F.R.I. 47

VERSLAG NR. REPORT NO. 66

VAN OF 1976

U1/E14/5

BRANDSTOFNAVORSINGSINSTITUUT
VAN SUID-AFRIKA

FUEL RESEARCH INSTITUTE
OF SOUTH AFRICA

ONDERWERP:
SUBJECT: INTERIM REPORT ON MINERALS IN COAL - THE DIRECT DETERMINATION OF THE MINERAL MATTER CONTENT IN SOME COAL PRODUCT SAMPLES

AFDELING:
DIVISION: CHEMISTRY

NAAM VAN AMPTENAAR:
NAME OF OFFICER: J L GAIGHER

Cosmi 5476-L48

AUTHOR	: J L GAIGHER
LEADER OF PROJECT	: J L GAIGHER
TITLE	: INTERIM REPORT ON MINERALS IN COAL - THE DIRECT DETERMINATION OF THE MINERAL MATTER CONTENT IN SOME COAL PRODUCT SAMPLES
ENQUIRIES TO	: J L GAIGHER
SECTION	: CHEMISTRY

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA

REPORT NO. 66 OF 1976

INTERIM REPORT ON MINERALS IN COAL - THE DIRECT DETERMINATION OF THE MINERAL MATTER CONTENT IN SOME COAL PRODUCT SAMPLES

SYNOPSIS

The mineral matter factors* for some coal product samples determined by the method of radio-frequency oxidation, compared with results from an earlier survey (Technical Memorandum No. 21 of 1971), appear to have an acceptable precision.

INTRODUCTION

The inorganic or ash-forming constituents in coal are usually designated the mineral matter, although typically "organic" elements such as carbon and sulphur are also represented, viz. in the mineral carbonates, sulphates and sulphides.

The practical importance of the nature and distribution of these inorganic constituents is linked with every aspect of the mining and utilization of coal. For example, the grindability of coal, its washing characteristics, behaviour on coking, gasification and hydrogenation, tendency to spontaneous combustion and the production of dust, clinker, slag and flue gases are all related to the mineral matter characteristics of the coal concerned.

The mineral matter as such, may also be of economic importance. Coal wastes and ash may be a future source of materials such as uranium, germanium, sulphur and alumina. Trace element enrichment in the mineral matter has in some instances in the Northern Hemisphere resulted in the formation of tin and copper ores.

NOTE: * $\frac{\text{mineral matter \%}}{\text{coal ash \%}}$

In view of the lack of data relating to South African coals, a survey has been started on the mineral matter content of coal produced commercially in the Republic. This report deals with the radio-frequency ashing of some coal product samples and the direct determination of the mineral matter content of coal.

MINERAL MATTER IN COAL - A REVIEW

Due to its relative ease in determination, a simple ash analysis is a popular measure of the inorganic matter content in coal. At the relatively high temperature at which ash analyses are carried out, most of the original minerals in the coal are altered or destroyed viz. water of hydration is driven off the clay minerals and hydrated sulphates and the carbonate and sulphide minerals are decomposed.

The ash content in coal is thus generally lower than the mineral matter content, with the mineral matter to ash ratios depending on the relative proportions of the minerals from which the ash is derived.

Indirect and direct methods have been used in the past to determine the mineral matter content of coal. By means of various formulae the ash content may be recalculated to the mineral matter content. However, certain variables must also be determined. The Parr (1928) relationship requires a total sulphur determination and the more elaborate King, Maries and Crossley (1936) formula, requires carbonate and chlorine analyses in addition to sulphur determinations. That results from these indirect methods are not accurate under all conditions, is reflected by suggestions for modifications in the formulae which occur from time to time viz. Brown, Caldwell and Fereday (1952), Pringle and Bradburn (1958) and Millot (1958).

For the acid digestion method (ISO recommendation R 602 (1967)) the acid soluble fraction of the mineral matter is extracted by means of HCl and HF, the coal residue is ashed, and by applying various correction factors, the mineral matter content can be calculated.

3/...

By means of low-temperature (ca 370°C) combustion in air (Brown, Durie and Schafer (1959)), moisture losses for the clay minerals are reversible, but pyrite and siderite ($FeCO_3$) are decomposed and have to be allowed for in the final calculation.

However, developments in plasma technology in the sixties made it possible to ash coal at an even lower temperature (ca 130-160°C) at which the principal minerals appear to be unaffected. By means of radio-frequency ashing it thus became possible to determine the mineral matter content of coal more directly.

METHOD

The low-temperature ashing was carried out in a commercially available radio-frequency asher, Model LTA 505 of the LFE Corporation.

Commercial grade oxygen is passed through a high energy electromagnetic field produced by a radio-frequency oscillator (frequency 13,56 mega H_z) in a partial vacuum. A plasma discharge takes place, the oxygen is activated and according to Gleit (1963) consists of a mixture of atomic and ionic species, as well as oxygen in electronically and vibrationally excited states. Combustion of organic material can thus take place at a relatively low temperature.

Previous experience (viz. Report No. 45 of 1975) indicated that the appearance of the low-temperature ash residue is not a reliable guide to the extent to which carbon has been removed. It is thus necessary to ash the residue to a constant mass.

Some preliminary tests were carried out. A half gram to 8 g lots of a coal with a moderate ash content (New Clydesdale 15,4% of ash) were placed in each of the five chambers of the radio-frequency asher, and ashed at 200 Watt and a 50 cc/min oxygen flow rate. The samples were stirred twice daily and weighed at 24 hour intervals, after allowing an hour for equilibrium with the laboratory atmosphere. Measurements of the infra-red radiation indicated that ashing occurred in the temperature range 130 - 160°C. In

4/...

spite of precautions, some ash was lost from the sample boats, as was shown by the fine powdery deposits on the ashing chamber windows.

Referring to Table 1, it is evident that the amount of coal placed in a sample boat strongly influences the ashing rate and the final result. For example, although 8 g of coal is easily accommodated in a sample boat, it is not readily ashed to completion. After 144 hours the 8 g sample still contained unoxidized carbon as shown by its high residue and residue to ash ratio of 19,7% and 1,28 respectively. The smaller samples required periods of time directly related to their size and the low end result for the 0,5 g sample (18,7% of residue and 1,22 residue to ash ratio) is probably due to some ash blow-over.

These results are explained by the nature of the ashing process. Active oxygen can only attack exposed carbon and the inert ash layer forming as oxidation proceeds, effectively prevents further access by the oxygen and thus combustion. It is therefore probably not possible to remove all the carbon from the sample, but by following a standardized procedure, reasonably reproducable results are obtainable. As they still contain residual carbon, the determined mineral matter contents may be expected to be too high.

RESULTS

For the data in Table II the radio-frequency ashing method was standardized as follows:- 1,0000 g of coal, weighed in a sample boat was ashed at 200 Watt and a 50 cc/min oxygen flow rate; the samples were stirred twice daily to expose unoxidized coal and weighed daily after allowing an hour for the residue to come to equilibrium with the laboratory atmosphere; the ashing was discontinued when the mass loss of the residue per 24 hour period was less than 1,0%.

From the data in Table II it appears that there is no simple relationship between the ash content and the time required for ashing to a negligible mass loss, for example the first two samples given in the Table had a nearly identical ash content of 25% but the Coalbrook sample required an average of

5/...

8 days for ashing as against the 4 days required for the Kilbarchan coal. The type of mineral matter and the reactivity of the coal probably also influence the ashing rate.

Bearing in mind that a period of 2 months elapsed between the first determination and the duplicate determination for each sample, and that the radio-frequency asher broke down and had to be modified and repaired after a few samples in the first series had been processed, the reproducibility of the results is good.

DISCUSSION

In Table III, some of the mean data from Table II are regrouped according to the different coalfields and are contrasted with earlier results (Technical Memorandum No. 21 of 1971) from the modified King, Maries and Crossley formula (KMC), acid extraction (AE), low-temperature oxidation (LTO) and kaolin methods. Where more than one analysis per colliery was given in the memorandum, the analysis closest in ash content was selected for comparison.

It is presumed that the mineralogical composition of the coal produced from most of the collieries, over the interim, has not altered significantly and that a comparison is valid.

Although some individual discrepancies occur, e.g. the radio-frequency oxidation mineral matter factor was rather lower for Wolvekrans, Tweefontein, New Clydesdale and New Largo and rather higher for Koornfontein and Utrecht coals, which could possibly be explained as due to a variation in carbonate compositions between the earlier and present coal samples, the overall agreement appears to be good.

On average (Table IV), the mineral matter factors determined by the radio-frequency oxidation method are slightly higher than for the KMC and acid extraction methods and slightly lower than the low temperature combustion and kaolin methods. The maximum difference is 1,5% (acid extraction method) and KMC as well as kaolin methods give mineral matter factors which are nearly identical to the radio-frequency oxidation method.

6/...

SUMMARY AND CONCLUSIONS

By means of radio-frequency oxidation, it is possible to combust coal at 130 - 160°C, which affords a method for the direct determination of the mineral matter content in coal.

Since only the surface carbon is attacked by the oxygen plasma, radio-frequency oxidation is a slow process requiring from 3 to 8 days to combust 1 g coal samples, with some residual carbon always remaining in the mineral matter.

Comparing data from the radio-frequency oxidation method with data from the modified KMC, acid extraction, low-temperature oxidation and kaolin methods given in Technical Memorandum No. 21 of 1971 for an earlier series of samples, the residual carbon does not appear to have an important influence on the results. On average, mineral matter factors determined by the radio-frequency oxidation method are likely to fall between factors from the KMC and acid extraction methods on the one hand and low-temperature oxidation and kaolin methods on the other hand. The maximum difference is 1,5%.

J L GAIGHER
SENIOR RESEARCH OFFICER

PRETORIA
16 SEPT. 1976
JLG/ug

REFERENCES

Brown H R, Durie R A and Schafer H N S (1959): Fuel 38 295 - 308.

Brown R L, Caldwell R L and Fereday F (1952): Fuel 31 261 - 273.

Gleit C E (1963): Am. J Med. Electr. 2 112 - 118.

King J G, Maries M B and Crossley H E (1936): J Soc. Chem. Ind. London 57 277 - 281.

Millot J O'N (1958): Fuel 37 71 - 85.

Parr S W (1928): Univ. Illinois Eng. Exp. Stat. Bull 180.

Pringle W J S and Bradburn E (1958): Fuel 37 166 - 180.

TABLE 1

RADIO-FREQUENCY ASHING OF A COAL SAMPLE

Orig. Mass (g)	Total Ashing Period (hours) 24	48	72	96	120	144
Residue %						
0,5	19,0	18,9	18,9	18,9	18,8	18,7
1,0	20,3	19,2	19,2	19,2	19,1	19,0
2,0	36,9	20,0	19,3	19,2	19,1	19,0
4,0	39,9	21,7	19,5	19,2	19,0	18,9
8,0	65,6	43,9	31,8	24,6	20,7	19,7
Residue: ash* ratio						
0,5	1,24	1,23	1,22	1,23	1,22	1,22
1,0	1,32	1,25	1,25	1,25	1,24	1,24
2,0	2,40	1,30	1,25	1,25	1,24	1,24
4,0	2,59	1,41	1,27	1,25	1,24	1,23
8,0	4,26	2,85	2,07	1,60	1,34	1,28
Mass loss per Ashing Period %						
0,5	-81,0	- 0,7	- 0,1	+ 0,3	- 0,7	- 0,3
1,0	-79,7	- 5,2	- 0,3	+ 0,3	- 0,9	- 0,3
2,0	-63,1	-45,7	- 3,7	- 0,2	- 0,8	- 0,2
4,0	-60,1	-45,7	-10,1	- 1,5	- 1,0	- 0,1
8,0	-34,4	-33,1	-27,5	-22,6	-16,1	- 3,8

Note: * Coal ash i.e. 15,4%

TABLE II

MINERAL MATTER AND MINERAL MATTER FACTORS* DETERMINED BY THE RADIO-FREQUENCY OXIDATION METHOD

Sample No.	Designation	Ash %	DUPLICATES				AVERAGE			
			Period** (days),	Δ	m.m. %	m.m./ash*	Period** (days),	m.m. %		m.m./ash*
75/45 A	Coalbrook No 2	24,6	9 7	0·2	30,7 30,5	1,25 1,24	8	30,6	✓	1,24
75/55 A	Kilbarchan	24,7	4 4	0·8	29,7 28,9	1,20 1,17	4	29,3	✓	1,19
75/144A	Blinkpan	20,1	4 3	0·5	25,0 24,5	1,24 1,22	4	24,8	✓	1,23
75/202A	Vierfontein	30,1	10 7	0·8	35,6 34,8	1,18 1,16	9	35,2	✓	1,17
75/38 D	Delmas	19,0	4 4	0·4	23,6 23,2	1,24 1,22	4	23,4	✓	1,23
75/128B	T.N.C.	11,8	4 3	0	14,3 14,3	1,21 1,21	4	14,3	✓	1,21
75/136B	Tavistock	10,7	3 3	0	13,3 13,3	1,25 1,24	3	13,3	✓	1,24
75/208D	Eikeboom	9,6	5 3	0·1	11,3 11,4	1,18 1,19	4	11,4	✓	1,18
75/124B	Union	13,0	5 4	0·2	15,9 16,1	1,22 1,24	5	16,0	✓	1,23
75/310B	Utrecht	13,5	4 3	0·1	16,6 16,7	1,23 1,24	4	16,7	✓	1,23
75/303B	Ballengeich	16,1	3 3	0·1	18,8 18,9	1,16 1,18	3	18,9	✓	1,17
75/504B	Newcastle-Platberg	23,2	5 3	0	26,5 26,5	1,14 1,14	4	26,5	✓	1,14
8434	Aloe Anthracite	11,8	3 3	0·2	12,6 12,8	1,07 1,08	3	12,7	✓	1,08
75/393A	Cornelia Bertha I	26,2	6 5	0·4	31,3 31,7	1,19 1,21	6	31,5	✓	1,20
75/394B	Cornelia Bertha II	25,0	7 6	0·2	29,7 29,9	1,19 1,20	7	29,8	✓	1,19
75/408D	Greenside No 5	11,5	3 3	0·1	13,7 13,6	1,19 1,18	3	13,7	✓	1,19
75/414A	New Clydesdale	15,4	3 3	0·5	19,3 18,8	1,25 1,22	3	19,1	✓	1,24
75/418B	Tweefontein	13,4	4 3	0·1	15,3 15,2	1,15 1,13	4	15,3	✓	1,14

TABLE II (Continued)

Sample No.	Designation	Ash %	DUPLICATES Period** (days)	Δ	 m.m. %	 m.m.* ash	AVERAGE Period** (days)	 m.m. %	 m.m.* ash
75/424A	Springbok No 2	13,7	4	0·2	16,2	1,20	4	16,3 ✓	1,19
			3		16,4	1,19			
75/425B	Van Dyks Drift	14,3	3	0	17,6	1,23	3	17,6 ✓	1,23
			3		17,6	1,23			
75/427B	New Largo	20,6	4	0·1	24,7	1,20	4	24,7 ✓	1,20
			3		24,6	1,19			
75/428D	Waterpan	14,4	4	0·1	17,3	1,20	4	17,4 ✓	1,20
			4		17,4	1,21			
75/555B	Kriel	15,0	3	0·4	17,8	1,19	4	17,6 ✓	1,17
			5		17,4	1,16			
75/572D	South Witbank	20,2	3	0·1	24,3	1,20	3	24,3 ✓	1,20
			3		24,2	1,20			
75/582A	Koornfontein	12,4	3	0·1	15,6	1,26	3	15,7 ✓	1,26
			3		15,7	1,27			
75/589B	Wolvekrans	15,7	3	0·2	18,5	1,18	4	18,4 ✓	1,17
			4		18,3	1,17			
75/557B	Sigma	30,2	7	0·3	35,0	1,16	7	34,9 ✓	1,15
			7		34,7	1,15			
75/559A	Coalbrook 3	33,4	6	0·1	41,3	1,24	6	41,3 ✓	1,24
			5		41,2	1,23			
75/562A	Springfield (Grootvlei)	26,8	5	0·1	32,1	1,20	5	32,1 ✓	1,20
			5		32,0	1,19			
75/569B	Navigation Coking	11,9	4	0·2	13,4	1,12	4	13,5 ✓	1,13
			4		13,6	1,14			
75/570B	Phoenix	14,8	4	0·2	17,8	1,20	4	17,9 ✓	1,21
			4		18,0	1,21			
75/574C	Witbank Cons.	21,9	4	0	26,2	1,20	4	26,2 ✓	1,20
			3		26,2	1,20			
75/576B	Albion	16,8	3	0·1	20,4	1,22	3	20,5 ✓	1,22
			3		20,5	1,22			
75/553A	Anglo Power (Kriel Sect.)	20,4	3	0·1	25,3	1,24	3	25,3 ✓	1,24
			3		25,2	1,24			
75/586B	Spitzkop	13,2	3	0·1	16,0	1,21	4	16,1 ✓	1,22
			4		16,1	1,22			

NOTE: * $\frac{\text{mm \%}}{\text{Ash \%}}$

** Ashing period to a mass loss of less than 1,0% per day.

Distribution in "ash" groups
"Ash range"

Δ	<15	15-19.9	20-29.9	30+
0	2	1	2	
0·1	2	6	4	2
0·2	2	4	1	①
0·3				1
0·4		1	1	1
0·5		1	①	
0·8			①	①

Δ	No of coals	Cum No
0	5	5
0·1	14	19
0·2	8	27
0·3	1	28
0·4	3	31
0·5	2	33
0·8	2	35

of these 4 are among first 5 coals on list.

○ = 1st five coals

Excluding ringed values not much correlation between Δ + "Ash" [illegible]

TABLE IV

AVERAGE DATA FOR MINERAL MATTER FACTORS

Designation	Number of samples	Ash %	KMC	AE	LTO	Kaolin	Ash %	RFO	Difference %[*]			
									KMC	AE	LTO	Kaolin
TRANSVAAL												
Witbank No. 2	12	13,45	1,206	1,205	-	1,223	14,37	1,212	-0,5	-0,6	-	+0,9
Witbank No.4	3	22,6	1,21	1,20	1,22	1,21	20,9	1,21	0	-0,8	+0,8	0
Heidelberg	1	19,3	1,21	1,17	1,25	1,24	26,8	1,20	+0,8	-2,5	+4,2	+3,3
O.F.S.	3	27,3	1,17	1,17	1,18	1,15	28,8	1,17	0	0	+0,9	-1,7
NATAL												
Klip River	3	20,6	1,17	1,13	1,17	1,17	22,7	1,17	0	-3,4	0	0
Utrecht	1	21,7	1,19	1,16	1,21	1,17	13,5	1,23	-3,3	-5,7	-1,6	-4,9
Average[**]	17	19,47	1,197	1,182	1,208	1,201	20,48	1,200	-0,2	-1,5	+0,7	+0,1
Overall Average	23	17,99	1,197	1,187	-	1,204	18,70	1,201	-0,3	-1,2	-	+0,2

NOTES [*] Relative to RFO method.

[**] Excluding samples for which no LTO data are given.

TABLE 111

MINERAL MATTER FACTORS OF TECHNICAL MEMORANDUM NO. 21 OF 1971 COMPARED WITH MINERAL MATTER FACTORS DETERMINED BY THE RADIO-FREQUENCY OXIDATION METHOD

Colliery	Technical Memorandum No. 21 of 1971 Mineral matter factors					Radio-frequency Ox. m.m. factors					
	Ash %	KMC	AE	LTO	Kaolin	Ash %	R.F.O.	KMC/RFO	AE/RFO	LTO/RFO	Kaolin/RFO
TRANSVAAL		Δ from R.F.O									
Witbank No. 2 Seam											
Delmas	12,2	1,22 −1	1,18 −5	1,25 +2	1,24 +1	19,0	1,23	0,99	0,96	1,02	1,01
Wolvekrans	14,9	1,20 +3	1,19 +2	1,19 +2	1,22 +5	15,7	1,17	1,03	1,02	1,02	1,04
Waterpan	14,1	1,17 −3	1,16 −4	-	1,18 −2	14,4	1,20	0,98	0,97	-	0,98
Tweefontein	11,9	1,18 +4	1,17 +3	-	1,18 +4	13,4	L 1,14	1,04	1,03	-	1,04
Phoenix	13,8	1,18 −3	1,19 −2	-	1,19 −2	14,8	1,21	0,98	0,98	-	0,98
Albion	15,5	1,23 +1	1,21 −1	-	1,26 +4	16,8	1,22	1,01	0,99	-	1,03
Tavistock	12,6	1,22 +2	1,25 +1	-	1,25 +1	10,7	1,24 1.2	0,98	1,01	-	1,01
New Clydesdale	13,3	1,27 +3	1,26 +2	1,30 +6	1,29 +5	15,4	1,24	1,02	1,02	1,05	1,04
Tvl. Navigation	14,9	1,20 −1	1,22 +1	-	1,22 +1	11,8	1,21	0,99	1,01	-	1,01
Van Dyks Drift	14,1	1,21 −2	1,20 −3	1,24 +1	1,23 0	14,3	1,23	0,98	0,98	1,01	1,00
Springbok	12,8	1,18 −1	1,19 0	1,19 0	1,19 0	13,7	1,19	0,99	1,00	1,00	1,00
Koornfontein	11,3	1,21 −5	1,24 −2	1,22 −4	1,23 −3	12,4	H 1,26	0,94	0,94	0,95	0,95
Witbank No. 4 Seam											
Blinkpan	20,9	1,20 −3	1,22 −1	1,19 −4	1,21 −2	20,1	1,23	0,98	0,99	0,97	0,98
New Largo	29,6	1,25 +5	1,22 +2	1,28 +8	1,24 +4	20,6	1,20 1.2	1,04	1,02	1,07	1,03
Witbank Consolidated	17,4	1,19 −1	1,17 −3	1,18 −2	1,19 −1	21,9	1,20	0,99	0,98	0,98	0,99
Heidelberg											
Grootvlei	19,3	1,21 +1	1,17 −3	1,25 +5	1,24 +4	26,8	1,20	1,01	0,98	1,04	1,03
ORANGE FREE STATE											
Bertha No. 1	23,3	1,18 −2	1,21 +1	1,21 +1	1,16 −4	26,2	1,20	0,98	1,01	1,01	0,97
Vierfontein	29,1	1,14 −3	1,15 −2	1,16 −1	1,14 −3	30,1	1,17 1.17	0,97	0,98	0,99	0,97
Sigma	29,4	1,19 +4	1,15 0	1,16 +1	1,16 +1	30,2	1,15	1,03	1,00	1,01	1,01
NATAL											
Klip River											
Kilbarchen	24,0	1,17 −2	1,13 −6	1,17 −2	1,16 −3	28,9	1,19	0,98	0,95	0,98	0,97
Ballengeich	17,6	1,16 −1	1,11 −6	1,15 −2	1,16 −1	16,1	1,17	0,99	0,95	0,98	0,99
Platberg	20,1	1,18 +4	1,14 0	1,19 +5	1,18 +4	23,2	1,14	1,04	1,00	1,04	1,04
Utrecht											
Utrecht	21,7	1,19 −4	1,16 −7	1,21 −2	1,17 −6	13,5	1,23	0,97	0,94	0,98	0,95

NOTES: KMC = King, Maries and Crossley formula as modified by Millot (1958).

AE = Acid Extraction method.

LTO = Low temperature oxidation method.

Kaolin = Indirect method assuming kaolinite to be the only clay mineral present.

RFO = Radio-frequency oxidation method.

	KMC	AE	LTO	Kaolin
No of comparisons	23	23	17	23
Max difference	±5	−7	+8	−6
Average difference	0.026	0.028	0.026	0.027
Algebraic Average difference	−0.002	−0.014	+0.008	+0.003
	−.33	−0.33	+0.14	+0.07