SULPHIDE ORE DUST EXPLOSION RESEARCH IN CANADA

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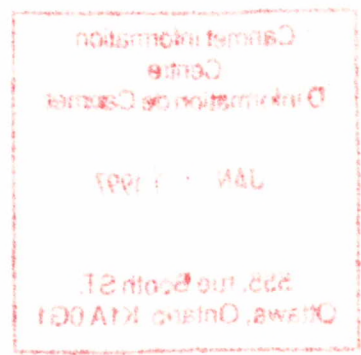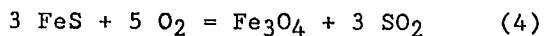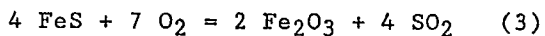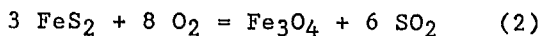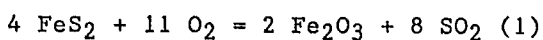Canada Centre for Mineral and Energy Technology,
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ABSTRACT

In recent years, the Canadian hard-rock mining industry has become aware of the need to eliminate sulphide ore dust explosions, which are initiated by blasting operations. The major source of injuries comes not from the explosions themselves but from the toxic sulphur dioxide gas produced. The mining industry, other related industries, academia and governments have started a collaborative program to carry out research on the causes and possible control methods of these sulphide dust explosions. Equipment is being developed to measure the quantity of sulphide dust produced during a blast and the quantity of sulphur dioxide produced by the explosion. Laboratory studies have determined some of the relationships between the mineralogy of ores and their explosibilities. The amount of sulphur dioxide produced during the laboratory tests was measured by infrared spectrometry.

INTRODUCTION

Sulphide ore dust explosions are caused by the explosive used for breaking rock in base metal mines igniting a cloud of metal sulphide dust. Both pyrite (FeS_2) and pyrrhotite (FeS) can react to form hematite (Fe_2O_3) or magnetite (Fe_3O_4), by the following reactions:

$$4\ FeS_2 + 11\ O_2 = 2\ Fe_2O_3 + 8\ SO_2 \quad (1)$$

$$3\ FeS_2 + 8\ O_2 = Fe_3O_4 + 6\ SO_2 \quad (2)$$

$$4\ FeS + 7\ O_2 = 2\ Fe_2O_3 + 4\ SO_2 \quad (3)$$

$$3\ FeS + 5\ O_2 = Fe_3O_4 + 3\ SO_2 \quad (4)$$

Unlike explosions of coal dust, the major problem is not usually the actual blast damage, but rather the toxic sulphur dioxide gas generated in the explosion. The identification of the cause of the ignition of a coal dust explosion in a mine can often be difficult, because the coal dust cloud can be ignited by various means, such as a methane/air explosion, electric sparks, flames, frictional sparks or the thermite reaction. Sulphide dust explosions can always be linked to the primary blast. Despite this apparent simplification, a solution has not been found, partly because there has not been until recently a recognition of the seriousness of the problem by the mining industry. A fatality in 1985 at the Geco Mine in Manitouwadge, Ontario, by poisoning from SO_2 generated in a sulphide dust explosion, has stimulated the present work. The advent of newer techniques, such as vertical crater retreat, has increased the probability of sulphide dust explosions. Recent legislation in Canada has given workers the right for a workplace environment free from safety and health hazards, which will increase the pressure on the mining industry to eliminate possible exposure to SO_2.

The earliest published reports on sulphide dust explosions were by the U.S. Bureau of Mines (Gardner 1926, 1928). Seven miners were killed by either SO_2 or by "inhaling burning sulphide dust" in the U.S. in the period 1924-1926. In addition to SO_2, H_2S was also detected when blasting high-sulphur ores in wet environments.

The Horne mine in Noranda, Quebec was reported to have had 76 fires caused

by dust explosions between 1949 and 1963 (Cant 1963); a number of other Canadian mines have had problems with dust explosions (Job 1975). Canada carried out studies on sulphide dust explosions from 1960-1968. Laboratory work indicated that more than 18% combustible content constituted a possible explosion hazard (Montgomery 1962).

Enright (1988) has given a detailed account of sulphide dust explosions that have occurred in Sweden, Australia, South Africa and Canada. Day (1980) gave a detailed description of a major sulphide dust explosion in Canada, along with a proposed mechanism, and attributed the increased frequency of such explosions to the increasing size of blastholes. In addition, Japan has also had a sulphide dust explosion, which occurred in their Yanahara mine in 1964 (Takagi 1987) and the U.S.S.R. have indicated that they have had explosions in some high-pyrite mines (Polikarpov 1982).

COLLABORATIVE RESEARCH PROGRAM

The first conference ever devoted to sulphide dust explosions was held at Manitouwadge, Ontario, sponsored by Geco Div. of Noranda Minerals Ltd., in October 1986 (Dainty 1987). Among the conclusions were: "problems of sulphide dusts are more frequent than previously considered by individual companies"; "precautionary measures currently in use may be unsuitable or inadequate"; and "dust explosions can be associated with stope blasting, development or secondary blasting".

Subsequently, a Sulphide Dust Control Group, consisting of representatives from mining companies, explosive manufacturers, universities and governments, was organized to coordinate research in this area; four meetings have been held. In addition, a session of 8 papers was held at the 90th Annual General Meeting of the Canadian Institute of Mining and Metallurgy in Edmonton in May 1988. In order to develop a data base for explosions, a standard occurrence report has been distributed to the mines;

18 incidents have been reported up to January 1989. A list of control measures has been prepared for the mines, based on current knowledge:

1. avoid long delay blasting, because a dust cloud can be formed and then ignited;

2. wash down area to prevent the blast from forming a dust cloud generated from previous blasts;

3. use finely-divided water sprays at entryways;

4. stem all holes where possible using inert plugs (not drill cuttings);

5. evacuate personnel from area before blasting;

6. confirm that area is free from SO_2 before re-entering.

LABORATORY STUDIES

Minimum Ignition Temperature (MIT)

A standard Godbert-Greenwald furnace (Dorsett 1960) was used to measure the MIT of seven pure minerals (diameter <38 μm), shown in Table 1, and 20 different ores.

TABLE 1 - MIT OF PURE MINERALS

Mineral	MIT (°C)
pyrrhotite	380
chalcopyrite	480
pyrite	510
tetrahedrite	530
galena	550
sphalerite	560
argentite	780

Unlike other dusts, sulphide ore dusts did not produce a flame in the Godbert-Greenwald furnace; they produced only sparks. The quantity of sparks increased with temperature, but even as high as 800°C, pyrrhotite generated only a shower of sparks, not a flame. The occurrence of a single spark was used as the limit criterion. It is a moot point as to whether indeed sparks should be used to define a MIT. As will be seen

later, the relative MIT values do not correlate with the explosibility tests. For example, sphalerite and tetrahedrite are in the same range of MIT as pyrite, yet they do not explode. MIT values of sulphide dusts are probably more closely related to their propensity for spontaneous combustion than their explosibility.

Hartmann Chamber Tests

Our first set of explosions were carried out using the standard Hartmann chamber (Dorsett 1960). A CEC 1000 strain-gauge pressure transducer was mounted on the top of the chamber; its output signal was amplified by a modified Honeywell 1885A-SGC module, then stored in a Nicolet 4094 digital oscilloscope. A control box was built to allow sequencing of events to a millisecond. Since the sulphide dusts would not explode in air using an electric spark discharge, the tests were carried out in pure oxygen. For convenience, all samples were tested at a concentration of 1600 g/m^3, which should be close to the optimum.

The maximum pressures during the explosion, P_m, and the maximum rate of pressure rise, $(dP/dt)_m$, of the pure minerals are given in Table 2. All of them have a particle size <106 µm, except for pyrrhotite, which is somewhat finer (38-75 µm). The explosion pressures are clearly not related simply to the percentage of sulphur present, as has been postulated. Galena is unusual, not only because it is explosible with relatively little sulphur, but because it formed the sulphate, rather than the oxide, and no SO_2 was detected. Thermodynamically, the sulphate is favoured over the oxide for reaction of all the metal sulphides. However, ferric sulphate decomposes at the relatively low temperature of 480°C, thus accounting for the lack of observance of iron sulphate.

In these explosion tests, pyrite produced only black powder (magnetite); by contrast, pyrrhotite produced only red powder (hematite). Using a finer fraction of pyrrhotite (which generated a higher explosion pressure), a mixture of hematite and magnetite was produced. Although at room temperature the reaction of both pyrite and pyrrhotite are thermodynamically favoured to form hematite, at higher temperatures, such as occur in strong explosions, thermodynamics predicts the reverse.

TABLE 2 – EXPLOSION PARAMETERS OF PURE MINERALS

mineral	%S	P_m (kPa)	$(dP/dt)_m$ (MPa/s)
pyrite	53.0	460	10
pyrrhotite	36.4	420	20
chalcopyrite	34.9	300	2
galena	13.4	310	4
sphalerite	32.9	no reaction	
tetrahedrite	26.0	no reaction	
argentite	10.0	no reaction	

Analyses of the residues from the explosion tests were carried out by scanning electron microscopy. Pyrite produced a variety of virtually perfect spheres between 5 and 50 µm in diameter (Fig. 1). Chalcopyrite produced less spherical particles. Although microanalysis indicated that these particles did not contain any sulphur, the distorted spheres indicate that the temperature reached during their formation was not sufficient to fuse the particles completely. Galena also produced highly spherical particles; microanalysis showed that these particles contained lead and sulphur, thus confirmining the formation of sulphate.
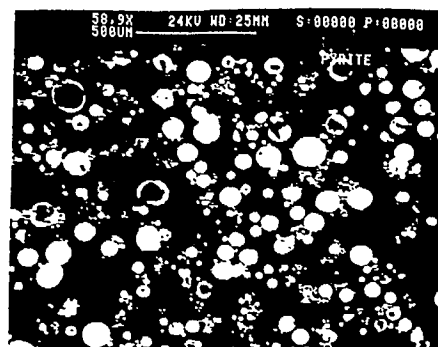

Figure 1

Table 2 shows that the explosibility is not simply a function of the sulphur content of the mineral. Twenty-seven ores of various composition were collected from 10 different mines and tested in the Hartmann chamber in the same way as was done for the pure minerals. For clarity, the explosibilities were normalized relative to pure pyrite, which should be the most explosive. Defining the relative explosibility (RE) of pyrite as 100, the relative explosibility of all the other samples are then:

$$RE = \frac{100 \ P_m \ (sample)}{P_m \ (pyrite)} \qquad (5)$$

Figure 2 shows the relative explosibility as a function of sulphur content for all the ores (but not the pure minerals). In general, explosibility increases with sulphur content, and there appears to be a cut-off at 26%, below which there are no explosions. However, the scatter of data is rather high; in addition, there were no ores with high galena content, which, as noted above, would probably explode at much lower sulphur contents.
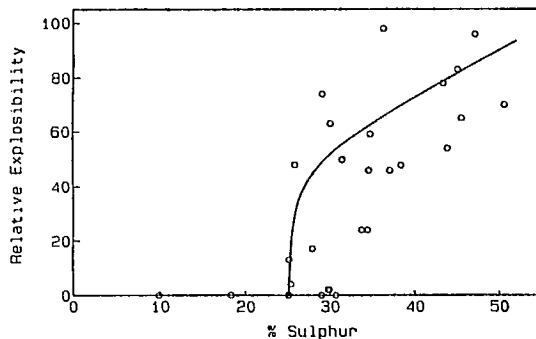
Figure 2

Equation 5 applied to the pure minerals yielded RE values of 90 for pyrrhotite, 65 for chalcopyrite, 70 for galena and 0 for sphalerite. Thus, using the mineralogical analysis, the RE of each ore sample can be predicted by multiplying the above values by the percentages of each component. A graph of the actual RE vs. the predicted RE for all the ore samples (but not the pure minerals) is shown in Fig. 3. The straight line shown is the theoretical line. It would appear that this line provides a prediction of the upper limit of the explosibility.
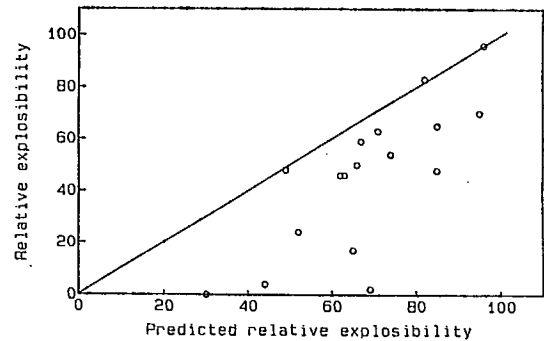
Figure 3

20-L Vessel Explosion Tests

A stainless-steel vessel similar to the one used by the U.S. Bureau of Mines (Cashdollar 1985) was used for these tests. The control and pressure-detection systems were the same as were used for the Hartmann apparatus. A paramagnetic oxygen analyzer was connected to the 20-L vessel to allow measurement of the oxygen remaining after the explosion test, as well as for making up mixtures for testing in oxygen-enriched or in oxygen-deficient atmospheres.

An infrared spectrophotometer (Miran-80 Computing Infrared Analyzer, with a 20-m gas cell) was also connected to the 20-L vessel for measuring the quantity of SO_2 produced in the explosion. The main absorption band of SO_2 at 7.3 µm was not used, because it is located in the midst of the absorption band due to water and thus is subject to interference. Instead, a weaker band at 9 µm, in a spectral region free from

interference by water and carbon dioxide, was used.

As mentioned above, the sulphide ore dusts cannot be ignited by an electric spark. Instead of testing in pure oxygen as was done for the Hartmann tests, a stronger ignitor (a 5-kJ Sobbe pyrotechnic) was used in a normal atmosphere. This system should provide a more realistic simulation of the actual occurrence. The Sobbe ignitor generates an explosion pressure of 50 kPa in our vessel under the operating conditions used. The maximum pressure in the explosion tests on a dust is approximately the sum of the explosion pressure due to that dust plus the pressure due to the ignitor. Therefore, the pressure trace of the ignitor carried out without dust was subtracted from the experimental trace to yield the "true" pressure trace. The justification for this procedure was that the maximum pressures thus obtained for lycopodium dust were the same as obtained for tests on lycopodium using electric sparks as the ignitor. On the other hand, $(dP/dt)_m$ was higher for lycopodium with dust than with electric sparks. This may be due to additional turbulence caused by the chemical ignitor, which affects that parameter much more than P_m.

Of critical importance in laboratory tests in dust explosions is the creation of a homogeneous dust cloud. The dispersion technique, the pressure of the dispersing air, the timing of the air injection and the ignition must be optimized. We have built a glass vessel of about the same size as the stainless-steel vessel and which uses the same dispersion system, so as to allow the dust dispersion process to be videotaped. Frame-by-frame viewing allows identification of appropriate parameters for testing.

Sulphide dusts, being much denser than coal and most other explosible dusts, require a shorter, more intense pressure pulse for adequate dispersion. The test conditions were

selected such that ignition occurred at a pressure of one atmosphere. It is known that the explosion pressure is proportional to the initial pressure. In the Hartmann apparatus, the initial pressure is about 30 kPa, thus the experimental pressures are about a factor of 1.3 too high (neglecting the other deficiencies of the Hartmann apparatus).

The explosion pressures obtained for pyrite and two size fractions of pyrrhotite are shown in Fig. 4. The curves are all S-shaped, making it reasonable to define the minimum explosible concentration (MEC) as being the steepest point on the curve. The maximum explosion pressure appears to be about the same for both size fractions of pyrrhotite, but the MEC of the finer fraction is much lower. The pyrite, which is coarser, has a smaller MEC than the pyrrhotite, indicating that it is more explosible.
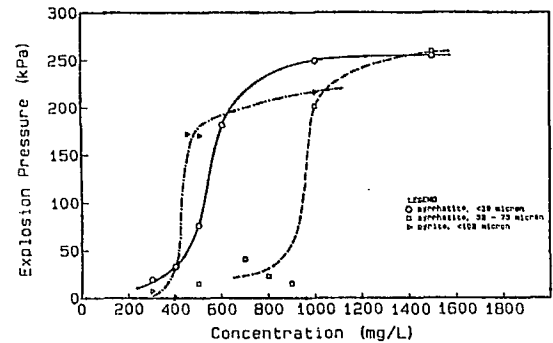

Figure 4

$(dP/dt)_m$ for the same three samples are shown in Fig. 5. The effect of particle size on this parameter is greater than it is on P_m. The separation of each curve into the regions of explosible and non-explosible is not as clear-cut, partly due to the intrinsically greater scatter of $(dP/dt)_m$ compared to P_m.
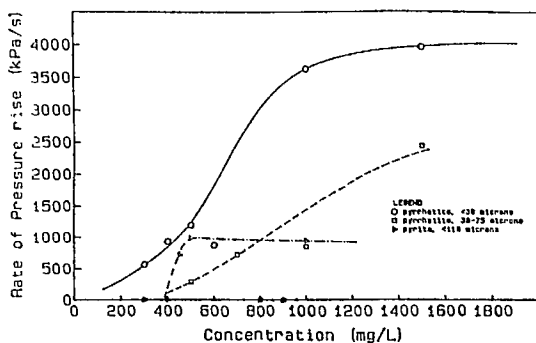
Figure 5

The quantity of SO_2 produced for the same three samples is shown in Fig. 6. The curves are quite similar to Fig. 4, because both P_m and $n(SO_2)$ are directly proportional to the amount of reaction that has occurred. The quantity of oxygen consumed (on a molar basis) was roughly two times the quantity of SO_2 generated. The theoretical values for reaction of pyrrhotite and pyrite are 1.75 and 1.38, assuming that they each react to hematite.
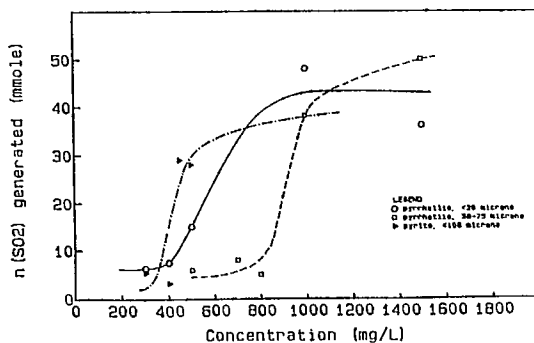

Figure 6

These tests produced mainly hematite, with some magnetite, for both pyrrhotite and pyrite. In the Hartmann apparatus, the same sample of pyrite produced magnetite; the difference being that the tests had been done in pure oxygen, which

produced stronger explosions, as shown also by the higher explosion pressures.

Chalcopyrite had only limited reaction up to 1200 g/m^3. Limited testing of galena indicated that the MEC is between 1000 and 1300 g/m^3. Galena produced significant quantities of SO_2, in contrast to the Hartmann tests, in which no SO_2 was detected. The reason is that the latter were carried out in pure oxygen, which would tend to favour reaction (7) that uses more oxygen than reaction (6):

$$PbS + 1\text{-}1/2\ O_2 = PbO + SO_2 \qquad (6)$$

$$PbS + 2\ O_2 = PbSO_4 \qquad (7)$$
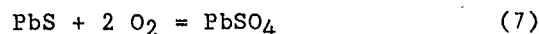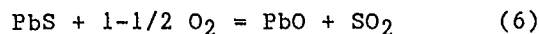
This hypothesis is supported by the ratio of SO_2 detected: O_2 consumed being 5, compared to a ratio of 1.5 predicted on the basis of (6) being the only reaction occurring.

Two explosion tests, at a concentration of 1000 g/m^3, carried out on different samples of sphalerite, both with particle size of <38 μm, yielded absolutely no evidence of explosion or reaction, thus confirming the tests carried out in the Hartmann chamber.

Figure 7 shows the explosion pressure for tests carried out on pyrrhotite, (38-75 μm fraction) at a concentration of 1500 g/m^3, as a function of oxygen concentration. The curve shows a sharp break between the region of explosibility and non-explosibility at 17.2% O_2, which can be defined as the minimum oxygen concentration for this sample.
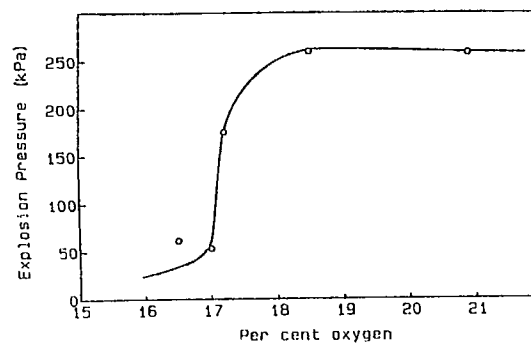

Figure 7

IN-MINE TESTS

Electrochemical SO_2 sensors were evaluated in a mine which has high pyrite ore and therefore has had many sulphide dust explosions. The sensors proved to be sufficiently reliable and stable that they are recommended for use by all mines having problems with sulphide explosions. The highest concentration of SO_2 measured was 910 ppm after a large blast.

Dust probes were constructed that would allow measurements of air-borne dust during four blasts, none of which had sulphide dust explosions. Most of the coarse dust settled within a second, but respirable dust took 10-15 minutes to decrease from 100 to 10 mg/m^3. Dust samples were also collected by pans placed on the floor at various distances from the blast; between 37 and 66% of this dust was below 38 µm. Laboratory tests reported above (Fig. 4-6) showed that the <38 µm size fraction was much more hazardous than larger fractions; hence, emphasis in the laboratory should be on the very fine fraction.

CONCLUSIONS

Laboratory tests have shown that pyrite, pyrrhotite, galena and chalcopyrite are all explosible when dispersed in air, and a sufficiently large ignitor is used. Sphalerite is non-explosible under those same conditions. The percentage of sulphur cannot be used as a reliable measure of the risk of explosion, except where the mineralogy of the ore is similar. The amount of SO_2 produced in the explosions of pyrite and pyrrhotite is proportional to the explosion pressure, indicating a quantitative conversion of the sulphur in the ore to SO_2. Explosions of galena produce sulphate in larger quantities than SO_2.

In the past three years, Canadian industry, industry and academia, with assistance from Australia and the U.S., have made significant progress in the understanding of sulphide ore dust explosions. It is hoped that application of this knowledge will lead to safer and more productive base metal mines.

ACKNOWLEDGEMENTS

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