

MOISTURE SORPTION ON COALS

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A considerable amount of work has been reported in the literature on moisture sorption on coals, carbon blacks, charcoals and graphitized carbon blacks. However, the results and interpretation of the data even for the same type of adsorbents have often been at variance with one another.

In the present study, moisture sorption isotherms have been determined at 0 and 20°C on a series of 200x325 mesh coals, varying in rank from anthracite to high volatile bituminous coals. Moisture sorption was followed gravimetrically using a helical quartz spring having a sensitivity of 2×10^{-5} g.

Both the isotherm shape and the extent of adsorption depend on the coal rank. Bituminous coals adsorb significantly more water at low relative vapor pressures than anthracites. Further, sorption on bituminous coals is characterized by Type II isotherms, while anthracite gives a Type III isotherm.

It has been reported that moisture sorption is influenced by the volatile matter content of the carbon. Our results show that for a given coal rank, the moisture sorption capacity does not vary necessarily in the same order as the volatile matter content. This could be due either to the influence of the amount or type of impurities or to the role of specific functional groups present on the carbon surface on moisture sorption.

A pronounced hysteresis has been observed in the case of bituminous coals. Anderson et al (1) have reported that in the case of coals, hysteresis loops usually do not close until the relative pressure is reduced to zero. However, in our work, sorption-desorption isotherms do not meet even at zero relative vapor pressure; a certain amount of water cannot be desorbed even on outgassing the system to a constant weight at 20°C. The irreversibly adsorbed water is presumably chemisorbed on impurities, or held tightly within the micropores, or, as suggested by Puri (2), held at the surface by a mechanism involving hydrogen bonding to certain oxygenated functional groups.

Conventional capillary condensation cannot explain hysteresis in the case of pores of molecular dimensions. An attempt has been made to explain the hysteresis in terms of swelling and shrinkage effects during adsorption and desorption (3,4), a "cluster" model (5), and the independent domain theory (6).

BET plots give sensible straight lines, even for the anthracite which gives a Type III isotherm. The uncertainty regarding the assignment of a definite value for the molecular area of water when adsorbed on a carbon surface has been discussed. The BET surface areas calculated from the moisture sorption isotherms are much less than those calculated from CO₂ adsorption isotherms obtained at 25°C. In this respect, these results differ from those of Anderson et al (7) who have reported that the surface areas of coals from CO₂ isotherms are of the same magnitude as those calculated from water and methanol isotherms.

The discrepancy in our water and CO₂ surface areas is explicable in terms of the difference in the nature of adsorptive forces involved in the sorption of water on carbons and those envisaged for the BET model. Since a carbon surface is essentially hydrophobic, the role of dispersive forces involved in moisture sorption is negligible. It appears reasonable that sorption of water on coals involves adsorption at the 'primary' specific oxygen sites. Because of the strong intermolecular forces in water, the adsorbed water could act as 'secondary' sites for the adsorption of additional water, thus leading to 'cluster' formation, the growth of the clusters increasing with increasing surface coverage. At a certain stage, the clusters could merge to cover the coal surface with a unimolecular layer of adsorbed water, leading ultimately to the filling of the entire micropore volume.

The isosteric heats of adsorption calculated from the 0 and 20°C isotherms show that the net heat of adsorption over the entire pressure range is zero, i.e., $E_1 = E_2$. This would imply that the value of the constant C in the BET equation is unity. This is in direct conflict with the values of C obtained from the BET plots, where the values vary from 5 for anthracite to 25 for the bituminous coals. For $C=1$, the BET equation predicts that the isotherm should be of Type III. However, the correlation of the isotherm shape with the relative values of E_1 and E_2 is based on certain faulty assumptions (8). If C is assumed ≈ 1 , the BET equation predicts that the amount adsorbed at a relative vapor pressure of 0.5 should correspond to monolayer capacity. This approach has recently been used successfully by Walker and Janov (9) to estimate the 'active' surface area of Graphon samples and the values agree remarkably well with those obtained from oxygen chemisorption. In the present work, arguments have been presented to emphasize that in the case of coals this approach can hardly be used to estimate the fraction of the surface which is hydrophilic in character.

Thermodynamic considerations show that when the net heat of adsorption is zero, a decrease in free energy and hence spontaneous adsorption can occur only if the process of adsorption is accompanied by an increase in entropy. Calculations show that the entropy of adsorption has a positive value over the entire relative pressure range, the value decreasing in magnitude with progressive increase in the extent of adsorption.

The BET surface areas calculated from the moisture sorption isotherms have been compared with those obtained by Harvey's method (10), and the significance of the results have been discussed in the light of the work of Puri and Sharma (11).

Brunauer and coworkers (12) have suggested recently that the t curves obtained from water vapor adsorption can be used for pore structure analysis. The feasibility of using this approach for the pore structure analysis of coals is discussed.

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