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TECHNICAL MEMORANDUM NO. 7 OF 1973

A STUDY OF THE WEATHERING OR ATMOSPHERIC OXIDATION OF A WITBANK NO. 2 SEAM LOW-ASH COAL.

OUTEUR :
AUTHOR : E.F.E. MÜLLER

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1. INTRODUCTION

The weathering or atmospheric oxidation of coal as evidenced by a change of properties, especially the coking propensity, is becoming of increasing importance now that low-ash blend coking coal from the Witbank area is being exported to Japan. It is essential to know whether the coal will retain its coking properties for a sufficient length of time, or to what extent and how rapidly these properties will deteriorate in the period from mining, through washing, storing, railing, shipping, etc., to charging the coke ovens. And further, will such deterioration have any marked effect on the resulting coke, taking into consideration the amount of this coal that may be used in the blend charged.

2. INFLUENCING FACTORS

Experience has shown that lower rank coals deteriorate more quickly than higher rank coals. It is also known that many factors influence the weathering rate. For example, storage of coal under water retards the oxidation rate.

The following factors should be considered when tackling the problem of weathering of coal, but the list should by no means be regarded as complete:-

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2.1 Storage conditions, such as

Under water
Moist
Air-dry
Bunker (open i.e. stockpile, or enclosed)
Nature of atmosphere (air or inert gases)

2.2 Size of coal

Presumably larger coal will deteriorate less rapidly than finely crushed coal.

2.3 Weather conditions

Rainy
Dry
Hot
Cold

2.4 Sampling procedures

e.g. It has to be realised that it can be extremely difficult to obtain representative samples of, say, nut coal from a stockpile, if these are to be taken at regular intervals. Presumably coal at the surface will have an oxidation rate different to that of coal in the middle of the mound.

Many factors are involved and a clear picture will only be formed over a long period.

3. PARAMETERS TO BE CONSIDERED FOR MEASURING CHANGES

Mr. Moodie of the Institute recently studied the effects of oxidation on two parameters, viz. the reflectance and swelling number of a Witbank No. 5 seam blend coking coal.[1] He proposes that parameters such as the dilatation and the Roga index should also be measured.

The author is in agreement with this and wishes to point out that a number of other parameters could also be of importance. However, whether they will prove useful will have to be established, e.g. by considering the following:-

(a) The Gieseler plastometer and Echterhoff Plastograph are useful for higher rank coals, but are practically valueless for low rank coals.

(b) It is considered that the composition of the volatile matter may throw some light on the oxidation mechanism. Thus differences could probably be detected in a gas-chromatographic analysis between volatile matters from fresh coal and from oxidized coal. Strict devolatilization conditions will have to be selected and maintained as rapid or slow heating will definitely lead to different gas compositions.

Reports on studies of some of the above as well as other parameters can be found in recent literature.

Iskra and Laskowski [2] investigated the change in flotation characteristics due to the surface oxidation of coal particles.

Ignasiak, Nandi, and Montgomery [3] discuss a chromatographic analysis of pyrolysis gases as a method for studying coal weathering. This new method appears to be more rapid, simpler, and more generally applicable to coals of widely differing dilatation properties, and is stated to be far superior to the Ruhr dilatometer when coals with small expansion characteristics are concerned.

In order to study the mechanism of low-temperature oxidation of coal, Ignasiak, Clugston, and Montgomery [4] oxidized a bituminous coal with $^{18}O_2$ and subsequently analysed the pyrolysis gases by mass spectrometry.

Parkash, Szladow, and Berkowitz [5] established that vigorous agitation of suspensions of coking coals in water often result in catastrophic loss of caking properties. They advance the hypothesis that the loss of caking properties during agitation is not a consequence of oxidation of the coals (by dissolved oxygen) but is mainly due to internal "solid-state" reactions which convert -OH into cyclic ethers with accompanying loss of lamellar mobility. The energy for these reactions derives from cavitation of the liquid.

The publications of Ignasiak et al [3,4] are being carefully studied in order to establish how the F.R.I. could make use of their methods. Ignasiak et al are expected to publish further information on their oxidation studies on coking coal related to weathering. These are being awaited with interest.

Burns, Miyazu, and Shibaoka carried out comparative tests of the Gieseler fluidity of coals and established that discrepancies between the results of Australian and Japanese laboratories were due, not to differences in equipment and technique, but to differences in the samples used. These differences can mainly be ascribed to weathering.

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4. PROPOSED PROCEDURE FOR INVESTIGATING THE WEATHERING OF COAL

Following on the work of Mr. Moodie [1)] on No. 5 seam coal where the parameters, reflectance and swelling number were studied, a similar study is to be undertaken on No. 2 seam low-ash coal. The number of parameters is to be extended to include laboratory-determined coking properties, especially the Roga index and dilatation, and possibly the Gieseler plastometer.

Bearing in mind the various combinations and difficulties, discussed above, it is proposed to adopt the following procedure:-

A fresh sample of washed coal is to be collected. After drying, and crushing to about -4 mm (3/16"), the coal will be subdivided into a suitable number of sub-samples (say 30) of about 1 kg quantities.

One sub-sample will be analysed immediately, and the rest stored in open seedling boxes in a dust-free space. At weekly intervals further samples will be prepared and analysed. As time progresses the intervals may be changed to, say, monthly.

The preparation of each sub-sample will be carried out as follows: It will first be split into two portions, one portion to be stored under water for analysis at a later stage. The second portion will be crushed carefully to -30 mesh (as required for the making of the microscope observation blocks) for petrographic analysis and reflectance measurements. Sufficient -30 mesh sample for the blocks is taken and the balance is crushed to -72 mesh for swelling number and Roga index tests and to - 100 mesh for the dilatometer test. If required, a portion will also be crushed to - 36 mesh for the Gieseler plastometer test.

At the same time an effort should be made to establish whether any other parameters, such as those mentioned in the literature, [2,3,4] can prove useful in elucidating the problem of the weathering of coal.

5. PRELIMINARY INVESTIGATION

Unfortunately the above programme could not be implemented immediately due to pressure of other work and to the fact that the assistants concerned with the determination of the coking properties were students and had to sit for their end-of-the-year university examinations.

However, in view of the importance attached to the weathering of coal, a preliminary investigation on Landau low-ash coal was initiated.

At this time a truckload of Landau No. 2 seam low-ash coal was received for a spontaneous combustion bunker test. The results of this test have been reported. [7] This bunker test* provided an opportunity to examine aspects of weathering. A sample of coal was collected during the loading of the bunker (Sample A). After completion of the bunker test a second sample (Sample B) was collected during discharging of the coal.

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* During a bunker test the coal is in a state of "aerated storage".

The analyses of these two samples could provide information concerning the behaviour or weathering of the coal during storage or in transit in a ship's bunker.

A second aspect of this preliminary work was to investigate the changes in laboratory samples, i.e. in finely crushed coal samples stored in the laboratory over a shorter or longer period. In other words, the weathering of laboratory samples was examined.

6. EXPERIMENTAL PROCEDURE

When the truckload of Landau coal was charged to the spontaneous combustion test bunker a sample of coal was collected - Sample A. This sample was subdivided into three portions and crushed to the sizes indicated for the following analyses:-

(i) -60 mesh for proximate analysis.
The proximate analysis, including a swelling number, was carried out almost immediately by the Survey Section.

(ii) -5 mm for microscopic examination.
The further preparation and analysis was carried out by the Coal Petrography Section.

(iii) -5 mm for the laboratory coking properties.
This sample was stored in a jar under water, as is customary for coal samples required for this purpose. It was a week before the sample could be analysed, and the following procedure was applied:

Sufficient sample was dried for about $1\frac{3}{4}$ hour in the sun, to enable the swelling number, Roga index, and dilatation tests to be carried out over a period of a few months at weekly intervals. Two sub-samples were prepared, one of -72 mesh B.S. size for swelling number and Roga index, and the other -100 mesh B.S. for the dilatometer test. These tests were carried out immediately and the balance of the two sub-samples were stored dry and exposed to the atmosphere in the laboratory in loosely covered containers.

At weekly intervals the stored samples were thoroughly mixed and a portion of each removed and analysed. These results are reported in Table 1. It will be seen that one week was missed (no assistants available), and that after 8/12/1972 the tests were done at roughly monthly intervals, one in January, 1973 and one in February, 1973.

About 4 weeks after sun-drying the first portion used for the above tests, a second portion was dried using a fan-heater to blow hot air over the wet sample. This happens to be the normal practice at the F.R.I. After half an hour the sample was dry. It was crushed to the required sizes and the tests were carried out. These results are reported in Table 2.

Approximately two months after charging the coal to the spontaneous combustion test bunker the coal was discharged again. During removal a laboratory sample, Sample B, was collected and subdivided into three sub-samples as before.

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The three coking property tests were carried out as soon as practically possible, which was the next day. These results are also reported in Table 2.

As with the original sample, (Sample A),the proximate analysis was also carried out on a sub-sample of Sample B. Both these sets of results are reported in Table 3.

The Maceral Analysis and Reflectance Measurements were carried out only on a portion of Sample A and on a portion of Sample B. The results are reported in Table 4.

7. DISCUSSION OF RESULTS

7.1 Change in coking properties of finely crushed, sundried coal stored dry and exposed to the atmosphere in the laboratory. (Table 1).

7.1.1 Swelling Number. From an initial swelling number of 3 on the sundried portion of coal the swelling number dropped to 2 after one week. The value of 2 was however maintained for some weeks, dropping to 1½ after a total of seven weeks. At eleven weeks it was still 1½, but dropped to 1 after sixteen weeks.

7.1.2 Roga Index. The Roga index was maintained at just under 50 over the first week. It then dropped to a lower level which it kept for about four weeks. At the seventh week it again dropped to a third level which was maintained up to the eleventh week. At sixteen weeks it had dropped further to a value of 25.

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7.1.3 Dilatometer. Normally it has been found by experience that the most convenient single criterion for evaluating the dilatometer results is the dilatation. In this particular study the effect of weathering is, however, best seen by examining the dilatation amplitude.

The first sample had a dilatation amplitude of 16, after one week it was 9, after two weeks only one. Subsequently all dilatometer curves showed only contractions. Although these contractions varied between 19 and 23%, it is not possible to follow any further oxidation. Of interest, however, is the shape of the last dilatometer curve (see 9/2/1973). Here the contraction curve did not become horizontal again but maintained a downward sloping trend. By convention if such a curve is obtained the contraction at 500°C is reported. This sort of curve indicates inferior coking properties and thus serves to prove that further weathering has occurred with respect to samples that previously gave contractions with horizontal ends.

No consideration has as yet been given to any changes in softening and resolidification temperatures.

7.1.4 Conclusions. It is evident that the coking properties deteriorate appreciably with finely ground samples stored in the laboratory.
It appears that with this coal the swelling number and dilatometer results are influenced more quickly while the Roga index alters at a slower rate.

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It must also be realised that it is quite possible that the two size gradings do not necessarily change at the same rate. This has, however, neither been proved or disproved.

7.2 Change in coking properties during storage in a bunker (Table 2)

Before the results are discussed a word of explanation is necessary on the samples mentioned in Table 2. The portion of Sample 72/813A used in the tests was dried, making use of a fan-heater to blow hot air over the wet coal which had been stored under water. This particular portion was analysed about a month after the first portion, yielding the results in Table 1, had been sun-dried.
It required about half an hour to dry the sample, after which it was crushed to the required sizes and tested. It is clear that this particular portion had better coking properties than those subjected to sun drying. For discussion see 7.3 below.

The second sample, 72/813B, is a portion of the coal sample collected after the spontaneous combustion bunker test.

7.2.1 Swelling Number. Over a period of nearly two months the swelling number of just under 4 had dropped to $2\frac{1}{2}$.

7.2.2 Roga Index. The Roga index changed from 56 to 45.

7.2.3 Dilatometer. From an initial dilatation amplitude of 17%, the sample collected after the bunker test gave only a contraction.

7.2.4 Conclusions. During aerated storage in a bunker for a period of two months the coal under test deteriorated with respect to coking properties. The rate of change is not as rapid as that of the finely crushed sample discussed under 7.1.

7.3 Influence of Drying Procedure on Coking Properties

The sample dried by exposure in the sunshine for 1¾ hours had coking properties inferior to those of another portion of the same coal dried by means of hot air from a fan-heater for ½ hour. Compare the figures in the first column of Table 1 and the first column of Table 2.

The swelling numbers are 3 and 3½ - 4 respectively. Compare also the swelling number 4 of the Sample A analysed by the Survey Section (Table 3 first column). The Roga indices are respectively 49 and 56. With the dilatometer results the dilatation amplitudes of 16 and 17 are very close; the contractions however differ, being 20 and 25.

These differences indicate that drying wet coal samples in the sun causes a deterioration of coking properties as compared to samples dried by means of hot air. One must, however, be careful in drawing conclusions. The sundried sample had been exposed for a period 4 times as long as for the other sample, so it may be the time factor that is important.

It should also be mentioned that when the Institute commenced carrying out the various coking properties on a regular scale, different methods of drying coal from under-water storage were investigated, viz. sun-drying, oven-drying at ca 105°C, drying a sample contained in a flask immersed in hot water, connected to a suction pump, and fan-heater drying.

The oven-drying method resulted in inferior coking properties; the suction method was rather cumbersome and time-consuming but otherwise satisfactory. Sun-drying and fan-heater drying were the most convenient. On a rainy day sun-drying could however not be employed, and it was also noticed that if exposure was too long the coking properties were adversely affected. By-and-large the fan-heater method proved to be the most convenient for most purposes. With larger portions of samples the fan-heater could be too slow and resort was taken to the sun, as in the present case where a fair amount of coal was required.

A method that appears still better is to spread the sample out thinly on a tray and to leave it exposed to the atmosphere in the laboratory overnight. Unfortunately this method is not always practicable, especially when analyses have to be carried out in a short time.

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7.4 Proximate Analysis

No differences are found in the proximate analyses of the two Samples A and B.

The swelling numbers determined by the Survey Section were 4 and 3 respectively. The swelling number determination has problems of its own. The Coking Property Section had found for Sample A in the sun-dried sample a swelling number of 3 and the fan-heater dried sample $3\frac{1}{2}$ - 4. The Survey Section had worked on another portion of the original sample quite soon after preparation and it does appear that Sample A should have a swelling number of near 4.

With Sample B the two sections found figures of 3 and $2\frac{1}{2}$. After much thought and discussion it was concluded that the following are contributing factors:-

(i) Different operators, and different interpretation of results. This is considered the most likely explanation for any differences that exist.

(ii) Different portions of the sample, i.e. sampling.

(iii) As the analyses were carried out at different times, temperatures may have differed as a result of change in gas pressure.

(iv) A possible effect of differing humidities.

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7.5 Maceral Analysis and Reflectance

A study of the results in Table 4 shows that the maceral analyses of the two Samples A and B, before and after the bunker test, are for practical purposes identical.

The percentage reflectance in the B sample has, however, increased, an indication that weathering or oxidation had taken place.

7.6 Change in coking properties after storage in water

In order to establish to what extent storage under water has an inhibiting effect on the oxidation of a coal, a further portion of coal was removed from the bottle on the 19th February, 1973, i.e. just over four months after it was sampled. The coking properties were determined and are reported in Table 5.

Comparing these results with those tabulated in Table 2, it is evident that the swelling number and Roga index values have deteriorated and have reached the level of the values obtained on the sample collected after the bunker test. The dilatometer still gave a dilatation amplitude of 14%, and there appears to be a shift in the temperature range. Apart from this the dilatometer result is not much changed.

Although water has the property of inhibiting oxidation of coal, deterioration over longer periods appears to be unavoidable.

The mechanism of oxidation is not clear at all. With the water-stored sample the swelling number and Roga index seem to deteriorate more quickly. With bunker storage and dry laboratory samples it is the dilatation that drops first.

All these findings show how complicated a study of the weathering of coal can be, and that a vast amount of time and labour will be required to gain an insight into all aspects.

8. SUMMARY

The coking properties of finely crushed laboratory samples of Witbank No. 2 seam low-ash coal deteriorate fairly rapidly on storage in the laboratory.

A nominal size of 32 mm x ½ mm of this coal stored in an aerated bunker for about two months also showed a loss in coking properties, and an increase in reflectance. The oxidation was however of a lesser degree than that of the finely crushed laboratory sample.

Storage of coal samples under water inhibits oxidation. Nevertheless deterioration does set in but at a slower rate.

(Signed): E.F.E. Müller
PRINCIPAL RESEARCH OFFICER

PRETORIA
6/3/1973
EFEM/KW

REFERENCES

1. The exposure of a Witbank No. 5 seam blend coking coal to the atmosphere at ambient temperatures and the influence of the subsequent oxidation on the reflectance of the vitrinites and the swelling properties - B. Moodie, F.R.I. Technical Memorandum No. 48 of 1972.

2. New possibilities for investigating air-oxidation of coal surfaces at low temperatures - J. Iskra, J. Laskowski, Fuel 46 (1967) pp 5-12.

3. Oxidation studies on coking coal related to weathering: (1) chromatographic analysis of pyrolysis gases as a method for studying coal weathering - B.S. Ignasiak, B.N. Nandi, D.S. Montgomery, Fuel 49 (1970) pp 214-221.

4. Oxidation studies on coking coal related to weathering: Part 2: The distribution of absorbed oxygen in the products resulting from the pyrolysis of slightly oxidized coking coal - B.S. Ignasiak, D.M. Clugston, D.S. Montgomery, Fuel 51 (1972) pp 76-80.

5. The deterioration of caking properties during prolonged agitation of coal in water - S. Parkash, A.J. Szladow, N. Berkowitz, The Canadian Mining and Metallurgical (CIM) Bulletin for November, 1971 - pp 92-94.

6. Comparative tests of Gieseler fluidity of coals - M.S. Burns, T. Miyazu, M. Shibaoka, Letters to the Editor, Fuel 51 (1972) pp 164-165.

7. Spontaneous heating of Landau coal - T.C. Erasmus, F.R.I. Technical Memorandum No. 6 of 1973.

TABLE 1

CHANGE IN COKING PROPERTIES OF FINELY CRUSHED, SUNDRIED COAL STORED DRY AND EXPOSED TO THE ATMOSPHERE IN THE LABORATORY.

F.R.I. Sample No. 72/813A (sundried)	Size of Sample	Date 1972							Date 1973	
		20/10	27/10	3/11	17/11	24/11	1/12	8/12	5/1	9/2
Swelling Number	-72 mesh	3	2	2	2	2	2	$1\frac{1}{2}$	$1\frac{1}{2}$	1
Roga Index		49	48	40	40	39	32	35	33	25
Dilatometer	-100 mesh									
Contraction %		20	25	23	23	21	19	21	21	25*
Dilatation %		-4	-16	-22	-23	-21	-19	-21	-21	at
Dil. Amplitude %		16	9	1	0	0	0	0	0	500°C
In. Soft Temp. °C		337	330	344	337	348	340	342	335	366
Temp. Max. Contr. °C		385	396	400	405	406	405	405	404	-
Temp. Max. Dil. °C		400	410	413	405	406	405	405	404	-
Plastic Range °C		63	80	69	68	58	65	63	69	-

*Where the contraction curve does not become horizontal, but maintains a downward sloping trend, the contraction at 500°C is conventionally reported (See F.R.I. T.M. No. 39 of 1972 or German L.V. 20/32/01 of May 1966).

TABLE 2

COKING PROPERTIES OF COAL SAMPLED BEFORE AND AFTER SPONTANEOUS COMBUSTION BUNKER TEST.

F.R.I. Sample No.	72/813A	72/813B
Description	Blower heater dried for ½ hr on 16/11/72 after storage in water from 11/10/72. Sample collected before bunker test.	Sample collected after bunker test on 7/12/72. Analysed 8/12/72.
Swelling Number	3½ - 4	2½
Roga Index	56	45
Dilatometer		
Contraction %	25	18
Dilatation %	- 8	-18
Dil. Amplitude %	17	0
In. Soft. Temp. °C	330	340
Temp. Max. Contr. °C	390	396
Temp. Max. Dil. °C	410	396
Plastic Range °C	80	56

TABLE 3

PROXIMATE ANALYSIS

Sample No.	72/813A (before bunker test)	72/813B (after bunker test)
Proximate Analysis:		
H_2O %	2,1	2,1
Ash %	6,7	6,7
V.M. %	32,4	32,2
F.C. %	58,8	59,0
Total Sulphur %	0,66	0,73
Swelling No.	4	3

TABLE 4

MACERAL ANALYSIS AND REFLECTANCE

Sample No.	72/813A (before bunker test)	72/813B (After bunker test)
Maceral Analysis (Vol.%)		
Vitrinite	60,1	59,9
Exinite	5,4	5,1
Inertinite	33,7	34,2
Visible Minerals	0,8	0,8
Ratio Reactives: Inerts	1,9:1	1,9:1
Reflectance, %	0,81	0,83

TABLE 5

COKING PROPERTIES OF COAL ANALYSED AFTER FOUR MONTHS STORAGE UNDER WATER.

F.R.I. Sample No.	72/813 A(4)
Description	Blower heater dried on 19 February, 1973 after storage in water from 11/10/72. (Compare Table 2 column 1)
Swelling Number	2½
Roga Index	44
Dilatometer	
Contraction %	22
Dilatation %	- 8
Dil. Amplitude %	14
In. Soft. Temp. °C	347
Temp. Max. Contr. °C	408
Temp. Max. Dil °C	425
Plastic Range °C	78