



An investigation of iron sulphide dust minimum ignition temperatures

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Abstract

An investigation of the ignition behaviour of iron sulphide dusts has been undertaken. Commercial samples of FeS and FeS₂ and mine samples of pyrrhotite and pyrite were tested for minimum ignition temperature (MIT) using a device known as the BAM oven. The mine samples were found to undergo a decrease in MIT as the mass mean particle diameter became smaller. Using available theoretical treatments, this experimental observation was interpreted as providing further evidence of the importance of heterogeneous combustion in the ignition of iron sulphide dusts. A dense cloud state was proven for the experimental apparatus used, and an alternate criterion for the boundary between a dilute and a dense dust cloud was proposed in terms of the number of dust particles present in the cloud. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Dust ignition is of considerable interest in terms of gaining a fundamental understanding of ignition phenomena, as well as from a practical perspective. Examples of the latter concern include the combustion of pulverised coal particles in boilers, process safety during handling of materials in powdered form, and propulsion systems. As reviewed by Essenhigh et al. [1], dust-ignition studies fall into two categories: single particles and dust clouds. The parameter of interest is the critical ambient temperature, also known as the minimum ignition (or autoignition) temperature, MIT, required for ignition of the particle/cloud.

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For single particles of coal, metals and several plastics, Cassel and Liebman [2] found an inverse relationship between the minimum ignition temperature (MIT) and particle size. A similar observation has also been made by Du and Annamalai [3], Chen et al. [4], and Bandyopadhyay and Bhaduri [5] for single coal particles. In the case of dust clouds, as opposed to single-particle ignition, the cloud concentration and reaction mechanisms are important. In general, one expects a lower critical ambient temperature for the ignition of a dispersed cloud of particles than for single-particle ignition of the same material. This lowering of the MIT can be attributed to the co-operative effect among particles in a dust cloud [2]. This effect also reduces heat losses from the cloud to the surrounding environment.

Theoretical treatment of the problem of dust cloud ignition has been provided by researchers such as Essenhigh et al. [1] and Zhang and Wall [6]. However, to our knowledge there has been no corresponding experimental validation for the iron sulphides, despite the fact that materials such as pyrrhotite and pyrite are prone to spontaneous ignition and have thereby caused fires in mines. We have therefore undertaken an investigation of iron sulphide dust cloud ignition with the objectives of:

- generation of minimum ignition temperature data for the iron sulphides,
- determination of the effect of particle size on minimum ignition temperature, and
- interpretation of the experimental results in light of the theoretical explanations posed by Zhang and Wall [6].

2. Experimental

2.1. Materials

Mine samples of pyrrhotite (Fe_{1-x}S) and pyrite (FeS_2) were obtained from Kidd Creek Mines, Falconbridge Operations in Timmins, Ontario. Tests were also done with FeS and FeS_2 , which approximate pure forms of pyrrhotite and pyrite, respectively. The sample of FeS was obtained from BDH Chemicals and the FeS_2 from EM Scientific. These commercial chemicals were tested as received. The mine samples were prepared for testing by first crushing the ore and reducing its size further by pulverising in a shatter box. The samples were then sieved into various size fractions. These are the same materials for which we have previously reported laboratory-scale (20-L) explosion data [7].

All dusts were analysed for composition and particle size. Sulphur and iron contents were determined to be those shown in Table 1. For the mine samples, the remaining components most likely include silicon, copper, zinc and other trace elements. Particle size measurements

Table 1
Iron and sulphur contents of sulphide dusts

Material	Fe (wt.%)	S (wt.%)
FeS	64.6	28.5
FeS_2	42.4	46.2
Pyrrhotite	38.6	32.7
Pyrite	34.2	46.4

Table 2
Particle size distributions of sulphide dusts

Material	<200 μm (wt.%)	<125 μm (wt.%)	<75 μm (wt.%)	<45 μm (wt.%)	<20 μm (wt.%)	D_w^a (μm)
FeS	100	100	100	99	86	11
FeS ₂	100	100	87	60	31	40
PO-90 ^b	100	87	33	3	1	90
PO-64	100	100	68	3	2	64
PO-49	100	100	90	39	14	49
PO-37	100	100	99	74	14	37
PO-16	100	100	100	100	66	16
PY-146 ^c	85	29	4	1	1	146
PY-85	99	92	29	3	2	85
PY-66	100	100	57	4	1	66
PY-50	100	100	85	27	6	50
PY-37	100	100	88	62	42	37
PY-35	100	100	100	68	16	35
PY-20	100	100	100	95	62	20

^a D_w : volume or mass mean diameter.

^b PO: pyrrhotite; number following dash: D_w (e.g. PO-90 is pyrrhotite with a mass mean diameter of 90 μm).

^c PY: pyrite; number following dash: D_w (e.g. PY-146 is pyrite with a mass mean diameter of 146 μm).

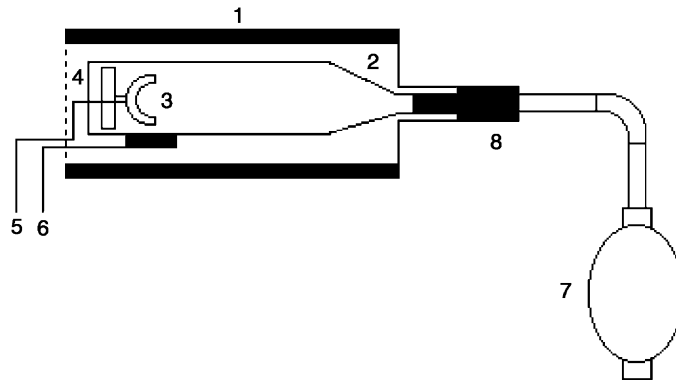
were made using a Malvern Instruments (2600 Series) analyser based on the principle of light scattering. The results of these measurements are given in Table 2; in most cases, the size distributions of the samples were fairly narrow.

2.2. Apparatus

The MIT tests were conducted in a BAM oven (Fig. 1). This device was developed by the Bundesanstalt für Materialforschung und -prüfung (BAM) in Germany [8], and is referenced in the ASTM E1491 standard for determination of minimum autoignition temperatures of dust clouds. The basic principle of the oven is that a dust cloud is exposed to a hot surface, with the lowest temperature of the surface that will ignite the dust being designated as the MIT of the dust.

In the operation of the BAM oven, a dust cloud is generated by squeezing a rubber bulb (previously charged with sample) which directs the dust against a circular, concave metal disc of about 20 cm² area and known temperature. If the cloud does not ignite directly in suspension, it will settle on the hot internal bottom of the oven and smolder. The smoldering gases may then ignite at a somewhat lower temperature than required for direct ignition of the dust cloud. If this occurs up to 5 s after the dust cloud has been generated, ignition is judged to have taken place (i.e. the temperature is at or above the MIT). If ignition occurs later than 5 s after dust cloud generation, or does not occur at all, ignition is judged not to have taken place (i.e. the temperature is below the MIT).

In all tests reported here, the oven was first set to its maximum operating temperature (about 620 °C). With the power source turned off and the oven temperature falling, dust was dispersed into the chamber at 20 °C intervals until no ignition was observed (1.5 ml of sample was used in each test). The oven was then cooled and cleaned for a second series



- 1) Oven
- 2) Test Chamber
- 3) Deflecting Surface
- 4) Flap
- 5) Measuring Thermocouple
- 6) Control Thermocouple
- 7) Rubber Bulb
- 8) Air Inlet Pipe and Sample Holder

Fig. 1. Schematic of the BAM oven.

of tests, in which the temperature was first set to 20 °C above the no-ignition temperature. Again, with the power off and the oven temperature falling, tests were done at 10 °C intervals until no ignition was recorded. In this manner the MITs were determined for all the particle sizes and the four different materials (FeS, FeS₂, pyrrhotite and pyrite) shown in Table 2.

3. Ignition temperature results

The experimental results are presented in Table 3. Minimum ignition temperatures are given as a 10 °C range, which is a standard method of reporting MITs measured in the BAM oven. For example, the MIT for the PY-20 sample lies between 480 °C (no ignition) and 490 °C (ignition). As noted in the third column of Table 3, the appearance of flame exiting the oven chamber could not always be used as the criterion for ignition. Some of the samples, particularly the coarser size fractions, generated only a shower of sparks. This is unlike the behaviour of most dusts, but is consistent with the observations of Mintz and Dainty [9] who tested sulphide ore dusts in another commonly used dust-ignition apparatus (the Godbert–Greenwald furnace).

The results in Table 3 show that, in general, the MIT decreased as the mass mean diameter decreased for the various pyrrhotite and pyrite mine samples. In the case of the commercial samples of FeS ($D_w = 11 \mu\text{m}$) and FeS₂ ($D_w = 40 \mu\text{m}$), the particle size effect dominates over the difference in sulphur contents. From Table 1, the sulphur contents are seen to be 28.5% for FeS and 46.2% for FeS₂; yet the FeS sample has a lower MIT than the FeS₂.

Table 3
Minimum ignition temperatures of sulphide dusts

Material	Minimum ignition temperature (°C)	Observations
FeS	520–530	Sparks
FeS ₂	550–560	Sparks
PO-90	600–610	Sparks
PO-64	580–590	Sparks
PO-49	560–570	Flame
PO-37	560–570	Flame
PO-16	580–590	Flame
PY-146	>620	No ignition
PY-85	550–560	Sparks
PY-66	540–550	Sparks
PY-50	510–520	Flame
PY-37	530–540	Flame
PY-35	510–520	Flame
PY-20	480–490	Flame

Also, in accordance with the previous paragraph, Table 3 indicates that the commercial samples ignited with a shower of sparks whereas mine samples of similar particle size yielded flames upon ignition. This can be explained by our previous study [7] in which closed-vessel explosion testing revealed that the rate of reaction (i.e. maximum rate of pressure rise) of the ore samples was two to three times that for the chemical samples. The current results support our earlier statement [7] that commercially prepared chemicals are of limited usefulness in predicting the explosion behaviour of mine samples of sulphide dusts.

In Table 3, it is observed that the PO-16 sample has a higher MIT than PO-37; similarly, the PY-37 sample has a higher MIT than PY-50. Referring to the particle size distributions given in Table 2, the PO-16 and PY-37 samples have a considerable percentage of fines (particles <20 µm in diameter). Further, Table 1 shows that the mine samples contain approximately 20–30% of components other than iron and sulphur. The effect of these undetermined components may be more prevalent when they are present as fines—in terms of both possible inerting effects and a tendency to cause particle agglomeration. This hypothesis is borne out for at least the PY-37 sample for which 20-L closed-vessel explosion data are available [10]. In these previous tests, the minimum explosible concentration for the PY-37 sample was determined to occur at a higher dust concentration than that for PY-50 (data which are consistent with the MIT data reported here, and which are explainable by a difference in physical makeup of the samples).

For comparable size fractions (e.g. PO-64 and PY-66), Table 3 shows that the MIT of pyrrhotite is greater than that of pyrite. This means that the pyrite samples are more reactive than the pyrrhotite, an observation that is important in assessing the relative probabilities of spontaneous combustion for the two materials. This finding is also consistent with the enhanced explosibility of pyrite over pyrrhotite that was determined in the previously mentioned 20-L explosion tests [7,10].

In comparing the present results with those of other workers, the study of Dunn and Chamberlain [11] is relevant. Their minimum ignition temperature results for synthetic FeS

Table 4
Ignition temperatures of FeS from TGA measurements [11]

Particle size (μm)	Ignition temperature ($^{\circ}\text{C}$)
90–125	755
63–90	740
45–63	720
20–45	660

(Table 4) confirm the general trend displayed in Table 3 with respect to particle size. The difference in the magnitude of the values between Tables 3 and 4 is caused by the difference in experimental techniques: a cloud-type arrangement in the present study and a static bed arrangement in the thermogravimetric work of Dunn and Chamnberlain [11].

4. Theoretical interpretation of results

Building on the review of Essenhigh et al. [1], and, in particular, the work of Krishna and Berlad [12], Zhang and Wall [6] proposed a model for the problem of coal dust cloud ignition. They gave expressions showing the relationship between the ignition temperature and particle size for three limiting cases:

$$\text{heterogeneous ignition (dense cloud)} : T^a = (\text{constant}) \left(\frac{r}{R\rho_{\text{cl}}} \right) \quad (1)$$

$$\text{heterogeneous ignition (dilute cloud)} : T^a = \frac{\text{constant}}{r} \quad (2)$$

$$\text{homogeneous ignition (dense cloud)} : T^a = \frac{\text{constant}}{R^2\rho_{\text{cl}}} \quad (3)$$

where T is the ambient temperature for ignition, a the empirical power index, r the particle radius, R the cloud radius, and ρ_{cl} is the cloud density.

Eqs. (1)–(3) illustrate that the effect of particle size on ignition temperature is predicted to be either directly proportional, inversely proportional, or invariant, respectively, depending on the mode of ignition and the physical state of the dust cloud. The experimental results in Table 4 show, in general, a direct relationship between MIT and particle size. Eq. (1) thus offers a theoretical interpretation of this experimental finding in terms of the importance of heterogeneous ignition of the iron sulphides in a dense cloud state.

The functional form of Eq. (1) is testable by a double-logarithmic plot, with the equation being supported if such a plot is linear. Incorporating the cloud radius and cloud density with the constant term in Eq. (1) and taking the logarithm of both sides, Eq. (1) becomes:

$$\ln T = \left[\left(\frac{1}{a} \right) \ln \left(\frac{\text{constant}}{R\rho_{\text{cl}}} \right) \right] + \left[\left(\frac{1}{a} \right) \ln r \right] \quad (4)$$

Fig. 2 gives a plot of Eq. (4) for the pyrite data shown in Table 3, with the exception of PY-146 which did not explode, and PY-37 which did not follow the general trend. In plotting

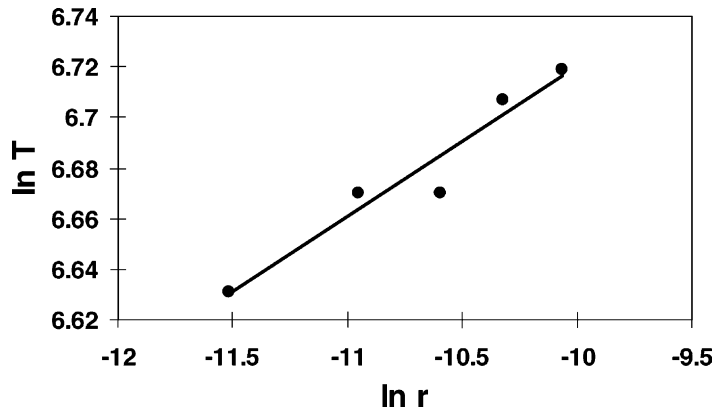


Fig. 2. Double-logarithmic plot of the MIT vs. particle size for pyrite (T : temperature (K), and r : radius (m)).

these data, the midpoint of the MIT range and the value of D_w were used (e.g. for PY-66, $T = 545^\circ\text{C} = 818\text{ K}$, and $r = 33\ \mu\text{m} = 33 \times 10^{-6}\text{ m}$). The exclusion of the PY-37 sample is justified based on the explanation previously given of excessive fines (such explanation being supported by our 20-L explosion data for this sample [10]). The pyrite data were judged to be more amenable to this theoretical treatment than the pyrrhotite data given that the pyrite experiments involved more samples, covered a wider range of particle sizes, and offered a viable explanation for data discrepancies based on explosion data. Nevertheless, the overall trend of MIT lowering with a decrease in particle size for pyrrhotite is evident in Table 3.

We have previously commented on the importance of heterogeneous ignition as a mode of closed-vessel explosion initiation for the iron sulphides [7]. The results in Table 3 and the linear relationship shown in Fig. 2 provide further evidence to support the contention that direct gas/solid interaction plays a role in ignition of iron sulphide dusts. Primary ignition may be due to direct oxygen attack on the whole solid particle, with sulphur evolution and homogeneous combustion occurring at a later stage. The evidence of hematite (Fe_2O_3) as a combustion product in the work of Mintz and Dainty [9] also suggests secondary ignition of remaining sulphur-containing material by rapid diffusion of oxygen through the pores of the solid.

The final point to be considered here is evidence for the existence of a dense cloud in the BAM oven, as would be required by Eq. (1) in light of the experimental results in Table 3. Essenhigh et al. [1] have given the following criteria for judging the physical state of a dust cloud:

$$\text{dilute cloud : } \frac{\rho_{\text{cl}} D^2}{\rho_{\text{p}} d^2} \ll 1 \quad (5)$$

$$\text{dense cloud : } \frac{\rho_{\text{cl}} D^2}{\rho_{\text{p}} d^2} \gg 1 \quad (6)$$

where D is the cloud diameter, ρ_{p} the particle density, and d is the particle diameter.

Table 5
Verification of dense cloud conditions in the BAM oven

Material	$\rho_{cl}D^2/\rho_p d^2$	$N_{critical}$	N
PY-85	5,300	880	4.7×10^6
PY-66	8,800	1100	1.0×10^7
PY-50	15,000	1500	2.3×10^7
PY-35	31,000	2100	6.7×10^7
PY-20	95,000	3800	3.6×10^8

In evaluating the ratio term on the left-hand side of Eqs. (5) and (6), the following conditions apply:

- The particle density is approximately 5000 kg/m³ (for pyrite).
- The particle diameter is taken to be the mass mean diameter.
- The cloud density is taken to be the ratio of the nominal dust loading to the chamber volume. The nominal dust loading (i.e. the mass of dust nominally dispersed) is 0.0075 kg (for a density of 5000 kg/m³ and a sample volume of 1.5×10^{-6} m³). The chamber volume is approximated by a sphere of diameter 0.075 m. (The actual chamber is cylindrical, but the placement of the heated deflector plate partway into the chamber necessitates this approximation.)
- The cloud diameter is the aforementioned diameter of 0.075 m.

With these approximations, the ratios given in the second column of Table 5 are calculated. Each of the pyrite samples is clearly seen to satisfy the dense cloud criterion of the ratio $\rho_{cl}D^2/\rho_p d^2$ being significantly greater than unity. As an alternative demarcation of the dilute/dense cloud boundary, we have introduced in Table 5 the concept of $N_{critical}$, the number of particles numerically equal to the ratio of cloud diameter to particle diameter. This parameter is suggested by a rearrangement of Eqs. (5) and (6) to the following forms:

$$\text{dilute cloud : } \frac{Nd}{D} \ll 1 \quad \text{or} \quad N \ll \frac{D}{d} \quad (7)$$

$$\text{dense cloud : } \frac{Nd}{D} \gg 1 \quad \text{or} \quad N \gg \frac{D}{d} \quad (8)$$

Eqs. (7) and (8) follow from Eqs. (5) and (6) by treating the particles as spheres of diameter D_w , and making use of the fact that the cloud mass is equal to the number of particles, N , times the mass of a single particle. The final column of Table 5 shows N for each of the pyrite samples. The values of N are clearly significantly greater than the corresponding values of $N_{critical}$, meaning that the dense cloud criterion given by Eq. (8) is satisfied. This is, of course, the same conclusion reached as when considering the dense cloud criterion according to Eq. (6). The potential usefulness of the criteria given by Eqs. (7) and (8) lies in the explicit emphasis placed on the number of particles in the cloud. This may be helpful in examining the ignition behaviour of dense and dilute dust clouds in relation to that of single particles.

5. Concluding remarks

The current work provides data for the minimum ignition temperature of commercial samples of FeS and FeS₂ and mine samples of pyrrhotite and pyrite. The mine samples were found to undergo a decrease in MIT as the mass mean particle diameter became smaller. This experimental observation has been interpreted as providing further evidence of the importance of heterogeneous combustion in the ignition of iron sulphide dusts. A dense cloud state has been proven for the experimental apparatus used, and an alternate criterion for the dilute/dense cloud boundary has been proposed in terms of the number of dust particles present in the cloud.

Further work on the problem of dust cloud ignition is planned in our laboratory. Development and implementation of an ignition chamber is currently underway based on a modification of the 6.8-L furnace introduced by the former US Bureau of Mines [13]. It is anticipated that the use of this chamber will enable exploration of the ignition behaviour of dilute and dense clouds of different materials undergoing both homogeneous and heterogeneous combustion.

Acknowledgements

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