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MOISTURE CONTENT AS A PREDICTOR OF COAL HYDROPHOBICITY W-7405-ENG-82

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Abstract

A statistical analysis of previously published experimental data showed that coal hydrophobicity correlates better with coal moisture content than with carbon content.

Introduction

Coals are heterogeneous complex solids which are generally classified according to various ranks such as lignite, subbituminous, bituminous, and anthracite. This classification reflects the stage of metamorphism that a coal has reached in a slow, progressive transformation of oxygen-rich plant debris to carbon-rich, oxygen-poor anthracite coal. As this transformation takes place, the following general changes in properties are noted: moisture content decreases, more rapidly in the early stages, slowly in the later stages; carbon content increases; oxygen content decreases; hydrogen content changes very little until later stages are reached when it decreases markedly; volatile matter content generally decreases; calorific value increases, levels off, and then drops slightly as the anthracite stage is reached; and total void volume (porosity) decreases, levels off among coals with 87-89% carbon before increasing again among anthracites (Berkowitz, 1979; Elliott and Yohe, 1981).

Carbon content is used most often for judging rank over the entire range of coal ranks as it is the most suitable criterion, although other parameters can be used for judging rank over limited ranges. Carbon is the major constituent of coal, and its determination is a direct and simple procedure. Other constituents which may reflect rank are present in smaller amounts and their determination is not always straightforward. For example, oxygen associated with the organic matrix is difficult to determine directly. Also, since coal is easily oxidized, the measured oxygen content may not be an accurate reflection of its inherent oxygen content. By the same token the moisture content of coal, determined "as received", may not correspond closely to its natural coal bed moisture content.

Many coals exhibit a certain degree of native hydrophobicity. The more hydrophobic coals (the higher rank coals) can be beneficiated by froth flotation or oil agglomeration, while the more hydrophilic coals (the lower rank coals) are difficult to float or agglomerate. Coals of different rank and sometimes even of the same rank differ greatly in hydrophobicity as measured by contact angle or natural floatability. Although the degree of

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hydrophobicity of a coal is related to its rank (Horsley and Smith, 1951; Brown, 1962) and the floatability of coal has been correlated with various indicators of hydrophobicity (Fuerstenau et al., 1983; Aplan, 1983; Gutierrez-Rodriguez and Aplan, 1984), the characterization of coal hydrophobicity is incomplete and its variation with rank has not been completely accounted for. One reason for this state of affairs is the heterogeneity of coal which makes it difficult to quantitatively account for the contribution of each constituent of the coal surface to hydrophobicity.

Traditionally, various hydrophobic indicators such as natural floatability and contact angle have been plotted against carbon content to illustrate the relationship between hydrophobicity and coal rank. These plots have shown that hydrophobicity increases with an increase in rank, reaches a maximum for medium-volatile bituminous and low-volatile bituminous coals (approximately 88-90% carbon content), and decreases for anthracite (Horsley and Smith, 1951; Brown, 1962; Gutierrez-Rodriguez et al., 1984). Because the natural hydrophobic character of some coals has been associated with their high carbon content and carbon content has been used in illustrating the variation of coal hydrophobicity with rank, the assumption has been made that the increase in hydrophobicity from lignite to low-volatile bituminous coal is due to an increase in carbon content. This led to numerous explanations to account for the "anomalous" behavior of anthracite coal, which is generally less hydrophobic than medium-volatile and low-volatile bituminous coals, even though anthracite has a higher carbon content.

Van Hatten (1982) based the selection of coals suitable for oil agglomeration on the inherent moisture content of coal (that is, he used inherent moisture content as a relative indicator of coal hydrophobicity). Fuerstenau et al. (1983) found an excellent correlation between as received moisture content and the flotation response of bituminous coals and coals on the borderline between bituminous and subbituminous. Labuschagne (1987) showed that the correlation probably applies to coals of all ranks, provided that the as received moisture content is a reasonable reflection of inherent moisture content (natural coal bed moisture).

It is well known that the floatability of coal is affected adversely by an increase in oxygen content and/or surface oxidation (Sun, 1954a; Iskra and Laskowski, 1967; Aplan, 1983; Fuerstenau et al., 1983; Gutierrez-Rodriguez and Aplan, 1984). Also it has been found that surface oxidation reduces the propensity for coal to undergo oil agglomeration (Sadowski et al., 1988). Therefore, the presence of oxygen functional groups on the surface directly affects the hydrophobicity of coal.

Another factor which may affect coal hydrophobicity is hydrogen content. As Brady and Gauger (1940) and Sun (1954b) observed, the most hydrophobic carbonaceous materials are paraffinic hydrocarbons and waxes which have a relatively high hydrogen-to-carbon ratio. Spitzer (1986) correlated the floatability of bituminous coals with the quantity of long-chain aliphatic compounds which are extractable with a mixture of chloroform and ethyl acetate. Moreover, the reduction in hydrophobicity associated with the transformation of low volatile bituminous coal to anthracite may be due to loss of hydrogen or alkyl groups.

Table 1. Parameters associated with coal rank

No.	Coal rank parameter	Group
1	Carbon content, as received (AR)	A
2	Carbon content, dry, ash-free (DAF)	A
3	Moisture content, as received (AR)	A
4	Hydrogen/carbon atomic ratio	B
5	Oxygen/carbon atomic ratio	B
6	Moisture/carbon molar ratio	B

From the preceding discussion it is apparent that coal hydrophobicity may be due to a number of factors or parameters which are associated with coal rank. The present study was undertaken to compare the degree of correlation between certain indicators of hydrophobicity and various parameters which are listed in Table 1. The parameters were placed in two groups (A and B) and comparisons were made within groups. The indicators of hydrophobicity which were used included the actual floatability (ACTF), the three-phase contact angle measured by the captive bubble (CB) technique, and the three-phase contact angle measured by the sessile drop (SD) technique. Experimental data were taken from the publications of Sun (1954b) and Gutierrez-Rodriguez *et al.* (1984). The degree of correlation between each indicator of hydrophobicity and any given parameter associated with coal rank was evaluated by two statistical methods. The first method was based on the well-known Spearman correlation coefficient which is a nonparametric measure of the association between two variables; it was used here as an index of monotonicity. The second method was based on R-square which is an index of the degree of conformance of the experimental data to a quadratic function. The degree of correlation was evaluated for two ranges of coal rank. Range I included the data for coals ranging from lignite to low-volatile bituminous coal (88-90% carbon content), whereas range II included the data for all coal ranks. The experimental data presented in Figures 1 to 4 suggest that hydrophobicity is a monotonic function of carbon content over range I but not over range II whereas hydrophobicity is a monotonic function of moisture content over both ranges I and II.

Statistical Methods

As indicated above, several parameters associated with coal rank were compared to see how well they correlate with hydrophobicity. The parameters are listed in Table 1. The degree of correlation between each parameter and an indicator of hydrophobicity was evaluated by two different statistical methods. The first method was based on the absolute value of the Spearman correlation coefficient, ρ , which was calculated by means of the following expression:

$$\rho = \frac{\sum_{i=1}^n (R_i - \frac{n+1}{2})(S_i - \frac{n+1}{2})}{\sum_{i=1}^n (i - \frac{n+1}{2})^2}$$

where n was the number of coal samples (i.e., data pairs X_i, Y_i) examined with X_i corresponding to the value of the parameter associated with coal rank and Y_i corresponding to the value of the hydrophobicity indicator of the i 'th coal sample, and R_i was the relative rank of X_i among the n values of X , and S_i was the relative rank of Y_i among the n values of Y . The second statistical method was based on the multiple correlation coefficient about quadratic regression,

$$R\text{-square} = \frac{\sum_{i=1}^n (Y_i - \bar{Y})^2 - \sum_{i=1}^n [Y_i - (a + b X_i + c X_i^2)]^2}{\sum_{i=1}^n (Y_i - \bar{Y})^2}$$

where $Y = a + bX + cX^2$ is the least squares quadratic regression function of Y on X .

The absolute value of ρ measures the degree of monotonicity of the observed (X,Y) relationship. It equals one, for example, when the relation is entirely monotonic, and it equals zero when the relation is completely disordered. A succession of steadily increasing values of Y associated with a succession of increasing values of X would be completely monotonic.

R -square measures the degree of conformance of the (X,Y) relation to the best-fitting quadratic function. It equals one when all (X_i, Y_i) values fall precisely on the best-fitting (least squares) quadratic function. It equals zero when the best-fitting quadratic function is a horizontal straight line, so that the dispersion of the Y values

$$\sum_{i=1}^n [Y_i - (a + b X_i + c X_i^2)]^2$$

about this line is no smaller than their dispersion as measured by the relation-insensitive variance numerator,

$$\sum_{i=1}^n (Y_i - \bar{Y})^2$$

For coals in range I, ρ is particularly appropriate for comparing the degree of correlation between different indicators of hydrophobicity and various parameters associated with coal rank because in this range hydrophobicity is generally a monotonic function of coal rank. Therefore, ρ is capable of identifying the most monotonic parameters among roughly monotonic ones in this range.

Table 2. Sources of experimental data

Indicators of hydrophobicity	Range	Data group	Data points No.	Data set ^a
Actual floatability	I	a	19	(1)
	II	b	27	(1)
Contact angle (CB)	I	c	14	(1)
	II	d	20	(1)
	I	e	17	(2)
	II	f	19	(2)
Contact angle (SD)	I	g	17	(2)
	II	h	19	(2)

^aSet (1): Sun, 1954b.

Set (2): Gutierrez-Rodriguez et al., 1984.

Discussion of Results

Experimental data reported by Gutierrez-Rodriguez et al. (1984) are replotted in Figures 1 to 4 to illustrate possible relationships between the three-phase contact angle (an indicator of hydrophobicity) and either coal carbon content or moisture content. Figures 1 and 3 indicate the classical variation of coal hydrophobicity with rank as represented by carbon content. Hydrophobicity increases with an increase in rank or carbon content, reaches a maximum at about 88% carbon (low-volatile bituminous coal), and decreases for coals of higher carbon content (anthracite). Since anthracite is not as hydrophobic as would be expected from its high carbon content, it appears anomalous. However, when hydrophobicity is plotted against moisture content as in Figures 2 and 4, the data for anthracite fall in line with those of other coals, and the resulting relationship appears to be monotonic. Similar behavior was observed when the data reported by Sun (1954b) were reanalyzed by Labuschagne (1987).

To quantify the degree of correlation between various indicators of hydrophobicity and different parameters associated with coal rank, the Spearman correlation coefficient ρ and R-square were calculated for the eight data groups listed in Table 2. These calculations were repeated for each of the parameters listed in Table 1 and the results are presented in Figures 5 to 12. The results are grouped according to hydrophobic indicator (floatability or contact angle), range of coal rank (I or II), and coal rank parameter group (A or B). Each bar in these charts is identified by a number corresponding to a coal rank parameter as indicated in Table 1.

Figures 5 to 8 show that values of ρ were generally as high and sometimes slightly higher for coal moisture content as for carbon content over range I of coal rank. Moreover, values of ρ were clearly greater for coal moisture content than for carbon content over range II. Therefore, moisture content

compares favorably with carbon content as a correlator of hydrophobicity for range I, and it is a much better correlator of hydrophobicity for range II.

Figures 5 to 8 also show that values of ρ were generally greater for the moisture/carbon ratio than for either the hydrogen/carbon ratio or the oxygen/carbon ratio over either ranges I or II. Values of ρ were consistently lower for the hydrogen/carbon ratio than for the other ratios. Consequently the moisture/carbon ratio is a better correlator of hydrophobicity than either the hydrogen/carbon ratio or oxygen/carbon ratio appear to be.

Figures 9 to 12 show that the trend in R-square values was generally similar to that noted for ρ values. However, Figure 9 indicates that the correlation between actual floatability and moisture content was far greater than that between floatability and carbon content for either range I or II. Furthermore, the correlation between floatability and the moisture/carbon ratio was markedly greater than that between floatability and either the hydrogen/carbon ratio or oxygen/carbon ratio for either range I or II. Consequently the correlation between floatability and moisture content is especially strong.

A summary of the information presented in Figures 5 to 8 is given in Table 3 which indicates the number of times any given coal parameter was ranked first, second, or third in its group (A or B) within a given range (I or II) on the basis of the ρ values presented in these charts. For example, within parameter group A and range I, the highest value of ρ was associated with carbon content (AR) once, with carbon content (DAF) once, and with moisture content twice. The second highest value of ρ was also associated with carbon content (AR) once, with carbon content (DAF) once, and with moisture content twice, whereas the third highest value of ρ was associated with carbon content (AR) twice, with carbon content (DAF) twice, and with moisture content not at all. Thus, within range I and group A, moisture content ranked as the best correlator of hydrophobicity more frequently than carbon content on either basis. Furthermore, within range II and group A, moisture content always ranked as the best correlator of hydrophobicity. The data further indicate that within group B the moisture/carbon ratio was almost always the best correlator of hydrophobicity within either range I or II.

A similar summary is given in Table 4 for the R-square values presented in Figures 9 to 12. The ranking of the R-square values follows a pattern very much like that for the ρ values. Consequently the results of the two statistical methods, i.e., the methods based on ρ and R-square, are very much in agreement.

The high degree of correlation between hydrophobicity and either of the two moisture-based parameters is remarkable inasmuch as the discovery is based on previous experimental work which was not conducted for the express purpose of proving such a relationship. Consequently, the moisture content may not have been specially controlled in that work. Therefore, the "as received" moisture content of the coal samples may not have reflected accurately the natural coal bed or inherent moisture content. Since the latter is a more fundamental property of the coal than "as received" moisture content, it could provide a better correlation with hydrophobicity. By conducting further measurements in which moisture content is carefully controlled and by correlating hydrophobicity with the natural coal bed moisture content, it may

Table 3. Spearman correlation coefficients ranked according to order

Parameter associated with coal rank	Group	Number of times ρ ranked					
		Range I			Range II		
		1st	2nd	3rd	1st	2nd	3rd
Carbon (AR)	A	1	1	2	0	2	2
Carbon (DAF)	A	1	1	2	0	2	2
Moisture (AR)	A	2	2	0	4	0	0
Hydrogen/carbon	B	0	0	4	0	0	4
Oxygen/carbon	B	1	3	0	0	4	0
Moisture/carbon	B	3	1	0	4	0	0

Table 4. R-square values ranked according to order

Parameter associated with coal rank	Group	Number of times R-square ranked					
		Range I			Range II		
		1st	2nd	3rd	1st	2nd	3rd
Carbon (AR)	A	1	2	1	0	2	2
Carbon (DAF)	A	1	0	3	0	2	2
Moisture (AR)	A	2	2	0	4	0	0
Hydrogen/carbon	B	0	1	3	0	0	4
Oxygen/carbon	B	1	2	1	0	4	0
Moisture/carbon	B	3	1	0	4	0	0

be possible to demonstrate an even tighter correlation between hydrophobicity and moisture content than the one revealed here.

Conclusions

Based on a statistical analysis of published experimental data, it is concluded that the correlation between coal hydrophobicity and moisture content is better than that between hydrophobicity and carbon content. Also, it is concluded that the correlation between hydrophobicity and the moisture/carbon ratio is better than that between hydrophobicity and either the hydrogen/carbon or the oxygen/carbon ratio.

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Fig. 1. Hydrophobicity vs. carbon content, data group (f).

Fig. 2. Hydrophobicity vs. moisture content, data group (f).

Fig. 3. Hydrophobicity vs. carbon content, data group (h).

Fig. 4. Hydrophobicity vs. moisture content, data group (h).

Fig. 5. ρ based on data groups (a) and (b).

Fig. 6. ρ based on data groups (c) and (d).

Fig. 7. ρ based on data groups (e) and (f).

Fig. 8. ρ based on data groups (g) and (h).

Fig. 9. R-square based on data groups (a) and (b).

Fig. 10. R-square based on data groups (c) and (d).

Fig. 11. R-square based on data groups (e) and (f).

Fig. 12. R-square based on data groups (g) and (h).

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