

ASSESSING OXIDATION AND THE WETTABILITY OF COAL BY A FILM FLOTATION TECHNIQUE

D. W. Fuerstenau, M. C. Williams, K. S. Narayanan and J. L. Diao

Department of Materials Science and Mineral Engineering
University of California
Berkeley, CA 94720

ABSTRACT

The wettability of various as-received and oxidized coals can be quantified by a film flotation technique developed in our laboratories. Film flotation response curves yield an average wetting tension, ($\bar{\gamma}_c$), that can be used as an index for correlating the behavior of coals with their composition, treatment, process behavior, etc. The shift in $\bar{\gamma}_c$ with oxidation provides a quantitative measure of the change in surface energy of the coal induced by the increase in oxygen functional groups.

INTRODUCTION

With the exception of anthracite, almost all coals are very sensitive to oxidation. Addition of oxygen even in amounts too small to quantify will alter the properties of coal. Oxidation can proceed in-situ for coal deposits at shallow depths or may occur during mining, transportation, storage and processing. Whether oxidation takes place in the bulk of the coal or is limited to a thin surface layer, can affect drastically the surface properties of coal. The rate of oxidation is further enhanced as the specific surface area of coal is increased through comminution. Much effort is being directed towards elucidating the effect of oxidation on wettability or flotability.

An earlier study by Sun (1) indicated that the flotability of coal decreases with oxidation. Others (2,3) have also observed the flotability of oxidized coals to decrease even in the presence of collectors. Yarar (4) found that the flotation yield decreases for coals mined from deposits closer to the surface of the earth. This is attributed to higher probability of oxidation in shallow beds.

Despite these useful observations, delineation of the alteration in surface characteristics (wettability) due to oxidation remains imprecise. Contact angle measurements are strongly influenced by the pronounced heterogeneity of coal. Immersion time measurements, which have been used quite extensively for this purpose are extremely arbitrary and are theoretically ambiguous. Hornsby and Leja (5) first published papers on the use of normal flotation tests in a series of methanol-water solutions of decreasing surface tension to characterize coal flotability. In this paper, we describe a new film flotation method for determining the wettability of coal particles and illustrate its use in assessing oxidation effects with various coals.

Materials and Methods:

The coals used in this study along with their proximate analysis (ash,

volatile matter and fixed carbon) are listed in Table 1. The coal samples, which were received in large lumps, were first crushed in a jaw-crusher and then ground in a small coffee-grinder to minimize contamination. After fractionating the sample by sieving, the material was stored in a glove box in air-tight glass bottles. The glove box was further purged with inert gas to minimize oxidation. For the film flotation experiments 48 x 65 mesh (295 x 210 μ m) particles were used.

Table 1 - Proximate Analysis (dry basis) of Raw Coals

Coal	Volatile Matter % wt.	Ash % wt.	Fixed Carbon % wt.	dmmf Carbon % wt.
Cambria #33	17.15	6.47	76.38	87.3
Geneva	40.96	8.23	50.81	82.2
Springfield	31.32	31.99	36.69	74.3
Kittanning	25.84	43.06	31.10	71.4
Anthracite	2.95	5.25	91.80	91.8

Film flotation, discussed in detail elsewhere (6,7), involves placing a monolayer of particles onto the surface of a liquid of given surface tension. The liquids used were solutions made of analytical grade methanol and triply distilled water. With this procedure, the particles are partitioned into lyophobic and lyophilic fractions which are filtered, dried and weighed. Similar tests are repeated using solutions having different surface tensions. The weight percent of the lyophobic fraction plotted as a function of solution surface tension yields what is called the wetting tension distribution diagram. The coal samples were oxidized in a natural convection oven at different temperatures (150°C, 200°C, and 244°C) for 19 hours. The oxygen functional groups were determined by wet potentiometric titration methods outlined by Schafer (8).

RESULTS AND DISCUSSION

Extensive experiments have been carried out to investigate the film flotation response of coal and the use of the results for characterizing coal behavior. Figure 1a, in which the cumulative percentage of particles not imbibed by the liquid is plotted as a function of the surface tension of that liquid, illustrates the film flotation response of 210 x 295 μ m particles of Cambria #33 coal (a hydrophobic Pennsylvania bituminous coal). This figure clearly shows that there is a distribution in the wettability of the coal particles. We consider the cumulative plot given in Figure 1a to be a surface-based partition curve, which gives the cumulative distribution of particles in relation to their effective surface energy or hydrophobicity. We have defined three parameters from the kind of results given in Figure 1a: the surface tension of the solution that wets all particles, $\gamma_c(\min)$, the mean surface tension of particles in the distribution, $\bar{\gamma}_c$, and the surface tension of the solution above which none of the particles are wetted, $\gamma_c(\max)$. Initially, we consider that particles are imbibed at a given surface tension when the contact angle of those particles has just reached a value of zero. However, due to gravitational effects, sinking occurs at contact angles slightly greater than zero. Thus, the surface tension of the solution that imbibes all the particles represents those

particles with the lowest surface free energy, that is $\gamma_c(\min)$. The mean critical wetting surface tension of particles in the assembly is designated as $\bar{\gamma}_c$, and this then must represent an average of the γ_c 's of the particles being tested.

Using the data from Figure 1a, the mass fraction of the particles which are lyophobic is plotted in Figure 1b as a function of the surface tension of the imbibing solution. This figure indicates the existence of a surface parameter distribution, even for a closely-graded size distribution of the coal. The average surface tension parameter for each distribution, $\bar{\gamma}_c$, can be calculated from the histogram.

Coal oxidation is known to proceed in stages, which lead progressively through the production of gases, changes in the properties of gases, and changes in the properties of the remaining solid (9). Surface oxidation is caused when coal is exposed to an oxidizing atmosphere. The initial stages of oxidation are characterized by chemisorption of oxygen and the formation of acidic functional groups, specifically carboxylic (-COOH), ketone (C=O) and phenolic (-OH). Prolonged oxidation under high severity conditions can result in substantial uptake of oxygen deep into the coal matrix. Oxidation in laboratory investigations has been carried either with chemical oxidants or by thermal oxidation. For the work reported here we have used the thermal oxidation procedure described.

In this work, the effect of oxidation on the wettability of powdered coal was investigated through film flotation response, by varying the surface tension of the liquid between that of pure methanol (22.5 mN/m) and distilled water (72.8 mN/m). The wetting surface tension distribution of Cambria #33 coal oxidized at 150, 200 and 244°C for 19 hours is shown in Figure 2. From the results presented here, it is clearly seen that the curves are shifted to the right with increased oxidation, indicating an increase in the average wetting surface tension ($\bar{\gamma}_c$) as the coal becomes more oxidized. In an ideal unoxidized coal, the carbonaceous material (macerals) is responsible for its natural hydrophobicity with the inorganic minerals generally being hydrophilic. Upon oxidation the carbonaceous substrate produces oxygenated functional groups (-COOH, -OH) at the surface, which increase the hydrophilicity of coal due to their interaction with polar water molecules.

The curves in Figure 2 suggest that different components of the hydrophobic fraction in this coal tend to oxidize at different degrees since $\bar{\gamma}_c$ changes markedly without $\gamma_c(\min)$ shifting appreciably. To test this, some contact angle results obtained by Yang (10) on the same sample of coal are reproduced in Figure 3, which gives plots of the cosine of the contact angle (θ), measured on coal samples oxidized at different temperatures, as a function of the surface tension of the aqueous methanol solution. These so-called Zisman plots yield the critical wetting surface tension, γ_c , by extrapolation of the line to cosine $\theta = 1$. The results given in Figure 2 indicate that γ_c for the coal is essentially independent of the extent of oxidation. Yet the contact angle in water indeed reflects oxidation behavior rather markedly with the contact angle being 90 degrees for as-received coal, 50 degrees when oxidized at 150°C and 40 degrees when oxidized at 200°C.

In regard to sensitivity of contact angle behavior, Parekh and Aplan (11) also observed that γ_c is the same for a wide range of coals, namely 45 mN/m.

This indicates probably some insensitivity in the contact angle technique for determining the critical wetting tension of coals and serving as a comparative index for differentiating coal subjected to different degrees of oxidation.

We believe that the mean wetting surface tension, $\bar{\gamma}_C$, provides a useful index with which to correlate process response among various coals or between degrees of oxidation of the same coal. To test this, the percentage of oxygen in functional groups was determined by wet potentiometric titration method outlined by Schafer (8). Figure 4 shows the correlation between the concentration of oxygen functional groups with $\bar{\gamma}_C$. In addition, Fuerstenau et al. (12) determined the flotation behavior of this same coal in 0.5M NaCl solutions and their results for maximum flotation yield are also included in Figure 4. This figure shows that the coal is rendered hydrophilic as the percentage of oxygen groups in the coal increases. This is also very well reflected by the film flotation results which show the γ_C to increase with oxidation, thus establishing its applicability in quantifying hydrophilicity.

The fact that the increase in hydrophilicity for a given coal is due to the increase in oxygen functional groups is further elucidated by determining the acidic and phenolic groups in the lyophilic and lyophobic fractions produced by film flotation. Film flotation of Geneva Mine coal (a Utah bituminous coal) was performed in 30% methanol solution ($\gamma = 45$ mN/m). Potentiometric titrations of the lyophobic and lyophilic fractions indicate that the particles imbibed into the solution (58% of the feed) have a considerably higher concentration of carboxylic and phenolic functional groups than the floating particles. The original feed was also titrated to determine the functional group closure. The results are presented graphically in Figure 5. There is a 99 percent closure on the phenolic and a 97 percent closure on the carboxylic groups. It is apparent from these studies that the presence of oxygen functional groups increases the hydrophilicity of coals, which in turn alters their processing response.

This procedure was extended to ascertain how a range of coals having wide range of proximate analysis (Table 1) were affected when oxidized and film floated. Table 2 presents the values of $\bar{\gamma}_C$ (or γ_{50}) obtained from the wetting tension diagrams for both as-received and oxidized (at 200°C, 19 hrs) coals used in this investigation. For some of the as-received coals and oxidized coals complete wetting tension distribution diagrams could not be obtained, because the most hydrophilic particles were engulfed into pure water. However, analysis of the curves for coals for which the full distribution could be obtained indicated that the $\bar{\gamma}_C$ is reasonably close to γ_{50} , that is the 50% point on the cumulative distribution plots. Some preliminary observations are that, of the bituminous coals, those with highest ash content are the most hydrophilic and the one with the highest volatile matter content is the most hydrophobic. Interestingly, anthracite is the least hydrophobic of the as-received coals and exhibits great resistance to oxidation. The initial behavior of coal and its susceptibility to oxidation will depend on the characteristics of the different carbonaceous species present in a given coal. This depends on the conditions of coalification to which the decaying plant matters are subjected.

Table 2 - Average Wetting Surface Tension from the Film Flotation of Raw Coal and Coal Oxidized for 19 hours at 200°C.

Coal	Average Wetting Tension (mN/m)	
	Raw	Oxidized
Cambria #33	46.8	75.5
Geneva	31.0	66.0
Springfield	51.5	76.5
Kittanning	49.0	90.0
Anthracite	69.0	71.0

SUMMARY AND CONCLUSIONS

In summary, by conducting film flotation with a series of alcohol-water solutions, the wettability of as-received and oxidized coals can be quantified. This quantification is achieved by estimating the mean wetting surface tension ($\bar{\gamma}_c$) for a given sample of coal. All the coals tested showed a marked increase in hydrophilicity on oxidation. The sensitivity of $\bar{\gamma}_c$ as an index for predicting the flotation response of coal is established through a correlation between oxygen content, $\bar{\gamma}_c$ and flotation yields. Potentiometric titrations of the hydrophilic and hydrophobic fractions of coal confirm that the concentration of oxygen functional groups is much higher in the hydrophilic fraction than in the hydrophobic fraction.

ACKNOWLEDGEMENT

This material was prepared with the support of the U.S. Department of Energy, Grant No. DE-FG22-84PC70776.

REFERENCES

1. Sun, S. C., Trans. AIME, 199, 396, 1954.
2. Wen, W. W., and Sun, S. C., Trans. AIME, 262, 174, 1977.
3. Celik, M. S., and Somasundaran, P., Colloids and Surfaces, 1, 121, 1980.
4. Yasar, B., Trans. AIME, 272, 1978, 1983.
5. Hornsby, D. T., and Leja, J., Coal Preparation, 1, 1, 1984.
6. Fuerstenau, D. W., Williams, M. C., and Diao, J. L., AIME Annual Meeting, New Orleans, March 1986.
7. Fuerstenau, D. W., Williams, M. C., and Urbina, R. H., Proceedings, Conference on Coal Science, Pergamon Press, 517, 1985.
8. Schafer, H. N. S., Fuel, 49, 271, 1970.
9. Tsai, S. C., Fundamentals of Coal Beneficiation and Utilization, Coal Science and Technology - 2, Elsevier, New York 1982.
10. Yang, G. C. C., Ph.D. Thesis, University of California, Berkeley, 1983.
11. Parekh, B. K., and Aplan, F. F., Recent Developments in Separation Science, 4, 107, 1974.
12. Fuerstenau, D. W., Yang, G. C. C., and Laskowski, J. S., Coal Preparation, in press, 1986.

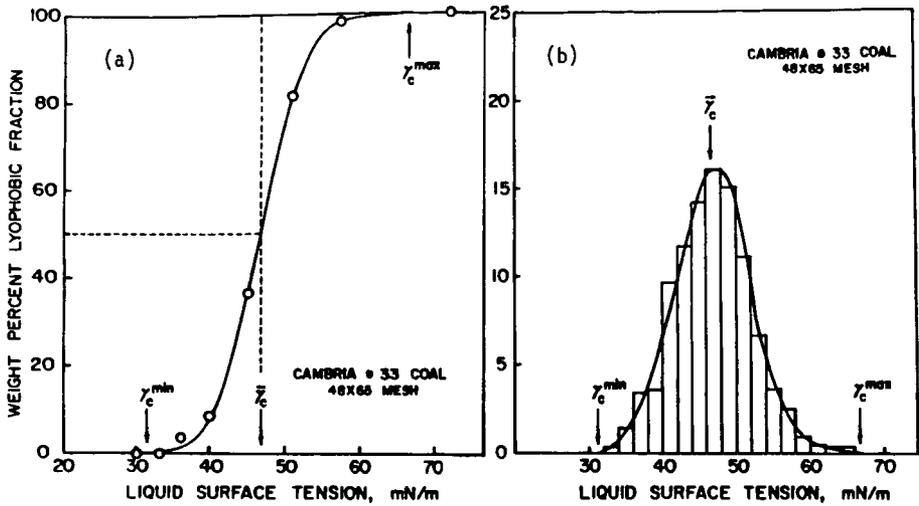


Fig. 1- a) Film flotation partition curve for Cambria #33 bituminous coal, and b) Frequency histogram for the lyophobicity of Cambria #33 coal.

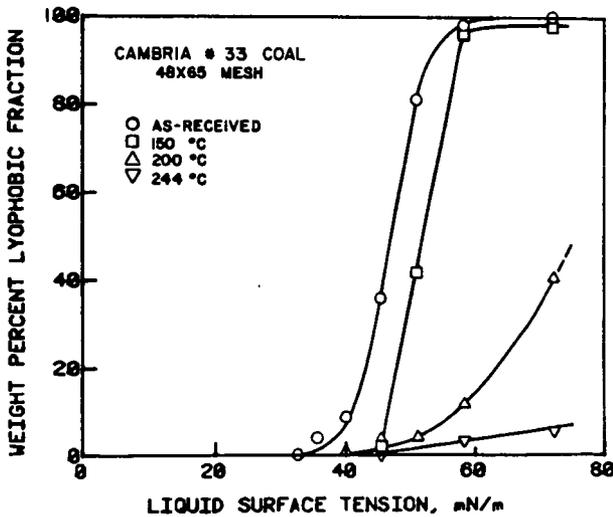


Fig. 2- Film flotation partition curves for as-received and oxidized Cambria #33 coal.

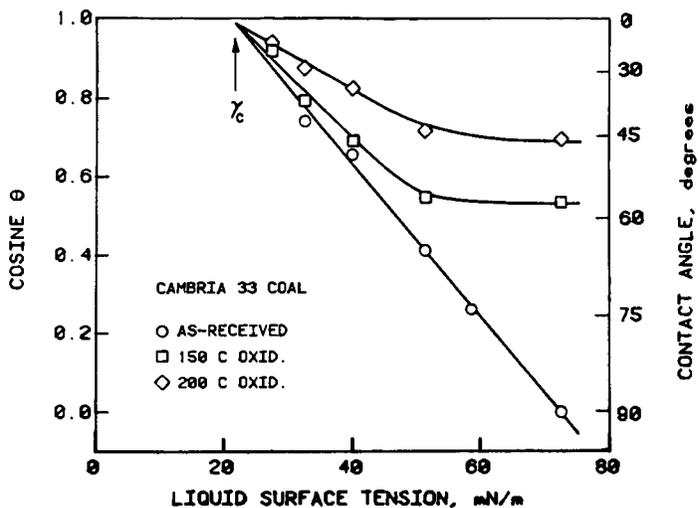


Fig. 3 - Zisman plots of the cosine of the contact angle of aqueous methanol solutions on as-received and oxidized Cambria #33 bituminous coal.

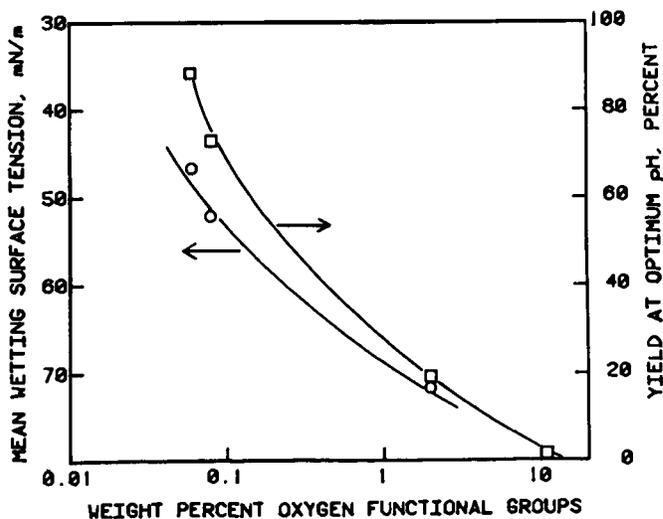


Fig. 4 - Correlation between the concentration of oxygen functional groups, average wetting tension and flotation yield for Cambria #33 coal.

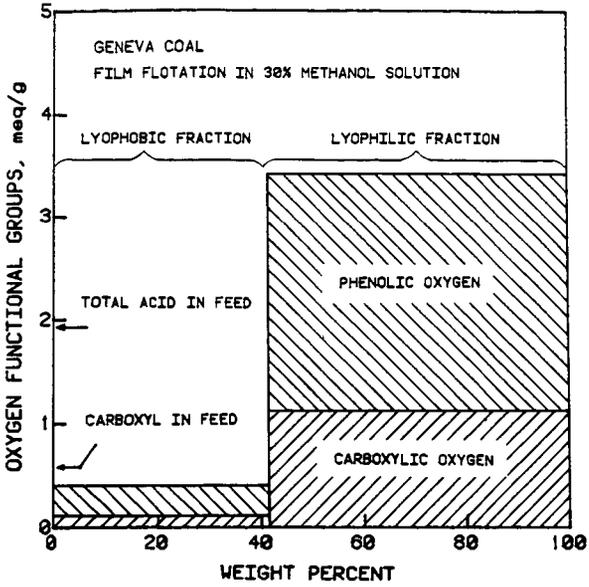


Fig. 5 - Graphical representation of the distribution of functional groups between the lyophobic and lyophilic fractions from the film flotation of Geneva coal.