On the explosiveness of suspensions of sulfide ore dust in air in shock waves

A V Pinaev* and P A Pinaev

Lavrentiev Institute of Hydrodynamics SB RAS, Lavrentiev av. 15, Novosibirsk, 630090, Russia

*E-mail: avpin@ngs.ru

Abstract. The explosiveness of suspensions of several powders of sulfide ores with a particle size of 1-5 µm in air is experimentally investigated. The air suspension is affected by high-temperature gas detonation products and shock waves with a temperature behind the front exceeding the pyrrhotite ignition temperature. Data on the changes in the content of chemical elements and compounds in ore powders after their exposure to shock waves are obtained by means of X-ray diagnostics. The effect of the air suspension on the parameters of incident and reflected shock waves is determined.

1. Introduction

Among air suspensions of coal, sulfuric, and sulfide dusts, sulfide dust is the least explosive one [1]. Iron sulfide in natural deposits occurs more often in the form of pyrite FeS₂. It is usually assumed that the lower and upper concentration limits of the sulfide dust explosiveness are 80 and 1800 g m⁻³, and the ignition temperature is 430–460°C (≈700–730 K). In mines, suspended dust with a particle size \( l_s \leq 75–100 \) µm usually has a mean bulk density \( \rho \leq 1-5 \) g m⁻³. A denser suspension of sulfide dust is formed near the site of high explosive initiation. When a compression wave propagates through the mine channel, additional rise of dust from the channel walls occurs and a dust cloud is formed. Dust ignition can be triggered by a thermal or mechanical pulse as a result of interaction of a shock wave (SW) and scattering high-temperature products of gas mixture or explosive detonation [2].

When sulfide dust ignites in the process of burning of the surface layer of particles, poisonous sulfur dioxide SO₂ is formed; its maximum allowable concentration in air is \( 3.8 \times 10^{-4} \)%. As the particle size decreases, the specific surface area increases, and sulfide dust explosion becomes more probable. Fine dust with \( l_s < 10-100 \) µm is the most explosive agent. To determine the degree of the response and the possibility of spontaneous combustion of ore powders at elevated temperatures, these mixtures are subjected to slow quasi-stationary heating, and a thermogravimetric study of oxidation of ore particles in special devices is performed [3-5].

The ignition and explosiveness of sulfide ores subjected to shock-wave heating have not been adequately studied. This work is a continuation of the research [6]. The purpose of this work is to propose an experimental method for studying the possibility of an explosion of sulfide ores exposed to shock and blast waves and to determine the effect of the air suspension density on the parameters of incident and reflected shock waves.
2. Ore samples

After grinding, ore sample Nos. 1–4 consisted mainly of loose lumps with sizes smaller than 100 µm. The lumps were easily dispersed into fine solid particles with $l_s \approx 1–10$ µm (mean size $l_s \approx 5$ µm) for ore No. 1 and $l_s \approx 0.5-3$ µm (mean size $l_s \approx 1$ µm) for other ores. The samples of natural ore Nos. 1–4 with a bulk density of 1.43–0.99 g/cm$^3$ were examined using a MERLIN Compact Zeiss electronic scanning microscope. Ore No. 1 contained the largest amount of S and Fe (35 and 30% of atoms, respectively); the contents of S and Fe atoms in ore Nos. 2–4 were smaller than 3.5 and 2.5%, respectively.

The atomic compositions of two powders of sulfide ores obtained by averaging the results of six measurements of the spectrum on an electron microscope are shown in Tables 1 and 2.

Table 1. Average percentage of the main chemical elements in ore No. 1.

| Chemical element | O    | Al   | Si   | S    | Fe   | Ni   | Cu   |
|------------------|------|------|------|------|------|------|------|
| Wt.%             | 12.19| 0.74 | 2.54 | 31.94| 46.70| 1.52 | 4.07 |
| At.%             | 26.60| 0.97 | 3.18 | 35.39| 30.00| 0.97 | 2.29 |

Table 2. Average percentage of the main chemical elements in ore No. 2.

| Chemical element | O    | Na   | Mg   | Al   | Si   | S    | K    | Ca   | Fe   | Ni   | Cu   |
|------------------|------|------|------|------|------|------|------|------|------|------|------|
| Wt.%             | 48.07| 2.13 | 0.44 | 4.95 | 23.21| 5.22 | 1.99 | 2.83 | 6.33 | 0.62 | 4.17 |
| At.%             | 65.27| 2.02 | 0.39 | 3.99 | 18.00| 3.54 | 1.11 | 1.54 | 2.47 | 0.23 | 1.43 |

The mass percentage composition of chemical compounds in sulfide ore powders was determined on a D8-Advance X-ray diffractometer, a device for measuring the intensity and direction of X-rays diffracted on crystals. The results of these measurements for ore powders are reported in Tables 3 and 4.

Table 3. Chemical compounds in ore No. 1.

| Compound          | Chemical compound formula | Wt.%  |
|-------------------|---------------------------|-------|
| Pyrrhotite-3T     | Fe$_7$S$_8$               | 61.56 |
| Chalcopyrite      | CuFeS$_2$                 | 10.76 |
| Pentlandite       | (FeNi)$_3$S$_8$           | 10.50 |
| Magnetite         | Fe$_3$O$_4$               | 8.00  |
| Quartz            | SiO$_2$                   | 7.22  |
| Troilite          | FeS                        | 1.96  |

Table 4. Chemical compounds in ore No. 2.

| Compound          | Chemical compound formula | Wt.%  |
|-------------------|---------------------------|-------|
| Pyrrhotite-3T     | Fe$_7$S$_8$               | 4.45  |
| Chalcopyrite      | CuFeS$_2$                 | 10.09 |
| Quartz            | SiO$_2$                   | 58.41 |
| Albite            | NaAlSi$_3$O$_8$           | 27.06 |

Reactions with substances capable of igniting and burning release pyrrhotite Fe$_7$S$_8$. Its amount in ore No. 1 is approximately 61.6 wt.%. For ore Nos. 3 and 4, the measurement results are close to the data in Table 4 and are characterized by a low content of pyrrhotite (<5 wt.%).
3. Thermogravimetric analysis of ore oxidation
To study the tendency of ores to oxidation under quasi-stationary heating from 20 to 1000°C, we measured the change in their wt.% (thermogravimetric analysis, TGA), the rate of change in wt.% in ores (differential thermal analysis, DTA), and the heat released from the ores (differential thermogravimetry, DTG). The measurement error did not exceed 5%. When ore Nos. 1–4 were heated from 20 to 450°C, no changes in their mass was detected (no heating and burning were observed).

When heated from 450 to 1000°C, ore No. 1 loses approximately 12% of its mass, and ore Nos. 2–4 lose approximately 2–4 wt.%. For ore No. 1, the contents of S and Fe and the total energy release are significantly higher than for ore sample Nos. 2–4. Therefore, ore No. 1 is the most interesting substance in terms of dynamic explosiveness.

4. Investigation of the explosiveness of sulfide ores in shock waves. Experimental setup, research methodology
The dynamic explosiveness of sulfide ores was investigated in a vertical shock tube with a length of 6.75 m and a diameter \( d=70 \) mm. Two initiating sections (IS) were separated from the test section by diaphragms. Before the experiment, the initiating sections were depressurized and filled with a \( \text{C}_2\text{H}_2+2.5\text{O}_2 \) mixture to an initial pressure \( p_{0i}=0.3–0.5 \) MPa. The mixture in the IS was initiated by a spark from a high-voltage source. The diaphragm was ruptured, and an SW with a Mach number in the interval \( M_{12}=2.9–4.1 \) (based on the data obtained by sensors S1 and S2) propagated in the tube. The products of gas detonation from the IS with a temperature of about 4000 K, which moved more slowly than the SW front, served as an additional source of sulfide dust heating.

Before the experiment, the test section of the shock tube was filled with air under normal conditions (sound speed \( c=343 \) m s\(^{-1} \), \( p_0=0.1 \) MPa). Then the air-dust mixture was uniformly fed from a cylinder through a gearbox, a container with the ore powder, and a dust generator at the top of the shock tube, forcing the air to leave through a bottom valve. When the shock tube was filled with the powder suspension, the valve was closed, and the gas mixture in the IS was initiated.

In the experiments, the density \( \rho \) in the shock tube was varied from 40 to 920 g m\(^{-3} \). The pressure and velocity profiles of the compression waves along the shock tube were recorded by using piezoelectric sensors S1–S9. Sensors S2 and S4 included optical fibers located close to the piezocrystals for simultaneous recording of pressure and luminescence. The optical inputs of photomultipliers PMT1, PMT2, and PMT3 were placed opposite sensors S2, S4, and S8, respectively.

The pressure and luminescence were recorded by three 4-beam Tektronix TDS2014 oscilloscopes. The signals from sensors S1–S9 were first fed to a source repeating amplifier with an input resistance \( R=1 \) GΩ and a block of capacitors. The time constant of the piezoelectric transducer was \( C=RC_0=0.1-1 \) s, where \( C_0 \) is the total electrical capacitance.

5. Results of experiments on dynamic initiation of air suspensions
The signal profiles on the oscillograms correspond to the numbers of the piezoelectric sensors and photomultipliers. The SW velocities in regions between the sensors with the numbers \( m \) and \( n \) were determined with an error of 1–2% within short time intervals. The error of pressure measurement did not exceed 5%. In the dust-free experiment with \( p_{0i}=0.3 \) MPa (figure 1), the gas detonation products from the IS moved behind the SW front with a delay \( \Delta t=0.25 \) ms at the S2 sensor location (see the PMT1 signal) and \( \Delta t=1.6 \) ms at the S4 sensor location (see the PMT2 signal).

At \( p_{0i}=0.4 \) MPa, \( \Delta t=0.11-0.14 \) ms, \( \Delta t=0.93-0.95 \) ms, PMT3 did not detect the flame at the bottom of the tube, similar to the case with \( p_{0i}=0.3 \) MPa. For the greatest value \( p_{0i}=0.5 \) MPa, \( D_{12}=1390 \) m s\(^{-1} \), \( \Delta p_{12}=1.93 \) MPa, \( T_{12}=1173 \) K (900°C), \( \Delta t=0.09 \) ms, and \( \Delta t=0.29 \) ms. It follows from the measurements that \( \Delta t_1 \) and \( \Delta t_2 \) decrease approximately linearly as functions of \( p_{0i} \). We had \( \Delta t_0=0 \) μs at the beginning of the tube \( (L=0) \) and \( \Delta t_1<\Delta t_2 \) further downstream, which means that the distance between the flame and the SW front increases nonlinearly with increasing \( L \).

In air suspensions, the ignition of dust Nos. 1–4 behind the shock front was not observed, and the shock waves gradually slowed down. The SW velocity along the tube for the same values of \( p_{0i} \) was...
lower than the SW velocity in the dust-free flow approximately by 40–60 m s⁻¹. Suspensions of ore No. 1 exposed to hot detonation products of the gas mixture from the IS did not explode.

Figure 1. Shock wave in the dust-free air flow, C₂H₂+2.5O₂ mixture in the IS, \( p_{0i} = 0.3 \) MPa; \( D_{12} = 1069 \) m s⁻¹, \( \Delta p_{12} = p_{12} - p_0 = 1.0 \) MPa, temperature \( T_{12} = 815 \) K, \( D_{23} = 1040, D_{45} = 1003, D_{56} = 923, D_{78} = 803, D_{89} = 795 \) m s⁻¹.

Glowing regions in the dust cloud were detected in reflected waves by PMT3 at \( M_{12} \geq 3.4 \) (figure 2). This luminescence is associated with the presence of chemical reactions whose energy release is insufficient for generation of additional compression waves and self-sustaining detonation regimes.

Figure 2. SW in the air suspension of ore No. 1, \( \rho = 760 \) g m⁻³, C₂H₂+2.5O₂ mixture in the IS, \( p_{0i} = 0.4 \) MPa; \( D_{12} = 1181, D_{23} = 1150, D_{45} = 1084, D_{56} = 1071, D_{78} = 926, D_{89} = 901 \) m s⁻¹.

In the experiment illustrated in figure 2, \( M_{12} = 3.44, \Delta p_{12} = 1.28 \) MPa, and \( T_{12} = 933 \) K. Extrapolation of the SW velocity yields the value \( D_{f0} = 820 \) m s⁻¹ close to the tube end (figure 3). The parameters of the reflected wave corresponding to this velocity are \( D_{3} = 350 \) m s⁻¹, \( \Delta p_{3} = 2.58 \) MPa, and
Therefore, the temperature in the reflected wave is approximately the same as that of the incident wave at the top of the tube, and the pressure is twice as high. These factors contribute to an increase in heat generation of ore No. 1 in the reflected wave and the emergence of luminescence in the lower part of the tube. A necessary condition for ignition of the ore suspension in air is the temperature behind the SW higher than the pyrrhotite ignition temperature (≈660°C).

Figure 3. Velocities of shock waves in the air flow (1, 1') and in the air suspension of ore No. 1 (2, 2'), ρ=760 g m⁻³; curves 1 and 2 refer to the incident SW; curves 1' and 2' refer to the reflected SW; $p_0=0.4$ MPa.

At a fixed pressure $p_0=0.4$ MPa, the velocities $D_{78}$ and $D_{89}$ decrease as the dust density $\rho$ increases up to 650 g m⁻³ due to the loss of momentum. At $\rho=650$ g m⁻³, $D_{78}$ and $D_{89}$ have the minimum values (=825 m s⁻¹). Then, due to the energy release in the air suspension, the velocities increase to 900–950 m s⁻¹ at $\rho=770$ g m⁻³. Then $D_{78}$ and $D_{89}$ again decrease to 870 m s⁻¹ at $\rho=920$ g m⁻³. A similar dependence $D(\rho)$ is also observed for reflected shock waves.

Table 5 shows the structural analysis results for ore powder No. 1 before the experiment and for three samples of the ore after the experiment. It is seen that the amount of pyrrhotite decreases, and the main agents reacting with oxygen are Fe and S. The most intense burnout of pyrrhotite (≈27 wt.%) and also sulfur in ore No. 1 is observed in the upper layer of the ore (Table 5, two extreme right columns). In all experiments, iron sulfide FeS (<2 wt.%) burns down completely.

Interaction of ore Nos. 2–4 with air is much weaker than that of ore No. 1. The luminescence in reflected waves is rather weak. The results of the X-ray analysis show that the fraction of reacted

| Compound      | Chemical formula | Wt.% before the experiment | Wt.% after the experiment | Change in wt.% | Wt.% after the experiment | Change in wt.% | Wt.% after the experiment | Change in wt.% |
|---------------|------------------|----------------------------|---------------------------|----------------|---------------------------|----------------|---------------------------|----------------|
| Pyrrhotite    | Fe₇S₈            | 61.56                     | 49.50                     | −12.06         | 46.18                     | −15.38         | 46.18                     | −15.38         |
| Chalcopyrite  | CuFeS₂           | 10.76                     | 6.24                      | −4.52          | 5.46                      | −5.30          | 4.96                      | −5.30          |
| Pentlandite   | (FeNi)(S₈)      | 10.50                     | 4.82                      | −5.68          | 4.13                      | −6.37          | 0.00                      | −10.50         |
| Magnetite     | Fe₃O₄           | 8.00                      | 32.33                     | +24.33         | 38.63                     | +30.63         | 57.99                     | +49.99         |
| Quartz        | SiO₂            | 7.22                      | 7.10                      | −0.12          | 5.60                      | −1.62          | 2.37                      | −4.85          |
| Troilite      | FeS             | 1.96                      | 0.00                      | −1.96          | 0.00                      | −1.96          | 0.00                      | −1.96          |
sulfur is small. The emergence of Fe$_3$O$_4$ is explained by oxidation of iron released after decreasing the mass fractions of Fe$_7$S$_8$ and CuFeS$_2$.

The thermogravimetric analysis suggests that oxidation reactions on particles of ore Nos. 1-4 proceed regardless of the presence or absence of luminescence if the temperature behind the SW is higher than 450°C.

The sulfur fraction is approximately 32 wt.% in the presented samples of ore No. 1 and approximately six times lower in the remaining ores. The studied ore samples cannot be classified as dangerous from the explosion viewpoint because their sulfur content is smaller than 35% [1].

**Conclusions**

During thermogravimetric oxidation of samples of sulfide ores, their mass begins to decrease at a temperature of 450°C. In the range of 450–1000°C, the ore mass decreases by 2-4 wt.% (ore Nos. 2-4) and by 12 wt.% (ore No. 1). This traditional technique is not enough to determine the explosiveness of these air suspensions.

An experimental technique was proposed for studying the dynamic explosiveness of air suspensions of finely dispersed sulphide ores exposed to shock and blast waves. The change in the elemental and chemical composition of ores in high-velocity flows is determined.

During the dynamic heating of ore suspensions in air by shock waves with Mach numbers $M_{12}=2.9$–4.1, SW attenuation is observed, and self-sustaining detonation regimes are not detected. Short-term luminescence of air suspensions without the formation of additional compression waves in reflected shock waves is observed at $M_{12} \geq 3.4$.

When air suspensions of ore particles are exposed to shock waves and gas detonation products, the amount of pyrrhotite decreases, and the main agents reacting with atmospheric oxygen are S and Fe. Oxidation reactions on the surface of ore particles occur regardless of the presence or absence of luminescence if the temperature behind the SW is higher than 450°C. The low reactivity to explosive ignition of the studied ores is explained by the high temperature (≈660°C) of pyrrhotite ignition, as well as by proceeding of chemical reactions in a narrow surface layer of particles.

Interaction of ore Nos. 2–4 with air behind the shock waves is significantly weaker than that of ore No. 1. All investigated samples of ores are not dangerous from the viewpoint of their explosion. Suspensions of ore particles with the size more than 10-100 µm are expected to be more chemically inert than the suspensions of fine particles considered in the present study.

**References**

[1] PB-03-553-03 2003 *Unified safety rules for the development of ore, non-metallic and gravel deposits of minerals by the underground mining method* Approved by the Russian Federation Gosgortekhnadzor Decree of May 13 2003 N30

[2] Weiss Eric S, Cashdollar Kenneth L, Sapko Michael J, and Bazala Eugene M 1995 *Report of Investigations* 9632 1–55

[3] Yang Fu-qiang, Chao Wu, Li Zi-jun 2014 *J. Central South University* 21 (2) 715–9

[4] Wei Pan, Chao Wu, Zi-jun Li, Zhi-wei Wu 2019 *In book: Proc. of the 11th Int. Mine Ventilation Congress* 991–1002

[5] Özdeniz A Hadi, Kelebek S 2013 *Int. J. of Mining Sci. and Technol.* 23 (3) 381–6

[6] Pinayev A V, Pinayev P A, Vasil’yev A A, Yeremenko A A, Pruuel E R and Shaposhnik Yu N 2018 *Vestnik Nauchnogo tsentra po bezopasnosti rabot v ugolnoi promyshlennosti - Herald of Safety in Mining Industry*Scientific Center. Industrial Safety Kemerovo ISSN 2072-6554 2 45–51