Journal of Thermal Analysis, Vol. 33 (1988) 435–440

POTENTIAL FOR COAL CALORIFIC VALUE CORRECTIONS, DEPENDENT ON THE CARBONATE MINERAL TYPE PRESENT

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In addition to calcite, other carbonate minerals in coal all undergo endothermic reactions on heating, i.e. dolomite, ankerite, siderite, aragonite, magnesite, rhodochrosite, witherite and strontianite. Of these, when determined in air, siderite and rhodochrosite give small exothermic resultants, while the amount of Fe in ankerites affects the actual endothermic values obtained. The magnitude of these carbonate decomposition reactions can be shown by DTA to be different and will need to be allowed for individually in calorific value corrections of coals containing them.

Detailed research has established that corrections to calorific values of lignites of the Hula Basin, Israel, due to the presence of calcite $CaCO_3$ are necessary [1]. This is due to the single strongly endothermic decomposition reaction of calcite by which it is characterised and identified [2]. Its presence will therefore influence detrimentally the calorific value determinations of coals of all other ranks.

In this case [1] only calcite was present, however it is well established [3, 4] that, in addition to calcite, other carbonate minerals are often present in coals of various ranks, i.e. dolomite $CaMg(CO_3)_2$, ankerite $Ca(Mg, Fe)(CO_3)_2$, siderite $FeCO_3$, aragonite $CaCO_3$ (orthorhombic), magnesite $MgCO_3$, rhodochrosite $MnCO_3$, witherite $BaCO_3$ and strontianite $SrCO_3$. Of these, only dolomite, ankerite and siderite may occur commonly and in sufficient proportions in coal to significantly affect the calorific value of individual coals (plus magnesite in oil shales).

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Akadémiai Kiadó, Budapest

Experimental

Natural minerals (purity confirmed by XRD) were crushed to pass a 200 mesh British Standard sieve and determined with a heating rate of 10 deg min^{-1} under the conditions with the equipment described elsewhere [5].

Results and discussion

The thermal reaction characteristics of these carbonates on heating have been established by differential thermal analysis (DTA) in a furnace atmosphere of flowing nitrogen, see Fig. 1 curves 1 to 5. Furthermore, a method has been established whereby, under controlled inert atmosphere conditions of flowing N_2 or CO_2 the presence of these carbonates in coal may be detected down to <1% and their content evaluated [2].

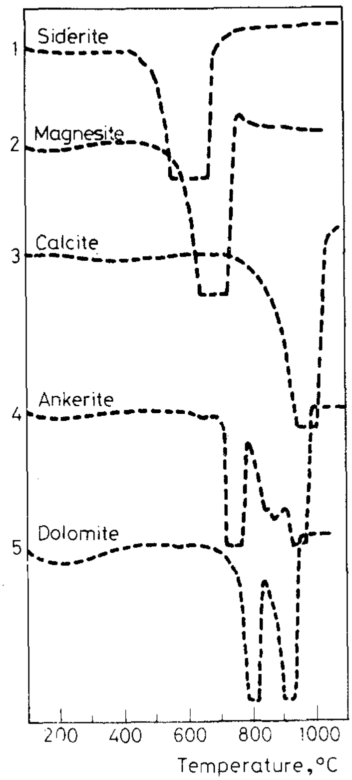

Fig. 1 DTA curves obtained in flowing N_2 from 100% samples of the minerals indicated

Under inert gas conditions it can be seen that in all cases for the minerals shown in Fig. 1, the decomposition reactions involve endothermic reactions. However, the decomposition temperatures differ as do the magnitude and number of the reactions involved, i.e. the decomposition of siderite, magnesite and calcite involves one reaction (Fig. 1 curves 1 to 3), while dolomite and ankerite have two and three respectively (Fig. 1 curves 5 and 4).

In air FeO (wustite) liberated by the decomposition of siderite or ankerite will oxidise exothermally, see Fig. 2 curves 2, 3 and 4 (even to the extent of reducing CO_2 present to CO). Such exothermic effects contribute towards negating the endothermic decomposition reactions involved.

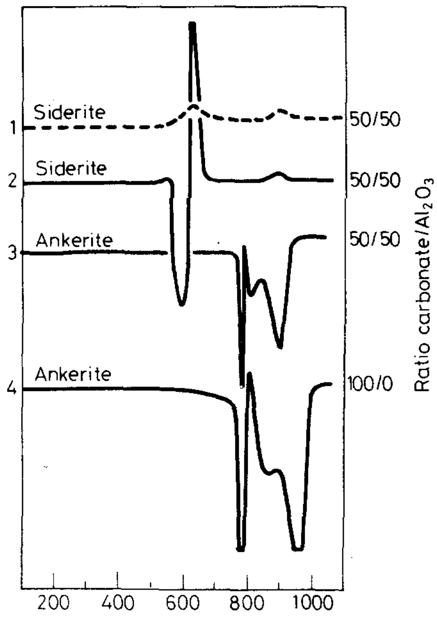

Fig 2 DTA curves obtained in static air ———— and flowing O_2 — — — — from samples of siderite and ankerite diluted where indicated with calcined Al_2O_3

For pure siderite determined in air it can be seen from Fig. 2 curve 2 that the endothermic and immediately following exothermic reactions overlap making the assessment of their thermal effects difficult. However, when the oxidation reaction is promoted by determination in flowing O_2, it can be seen that the resultant is a modest exotherm.

Thus pure or high Fe content siderites on decomposition will contribute, not detract from the calorific value of the coals which contain them. Conversely, as siderite forms a complete natural isomorphous substitution series with magnesite, many siderites will contain variable amounts of Mg substituted in the lattice of the series. Research using thermomagnetometry on a limited number of members of this series [6] has established that the presence of Mg results in the formation of magnesium ferrite $MgFe_2O_4$. This forms at the expense of oxidation, thus reducing the exothermic effect which, when enough Mg is present, will cease to exist. Thus only pure and high Fe content siderites will give exothermic resultants on heating in air.

In general terms, the same will apply to the isomorphous substitution series ankerite-ferroan dolomite-dolomite. In this series, as the Fe content falls, it will eventually provide no exothermic contribution, the presence of which negates to varying degrees the overall multi-peaked endothermic reactions involved.

The magnitude of the enthalpies of the endothermic decomposition reactions of the five carbonate minerals discussed herein may be calculated for pure examples when determined in the absence of O_2, i.e. in N_2. When placed in order of increasing magnitude (Table 1) it may be clearly seen that these effects will increasingly reduce the intrinsic calorific value of coals in the order siderite, magnesite, calcite and dolomite, whilst data for ankerites are not available.

Figures for the enthalpies of decomposition of ankerite are not available in the literature probably due to its variability with changing chemical composition. However, it is likely to be somewhat less than for dolomite due to the substitution of Fe in the lattice.

The enthalpy data (Fig. 2) show that the presence of these specific carbonates will require different calorific value corrections. Furthermore, in the presence of O_2 the values for magnesite, calcite and dolomite will be unaffected, remain endothermic and detract from the intrinsic calorific value of coal. However, the values for siderites (substituted with varying amounts of Mg) and ankerite (substituted with varying amounts of Fe) are not constant and will require a range

Table 1 Calculated enthalpies of carbonate mineral decompositions in nitrogen, as obtained from data stored in the CSIRO–SGTE thermodata system

Mineral name	ΔH (calc.), $kJ \cdot mol^{-1}$
Siderite	79
Magnesite	112
Calcite	170
Dolomite	294
Ankerite	n.a.

n.a. = not available

of different correction values dependent upon the degree of ionic substitution which has taken place. Specifically, however, high Fe siderites usually found in coals will contribute exothermally to increase the calorific values of coals containing them.

Conclusions

The technique of DTA has been shown to be suitable for detecting the presence, type and approximate amount of these carbonate minerals common in coals (and oil shale), thus allowing approximate positive and negative calorific value corrections to be made possible (the DTA characteristics of the lesser carbonates mentioned have previously been determined [7]).

It remains now to quantify the different thermal effects produced by the thermal decomposition of these carbonates by the new technique of high temperature differential scanning calorimetry (DSC). With the development of the necessary high temperature DSC calibration method [8] and the establishment of its general applicability to mineralogy [9], a follow-up study applying DSC to this topic was initiated. This is showing promise and is to be prepared for publication in the near future [10].

Of particular value will be the potential predictive applications to the upgraded calorific values likely to be produced from high ash coals ($\sim$25 to 35%). Such coal washing processes reduce the ash content including the carbonate minerals present.

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Zusammenfassung — Nicht nur Kalkspat, sondern auch andere in Kohle vorkommende Karbonatmineralien wie z. B. Dolomit, Ankerit, Spateisenstein, Aragonit, Magnesit, roter Braunstein, Witherit und Strontionit gehen bei Erhitzen endothermische Reaktionen ein. Von diesen zeigen Spateisenstein und roter Braunstein exotherme Ergebnisse kleinen Wertes, während der Betrag an Eisengehalt in Ankeriten den jeweils gemessenen endothermischen Wert beeinflußt. Das Ausmäß dieser Karbonatzersetzungsreaktionen kann durch DTA-Messungen als unterschiedlich nachgewiesen werden und muß bei den Kaloriewertkorrektionen für Kohlen, die diese Mineralien enthalten, berücksichtigt werden.

Резюме — В дополнение к кальциту и другие находящиеся в углаях карбонатные минералы, как доломит, анкерит, сидерит, арагонит, магнезит, родокрозит, витерит и стронцианит, при нагревании подвергаются эндотермическим реакциям. Из всех минералов, только сидерит и родокрозит в атмосфере воздуха дают небольшие экзотермические пики, тогда как различное содержание железа в анкеритах оказывает влияние на полученные эндотермические пики. Методом ДТА установлен различный характер реакций разложения этих карбонатов, вследствии чего в каждом отдельном случае требуется коррекция теплотворной способности углей, содержащих указанные карбонаты.