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Thermochimica Acta 293 (1997) 143–151

thermochimica
acta

Enthalpy determinations and adsorption behaviour in the coal pyrite–sodium acrylate co-polymer system: effects of pH

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Received 5 March 1996; accepted 10 December 1996

Abstract

The thermal oxidation of coal pyrite in an air atmosphere has been studied by differential scanning calorimetry (DSC) as a function of Magnafloc 74L addition and system pH. DSC heat flow curves show that the thermal oxidation of coal pyrite between 0° and 500°C is a three-stage exothermic process. Enthalpy data indicate that the adsorption of Magnafloc 74L at the coal pyrite–water interface is fundamentally different at pH 8 to that at pH 6 and 10. When considered in conjunction with electrokinetic (zeta potential) data, it is concluded that the anionic co-polymer adsorbs in an anionic form at pH 6 and pH 10, whereas at pH 8 adsorption is in the form of a non-ionic or charge reduced species. © 1997 Elsevier Science B.V.

Keywords: Adsorption; Coal pyrite; DSC; pH; Sodium acrylate

1. Introduction

In recent years, concerns over SO_2 emissions from coal-fired power generation plant have resulted in demands for coal products with a significantly lower pyritic sulphur content. Superimposed upon this, the quantity of fine (−0.063 mm) material in a typical raw coal entering the coal processing plant has, on average, increased by a factor of four [1] as a consequence of mechanised mining methods. At present, the treatment of this fine material is difficult, since conventional processing techniques are rendered ineffective or suffer from lower efficiencies at these particle sizes. Consequently, these troublesome fines are often simply discarded, representing not only an economic loss in terms of reduced recovery values, but also resulting in higher operating costs associated with its safe and environmentally acceptable disposal.

Two new processes being developed to meet the criteria of operating at ultrafine particle sizes and improving pyrite removal are selective flocculation and selective dispersion [2]. Both techniques have a common starting point, in that it is necessary to have at least one mineral species forming a stable phase with respect to particle sedimentation. Although this can be achieved, at least in part, by operating at reduced particle sizes, complications arise from the presence of a number of attractive interparticulate forces, which result in the aggregation of fine particles. In practice, the inherent instability of fine particulate minerals/solids can be overcome by the use of a suitable dispersing agent which provides either an enhanced electrostatic or steric repulsion mechanism, or both.

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PII S0040-6031(97)00010-5

This requires the adsorption of the dispersing agent at the mineral–solids interface, hence data relating to the various adsorption phenomena are of particular importance when identifying or designing suitable reagents with mineral selective properties.

In this study, differential scanning calorimetry (DSC) and zeta potential measurements have been used to examine the adsorption behaviour of Magnafloc 74L – a low molecular weight anionic polyelectrolyte dispersant – at the coal pyrite–water interface. The experimental data presented indicate that the adsorption mechanism present is dependent upon the pH of the system.

2. Experimental

2.1. *Materials and sample preparation*

The anionic dispersant selected for study was Magnafloc 74L (supplied by Allied Colloids, UK), as it has previously been shown to be a suitable dispersant for bituminous coals [3,4]. Manufacturer's data indicates that it is a co-polymer of sodium acrylate and a monomer containing sulphonate groups, with a 3000–5000 molecular weight range. Throughout the investigations, the liquid polymer was added in the form of a dilute 0.1% or 0.01% w/w solution, fresh solutions being prepared in distilled water prior to use. A solid sample of Magnafloc 74L was obtained by drying at 30°C over a period of two weeks and then hand grinding for evaluation by DSC.

Specimens of 'pure' coal pyrite were obtained as 'lily' pads from a source in Illinois, USA. X-ray diffraction and chemical analysis indicated that the samples were of very high purity. The samples were initially crushed to a maximum size of 0.5 mm and stored in sealed plastic bags. Prior to use in experimental investigations, 20 g sub-samples were pulverised in a laboratory Tema mill for 2 min. Subsequent size analysis indicated that sub-samples were reduced to 90% – 0.040 mm in size by this technique.

2.2. *Methods*

DSC studies were conducted using a Du Pont 2000 thermal analyser with standard DSC 10 cell base at a heating rate of 10°C min^{-1} in an air atmosphere and a sample mass of 0.032±0.002 g. Samples were prepared for each test by placing 20 g of pulverised coal pyrite in a conditioning tank and adding the appropriate quantity of distilled water, adjusted to the pH to be studied, to form a 2% w/v suspension. After 2 min conditioning at 1100 rev min^{-1}, the pH was adjusted back to its original value and a quantity of Magnafloc 74L was introduced. After a further 5 min conditioning, final pH adjustment was made and the system was allowed to condition for 10 min. The solids were then recovered by filtration and dried under vacuum before being presented for DSC. Identical 'blank' tests without any addition of Magnafloc 74L were also carried out.

Electrokinetic studies were undertaken using a Rank Brothers MKII electrophoresis unit with a flat cell configuration at 30°C. Measured electrophoretic mobilities were converted to zeta potential values by means of the Smoluchowski expression. In each determination, a 0.05 g sample was placed in a baffled conditioning vessel with 1.0 L of distilled water, previously adjusted to the pH to be studied. The suspension was conditioned for 10 min at 1100 rev min^{-1}; no further pH adjustment was made during this period. A pre-determined quantity of Magnafloc 74L was then introduced as a dilute (0.01% w/w) solution and conditioning continued for 8 min, after which the pH was readjusted to the original level and the suspension conditioned for a further 2 min. A 300 mL sample was then withdrawn from the vessel. To ensure a particle size range suitable for zeta potential determination, the sample was allowed to stand for 2 min before a small quantity was withdrawn from the upper portion and introduced to the flat cell of the electrophoresis unit.

3. Results and discussion

3.1. *DSC studies*

The DSC heat flow curve for dried solid Magnafloc 74L in an oxidising environment is shown in Fig. 1. The curve is characterised by the presence of both strong endothermic and exothermic features. The initial endotherm displays a maximum located at 113.84°C and is the result of sample dehydration

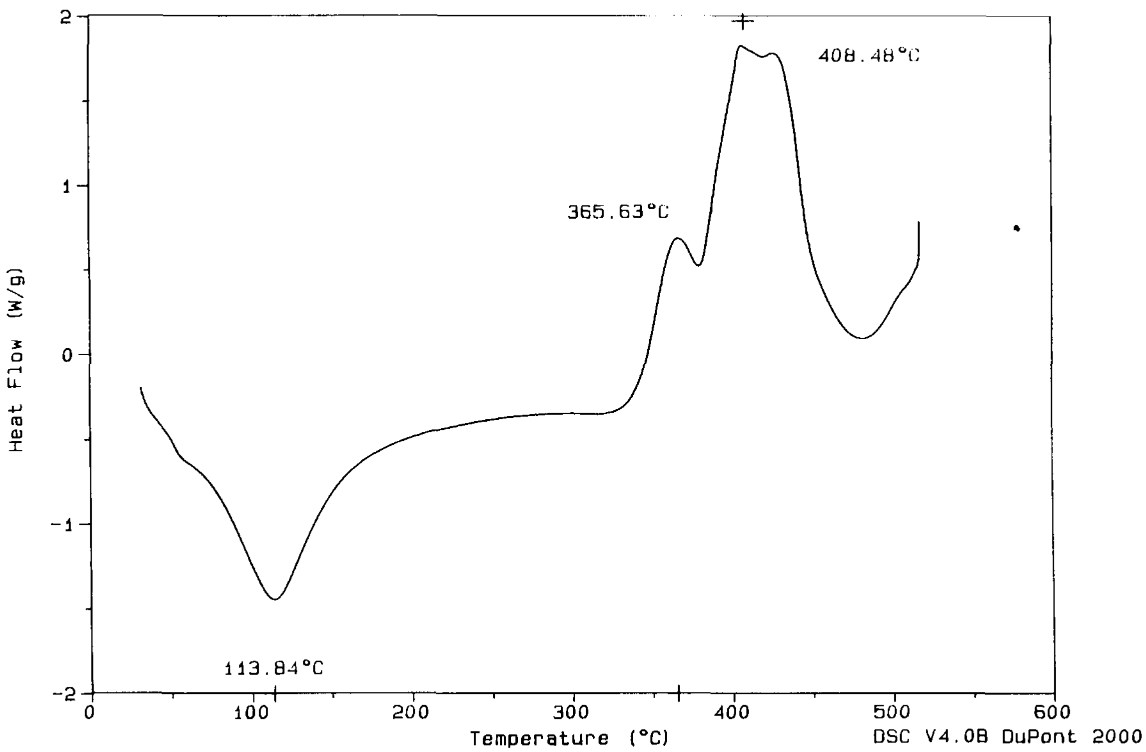

Fig. 1. DSC thermal oxidation curve for dried Magnafloc 74L.

effects caused by the loss of either surface adsorbed moisture or incomplete water removal during the drying of the liquid polymer sample. It is also evident that, at higher temperatures, the curve is characterised by two distinctive regions, each dominated by exothermic features located at 366° and 408°C, respectively. Previous NMR studies [5] have shown that heating polyacrylic acid (PAA) to temperatures ~350°C results in massive degradation of the polymer. At these temperatures, the PAA structure becomes increasingly aromatic in nature; the formation of a limited number of methyl groups, possibly from the breaking of methylenes, is also indicated. Continued heating of PAA to temperatures in excess of 400°C virtually eliminates the remaining traces of aliphatic structures, while hydroxy-bearing aromatics (phenols) appear. From Fig. 1 it can be seen that the onset of exothermic behaviour at 325°C and the subsequent peak maximum at 365°C show a marked similarity to the previously reported value of 350°C for the formation of aromatics [5]. Similarly, the second and larger exothermic feature located between 400° and 450°C is thought to be the result of the formation of phenolic type structures.

DSC heat flow curves for coal pyrite under oxidising conditions as a function of pH and Magnafloc 74L addition are presented in Figs. 2–4. Examination of the data recorded at temperatures below 200°C indicates that the thermal response of coal pyrite is endothermic in nature. At temperatures above 200°C, however, the response becomes exothermic and is characterised by the presence of two distinctive features – a sharp exotherm located at 260–270°C and a broad exotherm between 350° and 450°C, with a peak maximum around 390–420°C. A sharp endotherm is then observed at temperatures in the region of 480–490°C. The oxidation of mineral pyrite has already been studied by thermal analysis techniques [6–9] and the general consensus is that the final product is hematite, although various pathways invol-

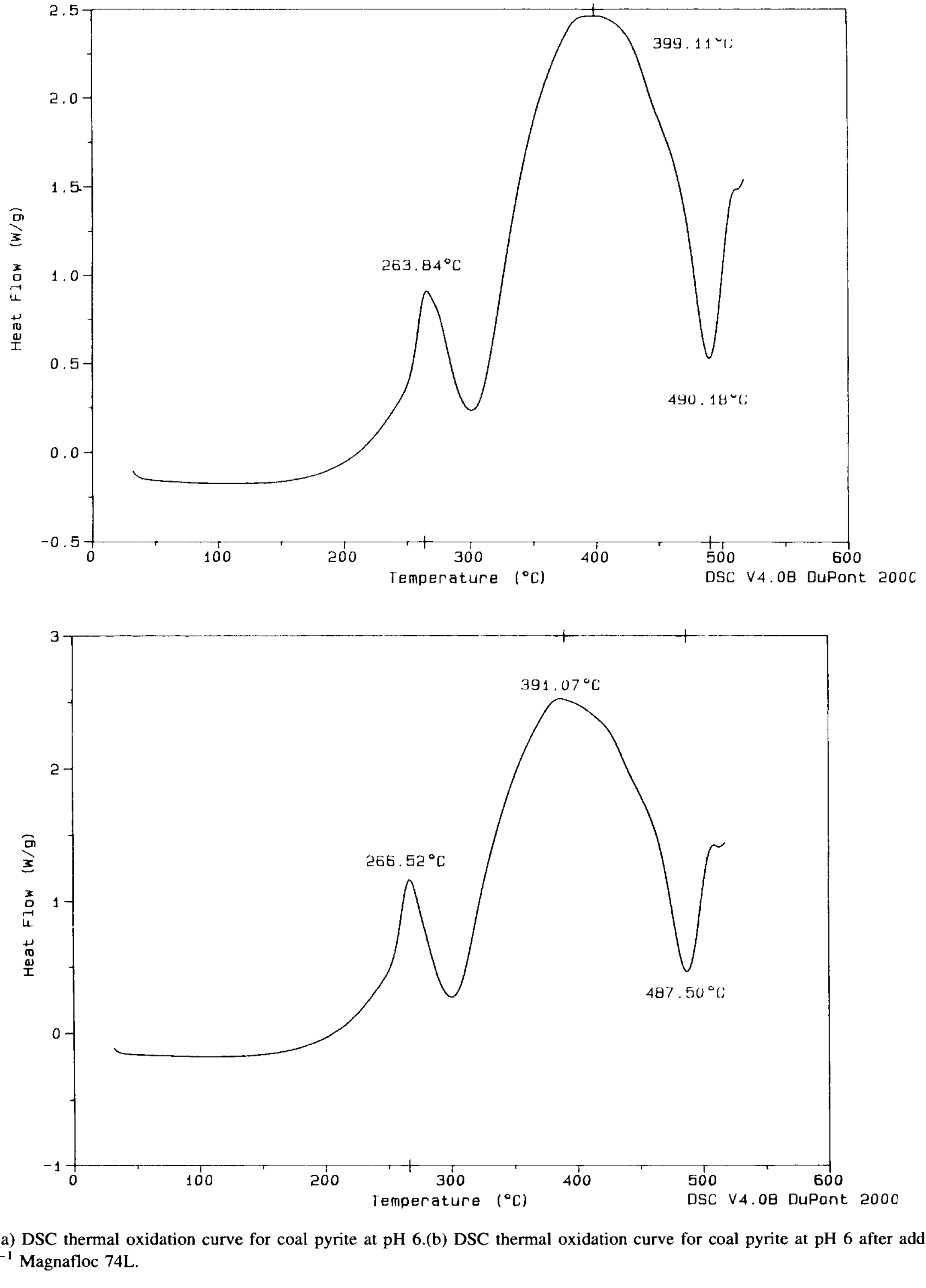

Fig. 2. (a) DSC thermal oxidation curve for coal pyrite at pH 6.(b) DSC thermal oxidation curve for coal pyrite at pH 6 after addition of 0.2 g kg^{-1} Magnafloc 74L.

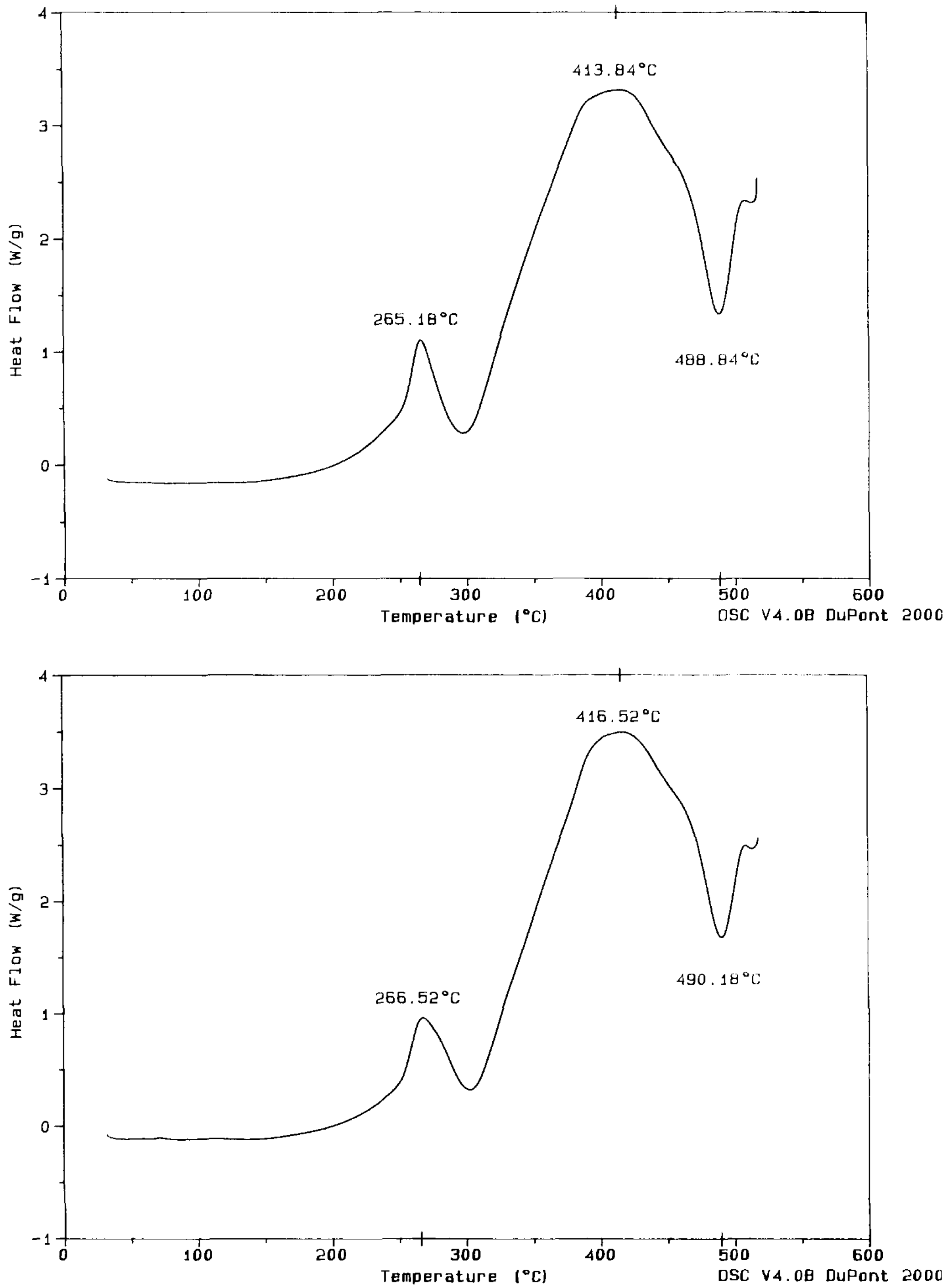

Fig. 3. (a) DSC thermal oxidation curve for coal pyrite at pH 8. (b) DSC thermal oxidation curve for coal pyrite at pH 8 after addition of 0.2 g kg^{-1} Magnafloc 74L.

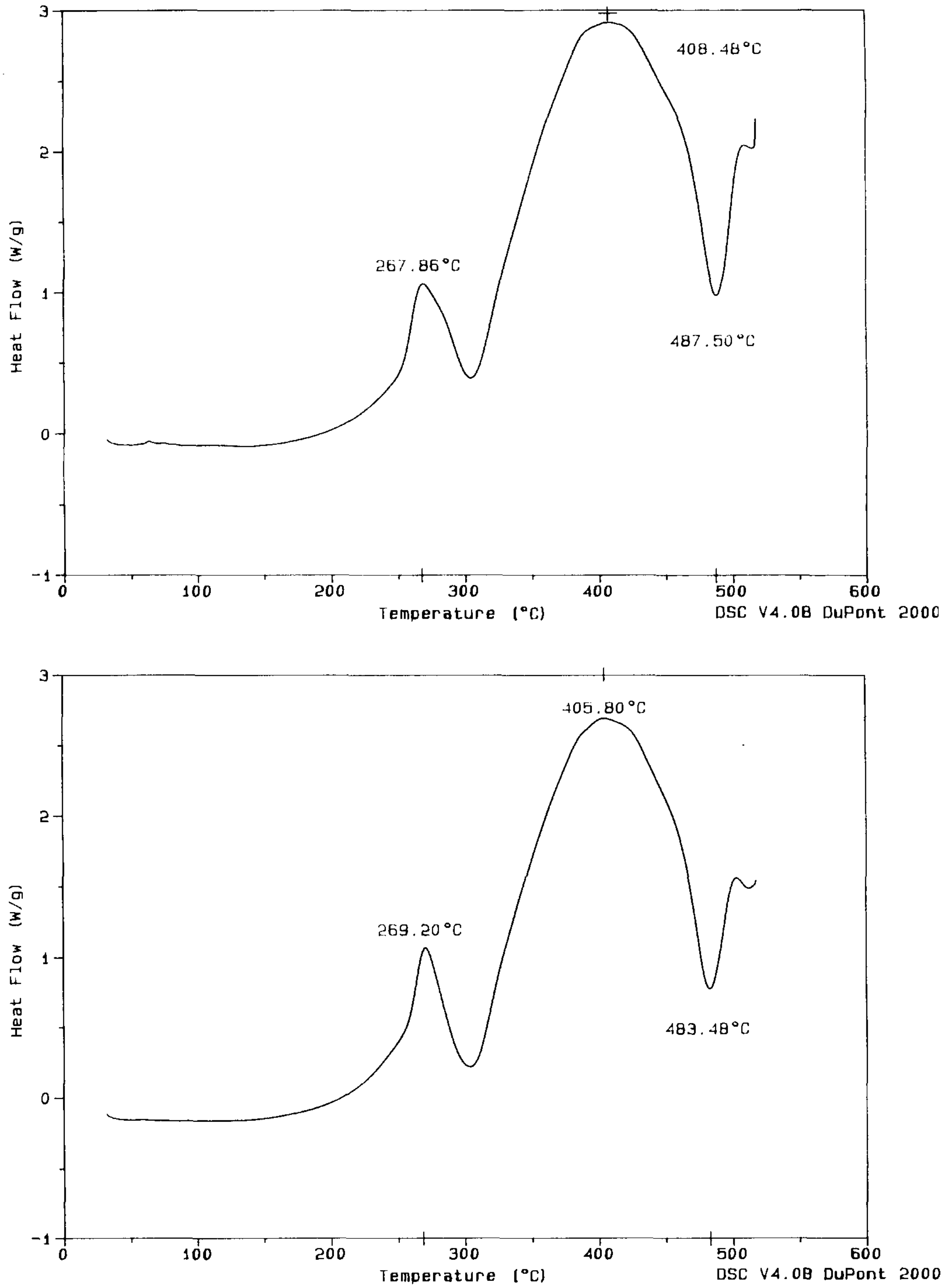

Fig. 4. (a) DSC thermal oxidation curve for coal pyrite at pH 10. (b) DSC thermal oxidation curve for coal pyrite at pH 10 after addition of 0.2 g kg^{-1} Magnafloc 74L.

ving both the direct oxidation and the involvement of intermediate iron sulphate moieties have been proposed.

From Figs. 2 and 4, two distinctive and separate observations can be made regarding the adsorption of Magnafloc 74L on coal pyrite at pH 6 and pH 10, respectively. The first of these relates to the presence of Magnafloc 74L at pH 6 (Fig. 2) at the coal pyrite surface which produces shifts in the recorded peak maxima of the two exothermic features, with the initial peak at 263°C being raised to 266°C and the second broad exotherm lowered from 399° to 391°C. The high-temperature endotherm observed at 490°C is also seen to be reduced to 487°C. Similarly, the data at pH 10 (Fig. 4) follow the same trends, with the initial exotherm being raised to 269° from 267°C and the second exotherm being lowered from 408° to 405°C. Again. the high-temperature endotherm is lowered from 487° to 483°C.

If the data in Fig. 3, which show the corresponding thermal oxidation effects for coal pyrite at pH 8 as a function of Magnafloc 74L addition, are considered in conjunction with the data in Fig. 2 and Fig. 4, a noticeably different sequence of temperature shifts is observed. The initial exothermic feature, in common with those seen at pH 6 and pH 10, is shifted to higher temperatures on addition of Magnafloc 74L, but the secondary exotherm and high-temperature endotherm are raised from 413° to 416°C and from 488° to 490°C, respectively, in the presence of Magnafloc 74L. The data summarised in Table 1 clearly demonstrate that the thermal response (as indicated by peak maxima) at pH 8 is contrary to that observed at pH 6 and 10.

A second feature observed from Figs. 2–4 is the relative effect of Magnafloc 74L addition on the enthalpy changes associated with the thermal air oxidation of coal pyrite. Enthalpy values were calculated for each of the systems under investigation by means of the internal software contained within the Du Pont 2000 thermal analyser and the results are summarised in Table 2. These results suggest the adsorption response of the polymer at the coal pyrite interface at pH 8 is very different to that observed at pH 6 and pH 10. From Table 2 it is evident that adsorption of Magnafloc 74L raises the enthalpy values obtained for the primary and secondary exotherms at both pH 6 and pH 10, whereas for pH 8 the enthalpy values are lowered for both the primary and secondary exotherms, under the same conditions. When considered with the DSC thermal peak maxima data, this reinforces the conclusion that the adsorption of Magnafloc 74L at the coal pyrite–water interface is fundamentally different at pH 8 to that at other pH levels studied.

3.2. *Electrokinetic studies*

Although results from the DSC investigations indicate that the adsorption phenomena associated with the Magnafloc 74L–coal pyrite interface are strongly dependent on the system pH, they provide little information on the form of adsorption at the surface. Therefore, the polymer adsorption behaviour was investigated further by means of an electrokinetic (zeta potential) technique as a function of Magnafloc 74L dosage and system pH. Zeta potential data presented in Fig. 5 show that, with the exception of pH 6,

Table 1
Summary of DSC thermal oxidation data for coal pyrite at pH 6–10

	1st exotherm (°C)	2nd exotherm (°C)	Endotherm (°C)
pH 6 (no polymer)	263.84	399.11	490.18
pH 6+ polymer	266.52	391.07	487.50
Net change	+2.68	−8.04	−2.68
pH 8 (no polymer)	265.18	413.84	488.84
pH 8+ polymer	266.52	416.52	490.18
Net change	+1.34	+2.68	+1.34
pH 10 (no polymer)	267.86	408.48	487.50
pH 10+ polymer	269.20	405.80	483.48
Net change	+1.34	−2.08	−4.02

Table 2
Enthalpy data for the coal pyrite-Magnafloc 74L system at pH 6–10

	No polymer addition			With polymer addition		
Peak start (°C)	200	305	470	200	305	470
Peak end (°C)	300	470	502	300	470	502
pH 6						
Peak maximum (°C)	263.8	399.1	490.1	266.5	391.1	487.5
Enthalpy (J g^{-1})	159.4	1034.0	78.2	189.8	1109.0	86.1
Enthalpy (kJ mol^{-1} FeS_2)	19.1	124.0	9.4	22.8	133.0	10.3
pH 8						
Peak maximum (°C)	265.2	413.8	488.8	266.5	416.5	490.2
Enthalpy (J g^{-1})	166.1	1127.0	95.9	148.1	991.1	76.1
Enthalpy (kJ mol^{-1} FeS_2)	19.9	135.0	11.5	17.8	118.0	9.1
pH 10						
Peak maximum (°C)	267.9	408.5	487.5	269.2	405.8	483.5
Enthalpy (J g^{-1})	149.6	1017.0	99.6	176.9	1106.0	74.6
Enthalpy (kJ mol^{-1} FeS_2)	17.9	122.0	11.9	21.2	132.0	8.9

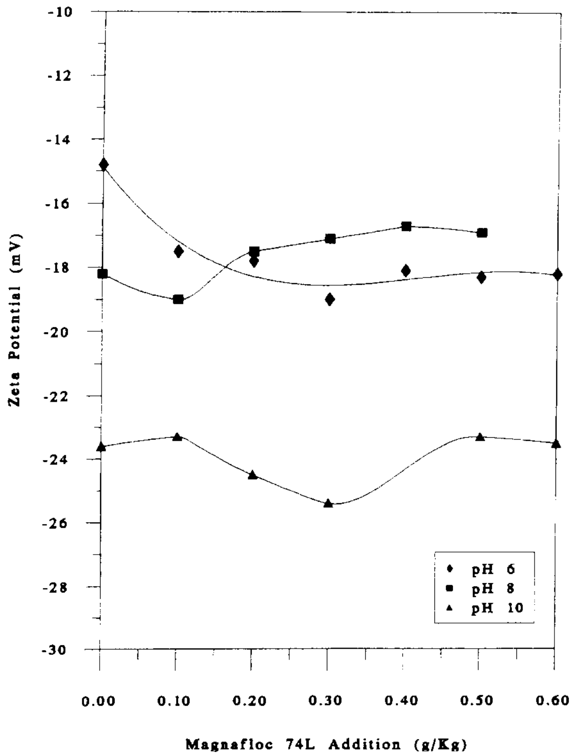

Fig. 5. Effect of Magnafloc 74L addition on zeta potential of coal pyrite at pH 6–10.

the presence of the sodium acrylate co-polymer at the coal pyrite surface produces very little increase in the electronegativity. Given that Magnafloc 74L is an anionic dispersant, it would be expected that adsorption would render the surface more negative, so the effects observed imply that uptake of polymer is slight. Further inspection of Fig. 5 reveals that dosage-dependent adsorption behaviour is displayed in the alkaline pH region. At pH 8, only a minor increase in zeta potential is observed at a dosage of 0.1 g kg^{-1}, with further additions resulting in lower zeta potentials. This type of behaviour is indicative of the adsorption of either cationic or non-ionic species at a mineral/solid surface. The results obtained at pH 10 show that zeta potentials are raised by $\approx$2 mV in the presence of 0.2–0.3 g kg^{-1} Magnafloc 74L, while remaining constant outside this range. Previously published data [4,5] indicate that the adsorption of Magnafloc 74L at the bituminous coal–water interface under conditions of alkaline pH results in significant increases in the observed zeta potential. This would tend to suggest that the adsorption phenomena observed at pH 8 in Fig. 5 are not simply the result of polyelectrolyte pH effects (degree of ionisation, chain extension, etc.), but are more complex mineral pH-specific adsorption phenomena. The zeta potential response at pH 8 also supports the DSC data, which indicated that the adsorption behaviour of the sodium acrylate co-polymer is indeed fundamentally different at pH 8 to that observed at other pH values.

It is likely that the coal pyrite response at pH 8 is the result of alterations in surface chemistry caused by changes in pH. Evidence for this is suggested in solution speciation diagrams for the iron aqueous system [10,11] which show the proportions and types of different iron species present in solution. At low total iron concentrations, ferric hydroxide $Fe(OH)_{3(aq)}$ and ferrous hydroxide $Fe(OH)^+$ are at, or close to, their maximum concentrations at pH 8. Since the presence of positively charged iron species at the solid–liquid interface would provide adsorption sites via enhanced electrostatic attraction and would, by definition, produce a net reduction in the electronegative charge of the anionic polyelectrolyte, it is possible that the apparently contradictory zeta potential response is due to the formation of a non-ionic or charge-reduced iron-sodium acrylate complex. However, it is not clear from the experimental data whether these complexes are formed at the mineral surface or in the bulk solution phase and, subsequently, adsorbed at the solid interface. It is already known that short-chain carboxylic acid (and sulphonate) based reagents are capable of forming complexes with multivalent metal cations [12]. These oxo-anions act as ligands with one or more oxygen atoms bound to the metal. In the case of larger chain polyelectrolytes, it might be possible for adjacent functional groups or, given the flexibility of the polymer backbone, for multiple interactions between carboxylates to allow the formation of a chelating structure. However, based on the evidence available at this stage, it is not possible to state with certainty which mechanism predominates in this system.

4. Conclusions

This study has examined the thermal oxidation of coal pyrite in an air atmosphere by DSC techniques as a function of Magnafloc 74L addition and system pH. The data indicate that a three stage exothermic process is involved in the 0–500°C range. Enthalpy data suggest that the adsorption of the co-polymer at the coal pyrite–water interface is different at pH 8 to that at pH 6 and pH 10. When additional electrokinetic data are taken into account, it is concluded that the co-polymer adsorbs in an anionic form at pH 6 and pH 10, but at pH 8 the adsorption is in the form of a non-ionic or charge reduced species.

The data presented also suggest that Magnafloc 74L has potential as a coal-selective dispersing agent in the removal of pyritic sulphur from coal by selective flocculation.

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