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CHARACTERIZATION OF THE LOW TEMPERATURE ASH COMPONENT OF COALS USING MULTIPLE ATMOSPHERE DTA, TG, AND DTG TECHNIQUES

C.M. Earnest*, W.P. Brennan, and R.L. Fyans

The Perkin-Elmer Corporation

Norwalk, CT USA

ABSTRACT

This paper will discuss sample handling and special analytical techniques leading to DTA, TG, and DTG pattern recognition in mineral mixtures and low temperature ash components of several coals from eastern Kentucky (USA) and southwestern Illinois (USA). The concepts of both atmospheric interaction, mineral-mineral interaction and their effect on the final thermal analysis pattern will be addressed.

INTRODUCTION

The types of minerals occurring in coals include carbonates, sulfides, sulfates, oxides, and various smectite, illite, kandite, and mixed layer clay minerals. The relative amounts and combinations of these minerals vary with the location of the coal seam. Prior to analysis for mineral matter composition, the coal is generally subjected to low temperature ashing (LTA) using an oxygen plasma. These LTA specimens are most commonly analyzed by x-ray diffractometry. Other options for analysis of LTA specimens include Infrared Spectroscopy, Mossbauer Spectroscopy, Atomic Spectroscopy, and the thermal methods of analysis: Differential Thermal Analysis (DTA), Thermogravimetry (TG), and Derivative Thermogravimetry. Whereas, each of the methods has its own specific advantage, the thermal methods of analysis can also provide the additional information of the behavior of the mineral content as a whole on heating in a variety of atmospheres.

Experimental

All DTA thermal curves reported in this work were obtained using a Perkin-Elmer microcomputer-based DTA 1700 High Temperature Differential Thermal Analysis System. In this study, only the DTA mode of operation of this instrument was used. In this case, the linearized ΔT (temperature difference) signal between two Pt/Pt-10% Rh thermocouples was displayed as the ordinate signal on either a Perkin-Elmer XY_1Y_2 Recorder or the Perkin-Elmer Thermal Analysis Data Station. In all cases, the linearized sample thermocouple temperature was displayed on the abscissa of the thermal curve. All TG and DTG thermal curves presented in this study were obtained with a Perkin-Elmer TGS-2 Thermogravimetric Analysis System used in conjunction with a System 4 Microcomputer Controller. Sulfur analyses and inorganic (carbonate) carbon determinations were made on the LTA specimens using a Perkin-Elmer Model 240C Elemental Analyzer and Perkin-Elmer Model 240DS Data Station. The low temperature ash specimens used in this study were obtained from the Univ. of Kentucky, Institute for Mining and Minerals Research, Lexington, KY (USA). A preliminary knowledge of the mineral composition of the ash was obtained from XRD studies performed at IMMR using a Philips Model 3100 X-Ray Diffractometer.

Results and Discussion

The LTA materials studied included specimens from the Herrin 6 seam (southwestern Illinois), the Hazard 8 seam (eastern Kentucky), and two specimens taken

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at different locations of the Hazard 7 seam (eastern Kentucky). Due to space limitations of this abstract, the Herrin 6 seam results will be the only ones given as an example. Figures 1, 2, and 3 give the DTA thermal curves obtained in dynamic nitrogen, dynamic air, and dynamic CO_2 atmospheres, respectively. The major features of these curves were dominated by a large pyrite (FeS_2) and hydrated iron sulfate component, illite and illite-smectite mixed layer clays and a small calcite component. The endothermic peaks observed near 110°C and 150°C in all three DTA thermal curves correspond to the loss of water from the clay mineral components as well as from the initial stages of dehydration of iron sulfates. The endothermic peak observed at 280°C in both dynamic nitrogen and dynamic CO_2 atmosphere corresponds to the dehydration of ferrous sulfate monohydrate to anhydrous ferrous sulfate. This peak is notably absent in the DTA curve obtained in dynamic air atmosphere. This is because there exists in dynamic air a two-way mechanism in which some of the $FeSO_4.H_2O$ may be oxidized to $Fe(OH)SO_4$ prior to decomposition to Fe_2O_3(1).

The weight losses assigned from the TG thermal curves for the dehydration step of ferrous sulfate monohydrate as observed in dynamic nitrogen used dynamic CO_2 atmospheres were used to quantitate the amount of $FeSO_4.H_2O$ to be 11.6 ± 0.3%. This corresponds to a $FeSO_4$ content of 10.4%.

The multi-step exothermic activity observed in Figure 2 at 407, 464, and 508°C corresponds to the oxidation of the large pyrite component (19% by XRD) in the presence of iron sulfates. The reader should consult a recent paper by Earnest (2) for details of the multi-step pyrite oxidative peak in LTA specimens. Additional studies using synthetic mineral mixtures found that the normal decomposition temperature of pyrite is lowered in the presence of significant iron (II) sulfates. The doublet observed here at 523°C and 550°C in the DTA thermal curves in both dynamic nitrogen and dynamic CO_2 atmospheres was also observed for the iron (II) sulfate/pyrite synthetic mixture.

In dynamic nitrogen atmosphere some overlap of the iron sulfate decomposition calcite decomposition occurs and a resultant peak maximum of 750°C is observed. In CO_2 purge (Figure 3), the calcite decomposition is shifted due to the PCO_2 effect to 910°C. In dynamic air atmosphere (Figure 2), a different type separation is observed. Due to the association of the calcite component with the relatively large amount of oxidation products of the pyrite, the calcite decomposition is both shifted to higher temperatures (890°C) and sharpened. The relatively strong endothermic peak at 667°C in Figure 4 is primarily the decomposition of anhydrous iron sulfate to iron (III) oxide. It should be mentioned that no kaolinite clay mineral was observed in this Herrin 6 LTA specimen at the level of detectability of DTA. In the other LTA specimens of this study (all from eastern Kentucky), kaolinite clay mineral was easily recognized by the characteristic ordering exotherm at 970-1000°C. This may be observed in Figure 5 where DTA thermal curves for all four LTA specimens are given. One will also note the difference in the exothermic pyrite oxidation profile as the content ranges from 2% in the Hazard 7 specimen to 19% in the Herrin 6 specimen.

References

(1) P.K. Gallagher, D.W. Johnson, and F. Schrey, J. Amer. Cer. Soc. 53 (1970) 666-670.

(2) Earnest, C.M., Thermochim Acta 75 (1984) 219-232.

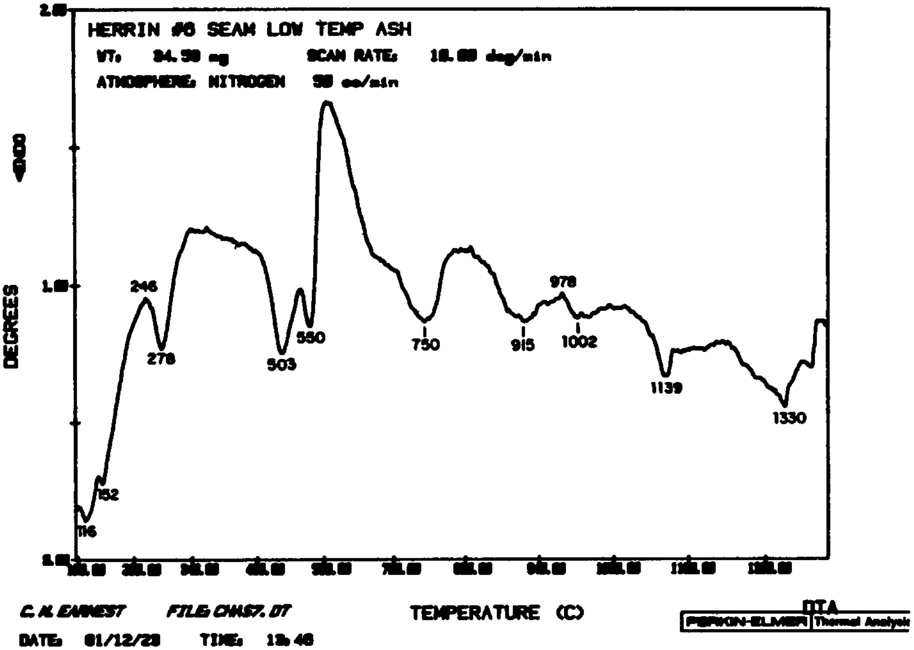

Figure 1

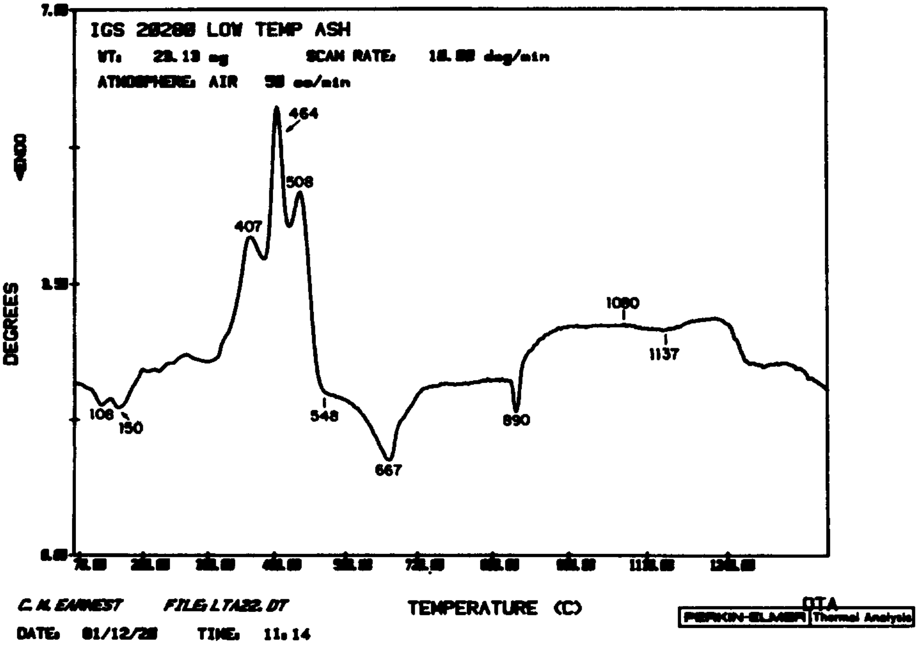

Figure 2

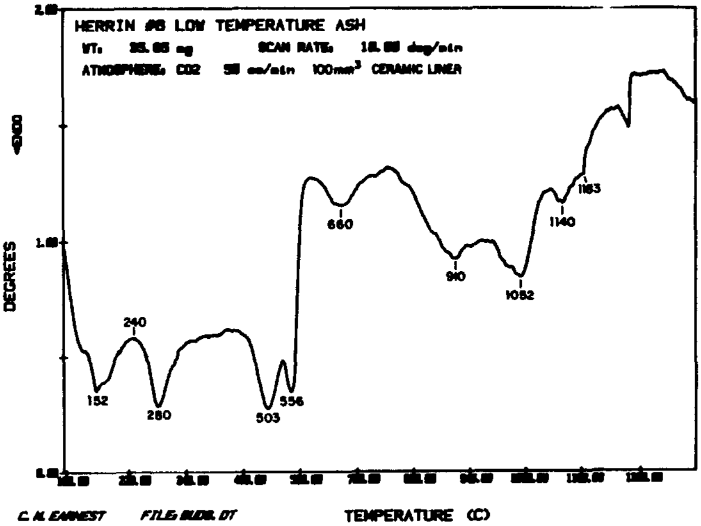

Figure 3

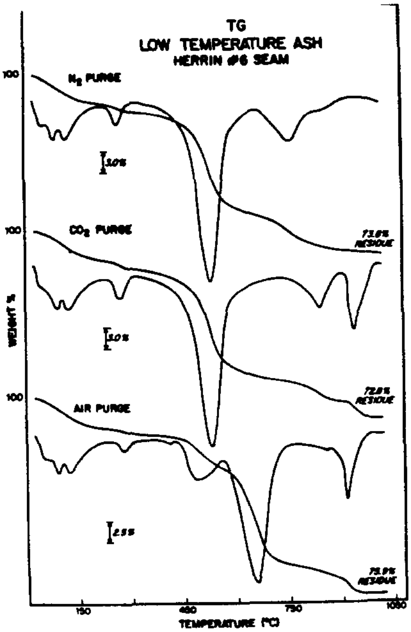

Figure 4

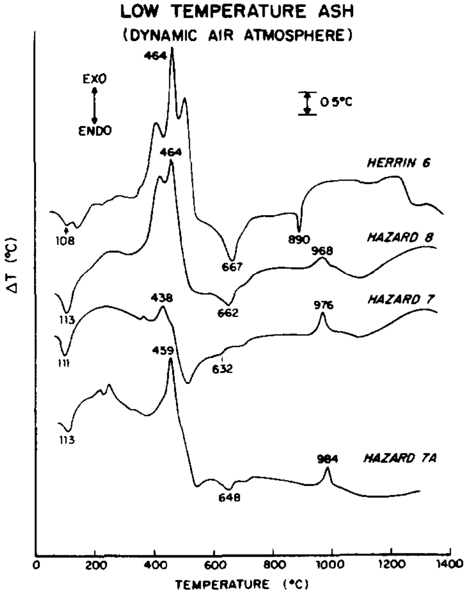

Figure 5