Experimental-theoretical approach to calculating the partial density of hydrogen cyanide during fires at energy facilities

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Annotation. It is made analysis of toxic effect of hydrogen cyanide on people during fire evacuation at energy facilities premises. The critical value of the partial density of hydrogen cyanide is substantiated. An experimental and theoretical approach is proposed for calculating the partial density of hydrogen cyanide indoor fire. The proposed approach is based on the analytical dependence of the average volumetric partial density of HCN on the change in the volumetric average partial density of oxygen in the premises. The results of experiments on measuring the partial density of HCN in the case of combustion of modern cable products used at energy facilities are presented. The results of experimental and theoretical studies make it possible to determine the time variation of the average volumetric partial density of hydrogen cyanide in a fire in a full-scale premises using the experimental values of the specific coefficients of formation of hydrogen cyanide and oxygen absorption obtained in a small-scale experimental setup, and the change of the volumetric average partial density of oxygen obtained from the solution of the conservation law equation mass of oxygen. It is substantiated that the calculation can also be made without solving the differential equation of the law of conservation of the mass of hydrogen cyanide using only the experimental dependence of the HCN density on the change in O₂ density.

1. Introduction
According to statistics for the causes of death in fires, the main cause of death is poisoning with toxic combustion products - in more than 70% of cases [1]. According to studies [1-3], while burning, various materials can release from 50 to 100 chemical compounds, which can have a toxic effect on the human body. As a rule, from the point of view of fire danger, the main toxicant actively formed in a fire is carbon monoxide. However, the results of forensic examinations [4] and studies of the toxicological picture of fire [5-12] indicate the presence of various toxicants in the blood of the victims in toxicologically significant concentrations. In [4, 6, 10], it was noted that hydrogen cyanide in many cases is the main toxicant, death from which occurs no less frequently than from carbon monoxide.

To justify fire prevention measures preventing negative effect of toxic combustion products, mathematical modeling of the toxic gases spreading in the premises volume and their effects on the human body is used. However, in the mathematical models used in Russia, the diffusion process of only two toxic gases (carbon monoxide and hydrogen chloride) is considered, not taking into account the extremely dangerous toxicant – hydrogen cyanide. The absence of hydrogen cyanide in the
calculation methods is explained by the lack of an experimental base for the formation of HCN during combustion of various materials.

In foreign standards, there are no data for the specific coefficients of the formation of hydrogen cyanide during the combustion of modern cable products used at energy facilities.

Thus, obtaining experimental values of the specific formation coefficients of hydrogen cyanide during the combustion of various materials and developing a methodology for calculating the concentrations of this gas during fire in premises has actual scientific and practical goals.

2. The critical concentration of hydrogen cyanide in a fire
Poisoning by hydrogen cyanide in a fire is a rather complicated process. According to studies [7,11-14], poisoning by gaseous hydrogen cyanide can be occurred by inhalation and as a result of resorption through the skin. As a rule, in a fire, inhalation is considered to be the main way of poisoning, due to certain psycho-physiological factors inherent in the evacuees (rapid breathing, increased heart rate, increased lung ventilation rate). The considered toxicant has a high diffusion ability in the alveoli of the lungs and quickly enters the bloodstream.

In accordance with the regulatory document [15], the critical partial density of hydrogen cyanide in air is taken to be $\rho_{HCN, kr} = 2 \times 10^{-4}$ kg/m$^3$. However, according to studies [16], irritation of the human mucosa of the eyes is already observed at a concentration of $1,11 \times 10^{-5}$ kg/m$^3$, and a fatal outcome occurs at a concentration of $1,11 \times 10^{-4}$ kg/m$^3$ with a 30-minute exposure. The concentration presented in the regulatory document is almost 2 times higher than the lethal concentration indicated above, and almost 20 times higher the concentration at which irritation of the mucous membrane of the eyes is observed, which significantly affects the process of safe evacuation of people.

Therefore, when calculating the concentration of hydrogen cyanide, it will be more justifiably to assume the critical partial density equal to $\rho_{HCN,kr} = 1,11 \times 10^{-5}$ kg/m$^3$.

3. Mathematical model for calculating the partial density of hydrogen cyanide during a fire in the premises
The scheme of fire in a sealed volume is shown on Figure 1.

The differential equation of the law of conservation of mass of hydrogen cyanide has the form [17-19]:

$$ V \frac{d\rho_{HCN}}{d\tau} = \eta \Psi L_{HCN}, \quad (1) $$

where $V$ – volume of a sealed room, m$^3$; $\rho_{HCN}$ – average volumetric partial density of hydrogen cyanide, kg/m$^3$; $\tau$ – time, s; $\eta$ – the coefficient of completeness of combustion; $\Psi$ – gasification rate of
combustible material, kg/s; \( L_{HCN} \) – the specific coefficient of the formation of hydrogen cyanide, kg/kg.

The differential equation of the law of conservation of oxygen mass for a sealed volume has the form [17-19]:

\[
V \frac{d\rho_{O_2}}{d\tau} = -\eta \Psi L_{O_2},
\]

where \( \rho_{O_2} \) – average volumetric partial density of oxygen, kg/m\(^3\); \( L_{O_2} \) – the specific oxygen consumption coefficient, kg/kg.

The dependence of the volumetric average partial density of hydrogen cyanide on the change of the average volumetric partial density of oxygen was obtained after the joint integration of equations (1) and (2) from \( \tau = 0 \) to the considered time moment:

\[
\rho_{HCN} = \frac{(\rho_{O_2,a} - \rho_{O_2})L_{HCN}}{L_{O_2}},
\]

where \( \rho_{O_2,a} \) – volumetric partial density of oxygen in premises before the fire, kg/m\(^3\).

It can be seen from equation (3) that when calculating the concentration of hydrogen cyanide, it is necessary to use the values of oxygen density, which varies over time, as well as the values of the specific coefficient of formation of hydrogen cyanide and the coefficient of oxygen consumption.

In addition, the equation (3) does not include the size of the premises. Therefore, this equation is valid for small-scale (experimental installation) and full-sized premises.

Equation (3) allows to calculate the concentration of hydrogen cyanide during fires in full-sized premises without solving the differential equation of the \( HCN \) mass conservation law using the experimental dependence of the hydrogen cyanide density on the change of oxygen density obtained in a small-scale experimental installation.

4. Experimental installation and method of conducting experiments
The scheme of experimental installation is shown on Figure 2 [20, 21].

The heat-insulated combustion chamber 1 is connected to the exposure chamber 2 by a heat-insulated transition sleeve 3 equipped with a thermal blocking device. An electric heating radiator 4 with a sensor for continuous temperature control and a sample holder 5 on a moving basis are installed in a combustion chamber with a volume of \( 3 \times 10^3 \) m\(^3\). The side wall of the combustion chamber is equipped with a quartz glass window that allows you to observe the sample during testing, as well as slide gates 6, used to change the test conditions [20].

The exposure chamber is a cubic volume (0.5887 m\(^3\)) with a conical upper part. Sliding openings are installed on two side walls. 32 low-inertia armored thermocouples are located throughout the exposition volume for continuous temperature control in the volume. These thermocouples have a measuring range from -40 to +1100 °C with an error of no more than ± 1,5t (°C).

The sample holder is placed on electronic scales 7, which are located on a movable table and have an error of measurements not more than ± 1 mg.

Control over the density of the heat flux falling on the test sample is carried out by using a Gordon-type water-cooled sensor and a recording device with a measurement range from 0 to 100 mV. The error in measuring the heat flux density does not exceed ± 8%.
Figure 2. Scheme of the modified experimental installation: 1 – combustion chamber; 2 – transition sleeve; 3 – exposure chamber; 4 – laser module; 5 – armored thermocouples; 6 – probe for extraction of gas; 7 – ventilator; 8 – photosensitive element; 9 – electronic scale; 10 – sample holder; 11 – electric heating radiator.

The composition of the gas-air mixture in the exposure chamber is controlled using a multi-channel gas analyzer measuring the concentration of carbon monoxide with a measurement range from 0 to 1% vol. and an error of ±10%; carbon dioxide concentration with a measurement range from 0 to 5% vol. and an error of ±10%; the concentration of hydrogen cyanide with a measurement range from 0 to 0.01% vol. and an error of ±1%; oxygen concentration with a measurement range from 0 to 21% vol. and an error of ±10% vol.

The experiment starts by turning on the electric heating radiator and recording programs with subsequent verification of the response of the sensors. After this, the operating temperature of 766 °C and the density of the falling heat flux of 60 kW/m² are set in steps. When the temperature and density reach the set values, the flap of the transition sleeve and the door of the combustion chamber are opened, after which a sample of material is placed in the combustion chamber and the door is closed.

During the experiment, the mass of the test sample, the temperature in the volume of the exposure chamber, and the concentration of gases generated during combustion of the test sample (CO, CO₂, HCN, O₂) were recorded.

The specific coefficient formation of hydrogen cyanide was determined on the basis of the gasification rate of combustible material and the partial density of hydrogen cyanide in accordance with the equation:

\[ L_{\text{HCN}} = \frac{V}{\varphi} \frac{d\rho_{\text{HCN}}}{d\tau}, \]  

where \( V \) – internal volume of installation, m³.

5. Results of numerical and full-scale experiments

Samples of modern cable products used at energy facilities were taken as test samples: power cable PVC insulated flame-resisting cable “BBГнг” (in rus. orin. abbr.) and communication cable “Low smoke”.

The initial mass of the test samples was 0.103 kg and 0.073 kg, respectively. The dimensions of the experimental samples were 100 × 100 mm. The room temperature at the time of the experiments was 22 °C, pressure 735 mm. Hg. Art., humidity 34%.
Dependences of the gasification rate of combustible material on time during burning of the insulation of “ВВГнг” and “Low smoke” cables are presented on figure 3.

![Figure 3. Dependences of the gasification rate on the burning time of the cable insulation: 1, 2, 3 – experimental values for the combustion of the “ВВГнг” cable; 4, 5, 6 – experimental values for the combustion of the “Low smoke” cable.](image)

Dependences of the volumetric average partial density of hydrogen cyanide on time during combustion of the test samples are shown on Figure 4.

![Figure 4. Dependences of the volumetric average partial density of hydrogen cyanide on the burning time of the cable insulation: 1, 2, 3 – experimental values for the combustion of the “ВВГнг” cable; 4, 5, 6 - experimental values for the combustion of the “Low smoke” cable; 7 – critical density of hydrogen cyanide.](image)
The dependences of the volumetric average partial density on the change in the volumetric average density of oxygen ($\Delta \rho_{O_2} = \rho_{O_2} - \rho_{O_2}'$) during combustion of the test samples are shown on Figures 5 and 6.

Figure 5. Dependences of the volumetric average density of hydrogen cyanide on the change in the volumetric average density of oxygen during combustion of the cable insulation “Low smoke”:
   1, 2, 3 – calculation in accordance with equation (3); 4, 5, 6 – experimental values.

Figure 6. Dependences of the volumetric average density of hydrogen cyanide on the change in the volumetric average density of oxygen during combustion of the cable insulation “ВВГнг”:
   1, 2, 3 – calculation in accordance with equation (3); 4, 5, 6 – experimental values.
The obtained experimental values of the volumetric average partial density of hydrogen cyanide, shown in figure 4, indicate the achievement of a critical partial density of cyanide at the initial stages of the experiment during the combustion of all the materials considered. Therefore, it is necessary to calculate the time for blocking evacuation routes at energy facilities using hydrogen cyanide.

The analytical solution (3) of the integrated fire model using the experimental values of the specific coefficients formation of $\text{HCN}$ and oxygen absorption with an error of no more than 1% coincides with the experimental values of the partial density of hydrogen cyanide for all materials considered (Figures 5 and 6).

Thus, the presented equation (3) allows to determine the time variation of the volumetric average density of hydrogen cyanide during fire in a full-scale premise without solving the differential equation of the law of conservation of mass of hydrogen cyanide only taking into account the experimental values of $L_{\text{HCN}}$ and $L_{\text{O}_2}$ obtained in a small-scale experimental installation and changes in the volumetric average partial density of oxygen. In this case, the dependence of the partial density of oxygen is determined from the solution of differential equation (2) for a full-scale premise.

The main disadvantage of measuring the time-averaged values of $L_{\text{HCN}}$ and $L_{\text{O}_2}$ is a significant their dependence from the time of the experiment [20, 22].

For this reason, and also in the absence of data for the specific coefficients formation of $\text{HCN}$ and $\text{O}_2$ absorption, only experimental dependences can be used $\rho_{\text{HCN}} = f(\Delta \rho_{\text{O}_2})$.

7. Conclusion

The proposed experimental and theoretical approach to calculating the partial density of hydrogen cyanide during fire in a full-scale premise allows to use the experimental dependences of the average volumetric density of hydrogen cyanide depending on the changing of the average volumetric partial density of oxygen obtained in a small-scale experimental installation. In this case, there is not necessary to solve the differential equation of the law of conservation of mass of hydrogen cyanide, which includes the $L_{\text{HCN}}$ value, which substantially depends on the averaging time of experiment.

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