

Investigation of the operation of thermocatalytic sensors in explosion hazard monitoring systems for technogenic objects

Vasyl Holinko^{1* \boxtimes}, Valentyna Zabelina^{1 \boxtimes}, Oleksandr Holinko^{1 \boxtimes}, Oleg Kuznetsov^{1 \boxtimes}

¹ Dnipro University of Technology, Dnipro, Ukraine *Corresponding author: e-mail golinkongu@gmail.com

Abstract

Purpose. The research aims to theoretically and experimentally investigate the operation of thermocatalytic sensors in the entire range of possible concentrations of explosion-hazardous vapors and gases to assess the unambiguous operation of explosion protection equipment.

Methods. Analytical methods, classical provisions of electrical engineering, thermodynamics and catalysis, experimental studies of serial single-chamber pellet-type thermocatalytic sensors with a platinum-palladium catalyst, as well as the evaluation and generalization of experimental results are used in the research.

Findings. It has been found that when monitoring the explosion hazard of gas mixtures using thermocatalytic sensors, the maximum measuring bridge output signal value is observed at a concentration of combustible gases where the complete reduction of oxygen sorbed by the catalyst is ensured. However, at higher concentration of combustible gases, when insufficient oxygen is available on the catalyst surface for complete oxidation, a decrease in the measuring bridge output signal value is observed. It is shown that, unlike gas-air mixtures, it is impossible to reduce the bridge output signal to zero in the region of high fuel-vapor concentrations, and the minimum bridge output signal value depends on the partial pressure value of oxygen in the fuel-air mixture when it is saturated with fuel vapors, which ensures the unambiguous operation of explosion protection equipment in the entire range of possible explosion-hazardous concentrations of fuel vapors.

Originality. It has been determined that when using thermocatalytic sensors to control the explosion-hazardous medium during the oxidation reaction of the fuel-air mixture in the diffusion region at the stoichiometric value of the diffusion fluxes of combustible components and oxygen to the surface of the catalytically active sensor element, short-term dips in the measuring bridge output signal of gas analyzers are observed. At high concentrations of fuel vapors, when oxygen becomes a limiting agent in the mixture, the bridge output signal is inverted, which is a consequence of a more active oxidation reaction on the comparative thermocouple.

Practical implications. The conducted research allows us to recommend thermocatalytic sensors for use in explosion hazard monitoring systems of oil-fuel complex facilities, the main tasks of which are to control the explosion hazard of the medium and timely adoption of control decisions aimed at eliminating the threat of explosion, and to substantiate their power supply modes.

Keywords: explosion hazard, control methods, methane, fuel-air mixtures, thermocatalytic sensors

1. Introduction

Coal mines, oil-fuel complex facilities, as well as any technogenic facility where explosive gases and volatile combustibles are emitted or used, pose a danger to humans [1]. The general problem of ensuring technogenic safety necessitates analyzing the existing level of danger and, if necessary, developing measures aimed at reducing this level.

One of the most pressing issues for both the mining industry and the oil-fuel sector is the prevention of gas-air mixture explosions. For example, the vast majority of coal mines in Ukraine are hazardous due to methane gas leaks, so special attention is paid to implementing measures aimed at preventing methane explosions. The most common high-risk facilities where explosive substances are used are storage facilities and fuel-filling stations. The main reasons for the formation of explosion-hazardous fuel-air mixtures at these facilities are leaks of volatile fractions of oil products due to overfilling of tanks when draining oil products from tank trucks, disconnection of joints in process piping and breakages in pressure-suction pipelines of tanks, overfilling of fuel tanks when refuelling vehicles, accidents on pipelines and in columns due to metal corrosion, malfunction of dispensing valves and damage to pressure hoses, malfunction of tank drainage-filling devices and breathing valves, depressurization of tank hatches, etc. [2], [3]. An important measure to prevent explosions is the use of explosion hazard monitoring systems for technogenic facilities. The main primary tasks of these systems are to monitor the explosion hazard of the medium and to ensure the timely adoption of management decisions aimed at eliminating the threat of explosions [4], [5].

Explosion hazard monitoring systems are widely used in coal mines [6]. These systems monitor, transmit, store, and

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provide information on the methane content in the mine atmosphere. Additionally, they issue a control signal for power outage, which is the primary source of ignition for the methane-air mixture.

The primary and most important elements of an explosion hazard monitoring system are the devices used to monitor the explosion hazard of the medium. These devices detect and measure the presence and concentration of explosive gases or vapors in the air. Difficult operating conditions, including exposure to temperature and humidity variations, changes in pressure and gas composition of the medium, accidental shocks, vibration, water flooding, dust contamination and other factors can affect the efficiency and stability of their operation. This in turn may lead to malfunction or false activations of explosion protection equipment, such as protective power outage, which could become contributing factor to explosions.

The development of methods and means of monitoring the explosion hazard of the medium is the subject of research by many scientists [6], [7]. Among the methods used for explosion hazard control, the most widespread are those based on thermocatalytic, semiconductor and optical techniques.

Thermocatalytic sensors have been used in explosion hazard monitoring systems for technogenic objects [6]. They are characterized by a simple design and low cost, as well as minimal impact from variations in gas composition, humidity, dust, temperature, and other factors. Studies of this method [6] have significantly improved the reliability and stability of thermocatalytic explosion hazard control devices.

Semiconductor (metal oxide) sensors are also characterized by a simple design and low cost. They have high sensitivity and a long service life. However, these sensors lack sufficient stability, which limits their application in explosion hazard control systems. They are most commonly used in air purification systems in homes, offices, ventilation and air conditioning systems [8], as well as in portable electronic devices. The instability of such sensors is mainly caused by the incomplete recovery of sensitivity after exposure to high concentrations of vapors or gases, which leads to gradual signal drift. To improve the stability of semiconductor sensors, it has been proposed to process signals received from a matrix of gas sensors that respond to different vapor concentrations [9]. However, this approach significantly complicates control systems, increases their cost, and reduces reliability.

The optical absorption method is advantageous due to its fast operation in explosion hazard control devices. However, the method has significant drawbacks, including the complexity and large size of the sensors, as well as a substantial sensitivity to temperature, pressure, humidity, and various gas impurities. Additionally, factors such as air dustiness, smoke, and smog at the sensor installation point pose challenges to its application.

Recent studies of the optical method have made it possible to develop sufficiently sensitive, small-sized optical sensors. These developments have improved the dynamic performance of control devices through software methods and partially compensated for the influence of factors like dustiness on measurement results [10], [11]. However, this progress has led to a significant increase in the complexity of control systems, including the need to use additional optical sensors with altered spectral characteristics.

Other control methods used to detect petroleum vapors in the air include chromatographic, flame ionization, and photo-

ionization methods [12], [13]. These methods are highly sensitive and allow monitoring fuel vapor concentrations at a level close to the maximum permissible concentrations. However, their complex structure, high cost, and intricate measurement processes limit their use primarily to environmental monitoring systems.

The analysis and practical results of the application of various methods for explosion hazard monitoring show that thermocatalytic sensors are the most suitable for use in explosion hazard monitoring systems at fuel storage facilities and fuel-filling stations.

Modern explosion hazard control equipment utilizes thermocatalytic sensors consisting of two elements with identical geometric dimensions and electrical parameters: a working (active) element and a reference element. These elements are typically placed within a common reaction chamber. The supply of reacting gases to the working element and the removal of reaction products from it occur due to the presence of a gas concentration gradient and are facilitated by diffusion and convection. Heat exchange between the elements and the analyzed mixture is achieved through thermal conductivity and convective heat transfer. The reaction chamber is made of ceramic or cermet material with an internal diameter of 5-6 mm.

The sensing elements of modern sensors resemble a miniature ball made of aluminum oxide with a platinum wire spiral embedded inside. This spiral serves simultaneously as a heating element and a resistance thermometer. The surface of the catalytically active element is coated with a platinum-palladium catalyst. The working and compensation elements are typically included in one arm of the bridge measuring circuit [6], [14].

The oxidation reaction of combustible gases and vapors on a platinum-palladium catalyst can occur in both the kinetic and diffusion regions [14]. The rate of the oxidation reaction in the kinetic region depends on the type and temperature of the catalyst, as well as the concentration of the reacting components. For a platinum-palladium catalyst used in methane oxidation, this region is characterized by temperatures in the range of 350 to 360°C. The oxidation process involves the simultaneous adsorption of oxygen and combustible components on the catalyst surface, and the reaction rate is influenced not only by the concentration of combustible components, but also by the concentration of oxygen in the atmosphere.

As the catalyst temperature increases, the chemical reaction rate rises significantly, resulting in a zero concentration of the limiting component and a deficit of the excess component on the active surface of the catalyst. The reaction rate and, consequently, the amount of heat generated are determined by the diffusion rate of the limiting component. For a platinum-palladium catalyst in methane oxidation, the diffusion region occurs at temperatures above 360°C [14].

When an oxidation reaction occurs on a working element in the diffusion region with a low concentration of combustible gas, such as methane, its flow to the sensitive element surface depends linearly on the gas concentration in the reaction chamber and the effective diffusion conductivity of the working thermocouple [6]:

$$Q_m = \gamma_e C_{mk} \,, \tag{1}$$

where:

 $\gamma_e = 10^{-2} K_{ef} \beta_m F_e$ – an effective diffusion conductivity of the thermocouple, m³/s;

 C_{mk} – the methane concentration in the reaction chamber;

 K_{ef} - the methane oxidation efficiency factor;

 β_m – the mass transfer coefficient, m/s;

 F_e – the element surface area, m.

The mass transfer coefficient depends on the diffusion properties of the gas and is generally proportional to the molecular diffusion coefficient [6].

Due to the oxidation of methane on the catalytically active element, its concentration in the reaction chamber differs significantly from the concentration of methane in the C_{mm} mixture. The correlation between these values when methane enters the chamber by diffusion can be represented as:

$$C_{mk} = C_{mm} \frac{\gamma_f}{\gamma_f + \gamma_e} , \qquad (2)$$

where:

 γ_f – the diffusion conductivity of the filter element, m³/s.

The difference between the methane concentration in the mixture and in the chamber is:

$$\Delta C_m = C_{mm} \left(1 - \frac{\gamma_f}{\gamma_f + \gamma_e} \right). \tag{3}$$

This difference determines the volume of methane flow into the chamber and, consequently, the amount of heat generated by the working element, its temperature increase, as well as the output signal value of the measuring bridge.

It should be noted that Expressions (2) and (3) are valid for cases where methane is the limiting agent in the gas mixture that determines the reaction rate. When the methane volume fraction exceeds 9%, air oxygen becomes the limiting component, and the amount of heat generated on the working element becomes proportional to the flow of oxygen reaching its surface. In this scenario, the output signal value decreases from its maximum at a methane volume fraction of 9% to zero at 100% methane in the mixture. Assuming that the value in this case decreases linearly, the dependence of the output signal value U_{out} of the bridge measuring circuit on the concentration of combustible gas takes the form shown in Figure 1.



Figure 1. Theoretical dependence of the output signal value U_{out} of the bridge measuring circuit on the methane concentration

The dependence shown in Figure 1 has been obtained under the assumption of a constant value for the oxidation efficiency and mass transfer coefficient in the entire range of possible combustible gas concentrations. Additionally, it does not account for the fact that the heat transfer mechanism changes significantly with variations in the composition of the mixture, as the methane thermal conductivity is much higher than that of air.

Experimental studies on the dependence of the output signal value of the bridge measuring circuit (assuming the measuring bridge is powered by a stable voltage source) on the methane concentration, as presented in [14], have revealed that no sensors exhibit completely identical characteristics in the region of high methane concentrations. Each sensor has its own dependence $U_{out} = f(C)$.

Despite the differences in the dependences at high methane concentrations, in the range of 0 to 9 vol.%, the dependence $U_{out} = f(C)$ for all the studied sensors is characterized by an almost linear increase in the output signal as the methane concentration rises to 7 vol. %. A sharp decrease in the output signal value (failure of the output characteristic) is observed when the methane concentration increases from 8 to 9 vol. %. Since the oxidation of one methane molecule requires two oxygen molecules, this corresponds to a ratio of methane and oxygen flows to the surface of the catalytically active element of 1:2. Given the similarity of the molecular diffusion coefficients of methane and oxygen, this ratio nearly coincides with the stoichiometric concentration of the components.

The type of downward dependence $U_{out} = f(C)$ in the region of high methane concentrations for most of the studied sensors is approximately linear. Furthermore, at a gas content of 100%, there is a shift of the bridge zero toward positive values, accompanied by an output signal inversion. This phenomenon is attributed to significant changes in the heat transfer mechanism of the sensors in air and methane.

Many sensors in the range of 60 to 80 vol. % methane exhibit a notable increase in the steepness of the characteristic, followed by its subsequent levelling. These changes are evidently associated with a decrease in the temperature of the working element in a mixture with a high methane concentration, due to a significant increase in the thermal conductivity of the gas medium. This decrease in temperature causes the oxidation reaction to transition from the diffusion region to the kinetic region.

An example of an experimental dependence obtained by varying the methane concentration in the test chamber from 0 to 100 vol. % is shown in Figure 2.



Figure 2. Experimental dependence of the output signal value U_{out} of the bridge measuring circuit on the methane concentration

The presence of a dip in the measuring bridge output characteristic within the range of explosive concentrations, as well as a decrease in the bridge output voltage below the threshold of the explosion protection system at high concentrations, necessitates several measures to ensure the unambiguous operation of the protection system. These measures include the additional incorporation of thermoconductometric sensors into mine methane analyzers [14] and the application of various control methods based on specific situations.

However, such solutions significantly complicate and increase the cost of explosion hazard control equipment. They also fail to align with modern approaches to the development of technological safety systems for technogenic facilities, which emphasize the integration of advanced information technologies [15]. The rapid advancement of digital tools for sensor data processing, and primarily microcontrollers, the cost of which has now become comparable to those of analog chips, creates opportunities for shifting the focus away from complex measuring equipment designs to the use of simple, low-cost sensors and achieving desired outcomes by controlling their operating modes and employing appropriate software [16]. For instance, software-based solutions enable the control and adjustment of methane analyzers' zero readings [17], sensor sensitivity [18], contamination of gas diffusion filters, and restricted access to the sensors by the gas-air mixture [19]. They also support the optimization of thermocouple power supply modes [20] and the estimation of measurement errors based on the presence of unmeasured components in the atmosphere [21].

Explosion-hazardous concentrations of petroleum product vapors are formed during various processes related to the processing, transportation, storage, and use of petroleum products. At storage facilities and fuel-filling stations, the greatest danger of explosion-hazardous mixtures is associated with the evaporation of gasoline from tanks [22], [23]. The introduction of promising technical measures aimed at reducing gasoline vapor emissions into the environment during transportation [24], [25] and minimizing the intensity of gasoline evaporation during storage [26]-[28] has helped mitigate the risks. However, these measures do not eliminate the threat of explosions. This risk remains particularly significant in extreme situations, such as those related to military operations and psychophysiological factors [29]-[31].

One key indicator characterizing the content of fuel vapors in a mixture is the partial vapor pressure. DSTU 4160-2003 "Petroleum products. Determination of saturated vapor pressure. Reid technique" defines a method for determining saturated vapor pressure, which is one of the primary characteristics of any type of fuel. This method involves measuring the saturated vapor pressure of petroleum pro-ducts at a temperature of 37.8°C and a volume ratio of the tested petroleum product to its vapors in the air of 1:4. Changes in the volume ratio or temperature lead to variations in the pressure of saturated vapors [32].

Under real-world conditions, when evaporating from an open fuel surface, vapors are continuously and completely released into the atmosphere, and evaporation proceeds at maximum velocity. In a sealed container, the evaporation process initially occurs at maximum velocity, but gradually slows down as the vapor-air mixture pressure and fuel vapor content increase.

Thus, research conducted in this area has significantly improved the metrological and operational characteristics of explosion hazard control devices based on the thermocatalytic control method, enhancing their reliability and stability. However, issues related to explosion hazard control in the presence of combustible gases and vapors with varying self-ignition temperatures remain unresolved. Cases of malfunctioning explosion hazard control devices at high concentrations of vapors and gases have been reported. Existing thermocatalytic control devices and methane analyzers do not provide reliable protection in the entire range of possible vapor and gas concentrations, with some cases of ambiguous operation at high concentrations [14].

These challenges necessitate further research to refine this method and improve the methods for controlling the explosion-hazardous fuel-air mixtures.

The purpose of this publication is to theoretically and experimentally investigate the operation of thermocatalytic sensors in the entire range of possible concentrations of explosion-hazardous vapors and gases to ensure the unambiguous operation of explosion protection equipment.

2. Methods

Analytical methods based on the fundamental principles of heat and mass transfer theory, as well as molecular diffusion in gases are used in this study. Additionally, experimental studies of serial pellet-type thermocatalytic sensors with a platinum-palladium catalyst are conducted, and the research results are assessed and summarized.

To assess the unambiguous operation of explosion protection systems in the range of explosive concentrations of fuel-air mixtures using thermocatalytic sensors, observations are made of the change in the output signal values of serial sensors manufactured by the Red Metalist Research and Production Association, Konotop. The observations are performed by placing the sensors in a small-sized semi-hermetic chamber (without complete sealing), into which porous material impregnated with gasoline is introduced.

The average sensitivity of the 10 methane sensors used in the study, powered by a stable current source of 205 mA, is 18.8 mV/vol.%. The calculated preheating temperature of the working element of the sensors is approximately 430°C, indicating that the catalytic oxidation reaction occurs in the diffusion region. Given that the self-ignition temperature of many volatile gasoline components is below 430°C, which can lead to combustion of fuel components on the comparative sensor element, the experiments are conducted at varying current values through the thermocouples. The sensors are powered by a stable current source.

3. Results and discussion

This is a revised version with minor corrections for clarity and flow. In view of the above, to assess the feasibility of ensuring the unambiguous operation of the coal mine explosion protection system using only thermocatalytic sensors, a theoretical analysis is performed of their operation when the measuring bridge is powered by a stable current source.

Based on the analysis of the experimental dependences of the output signal value of the bridge measuring circuit on methane concentration (Fig. 2), the ambiguous operation of the explosion protection system may result from the dip of the measuring bridge output characteristic in the region of stoichiometric concentrations of methane and air, as well as at methane concentrations ranging from 60 to 100 vol. %. The dips in the output characteristic, observed within the 8-9 vol. % methane range, are short-lived and unstable (lasting up to several seconds). Even under laboratory conditions, it is challenging to create scenarios in which a prolonged disruption of the oxidation reaction occurs. This is attributed to changes in the temperature regime of the catalytically active element during oxidation reaction disruptions, variations in the effective diffusion conductivity of the thermocouples and filter element, and, in mine conditions, the presence of turbulent pulsations in the medium. The unambiguous operation of the explosion protection system is achieved through software-based solutions, such as introducing a restriction on restoring power supply to electrical equipment disconnected by the protection system without a time delay.

The decrease in the output signal of the thermocatalytic sensor at methane concentrations ranging from 60 to 100 vol. %, which can lead to ambiguous operation of the explosion protection system, may persist for a significant duration. Without the additional integration of thermoconductometric sensors to methane analyzers, this necessitates the search for solutions to ensure the unambiguous operation of explosion protection systems using only thermocatalytic sensors.

The theoretical dependence of the voltage on the comparative thermocouple of the thermocatalytic sensor on the current value is as follows:

$$U_{e} = I_{e}R_{eg} + \beta b_{e}R_{0e}I_{e}^{3}, \qquad (4)$$

where:

 U_e – the voltage on the thermocouple, V;

 I_e – the current through the thermocouple, A;

 R_{eg} – the resistance of the thermocouple at the current temperature of the gas mixture, Ohm;

 β – the temperature coefficient of the thermocouple resistance, 1/°C;

 b_e – the thermal resistance coefficient of the thermocouple, °C/A²;

 R_{0e} – the thermocouple resistance at 0°C, Ohm.

The thermocouple resistance at air temperature for a platinum resistor is determined by the known Expression:

$$R_{eg} = R_{0e} \left(1 + \beta t_g \right), \tag{5}$$

where:

 t_g – the air temperature, °C.

In this case,

$$U_e = I_e R_{0e} \left(1 + \beta t_g \right) + \beta b_e R_{0e} I_e^3.$$
(6)

The thermocouple thermoresistive coefficient determines the correlation between its electrical, thermal and geometric characteristics:

$$b_e = \frac{R_e}{\alpha_e F_e},\tag{7}$$

where:

 α_e – the total heat transfer coefficient of the element, W/(m^{2.o}C);

 F_e – the surface area of the element, m².

From Expressions (6) and (7), it follows that, provided the thermocouple is powered by a stable current source [20] and the ambient temperature is known, the voltage across the comparison element depends directly on the process of heat exchange between the thermocouple and the medium. This means that the comparison element can effectively function as a thermal conductivity sensor.

The total heat transfer coefficient of an element is the sum of the heat transfer coefficients of the element due to thermal conductivity of the medium, convection, radiation, and thermal conductivity of the conductive lead ends. When designing the transducer elements of sensors, it is crucial to minimize the influence of all heat transfer components, except for the thermal conductivity of the gas medium, on their temperature. Under such conditions, the temperature dependence of the heat transfer coefficient is directly linked to changes in the thermal conductivity of gases, which increases with temperature in accordance with the following dependence:

$$\lambda = \lambda_0 \left(\frac{T}{T_0}\right)^n,\tag{8}$$

where:

T- the gas temperature, K;

 T_0 – the temperature equal to 273 K;

 λ_0 – the thermal conductivity of gas at a temperature of 273 K, W/m K;

n – the temperature coefficient of thermal conductivity change (for air – 0.82, for methane – 1.33).

Due to methane oxidation on the catalytically active element, the composition of the analyzed gas mixture differs from that of the mixture within the reaction chamber. Table 1 presents information on the composition of the mixtures when the methane content in the medium is 60 vol.% under specified conditions $\gamma_f = \gamma_e$.

Table 1. Composition of the analyzed gas mixture and the mixturein the reaction chamber at a methane content of60 vol. % in the medium

Mixture type	Volumetric content of gas components, %				
	CH ₄	O_2	CO ₂	H ₂ O	N ₂ and
					others
Atmospheric air	0	21	0	0	79
Gas mixture	60	8	0	0	32
to be analyzed					
Mixture in the	59	4	2	4	20
reaction chamber	50	4	2	4	32

The thermal conductivity coefficients of air, the analyzed gas mixture, and the mixture in the reaction chamber for this case, calculated using expressions from [21], at a heating temperature of the comparative sensor element of 400°C, are respectively:

$$\lambda_a = 39.4 \cdot 10^{-3} \text{ W/m} \cdot ^{\circ}\text{C};$$

 $\lambda_{as} = 54.3 \cdot 10^{-3} \text{ W/m} \cdot ^{\circ}\text{C};$
 $\lambda_{ck} = 53.6 \cdot 10^{-3} \text{ W/m} \cdot ^{\circ}\text{C}.$

From the data in Table 1, the calculated measurement error due to the discrepancy between the gas composition in the reaction chamber and the analyzed mixture at a methane volume fraction of 60% and a heating temperature of 400°C is 1.3%.

In modern thermocatalytic sensors, heat removal from the thermocouple due to convection and the thermal conductivity of the conductive lead ends is negligible. However, heat dissipation due to radiation accounts for up to 50% of the total heat transfer of the element [6]. In this case, based on Dependence (6), an increase in the thermal conductivity coefficient from $39.4 \cdot 10^{-3}$ to $53.6 \cdot 10^{-3}$ W/m·°C, when the thermoelectric group is powered by DC source of 0.2 A and the platinum

thermoelectric element resistance is 2 Ohm (at 0°C), leads to a decrease in the voltage on the comparative element by almost 100 mV. Under such conditions, the use of a comparative element of the thermocatalytic sensor as a thermal conductivity sensor allows these voltage changes to ensure the unambiguous operation of the explosion protection system, even without medium temperature control. Furthermore, the integration of a temperature sensor into mine analyzers enables not only unambiguous operation of methane concentration in the mixture during emergency gas gassing of mine workings.

The revealed peculiarities of thermocatalytic sensors at high methane concentrations necessitate the study of their operation in the field of explosion-hazardous concentrations of oil vapors and when the oxidizing agent in the fuel-air mixture becomes the limiting agent. It should be noted that the fuel-air mixture formed as a result of the evaporation of volatile gasoline fractions differs significantly from the methane-air mixture in terms of properties and physical characteristics.

First, the thermal conductivity of the fuel-air mixture decreases rather than increases with an increase in the content of combustible components, unlike the methane-air mixture. Secondly, gasoline contains volatile hydrocarbons with a selfignition temperature significantly lower than the temperature of the working element, which in methane analyzers is selected based on the condition of the oxidation reaction in the diffusion region. Thirdly, under the possible conditions of operation of explosion protection equipment and fuel use, it is impossible to reduce the oxygen content in the fuel-air mixture to zero.

Given the variability of the fuel composition and the uncertainty of the processes of evaporation and oxidation of individual fuel components in the diffusion region, it is impossible to theoretically describe the dependence of the output signal U_{out} of the bridge measuring circuit on gasoline vapors. The process can only be qualitatively evaluated for individual volatile components of the fuel mixture, such as the most volatile component of gasoline – butane (Fig. 3).



Figure 3. Theoretical dependence of the output signal value U_{out} of the bridge measuring circuit on the concentration of butane vapors

The maximum value of the output signal of the measuring bridge in this case is observed at a volume concentration of butane of about 7%, when the flow to the surface of the butane sensing element becomes sufficient for the complete reduction of oxygen sorbed by the catalyst surface, i.e., at the stoichiometric value of the diffusion fluxes of gasoline vapors and oxygen. At a higher concentration of butane, when there is not enough oxygen on the catalyst surface for its complete oxidation, a linear decrease in the bridge output signal is expected.

It should be noted that, given the significantly lower value of the diffusion coefficient of butane compared to the diffusion coefficient of oxygen, which under normal conditions are 0.081 and 0.19 cm²/s, respectively, the maximum value of the output signal does not coincide with the stoichiometric concentration of components. The stoichiometric concentration is achieved at a butane content in air of about 3.1 vol. %.

A peculiarity of testing thermocatalytic sensors in a mixture of gasoline vapors and air is that it is impossible to create a vapor-air mixture with specific parameters for calibration and adjustment of gas analyzers or alarms. For this purpose, mixtures of specific gases or volatile liquids are used, such as methane-air mixtures, propane-air mixtures, or hexane-air mixtures. In such cases, the results of measuring the concentration of gasoline or diesel fuel vapors, expressed either in vol. % or in mg/m³, are arbitrarily conditional values equivalent to the values for gases or vapors of substances for which the analyzers are calibrated.

Under real conditions, when evaporating from an open fuel surface, vapors are continuously and completely discharged into the atmosphere, and evaporation proceeds at maximum velocity. In a sealed container, the evaporation process initially occurs at maximum velocity, but gradually slows down as the vapor-air mixture pressure in the container increases, along with the fuel vapor content.

In a leaky tank, such as one with an opening in its wall, the content of fuel vapors in the gas mixture is determined by the ratio of the rate of fuel diffusion from the open surface to the rate of diffusion of fuel vapors through the opening into the atmosphere. Clearly, by altering the size of the opening or the ambient temperature, it is possible to change the content of fuel vapors in the gas from zero to the maximum achievable value at a given temperature and degree of container leakage.

To evaluate the unambiguous operation of explosion protection equipment using thermocatalytic sensors, experimental studies are conducted on their performance during the accumulation of gasoline vapors in the measuring chamber.

The study of the change in the output signal of the measuring bridge over time after the introduction of gasoline into the chamber is conducted at current values through the thermocouples of 205, 185, 165 145 and 135 mA. At these current values, the initial heating temperatures of the thermocouples are approximately 430, 360, 290, 220 and 180°C, respectively. This setup allows for the study of sensor operation during the oxidation reaction in both the diffusion region (430 and 360°C) and the kinetic region (290, 220 and 180°C).

In the initial period of time, as the vapor accumulates, in all cases, an increase in the output signal of the measuring bridge to the maximum is observed. However, with further accumulation of fuel vapors and a decrease in the partial pressure of oxygen in the mixture, the output signal value decreases. The maximum output voltage of the measuring bridge at currents of 205, 185, 165, 145 and 135 mA is 76, 90, 118, 106 and 8.2 mV, respectively. At a current value below 135 mA, when the initial heating temperature of the thermocouples is less than 180°C, the oxidation of gasoline vapors on the catalytically active element does not occur.

A characteristic view of the change in the output signal of the measuring bridge over time after the introduction of gasoline into the chamber and during the oxidation reaction in the diffusion region is shown in Figure 4.



Figure 4. Time variation of the sensor output signal during the evaporation of gasoline in the chamber and the oxidation reaction in the diffusion region ($I_e = 185 \text{ mA}$)

As a result of the experiment, it has been found that after the introduction of gasoline into the chamber, during the initial period, as vapors accumulate at preheating temperatures of 430 and 360°C, an increase in the measuring bridge output signal to a maximum is observed. Subsequently, with further accumulation of fuel vapors and a decrease in the partial pressure of oxygen in the mixture, a decrease in the output signal and its inversion are observed. In this case, it is evident that oxygen becomes the limiting agent in the mixture, and the inversion of the output signal occurs due to more intense oxidation of fuel vapors on the comparison element than on the working element.

In the zone of maximum output signal at high thermocouple preheating temperatures, short-term disturbances (characteristic dips) were observed, indicating the achievement of the stoichiometric concentration of diffusion flows of gasoline vapors and oxygen to the catalytically active thermocouple. However, the amplitude of these disturbances is smaller than in a binary mixture of air and methane and does not disrupt the unambiguous operation of explosion protection systems. This may be attributed to the peculiarities of the oxidation reaction of a multicomponent mixture on catalysts in the diffusion region.



Figure 5. Time variation of the sensor output signal during the evaporation of gasoline in the chamber and the oxidation reaction in the kinetic region ($I_e = 145 \text{ mA}$)

It is notable that the maximum output signal value of the bridge measuring circuit at thermocouple preheating temperatures of 430 and 360°C is significantly lower than at preheating temperatures of 290 and 220°C. This is due to the presence of fuel components with low self-ignition temperatures, which undergo oxidation at higher thermocouple temperatures, both on the working element and the comparison element. Evidence of such oxidation on the comparison element is provided by an increase in the voltage across this element during vapor accumulation when the thermogroup is powered by a stable current source, indicating an increase in its temperature.

The oxidation reaction of fuel vapors on the comparison element is practically not observed at heating temperatures of 290°C or lower. At this temperature, the maximum output signal value of the bridge measuring circuit is recorded at 118 mV. A further decrease in current is accompanied by a gradual reduction in the maximum output signal value, and at an initial heating temperature of the catalytically active element of 220°C, the maximum signal value is 106 mV.

The cessation of oxidation of fuel vapors on the comparison element at a preheating temperature of 290°C, despite the presence of components with lower self-ignition temperatures in gasoline, can be explained by the significant difference in the gas mixture composition of the sensor reaction chamber compared to that of a mixture determined by self-ignition temperatures. This is primarily due to a significantly lower oxygen concentration in the chamber compared to its concentration in air.

With a further reduction in the current through the thermocouples, and consequently a decrease in their initial heating temperature, the maximum output signal value of the bridge measuring circuit decreases sharply. At a thermocouple preheating temperature below 180°C, the oxidation of fuel vapors on the working thermocouple with a platinumpalladium catalyst practically ceases.

As shown by the research results, the use of serial thermocatalytic sensors in explosion protection systems at oilfuel complex facilities, when choosing a power supply mode that ensures the oxidation reaction occurs in the diffusion region, does not guarantee the unambiguous operation of the explosion protection system. This is because, at initial thermocouple heating temperatures of 360°C and above, where oxidation of fuel vapors occurs in the diffusion region, oxidation of gasoline components with low self-ignition temperatures is observed on the comparison thermocouple. Furthermore, the oxidation reaction velocity on the comparison element increases significantly when oxygen becomes the limiting agent in the mixture. This results in not only a decrease in the sensitivity of the sensor, but also in an inversion of the measuring bridge output signal, which can lead to erroneous actions of the explosion protection system.

When the preheating temperature of the thermocouples is reduced to 290°C, oxidation of fuel vapors does not occur on the comparison element. In this case, the oxidation reaction takes place in the transition zone between the diffusion and kinetic regions. This ensures high sensor sensitivity and eliminates signal inversion, enabling the unambiguous operation of explosion protection equipment. Stable and high sensitivity is also observed when the initial heating temperature of the elements is reduced to 220°C. Considering this temperature range, for practical use of sensors in explosion protection systems at oil-fuel complex facilities, the initial heating temperature should be set to approximately 255° C. When powering the sensors from a DC source, the current should be about 155 mA, and when using a stable voltage source, the recommended voltage is 1.5 V.

This power supply mode ensures the unambiguous operation of the explosion protection system in the full range of possible ambient temperature variations. When microcontrollers are used to process information from sensors, the optimal power supply mode for a thermocatalytic sensor involves stabilizing the temperature or voltage on the comparison element and the voltage across the comparison element [6]. It is also advisable to set the operational thresholds for explosion protection equipment using a certified hexane-air mixture.

4. Conclusions

The use of a thermocatalytic sensor comparison element as a thermal conductivity sensor ensures the unambiguous operation of the coal mine explosion protection system in the entire range of possible methane concentrations. Additionally, the introduction of a temperature sensor into mine analyzers not only ensures the unambiguous operation of the explosion protection system, but also enables the calculation of methane concentration in the mixture within the entire range of possible concentrations.

Given the uncertainty and variability of the composition of gasoline vapors in space and time, it is impossible to theoretically describe the dependence of the output signal of the bridge measuring circuit on the concentration of gasoline vapors. However, a theoretical analysis of the dependence of the thermocatalytic sensor output signal on the concentration of a specific volatile component of the fuel mixture such as butane, indicates that the maximum value of the measuring bridge output signal is observed in the area of the stoichiometric value of the diffusion fluxes of butane and oxygen to the surface of the catalytically active element. This corresponds to a volume concentration of butane of approximately 7 vol. %. At higher butane concentration, when oxygen becomes the limiting component in the mixture, a linear decrease in the bridge output signal is expected. Unlike gas-air mixtures, it is impossible to reduce the bridge output signal to zero in the region of high concentrations of combustible vapors. The minimum value depends on the partial pressure of oxygen in the fuel-air mixture when it is saturated with gasoline vapors.

Experimental studies of the change in the output signal of a measuring bridge with a thermocatalytic sensor during the accumulation of gasoline vapors in a semi-hermetic chamber demonstrate that when a sensor power supply mode ensures the catalytic oxidation of fuel vapors in the diffusion region, the unambiguous operation of the explosion protection system is not guaranteed. It has been shown that the unambiguous operation of explosion protection systems is ensured at preheating temperatures of thermocouples ranging from 220 to 290°C. The recommended power supply modes for sensors in explosion protection systems for fuel complex facilities are provided.

The conducted research allows us to recommend thermocatalytic sensors with a platinum-palladium catalyst for use in explosion hazard monitoring systems not only in coal mines, but also at oil-fuel complex facilities. The primary tasks of these systems are to control the explosion hazard of the medium and enable timely decision-making aimed at eliminating potential threats.

Author contributions

Conceptualization: VH; Formal analysis: VZ, OH, OK; Investigation: VZ, OH, OK; Methodology: VH; Project administration: VH; Supervision: VH; Validation: VZ, OK; Visualization: VZ, OH; Writing – original draft: OH; Writing – review & editing: VZ, OK. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interests

The authors declare no conflict of interest.

Data availability statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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Дослідження роботи термокаталітичних датчиків в системах моніторингу вибухонебезпеки техногенних об'єктів

В. Голінько, В. Забеліна, О. Голінько, О. Кузнєцов

Мета. Теоретично та експериментально дослідити роботу термокаталітичних датчиків в усьому діапазоні можливих концентрацій вибухонебезпечних парів і газів для оцінки однозначності роботи засобів вибухозахисту.

Методика. В роботі застосовані аналітичні методи, класичні положення електротехніки, термодинаміки та каталізу, експериментальні дослідження серійних однокамерних термокаталітичних датчиків пелістерного типу з платино-паладієвим каталізатором, оцінка й узагальнення результатів експериментальних досліджень.

Результати. Встановлено, що при контролі вибухонебезпечності газових сумішей термокаталітичними датчиками, максимальне значення вихідного сигналу вимірювального моста спостерігається при концентрації горючих компонентів, за якої забезпечується повне відновлення сорбованого каталізатором кисню, а при більшій концентрації горючих компонентів, коли для їх повного окислення на поверхні каталізатора недостає кисню, спостерігається зниження вихідного сигналу вимірювального моста. Показано, що на відміну від газоповітряних сумішей, зниження вихідного сигналу моста в області високих концентрацій парів горючих компонентів до нуля неможливе, а мінімальне значення вихідного сигналу моста залежить від величини парціального тиску кисню в паливоповітряній суміші при її насищенні парами пального, що забезпечує однозначність спрацювання засобів вибухозахисту в усьому діапазоні можливих вибухонебезпечних концентрацій парів палива.

Наукова новизна. Встановлено, що при використанні термокаталітичних датчиків для контролю вибухонебезпечності середовища при протіканні реакції окислення паливоповітряної суміші в дифузійній області за стехіометричного значення дифузійних потоків горючих компонентів і кисню до поверхні каталітично активного елемента датчика спостерігаються короткочасні провали вихідного сигналу вимірювального моста газоаналізаторів. Крім того, при високій концентрації парів палива коли лімітуючим агентом в суміші стає кисень, виникає інверсія вихідного сигналу моста, що є наслідком більш активного протікання реакції окислення на порівняльному термоелементі.

Практична значимість. Проведені дослідження дозволяють обґрунтувати режими живлення термокаталітичних датчиків та рекомендувати їх для використання в системах моніторингу вибухонебезпеки об'єктів нафтопаливного комплексу, основними задачами яких є контроль вибухонебезпечності середовища та своєчасне прийняття управляючих рішень спрямованих на усунення загрози вибуху.

Ключові слова: вибухонебезпека, методи контролю, метан, паливоповітряні суміші, термокаталітичні датчики

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