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Detection of the incipient oxidation of coal by petrographic techniques

Krystyna J. Kruszewska and Vivien M. du Cann*
Faculty of Earth Science, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec, Poland
**Division of Materials Science and Technology, CSIR, PO Box 395, Pretoria 0001, South Africa*
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Two petrographic methods, namely long-wave fluorescence intensity measurements and a vitrinite elasticity index, were developed and used to detect incipient oxidation in coals subjected to simulated weathering conditions. The two methods are based on different physical properties of coal. However, their sensitivity in detecting changes caused by oxidation was found to be equally high. Copyright © 1996 Elsevier Science Ltd.

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Coal, being a very heterogeneous material, behaves in different technological processes according to (among other factors) the proportion of reactive/inert components and the degree to which they are affected by oxidation.

Oxidation affects coal reactivity and can have a significant impact on coal properties. Oxidation is a process of deterioration and adversely affects coal performance in industrial processes such as carbonization (for cokemaking). In addition, oxidation influences surface properties, altering wettability and flocculation. It is therefore of great importance to be able to assess oxidation levels.

There have been many investigations of coal oxidation[1-4]. However, the complex nature of coal, together with a lack of reliable analytical methods sensitive to changes during coal oxidation, have made it very difficult to quantify oxidation.

In recent years, fluorescence microscopy has developed as a promising tool for the detection of coal oxidation[5,6]. The aim of this study was to develop two parallel microscopic approaches to the problem, based on fluorescence photometry and vitrinite micro-elasticity, to detect the early stages of coal oxidation, which are difficult to evaluate by physicochemical analyses.

EXPERIMENTAL

Conventional methods

To assess the applicability of conventional methods in detecting incipient oxidation, the following analyses were carried out: (a) *petrographic techniques*: maceral analyses for the evaluation of coal type, reflectance measurements for the determination of rank, and total maceral reflectance scans for the determination of reactive maceral content[7]; (b) *chemical analyses*: proximate and ultimate analyses and calorific value determinations; (c) *assessment of caking properties*: swelling number and Roga index.

Specific petrographic methods for assessing intensity of oxidation

Both long-wave fluorescence relative intensity (FRI) measurements and a vitrinite elasticity index (EI) were developed in the Petrographic Laboratory of the Division of Energy Technology of the CSIR in Pretoria.

Long-wave fluorescence relative intensity measurements. The basic equipment used for fluorescence measurements was the Zeiss Universal microscope designed for reflectance measurements. For fluorescence intensity measurements some instrumental changes were necessary. These were as follows:

(a) *Illumination changes*: a 100 HBO lamp with a stabilizer was fitted to the microscope.
(b) *Addition of an irradiation system*: a system comprising an excitation filter (within the blue light range, 450–490 μm wavelength) and a barrier filter was inserted.
(c) *Interference filter*: a filter of 650 μm wavelength was used.
(d) *Measuring field*: 36 μm.
(e) *Standard*: A Zeiss uranyl glass standard was used as a relative intensity standard.

100 measurements were taken on all vitrinite macerals, using the computer program designed for reflectance measurements to calculate results. For further interpretation, mean fluorescence values were taken into account.

Table 1 Chemical analyses and caking properties of the fresh coals

Coal	Proximate analysis (wt% air-dry)			Calorific value	Ultimate analysis (wt% daf)					Swelling no.	Roga index
	H_2O	Ash	VM	($MJ\,kg^{-1}$ daf)	C	H	O	N	S		
1	3.2	10.5	36.2	33.9	81.5	5.9	10.0	1.6	1.0	4.0	67
2	2.6	7.1	33.2	34.5	84.4	5.5	7.5	2.0	0.6	2.0	62
3	1.6	11.9	29.9	35.5	85.3	5.6	5.2	2.3	1.6	5.5	79
4	1.2	13.7	24.2	36.0	88.7	5.0	3.2	2.2	0.9	5.0	83
5	0.8	18.6	22.3	36.1	89.0	5.2	2.7	2.1	1.0	8.0	89

Table 2 Petrographic analyses of the fresh coals[a]

Coal	V	E	RSF	I	Vitrinite reflectance[b] Max	Random	Σ Re	FRI	EI
1	93.9	2.7	0.5	2.9	0.69	0.64	96.4	1.53	52
2	54.9	4.2	14.9	26.0	0.72	0.67	66.0	1.36	50
3	59.1	2.4	15.2	23.3	0.86	0.82	67.6	2.46	39
4	60.9	0.0	14.3	24.8	1.02	0.98	67.6	1.86	27
5	87.1	0.0	3.4	9.5	1.20	1.16	89.2	1.67	22

[a] V: vitrinite, E: exinite, RSF: reactive semifusinite, I: inertinite, Σ Re: sum of reactives, FRI: fluorescence relative intensity: all figures in per cent; EI, elasticity index
[b] In oil immersion

Vitrinite elasticity tests. Nandi *et al.*[3] found that different of types of microhardness impressions were obtained on coals of different rank, and that oxidation could affect the physical state of fresh vitrinite so that a plastic state could, depending on the rank of the coal, be transformed into an elastic state.

Based on these findings, impression types were used to evaluate the changes in the physical nature of vitrinite in coals brought about by weathering. Impressions were made on vitrinite particles using a Leitz Miniload 2 microhardness tester. The measuring force selected was 490.3 mN. This force was found to produce suitable indentations of appropriate dimensions for vitrinite particles of size <1 mm in the coals used in this study.

The impressions obtained were categorized according to their nature: plastic, plastic brittle, brittle, elastic brittle or elastic. This information was used to develop an empirical formula for calculating an elasticity index (EI) for each sample. An EI of 0–20 indicated that the majority of vitrinite particles exhibited predominantly plastic properties, 20–40, brittle properties, 40–60, elastic-brittle properties, 60–80, elastic properties, and 80–100, highly elastic properties.

Simulated weathering

It is well known that the weathering of coal is a natural process in response to physical and chemical actions. To test the suitability of the two new petrographic techniques, a simulated weathering programme was set up. Five coals of different type and rank were selected. The fresh coals were characterized by their chemistry, caking properties and petrography (*Tables 1* and *2*).

15 kg portions of these samples (<5 mm material) were subjected to simulated weathering conditions on the roof of the CSIR Enertek building for up to 134 weeks. Representative samples were riffled out periodically and analysed.

Petrographic blocks were made of the weathered coals and routine analyses (maceral analyses and reflectance measurements) were carried out. A total maceral reflectance scan[7] was also carried out on all samples and the sum of reactives calculated in each case. In addition, fluorescence intensity measurements and vitrinite elasticity tests were applied to the coal samples.

Finally, mean fluorescence intensity values and elasticity indices were correlated with weathering time and with each other.

RESULTS AND DISCUSSION

The results of the petrographic and other analyses of the weathered samples are shown in *Tables 3–7*. Only those results relevant to changes due to oxidation are reported in this paper.

Computed daf values are provided for the calorific value and volatile matter of the weathered coal samples, due to the wide scatter of results in these cases. For all five coals, trends were apparent in response to weathering. In each case there were slight decreases in calorific value and percentage of volatile matter.

These trends were most obvious for Coal 1, the coal of lowest rank. This coal also showed the most marked decline in Roga index and swelling number, while the coal of highest rank, Coal 5 (a prime coking coal), showed the least decline in Roga index and no drop in swelling number even after 130 weeks of weathering.

However, routine microscopic examination of the weathered samples revealed no change in the appearance of the macerals. No oxidation rims or additional microfissures were seen. There was no significant change in vitrinite reflectance with weathering up to 134 weeks. There was no change in the sum of reactives or the percentage of reactive inertinite calculated from the reflectance scans in the weathered samples.

To investigate changes in fluorescence intensity and vitrinite elasticity with coal rank, the results of both fluorescence and elasticity measurements on the fresh coals were correlated with R_{max} values.

The fluorescence intensities of the fresh vitrinites increased rapidly with rank between 0.60 and 0.90% R_{max}, thereafter decreasing rapidly towards the higher-rank coking coals (*Figure 1*). This phenomenon is closely related to the secondary character of the long-wave fluorescence intensity, which in turn is confined to the sequence between the end of the first and the end of the second coalification jump.

Table 3 Weathering data: Coal 1

Weathering time (weeks)	Vitrinite reflectance (%) Max.	Random	Σ Re (%)	RI (%)	EI	FRI (%)	CV ($MJ\,kg^{-1}$ daf)	VM (wt % daf)	Swelling no.	Roga index
0	0.69	0.64	96.4	0.0	52	1.53	33.7	41.1	4.0	67
2	0.70	0.64	93.2	0.0	53	1.43	33.7	41.0	4.5	62
4	0.72	0.67	96.8	0.2	57	1.44	33.6	41.0	4.5	66
6	0.70	0.65	95.6	0.5	55	1.37	33.6	40.9	4.5	58
10	0.72	0.67	95.6	0.1	58	1.28	33.5	40.9	3.5	54
15	0.71	0.66	96.0	0.1	60	1.16	33.4	40.8	3.5	57
24	0.71	0.65	94.0	0.1	65	1.06	33.2	40.6	1.5	27
30	0.72	0.67	96.4	0.1	72	1.01	33.1	40.5	0.5	20
35	0.73	0.68	94.0	0.1	72	0.87	33.0	40.4	0.5	16
40	0.72	0.67	93.6	0.1	77	0.81	32.9	40.3	1.0	17
45	0.72	0.67	96.4	0.1	79	0.79	32.8	40.2	1.0	12
49	0.70	0.64	95.2	0.1	79	0.71	32.7	40.1	0.5	5
54	0.70	0.64	93.6	0.1	78	0.72	32.6	40.0	0.5	19
59	0.73	0.67	95.6	0.1	80	0.66	32.6	39.9	1.5	13
64	0.72	0.67	94.8	0.0	80	0.53	32.5	39.8	1.5	9
73	0.69	0.64	94.8	0.0	83	0.51	32.4	39.6	0.0	5
79	0.70	0.64	95.2	0.1	84	0.51	32.3	39.5	0.5	4
83	0.72	0.66	96.8	0.2	83	0.51	32.3	39.5	0.5	2
102	0.73	0.67	97.2	0.2	83	0.47	32.1	39.1	0.0	–
120	0.74	0.69	95.2	0.1	85	0.48	32.0	38.8	0.5	–
134	0.73	0.68	94.0	0.1	85	0.44	32.0	38.5	0.0	–

Table 4 Weathering data: Coal 2

Weathering time (weeks)	Vitrinite reflectance (%) Max.	Random	Σ Re (%)	RI (%)	EI	FRI (%)	CV ($MJ\,kg^{-1}$ daf)	VM (wt % daf)	Swelling no.	Roga index
0	0.72	0.67	66.0	9.5	50	1.36	34.5	36.6	2.0	62
2	0.73	0.67	68.8	7.8	54	1.27	34.4	36.6	2.0	57
4	0.74	0.69	68.4	8.0	54	1.22	34.4	36.6	2.0	58
6	0.75	0.70	67.2	8.8	56	1.17	34.4	36.5	2.0	45
10	0.76	0.70	67.6	8.5	57	1.15	34.3	36.5	2.0	40
15	0.72	0.66	69.2	7.6	58	1.13	34.2	36.5	1.5	39
24	0.74	0.69	66.0	9.5	59	1.09	34.1	36.4	0.5	28
30	0.73	0.67	67.6	8.5	62	1.04	34.0	36.3	1.0	24
35	0.73	0.68	68.0	8.2	63	–	33.9	36.3	0.5	20
40	0.73	0.68	69.2	7.5	63	1.02	33.9	36.2	1.0	19
45	0.74	0.69	66.8	9.0	64	0.97	33.8	36.1	1.0	17
49	0.73	0.68	67.2	8.7	66	0.95	33.8	36.1	0.5	12
54	0.73	0.67	70.0	7.0	66	0.94	33.7	36.1	1.0	22
59	0.73	0.68	66.0	9.5	66	0.82	33.7	36.0	1.0	19
64	0.73	0.67	68.8	7.8	67	0.79	33.6	36.0	1.0	13
73	0.72	0.67	68.4	8.0	68	0.77	33.5	35.9	0.5	11
79	0.72	0.67	66.8	9.0	68	0.67	33.5	35.8	0.5	8
83	0.75	0.70	67.2	8.7	68	0.65	33.4	35.8	0.5	9
102	0.75	0.70	68.0	8.2	69	0.57	33.3	35.6	1.0	–
120	0.75	0.70	66.4	9.3	69	0.55	33.3	35.4	0.5	–
134	0.77	0.72	67.2	8.7	70	0.56	33.2	35.2	0.5	–

The elasticity of the fresh vitrinites was inversely related to rank (*Figure 2*).

Fluorescence relative intensity (FRI)

Coal 1. The initial fluorescence intensity of this coal was established at 1.53%. A very regular decline in fluorescence intensity with time was apparent. The correlation curve was a parabola and the correlation coefficient was high, 0.99.

Table 5 Weathering data: Coal 3

Weathering time (weeks)	Vitrinite reflectance (%) Max.	Random	Σ Re (%)	RI (%)	EI	FRI (%)	CV ($MJ\,kg^{-1}$ daf)	VM (wt % daf)	Swelling no.	Roga index
0	0.86	0.82	67.6	8.5	39	2.46	35.2	34.2	5.5	79
2	0.86	0.81	66.4	9.3	38	2.42	35.2	34.1	6.0	78
4	0.87	0.82	68.4	8.0	39	2.31	35.2	34.1	5.0	76
6	0.86	0.83	65.6	9.8	38	2.26	35.2	34.1	5.5	74
10	0.85	0.81	69.2	7.5	40	2.24	35.1	34.0	5.5	65
15	0.86	0.81	66.4	9.3	41	2.17	35.1	33.9	5.5	75
24	0.87	0.83	66.4	9.3	44	1.97	35.0	33.8	5.5	66
30	0.88	0.83	67.6	8.5	44	1.82	34.9	33.7	5.5	58
35	0.86	0.82	66.0	9.5	47	1.79	34.9	33.6	4.5	42
40	0.85	0.80	67.2	8.7	48	1.65	34.8	33.6	4.5	46
45	0.87	0.83	65.6	9.9	49	1.60	34.8	33.5	5.0	47
49	0.85	0.81	67.6	8.5	51	1.56	34.7	33.4	5.5	39
54	0.88	0.85	67.6	8.5	52	1.57	34.7	33.4	4.5	48
59	0.88	0.83	66.4	9.3	53	1.40	34.7	33.3	4.5	35
64	0.87	0.82	66.8	9.0	53	1.44	34.6	33.2	4.0	44
73	0.86	0.81	67.6	8.5	54	1.19	34.6	33.1	2.5	33
79	0.85	0.81	65.6	9.7	54	1.11	34.6	33.0	4.5	31
83	0.86	0.81	67.6	8.5	55	1.02	34.6	32.9	3.0	34
102	0.87	0.82	66.4	9.3	56	0.97	34.5	32.7	2.5	30
120	0.86	0.81	65.6	9.9	56	0.86	34.5	32.4	2.0	–
134	0.86	0.81	68.4	8.0	57	0.79	34.5	32.2	2.0	–

Table 6 Weathering data: Coal 4

Weathering time (weeks)	Vitrinite reflectance (%) Max.	Random	Σ Re (%)	RI (%)	EI	FRI (%)	CV ($MJ\,kg^{-1}$ daf)	VM (wt % daf)	Swelling no.	Roga index
0	1.02	0.98	67.6	8.5	27	1.86	35.8	28.0	5.0	83
1	1.03	0.99	67.2	8.7	28	1.86	35.8	28.0	5.5	83
3	1.06	1.03	67.2	8.7	29	1.90	35.8	28.0	5.0	76
7	1.06	1.04	67.6	8.5	28	1.72	35.8	27.9	5.0	77
12	1.04	1.01	67.6	8.5	29	1.60	35.7	27.8	5.0	80
20	1.03	0.99	68.4	8.0	32	1.57	35.7	27.7	4.5	75
26	1.04	1.00	69.6	7.3	32	1.56	35.7	27.7	5.0	78
31	1.04	1.01	68.0	8.2	33	1.46	35.6	27.6	4.0	58
36	1.04	1.00	68.4	8.0	35	1.42	35.6	27.5	5.0	62
40	1.04	1.00	66.8	9.0	37	1.28	35.6	27.5	5.0	53
45	1.02	0.99	69.2	7.5	38	1.27	35.6	27.4	5.0	52
51	1.05	1.01	67.2	8.7	40	1.25	35.5	27.3	4.5	55
56	1.04	1.00	68.0	8.2	39	1.18	35.5	27.3	4.0	54
60	1.05	1.03	66.4	9.3	39	1.23	35.5	27.2	4.5	54
69	1.05	1.02	65.6	9.8	40	1.10	35.5	27.1	4.0	47
75	1.03	0.99	66.4	9.3	41	1.04	35.4	27.0	4.5	46
79	1.06	1.03	69.6	7.3	42	0.80	35.4	27.0	3.5	39
98	1.03	1.00	66.8	9.0	42	0.80	35.3	26.7	3.0	39
116	1.03	0.99	68.4	8.0	44	0.81	35.2	26.5	2.0	–
130	1.05	1.02	66.8	9.0	43	0.71	35.2	26.3	2.0	40

Coal 2. The initial fluorescence intensity was lower than that of Coal 1, 1.36%. The measurements also showed a significant decline in fluorescence intensity with weathering time. However, this decline was less regular than that recorded for Coal 1. In Coal 2, the FRI declined rapidly during the first 6 weeks of weathering, then more slowly, and finally more or less regularly over the rest of the weathering period. The correlation coefficient was still good, 0.97.

Coal 3. This coal showed a very regular decline in the average fluorescence intensity. The intensity was initially

Table 7 Weathering data: Coal 5

Weathering time (weeks)	Vitrinite reflectance (%) Max.	Random	Σ Re (%)	RI (%)	EI	FRI (%)	CV ($MJ\,kg^{-1}$ daf)	VM (wt % daf)	Swelling no.	Roga index
0	1.20	1.16	89.2	0.6	22	1.67	36.1	27.5	8.0	89
1	1.25	1.21	89.2	0.6	22	1.61	36.1	27.5	8.0	88
3	1.22	1.19	90.8	0.2	23	1.52	36.1	27.4	9.5	91
7	1.22	1.18	89.2	0.6	24	1.48	36.1	27.4	9.0	86
12	1.22	1.18	88.0	0.5	24	1.40	36.0	27.4	9.5	85
20	1.24	1.21	86.4	0.8	25	1.30	36.0	27.3	9.5	86
26	1.20	1.17	86.8	0.7	26	1.27	36.0	27.3	9.0	83
31	1.22	1.18	86.4	0.8	28	1.20	36.0	27.3	9.0	78
36	1.21	1.17	86.4	0.8	27	1.22	36.0	27.2	9.5	85
40	1.22	1.19	86.8	0.7	28	1.22	36.0	27.2	9.5	85
45	1.21	1.18	88.4	0.5	27	1.19	35.9	27.2	9.5	76
51	1.20	1.17	86.8	0.7	28	1.14	35.9	27.1	8.5	77
56	1.20	1.17	88.4	0.5	29	1.11	35.9	27.1	9.0	78
60	1.20	1.17	87.2	0.6	29	1.05	35.9	27.1	9.0	73
69	1.20	1.16	88.0	0.5	31	1.10	35.9	27.0	9.5	75
75	1.21	1.17	88.0	0.5	30	1.08	35.8	27.0	9.5	77
79	1.20	1.17	86.8	0.7	31	0.79	35.8	27.0	9.5	74
98	1.21	1.18	85.6	0.9	31	0.73	35.8	26.8	9.0	81
116	1.23	1.19	86.0	0.9	31	0.69	35.7	26.7	9.0	72
130	1.24	1.20	88.0	0.5	32	0.66	35.7	26.6	9.0	73

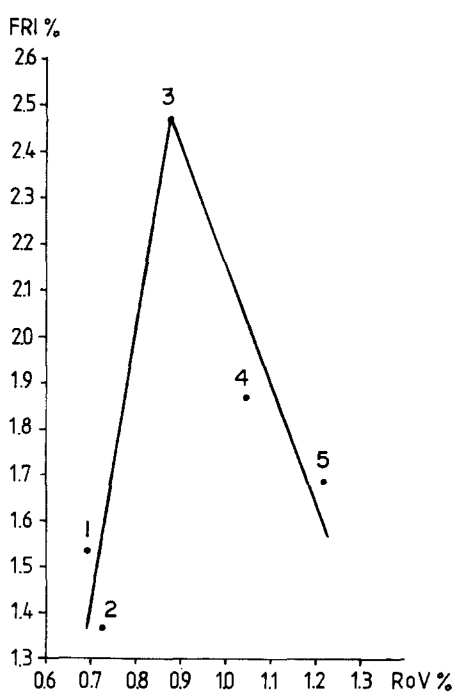

Figure 1 Relation between vitrinite maximum reflectance (RoV) and FRI for the fresh coals

very high (2.46%) but decreased steadily over the weathering period, reaching 0.79% after 134 weeks. The correlation line was practically straight and the correlation coefficient was similar to that for Coal 1, 0.99.

Coal 4. This coal showed a pattern of change in FRI similar to that of Coal 3, but rather less uniform. During the first 3 weeks there was no change in FRI, a significant decrease being observed only from the third week onwards. However, the correlation coefficient was good, 0.97.

Coal 5. This coal, with an initial FRI of 1.67%, also showed an individual pattern of response to weathering. The FRI declined sharply within the first 3 weeks and thereafter less sharply over the following 36 weeks. Over the next 24 weeks, the intensity level changed only slightly. The course of fluorescence decline with time was a parabola. The correlation coefficient of fluorescence intensity with time was also high, 0.95.

Vitrinite elasticity

For the fresh samples, a variation of EI was observed: for Coal 1 it was calculated to be 52, for Coal 2 50, for Coal 3 39, for Coal 4 27 and for Coal 5 22.

For all five coals, an increase in EI with weathering time was seen and good correlation coefficients were obtained. The lower-rank coals, 1 and 2, displayed distinctly parabolic correlation curves, this effect becoming less marked with increasing rank.

For all five coals subjected to weathering, the increase in elasticity index and the decrease in fluorescence intensity showed a good correlation.

CONCLUSIONS

1. Chemical responses to weathering were not dramatic but were most pronounced in the lower-rank coals, 1 and 2. However, the results were scattered.
2. Significant decreases in Roga index were observed with weathering, these being least marked in the highest-rank coal, Coal 5.
3. The fact that no classical oxidation features were seen in any of the five coals undergoing weathering for up

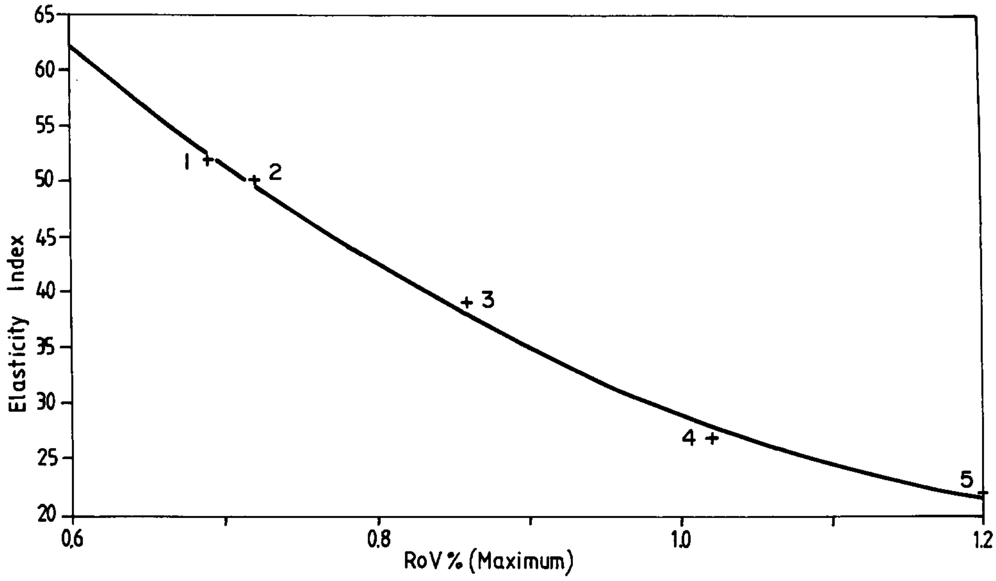

Figure 2 Relation between vitrinite maximum reflectance and elasticity index for the fresh coals

to 134 weeks indicates that oxidation was still not very advanced.

4. The absence of significant changes in vitrinite reflectance in the weathered samples demonstrates that reflectance cannot be used as an oxidation indicator at low oxidation levels.
5. There was no change in the sum of reactives with weathering. This is explained by the fact that the determination of this factor depends on reflectance.
6. Fluorescence measurements and elasticity tests showed very good agreement in the evaluation of oxidation levels. They appear to be more reliable than chemical or rheological methods. This may be because the determinations of chemical, swelling and caking properties are bulk-oriented techniques, whereas fluorescence and elasticity measurements are taken exclusively on vitrinite, the most predominant reactive component in the five coals investigated. The two methods are based on different physical properties of coal. However, their sensitivity in detecting changes caused by oxidation is equally high. The practical applications of both techniques may be wide-ranging. They have already been successfully used for the detection of oxidation of coals in stockpiles.

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