Thermal behaviour of mineral fractions separated from selected American coals

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The thermal behaviour of four samples of mineral matter, whose quantitative mineralogical compositions had previously been determined, was investigated using thermogravimetric and derivative thermogravimetric analysis methods. The mineral fractions were initially separated from the coal substance by a low-temperature ashing technique. The decomposition of the individual mineral species associated with coals is briefly reviewed. A synthetic standard mineral mixture was examined under various combustion atmospheres. X-ray diffraction analysis was utilized to study the high-temperature phases yielded by the mineral fractions. Ash-fusion data were also obtained, and can be understood in relation to the corresponding mineralogical analyses. No evidence was found of solid-state interactions below $1100°C$.

Much of the research into coal utilization today is particularly concerned with combustion and gasification, fields in which the mineral constituents of the coal can be of great importance. Chemical reactions which occur in the mineral-matter phase during combustion and gasification of coal at high temperatures are not as yet fully understood. This investigation, which involved a thermal study of mineral-matter fractions in selected coals and how their properties changed chemically and physically upon heat treatment, was aimed at expanding our knowledge in this area.

Coals contain mineral components in varying amounts; and, in general, these minerals are intimately mixed with the combustible organic material. During the pyrolysis of a coal, its mineral matter can contribute thermal effects which are worthy of investigation. The behaviour of coal minerals during combustion and gasification is governed by several factors including chemical composition, the initial distribution of minerals within the fuel particles, the degree of mixing of different constituents which may occur as reaction proceeds, and the composition of the incoming and product gases. By evaluating these thermal effects, some predictions may be made concerning the behaviour of the inorganic fraction of coals in various thermal processes.

Four coal samples of different rank were selected for this study: an Illinois high-volatile bituminous coal (PSOC–24), a Pennsylvania anthracite (PSOC–82), a West Virginia low-volatile bituminous coal (PSOC–132), and an Alabama medium-volatile bituminous coal (PSOC–135). Quantitative analysis of the mineral matter of these samples had revealed significant differences in their mineralogical compositions[1]. Mineralogical composition was, therefore, the primary basis for sample selection.

EXPERIMENTAL

The mineral-matter fractions were separated from the coals by low-temperature ashing in an oxygen plasma. Details of this procedure have been described previously[2].

Thermogravimetric analysis (TGA), differential thermal

analysis (DTA), and derivative thermogravimetric analysis (DTGA) experiments were carried out with a Fisher Series 100A thermal analysis system. In the TGA system, the sample (here 5–10 mg) is suspended from the beam of an automatic recording balance (Cahn RG Electrobalance) installed in the top compartment of a support cabinet. The platinum sample pan is enclosed in a quartz 'hangdown' tube inserted in the furnace. The weighing cabinet has gas connections that enable one to surround the sample with an inert or reactive atmosphere of static or flowing gas. The programming unit controls the temperature of the furnace and increases or decreases it at a rectilinear rate. The programmer allows a choice of 8 program rates from 0·5 to $25°C/min$ ($10°C/min$ was used); the operating range is from ambient temperature to $1100°C$. When the temperature of the sample changes, any change in its weight is automatically recorded by the Electrobalance and charted on a two-channel recorder. A Platinel I thermocouple in the hangdown tube, close to the suspended sample, records its temperature throughout the analysis.

Derivative thermogravimetric analysis (DTGA) was carried out by utilizing an accessory time-derivative computer with the TGA system. In this arrangement the second recorder channel is used to record the rate at which the sample gains or loses weight, simultaneously with the absolute change in weight. In the Figures, DTG plots are shown on an arbitrary, relative scale basis.

A controlled-atmosphere DTA sample holder was used for the DTA studies. This provided facilities for introducing a flowing gas stream into and around the DTA sample, thereby creating a controlled gaseous environment for thermal reactions. The gaseous environment used in the DTA studies reported here was 1 atm* of nitrogen. Other operating parameters of importance are: sample weight 150 mg and particle size, –150 mesh Tyler; and heating rate, $10°C/min$.

X-ray diffraction analysis was utilized to evaluate the

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* 1 atm = 1·013 bar = 101·3 kN/m²

phases present in the high-temperature residues. Ash-fusion data were obtained in accordance with standard ASTM procedures.

RESULTS AND DISCUSSION

Thermal behaviour of individual mineral species

Before considering the polymineralic systems which comprise the mineral fraction of coals, it was deemed desirable to review briefly the thermal behaviour of the individual mineral species associated with coals. Standard minerals representative of the most commonly occurring minerals in coal were studied. Additional information on these minerals is given elsewhere[1].

The thermal decomposition of the individual mineral species was investigated using DTA methods (see *Figure 1*). The results obtained are summarized in *Table 1*, the peak maxima being shown in parentheses. The temperature range covered was from ambient to 1000°C, but some additional comments are included concerning phases formed at higher temperatures. Some TG and DTG analyses were also carried out on the samples whose DTA curves showed poor resolution. These curves are shown in *Figure 2*.

Kaolinite. The mechanism of the decomposition of kaolinite has been studied very extensively; and although there is general agreement on the phenomena accompanying the decomposition, there has been much controversy over the nature of the intermediate phases produced.

The shape of the DTA curve for different samples of kaolinite is fairly constant. It shows two endothermic peaks, the first between 100 and 120°C and the second between 550 and 600°C, followed by an exothermic peak between 950 and 1000°C. The first endothermic reaction, which is barely discernible in *Figure 1*, is due to the loss of adsorbed water, and the second to the removal of combined water from the hydroxyl groups surrounding the aluminium atoms, resulting in the formation of an amorphous phase (metakaolin). Metakaolin remains unaltered up to the first exothermic peak (950–1000°C), at which stage it becomes converted either to a spinel-like form of γ-alumina or to mullite ($2SiO_2.3Al_2O_3$). With further increase in temperature the γ-alumina is replaced by increasing amounts of mullite; and, at still higher temperatures, a tetragonal modification of silica (cristobalite) appears and persists with the mullite up to a temperature of 1500°C at which mullite is the only stable phase.

The DTA trace of the standard kaolinite used in this study is illustrated in *Figure 1*. This sample has a somewhat low endothermic peak and a subdued exothermic peak, both of which are characteristic of fine particle size[3].

Illite. This exhibits endothermic peaks at 50–150°C, 370–620°C and 850–900°C and an exothermic peak immediately following the third endothermic effect. The first endotherm corresponds to the loss of hygroscopic moisture, the second and third to the expulsion of water from the lattice and the destruction of the illite structure, respectively. The exothermic peak is attributed to the formation of a spinel phase.

At higher temperatures Grim and Bradley[4] found that the crystals of spinel increased in particle size with increasing temperature and finally disappeared at 1300°C by dissolution in a glass phase that made its appearance at 950°C. Mullite began to form at 1100°C and persisted up to 1400°C. Quartz appeared at lower temperatures and dissolved finally in the glass at 1050°C. The authors explained these changes in terms of the crystal structure of
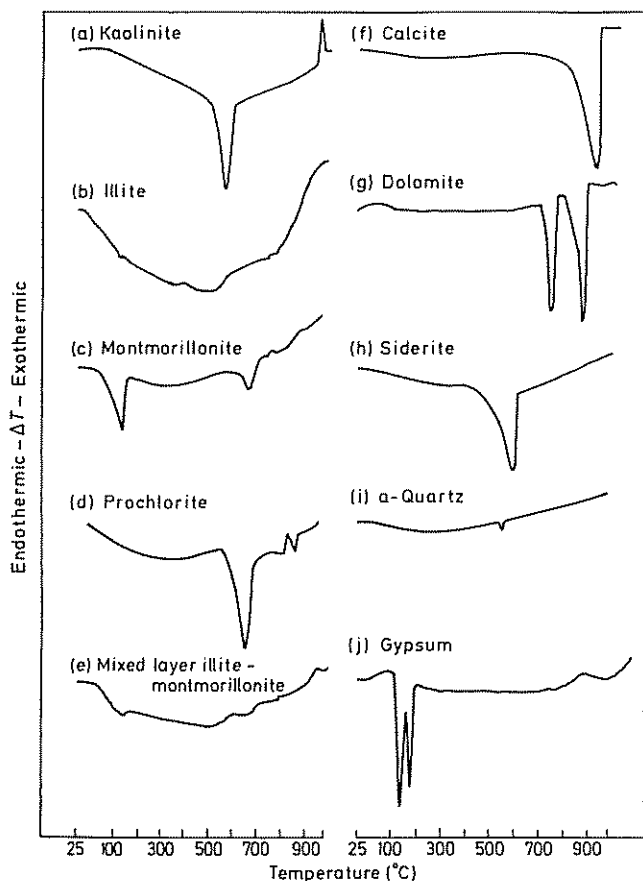

Figure 1 DTA curves (in nitrogen) of the individual mineral species associated with coals
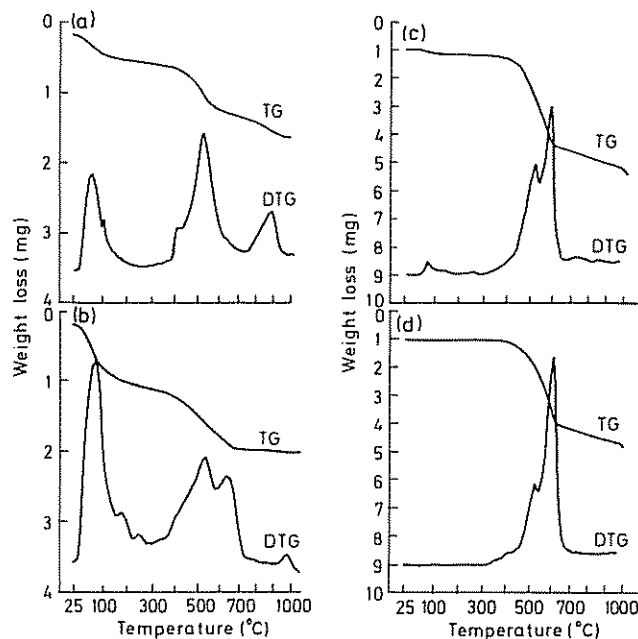

Figure 2 Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for (a) illite, (b) mixed-layer illite—montmorillonite, (c) marcasite, and (d) pyrite. Run in 1 atm of nitrogen

the illite by supposing that the middle sheet of the lattice carrying the alumina and magnesia was utilized to form the spinel, the alkali and silica from the outer layers interacting to form the amorphous glass phase.

The intensity of the peaks in illites is of much lower magnitude than that in kaolinite; that is, the DTA curve in

Table 1 DTA data for minerals commonly occurring in coals — determined in a nitrogen atmosphere

Mineral	Chemical formula (idealized)	Endothermic effects			Exothermic effects		
		Peak temp. range ($^{\circ}$C)	Intensity	Interpretation	Peak temp. range ($^{\circ}$C)	Intensity	Interpretation
Kaolinite	$Al_4Si_4O_{10}(OH)_6$	100—120	Small	Release of adsorbed water	950—1000 (980)	Intense	Phase transformation to γ-Al_2O_3 and nucleation of mullite
		500—600 (558)	Intense	Dehydroxylation			
Illite	$K_{1-x+y}(Al, Fe^{+3})_{2-y}$ $(Mg_1Fe^{+2})_ySi_{3+x}$ $Al_{1-x}O_{10}(OH)_2$	50—150 (135)	Small	Release of interlayer water	940—950	Small	Phase transformation to spinel phase
		370—620 (535)	Moderate	Dehydroxylation			
		850—900	Small	Lattice destruction			
Montmorillonite	$Al_{2-x}Mg_xSi_4O_{10}(OH)_2$	100—150 (137)	Moderate	Release of interlayer water	900—920	Small	Phase transformation to spinel phase
		600—730 (685)	Moderate	Dehydroxylation			
		850—900	Small	Lattice destruction			
Prochlorite	$Mg_6Si_4O_{10}(OH)_8$	550—750 (650)	Intense	Decomposition of brucite layer	860—900 (870)	Small	Formation of olivine $(Mg,Fe)_2SiO_4$
		750—820 (795)	Small	Dehydration of talc layer			
		820—860 (842)	Small	Dehydration			
Mixed-layer illite-montmorillonite	—	50—150 (115) (137)	Small	Release of adsorbed and interlayer water	900—950 (945)	Small	Phase transformation
		450—580 (530)	Small	Dehydroxylation			
		600—650 (640)	Small	Dehydroxylation			
		950—1000	Small	Lattice destruction			
Calcite	$CaCO_3$	710—950 (915)	Moderate	Decarbonation			
Dolomite	$CaMg(CO_3)_2$	740—800 (780)	Intense	Decarbonation			
		815—910 (890)	Intense	Decarbonation			
Siderite	$FeCO_3$	425—610 (570)	Moderate	Decarbonation			
Quartz	SiO_2	570 ± 3 (570)	Very small	Quartz inversion			
Gypsum	$CaSO_4.2H_2O$	100—150 (145)	Intense	Dehydration	350—370	Very small	Phase transformation
		150—200 (174)	Intense	Dehydration			γ-$CaSO_4 \rightarrow$ β-$CaSO_4$

Figure 1 is relatively featureless. However, the more sensitive differential thermogravimetric (DTG) curve in *Figure 2* provides more detail; and the three main endothermic effects are clearly shown.

Montmorillonite. This mineral shows an initial endothermic peak at 100–150°C which is due to the loss of interlayer water, and another at 600–730°C corresponding to loss of lattice water. A third endothermic peak at 850–900°C corresponds to the destruction of the montmorillonite lattice. Again an exothermic peak occurs immediately after the third endotherm and is attributed to the formation of a spinel phase.

Bradley and Grim[5] found that the decomposition of montmorillonite followed much the same course as for illite over the range 1000–1300°C. The products were silica (as quartz or cristobalite), cordierite ($2MgO.2Al_2O_3.5SiO_2$), enstatite ($MgSiO_3$), mullite and a spinel. With increasing temperature the mullite, cordierite and cristobalite phases increased in quantity, while the other phases decreased.

In the differential thermal curve, the first two endotherms are well defined; but the third endotherm and the subsequent exotherm are not clearly outlined.

Prochlorite. This shows little or no thermal changes between 25 and 500°C. The major endothermic reaction occurs at 550–750°C; this corresponds to the decomposition of the brucite layer in the structure. A second endothermic effect is noted between 750 and 820°C, which is due to the dehydration of the talc layer. An unexplained endotherm is noted at 820–860°C, followed immediately by an exothermic reaction at 860–900°C which is attributed to the initial crystallization of olivine ($(Mg,Fe)_2SiO_4$).

Mixed-layer illite–montmorillonite. Although not a standard mineral, a sample of this material was included in the study as it was found to occur in the mineral matter of quite a few seams. The DTA curve exhibits poorly-defined peaks, whereas the DTG curve (*Figure 2*) provides a better insight into the decomposition of this material. After the initial loss of interlayer and adsorbed water, two smaller weight losses are evident between 160 and 260°C. These may indicate the presence of water molecules in stronger association with the clay. Between 450 and 650°C the dehydroxylation of the illite and montmorillonite layers is evident; the final weight loss at 950–1000°C is probably attributable to final destruction of the lattice.

Calcite. The differential thermal curve of calcite shows a rather intense broad endothermic reaction commencing at 710°C and ending about 950°C with a peak at 915°C.

Dolomite. Two endothermic reactions are shown in the dolomite curve, both of which are sharper than with either calcite or siderite. The first starts at about 740°C and has a peak at 780°C; the second has a peak at 890°C and ends at 910°C.

Siderite. This exhibits a single endotherm starting at about 425°C and ending about 610°C, reaching a maximum at 570°C.

Quartz. This substance exhibits a small endotherm at about 570°C, produced as a result of the $\alpha \to \beta$ quartz inversion.

Gypsum. Gypsum undergoes a two stage dehydration, which is characterized by two sharp endotherms with peaks at 145°C and 174°C. The small exotherm occurring at about 364°C is not defined in the DTA curve. This exotherm has been attributed to a $\gamma\text{-CaSO}_4$–$\beta\text{-CaSO}_4$ phase transition.

Pyrite. It was not possible to run a DTA curve for pyrite owing to its corrosive effect on the thermocouples. However, the TG and DTG curves in *Figure 2* illustrate the decomposition of pyrite in an inert atmosphere. Decomposition commences at about 325°C and is complete at 700°C. From the DTG curve it appears that decomposition takes place in essentially two stages. This would concur with the evidence of Karavaev and Amagaeva[6], who found that the first dissociation product was $FeS_{(1-x)}$ ($x = 0.1-0.3$) and the second dissociation products were pyrrhotite (FeS) and sulphur. These thermal effects are endothermic by nature.

Marcasite. This behaves similarly to pyrite but additional effects are noted on the DTG curve between 80 and 250°C. From this it would appear that the marcasite had undergone partial oxidation to a hydrated sulphate form and that these effects correspond to a dehydration reaction.

The behaviour of the iron-containing minerals is largely governed by the combustion atmosphere utilized. In an oxidizing atmosphere pyrite shows a large single exothermic effect with a peak at about 500°C. This would correspond to the following decomposition reaction:

$$2FeS_2 + 5\tfrac{1}{2}O_2 = Fe_2O_3 + 4SO_2$$
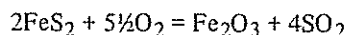
Marcasite behaves similarly but has its peak at a somewhat lower temperature, i.e. 460°C, as it is the less stable form of the two polymorphs.

Siderite, in an oxidizing atmosphere, shows a single endothermic peak beginning at about 500°C and peaking at about 585°C. In addition, there are two exothermic peaks, one at about 670°C and the other at about 830°C. The endothermic peak represents the decomposition of siderite to FeO. This is oxidized to Fe_2O_3 giving the major exothermic peak at 670°C. The product after the first exothermic peak is a mixture of hematite ($\alpha\text{-Fe}_2O_3$) and maghemalite ($\gamma\text{-Fe}_2O_3$). The second exothermic peak is due to the transformation of $\gamma\text{-Fe}_2O_3$ to $\alpha\text{-Fe}_2O_3$. These reactions can be summarized by the following equations:

$$FeCO_3 \to FeO + CO_2 \text{ (endothermic)}$$

$$4FeO + O_2 \to 2Fe_2O_3 \text{ (exothermic)}$$
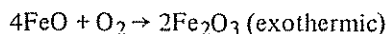
From the data in *Table 1*, it can be seen that most of the reactions which the minerals undergo are of an endothermic nature. Thus, on combustion the presence of these minerals will have an influence on the heat of combustion of coal.

Thermal behaviour of a synthetic standard mineral mixture in various gas atmospheres

To gain some insight into the behaviour of a complex system of minerals on heating in various atmospheres, an investigation was made of a standard mineral mixture. Some six minerals were selected to represent the major groups of minerals found in coals, viz. illite (shale minerals group), kaolinite (kaolin group), pyrite (sulphide group), calcite (carbonate group) and quartz and gypsum as the main accessory minerals. A mineral mixture of the following composition, by weight, was prepared: 20% kaolinite, 20% illite, 20% calcite, 20% pyrite, 10% quartz, and 10% gypsum. The mixture was prepared by hand blending the minerals (–150 mesh) in an agate mortar and pestle for a period of 10 min.

Gas atmospheres were chosen to simulate probable conditions met during combustion and to provide as wide a contrast as possible. The following gas mixtures were

utilized: air (oxidizing), nitrogen (neutral), 10% hydrogen + 90% nitrogen (reducing), 12% carbon monoxide + 88% nitrogen (mildly reducing), and 18% carbon dioxide + 2% carbon monoxide + 80% nitrogen (synthetic flue gas). TG and DTG results are shown in *Figure 3*. The temperature range covered was from ambient to 1100°C. It was not possible to obtain the corresponding DTA curves, owing to the corrosive effect of the pyrite in the mixture on the differential thermocouple.

In curves (a) and (b) of *Figure 3*, the TG and DTG analyses of the standard mineral mixture in air are shown. Between 25 and 85°C, a loss of adsorbed water is indicated; this is followed by the dehydration of gypsum. This latter reaction is complete at about 175°C. It is well established that a two-stage transition takes place, first with the loss of 1·5 mol of water to produce the hemihydrate, then loss of the remaining 0·5 mol to produce anhydrous calcium sulphate. However, the resolution of the two stages was not evident in the DTG curve in any of the gas atmospheres used. This can probably be explained by the fact that the resolution of the two stages is very susceptible to water-vapour pressure. It is only when a steam atmosphere is introduced that the two processes are clearly distinguished[7].

From 175°C to 325°C the TG curve shows a plateau region. At about 325°C a gradual loss of hydroxyl water from the clay minerals occurs and this reaction becomes quite marked at 425°C. The DTG curve fails to show a resolution of the dehydroxylation of kaolinite and illite. In addition, the decomposition of pyrite at about 520°C, which commences before completion of the dehydroxylation reaction, is accompanied by a marked increase in the reaction rate. At 620°C both of these reactions are complete and the TG curve again shows a plateau region. Between 700 and 830°C, the decomposition of calcite takes place; and then the TG curve levels off, no further weight-loss reactions taking place.

The same mineral mixture run in a nitrogen atmosphere shows somewhat similar reactions (see curves (c) and (d)). The dehydroxylation reactions of kaolinite and the decomposition of pyrite are not resolved on the DTG curve. They are shown on this curve as a rather broad hump between 310 and 685°C. At 1030°C the decomposition of the calcium sulphate from the gypsum commences.

In the hydrogen—nitrogen atmosphere (curves (e) and (f)), partial resolution of the pyrite decomposition reaction is achievable. The rate of this reaction reaches a maximum at about 570°C. The decomposition of calcite is found to commence at 625°C, which is some 75°C lower than was found in the nitrogen or air atmospheres. Following the calcite decomposition, it can be seen from the TG curve that a further gradual loss in weight occurs. This appears as a rather broad peak on the DTG curve and is attributed to the decomposition of calcium sulphate. It would appear that the decomposition of this constituent occurs at substantially lower temperatures in a reducing-gas environment.

The principal feature to note from the traces run in a carbon monoxide—nitrogen atmosphere (curves (g) and (h)) is that the calcium sulphate decomposition is even more pronounced. This reaction commenced at 820°C and is essentially complete at 1100°C.

In the flue-gas atmosphere (curves (i) and (j)), the decomposition of calcite takes place between 780 and 960°C. This higher decomposition range is undoubtedly due to the presence of carbon dioxide in this dynamic gas atmosphere. This is explained by the fact that the dissociation of calcium carbonate is a reversible process, and is
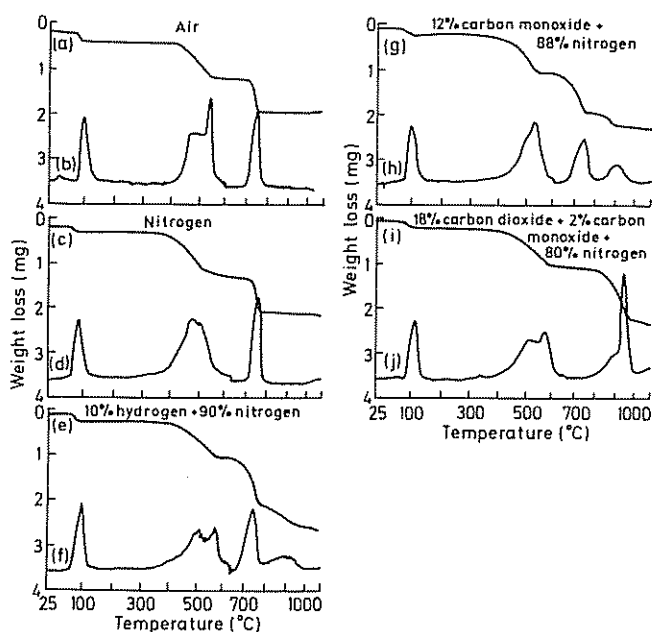

Figure 3 TG and DTG curves for the synthetic standard mineral mixture in various gas atmospheres

influenced by the partial vapour pressure of carbon dioxide. An additional run using moist flue gas ($\approx$3% moisture) revealed a decomposition pattern almost identical with that obtained in the dry atmosphere.

No evidence for solid-state interactions between the minerals below 1100°C was found. This was confirmed by an X-ray diffraction analysis of the combustion residues; and it is in agreement with the findings of Warne[8], who studied several synthetic mineral mixtures by a DTA procedure. The clay minerals appear to be unaffected by variation in the combustion-gas atmosphere, while pyrite, calcite, and gypsum exhibit some changes in their thermal behaviour. As might be expected, the oxidation of pyrite in air was accompanied by a marked increase in reaction rate. The decomposition of calcite in the flue-gas atmosphere took place over a somewhat higher temperature range. The initial decomposition temperature of gypsum was lowered considerably in the reducing-gas atmospheres. This prompted a further investigation of the decomposition reaction of pure gypsum.

Gypsum was studied by the simultaneous TG/DTG method in the five furnace atmospheres. The initial dehydration of the gypsum did not appear to be affected by varying the gas atmosphere. However, in the carbon monoxide—nitrogen, hydrogen—nitrogen, and flue-gas atmospheres the decomposition of the anhydrite started at about 780°C. In the neutral or oxidizing atmospheres this decomposition did not take place below 1000°C. In the hydrogen—nitrogen and flue-gas atmospheres a single-stage reaction was indicated from the DTG curve. By comparison, the DTG curve for the sample run in a carbon monoxide—nitrogen atmosphere provided evidence of a two-stage reaction (see *Figure 4*).

A subsequent X-ray analysis of the sample residue from this latter run revealed the presence of both calcium sulphide and calcium oxide. The anhydrite decomposition probably takes place according to the following reactions:

$$CaSO_4 \rightarrow CaO + SO_3$$

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2$$
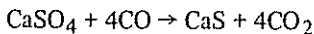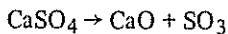
In coal, gypsum would be quite likely to dissociate under certain conditions, e.g. in a kiln furnace; and the sulphur trioxide gas evolved might react with the surface of brick or ceramic ware.
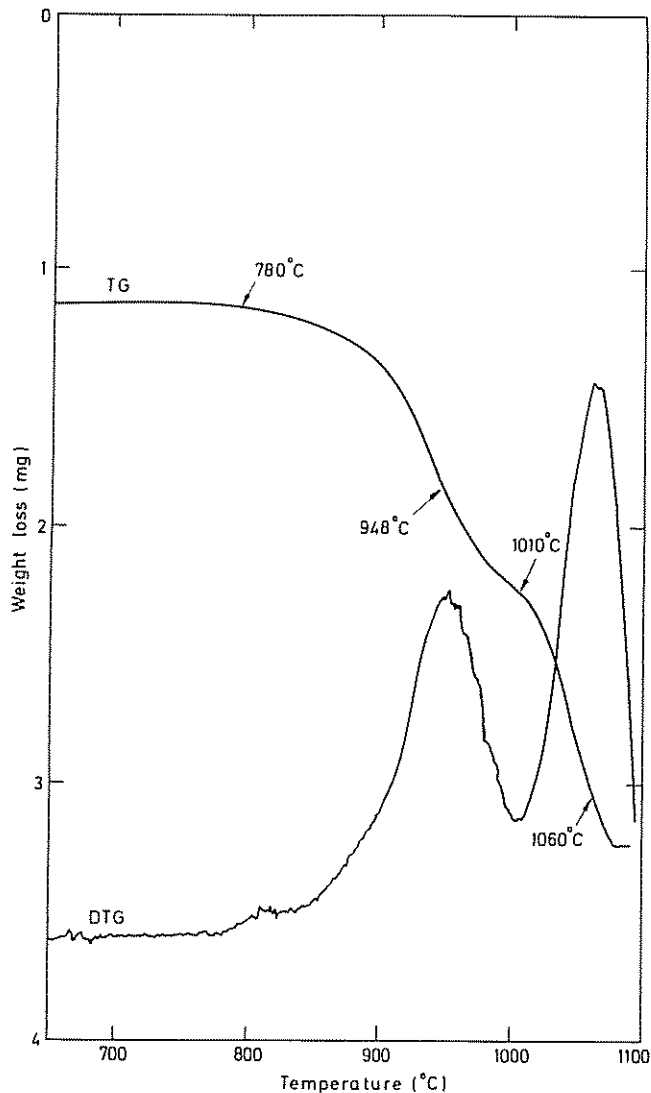

Figure 4 Thermal decomposition of anhydrite in a reducing-gas atmosphere (12% CO, 88% N_2)

Figure 5 TG and DTG curves for (*a*) the parent coal and (*b*) the mineral-matter of PSOC—24. Run in 1 atm of air

Thermal analysis of the mineral-matter fractions of four selected coal samples

In *Figure 5* the TG and DTG curves for both the parent coal and the mineral matter of PSOC—24 are illustrated. Determinations were made in an atmosphere of flowing air. From the TG curve of the coal sample, it can be seen that upon heating in the range 25—200°C there is small loss of adsorbed moisture. At a temperature slightly above 200°C, the TG curve shows a slight increase in weight. This effect was noticeable in each of the four coal samples and it is possible to postulate that between 200 and 300°C the coal
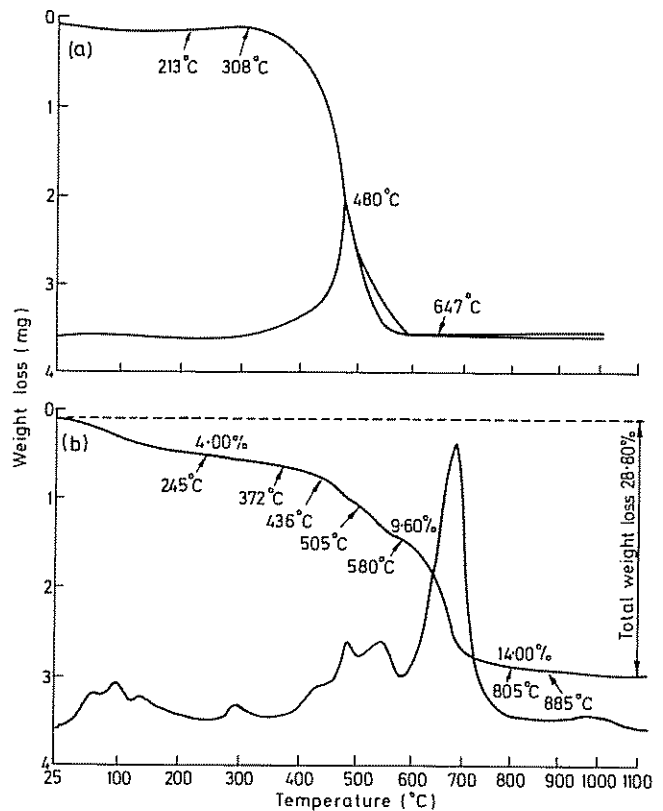
shows a tendency to chemisorb oxygen[9]. From the DTG curve it is seen that ignition commences at 308°C and that reaction is complete at 647°C. The DTG curve indicates accurately the initial decomposition temperature, i.e. the temperature at which the rate of weight change becomes detectably different from zero, the maximum rate, and the temperature at which it returns to zero, corresponding to complete reaction.

The corresponding curves for the mineral-matter fraction are shown in *Figure 5 (b)*. A quantitative mineralogical analysis of the mineral matter, determined using infra-red analytical techniques as described previously by us[2], revealed the following composition: 30% kaolinite, 21·6% illite + mixed-layer illite—montmorillonite, 1·5% gypsum, 14·5% quartz, and 32·4% pyrite. Between 25 and 245°C there is a loss of adsorbed and interlayer water from the clays, plus the dehydration of gypsum corresponding to 4% by weight. From the DTG curve, a further small weight loss is indicated at about 300°C. This may be due to the presence of some water molecules which were strongly bound in the lattice of the mixed-layer illite—montmorillonite. This also illustrates a further advantage of DTG analysis, in that it allows the detection of phenomena that may go completely unnoticed on the TG curve alone. In the temperature range 245 to 580°C, there is an additional weight loss of 9·60%. In this region the dehydroxylation of the clay minerals occurs and kaolinite, illite, and mixed-layer illite—montmorillonite all contribute effects. There appears to be a partial resolution of these reactions in the DTG curve, but they generally appear as overlapping effects. Above about 580°C there is a marked increase in the rate of weight loss, which is coincident with the decomposition of pyrite. This reaction
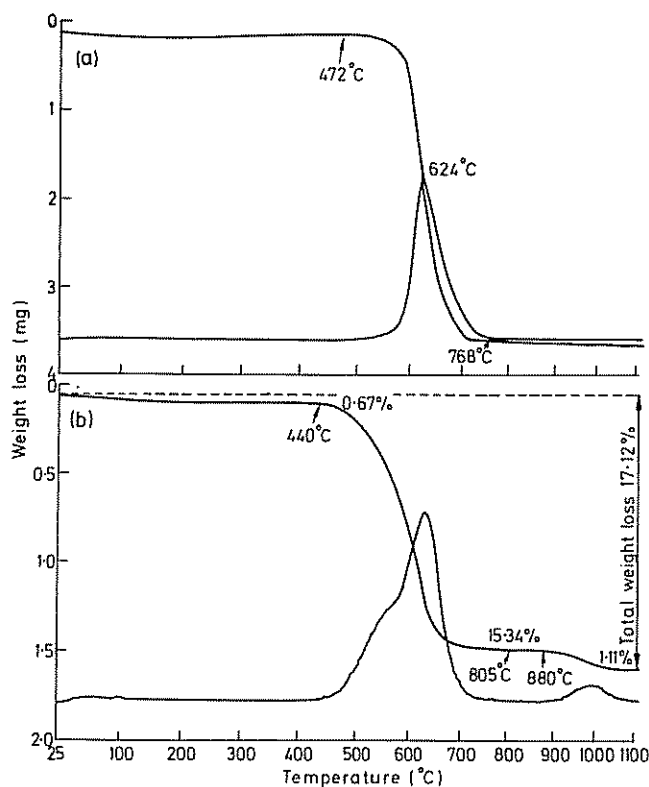
Figure 6 TG and DTG curves for (a) the parent coal and (b) the mineral matter of PSOC—82. Run in 1 atm of air
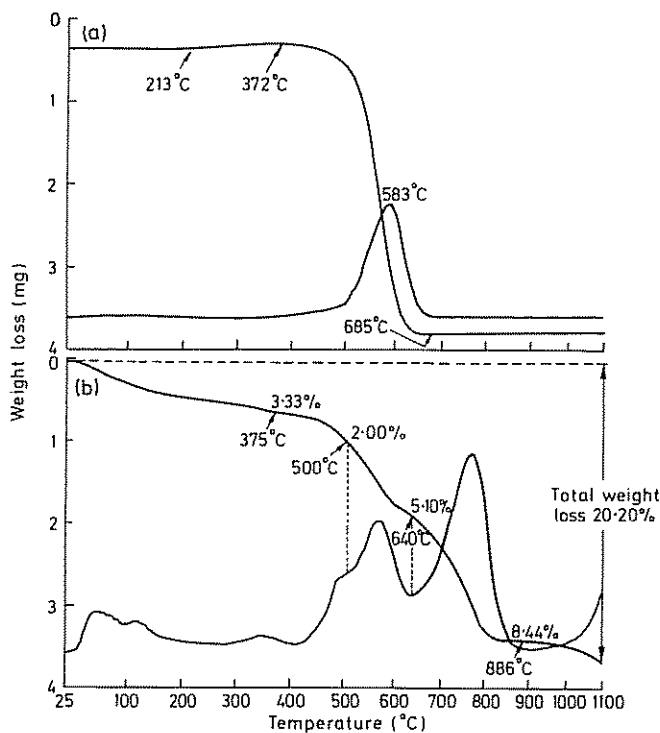

Figure 7 TG and DTG curves for (a) the parent coal and (b) the mineral matter of PSOC—132. Run in 1 atm of air

is complete at about 800°C and accounts for the major portion of the total weight loss. The decomposition range is somewhat higher than that of pyrite in air. This may be due to an indirect effect of some other component in the mineral mixture. Between 950 and 1050°C an additional small weight loss is indicated, which is probably associated with lattice destruction in the clay minerals.

The equivalent curves for sample PSOC—82 are shown in *Figure 6*. The temperature range over which combustion of the parent anthracite occurred was considerably higher than that for the high-volatile bituminous sample (PSOC—24), i.e. 472 to 768°C. The TG curve for the mineral matter was almost identical with that of pure kaolinite, which one would expect from the mineralogical analysis: 72·2% kaolinite, 5·1% illite, 5·4% pyrite, 2·9% calcite, 3·3% rutile, and 11·1% quartz. From 25 to 440°C there is a small weight loss of 0·6%. At this latter temperature, dehydroxylation of kaolinite begins. This reaction is illustrated in the DTG curve as one large peak with a slight shoulder. Minor effects due to the decomposition of pyrite and the dehydroxylation of illite are essentially overlapped. At a temperature of 880°C, a further weight-loss reaction takes place which is attributed to the decomposition of calcite.

In *Figure 7* the curves for sample PSOC—132 are shown. For the TG curve of the coal a slight gain in weight is again indicated between 213 and 372°C. In this temperature range an apparent gain in weight, due to oxygen adsorption, proceeds up to the onset of ignition, i.e. 372°C. Combustion is found to be completed at a temperature of 685°C. The mineral matter of this sample had a more complex composition, i.e. 14·0% kaolinite, 7·7% chlorite, 21·3% gypsum, 13·5% siderite, 17·5% dolomite, 8·0% pyrite, 17·0% quartz and 1·0% rutile. In the corresponding mineral-matter curves, a weight loss of 3·33% is recorded in the temperature range of 25 to 375°C. This is primarily due to the loss of adsorbed water from the clays and the dehydration of gypsum. At about 400°C the dehydroxylation of clays commences and this is followed by the decomposition of siderite. This latter reaction commences at approximately 500°C and appears on the DTG curve as a superimposed peak. The DTG curve then shows a minimum at 640°C, and at a temperature slightly beyond this the decomposition of dolomite starts. The two-stage decomposition associated with this mineral is not resolved in the DTG curve. The overall reaction was complete at 886°C. At about 970°C a final weight-loss reaction starts which is incomplete at the cut-off temperature of 1100°C. This corresponds to the decomposition of anhydrite, even though the temperature range is somewhat lower than that recorded for anhydrite derived from pure gypsum. This may indicate the presence of a less stable form of gypsum in the mineral matter of this sample.

By projecting the minima of the DTG curve onto the TG curve, the weight changes in the two steps of the decomposition of the carbonate minerals can be determined, although only approximately because of overlapping of the processes. Between 500 and 640°C, there is a weight loss of 5·10%. Assuming this weight loss to be derived essentially from the decomposition of siderite, the siderite content of the mineral mixture can be estimated to be 13·4%. Similarly by assuming the weight loss between 640 and 886°C to be due to the loss of carbon dioxide from dolomite, its concentration was estimated at a level of 17·7%. Both these figures show good agreement with those derived by the infra-red procedure utilized in the mineralogical analysis[2].
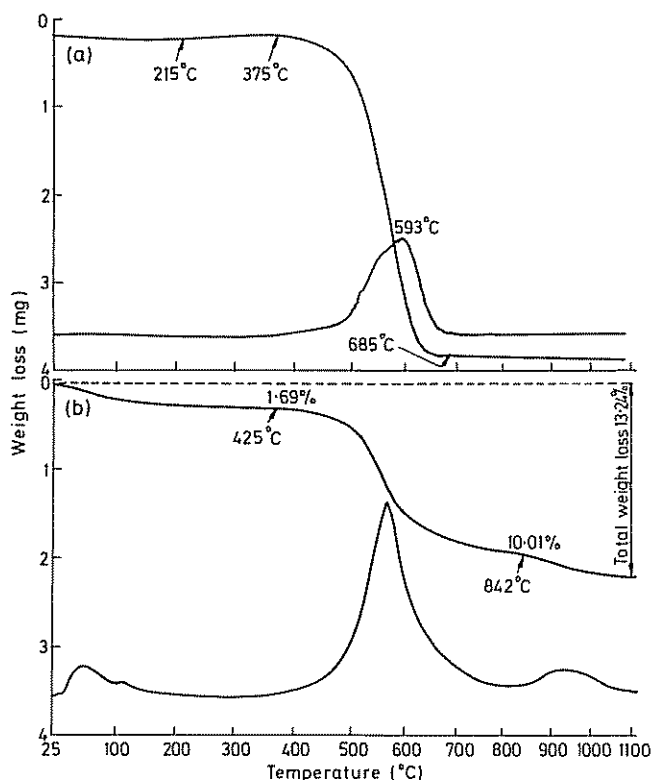
Figure 8 TG and DTG curves for (a) the parent coal and (b) the mineral matter of PSOC—135. Run in 1 atm of air

Table 2 High-temperature phases given by mineral-matter fractions

PSOC Sample No.	1100°C	1200°C	1300°C	1400°C
24	Quartz Hematite Corundum Mullite	Hematite Mullite	Hematite Mullite	Hematite Mullite Glass
82	Quartz Mullite Corundum Cristobalite Rutile	Quartz Mullite Cristobalite Rutile	Quartz Mullite Cristobalite	Mullite Cristobalite
132	Quartz Hematite Anhydrite Anorthite	Hematite Anorthite Glass	Anorthite Glass	—
135	Quartz Mullite Hematite Corundum	Mullite Hematite	Mullite Hematite	Mullite

The curves obtained for the coal and mineral matter of sample PSOC—135 are shown in *Figure 8*. For the coal sample, ignition commences at 375°C and combustion is complete at 685°C. The mineral matter of this sample was found to have the following composition: 52·3% kaolinite, 22·0% muscovite, 13·0% quartz, 2·5% gypsum, 1·4% rutile, 6·8% siderite, and 2·0% pyrite. There is a loss in weight in the mineral matter of 1·69% over the temperature range 25 to 425°C. Between 425 and 842°C a further weight loss of 10·01% occurs, which accounts for the major portion of the total weight loss. In the DTG curve very little appears resolved. The dehydroxylation effect of kaolinite completely overlaps the minor effects that are due to muscovite dehydroxylation and pyrite and siderite decomposition. Over the temperature range 842 to 1050°C, an additional weight-loss effect is evident, which may originate from the final destruction of the muscovite lattice.

High-temperature phases yielded by the mineral-matter fractions

As the limiting temperature in the thermal-analysis equipment was approximately 1100°C, some additional studies were made on the ashes in the temperature range 1100 to 1400°C. Samples were maintained at each of the elevated temperatures for a period of 3 h in an atmosphere of air. They were allowed to cool in a desiccator, and the combustion residues were subsequently analysed by X-ray diffraction. Results of this analysis are summarized in *Table 2*.

In the ash of sample PSOC—24, at 1100°C quartz and hematite were the principal phases present, with small amounts of corundum (Al_2O_3) and mullite ($2SiO_2.3Al_2O_3$). At 1200°C the quartz phase was no longer in evidence and the mullite content had increased markedly. At 1400°C there was evidence of the formation of a vitreous phase and a reduction in the hematite content.

Five distinct phases were identifiable in the ash of PSOC—82 at 1100°C, i.e. quartz, mullite, corundum, cristobalite (SiO_2), and rutile (TiO_2). With increasing temperature, the quartz content decreased and the mullite content increased. At 1400°C only mullite and cristobalite were detected.

Some anhydrite was in evidence in the ash of PSOC—132 at 1100°C together with quartz, hematite, and anorthite ($CaO.Al_2O_3.2SiO_2$). A glass phase formed at 1200°C. At 1300°C the hematite seemed to have been absorbed in the vitreous phase and the anorthite content was also reduced. At 1400°C the ash of this sample was completely molten, and on cooling it firmly adhered to the combustion crucible.

Mullite and hematite were the principal phases yielded by the ash of PSOC—135, with mullite the predominant phase at 1400°C.

Ash-fusion data

Further information concerning the behaviour of the ashes at high temperatures can be gleaned from a study of their ash-fusion properties. These data are shown in *Table 3*. The softening temperature of the ash of PSOC—24 shows a difference of some 155°C when examined under reducing and oxidizing conditions. This is primarily due to the fluxing action of the high iron content of this sample. Ferrous oxide which is formed under reducing conditions has a more marked depressing influence on the melting point of the ash than the higher oxide, because of the formation of the very fusible iron silicates.

In contrast, the ash of the anthracite sample (PSOC—82) is highly refractory, which is due to the high kaolinite content of this sample. Illite which is much less refractory than either kaolinite or quartz would tend to act as a flux and lower the softening point somewhat. However, the overall fusion behaviour in this sample is governed by the kaolinite decomposition products, i.e. mullite and silica.

Table 3 Ash-fusion temperatures (°C)

PSOC Sample No.	24		82		132		135	
Observation	Reducing	Oxidizing	Reducing	Oxidizing	Reducing	Oxidizing	Reducing	Oxidizing
Initial deformation	1060	1280	1549+	1549+	1043	1088	1454	1516
Softening (H = W) *	1149	1304	1549+	1549+	1054	1193	1477	1527
Softening (H = 0·5 W)	1182	1338	1549+	1549+	1071	1204	1493	1549+
Fluid	1288	1366	1549+	1549+	1110	1232	1510	1549+

* H is cone height, W is cone width
+ Temperature higher than 1549°C

Under reducing conditions the softening point of the ash of PSOC−132 was 139°C lower than when an oxidizing atmosphere was used. This can again be associated with the iron content of the sample but additional effects are also important. The clay-mineral content of this sample is relatively low which means that the amounts of refractory silica and alumina are also low. Lime and magnesia, which derive from the carbonate mineral dolomite, will also act as fluxes. The overall result of these effects is to produce a comparatively low-melting-point ash.

For the ash of PSOC−135, the variation in the softening-point temperatures under the different atmospheres is only 50°C. In this instance the refractory mineral content is high relative to that of the minerals which would contribute a fluxing effect. Ash melting does not take place until a temperature in excess of 1510°C is achieved.

CONCLUSIONS

The most important finding to be derived from the study of the thermal behaviour of the synthetic standard mineral mixture was that there was no evidence for solid-state interactions below 1100°C. The composition of the furnace atmosphere can affect the initiation and course of reactions accompanied by changes in weight. Apart from the loss of adsorbed and combined water from the silicate minerals, it appears that little reaction with the other minerals can be expected until much higher temperatures are attained.

In the thermogravimetric study of some parent-coal samples, evidence for the adsorption of oxygen on the coal particles was obtained. This effect initially occurs at a temperature of 200°C and appears to increase up to the onset of ignition. The thermogravimetric analysis of the mineral-matter fractions, together with a knowledge of the mineralogical compositions, permits a prognosis to be made concerning the behaviour of the inorganic fraction of coals during the reaction of coals at elevated temperatures. Where overlapping peak effects in the DTG curves are not complex, estimates of the actual mineral concentrations present are feasible.

X-ray diffraction studies of the ashes at elevated temperatures (up to 1400°C) shed some light on the phase transformations that the mineral systems undergo. Interaction between the components of the coal ashes proceeds within the system $CaO-Al_2O_3-SiO_2-Fe_2O_3$, with minor amounts (total 2 to 6%) of MgO, Na_2O, K_2O and TiO_2. Interpretation of phase data for such a system is difficult. From ash-fusion data, it can be seen that the ashes do not melt sharply and completely at a given temperature; and, in most instances, there is a wide interval of temperature between the onset of sintering and completion. Again a knowledge of the original mineralogical composition can be of assistance in interpreting both the high-temperature phases formed and the ash-fusion properties.

A knowledge of the mineral species involved is of great importance in any detailed consideration of the reactions taking place in combustion and gasification systems. When the mineralogical composition of the mineral matter is known, it can be of practical significance in interpreting such problems as high-temperature corrosion, boiler-deposit formation, and catalytic effects in hydrogasification processes.

ACKNOWLEDGEMENTS

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