SPECIFIC HEAT MEASUREMENTS OF TWO PREMIUM COALS

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Introduction

Our purpose in initiating the study of the premium coal was threefold. Our first aim was to observe the behavior of the premium coal. Second, we wished to obtain reliable heat capacity data to add to the pool of available information on the premium coals and thus extend the data base available for the development of useful correlations. Third, we wished to compare the results obtained for premium coals with those obtained on a nonpremium coal during our development of transferable measurement techniques. The heat capacity measurements made on the nonpremium coals had shown the development of a deep exotherm on initial heating as the coal became more oxidized. We surmised that the difference between the initial and repeat measurements on the oxidized coal could be ascribed in some way to the increased oxidation level of the nonpremium coal. However, the contributions to that effect were not clear.

The heat capacity measurements have been made in sealed cells with no significant mass loss. Water has been shown to be released from the coal as it is heated above the temperature at which it was dried in the course of specimen preparation.(1,2) Three possible sources of this water have been identified. First, it may be water physically trapped in the coal structure that is released as the coal is heated above its drying temperature. Second, the water could be produced by mineral reactions that occur as the coal is heated. Carling has applied a thermodynamic predictive program, which identifies the most likely mineral reactions at various temperatures, to the nonpremium coal used in our studies.(3) Reactions that produce significant amounts of water are predicted to occur between 400 and 450 K, which is within the range of our measurements. Third, the water may be generated by condensation reactions occurring within the organic component of the coal. These would increase as the coal becomes more oxidized.(4)

One possible contribution to the deepening of the exotherm with increased oxidation was the increased exothermicity expected on readsorption of water on a more oxidized surface. Barton has evaluated the effects of increased oxidation on the enthalpy of adsorption of water on coal surfaces.(5)

Two investigations in our laboratory have shed light on the causes of the observed exotherm: The heat capacity of both premium coals and

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macerals have been measured. Measurements on the macerals will allow separation of the mineral contributions from those of the organic moieties of coal. The studies on the premium coal aid in the evaluation of the effects of oxidation. It is the studies of the premium coals which are discussed in this contribution.

Experimental

(i) Materials

The premium coals used in this study were the medium volatile bituminous coal from the Upper Freeport Seam and the high volatile bituminous coal from the Pittsburgh #8 Seam.(6) The Upper Freeport Seam coal was the first of the premium coals available and was obtained at the very beginning of this study. During the analysis of the results of these measurements it became evident that measurements on a high volatile premium coal would be most helpful and the Pittsburgh Seam coal was obtained. Comparisons are made with measurements on a high volatile Colorado coal, PSOC-854, that was obtained from the Coal Sample Bank at Pennsylvania State University. The as-received oxygen content of the premium coal was less than two percent; for the nonpremium coal, it was 11 percent.

(ii) Sample preparation

The premium coals were opened in a controlled-atmosphere chamber with low oxygen and moisture levels.(7) They were dried to constant weight at 383 K in a stream of dry nitrogen; the premium coals reach constant weight within 24 hours. The sample is then riffled to ensure representative sampling. The coal is pelletized and sealed in an inert atmosphere within the controlled-atmosphere chamber. Specimen masses ranged from 11-25 mg. Forty specimens of each coal were prepared. Some were used in the initial studies reported here; other, sealed at the same time under the same conditions, are available for further work.

(iii) Measurements

Heat capacity measurements were made in sealed cells with a power-compensated differential scanning calorimeter (DSC) over the temperature range 300-520 K at a heating rate of 5 K/min. Calorimetry Conference sapphire was used as a standard.(8) The heat capacity of the sapphire standard, determined before beginning the measurements reported here with the instrument settings to be used, was accurate to ±1.5 percent. Heat capacity measurements were made on 20 specimens of the Upper Freeport Seam coal; 10 specimens of the Pittsburgh Seam coal were used.

The standard operating procedures and data acquisition and reduction methods used for heat capacity measurements in our laboratory have been described.(9) Modifications have been made to these procedures for a material that undergoes an irreversible reaction on the first heating.(10)

The moisture content of the specimens as used was determined by means of a thermogravimetric balance (TGA).

Results and Discussion

In Figure 1 the heat capacities of the Upper Freeport Seam coal, for both initial and repeat runs, are shown. For purposes of comparison, similar measurements on an oxidized coal, PSOC-854, are shown in Figures 2 and 3. Though this coal, not a premium coal, had an as-received oxygen content of 11 percent, it was ground to -100 mesh in our laboratory before we had the capability of protecting it from the atmosphere. Because it was already well-oxidized when our protective facility was ready, no attempts were made to prevent further oxidation. The moisture content of the specimens actually measured, as determined by TGA, was less than 0.3 percent.

A significant difference between the premium and the nonpremium coals is evident on comparison of Figures 1, 2 and 3. The premium coal does not exhibit the deep exotherm on initial heating that is observed for the nonpremium coal. Both coals manifest expected, or normal, heat capacity behavior on the repeat runs. Differences between initial and repeat runs similar to those for the oxidized coal have also been reported by Singer and Tye(11) and by Richardson.(12) The differences noted strengthen our supposition that the exotherm is associated with the increased oxidation level of the coal.

The exotherm is now believed to result from exothermic condensation reactions which occur on the oxidized coal surface.(4) In the course of development of measuring techniques which will give valid results universally (transferable measuring techniques) we have made heat capacity measurements during several years on the PSOC-854 coal. As the coal has become more severely oxidized, the exotherm has deepened. A quantitative evaluation of the exotherm for coal specimens sealed in an inert atmosphere shows an increase from 6 J/g for a coal containing minimal amounts of oxygen to 38 J/g for a severely oxidized coal. For coals sealed in air, the enthalpy difference between initial and repeat runs is 60 J/g. The small energies stated here, when translated to tons, of coal are on the order of 5-34 MJ.

As our measurements were made in sealed specimen cells, the possibility of a contribution from readsorption of water exists. The water that was released during the heating of the coal to a temperature above that at which it was dried has the potential to react with the altered coal surface. Barton has shown that the exothermicity of the enthalpy of adsorption of water on a coal surface increases significantly as the coal becomes more oxidized.(5)

Another contribution to the differences observed between initial and repeat runs on premium and nonpremium coals arises from the difference in the volatile matter content of the two coals studied. Proximate analysis of the medium volatile premium coal gives a volatile matter content of 32 percent; for the high volatile coal, it gives 43 percent. In analyzing the results of measurements on the Upper Freeport seam (a medium volatile coal) and comparison with the PSOC-854 coal (a high volatile coal) the effects of the difference in volatile matter content of the two coals were of concern.(4) These effects, however, could not be evaluated until measurements on a premium high volatile coal were completed. The Upper Freeport Seam coal was the first of the premium coals to be distributed and was the only one available at the time this study was initiated. A sample of a high volatile premium coal (Pittsburgh #8 Seam) has since been obtained; measurements in progress on this coal will permit the effects of volatile matter content to be assessed.

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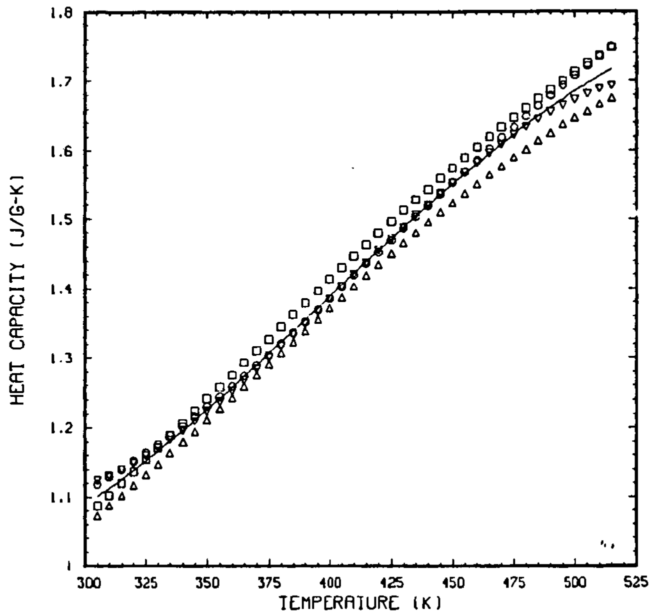

Figure 1. Initial and repeat measurements of premium coal. Fitted value for all measurements, —; fitted values for sets of five replicates, symbols; repeat measurements, Δ; initial measurements, other symbols.

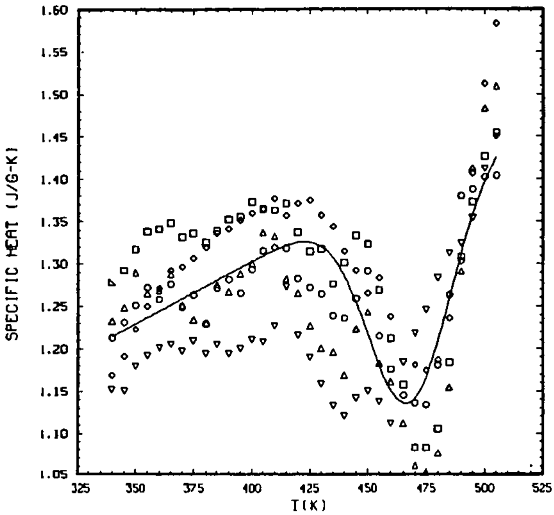

Figure 2. Initial measurements on nonpremium coal. Fitted value for five replicates, ; individual measurements, symbols.

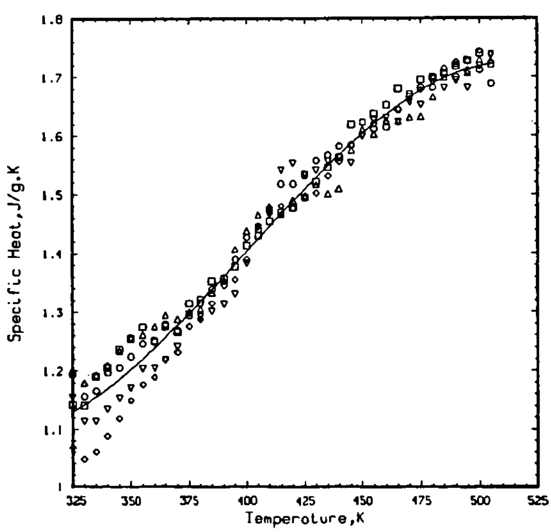

Figure 3. Repeat measurements on nonpremium coal. Fitted value for five replicates, ; individual measurements, symbols.