

COAL DUST NANOPARTICLES IN THE AMBIENCE OF MINE WORKINGS AND THEIR ENVIRONMENTAL HAZARD

Onischuk A.A.¹, Paleyev D.Yu.², Baklanov A.M.¹, Dubtsov S.N.,
Zamaschikov V.V., Korzhavin A.A.

¹Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia, onischuk@kinetics.nsc.ru,

²Institute of Coal SB RAS, Kemerovo, Russia, pal07@rambler.ru

The authors studied the mechanism of formation of nanoscaled aerosol at mechanical destruction of coal both by a shearer and in a continuous flow mill under laboratory conditions. They found that the spectrum and morphology of particles formed in a laboratory mill are in line with those of the nanoaerosol formed in a mine. The investigation of ignition of a methane-air-nanoaerosol mixture in a spherical reaction vessel with 10 liters volume showed that such a mixture becomes essentially more explosive. This made itself felt both by the growth of the maximum explosion pressure, and a significant increase in its rate of rise. The studies suggested that the nanoaerosol was originated from organic compounds contained in the coal transforming into the gaseous phase at the local heating of the coal on shearer bits.

Keywords: nanoaerosol, coal dust, nucleation, methane-air mixture, ignition, explosion, flame front.

Introduction

In recent years explosions involving coal dust have begun to turn into disasters with a large number of human losses and bad economic effects. The main danger is the coal dust deposited on the walls of mine openings, turned by a shock wave in suspension and ignited by the flame front following the shock wave. Another danger is methane in the mine openings [1]. Despite the taken measures in the coal-producing countries, the explosive risk of coal dust in coal mines is not fully eliminated. The introduction of high-tech coal extraction leads to rise of the risk of dust explosion due to a sharp increase in its highly dispersed fractions (including nanoscaled ones), transported by air flow over long distances, followed by its deposition on the walls of mine workings. However, the coal dust control apparatus used in mines only registers particles of 200 microns and greater in size. Therefore, investigations of explosive characteristics of nanoscaled particles of coal dust have not been carried out. It is this fact that made for poor state of knowledge on physical and chemical processes of coal aerosol formation and its effect on the ignition and combustion of dust-methane-air mixtures.

Recent studies have shown that the level of explosive risk of mine workings should not be only determined taking into account the concentration of coal particles, originated in a mining combine operation area but also their degree of dispersion and chemical composition. A virgin coal seam rich in methane is a “coal-methane-natural moisture” balanced system. When strain-stress state of the coal bed changes by technogenic burden, irreversible structural variations take place in it. These changes occur at the level of microstructures containing methane molecules. It was found that when a shearer operates, not only mechanical, but also a complex mechanic and chemical processes take place [2]. It comprises crushing a solid body, its pyrolysis, the escape of volatile organic compounds in the gaseous phase and their condensation to form a large number of aerosol particles less than one micron in size.

This article reviews the degree of dispersion of coal dust forming at mechanochemical coal crushing at a mine in Kuzbass. Main results of laboratory studies of the mechanism of organic nanoaerosol formation by mechanical destruction of coal and the impact of the aerosol on the risk of explosion in coal mines.

1. Experiment technique

To study the nanoscale component of the coal aerosol developed by the Institute of Chemical Kinetics and Combustion SB RAS, a portable aerosol diffusion spectrometer (ADS) (Figure 1) was used. It made possible to measure the nanoaerosol concentration within the range of 101-109 particles/cm³ and the size spectra within the range of 3-200 nm.



Fig.1. The outside appearance of the aerosol diffusion spectrometer

The device control, processing, displaying and storing measurement data are performed using the PC program. Measurement cycles can be performed automatically. The device consists of three main functional blocks: a diffusion battery (to separate an aerosol by size due to the diffusion mobility), the condensing coagulant of aerosol particles and an optical particle counter.

The morphology of the nanoscaled dust coal component was studied by transmission electron microscope (TEM) JEM 100 SX. Sample collection was carried out in the longwall face of Erunakovskaya VIII mine using a device, shown schematically in Figure 2. The device was a quartz tube (with 1.0 cm internal diameter), inflowing the air stream in the longwall face when a shearer was operating. The volumetric flow rate through the tube was 1 l/min. The airflow containing the nanoaerosol passed over a special copper electron-microscopic grid (with 50 microns step) coated by a polyvinylformal film (transparent to the electron beam in the microscope). The outside tube area containing the grid was cooled by liquid nitrogen. Thus, in the grid area there was a radially directed temperature gradient, which caused the deposition process of aerosol particles on the grid (a thermophoresis phenomenon).

To carry out laboratory experiments on the dispersion of coal and study of the role of nanoscaled aerosol component in the process of combustion of a coal-methane-air mixture, a dust generator (a mill) with 500 cm³ working volume was developed. The operation principle of the generator was based on mechanical coal crushing by rotating knives in a chamber through which the filtered air or a methane-air mixture at a volume flow rate of 1/min was blown. The radius of rotation of the crushing blade edge was 90 mm, the rotation speed was 3000 rev/min.

To compare the chemical composition of the initial coal and the nanoaerosol formed at its mechanical crushing, a chromatographic-mass-spectrometric method was used.

To investigate the effect of the coal aerosol on the gas mixtures combustion process, the experimenters used a spherical reaction vessel equipped with optical windows (a bomb). The vessel with 10 l volume was made at the Institute of Chemical Kinetics and Combustion SB RAS. To register the combustion front at different moments of time the schlieren method was used.

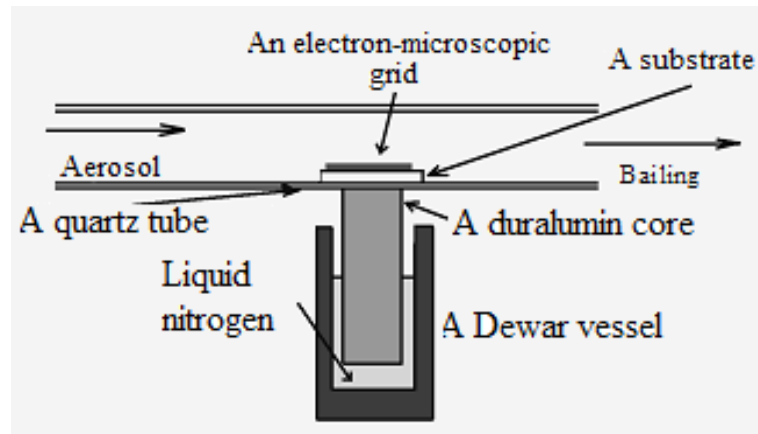


Fig. 2. The device for thermophoretic selection of aerosol samples

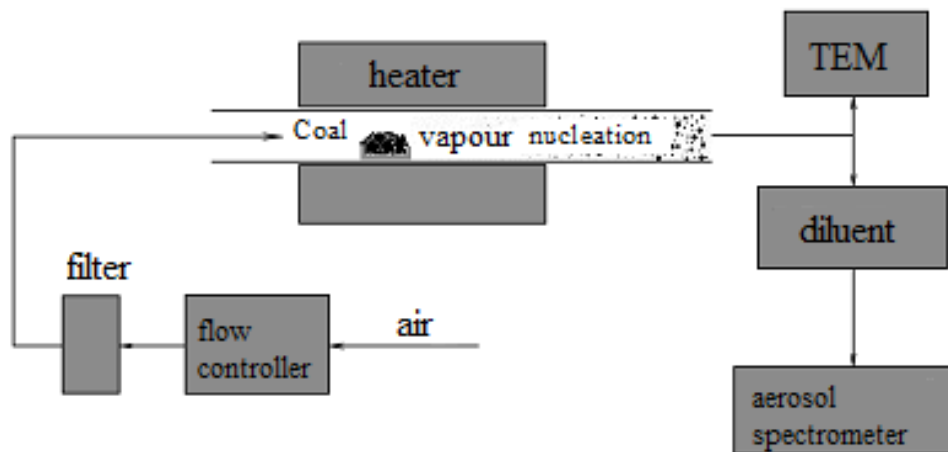


Fig.3. The layout of the experimental setup for the production of aerosol from coal by volatility process

The study of the formation of aerosol during nucleation of supersaturated vapour of organic coal components was carried out at a special flow-through thermal condensation plant (Figure 3). The plant was a quartz tube with 0.9 cm inner diameter. Outside it there was a heater, making possible to vary the temperature inside the tube within the range of 300-1000 C°. In the hot area inside the tube a quartz spoon with coal (from Erunakovsky deposit) was placed. At the input of the tube a filtered air stream was blown at 1 l/min volume flow rate. When passing along the hot area the stream was saturated with organic components vapour. The farther the distance from the hot area the lower the temperature of the stream; the vapour became supersaturated, and homogeneous nucleation process started. The output aerosol concentration and its size were recorded using an aerosol spectrometer. Besides, using a thermoprecipitator a selection was carried out on a transmission electron microscope. The investigators measured the mass concentration and the rate of accumulation of aerosol mass at an aerosol filter installed on the output of the thermal condensation plant. The chemical composition of the aerosol formed at heating coal, was determined using the chromatographic-mass-spectrometric method.

The investigation of the effect of thermal condensation aerosol on the process of combustion of the methane-air mixture was carried out in a 10 liters-"bomb" in the same way as it was performed with the aerosol formed in the mill.

2. Results and discussion

Figure 4 shows a typical spectrum of the nanoaerosol measured with a spectrometer ADS in a transfer gallery of "November 7" mine (coal of rank "G", 33.5% volatile content [3]). The total count concentration of particles was 10^5 particles/cm³; and the particle sizes of 90% of the total particles were less than 200 nm. It is significant that the typical aerosol formed by crushing solid bodies had size spectra within the range of one to several tens of microns with a distribution maximum about 10 microns [4].

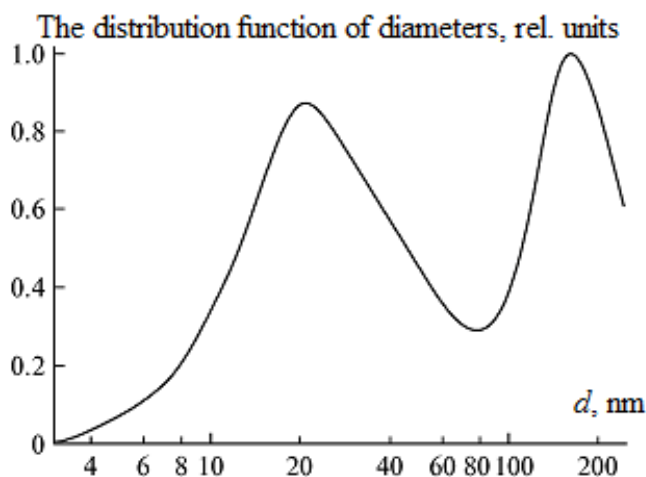


Fig.4. The size spectrum of the nanoaerosol measured in the gallery of "November 7" mine

As seen in Figure 4, the measured size spectrum shows peaks with maxima at 20 and 150 nm. Such aerosol may only be formed during nucleation process from gaseous phase [5]. Moreover, the measured concentration is significantly higher (at least by an order of magnitude), than the typical concentration of the aerosol formed when crushing solid substances. Such a high concentration may only be obtained when aerosol forms from the gaseous phase (pyrolysis of hydrocarbons, nucleation from a supersaturated vapour) [4, 5].

Thus, we can assume that the original substances of the aerosol, whose spectrum is shown in Figure 4 are the coal organic compounds, transforming into the gaseous phase at local heating of the coal in the course of operation of a shearer. Note that the peak in the vicinity of 20 nm represents an initial aerosol formed during the homogeneous nucleation process; the peak in the range of 150 nm is due to the coagulation of the original aerosol. The presence of the coagulation aerosol indicates that the local concentration of the initial aerosol was quite high – not less than 10^8 particles/cm³ (coagulation limit), since at lower concentrations coagulation is not possible during real time [6].

To study the morphology of the nanoparticles formed in the mine, selections of samples on the electron-microscopic grids were carried out to analyze them at the transmission electron microscope. Sample collection was carried out in the longwall face of «Erunakovskaya VII» mine (coal of rank "GZh", 37% volatile content) when a shearer was operating. The analysis of the images showed that the nanoaerosol was formed in the form of individual particles with 10-50 nm diameters as well as in the form of aggregates consisting of primary particles. An average aggregate consisted of 10 primary particles. Formation of aggregates indicated a high rate of coagulation process in the area of aerosol formation when the local concentration of aerosol was at least 10^8 particles/cm³ in operating area of the combine. Thus, the electron microscopic analysis confirmed the assumption based on ADS measurements that at mechanical destruction of coal a nanoaerosol is

formed which consists of particles of two types – single particles and aggregates formed by coagulation of individual particles.

To test the assumption that the fraction of nanoscale aerosol was formed as a result of mechanical destruction of coal, laboratory studies of the formation process of coal aerosol in the mill were carried out. The observed range of particle size distribution is in qualitative agreement with the spectrum measured at the mine "November 7". In both cases, the main contribution to the total number of particles was made by nanoscale nanoaerosol fraction (80-90%), and the typical diameter of the nanoscale mode was about 20 nm. By changing the temperature at the knife edge of the crushing mill and the time of its operation it was shown that the reason for the formation of nanoaerosol was the evaporation of the organic coal components to form the supersaturated vapour with its subsequent nucleation.

To compare the chemical composition of the initial coal and the nanoaerosol formed by mechanical destruction of the coal in the mill, the experimenters made a chromatographic-mass-spectrometric analysis of coal extract and the solution obtained from aerosol particles selected on a filter. The analysis showed that the aerosol and coal spectra were similar. The most intense were alkane lines. Besides the alkanes, the aerosol particles included polyaromatic molecular entities containing 3 or 4 condensed aromatic rings; those were alkyl derivatives of phenanthrene, anthracene, pyrene. In the aerosol spectrum, unlike coal spectrum there were no light alkanes C10-C13. It was apparently due to the fact that they were discharged during the heating process earlier than other alkanes, before the aerosol began to form in large amounts. The composition of aromatic compounds in the aerosol and in the starting coal was nearly the same. The total ratio of alkanes and aromatic compounds in both spectra was about 1:1. Thus, we can assume that the origin of the aerosol were organic components contained in the coal, and transformed into the gaseous phase at local heating of the coal during the operating process of a shearer.

Since the mass of the organic components vapour released from the coal could be quite large, to determine the effect of the resulting nanoaerosol on the process of ignition and combustion of methane-air mixtures, investigations in a 10-liter volume bomb with optical windows were conducted. Figure 5a shows that presence of the aerosol in the mixture increases the rate of pressure rise and the value of the maximum pressure.

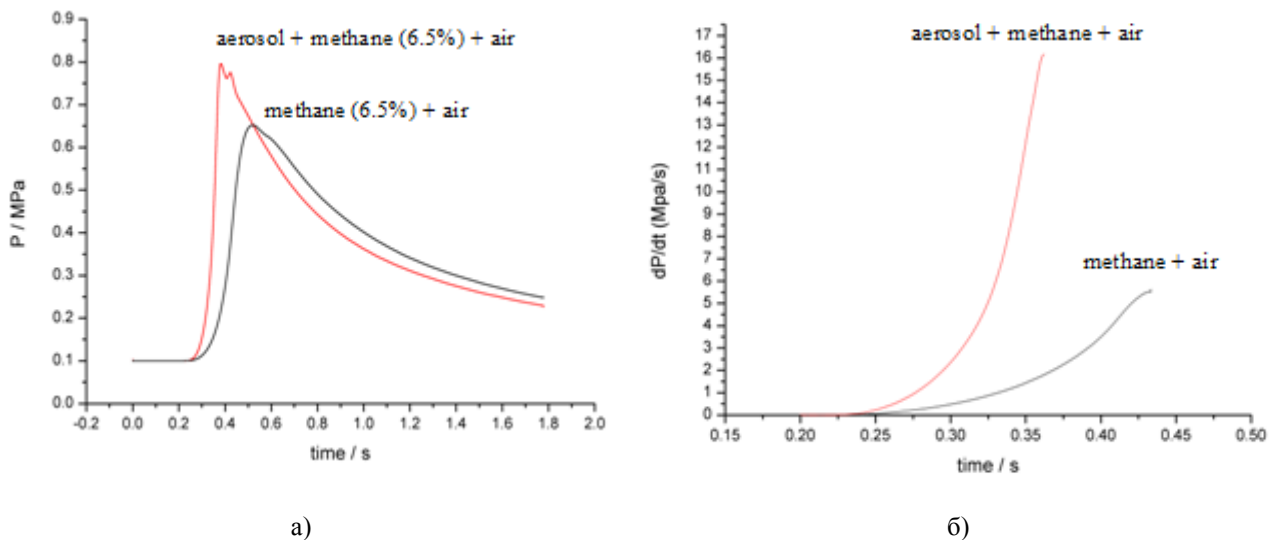


Fig.5. Dependence of the pressure in the bomb (a) and the pressure rise rate in the bomb (b) on the time at the ignition of a methane-air mixture and of thermal condensation aerosol-methane-air mixture

Thus, in the case of a pure mixture the maximum pressure was 0.65 MPa, and in the case of an aerosol mixture it was 0.8 MPa. Such increase in the maximum pressure corresponded to the increase in the fuel content in the aerosol by about 20% as compared with the pure compound. Figure 5b shows the dependence of the pressure rise rate in the bomb on the time, at ignition of a pure mixture and the mixture with the aerosol. It is seen that the addition of the aerosol increases the rate of pressure rise by about an order of magnitude.

Addition of a large sized coal aerosol to the methane-air mixture did not change the pattern of the ignition. The flame images obtained by schlieren method, showed that the presence of nanoaerosol lead to a change of the flame structure, making it more cellulous (Figure 6).

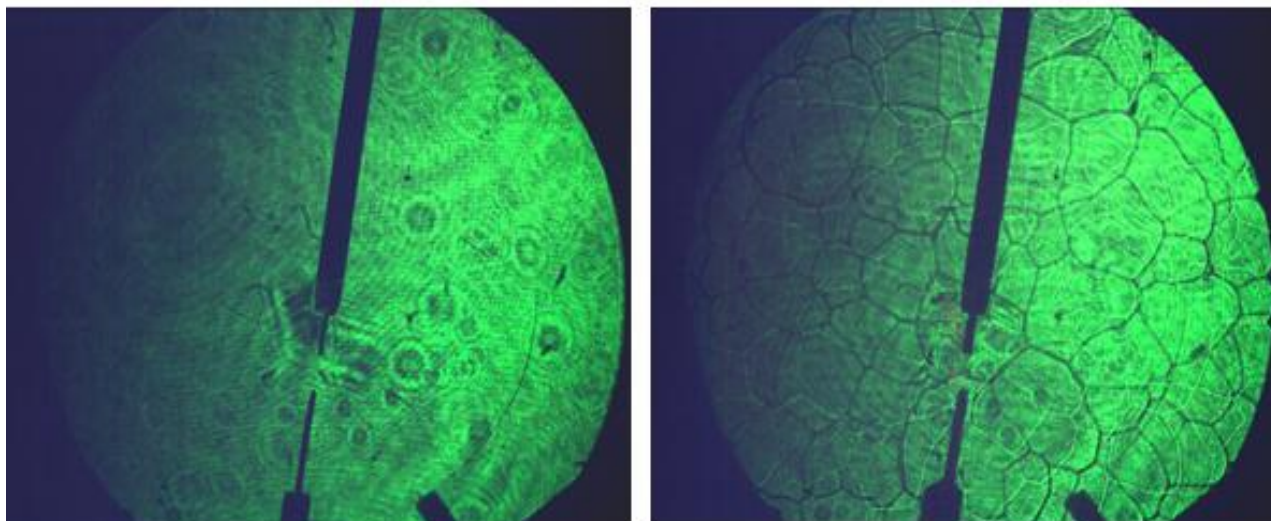


Fig.6. The flame structure captured using a rapid video shooting: on the left there is a pure mixture; on the right there is a mixture with the nanoaerosol

In order that the effect of the nanoaerosol on the combustion of the methane-air mixture was significant the mass concentration of the organic aerosol should be comparable with the mass concentration of methane in the mixture. The ordinary concentration of the nanoparticles, obtained in the mine and in the laboratory experiments was 10^{-5} - 10^{-6} cm^{-3} and their average size was 20-100 nm. In order to estimate the upper limit of the mass concentration of those particles, if we take 10^{-6} cm^{-3} concentration, 100 nm diameter and 1 g/cm^3 substance density in the particles, then the mass concentration of the particles will be $5 \cdot 10^{-4}$ g/m^3 . In this case the mass concentration of methane in the mixture 6.5% CH_4 +air will be 42 g/m^3 . It is obvious that we cannot talk about the possible impact of aerosol on the combustion process at such a low mass concentration of nanoparticles. The cause of the observed effect of the nanoaerosol on the combustion is that in the process of coal crushing besides the aerosol there formed a large sized fraction. It was low-inactive in the combustion process, but on its surface a large amount of organic vapour and nanoparticles deposited.

Taking into consideration that the constant the of coagulation of micron particles with nanometer particles is by five orders of magnitude greater than the constant of coagulation of nanoparticles of the same size, in the aerosol formation area the bulk of nanoparticles formed during the nucleation from the supersaturated vapour, will not be in the gaseous phase but on the surface of large particles formed at crushing coal. During ignition the organic compounds vaporize from the surface of micron and submicron particles into the gaseous phase, resulting in a mass concentration of organic compounds in the mixture comparable to that of the methane that causes an increase in the maximum pressure and the rate of its rise.

Conclusion

The study of concentration, dispersivity and morphology of the aerosol formed in Kuzbass mines, as well as laboratory studies of aerosol formation at mechanical action on the coal and the heating of the latter allow the following assumptions. Mechanical destruction of coal by operating shearer or in a laboratory mill cause local heating of the coal in the course of which large amounts of organic compounds in the gaseous phase are discharged from the coal. After the temperature of the generated vapour becomes equal to the ambient temperature it becomes supersaturated. The high supersaturation of the vapour leads to the formation of organic nanoaerosol as a result of homogeneous nucleation.

Moreover, there takes place the vapour condensation and deposition of the nanoparticles on the surface of large micron and submicron particles formed directly during coal crushing. The high concentration of the nanoaerosol in the aerosol-formation area (not less than $10^8 \text{ cm}^{-3} \text{ c}^{-1}$) indicates a large amount of organic compounds discharged from the coal into the gaseous phase, which can be compared with methane content in an explosive methane-air mixture. The investigation of ignition of dust and methane-air mixture suggests that the addition of coal aerosol to a methane-air mixture significantly increases the rate of pressure rise at ignition and the value of the maximum pressure. The presence of the aerosol in the methane-air medium can significantly shift the ignition threshold.

It is significant that the mass concentration of the organic nanoaerosol itself in the air at mechanical coal crushing is relatively small. However, the nanoaerosol concentration of 10^5 cm^{-3} can indicate the presence of organic compounds deposited on the surface of the large dispersed aerosol in an amount sufficient to appreciably affect the methane-air mixture ignition. In other words, the nanoaerosol can serve as an indicator of explosive situation. However, this aerosol is not registered by modern methods of explosion safety control in mines. The only way of monitoring organic aerosol is using flameproof means of measuring the concentration and size of the nanoaerosol, which are not available in the coal mines to date.

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