Relating coal oxidation and hydrophobicity: a petrographic approach

Krystyna J. Kruszewska, Barend C. J. Labuschagne* and Vivien M. du Cann†

Faculty of Earth Science, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec, Poland
* Faculty of Medicine, University of Stellenbosch, PO Box 19063, Tygerberg 7505, South Africa
†Division of Materials Science and Technology, CSIR, PO Box 395, Pretoria 0001, South Africa

Long-wave fluorescence relative intensity measurements and a vitrinite microelasticity index were used to determine oxidation levels in a suite of artificially oxidized coals. These petrographic parameters were correlated with the agglomeration responses of the coals. Very definite relations were found between the petrographic indicators of oxidation and the agglomeration rates of the coals. *Copyright © 1996 Elsevier Science Ltd.*

The oxidation of coal can have a negative impact on coal quality and technological behaviour. Oxidation can also affect preparation plant performance by reducing coal hydrophobicity[1]. Changes in the surface characteristics of coal affect wettability and thus the flotation and agglomeration responses. Reduction of hydrophobicity results in decreases in the floatability or agglomerability of the coal[2]. The aims of this study were to use two petrographic techniques, namely long-wave fluorescence relative intensity (FRI) measurements[3] and a vitrinite elasticity index (EI) based on Vickers microhardness impression types[3,4], to assess the degree of oxidation of a set of four artificially oxidized coals and to correlate these parameters with the agglomeration responses of the coals.

EXPERIMENTAL

Coals

Four coals of different rank and type were selected and characterized by their chemistry and swelling number (*Table 1*) and by their maceral composition[5], vitrinite reflectance and reactive maceral content[6] (*Table 2*).

Agglomeration

A portion of each of the four fresh coal samples was ball-milled in water to an average size of $10 \mu m$ for use in the agglomeration tests. The agglomeration experiments were carried out in a 500 mL beaker on 200 mL of slurry containing 20 g of solids (10 wt% solids). A Morat R20S Digitronic stirring machine was used at the selected speed of $1000 \, \text{rev} \, \text{min}^{-1}$. The coals were agglomerated with 15 mL of tetralin (1,2,3,4-tetrahydronaphthalene) as the bridging liquid.

The average rate of organic recovery, k, was calculated using the formula:

$$k = R/t$$

where R = organic recovery (wt%) obtained at time t and t = agglomeration time in seconds. The agglomeration time was the minimum time needed for complete agglomeration. When agglomeration was incomplete after 5000 s, the process was stopped and the organic recovery measured at the end of this period. The average rate of organic recovery was used as an indicator of hydrophobicity.

The organic recovery on an oil-free basis, R (wt%), and degree of de-ashing, E (wt%) were determined using the formulae:

$$R = 100[(y_3 - y_1)(100 - y_2)]/[(y_3 - y_2)(100 - y_1)]$$
$$E = 100(y_1 - y_2)/y_1$$

where y_1, y_2 and y_3 are the proportions (wt%) of ash in the feed, agglomerated coal and tailings respectively. These percentages (y) were determined by ashing the fractions (feed, agglomerates and reject) at 825°C for 10 h.

Oxidation

A portion of each of the four fresh coals was crushed to <1 mm and 40 g of this material was spread evenly in a very thin layer (~1 mm) in a stainless steel tray. The coals were oxidized in air at 150°C. Samples were removed at 0.25, 0.5, 2.0, 5.0 and 10.0 h intervals.

For each of the four coals under study, a portion of coarse oxidized material (<1 mm) was subjected to

Table 1 Chemical analyses and swelling numbers of the fresh coals

	Proximate analysis (wt% air-dry)				Ultimate analysis (wt% daf)					Swelling no.
	H_2O	Ash	VM	FC	C	H	O	N	S	
Coal 1	2.6	9.8	35.6	52.0	80.6	5.8	11.2	1.6	0.8	3.5
Coal 2	1.5	11.6	20.2	66.7	84.8	5.4	6.3	2.1	1.4	6.0
Coal 3	0.9	12.4	21.1	65.6	88.3	5.1	3.7	2.2	0.7	6.0
Coal 4	0.6	15.9	23.4	60.1	89.5	5.3	2.6	1.8	0.8	8.0

Table 2 Petrographic analyses of the fresh coals

	Maceral composition (vol. % mmf)[a]				Rank, R_o (%)[b]	Maceral scan analysis (vol. % mmf)[c]		FRI (%)[d]	EI[e]
	V	L	RSF	I		RI	Σ Re		
Coal 1	87.7	5.5	2.8	4.0	0.64	0.1	94.4	0.54	54
Coal 2	52.4	3.3	17.3	27.0	0.82	10.9	64.0	1.72	38
Coal 3	50.3	0.4	18.9	30.4	1.12	12.7	61.6	1.00	23
Coal 4	93.6	0.0	0.5	5.9	1.18	0.1	94.4	1.12	21

[a] V, vitrinite; L, liptinite; RSF, reactive semifusinite; I, inertinite
[b] Random reflectance of vitrinite in oil immersion
[c] RI, reactive inertinite; Σ Re, sum of reactives (vitrinite + liptinite + reactive inertinite)
[d] Fluorescence relative intensity
[e] Elasticity index

Table 3 Oxidation data: coarse material (particle size <1 mm)

		Petrographic analyses			Percentage change	
	Oxidation time (h)	Vitrinite reflectance, random (%)	FRI (%)	EI	FRI	EI
Coal 1	0.00	0.64	0.54	54	—	—
	0.25	0.66	0.40	60	25.9	11.1
	0.50	0.65	0.37	62	31.5	14.8
	2.00	0.66	0.33	70	38.9	29.6
	5.00	0.67	0.32	79	40.7	46.3
	10.00	0.66	0.29	85	46.3	57.4
Coal 2	0.00	0.82	1.72	38	–	–
	0.25	0.80	1.29	38	25.0	0.0
	0.50	0.80	1.23	39	28.5	2.6
	2.00	0.81	1.19	43	30.8	13.2
	5.00	0.80	1.20	46	30.2	21.1
	10.00	0.80	0.95	53	44.8	39.5
Coal 3	0.00	1.12	1.00	23	–	–
	0.25	1.14	0.89	24	11.0	4.3
	0.50	1.15	0.74	26	26.0	13.0
	2.00	1.13	0.76	29	24.0	26.1
	5.00	1.15	0.59	32	41.0	39.1
	10.00	1.15	0.46	35	54.0	52.2
Coal 4	0.00	1.18	1.12	21	–	–
	0.25	1.19	0.97	21	13.4	0.0
	0.50	1.18	0.91	22	18.8	4.8
	2.00	1.20	0.92	25	17.9	19.0
	5.00	1.19	0.84	27	25.0	28.6
	10.00	1.19	0.74	29	33.9	38.1

Table 4 Oxidation data: fine feed material (particle size 10 μm)

	Oxidation time (h)	Agglomeration response			Petrographic analyses	
		Agglomeration rate (wt % s^{-1})	Organic recovery (wt %)	De-ashing (wt %)	Vitrinite reflectance, random (%)	FRI (%)
Coal 1	0.00	0.83	98.5	57.4	0.60	0.54
	0.25	0.74	98.6	55.6	0.61	0.42
	0.50	0.68	99.0	53.5	0.61	0.38
	2.00	0.44	99.0	55.6	0.59	0.24
	5.00	0.21	98.6	55.6	0.60	0.23
	10.00	0.02	26.8	72.2	0.61	0.20
Coal 2	0.00	0.23	54.7	44.8	0.75	—
	0.25	0.20	33.7	33.6	0.76	—
	0.50	0.19	32.9	33.6	0.75	—
	2.00	0.12	33.6	33.6	0.73	—
	5.00	0.06	30.9	43.1	0.74	—
	10.00	0.03	33.1	45.7	0.76	—
Coal 3	0.00	1.18	>98.0	—	1.05	—
	0.25	1.18	>98.0	—	1.05	—
	0.50	1.05	>98.0	—	1.08	—
	2.00	1.00	>98.0	—	1.06	—
	5.00	0.74	>98.0	—	1.07	—
	10.00	0.63	>98.0	—	1.06	—
Coal 4	0.00	2.86	>98.0	—	1.13	—
	0.25	2.50	>98.0	—	1.11	—
	0.50	1.82	>98.0	—	1.12	—
	2.00	1.54	>98.0	—	1.13	—
	5.00	0.80	>98.0	—	1.11	—
	10.00	0.56	>98.0	—	1.13	—

petrographic investigations, namely reflectance, fluorescence and elasticity measurements. The latter two procedures have been described in detail by Kruszewska and du Cann[3].

A second portion of each fresh coal was ball-milled in water to a particle size of 10 μm, air-dried, oxidized under the same conditions as in the case of the <1 mm material and used for agglomeration experiments.

To determine the most suitable particle size for fluorescence measurements, further work was carried out on the 10 μm fine feed material of coal 1. Fluorescence and reflectance measurements were carried out, but this particle size was too small for conducting elasticity tests. The fluorescence measurements were made in a manner similar to that for the coarser material, except that the diameter of the measuring field was decreased to 8 μm for measurements on the 10 μm vitrinite particles.

The agglomerates (coal 1 only) in each case were also subjected to reflectance and fluorescence measurements.

RESULTS AND DISCUSSION

The results of petrographic analyses and agglomeration tests carried out on the initial and oxidized samples are shown in *Tables 3, 4* and *5*. Characterization of the initial samples showed that the samples could be considered as fresh at the outset of the investigation.

The results of the agglomeration tests on the fresh coals revealed that coal 4 was the most hydrophobic,

Table 5 Oxidation data: agglomerates (particle size 10 μm) of coal 1

Oxidation time (h)	Petrographic analyses[a]	
	Vitrinite reflectance, random (%)	FRI (%)
0.00	0.52	0.67
0.25	0.51	0.59
0.50	0.51	0.51
2.00	0.54	0.31
5.00	0.51	0.23
10.00	0.54	0.22

[a] Particle size too small for EI measurements

followed by coal 3 and then coal 1. Coal 2 was identified as the most hydrophilic of the four fresh coals.

Analyses of the oxidized samples revealed the following trends with increasing oxidation time:

(1) a marked decrease in the fluorescence intensity values;
(2) an increase in the vitrinite elasticity;
(3) no significant change in the reflectance;
(4) a decrease in the agglomeration rate.

Coal 1

A good correlation between the decrease in the fluorescence intensity and the increase in the elasticity index with oxidation was obtained in the case of the <1 mm material (*Figure 1*), the correlation coefficient
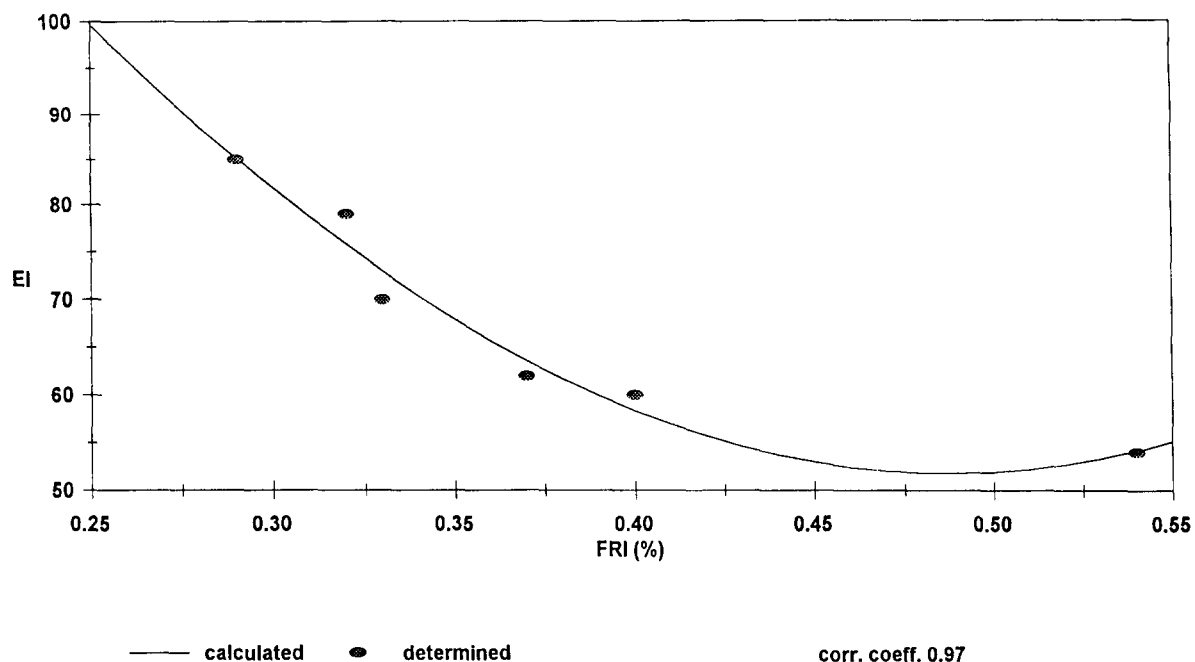
calculated ● determined   corr. coeff. 0.97

Figure 1 Coal 1: relation between fluorescence relative intensity and elasticity index with oxidation (<1 mm material)

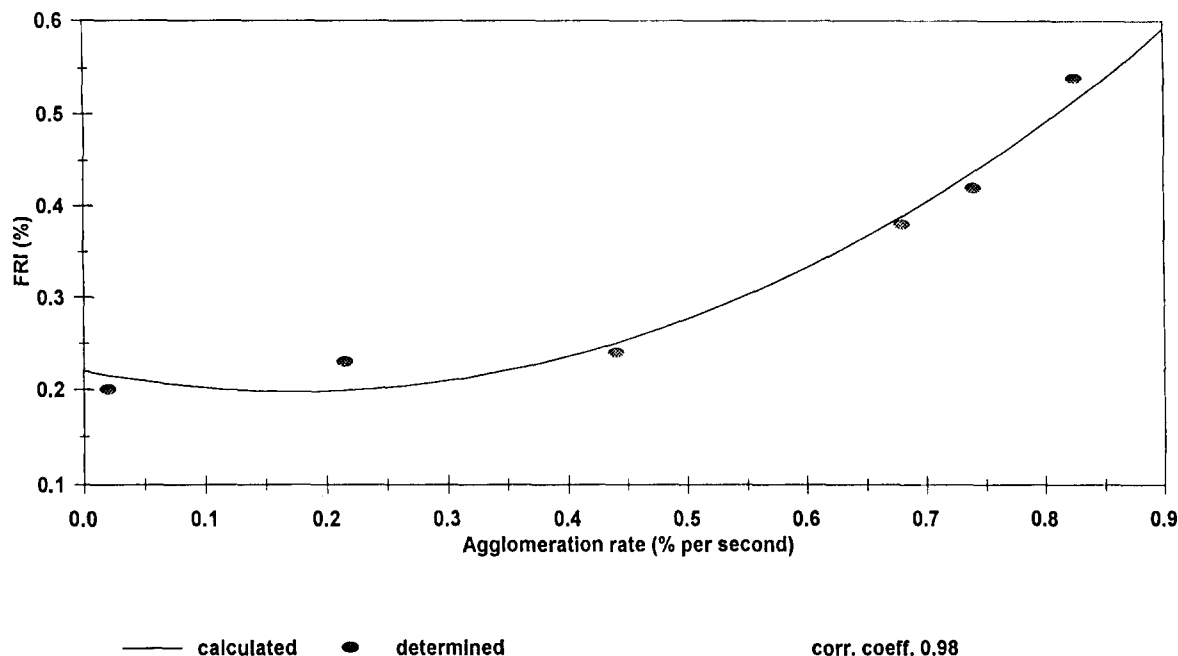calculated ● determined   corr. coeff. 0.98

Figure 2 Coal 1: relation between agglomeration rate and fluorescence relative intensity as a result of oxidation (10 μm material)

being 0.97. Both methods revealed increasing oxidation levels over time.

For the fine feed samples the decline in the agglomeration rate with increasing levels of oxidation indicated that the surface of the coal became less hydrophobic (more hydrophilic). A close relation was observed between the decrease in the agglomeration rate and increase in oxidation time (*Table 4*).

The organic recovery remained at >98 wt% for up to 5 h oxidation but then decreased to 26.8 wt% after 10 h.

The decrease in the agglomeration response corresponded with a decrease in the FRI values, a closer correlation being obtained where FRI measurements were taken on the fine feed particles (correlation

coefficient 0.98) (*Figure 2*) than on the coarse particles (correlation coefficient 0.84) (*Figure 3*).

Although the agglomeration tests were carried out on 10 μm material and the elasticity measurements on < 1 mm material, there was a very close relation between the decrease in the agglomeration rate and the increase in the vitrinite elasticity with oxidation (*Figure 4*).

The reflectance measurements on the samples in all three sets did not reveal changes within the set, although the reflectances of the samples in the first set (<1 mm material, *Table 3*) were significantly higher than those of the corresponding samples in the following two sets (fine feed, *Table 4*, and agglomerates, *Table 5*). This difference could be explained by the fact that since the particle size of the coal in the fine feed and product
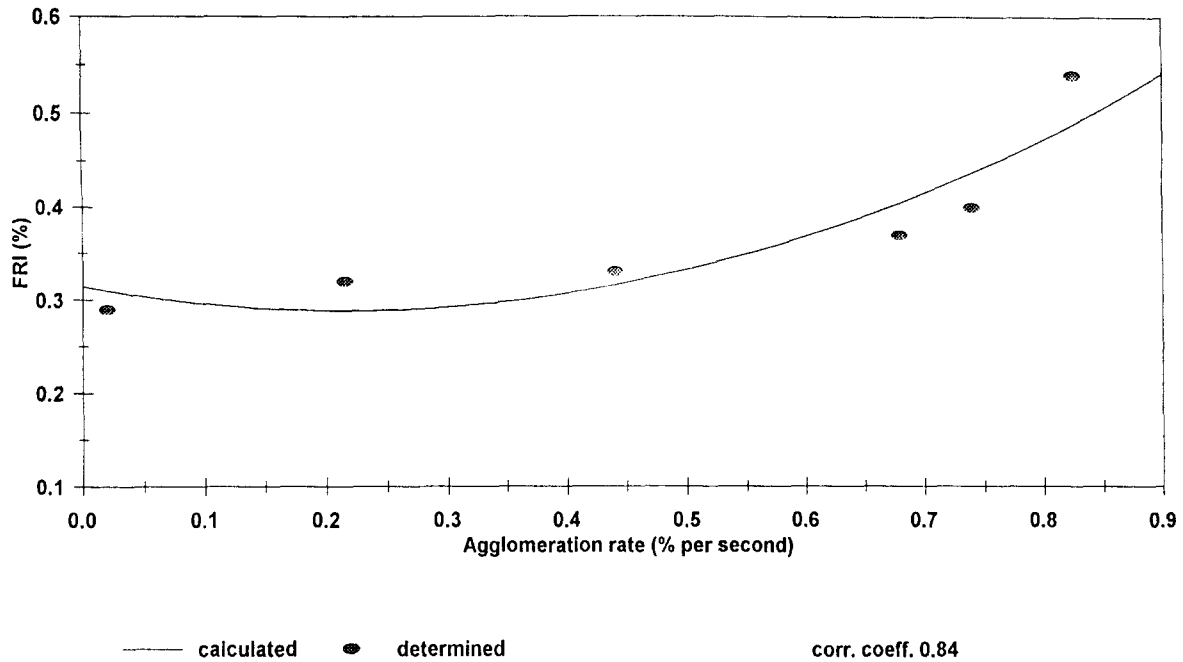
Figure 3 Coal 1: relation between agglomeration rate (10 μm material) and fluorescence relative intensity (<1 mm material) as a result of oxidation
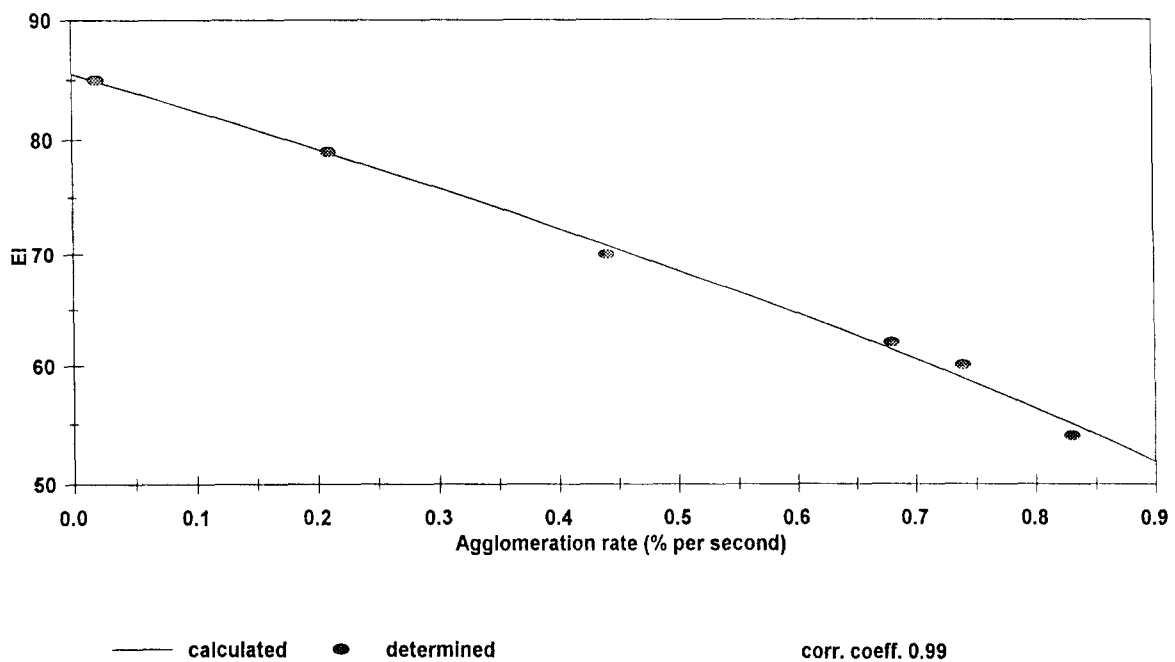

Figure 4 Coal 1: relation between agglomeration rate (10 μm material) and vitrinite elasticity index (<1 mm material) with oxidation

samples was much smaller, the reflectance readings would have tended to be lower, being taken rather too close to particle edges. However, since no change in the reflectance was observed in each individual set, it can be confirmed that the vitrinite reflectance did not alter during the low-level oxidation treatment used in this study.

The fluorescence values obtained on the 10 μm material in the samples taken at 2, 5 and 10 h of oxidation (*Table 4*) were significantly lower than the values obtained on the corresponding <1 mm samples (*Table 3*). This indicates that the rate of oxidation of the

vitrinite particles was more rapid in the 10 μm material during this period.

Coals 2, 3 and 4

Generally, the less regular changes in these coals in response to oxidation were associated with somewhat poorer correlations between the oxidation parameters themselves and between the oxidation parameters and the agglomeration responses for each coal. A probable explanation for this is that coal 1 is the one of lowest rank among the four coals selected for this investigation and hence responds more dramatically to oxidation

treatment. This, coupled with the fact that it is also very high in vitrinite content (vitrinite being the most predominant reactive maceral in all four coals under study), would render coal 1 more sensitive to low-level oxidation. This coal also showed a greater sensitivity to natural oxidation with time[3].

The results of FRI analyses on coal 2 (coarse material) showed a rapid decrease in the intensity during the first 15 min. A loss of 25.0% in fluorescence intensity was observed, this trend being similar to that observed for coal 1 (*Table 3*).

For coal 2 (the most hydrophilic of the four coals) the agglomeration response was poor and the final organic recovery was low, decreasing from 54.7 wt% for the initial sample to 33.1 wt% for the sample oxidized for 10 h (*Table 4*).

The coals of higher rank (i.e. 3 and 4) lost 11.0 and 13.4% in fluorescence intensity respectively during the first 15 min and 26.0 and 18.8% respectively after 30 min (*Table 3*). In both cases, the loss in intensity ceased during the interval between 30 min and 2 h of oxidation, but further decreases occurred during the period between 2 and 10 h. This pattern of behaviour could be explained by the characteristic development of the FRI phenomenon when related to coal rank[3]. Both coals 3 and 4 are prime coking coals, which probably determines their behaviour during artificial oxidation.

Again there was a close relation between the decrease in agglomeration rate and increase in oxidation time in each of these two higher-rank coals. In both cases the organic recovery was always >98 wt%, even after 10 h of oxidation.

CONCLUSIONS

1. Fluorescence intensity and elasticity values proved to be closely related to each other and were shown to be sensitive indicators of oxidation.

2. The responses of the coals subjected to artificial low-level oxidation seemed to depend on both their type and rank: the higher the vitrinite content, the higher the rate of oxidation, and the higher the rank, the lower the rate of oxidation.
3. According to the results of this study, reflectance was not a sensitive indicator of the low oxidation levels of the coal investigated.
4. The agglomeration rate was shown to be a sensitive method for detecting changes in coal hydrophobicity due to oxidation.
5. Very definite relations were revealed between the fluorescence and elasticity measurements and the agglomeration rates of the four artificially oxidized coals. However, refining these methods for practical use requires thorough additional research work. In future investigations, coarse material of <1 mm particle size should be used for elasticity tests, whereas finer material (10 μm) is more suitable for fluorescence measurements and gives more accurate results.

ACKNOWLEDGEMENTS

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