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THE MEASUREMENT OF THE IGNITION TEMPERATURES OF COMMERCIALLY IMPORTANT SULFIDE MINERALS

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Drop tube furnaces and thermal methods of analysis are techniques used to measure the ignition behaviour of reactive minerals such as sulfides and coals. The use of the two techniques is discussed critically, and results obtained for pyrite and pyrrhotite have been compared. The values for ignition temperature are lower when determined by thermal methods relative to a drop tube furnace. Care must be exercised when comparing results as variables associated with the mineral such as its particle size, stoichiometry, and surface area, all influence its reactivity.

Keywords: drop tube furnaces, ignition temperature, sulfide minerals

Introduction

The ignition reactions of solid materials are of some importance in the industrial context and occur, for example, in pyrotechnic systems, flash smelting and coal combustion. Jorgensen [1] quotes the Shorter Oxford Dictionary definition of ignition as 'the action of igniting, especially heating to the point of combustion or of chemical change: a condition of being so heated or on fire'. Ignition reactions are very fast, and are usually complete in less than one second.

The conditions necessary to induce ignition tend to be more vigorous than those used for normal oxidation reactions. This usually means fast heating rates, high concentrations of oxidant and small particle size. In industrial flash smelting practice, sulfide concentrate is introduced with preheated air as a gas/solid suspension into the top of a reaction shaft. The particles experience heating rates of several thousands of degrees per minute. The hot air environment is such that energy loss from the particles is minimised, causing the temperature of the particles to increase rapidly and to exceed

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the furnace temperature. This overheating effect is sufficient to produce particle melting.

Two parameters of particular interest are the:

– ignition temperature, which is defined as the minimum temperature that the particles need to experience in order to generate a sufficient heating rate to cause ignition. The ignition temperature is not a thermodynamic constant, and hence the value will vary with the technique and conditions used.

– extent of oxidation of samples at various furnace temperatures.

Consequently most studies have measured ignition temperatures and extents of oxidation as a means of assessing the relative reactivity of different minerals. However, other studies have identified the variables that affect these values, and attempts have been made to determine the mechanisms of reaction.

Drop tube furnaces and thermal methods of analysis are two major techniques used for the laboratory scale investigation of ignition reactions. This paper describes these techniques, critically reviews the results obtained, and discusses other factors that can confuse the interpretation of results.

Experimental methods for the examination of ignition reactions

In view of the dependency of the ignition temperature and extent of oxidation on the experimental variables, it is obviously necessary to control these variables in order to make viable comparisons between data.

Drop tube furnaces

A drop tube furnace consists of a vertical tube contained within a furnace [2–4]. Solids can be fed into the top of the tube via screw feeder devices, together with gas which is capable of being preheated. Exit gas can be monitored for composition.

In operation, the tube and input gas are heated to some predetermined temperature. The solid is introduced into the top of the tube where it contacts the gas and forms a suspension. Collection of the quenched product permits chemical and microscopic analysis to be carried out to determine the extent of oxidation and the particle morphology. If no reaction is evident, the furnace and/or preheat gas temperature is raised until ignition is observed.

Two main criticisms can be made of this method:

(a) The solids/gas ratio is usually low compared with industrial systems, meaning that the particles are in a dilute suspension in the carrier gas. Heat generated in the oxidation process tends to be taken up by the environment, and not used for particle self-heating. The heat evolved is also not significant in providing additional heating to the gas phase.

(b) The determination of the ignition temperature is not very precise, and is rarely quoted to better than 50°C. Consequently it is not easy to differentiate between materials of similar ignition temperature.

Thermal methods of analysis

Provided the oxidation conditions are sufficiently vigorous, both DTA and TG can be used to study ignition reactions [5, 6]. The large exothermic effect that occurs on ignition can be detected by DTA, and the rapid mass loss that occurs can be determined by TG.

A more appropriate method is to use TG in an isothermal mode [6]. This method can only be employed if the furnace can be preheated prior to being placed around the sample. The sample is loaded into the pan. The furnace is preheated to a specific temperature and placed around the sample. This produces a heating rate of the order of 5000 deg/min. If no rapid mass loss occurs, the furnace is lowered and a fresh sample loaded. The furnace temperature is raised incrementally until rapid oxidation is evident, and this value, which can be determined to ±5°C, is taken as the ignition temperature. The mass loss is directly proportional to the extent of oxidation, and so by increasing the furnace temperature beyond the ignition temperature plots of percent extent of oxidation against furnace temperature can be constructed. This method enables both parameters to be determined, whereas applying DTA or TG in the usual dynamic heating mode permits determination of the ignition temperature only.

There are criticisms of the use of thermal methods of analysis.

(a) The sample is not suspended in the gas stream, but is in a static bed. Heat and mass transfer effects are thus different to those which prevail in drop tube furnaces or in industrial smelters. This is emphasized by the dependence of the TG ignition temperature on the sample mass, with a decrease in the latter producing a corresponding increase in the former.

(b) Ignited particles still show the angular morphology typical of the unreacted material. Hence the overheating effect is not large enough to cause melting and give the rounded shapes typical of material isolated from industrial flash furnaces.

Table 1 Comparison of the ignition temperatures of sulfides measured using drop tube furnaces and isothermal TG. Numbers in parentheses indicate references

Mineral	Drop tube furnace air atmosphere		Isothermal TG oxygen atmosphere	
	Particle size/μm	Ignition Temp./°C	Particle size/μm	Ignition Temp./°C
Pyrite	37–53	600 [7]	45–75	395 [8]
Pyrrhotite	51	511–623 [3]	45–75	500 [8]

Comparison of results

Relatively few sulfides of similar properties have been studied by the different methods, and so comparative data is scarce. The data collected is given in Table 1.

The first sign of reaction of pyrite in a drop tube furnace was found to occur at 500°C, but the maximum rate of reaction did not take place until 600°C [7]. On the other hand, the isothermal TG method caused samples to be virtually 100% oxidised at a temperature of 395°C [8].

In a drop tube furnace pyrrhotite particles showed a small amount of reaction at a furnace temperature of 511°C [3]. However, the particles still showed the angular shape of the unreacted material. At the next temperature examined of 623°C the particles had melted. Hence the ignition temperature was somewhere between these two values. Using the isothermal TG method an ignition temperature of 500°C was measured for pyrrhotite [8].

Some of the difficulties associated with comparing results can be seen from the above discussion. What do you take to be the ignition temperature? In the isothermal TG method the temperature at which the first major reaction occurs is taken. For the iron sulfides this is easy to detect as over 90% oxidation occurs. In the drop tube furnace experiments, the oxidation takes place over a range of temperatures, with increasing extent of oxidation as the furnace temperature increases. This effect may be due to the time factor, as it has been demonstrated that in a drop tube furnace pyrite takes approximately 0.06 second to be 90% reacted [9] even at 700°C. Hence at lower temperatures the rate of reaction will be slower and the particles may not have sufficient residence time in the hot zone of the furnace to react completely. In the TG method the time factor is less important, as the particles are in the furnace longer. The decay curve for pyrite is typically several seconds at the lower temperatures. If the temperature at which the first reaction occurs is taken as the ignition temperature then the results obtained from the two different methods are closer. However, in general the values obtained from the TG method are lower than those from the drop tube furnace. The contact of the particles in the TG method assists in the heat transfer process, so that when one particle ignites it triggers the ignition of near neighbours.

There is still some confusion in the literature about the effect of oxygen concentration on the ignition temperature, although the balance of evidence suggests that the ignition temperature decreases as the oxygen content increases [10]. Hence the differences between the drop tube furnace and TG methods may be in part due to the significant differences in the atmosphere used.

Other factors affecting ignition temperature measurements

Besides the need to control variables such as the oxygen concentration, isothermal TG work has identified the effects of several variables which

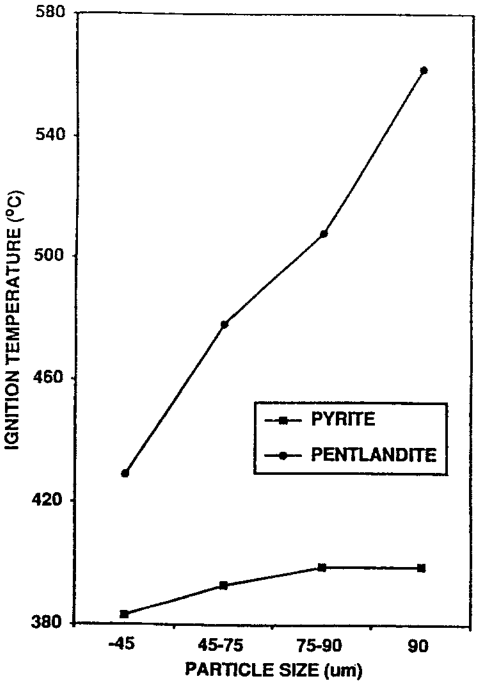

Fig. 1 The influence of particle size on the ignition temperature of pyrite and pentlandite

must be taken into account in order to make viable comparisons between data.

The particle size effect has been shown to vary with the mineral [8]. For example, pyrite exhibits a 15°C difference in ignition temperature between <45 and 90–125 μm fractions compared with a value of 135°C for pentlandite, as shown in Fig. 1. For mixtures, such as sulfide concentrates, the composite minerals will affect the reactivity. For example, pyrite and violarite are much more reactive than pentlandite or pyrrhotite, and so concentrates containing the former will ignite at much lower temperatures than those containing the latter minerals [8]. Hence it is not possible to make valid comparisons between studies made by different workers unless the quantitative phase analysis of the mixture is given. Bulk elemental analysis alone is insufficient.

A more recent finding [11] is that the stoichiometry of an individual sulfide has an effect on reactivity. Pyrrhotite has a range of stoichiometries, from FeS to $Fe_{0.83}S$. The reactivity of synthetically prepared samples increased as they became increasingly sulfur rich. Differences in ignition

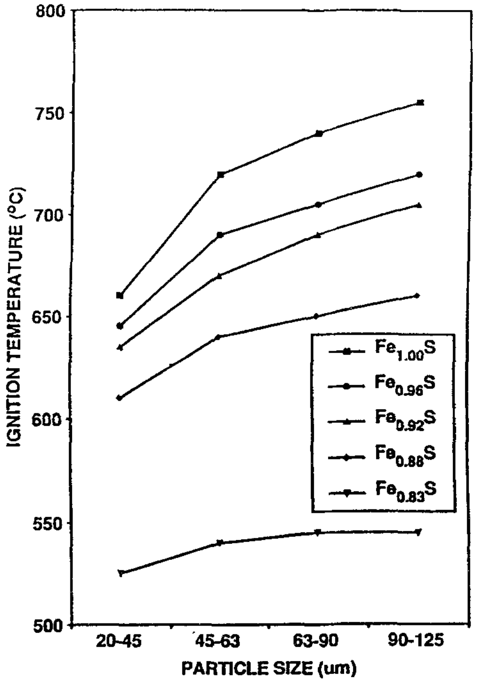

Fig. 2 Variation of ignition temperature with iron-sulfur ratio in a series of pyrrhotites

temperature were as much as 180°C for the particle size range 45–63 μm as shown by Fig. 2.

This information provides some explanation for the different results reported for pyrrhotite. Unless the pyrrhotite has been characterised as an individual mineral comparisons between results are not valid.

Another factor that needs to be taken into account is the surface area of the minerals. Pyrite is capable of being formed by two different mechanisms, giving rise to what are called primary and secondary pyrite. The former is produced directly, whereas the latter is produced by a supergene alteration process whereby pyrrhotite is dissolved and reprecipitated as pyrite [12]. The ignition temperature of the secondary pyrite was some 40°C lower than that of the primary pyrite [13]. The only difference in property that could be detected was the surface area, which was 0.6 $m^2 g^{-1}$ for the secondary form as opposed to 0.1 $m^2 g^{-1}$ for the primary material.

Conclusions

The ignition temperatures and extents of oxidation of sulfides can be measured by drop tube furnace and thermal analytical methods. The results obtained by the two classes of technique vary significantly, with the thermal analysis techniques producing lower values of ignition temperature relative to the drop tube furnace method. Each technique has its advantages. The TG method is fast and gives precise values for the determination of ignition temperatures and extents of oxidation. It is especially useful for investigating the variables that affect the ignition reaction. The drop tube furnace method is useful for studying the morphology of, and phases present in, the particles after they have been ignited. Neither method simulates true industrial flash smelting for the reasons outlined previously. The value of these techniques therefore lies in comparative studies.

Some of the difference in the reported values may not be due entirely to the techniques used, but to differences in the properties of the minerals studied. For true comparisons to be made, the particle size and oxygen concentration need to be controlled. In addition the quantitative phase analysis needs to be known for mixtures, as well as the stoichiometric composition of the individual minerals. Finally other factors which influence the reactivity of solids, such as the surface area, need to be measured.

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Zusammenfassun — Tropfenbombenöfen und thermoanalytische Methoden sind Techniken, die bei der Messung des Entzündungsverhaltens reaktiver Substanzen wie z.B. Sulfide und Kohlen verwendet werden. Die Anwendung beider Techniken wird kritisch diskutiert und erhaltene Ergebnisse für Pyrit und Pyrrhotin miteinander verglichen. Mit thermoanalytischen Methoden erhält man niedrigere Werte für die Entzündungstemperatur als mit Tropfenbombenöfen. Beim Vergleich von Ergebnissen muß Vorsicht gelten, denn alle mit dem Mineral verknüpfte Parameter, wie z.B. Partikelgröße, Stöchiometrie, Oberflächengröße beeinflussen seine Reaktivität.