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APPLICATIONS OF THERMAL ANALYSIS METHODS TO IRON MINERALS IN COAL—A SYNTHESIS *

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ABSTRACT

Iron minerals in coal belong to the carbonate, sulphide and clay groups. Individual mineral contents, their compositions, iron contents, thermal stability, types and magnitudes of reactions on heating, recarbonation and sulphation are particularly suitable to investigation by thermal analysis. These are important as iron acts as a natural catalyst in hydrogenation processes, lowers coal ash fusion temperatures, may be related to pyrite/inorganic sulphur contents and their exothermic reaction component on heating. Investigations using DTA, DSC, TG, DTG, thermagnetometry and evolved gas analysis, often involving " variable atmosphere TA," illustrate their complementary nature and highlight the increased potential of a multi-technique approach to applied research.

INTRODUCTION

The world consumption of energy relentlessly continues to increase but most heavily industrialized countries are disproportionately dependent on petroleum but conspicuously lack indigenous self-sufficiency.

During the 1970–1982 "energy crisis" the rapid price escalation of oil (~ 1600%) coupled with restricted and unreliable sources of supply and predicted diminution of reserves resulted in a search for alternative sources of energy.

The most readily available with efficient utilization technology available was coal and, potentially, oil shale, (solid hydrocarbon fossil fuels). Further advantages of coal are its much wider geographic distributions, rapidly

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advancing extraction techniques and enormous known reserves compared to petroleum.

The continuing depletion of high quality coal deposits, constant downwards pressure on prices and demand for diversification of sources of supply has led to the utilization of progressively more impure (dirty) coals. Such impurities are essentially composed of mineral matter, the amount of which is expressed as wt.% ash, i.e. the residue after oxidizing away the organic coal components by heating.

Such is the magnitude of the trend towards the use of high ash, as mined coals, that they have been burnt directly in large pulverized-coal-fired power stations (driving 550 MW generators) with ash contents as high as 35%. Further, in India, currently on a much smaller scale, coal washery reject material up to 68% ash is used for local electricity generation.

RESEARCH DIRECTIONS

It is not surprising, therefore, that much recent and current research is being directed towards the hitherto somewhat neglected area of the mineral matter (inorganic constituents) in coal. A major question being between the merits of burning high ash coals direct and designing for the problems this generates or directing the available funds at the earlier stage of coal beneficiation to physically remove much of the mineral matter present before burning. As a result, emphasis is being placed on the following areas of coal mineralogical investigations.

(1) What minerals are present?
(2) Which minerals occur most commonly?
(3) What are their origins?
(4) In what physical and distribution forms do they occur?
(5) What are their compositions?
(6) To what extent can mineral components be removed to increase coal quality (i.e. coal beneficiation—washing)?
(7) What are their effects on combustion, calorific value and coke quality?
(8) What are their effects on the residual slag and ash composition and constitutions?
(9) Do the waste products have any economic uses?
(10) Does their utilization have environmental implications either negative or positive?

It is pertinent to note that 8 out of the 10 group topics listed above have been investigated by TA using a wide range of techniques [1], i.e. DTA, DSC, TG, DTG, thermomagnetometry (TM), thermomechanical analysis, derivative thermomechanical analysis, evolved gas analysis, emanation thermal analysis, thermomicroscopy and thermodilatometry.

In addition the simultaneous use of more than one TA technique often employing also the method of "variable atmosphere thermal analysis" to obtain complementary determinations from a single sample under the same conditions, has proved increasingly valuable, e.g. for quantification of DTA results (DTA/TG) [2], the resolution of multi-reaction TG curves (TG/DTG) [3–5] and the nature and evolution temperatures of evolved gases [6], while a large range of fossil fuel examples are excellently presented in the recent ASTM special publication No. 997 [7].

The second major question involves several aspects.

(1) What minerals are known to occur in coal? The most comprehensive compilation lists 83 [8].
(2) In what forms are they present—mainly crystallized mineral entities, bands, veins, nodules, crystals, etc.
(3) Of the main minerals occurring in coal which contain Fe—clays, carbonates and sulphides [8], see Table 1.
(4) What is the significance of the Fe bearing minerals? This requires further amplification.

The significance of Fe-bearing minerals in coals is that the presence of Fe lowers the ash fusion temperatures, acts as a catalyst in hydrogenation processes, may be related to the content of pyrite (and marcasite in brown coal) and therefore the inorganic S content present. Furthermore, it is relatable to exothermic effects from carbonate and sulphide minerals. On coal combustion, Fe oxides become readily available from the decomposition of its host mineral carbonates and sulphides although it may recombine to form ferrites [9]. However, it remains unavailable as silicates if present in clays which essentially give off water.

TABLE 1

Minerals commonly found in coal, not in order of frequency as this varies. Those underlined contain Fe; prefixes Cl, Si, C, and S indicate clay, silica, carbonate and sulphide minerals respectively

Mineral name	Mineral composition
(Cl) Illite	$(KH_3O)(AlMgFe)_2(SiAl)_4O_{10}[(OH)2H_2O]$
(Cl) Kaolinite	$Al_2Si_2O_5(OH)_4$
(Cl) Montmorillonite	$NaCa(AlMgFe)_2Si_4O_{10}(OH)_2 \cdot nH_2O$
(Si) Quartz	SiO_2
(C) Calcite	$CaCO_3$
(C) Dolomite–ankerite	$CaMg(CO_3)_2$–$Ca(MgFe)(CO_3)_2$
(C) Siderite	$FeCO_3$
(S) Pyrite and marcasite	FeS_2 (both)

RESULTS AND DISCUSSION

The question of the pyrite (FeS_2) and pyritic sulphur in coal has been investigated in several different ways.

First, the mineral pyrite has been identified under inert atmosphere conditions by its characteristic endothermic decomposition peak between 510 ° C and 570 ° C on DTA curves of coal and oil shale containing pyrite [2,10] and its amount confirmed by simultaneous DTA/TG. Its presence with siderite ($FeCO_3$) which decomposes endothermically at a similar temperature (in inert gases), may be confirmed from a comparison of duplicate runs in flowing oxygen free N_2 and CO_2 [11]. In N_2 their similar endothermic peaks occur superimposed to produce a composite resultant simple endothermic peak. However, in CO_2 the decomposition of siderite has to overcome the increased partial pressure of CO_2 and so its peak occurs at a higher temperature (moves up scale) leaving the pyrite peak (unaffected by CO_2) with its original decomposition temperature. Thus in flowing CO_2 the similar peaks of pyrite and siderite may be resolved if both are present and siderite diagnosed, if up scale peak shift occurs [11].

The pyritic sulphur content of coals has been determined by the development of an elegant combination of TG/TM methods coupled with variable atmosphere TA involving flowing N_2, O_2 and H_2 [12]. This gives an Fe content which can be directly related to pyrite content for coals devoid of siderite which is almost always the case for U.S. and many other specific coals. However, when both pyrite and siderite are present (particularly in Gondwana coals) this method, while not accurately indicating Fe of pyritic origin, will accurately indicate total Fe derived from pyrite plus siderite contents [13]. This aspect has been addressed by EGA in flowing "air" using non-dispersive IR detectors. In this way evolved SO_2 peaks could be recorded and measured to indicate the amount of S produced [14], which when related to the Fe determinations in H_2 indicates the proportions of pyrite and or siderite present. Also, this EGA method appears to have the potential of separating pyritic and organic S contents [14].

Thermomagnetometry studies of siderite [15] and pyrite [16] have shown that in atmosphere conditions of strongly restricted O_2, both minerals decompose to form magnetite (Fe_3O_4). From this it has been suggested [17] that the pyrite in coal , heated to between 393° C and 455 ° C under O_2-poor conditions, will form magnetite rims. When subjected to a magnetic field of ~ 500 Oe these grains will be separated by magnetic attraction from crushed coal, thus reducing its S content. Similarly, magnetic residues of coal liquefaction may be extracted [17]. Recent isothermal studies under the same O_2-poor conditions and temperature range have confirmed that magnetite is also produced from siderite ($FeCO_3$). Thus it will be similarly extracted but, of course, without any related diminution in the S content of the coal preheated as above. The extraction of both the "pyritic and sideritic" Fe in this way may not always be advantageous as its inherent catalytic effects will be lost. This must be weighed against the retention of Fe leaving the increased S content to be extracted later from the flue gas by sorption and regeneration using variable atmosphere TG [18].

It has been established [19] that, under conditions of flowing CO_2, DTA curves of members of the dolomite–ankerite series: (1) preserve their diagnostic 2- and 3-peak DTA curves right down to the limits of detection; (2) clearly show a middle peak if Fe is present in the lattice of this isomorphous substitution series; (3) have an increasing middle peak size with increasing Fe content; and (4) allow the Fe present as siderite and ankerite to be identified separately for physical mixtures.

Furthermore, Fe present in ankerite provides a variable source of Fe in the oxide form as in CO_2 and N_2 it immediately forms Ca and Mg ferrites [20,21]. However, in readily available O_2 hematite forms, increasing Fe contents cause progressively decreasing decomposition enthalpies [22]. Thus the presence of Fe in carbonates decreases their resultant endothermic decomposition values to the extent that high Fe content siderites produce a small exothermic resultant; such effects may be qualified using DSC [23].

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