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FUEL RESEARCH INSTITUTE OF SOUTH AFRICA

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THE OCCURRENCE OF VANADIUM IN SOUTH AFRICAN COALS

by

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and

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Apart from the major constituents of the ash of a coal, every coal contains a great number of trace elements. In many cases the suitability of a coal for certain purposes depends on the concentration of these trace elements in the coal. Trace elements can become dangerous because of their toxic effect if passed on to edible products with flue gases or flue dust. Catalytically active metals such as vanadium, nickel, cobalt and molybdenum may influence the course of a catalytic hydrogenation process or other catalytic processes. Other trace elements, volatilized during combustion, may completely inhibit the action of catalysts. Finally trace elements may be involved in the formation of boiler deposits.

Special merit for the investigation of trace elements in coal must go to Goldschmidt (1). He also developed a theory explaining the enrichment of trace elements in coal, but he himself expressed his doubts that this theory is applicable to the enrichment of metals like vanadium, molybdenum and nickel.

A very comprehensive paper on rare elements in coal was published in 1944 by Gibson and Selvig (2). The authors gave inter alia a detailed report on the occurrence of vanadium in coal.

The first report on the occurrence of vanadium in coal may have come from Kyle (3) in 1892. He discovered in the ash of lignite, found in San Rafael in Argentina, 38.22% V_2O_5. Forty years later Hess (4) expressed his doubts that the material analysed by Kyle was lignite and he suggested that it may have been asphaltite.

In .../

In Peru asphaltite was found containing 7.1% V_2O_5 in the ash. Two Peruvian coal samples, with ash contents of 13.9% and 29.2%, examined by the Bureau of Mines (USA) for vanadium (2) showed V_2O_5 contents of 0.21% and 0.13% only.

According to a report published by Simpson (5) the ashes of Australian coals contain from a trace to 0.21% V_2O_5. A fairly recent paper on trace elements in New South Wales coal, published by Clark and Swaine (6), gives for the vanadium content of the ashes a figure of 0.0020 - 0.15% (= 0.0035 - 0.26% V_2O_5). Zilbermintz (7,8) reported low V_2O_5 contents of 0.02 - 0.3% in most of the Russian coal ashes analysed. Coals from deposits of the eastern slopes of the Ural showed, however, V_2O_5 contents of 0.56 - 8.79% in the ash. Radmacher and Schmitz (9) found in the ash of coal from the Ruhr-Area V_2O_5 contents from 0.018 to 0.089%. Headly and Hunter (10) carried out 596 spot analyses from 35 columns representing 16 major coal seams in West Virginia and found V_2O_5 contents from 0.016 to 0.149% in the ashes.

Reynolds (11) observed that ashes of certain bands of vitrain interbedded with Coal Measure rocks in North Staffordshire and North Wales contain abnormally high quantities of vanadium, chromium, titanium and nickel. "Cauldron" vitrains from the Durham Coalfield show the same phenomenon. A sample of vitrain associated with the Peacock seam in North Staffordshire gave, according to Reynolds, the following ash analysis after being separated at a specific gravity of 1.35.

TABLE 1.

Analysis of the Ash of a Special Vitrain
(Floats at sp.gr. 1.35)

	%		%
SiO_2	18.8	Na_2O	0.5
Al_2O_3	23.5	K_2O	0.8
Fe_2O_3	11.2	SO_3	6.0
TiO_2	15.0	P_2O_5	0.4
NiO	1.5	Cr_2O_3	1.0
MnO	Trace	V_2O_5	14.1
CaO	6.4	B_2O_3	0.4
MgO	0.7		

No satisfactory explanation has been found for this enrichment which is outstanding in two respects, namely, the high degree of enrichment and its selectivity. Reynolds guesses that the presence of certain organic compounds, e.g. porphyrines, which form water-insoluble organo-metallic complexes with these few elements could explain the selective enrichment.

No figures concerning the vanadium content of South African coal were published previously.

For the determination of traces of vanadium, apart from spectrographic methods several colorimetric methods are recommended in the literature. The two best known colorimetric methods are the "Peroxide Method"(12) and the "Phosphotungstate Method"(13). The first is based on the reddish-brown colour reaction which quinquevalent vanadium gives with hydrogen peroxide. The sensitivity of this method is somewhat lower than that of the phosphotungstate method and therefore the latter was chosen in the present study. The phosphotungstate method, introduced in colorimetry by Willard and Young (14) makes use of the yellow compound which is formed when sodium tungstate and phosphoric acid are added to an acid solution containing quinquevalent vanadium. The measuring of the absorbance of the coloured solutions was done with a spectrophotometer.

Table 2 shows the vanadium content of 21 South African coals and of their ashes. The vanadium content of these coals lies between 0.0023 and 0.0132% (V) and that of their ashes between 0.016 and 0.056% (V). From these 21 samples an average vanadium content of 0.0046% is calculated for coal and of 0.027% for the ash. There are not enough figures to be able to draw definite conclusions about regional differences in the vanadium content of South African coals. It may be mentioned, however, that Table 2 shows only low values in the Witbank Area but some relatively high values for Free State and Natal coals.

Table 2...../

TABLE 2.

The Vanadium Content of Some South African Coals.*

Colliery	Sample No.	Ash %	% V_2O_5 in Ash	% V in Ash	% V in Coal
Greenside	65/1897C	16.6	0.029	0.016	0.0027
Wolvekrans	65/1904C	14.1	0.052	0.029	0.0041
Douglas	65/1886C	11.3	0.036	0.020	0.0023
Klipportjie	65/1890D	18.6	0.039	0.022	0.0041
South Witbank	65/1891D	17.4	0.041	0.023	0.0040
Navigation S.A.C.E.	66/480A	12.5	0.045	0.025	0.0031
Kendal	66/477C	17.6	0.030	0.017	0.0030
Consolidated (Bankfontein)	65/1876C	15.4	0.050	0.028	0.0043
Bellevue	66/450B	13.7	0.052	0.029	0.0040
Springfield(Grootvl.)South	65/2127A	19.3	0.029	0.016	0.0031
Cornelia (Betty Shaft)	65/2150C	31.4	0.041	0.023	0.0072
Sigma	66/533A	23.7	0.052	0.029	0.0069
Utrecht	66/504B	18.4	0.071	0.040	0.0074
Vryheid Coronation	66/993A	14.0	0.052	0.029	0.0041
Hlobane	66/814A	18.6	0.030	0.017	0.0032
Natal Ammonium	6266	8.2	0.057	0.032	0.0026
Enyati	66/382A	19.5	0.055	0.031	0.0060
Kilbarchan	66/599A	21.7	0.048	0.027	0.0059
Durban Navigation	66/985A	11.2	0.059	0.033	0.0037
Indumeni	66/987A	15.4	0.029	0.016	0.0025
Natal Steam	66/601A	23.6	0.100	0.056	0.0132

* Mostly Power Station Coal.

% V in Ash: 0.016 - 0.056
% V in Coal: 0.0023 - 0.0132

Table 3 gives the vanadium content of the fractions of a fractional float-sink separation. The figures show that the lowest ash, the ash of float 1.30, has the highest vanadium content. The vanadium content of the ash of the fractions decreases with rising specific gravity up to the fraction float 1.45 - 1.50, then increases again slightly. The sink 1.80 has a somewhat lower vanadium content than the float 1.80. The vanadium contents of the fractions, calculated on coal, show smaller differences than those calculated on the ash. These values decrease from the float 1.30 to the float 1.36 - 1.40 and increase again up to the sink 1.80.

Table 3...../

TABLE 3.

Vanadium Contents of the Fractions of a Fractional Float-Sink Separation.

	% Yield	% Ash	% V_2O_5 in Ash	% V in Ash	% V in Coal
59/898E Float 1.30	10.6	2.5	0.237	0.133	0.0033
" Fl. 1.30-1.33	17.0	4.1	0.148	0.083	0.0034
" Fl. 1.33-1.36	16.2	5.8	0.061	0.034	0.0020
" Fl. 1.36-1.40	22.4	8.1	0.036	0.020	0.0016
" Fl. 1.40-1.45	15.5	11.1	0.029	0.016	0.0018
" Fl. 1.45-1.50	5.8	14.2	0.025	0.014	0.0020
" Fl. 1.50-1.60	4.9	16.2	0.029	0.016	0.0026
" Fl. 1.60-1.80	3.9	21.9	0.036	0.020	0.0044
" Sink 1.80	3.7	53.6	0.030	0.017	0.0091
59/898E Whole Coal	100.0	9.6	0.054	0.030	0.0029

Vanadium is known to play an important role in the formation of external deposits in oil-fired boilers. An article published by Konopicky (15) shows which harmful effects have to be reckoned with when fuels giving ashes rich in vanadium are fired. Because of its low surface tension fused V_2O_5 has a strong wetting action on all the surfaces with which it comes in contact and creeps up the walls of the fire box corroding the fireproof masonry. It also causes rapid corrosion of steel and special steels by removing the protecting surface layer.

The generally low vanadium contents of South African coals should not lead to corrosion or deposit forming troubles.

As can be seen from a monograph on the toxicology and biological significance of vanadium, written by Faulkner Hudson (16), there is already an extensive literature on the toxic effect of vanadium. The reports on ill effects concern, with few exceptions, only workers in the vanadium mining or processing industries and people

employed...../

employed in the cleaning of oil-fired boilers.

The first signs of poisoning through inhalation of vanadium dust or fumes are an irritation of the nose, eyes and throat, followed by a dry, often paroxysmal cough. Occasionally, also, a discolouration of the tongue, the so-called "green tongue" is observed.

Values for the maximum permissible concentration of vanadium pentoxide, as adopted at an American Conference of Governmental Industrial Hygienists 1961 (16), are the following:

Vanadium pentoxide dust: .... 0.5 mg/m^3
Vanadium pentoxide fumes: .... 0.1 mg/m^3
Ferrovanadium dust: .... 1.0 mg/m^3

Cessation of the exposure to vanadium compounds mostly leads to a complete recovery and no reports of a cumulative action of vanadium have been found.

No reports of ill effects due to the vanadium content of coal could be found. This is not surprising when one considers that the vanadium content of coal ash seldom exceeds 0.10% (V_2O_5) whilst the vanadium content of the ash of furnace oils often exceeds 50% (V_2O_5).

PRETORIA.
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