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ONDERWERP: THE MANGANESE CONTENT OF SOUTH AFRICAN COALS.
SUBJECT:

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DIVISION:

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NAME OF OFFICER:

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

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THE MANGANESE CONTENT OF SOUTH AFRICAN COALS.

SUMMARY.

The presence of manganese in South African coals is well known, but no figures on the manganese content of these coals or their ashes were hitherto available. In this paper the manganese content of 33 South African coals is reported, and some information about the behaviour of manganese during specific gravity separations is given. Results of extraction experiments carried out by the authors indicate that manganese occurs in South African coals mainly as carbonate, presumably ankerite.

INTRODUCTION:

Manganese is about fifteenth in the list of the most abundant elements in the earth's crust. Its concentration in the crust is about 0.09%. It occurs in igneous rocks as well as in sedimentary rocks and it is also found in coal. Manganese often partially replaces calcium and magnesium in carbonates of the dolomitic group. It can also partially displace divalent iron in some minerals.

Manganese is an indispensable trace element for most forms of organic life, plant life as well as animal life. Little is known about the role manganese plays in plant and animal

life

life. It has been suggested (1a) that manganese, together with iron, has some function in the formation of haemoglobin. In plants it often occurs in higher concentration in parts rich in chlorophyll. Apparently the physiological effect of manganese is connected with its ability to assume various states of oxidation.

The amount of manganese in soils usually varies between 2000 and 5000 p.p.m. (1b) and it is often found in higher concentration in the surface than in the subsoils. A very important fact is the liability of manganese to be leached from certain soil horizons and to be concentrated in others. These two opposing processes of leaching and precipitation are governed by two factors. The first is the access of atmospheric oxygen causing fixation by oxidation of the manganese, the second is the pH, a low pH favouring the solution and leaching of the manganese.

The presence of manganese in coal ashes is indicated by the bluish-green colour of their sodium carbonate melts. Its presence in South African coals is well known but no figures on the manganese content of coals or coal ashes were hitherto available.

ANALYTICAL METHODS FOR THE DETERMINATION OF SMALL AMOUNTS OF MANGANESE:

Apart from spectrographic and flame photometric methods, mainly colorimetric methods are used for the determination of small amounts of manganese. The best known methods for the colorimetric determination of manganese are based on the intense purple colour of the permanganate ion. Different reagents are recommended for the oxidation of manganese to the 7-valent state. In the British Standard Method for the analysis of coal ash and coke ash, potassium periodate is used for the oxidation (2).

Another oxidizing agent used for this purpose is sodium bis-muthate (3). With this reagent the oxidation occurs even at room temperature. A third, widely used, oxidizing agent is ammonium peroxy-disulfate, briefly called ammonium persulfate (4). The oxidation of manganese with peroxy-disulfate is carried out in the presence of a small amount of a silversalt which catalyses the reaction.

There are also a few organic reagents which give a coloured complex with the manganese ion and are therefore used for its colorimetric determination. Sodium diethyl dithiocarbamate (5) gives with divalent manganese a chloroform-soluble colourless complex which is quantitatively oxidized to the brown-violet thiocarbamate of the trivalent manganese by a short agitation of the solution in contact with air. Formaldoxine (6) forms with manganese an orange-red complex which also allows its colorimetric determination.

For the investigation in hand a method proposed by Radmacher and Schmitz (7) was used. In this method the ash of the coal is treated with hydrofluoric and sulfuric acid and the manganese is extracted from the residue with diluted nitric acid. In the extract the manganese is determined spectrophotometrically, after oxidizing it to permanganate with ammonium peroxy-disulfate in the presence of silver ions. The reproducibility of the values obtained with this method is excellent.

THE MANGANESE CONTENT OF SOUTH AFRICAN COALS:

Table 1 shows the manganese content of 33 South African coal samples and of their ashes. The manganese content of the ashes lies between 0.005 and 0.083% Mn and that of the coals between 0.0011 and 0.0129% Mn. From the 33 samples listed in Table 1 an average content of 0.033% Mn was calculated for the ash and 0.0053% for the coal. Manganese is therefore

not enriched in the coal ash compared with its concentration in the earth's crust. On the contrary, it occurs in coal ash in a considerably lower concentration.

Radmacher and Schmitz (8) give for the manganese content of the ashes of coals from the Ruhr area limits of 0.003 and 0.060% Mn. Clark and Swaine (9) found in the ashes of New South Wales coal manganese contents ranging from 0.003 - 0.30% Mn. For West Virginian coal ashes Headlee and Hunter (10) give figures of 0.005 - 0.90% Mn with an average of 0.035%.

No distinct relationship between the manganese content of the coal or coal ash and the geographical area could be established. It may be mentioned, however, that all the ashes of the samples from the No. 2 and No. 4 seams from the Witbank area show a manganese content which lies above the average for South Africa.

Table 2 shows the manganese content of the fractions of fractional specific gravity separations of two coal samples. In both samples the manganese content of the coal increases with increasing specific gravity of the fractions. The manganese content of the ash increases only in the first sample from the Float 1.40 to the Sink 1.60. In the second sample the manganese content of the ash drops from the Float 1.35 to the Fraction 1.35 - 1.40 but increases then again slightly up to the Sink 1.60.

To investigate the mode of occurrence of manganese in South African coals, 8 coal samples were extracted with cold 5% acetic acid and with boiling 2N nitric acid. Manganese was then determined in the extracts. In the first method the acetic acid had to be removed by evaporation with sulfuric acid before the manganese could be determined with ammonium peroxydisulfate.

TABLE 1. MANGANESE CONTENT OF SOUTH AFRICAN COALS AND COAL ASHES.

<u>Witbank Area</u>					
Colliery	Sample No.	% Ash	% Mn in Ash	% Mn in Coal	
Seam 2	Landau	67/409 C	18.3	0.050	0.0092
	Waterpan*	67/404 D	14.8	0.046	0.0068
	Wolvekrans*	67/405 C	13.8	0.056	0.0077
	Douglas	67/394 C	11.7	0.042	0.0049
	Springbok	67/387 B	12.3	0.044	0.0054
	Koornfontein	67/389 C	14.9	0.041	0.0061
	Phoenix*	67/402 C	14.9	0.060	0.0089
	Tweefontein*	67/403 C	18.1	0.049	0.0089
Seam 4	Klippoortjie	67/412 E	16.7	0.044	0.0073
	Witbank Consolidated	67/414 D	16.4	0.041	0.0067
	South Witbank	67/411 E	17.9	0.036	0.0064
Seam 5	Navigation (SACE)	67/407 B	11.4	0.039	0.0044
	Blesbok	67/392 A	10.4	0.011	0.0011
	Springbok	67/387 C	10.1	0.011	0.0011
*Mining more than one seam.					
<u>Ermelo - Breyten</u>					
Union	67/396 C	13.4	0.038	0.0051	
Bellevue	67/386 B	15.7	0.025	0.0039	
<u>Heidelberg</u>					
Springfield (Grootvlei)					
North	67/373 C	20.7	0.030	0.0062	
Springfield (Grootvlei)					
South	67/542 A	21.3	0.022	0.0045	
<u>Orange Free State</u>					
Cornelia Bertha Shaft 1	67/420 C	29.1	0.014	0.0041	
Cornelia Betty Shaft	67/419 C	26.7	0.040	0.0107	
Sigma	67/424 A	27.7	0.026	0.0072	
<u>Natal</u>					
Utrecht	67/452 C	17.3	0.038	0.0066	
<u>Vryheid</u>					
Hlobane (Duff)	67/450 A	12.5	0.014	0.0018	
Hlobane (Coking)	67/450 B	13.2	0.015	0.0020	
Natal Anthracite	6543	10.0	0.030	0.0030	
Natal Ammonium	6533	12.9	0.039	0.0050	
Enyati (Mixed Smalls)	67/449 B	22.8	0.005	0.0011	
<u>Klip River</u>					
Kilbarchan	67/490 A	21.0	0.023	0.0048	
Durban Navigation	64/112	11.2	0.032	0.0036	
Natal Navigation (Peas)	67/492 B	11.7	0.024	0.0028	
Natal Navigation (Coking)	67/492 C	12.7	0.025	0.0032	
Indumeni (Steam)	67/488 E	15.6	0.083	0.0129	
Natal Steam	67/493 D	22.9	0.007	0.0016	

TABLE 2. MANGANESE CONTENT OF THE FRACTIONS OF FRACTIONAL SPECIFIC GRAVITY SEPARATIONS.

64/391	Float 1.40	Fl. 1.40-1.45	Fl. 1.45-1.50	Fl. 1.50-1.55	Fl. 1.55-1.60	Sink 1.60	Whole Coal
% Yield	49.60	25.74	10.78	2.95	2.66	8.27	100.00
% Ash	6.8	11.4	16.4	20.6	25.1	45.6	13.1
% Mn in Ash	0.032	0.034	0.035	0.036	0.038	0.045	0.037
% Mn in Coal	0.0022	0.0039	0.0057	0.0075	0.0095	0.0205	0.0048
67/452	Float 1.35	Fl. 1.35-1.40	Fl. 1.40-1.45	Fl. 1.45-1.50	Fl. 1.50-1.60	Sink 1.60	Whole Coal
% Yield	28.8	14.1	11.4	15.3	7.0	23.4	100.00
% Ash	4.4	6.7	9.4	14.0	20.1	44.9	17.3
% Mn in Ash	0.039	0.030	0.031	0.035	0.037	0.040	0.038
% Mn in Coal	0.0017	0.0020	0.0029	0.0049	0.0074	0.0180	0.0066

10

TABLE 3. MANGANESE CONTENT OF 8 COAL ASHES DETERMINED ACCORDING TO RADMACHER AND SCHMITZ AND CALCULATED FROM THE AMOUNT OF MANGANESE EXTRACTED FROM THE COAL WITH BOILING 2 N NITRIC ACID AND COLD 5% ACETIC ACID.

Sample No.	% Ash	% Mn determined accord. to Radmacher and Schmitz	% Mn calcul. from extraction with boiling 2 N HNO ₃	% Mn calcul. from extraction with cold 5% Acetic Acid
67/488 E	15.6	0.083	0.082	0.084
67/402 C	14.9	0.060	0.058	0.057
67/405 C	13.8	0.056	0.056	0.051
67/414 D	16.4	0.041	0.042	0.039
67/409 C	18.3	0.050	0.052	0.052
67/407 B	11.4	0.039	0.039	0.035
6533	12.9	0.039	0.038	0.026
6543	10.0	0.030	0.030	0.018

Column 3 of Table 3 shows the total manganese content of the 8 ashes determined by the above described method of Radmacher and Schmitz. In column 4 the manganese content, calculated from the amount of manganese extracted from the coal with boiling 2N nitric acid, can be seen. It is obvious that all the manganese is extracted with boiling 2N nitric acid. The small deviations from the values given in column 3 must be interpreted as experimental deviations. Column 5 shows the manganese extracted from the coal with cold 5% acetic acid. It is assumed that only manganese occurring in coal as carbonate is extracted by acetic acid. The high figures in column 5 indicate therefore that manganese occurs mainly as carbonate, presumably as ankerite $\text{Ca}(\text{MgFeMn})(\text{CO}_3)_2$, in South African coals. With the last two samples 6533 and 6543 a second extraction with acetic acid was carried out without noticeably improving the result. By means of an additional extraction with hot 2N nitric acid, however, the missing manganese was fully recovered. There is no doubt that in these two samples part of the manganese occurs in a compound which is not soluble in acetic acid.

In conclusion it may be stated that manganese occurs in South African coals in concentrations which have no detrimental influence on their commercial use. It may be important, however, for the analyst to be aware of the interferences which can be caused by its presence in coal or coal ash in the analytical field.

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PRETORIA.

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