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DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

Note on spontaneous heating and ignition in iron pyrites

by

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Summary

In response to an enquiry on the risk of spontaneous heating and ignition in finely divided iron pyrites a review has been made of the relevant information available in the literature. While heating is certain to occur its severity cannot be predicted in detail.

Introduction

In response to an enquiry on the risk of spontaneous heating and ignition in finely divided iron pyrites a review has been made of the relevant information available in the literature.

Nature of material and reactions

Iron disulphide, FeS₂, occurs naturally in two forms, pyrite and marcasite, which differ in crystal structure. Except where a distinction is necessary the word "pyrites" will be used in this note to cover both forms.

The occurrence of spontaneous heating in pyrites is due to atmospheric oxidation of the pyrites with the formation of ferrous sulphate and sulphuric acid and with the evolution of heat, at a rate which is appreciable at ordinary temperatures. Ferric sulphate as a product of pyrites oxidation in a coal seam was observed by Sinnatt and Simpkin¹, but this was unusual as coal is apparently normally capable of reducing ferric salts. Winmill⁶ states that ferric sulphate does not occur to any extent until all the pyrites has been oxidised, since ferric sulphate, in slightly acid solution, is reduced to ferrous sulphate in the presence of pyrites. It appears to be generally accepted that the main reaction in the presence of air and moisture may be represented as follows:



Burke and Downs¹ have obtained evidence that the reaction may occur in two stages:



The first stage, which is slow compared with the second, occurs in dry air and leads to an accumulation of ferrous sulphate on the surface of the pyrites which eventually retards the reaction; this retardation was also observed by Winmill⁶. Ivon Graham noted that as soon as all moisture was used up the absorption of oxygen by pyrites practically ceased¹⁰.

Oxidation of pyrites to iron oxides and sulphur dioxide only becomes appreciable at high temperatures. Ruiss *et al*⁹ found that the rate of sulphur dioxide production increased rapidly as pyrites was heated above 340° - 360°. These authors found ignition temperatures for pyrites which varied between 330° and about 450°; the lower values occurred with samples of small particle size and in the presence of increasing amounts of copper in the ore. Cawley, Carlisle, King and Kingman¹⁶ obtained ignition temperatures of 410° and 440° respectively for coal pyrites and commercial iron pyrites.

Continued oxidation of pyrites at atmospheric temperatures accompanied by leaching by water results ultimately in the formation of limonite, i.e. hydrated ferric oxide.

Heat Production

Using the value 42.5 K.cal per mol for the heat of formation of pyrite (Lipin, Uskov and Klokman³), and tabulated values⁴ for the other substances, the calculation by Parr and Kressman⁵ and Winmill⁶, of the heat evolved in reaction (1) is revised to 296 K.cal per mol of pyrite oxidised; which is equivalent to 3.8 cal per cc of oxygen at N.T.P. reacting. If the ferrous sulphate produced is fully hydrated ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) the corresponding values for the heat evolved are 316 K.cal per mol of pyrite and 4.0 cal per cc of oxygen. Winmill⁶ obtained, experimentally, a value of 4.5 cal per cc of oxygen reacting, with an error of ± 0.3 cal.

For marcasite the heat of oxidation will be greater by 5.6 K.cal per mol, which is the heat evolved in the transformation marcasite \rightarrow pyrite³.

Most of the heat of oxidation appears in the stage represented by (2), the oxidation in dry air, for which the heat evolved is calculated as 244 K.cal per mol of pyrite.

Winmill⁶ points out that the heat produced per cc of oxygen used in the spontaneous heating of pyrites is twice the value he obtained for the spontaneous heating of coal¹² and that, since the specific heat of pyrites is about two thirds that of coal, the low temperature oxidation of equal weights of pyrites and coal, by equal amounts of oxygen, would raise the temperature of the pyrites by three times as much as for the coal. Winmill does not give the specific heat values on which this estimate is based but tabulated values, viz. 0.118 cal/g/°C for pyrites⁴ and 0.27 cal/g/°C for a bituminous coal with 5% moisture content¹³, indicate that the ratio of the pyrites and coal temperatures would be nearer four than three.

Rate of oxidation

Winmill⁶ found that although samples of pyrites of different origin oxidised at different rates in the massive state they tended to oxidise at the same rate when reduced to fine powder. Results on different sieve fractions indicated that the rate of oxidation is proportional to the pyrites surface exposed, or, as was later found by Li and Parr², approximately inversely proportional to the particle diameter.

Information on the relative rates of oxidation of pyrite and marcasite is conflicting but Li and Parr ² found that similar sieve fractions of each oxidised at about the same rate; marcasite tended to break down more readily with the production of fine particles, thus facilitating its oxidation.

For the temperature range 30°C to 60°C Winmill ⁶ found that the rate of oxidation of pyrites doubled for each 10°C rise in temperature. Li and Parr ² state that the rate of oxidation is directly proportional to the temperature, but it is not easy to reconcile this statement with their published curves for the oxidation of pyrite and marcasite at 25°C and 100°C.

The rate of oxidation was found by Winmill ⁶ to be directly proportional to the percentage of oxygen present in the gas phase for the range 10.6% to 89.0%.

For pyrite in coal Li and Parr ² found that oxidation occurred most rapidly in a stream of air or oxygen which saturated with moisture and when the solid had a high moisture content. For example, in a stream of laboratory air of unspecified relative humidity the oxidation of available sulphur reached a stationary value of 2% in about two and a half weeks, the rate having been relatively small since the end of the first week, while in saturated air the oxidation was about 5.5% at the end of two and a half weeks and was still increasing at the rate of about 2% per week; in both cases the moisture content of the solid was 10.5%.

Spontaneous heating and ignition

Most investigations of the spontaneous heating of pyrites have been directed to the determination of its role in the spontaneous heating and ignition of coal; this work has recently been reviewed by Scott ⁷ in relation to anthracite mine fires. Although pyrites is not necessary for the occurrence of spontaneous heating and ignition in coal its presence will assist the process and it may sometimes be the primary cause ¹⁰, although a considerable quantity in a finely divided state is likely to be necessary ⁶.

The self heating of pyrites placed in heaps either for storage or, as formerly, for the manufacture of concentrated sulphuric acid by weathering of pyrites has long been known ^{6, 10}; and the heating arising from the oxidation of iron sulphides in spent oxide from gas purifiers is a known fire hazard. Pyrites in the finely divided state has a reputation for being hazardous ⁸.

It is evident, from Winmill's work ⁶ especially, that, under conditions suitable for unretarded reaction, finely divided pyrites would present a greater fire hazard from spontaneous ignition than does coal. Assuming the heat loss to be zero Winmill ⁶ calculated that a sample of pyrites could heat from an initial temperature of 30°C to 90°C in three hours, while an average oxidisable coal would require forty eight hours under the same conditions. However, the presence or absence of water is likely to be decisive for the occurrence or otherwise of dangerous heating in practice. Thus, although most of the heat available from the oxidation in the presence of moisture is evolved in the reaction in the absence of moisture, the rate of heat production in the absence of moisture may be too low to cause an appreciable rise of temperature in a mass of pyrites unless the heat losses are very small.

Records of detailed observation of fires associated with the self-heating of pyrites are few in the literature. Brown ¹⁴ describes experience of fires in the Huelva pyrites mines, Spain. The ore in these mines consists mainly of cupreous iron pyrites, which consists of an intimate mixture of iron pyrites

and chalcopyrite ($\text{Cu}_2\text{S}, \text{Fe}_2\text{S}_3$), occurring with zones in which the chief copper mineral is chalcocite (Cu_2S). Fires occurred either in zones containing the softer and more readily oxidised chalcocite or in primary ore which was either unusually soft or which had been moved or had fallen naturally; fires would break out several weeks after such a fall. Evidence indicated that the primary cause of the fires was the exothermic oxidation of the fractured mineral. In the absence of combustible material, such as timber, the temperature would rise until sulphur dioxide was evolved. If timber was present, and if the air supply was adequate, the timber would eventually be ignited and cause a "sudden" outbreak of fire; in a limited supply of air the timber was reduced to charcoal which would ignite when exposed to air during digging-out operations in the fire area. Fires also occurred in heaps of broken mineral and it was noted that heaps of lumps were more likely to heat than heaps of fines, presumably because of reduced air access to the interior of the latter.

Control of the fires was difficult; flooding, mining out, and cooling by copious forced ventilation were employed. In opening up an area which had been flooded the fire was apt to break out again. Cooling by ventilation was effective only if large volumes of air could be passed at a high rate, otherwise the rate of reaction was merely increased. It appears probable that provided the temperature is below 100°C , forced ventilation will be effective by virtue of the removal of moisture and retardation of the reaction as much as by cooling.

Investigations on the causes and control of fires in pyrites mines have been carried out more recently in the U.S.S.R. 9, 15.

Ruiss et al studied the oxidation of pyrites mainly at high temperatures but, to a limited extent, also followed the self-heating of pyrites from about 35°C in an adiabatic furnace. Self-ignition from low ignition temperatures was not reproduced. It was concluded that the oxidation of pyrites, particularly in the finely divided state and in the presence of small amounts of water, is accompanied by a rapid rise of temperature; but this does not continue to the ignition temperature of the pyrites because of the greatly reduced rate of oxidation of dry pyrites. These authors reproduce some graphs of Miagav which show that moist pyrites heated from 53°C to 90°C in about 75 minutes, whereas dry pyrites heated from about 48°C to only 53°C in the same period; experimental details are not given. They suggest that mine fires could be caused by the self-heating of pyrites dust in contact with wood hydrolysed by acid mine water; stating that hydrolysis of the wood can lower its ignition temperature from 280°C - 290°C to 200°C .

Discussing the control of fires Ruiss et al say that carbon dioxide can be used for small fires.

Conclusions

The information obtained leads consistently to the conclusion that freshly pulverized iron pyrites will certainly heat if accumulated in bulk, e.g. stored in hoppers, to which air has access, and it may present a greater hazard than pulverized coal. If the pyrites is free from moisture the risk of dangerous heating may be considerably reduced but it certainly cannot be regarded as non-existent. There should be no wood or other combustible material in the hoppers.

It is not at present possible to predict the size of pile for dangerous heating to occur or the safe dimensions for storage hoppers. The fire hazard in any particular storage system can only be gauged by careful observation of the behaviour of the temperature.

If heating is found to be sufficiently great in storage hoppers to require counter measures it is suggested that these may consist of one or more of the following:

1. reducing the amount stored,
2. reducing the period of storage,
3. filling the hoppers, or at least diluting the contained air, with inert gas, e.g. flue gas or carbon dioxide.

Cooling by ventilation, if at all practicable, should be tried only with great caution. It has been noted that heaps of finely divided pyrites tend to heat less readily than coarse material, consequently there is likely to be a wide range of air-flow rates within which ventilation will increase the heating.

Attempts to control the heating by sealing the hoppers may be difficult since, in the oxidation of dry pyrites, three volumes of oxygen are used in the production of one volume of sulphur dioxide which, in a closed hopper, will lead to a pressure reduction of two fifteenths of an atmosphere, i.e. about 2 lb/in².

Acknowledgement

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Addendum

The following references are to recent work in the U.S.S.R. on explosions in pyrites-air mixtures; Ruiss et al. recommend that the precautions against explosions in sulphuric acid plant using pulverised pyrites should be similar to those observed in pulverised coal plant.

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