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Note

COAL PROXIMATE ANALYSIS AND PYRITE CONTENTS BY THE TM/TG METHOD. THE PROBLEM OF IRON-BEARING CARBONATES

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The new combined thermomagnetometry/thermogravimetry (TM/TG) technique provides an excellent method for the determination of the pyrite contents of coals, providing the carbonate mineral siderite is not present. Siderite will contribute additional magnetic products which will lead to a spuriously high pyrite determination. Members of the Fe-bearing dolomite–ferroan dolomite–ankerite series on decomposition yield dicalcium ferrite which is not only non-magnetic but is not reduced in H_2 to the magnetic Fe form. Their presence does not affect the new TM/TG method for pyrite content determination. The contents of the Fe-bearing carbonates may be detected and assessed or their absence confirmed by variable atmosphere DTA, under conditions of flowing N_2 and CO_2.

INTRODUCTION

In the excellent and thorough paper "A New Method for the Simultaneous Determination of Pyrite Content and Proximate Analysis in Coal", Aylmer and Rowe [1] have described a new method which offers several advantages over the ASTM method. Furthermore, from the large range of American coals studied it has been established as a valid method of wide application. No mention of the minerals present with pyrite in the coals tested is made, however, and of these siderite ($FeCO_3$) and ankerite Ca(Mg, Fe)$(CO_3)_2$ are of particular relevance. From the previous detailed work of Mitchell and Gluskoter [2] these two minerals do not appear to be present in a wide range of American coals but, as has been pointed out by Warne and French [3], this is not the case for other coals in which siderite and ankerite are listed as common [4], in particular those from Australia (siderite) [5,6] and the United Kingdom (ankerite) [6,7].

In addition, there is the isomorphous substitution series where Fe substitutes for Mg in the dolomite $CaMg(CO_3)_2$ structure to form the continu-

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ous dolomite–ferroan dolomite–ankerite series. The DTA and TG decomposition characteristics of this series have been described previously [3,8]. It is likely that much of the dolomite in coal will contain some Fe substituted for Mg in its structure.

If present in coal (or oil shales) these iron-bearing carbonates could be expected to contribute their own magnetic Fe fraction as both decompose below 750°C in N_2. This material added to that produced from pyrite would result in a spuriously high determination for the pyrite content as obtained by the new thermomagnetometry/thermogravimetry (TM/TG) method.

RESULTS

Siderite-pyrite decomposition temperatures and solid products

As part of related research concerning the DTA of these minerals in oil shales [3,9], the present author has established that in an N_2 atmosphere the single endothermic decomposition peaks of siderite and pyrite in oil shale are very similar, i.e., showing DTA peak temperatures of 500 and 525°C, respectively. However, when present together only one single composite endothermic decomposition peak occurs which indicates that their decomposition reactions completely overlap (ref. 9, fig. 1, cf. curves 2, 3 and 6).

The solid decomposition product in each case is FeO, which, during the oxygen-rich atmosphere purge stage at 950°C proposed by Aylmer and Rowe [1], will collectively oxidise to hematite (Fe_2O_3). The Fe_2O_3 derived from both siderite and pyrite will then be reduced to metallic iron in the H_2-flow phase and thus give an additional weight variation due to the "siderite-derived Fe" in the thermomagnetometry phase of the procedure.

Ankerite decomposition temperatures and solid products

The decomposition of members of the ankerite–ferroan dolomite series is complex and has been shown in a related study to occur in three stages if determined in flowing CO_2 [8]. However, when determined in flowing N_2, in the amounts likely to occur in coal, i.e., $< 20\%$, these reactions occur so close together that they appear on the resultant DTA curve as a single endothermic peak at 725°C (ref. 9, see fig. 1, curve 5).

The final solid decomposition products are non-magnetic dicalcium ferrite, MgO and excess CaO [10]. The end-product mixtures from different members of the ferroan dolomite–ankerite series are not reducible to produce metallic Fe under the H_2-flow phase and on subsequent thermomagnetometry investigation do not show any deflections (A.E. Milodowski, personal communication, 1984). Thus, the presence of these iron-bearing carbonates do *not* affect the results of pyrite determinations by the new method.

DISCUSSION

Recent relatable research on oil shales by Warne and French [9] has indicated that the application of "variable atmosphere DTA" in conditions of flowing CO_2 compared to N_2 are capable of separating the endothermic peaks of siderite, pyrite and ferroan dolomite/ankerite. This is possible because for a single gas-liberating mineral decomposition reaction to take place it has first to overcome the partial pressure of any of the sample-generated gas type present in the purge gas.

In the case of siderite the substitution of a purge gas of CO_2 instead of N_2 causes a delay in the decomposition of siderite which then occurs at a higher temperature, whilst the SO_2-liberating decomposition reaction of pyrite is unaffected. Thus, on the resultant DTA curves of oil shale containing both siderite and pyrite their decomposition peaks now occur some 50°C apart and their individual peaks are almost completely separated. This allows for the assessment of their individual contents by peak area measurements and comparison with reference DTA curves for samples of known siderite/pyrite contents.

Coal DTA curves are similarly modified by the presence of siderite and pyrite.

In the case of the ferroan dolomite/ankerites in CO_2, their three reaction peaks are clearly produced and occur at sufficiently high temperatures to distinguish them from those of siderite or pyrite [8,9].

CONCLUSIONS

In the application of the proposed new TM/TG method for the determination of pyrite in coal, the presence of siderite will give too high a value due to the extra Fe contributed by the decomposition of this mineral. However, the presence of the Fe-containing members of the ferroan dolomite/ankerite series of carbonates does not contribute Fe decomposition products in a form which will affect the determination of pyrite.

The presence or absence of these carbonates may be assessed by the technique of variable atmosphere DTA under conditions of flowing N_2 and CO_2.

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