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APPLICATIONS OF THERMOANALYTICAL METHODS TO STUDIES OF FLASH SMELTING REACTIONS

J G DUNN[1] and S A A JAYAWEERA[2]
[1]School of Applied Chemistry, WAIT, Kent St, Perth, Western Australia 6102
[2]Department of Environmental Sciences, Plymouth Polytechnic, Plymouth, Devon UK

ABSTRACT

DTA and TG techniques were used to measure the ignition temperatures and extents of reaction of nickel sulphide concentrates used as feedstock in flash smelting processes. The values obtained were dependent on the experimental conditions chosen. Under standardised procedures, the thermal properties of concentrates from different sources were measured, and indicated differences in ignition temperatures in the range 20-30°C and differences in extent of reaction of about 20%. These values are significant in terms of smelter operations.

INTRODUCTION

There are many examples in the literature (see for example, ref 1) of mineral sulphide oxidation studies carried out under conditions designed to examine the stepwise oxidation sequence of the various mineral phases present or formed during reaction. However, although DTA and TG have been used to study ignition reactions in pyrotechnic systems (2) and coal (3), this present paper appears to be the first in which the correct conditions are used to study the ignition reactions of mineral sulphides, specifically nickel sulphide concentrates typical of those used in flash smelting processes.

EXPERIMENTAL

Nickel sulphide concentrates were provided by the Kalgoorlie Nickel Smelter, Western Australia and were tested as received. The major sulphide phases present were pyrite, pyrrhotile, pentlandite and violarite.

All DTA experiments were performed using a DuPont 1090 Thermal Analyser equipped with a high temperature (1600°C) DTA cell. Refractory alumina was used as an inert reference material.

TG experiments were performed on a Stanton Redcroft TG 750 thermobalance.

RESULTS AND DISCUSSION

DTA Investigations

Figure 1 shows a DTA record of the same nickel sulphide concentrate heated

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under different experimental conditions. The lower trace was obtained at a heating rate of 10 degrees per minute with 5 mg of sample and a flowing air atmosphere. These conditions favour the stepwise reaction of the individual phases present, and the exothermic peaks are evidence of the sequential oxidation of various iron-nickel sulphides. The reaction scheme is complex (4) and oxidation not complete until 800°C.

Using the more vigorous conditions of a heating rate of 20 degrees per minute, a 15 mg sample, and an oxygen atmosphere caused the sulphide to ignite, producing a very intense DTA peak which occurred over a temperature range of 30°C (Figure 1). A perturbation of the temperature record was also apparent. No further reaction was detected by the DTA above 500°C.

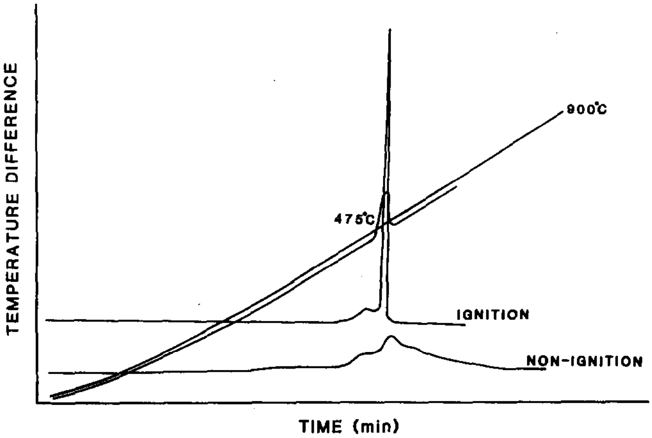

Fig. 1. DTA traces of the oxidation of nickel sulphide concentrate under ignition and non-ignition conditions.

It would obviously be incorrect to derive any information on ignition reactions from the non-ignition experiment. It would also be incorrect to take the ignition temperature as the first exothermic deviation from the baseline in the ignition DTA curve, since this is evidently the exothermic peak from the oxidation of a minor sulphide phase which under these conditions had no significant effect on the ignition reaction. Hence the only correct interpretation of the ignition temperature is the extrapolated onset temperature of the main DTA peak, which had a value of 475°C.

TG Investigations

Thermogravimetric studies on the oxidation of nickel sulphide concentrate under ignition and non-ignition conditions have been previously reported (5). Under non-ignition conditions significant weight gains due to the formation of iron and nickel sulphates were evident followed by decomposition of sulphates and oxidative decomposition of the remaining sulphides. Under ignition conditions, the sulphation reaction was much reduced, and the oxidation occurred over a much smaller temperature range and at a much lower temperature.

The thermobalance used in this work has a small water cooled furnace which is raised around the sample on a cam shaft (6). These characteristics enabled the thermobalance to be used in a novel manner which permitted very fast heating rates to be achieved. The sample was placed in the sample crucible, and the furnace preheated to a specific temperature before raising it around the sample. It was calculated that heating rates of between 4000-5000°C min^{-1} were attained. This technique could be used to determine the ignition temperature, by heating the furnace to a set temperature below the ignition temperature determined by the dynamic TG method and then raising the furnace around the sample. This procedure was repeated on fresh samples until ignition occurred (See Figure 2). Below the ignition temperature the only change was a weight gain due to sulphation but above the ignition temperature a very rapid weight loss occurred.

FIGURE 2.

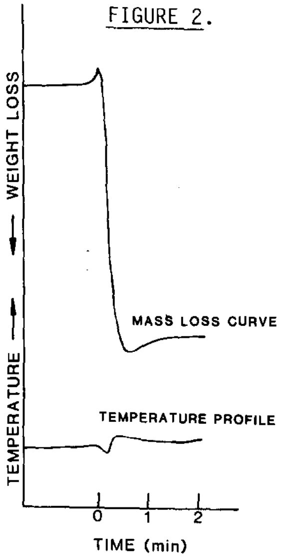

FIGURE 3.

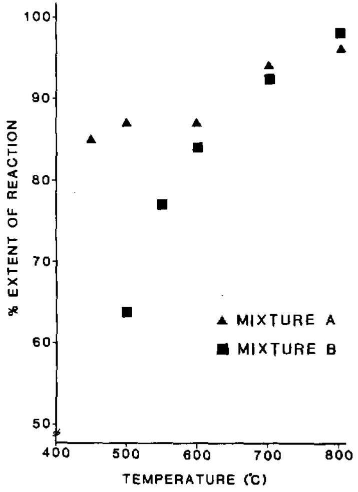

Fig. 2. TG trace of the oxidation of nickel sulphide concentrates using an isothermal technique.

Fig. 3. Extents of reaction for nickel sulphide concentrate as a function of temperature.

Generally the ignition temperatures determined by this approach were lower than those determined by either conventional DTA or TG, although the values were lower only by about 30 degrees at a maximum and were not in proportion to the 200 times increase in heating rate. This suggests that once a heating rate has been reached sufficient to cause ignition then further increments in heating rate have a relatively small effect.

Some ignition temperature values determined by the three methods are given in Table 1.

TABLE 1

Ignition temperatures determined by thermoanalytical methods.

Sample	Ignition Temperature °C		
	DTA	TG	Isothermal TG
Nickel Sulphide Concentrate	475	500	470

The weight loss at any particular temperature is directly proportional to the extent of oxidation at that temperature. Hence by determining the maximum possible weight loss, plots of percentage extent of reaction against temperature can be obtained (see Figure 3). These plots give an indication of relative extents of reaction for different nickel concentrates or concentrate blends at various air pre-heat temperatures. In the example shown, it is evident that the mixture A is much more reactive than mixture B, the former having achieved 85% reaction at 500°C compared with only 63% reaction at the same temperature for the latter.

CONCLUSION

DTA and TG techniquescan be used under well controlled standardised conditions to compare the ignition temperatures and extents of reactions of nickel sulphide concentrates and mixtures. This information is of value to efficient flash smelter management.

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