

Differential Thermal Analysis of Lignite Coals/Mineral Mixtures and Decomposition Studies of Carbonate Minerals in Coal Ashes by Isothermal Thermogravimetry

¹G. M. KUMBHAR, ²A. G. M. VASANDANI, ¹S. W. SHAH AND ¹M. I. BHANGER

¹Center of Excellence in Analytical Chemistry, University of Sind Jamshoro

²Dr. M. A. Kazi Institute of Chemistry, University of Sind Jamshoro

(Received 7th August, 2002, revised 26th March, 2003)

Summary: In the present work, the rates of decomposition for Siderite and Magnesite minerals found in lignite ashes have been evaluated by isothermal thermogravimetry by monitoring the weight loss for 60 min at 350 °C, 400 °C, 500 °C and 575 °C and the mineralogical composition of coal ash was evaluated. The comparative account is also given for DTA of coal/mineral mixtures in air atmospheres which show the major exothermic effects in the initial and final temperature zones of major peak configurations.

Introduction

Coal is principle source of energy, which is used for variety of purposes. The use of coal as fuel has direct influence on its budget for the mineral constituents. The ash produced by coal fired power plants is finding applications in water logging and as blend in cement, therefore it is essential that their decomposition of mineral constituents be thoroughly understood. A number of studies of the mineralogy, chemistry and low/high temperature ashing of coal inorganic constituents reported during past years [1-6].

The thermal methods of analysis based on techniques of TG, DTA, DSC and TMA have found wider as a role in these investigations [4-8]. Present study was therefore carried out to understand the decomposition behavior of minerals in lignitic coal ashes derived from lakhara coal mines, which is also used as fuel in coal fired power plant. The results of thermal analysis of coal ashes were compared with those of coal/ mineral mixtures, to understand the nature of decomposition reactions in both coal and coal ashes.

Results and Discussion

The comparison of detailed TG curves (Fig-1) shows that the decompositional characteristics of siderite and magnesite carbonate minerals manifest great variation with respect to change of environment using carbon dioxide (CO₂) instead of air and nitrogen, surrounding the sample. The TG profile of siderite (Fig-1-cf A₁) in nitrogen atmosphere has decomposition zones in the temperature region 430°C to 610°C with weight loss of 35% up to the final

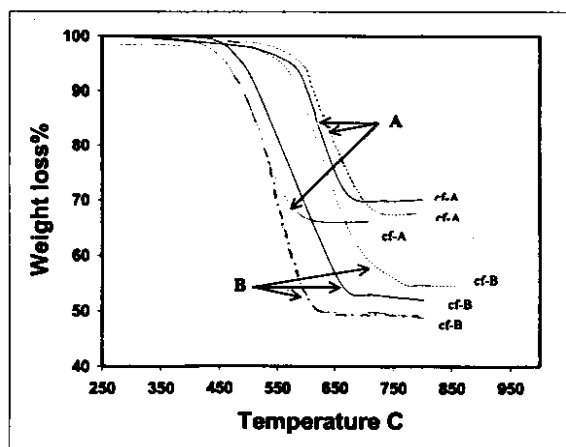


Fig.1: TG curves of (A) Sederite and (B) Magnesite determined at the heating rate of 5 °C /min in (-----) nitrogen, (————) static air and (.....) carbon dioxide (-----)

temperature of 700 °C. The corresponding curve (Fig-1-cf A₂) recorded in static air has decomposition zone between 530-650 °C. The curves (Fig-1-cf A₃) recorded in CO₂ atmospheres show slightly upper limits of variation as compared to curves recorded in air.

The variations are in the range of initial ± 70 °C and final ± 60 °C in weight loss zones with a 10% difference in weight loss. The curves recorded for magnesite (Fig-1cf B_{1,3}) in CO₂ atmosphere show the variation of 80 °C in initial weight loss and 60 °C in final weight loss instead of air and nitrogen atmospheres.

According to works reported [7-11], the decomposition characteristics of these carbonate minerals are a highly dependent on the nature of atmosphere surrounding the sample. During the decomposition process of these carbonate minerals the partial pressure increases in the order from pure nitrogen to air to pure CO_2 (at ambient pressure) resulting in to the shift of decomposition zones to higher temperatures.

Isothermal mass changes

To evaluate mineral decomposition characteristics clearly. The quantity of sample and time was varied isothermally at 375 °C, 400 °C, 425 °C and 450 °C for the individual carbonate minerals in air and nitrogen atmospheres. The results for siderite (Figs-2-cf-A) at the isothermal mass change in static air and nitrogen at the temperature of 375 °C show that the weight of sample is unchanged except a initial loss of moisture and or water of crystallization. The isothermal changes at 400 °C (Figs-2-cf- B) show 5% weight loss at 20 minutes, 7% at 30 minutes and 10% at 40 minutes. The isothermal profiles of same sample in nitrogen atmosphere show weight loss of 1%, 1% and 2% at the 20,30 & 40 minutes respectively.

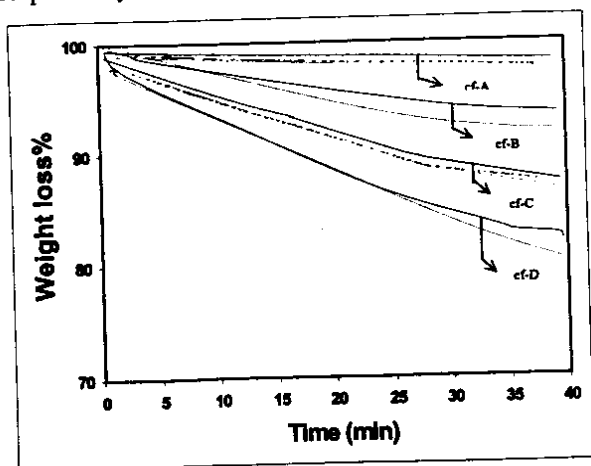


Fig-2. Isothermal weight loss curves of siderite at (A) 375 °C, (B) at 400 °C, (C) at 425 °C in (-----) nitrogen atmosphere and (————) in air atmosphere

The isothermal weight loss recorded at 425 °C (Figs-2-cf-C) show slightly rapid decomposition of sample with weight loss of 10%, 13% and 15% after the times of 20, 30 and 40 minutes respectively as compared to previous temperatures. The isothermal

weight loss profiles taken on 475 °C (Figs-2-cf -D) show the variable differences in curves at 20 min with weight loss of 14% and at 30 min 18%. While in air at 40 min 20% of loss and in nitrogen 20%, 22% and 25% at respective times.

The corresponding isothermal profiles for the samples of magnesite (Fig-3a, 3b, & 3c) were recorded at 375 °C, 400 °C and 425 °C in air and nitrogen. There is change of weight loss in air at 375°C and the initial loss of absorbed water, but in nitrogen it shows 3% loss at 40 min.

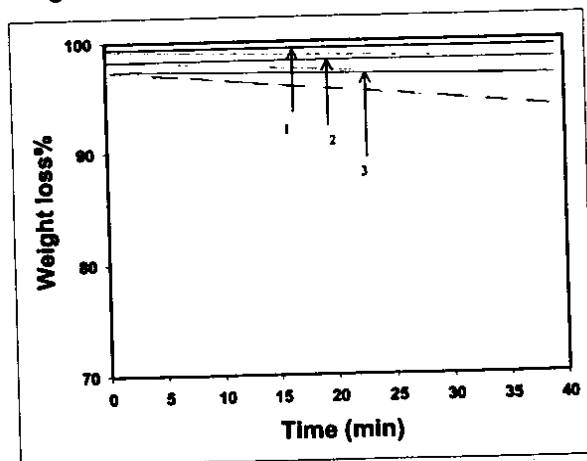


Fig 3a Isothermal weight loss changes of Magnesite at 375 °C (-----) for nitrogen and for air (————)

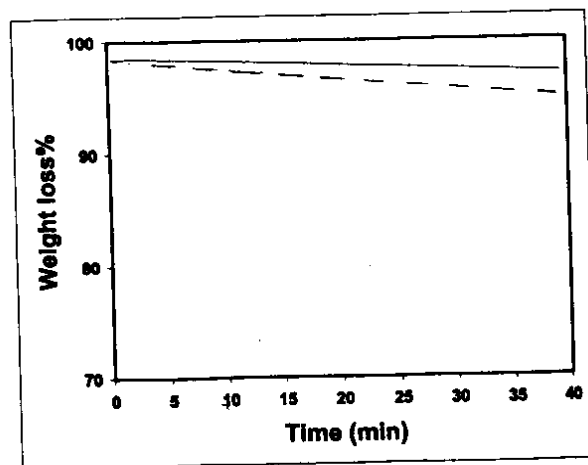


Fig 3b. Isothermal weight loss changes of Magnesite at 400 °C

The pure samples of magnesite show great variation in weight loss with sample two, 5% in air & 7% in nitrogen and sample three, 6% in air and 9% in

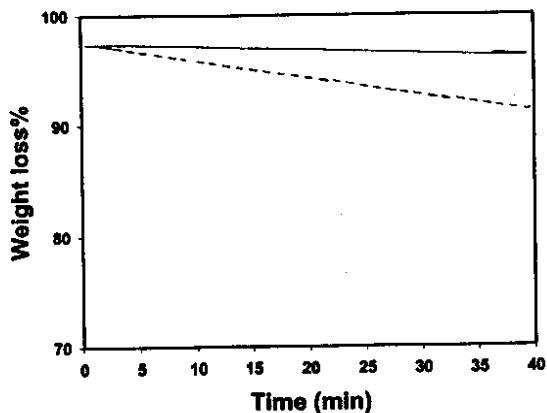


Fig 3c Isothermal weight loss changes of Magnesite at 425 °C

nitrogen at 40 minutes. The isothermal weight loss of magnesite (Fig-3b, 3c & 3d) sample at 400 °C shows the higher weight losses of 5% in air & 7% in nitrogen whereas at 425 °C 6% in air and 10% in nitrogen.

Differential thermal analysis of mixtures

DTA of coal sample with sederite

DTA curves for pure coal sample (Fig-4) show, broad endothermic hump in the region of 50 to 200 °C, due to the loss of moisture and low temperature organic volatile matters. Following this hump, there is small but wide exothermic peak situated beside the main exothermic peak resulting from the smooth releasing of any inorganic constituents present in the sample, that may cause slow burning of coal in air atmosphere. The later events lying with small initial shoulder peak in region of 300 -520°C are main exothermic peak due release of high temperature volatile matters and the fixed carbon responsible for the high calorific values of coal.

At the end these events, there is a small endothermic peak situated in the region of 510-530 °C. This peak is a significant sign of the decomposition of sederite, which has been confirmed by the addition of known grade sederite diluent to coal samples in the proportion of 10%, 20%, 30%, 40% and 50%. The DTA results of diluent sequence show that, original configuration of peak related to coal sample has suffered negatively due to the addition of diluent (sederite). The position of the peak for sederite became clearer, wide and tends to shift

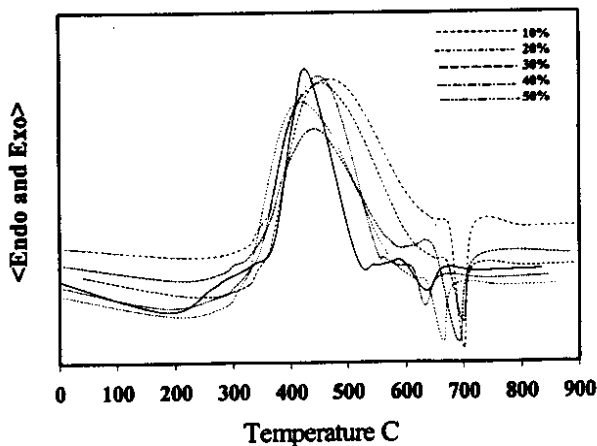


Fig-4 DTA curves of dilution sequence of various percent mixture containing coal and Sederite (FeCO_3)

towards high temperature at 520, 522, 525, 530, 535, & 540 °C with increase subsequent amount (10-50% of diluent).

The effects on the events including main exothermic peak along its all shoulders and humps are wider with increase of final peak temperature 420, 430, 432, 435, 440 & 450 °C, and decrease in initial temperature peak at 317, 310, 295, 290, 280 & 275°C is noticeable. The disturbed configuration of the remaining peaks in the profile shows that, the addition of diluent hampers the release of the high temperature volatile matters in nitrogen and have negative effects on burning process in air atmosphere.

DTA of coal sample with magnesite

The coal samples blended with various amount of magnesite as 10%, 20%, 30%, 40% and 50% (Fig-5) show different differential thermal analysis characteristics as compared to sederite blending. The DTA curve of this sample shows the big hump at the temperature zone of ambient to 200 °C with pattern of smooth release of water contents and low temperature organic volatile.

The major exothermic peak in the region of 380-550 °C appears without any initial shoulder peak. A small shoulder peak in the end of major exothermic peak in the region of 630-690 °C may be due to the decomposition of magnesite in coal sample. To confirm this, the magnesite sample was mixed as 10-

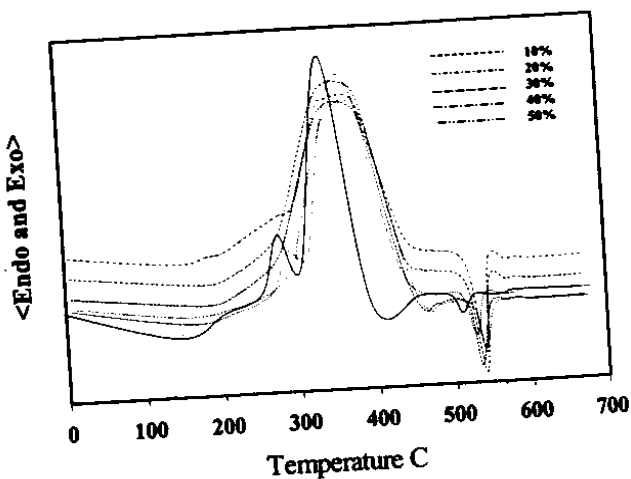


Fig-5 DTA curves of dilution sequence of various percent mixture containing coal and Magnesite (MgCO_3)

50%, with coal sample and subjected to differential thermal analysis. The resulting curves show that the peak configuration for the proportion 10% and 20% magnesite do not affect normal peak configuration, where as higher proportions result in initial small shoulder peaks.

The addition of more proportions of magnesite (30%, 40% and 50%) show more negative effects such as depression of major exothermic peak and its shifting of final temperature peak towards 560, 570, 580, 600 & 620 °C and decrease in initial temperature peak from 380°C to 360, 358, 355, 340 & 330 °C.

Experimental

Thermogravimetry (TG) experiments were carried out using Perkin Elmer TG-2 systems in the temperature range from ambient to 1200 °C. The curves were recorded applying twin modes, one as non-isothermal facilitated as continuously recording the weight changes of sample as the temperature is varied (Figs- 1) and second one as isothermal mode under which samples were maintained at a constant temperature for various times (Fig-2, 3a, 3b & 3c). The furnace atmosphere conditions were static air, nitrogen and high purity carbon dioxide flowing at

The DTA experiments of coal/mineral mixtures were carried out using Sh madzu DT-30B thermal analyzer equipped with DGC-30 thermo-balance and R-123T multi channel recorder. Prior to all the experiments the instruments were calibrated with ICTA certified standards. The specific mineral sample magnesite and sederite used in these experiments were obtained from PMDG (Pakistan mineral development cooperation).

Conclusions

On the basis of resultant DTA events of coal with mineral mixture, it can be concluded that, the presence of these minerals in coal samples has profound impact on its burning characteristics. The thermal methods of analysis of analysis especially alongwith technique of DTA is powerful tool to characterize such minerals in coal, which is used as fuel in power generation plants.

References

1. R. S. Mitchell and H. J. Gluskoter, *Fuel*, **55**, 90 (1976).
2. R. G. Jenkins and P. L. Walker, in C. Karr, Jr. (eds.), "Analytical Methods for Coal and Coal Products", Vol. II, Chap. 26, Academic Press, New York, pp. 265 (1978).
3. F. W. Frazer and C. B. Belcher, *Fuel*, **52**, 41 (1973).
4. S. St. J. Warne. *J. of Inst. Fuel*, **38**, 207 (1965).
5. S. St. J. Warne. *J. of Inst. Fuel*, **43**, 240 (1970).
6. S. St. J. Warne and P. Balyiss. *Amer. Mineral*, **47**, 1011 (1962).
7. S. St. J. Warne in C. Karr, Jr. (eds.), "Analytical Methods for Coal and Coal Products", Vol. III, Chap. 52, Academic Press, New York, pp. 447 (1979).
8. E. Hodzic, Z. Pasic. *Thermochim. Acta*, **93**, 365 (1985).
9. S. St. J. Warne and D. H. French, *Thermochim. Acta.*, **75**, 149 (1984).
10. D. J. Morgan, Thermal Analysis Vol. 3, Proc. 3rd Int. Conf. Pub. "Thermal Analysis", Davos, Birkhauser Verlag, Stuttgart, p. 675 (1972).
11. H. Bilinski, R. Ciovanoli, A. Usui and D. Hanzel. *American Mineralogist*, **87**, 580 (2002).