-oxygen mixture of i -th composition) into the air in

fire-extinguishing concentrations, using the mixing rules. For a mixture of air and pure nitrogen:

$$X = C_{N_2}^1 C_{FC}^1 + C_{N_2}^n (1 - C_{FC}^1) = C_{N_2}^n + C_{FC}^1 (C_{N_2}^1 - C_{N_2}^n); \quad (3)$$

for a mixture of air and nitrogen that contains an admixture of oxygen (i -th composition):

$$X = C_{N_2}^i C_{FC}^i + C_{N_2}^n (1 - C_{FC}^i) = C_{N_2}^n + C_{FC}^i (C_{N_2}^i - C_{N_2}^n). \quad (4)$$

Equating the right parts of equations (3) and (4), we get:

$$C_{FC}^1 (C_{N_2}^1 - C_{N_2}^n) = C_{FC}^i (C_{N_2}^i - C_{N_2}^n), \quad (5)$$

hence:

$$C_{NO}^i = \frac{C_{N_2}^1 - C_{N_2}^n}{C_{N_2}^i - C_{N_2}^n} C_{FC}^1 = K_i C_{FC}^1, \quad (6)$$

where K_i is a coefficient constant for the i -th composition of the nitrogen-oxygen fire extinguishing mixture if the air composition is constant. For air of normal composition:

$$K_i = 0.21 / (C_{N_2}^i - 0.79). \quad (7)$$

By setting arbitrary discrete $C_{N_2}^i$ values (from 0.90 to 0.98) and C_{FC}^1 (from 0.28 to 0.51), K_i can be calculated using equation (6), and C_{FC}^i from equation (6). The obtained data are given in Table 2.

Table 2

Calculated values of concentrations of nitrogen-oxygen mixtures (C_{FC}^1 , vol. parts), which correspond to the minimum fire-extinguishing concentrations of nitrogen C_{FC}^i , depending on the nitrogen content in these mixtures ($C_{N_2}^i$)

$C_{N_2}^i$, vol. %	C_{FC}^1 , vol. %								
	0.28	0.30	0.33	0.36	0.39	0.42	0.45	0.48	0.51
0.98	0.30	0.33	0.36	0.40	0.43	0.46	0.50	0.53	0.56
0.95	0.35	0.39	0.43	0.47	0.51	0.55	0.59	0.63	0.67
0.92	0.42	0.48	0.53	0.58	0.63	0.68	0.73	0.78	0.82
0.90	0.51	0.57	0.63	0.69	0.74	0.80	0.86	0.92	0.97

As can be seen from Table 2, with increasing C_{FC}^1 the requirements for the purity of nitrogen as a fire extinguishing agent increase. Values C_{NO}^i that exceed 1.00 have no physical meaning, that is, the corresponding combinations C_{FC}^1 and $C_{N_2}^i$ are impossible. Therefore, conditionally limiting the C_{FC}^1 value, it is possible to preliminarily identify a part of the table ($C_{N_2}^i$ from 0.90 to 0.98; C_{NO}^i from 0.28 to 0.51), which reflects the conditions under which there is a fundamental possibility of practical application of nitrogen-oxygen mixtures of a certain composition for fire extinguishing.

6. Discussion of results based on studying the process of fire protection of wood with a reactive coating

When studying the process of anthracite burning (Fig. 5), it was found that a sample of heated coal in a normal air atmosphere continues to burn with greater intensity since an average increase in temperature by 20 °C was recorded

for 40–45 s. Adding nitrogen to the air in an amount of 12.85 % reduces the ignition temperature of the anthracite site by 2 % but the cooling time of ignition below the ignition temperature exceeds 120 s. For a nitrogen-air mixture with a nitrogen concentration of 23.81 %, a decrease in the ignition temperature of the sample below its ignition temperature was recorded for 120 s. A further increase in the amount of nitrogen in the nitrogen-air mixture to 28.57 % more effectively cools the ignition of anthracite below the ignition temperature for 70 s. This indicates the inhibition of the anthracite ignition process due to a decrease in the oxygen concentration, which can be identified directly by forming a gas-air mixture of a certain composition around a model anthracite fire [15, 16]. However, the plot of dependence of nitrogen concentration on the oxygen impurity content in the fire extinguishing substance, at which the anthracite ignition process is effectively inhibited (Fig. 6) shows that with a decrease in the oxygen content, the curve deviates from the x-axis and naturally ends at points corresponding to the nitrogen concentration values $C_{NO}=100$ %. The fire extinguishing effect, as when using pure nitrogen in concentration C_{FC}^1 , for the i -th nitrogen-oxygen composition, must be introduced in such a concentration C_{FC}^i , that the nitrogen content in the formed mixtures with air in both cases is the same and is described by the above dependences.

Unlike previous studies [2, 8, 10], in which attention was mainly paid to the use of gels containing flame retardants, our study considered a gas fire extinguishing agent, which is widely available in the market.

In contrast to the results reported in [17–19] regarding the mechanism for ignition inhibition, the following can be stated:

- the main regularity of the ignition inhibition process of anthracite fire site is not so much the use of the amount of nitrogen that affects the flame since individual fire extinguishing agents, for example, foaming agents, emit a significant amount of water vapor, and halons inhibit active radicals;
- the processes of ventilating the coal embankment with nitrogen, maintaining the required level of oxygen concentration, exert a significant impact on the process of eliminating the fire.

This approach guarantees greater practical significance of the results since the studied fire extinguishing substance was tested for reaction to the action of a high-temperature flame, which reflects the real circumstances of its operation. The results of our experiments showed that this approach has the potential, which is manifested, first of all, in the formation of an inert atmosphere. Determination of the oxygen concentration during the tests shows how nitrogen affects the inhibition of the ignition process of anthracite.

Our results on the localization of a fire site have certain limitations when determining the amount of nitrogen due to the unpredictability of the inhibition of the ignition process of the material. Taking into account the effectiveness of the use of nitrogen is possible provided that a certain concentration of oxygen is ensured, which is formed when nitrogen is supplied.

In addition, the response of the fire site to the influence of the nitrogen-oxygen mixture may give insufficiently predictable indicators due to the small amount of data on the reduction of the oxygen level by the use of membrane nitrogen, which limits the use of the results obtained. The disadvantage of the established experimental approach is a certain complexity, which may limit the determination of the effect

of extinguishing the anthracite fire site. However, thanks to fire tests, it is possible to obtain reliable results, which make it possible to establish the mechanism of operation of nitrogen-oxygen mixtures. Further development of the research area on technologies for eliminating anthracite fires can be based on potentially promising areas of further research, particularly in optimizing experimental data on formulation development.

7. Conclusions

1. Based on the results of our experiments on the process of inhibiting the ignition of anthracite with nitrogen, it was found that a sample of heated coal in a normal air atmosphere continues to burn with greater intensity. An average temperature increase of 20 °C was recorded for 40–45 s. Adding nitrogen to the air in an amount of 12.85 % reduces the ignition temperature of the anthracite site by 2 %, but the cooling time of ignition below the ignition temperature exceeds 120 s. For a nitrogen-air mixture with a nitrogen concentration of 23.81 %, a decrease in the ignition temperature of the sample below its ignition temperature was recorded for 120 s. A further increase in the amount of nitrogen in the nitrogen-air mixture to 28.57 % more effectively cools the ignition of anthracite below the ignition temperature for 70 s.

2. According to the results of changes in nitrogen concentration, it was found that with an increase in the concentration of pure nitrogen in the nitrogen-air mixture, the requirements for the purity of nitrogen as a fire extinguishing agent increase. Therefore, conditionally limiting the concentration of nitrogen in the *i*-th nitrogen-oxygen composition it is necessary to introduce it in such a concentration that the nitrogen content in the formed mixtures with air in both cases is the same. The purity of the nitrogen-oxygen mixture and its fire-extinguishing concentration reflect the conditions under which there is a fundamental possibility of practical applica-

tion of nitrogen-oxygen mixtures of a certain composition for fire extinguishing.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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