

VERSLAG No.

REPORT No. 12

VAN

OF 1955.



U1101417

BRANDSTOFNAVORSINGSINSTITUUT

VAN SUID-AFRIKA.

FUEL RESEARCH INSTITUTE

OF SOUTH AFRICA.

ONDERWERP:
SUBJECT: THE OCCURRENCE OF GERMANIUM IN SOUTH AFRICAN

COAL AND DERIVED PRODUCTS.

AFDELING:
DIVISION: CHEMISTRY.

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FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

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THE OCCURRENCE OF GERMANIUM IN SOUTH AFRICAN
COAL AND DERIVED PRODUCTS.

INTRODUCTION:

Although discovered in 1886, germanium was, until recent years, more a chemical curiosity than an economically important element. Its discovery resulted from a consistent deficit of 6 %-7 % observed by Clemens Winkler in the analysis of a silver mineral and, after isolation, it proved to be the "Ekasilicon" predicted by Mendelejeff from his periodic table of the elements.

The metal is brittle, of light grey colour and regular crystal structure. While insoluble in hydrochloric and dilute sulphuric acid, it dissolves in aqua regia and hot concentrated sulphuric acid. Nitric acid oxidises it to GeO_2 ¹⁷⁾.

In its compounds germanium is either bi- or tetra-valent but the bi- form is less stable and tends to oxidise to the tetra- form.

The element lies between carbon-silicon and tin-lead in Group IV of the periodic system. Its chemical behaviour also places it in the transition stage between non-metals and metals.

The chemical behaviour of germanium has been studied extensively but its present economic value results from its physical properties. Germanium is a semi-conductor. These substances are characterised by the fact that they are non-conductors in their purest state and at low temperatures. They become conductive, however, by the introduction of mere traces of foreign metals into their crystal lattice and also when heated. The latter behaviour is contrary to that of metals whose conductivity decreases with rise in temperature. They also differ from metallic conductors in that the latter conduct the current by electrons only whereas both electrons and

"defect electrons"/.....

"defect electrons" are responsible for conduction in semi-conductors.

Germanium is mainly used in the construction of diodes and transistors. The latter, a new type of an electronic amplifier were developed by W.H. Brattain and J. Bardeen in 1948. These transistors have several advantages over conventional vacuum tubes. Thus, for the same performance, the size of the transistor may be only one-tenth of that of the vacuum tube. The transistors need no heating current and there is no heating-up period. They are also more shock-proof.

STATISTICS:

The available reports on germanium production and consumption were found to be somewhat inconsistent but the following data, abstracted from a paper by W. von Haken¹⁸⁾ appear fairly reliable.

The world production of germanium has risen as follows:-

<u>Year.</u>	<u>Production (Kg)</u>
1948	500
1951	5,000
1953	10,500
1954	18,500
1955 (estimate)	32,000

The largest producers are the United States and Belgium (including Congo). Production in the United Kingdom is estimated at 500-700 Kg. Apparently this meets the present demand and production could probably be doubled.

The United/.....

The United States of America is also the largest consumer of germanium. Consumption, for non-military purposes rose in that country from 5,400 kg in 1953 to 10,000 kg in 1954 and may reach 17,700 kg in 1955.

In 1953 the dioxide was quoted at \$ 142 per lb. and the pure metal at \$ 340 per lb. The latest available quotation for germanium (99.9 % germanium) is \$ 295.

This high price does not affect the price of diodes and triodes appreciably as very little germanium is required per unit. Diodes sold in the United States of America at \$ 1.25 each in 1953 contained only a few cents worth of germanium.

SOURCES:

At present most of the germanium is won as by-product in the production of zinc from certain ores (e.g. Missouri and Wisconsin zinc-blends with 0.01 % germanium. Tsumeb mine in South West Africa is also starting with production of germanium¹⁹⁾).

With the rapid increase of demand there has been a general search for other sources of germanium and one that has commanded most interest in recent years is coal.

OCCURRENCE OF GERMANIUM IN COAL OR DERIVED PRODUCTS:

V. M. Goldschmidt¹⁾ first established the presence of germanium in coal (1930) and G.T. Morgan and G.R. Davies²⁾ studied its occurrence in coal ash (1937). They found that under certain conditions of combustion of the coal, up to 60 % of the germanium was volatilised. This led them to an investigation of flue dusts and they found up to 1 % germanium in some of these.

P. Belugou and P. Dumoutet³⁾ consider that volatilisation of the germanium mainly occurs as germanous-oxide or sulphide. These compounds will be formed if conditions in the fuel bed are sufficiently reducing. The germanous compounds are more volatile than the germanic compounds so that if complete combustion takes place in the gas phase germanic compounds may be formed and
deposit/.....

deposit with dust in the flues of the appliance.

The conditions for concentration of germanium are especially favourable in gas producers forming part of an appliance such as a gas retort where the producer gas is burnt before it has cooled appreciably. They actually found up to 2 % germanium in the flues of gas-work's retorts although the average germanium content was 0.5 %.

Similar conditions do not obtain in watergas generators as the conditions in the bed are too highly reducing. The germanium is probably reduced completely, it combines with the (free) iron and is thus retained in the ash.

A. J. W. Headlee and R. G. Hunter⁴⁾ studied coal in the West Virginia coalfield and found the germanium content to vary from the top to the bottom of the seams. The highest germanium contents were usually found either in the top or bottom three inches.

This finding led them to conclude that while some germanium was introduced into the seam at the time of deposition e.g. as integral part of the coal forming plants, germanium was probably also introduced in solution or as vapour from adjacent strata at a later stage. This germanium was mainly absorbed in the parts of the seam first penetrated.

A similar variation in the concentration of germanium over the cross-section of the seam was also observed in the present investigation.

ANALYTICAL METHODS:

Germanium has been determined gravimetrically^{5,11)}, volumetrically⁶⁾, colorimetrically^{7,8,9,10)} and spectrographically^{4,12,13)}.

In the initial stages of this investigation the National Physical Laboratory (C.S.I.R.) kindly agreed to undertake the/.....

take the spectrographic determination on a number of samples. Meanwhile the micro method described by H.J. Cluley¹⁰⁾ was studied at the Institute. It was adopted with only slight modification for routine determinations and all the germanium data given in this report were obtained by this method.

PROCEDURE:

Half a gram to one gram of coal (an amount equivalent to not more than 30 μ gram germanium) is weighed into a porcelain or quartz crucible (20 ml. capacity) and is mixed with 2 grams of calcined sodium carbonate. After covering the mixture with 1 gram of sodium carbonate it is heated in a muffle furnace at 600°C for 4-6 hours until combustion is complete. The contents of the crucible are transferred quantitatively to a platinum crucible and heated at 1000°C for a further period of 20 minutes.

After cooling, 8 ml. of distilled water are added and the crucible is covered with a watch-glass having a small opening at its centre. Now, 4.5 ml. of sulphuric acid (50 % wt.) are added drop-wise through this opening from a burette with finely drawn out point (see Fig. 1) (solution of the contents of the crucible in water alone, as suggested by Cluley was found too tedious).

The solution in the crucible is transferred to a 100 ml. distillation flask and crucible and watch-glass are washed with about 12.5 ml. of distilled water.

The distillation apparatus (Fig. 2) is assembled, 5 ml. of distilled water are placed in the receiver (a stoppered measuring cylinder) and then 25 ml. of HCl (s.g. 1.18) are run into the distillation flask.

The flask/.....

The flask is heated and 10 ml. are distilled over at a rate of about 2 ml. per minute. The condenser is rinsed with a few ml. of distilled water and the receiver is then removed.

After adding 5 ml. of gum arabic solution (1 %) and 15 ml. phenylfluoron solution^{*} the contents of the receiver are brought to 50 ml. by adding distilled water. The stoppered cylinder is allowed to stand for one hour before taking readings in the spectrophotometer.

The solution for the blank determination is prepared in exactly the same way, starting with 3 grams of calcined soda.

The colorimetric evaluation was conducted in a Beckman spectrophotometer (wavelength 510 m μ , slit 0.045 mm.). Standardisation was done as described by Cluley but all standard solutions were distilled as described and measurements were only taken after the final mixture had stood for one hour.

Some tests in which chromate solutions were used for reference indicated, that the colour of phenylfluoron solutions as prepared for testing in the spectrophotometer fades somewhat with time. The blank as well as the test solutions are similarly affected and therefore this defect will have little influence on results provided that the time interval between preparation of solutions and their evaluation is about the same and blank tests are conducted more or less simultaneously with routine determinations. It was considered advisable, therefore, to conduct determinations in batches of not more than 8 at a time and to prepare the solution for the blank about midway between the others./.....

* 0.03 grams of phenylfluoron are dissolved with slight heating in a mixture of 85 ml. ethyl alcohol and 5 ml. sulphuric acid (14 vol %). After cooling the solution is made up to 100 ml. by adding ethyl alcohol.

others.

The accuracy of this method as indicated in Tables 1 and 2 was considered adequate for the present investigation:-

TABLE 1.

Check determinations on various coal samples.

Coal sample	ppm. Ge.	Coal sample	ppm. Ge.	Coal sample	ppm. Ge.
1.) A 9454	4.9	55/10 C	56.3	55/15 C	121
2.) "	5.0	"	57.3	"	118
3.) "	4.8	"	56.5	"	124
4.) "	4.6	"	55.0	"	123
5.) "	5.1	"	57.8	"	125
6.) "	4.7	"	56.3	"	123
Average :	4.85		56.5		122

TABLE 2.

Control tests to determine germanium recovery.

(Germanium values in μ gr. Ge.)

Coal sample	Ge. content	Ge. added	Total	Found
4035	10.5	10	20.5	20.7
55/8 E	5.1	10	15.1	14.4
53/443	17.2	10	27.2	28.1
54/389 A	19.3	10	29.3	28.8

THE GERMANIUM CONTENT OF SOUTH AFRICAN COAL.

The survey of the germanium content of South African coal was conducted on samples of commercial products of various collieries. Detailed work on face samples was only done in a few instances.

Table 3 provides information on the general survey. It will be noted that the germanium content is rather variable and any generalisation must be treated with some reserve.

Nevertheless, there is evidence that coal from the Vryheid area has the highest germanium content (average 6.2 ppm.). The Breyten-Ermelo coalfield comes second with an average value of 5.9 ppm. and is followed by the Klip River coalfield with 4.0 ppm. Coal from the Witbank area has a low germanium content (average 2.8 ppm.).

The overall average for all the coalfields is about 3.8 ppm. whereas K.V. Aubrey¹⁴⁾ quotes an average of 7 ppm. for British coal.

If one accepts, as suggested by Headlee and Hunter¹⁴⁾ that the germanium may have been introduced into the seam from adjacent formations, a high germanium content in the coal might be considered to provide evidence of the occurrence of a germaniferous ore deposit in the vicinity.

To test Headlee and Hunter's findings, face samples were taken at three collieries for more detailed study.

VARIATION OF GERMANIUM CONTENT WITHIN A COAL SEAM.

Referring again to Table 3 it will be observed that the highest values were obtained on commercial products from Colliery No. 48 and Colliery No. 49. Accordingly these were selected for the first more detailed study. The seam mined (Gus seam) was divided for sampling into sections,
as shown/.....

TABLE 3.

Germanium in South African coal.

Colliery.	Area.	Sample No.	ppm. Ge.
		<u>Seam</u>	
1 Coronation.	Witbank	No. 1 W 5424	5.7
2 Tavistock-Uitspan....	"	" 2 54/264 B	3.9
3 Navigation.....	"	" 2&5 55/69 B	3.3
4 Landau.....	"	" 2 W 5425	2.5
5 Greenside.....	"	" 2 Comp. 12	4.3
6 Wolvekranz.....	"	" 2 54/285 B	1.7
7 Alpha Consolidated...	"	" 4 54/255 A	2.4
8 Waterpan.	"	" 2 54/259 A	2.6
9 Tweefontein	"	" 2 A 9455	2.9
10 Kendal	"	" 5 54/565 B	8.4
11 W.C.C.M.	"	" 4 54/265 B	1.8
12 Phoenix	"	" 2 A 9456	4.9
13 Van Dyksdrift	"	" 2 Comp. 6	1.6
14 Springbok	"	" 2 A R 7/9	1.5
15 New Clydesdale	"	" 2 A 9457	1.0
16 Douglas	"	" 2 A 9459	1.4
17 Blesbok	"	" 5 54/586 A	3.8
18 Schöongezicht	"	" 2 54/100 B	1.4
19 Koornfontein	"	" 2 53/323 A	1.4
20 Klippoortje	"	" 4 Comp. 7	2.4
21 South Witbank	"	" 4 54/261 C	2.6
22 Albion	"	" 2 54/101 B	1.2
23 T.N.C.	"	" 2 54/98 B	1.7
24 Waterberg	Waterberg	52/428 A	3.8
25 Cornelia	Vereeniging.	54/153 C	2.1
26 Sasol-Clydesdale	"	-	1.4
27 Union	Breyten-Ermelo	Comp. 10	5.9
28 Bankfontein	"	Comp. 1	5.9
29 Marsfield	"	A 9454	4.9
30 Bellevue	"	Comp. 11	6.9
31 Utrecht	Utrecht	Comp. 8	1.0
32 Kilbarchan	Klip River.	Comp. 4	1.0
33 Ballengeich	"	Comp. 9	3.5
34 D.N.C.	"	54/44 A	6.0
35 Natal Navigation ...	"	54/210 B	3.3
36 Cambrian	"	54/41 A	3.9
37 Burnside I	"	54/204 C	1.9
" II	"	54/204 D	3.3
38 Natal Steam	"	54/203 B	4.6
39 Newcastle Platberg ..	"	Comp. 3	11.0
40 Carnarvon	"	4037	1.0
41 Zuinguin	Vryheid	55/97 B	1.8
42 Vryheid Coronation...	"	53/274 A	4.1
43 Tshoba	"	Comp. 2.	4.1
44 Hlobane	"	Comp. 5	5.3
45 Enyati	"	54/40 A	4.4
46 Natal Ammonium	"	4036	2.2
47 Natal Anthracite	"	4034	3.6
48 Alpha Anthracite ...	"	AAD/S	15.6
49 Jackson's Anthracite.	"	4040	14.6

TABLE 3.
Germanium in South African coal.

Colliery No.	Sample No.	Area.	ppm. Ge.
1.	W 5424	Witbank No. 1	5.7
2.	54/264 B	" " 2	3.9
3.	55/69 B	" " 2 & 5	3.3
4.	W 5425	" " 2	2.5
5.	Comp. 12	" " 2	4.3
6.	54/285 B	" " 2	1.7
7.	54/255 A	" " 4	2.4
8.	54/259 A	" " 2	2.6
9.	A 9455	" " 2	2.9
10.	54/565 B	" " 5	8.4
11.	54/265 B	" " 4	1.8
12.	A 9456	" " 2	4.9
13.	Comp. 6	" " 2	1.6
14.	A R 7/9	" " 2	1.5
15.	A 9457	" " 2	1.0
16.	A 9459	" " 2	1.4
17.	54/586 A	" " 5	3.8
18.	54/100 B	" " 2	1.4
19.	53/323 A	" " 2	1.4
20.	Comp. 7	" " 4	2.4
21.	54/261 C	" " 4	2.6
22.	54/101 B	" " 2	1.2
23.	54/98 B	" " 2	1.7
24.	52/428 A	Waterberg.	3.8
25.	54/153	Vereeniging.	2.1
26.	-	"	1.4
27.	Comp. 10	Breyten-Ermelo.	5.9
28.	Comp. 1	"	5.9
29.	A 9454	"	4.9
30.	Comp. 11	"	6.9
31.	Comp. 8	Utrecht.	1.0
32.	Comp. 4	Klip River.	1.0
33.	Comp. 9	"	3.5
34.	54/44 A	"	6.0
35.	54/210 B	"	3.3
36.	54/41 A	"	3.9
37. I	54/204 C	"	1.9
II	54/204 D	"	3.3
38.	54/203 B	"	4.6
39.	Comp. 3	"	11.0
40.	4037	"	1.0
41.	55/97 B	Vryheid	1.8
42.	53/274 A	"	4.1
43.	Comp. 2	"	4.1
44.	Comp. 5	"	5.3
45.	54/40 A	"	4.4
46.	4036	"	2.2
47.	4034	"	3.6
48.	AAD/S	"	15.6
49.	4040	"	14.6

as shown in Table 4. In both cases the highest germanium content was found in the coal adjacent to the roof of the seam with a sharp fall to lower values in subsequent sections. Analysis of roof material proved this to contain very little germanium.

Some samples of the Lower Alfred seam, the seam immediately overlying the Gus seam, had been taken from an adit above the workings of Colliery No. 48 on a previous occasion for other investigations. On analysis of these samples (see Table 5) the interesting fact was revealed that in this case the highest concentration of germanium was in the coal at the floor of the seam. A concentration of 100 ppm. over 7 inches is high. Unfortunately this adit is now inaccessible and further samples could not be taken to confirm this high value.

TABLE 4.

Variation in germanium content over a vertical section of the Gus seam at Collieries No. 48 and No. 49.

a.) Colliery No. 48 (Gus Seam).

		ppm. Ge.
	<u>ROOF:</u> Sandstone.	
3½"	Finely banded very bright coal.	48.0
7½"	Mainly bright coal, slightly pyritic.	11.0
6"	Dull lustrous coal with bright bands.	4.3
5"	Very bright coal, slightly banded and pyritic.	5.1
3½"	Dull coal with bright bands.	1.4
9"	Dull lustrous coal.	1.7
6"	Mixed coal.	1.9
3½"	Finely banded bright coal.	2.8
	<u>FLOOR:</u> Shale.	

b.) Colliery No. 49 (Gus Seam).

		ppm. Ge.
	<u>ROOF:</u> Sandstone.	
6"	Mainly bright coal.	59.0
2"	Carbonaceous shale (not sampled)	-
24"	Dull lustrous coal.	5.3
12"	Dull coal, occasional bright bands.	4.5
12"	Bright banded dull coal.	6.0
7"	Bright banded coal.	7.3
	<u>FLOOR:</u> Shale and sandstone.	

TABLE 5.

Distribution of germanium in the Lower Alfred Seam
at Colliery No. 48.

	<u>ROOF</u> : Sandstone and shale.	ppm. Ge.
10"	Coal with shale bands.	1.8
26"	Mainly dull coal.	2.2
6"	Dull shaly coal.	2.4
7"	Mixed coal.	100.0
	<u>FLOOR</u> : Carbonaceous shale.	

The analysis of face samples taken from the C-seam at Colliery No. 30 (Ermelo) also showed a variable germanium content (see Table 6) with the highest concentration at the bottom of the seam.

TABLE 6.

Distribution of germanium in the C-seam at
Colliery No. 30 (Ermelo).

	<u>ROOF</u> : Sandstone.	ppm. Ge.
7"	Bright coal.	4.8
10"	Dull coal, conchoidal fracture.	2.4
6"	Bright coal.	1.6
5"	Dull coal, sugary.	1.2
14"	Mixed coal, mainly bright.	1.1
5"	Dull coal.	1.2
14"	Mixed coal, mainly bright.	0.7
5"	Mixed coal, mainly bright.	24.0
	<u>FLOOR</u> : Sandstone.	

These results are in accordance with the findings of Headlee and Hunter for West Virginian coal. They support the theory that germanium may have entered the seam by infiltration after formation of the coal seam.

Under such circumstances variations in the germanium content might occur in the plane of the seam. Therefore a survey was made at the Collieries No. 48 and No. 49.

Sampling was/.....

Sampling was confined to the uppermost 3" to 4" of the seam. In view of the rapid decrease in germanium content with distance from the roof, some of the variation in results may be due to variations in the thickness of the section actually sampled. It might have been desirable to sample at even smaller intervals but this was not practicable at the time.

Results of the survey in Colliery No. 49 are given in Table 7. While some relatively low values were found, the majority of values were high. The average value is high at 121 ppm. over 3-4 inches. A composite sample made up of equal parts of these samples gave a value of 128 ppm. germanium.

Variability was greater at the Colliery No. 48 sampled at 14 places. (See Table 8).

TABLE 7.

Germanium content of the uppermost 3" - 4" of coal in Colliery No. 49 at 24 faces.

	ppm. Ge.		ppm. Ge.		ppm. Ge.
1.)	99.0	9.)	122.0	17.)	99.0
2.)	84.0	10.)	122.0	18.)	136.0
3.)	91.0	11.)	96.0	19.)	118.0
4.)	137.0	12.)	178.0	20.)	78.0
5.)	171.0	13.)	140.0	21.)	135.0
6.)	113.0	14.)	150.0	22.)	91.0
7.)	126.0	15.)	150.0	23.)	137.0
8.)	149.0	16.)	154.0	24.)	36.0

TABLE 8.

Germanium content of the uppermost 3"-4" of coal
in the Colliery No. 48.

	ppm. Ge.		ppm. Ge.		ppm. Ge.
1.)	95.0	6.)	9.3	11.)	7.7
2.)	84.0	7.)	10.2	12.)	53.0
3.)	122.0	8.)	95.0	13.)	56.0
4.)	7.3	9.)	10.7	14.)	41.0
5.)	9.0	10.)	5.3		

In this table samples 1-3, 8 and 12-14 represent an area of the colliery bounded approximately by the lines joining the places 1, 3, 8 and 12.

Similar surveys are being undertaken at other collieries where reasonably high values were obtained on product samples.

DISTRIBUTION OF GERMANIUM IN FLOAT AND SINK FRACTIONS.

With a view to commercial recovery it appeared of interest to ascertain whether the germanium is associated specifically with any specific gravity fraction of the coal.

The results of analysis of float and sink fractions of five coal samples, given in Table 9 reveal no definite trend. They rather confirm the opinion expressed by K.V. Aubrey that the germanium is associated with the organic as well as with the inorganic matter in the coal.

Whenever the germanium concentration is high enough, recovery from the ash is conceivable and in that case reduction of the mineral matter in the coal by washing before combustion

becomes/.....

becomes important.

The advantage of washing may be illustrated by reference to sample 55/15 C in Table 9 on which the following results were obtained :-

	Yield	Ge. content.	Ge. content of ash (%)	
	(% whole Coal).	(% of Ge. in whole coal).	Calculated from % Ge. of whole coal.	Found in ash.
Whole coal	100	100	0.139	0.132
Float s.g. 1.58	93	91	0.219	0.212

The results indicate, incidentally, that very little if any germanium is lost when ashing according to the British Standard procedure at 800°C in the presence of excess oxygen. This observation led to preliminary tests to determine:-

THE BEHAVIOUR OF GERMANIUM DURING COMBUSTION OR GASIFICATION OF THE COAL.

Further tests, the results of which are reported in Table 10 confirmed the previous finding that germanium losses do not occur or are negligible when ashing a coal at low temperature (800°C) in the presence of excess oxygen.

Even when igniting a coal at a temperature of 1050° in an oxidising atmosphere (combustion tube) the germanium losses are still relatively low (see Table 11).

Since it is known that germanous compounds are more volatile than germanic compounds and Belugou and Dumoutet³⁾ consider the concentration of germanium in the flue dust of gaswork's/.....

TABLE 2.

Germanium content of float and sink fractions.

Sample:	Colliery No. 48.						Colliery No. 49.								
	AAD/S.			4117.			7" from floor 55/83 A.			4124			55/15 C 4" (under- neath the roof).		
	% of Sample	% Ash	ppm. Ge.	% of Sample	% Ash	ppm. Ge.	% of Sample	% Ash	ppm. Ge.	% of Sample	% Ash	ppm. Ge.	% of Sample	% Ash	ppm. Ge.
Float 1.40	58.0	3.1	13.0	54.0	2.8	10.8	26.0	4.27	75	2.7	1.8	8.9	1.0	4.7	76.5
Float 1.40-1.58	36.3	11.3	10.3	42.5	9.8	10.6	54.0	11.7	94	91.0	8.2	13.4	92.0	5.4	118.5
Float 1.58-1.80	2.2	32.7	49.4	1.4	33.2	61.7	8.5	27.8	147	4.5	27.5	18.5	2.7	22.9	236.0
Sink 1.80	3.5	69.9	102.6	2.1	59.0	76.0	11.5	58.7	148	1.8	62.9	33.8	4.3	79.4	98.0
Whole coal.	100.0	9.2	15.4	100.0	7.3	12.4	100.0	16.5	100	100.0	9.8	13.3	100.0	8.8	122.0

gasworks retorts to be largely due to volatilisation of germano compounds, a few laboratory gasification tests were done in the absence of free oxygen.

The coal was gasified in a furnace kept at 1050°C by passing carbon dioxide over it. The results given in Table 12 indicate that over 80 % of the germanium may be volatilised under these conditions.

TABLE 10.

Germanium content of coal samples and their ash prepared according to the standard laboratory method for ash determination.

Coal Sample.	% Ash (Average)	ppm. Ge. in coal.	Average.	ppm. Ge. in ash calcul.	ppm. Ge. in ash found.	Average.
55/10 C	5.0	56.3	56.5	1130	1128	1135
"		57.3			1156	
"		56.5			1160	
"		55.0			1124	
"		56.3			1128	
"		57.8			1116	
55/15 C	9.0	121	122	1356	1355	1330
"		118			1340	
"		123			1315	
"		125			1385	
"		123			1300	
"		124			1285	
Comp. 3	20.9	10.8	11.0	52.6	54	54
"		11.2			54	

TABLE 11/.....

TABLE 11.

Loss of germanium by burning coal in excess oxygen at 1050°C.

Coal Sample.	% Ash.	ppm. Ge. in coal average.	ppm. Ge. in ash calcul.	ppm. Ge. in ash found	% Loss in Ge.	% Average loss
55/83 A	16.5	100	606	552	8.9	8.6
"	16.5		606	556	8.3	
55/15 C	8.5	122	1435	1320	8.0	6.1
"	8.4		1452	1395	4.1	
53/443	11.4	17.9	157	147	6.4	5.1
"	11.3		158	152	3.8	

TABLE 12.

Volatilisation of germanium by gasification with CO₂ at 1050°C.

Coal Sample.	% Ash.	ppm. Ge. in coal.	ppm. Ge. in ash calcul.	ppm. Ge. in ash found.	% Loss in Ge.
55/15 C	9.3	122	1312.	204	84
55/83 A	16.5	100	606	110	82
55/10 C	4.7	56	1191	142	88

Tests under more strongly reducing conditions have not yet been completed.

BEHAVIOUR/.....

BEHAVIOUR OF THE GERMANIUM DURING CARBONISATION.

In order to obtain some insight into the behaviour of the germanium during carbonisation, standard High Temperature Gray-King assays were done on six coal samples.

The germanium contents of the coal samples and the coke residues were determined and are reported in Table 13.

TABLE 13.

Loss of germanium during carbonisation.

Coal sample.	% Coke.	ppm. Ge. in coal.	ppm. Ge. in coke calcul.	ppm. Ge. in coke found.	% Loss in Ge.
55/83 A	86.4	100	116	107	7.8
55/15 C	89.1	122	137	128	6.6
55/183 A	64.7	25.1	38.8	37.2	4.1
53/443	75.5	17.9	23.6	20.9	11.4
Comp. 3	78.1	11.0	14.1	12.7	9.9
4130	74.5	7.0	9.4	8.4	10.6

The differences between the "found" and "calculated" germanium contents of the coke are quite small. One may therefore conclude that, only small quantities of germanium are lost during carbonisation in practice.

One is inclined to conclude from these preliminary tests that appreciable volatilisation of germanium, during the combustion of coal, only takes place at high temperatures and reasonably reducing conditions in the fuel bed. This conclusion is subject to confirmation by further research.

THE GERMANIUM/.....

THE GERMANIUM CONTENT OF FLY-ASH, FLUE DUST AND BOILER DEPOSITS.

It has been variously stated in the literature that an appreciable concentration of germanium may occur in the fly-ash or flue dust of boilers.

Analysis of flue dust samples from a number of power stations in the Union yielded disappointing results. As will be seen in Table 14 the highest value found was 0.011% germanium while the average value was about 0.03 % germanium and thus much below the accepted concentration for economic exploitation.

TABLE 14.

Germanium content of fly-ash and ash from Power Stations.

Power Station.	Place where sampled.	No.	% Ge.
Pretoria Power St.	Primary Grit Collector	53/516 A	0.00075
	Secondary Grit Collector	" B	0.0054
	Economiser	" C	0.0039
Orlando Power St.	Grit Arrester (after Econom.)	53/574	0.0011
Klip Power St.	Ash from End of Grate	53/434 A	-0-
	Cyclon Grit Extractor	" B	0.00045
	Economiser	" C	0.0003
Vaal Power St.	Ash from End of Grate	53/435 A	0.0003
	Economiser and Airheater	" B	0.0031
	Economiser	" C	0.0025
Carolina Power St.	from Base of Chimney.	53/575	0.0035
Ermelo Power St.	from Base of Chimney.	53/576	0.0097
Vryheid Power St.	before Economiser	53/577 A	0.0051
	after Economiser	" B	0.0111
Colenso Power St.	from Economiser	53/578 A	0.0037
	" Base of Chimney	" B	0.0024
	Ash from End of Grate	" D	0.0007
Congella Power St.	from Electrostatic Precipitator.	53/580 A	0.0021
	" Airheater	" B	0.0008
	" Economiser	" C	0.0009

As these samples might have been taken in an unfavourable temperature region, the opportunity was taken to obtain flue dust samples at various points in a boiler when one of the boilers at the Pretoria Power Station was taken off the range for inspection. The germanium content of these samples is given in Table 15. As no definite relation between germanium content and temperature of deposition could be established, and the values were generally too low to be of economic interest, no further work was done in this direction.

TABLE 15.

Germanium content of Flue dust deposited in different temperature regions of a Power Station boiler.

Power Station.	Place where sampled.	% Ge.
Pretoria Power St.	Flue dust before entering the Superheater	$\pm 900^{\circ}\text{C}$ 0.0047
	Between Superheater tubes	0.0041
	After Superheater	0.0040
	Between first and second passage through last bank of Watertubes.	0.0036
	In the Economiser	$\pm 300^{\circ}\text{C}$ 0.0038

The results of analysis of some bonded and fused fly-ash deposits are given in Table 16.

TABLE 16/.....

TABLE 16.

Germanium content of bonded and fused Fly-ash Deposits.

<u>Power Station.</u>	<u>Type of sample.</u>	<u>% Ge.</u>
Salt River Power St.	Bonded Deposit from Boiler Tubes	0.047
	" " " Economiser	0.025
P. Elizabeth Power St.	Partly fused Fly-ash Deposit from Boiler Tubes.	0.089
	Fused Fly-ash Deposit from Boiler Tubes.	0.026
Newtown Power St.	Loose Fly-ash Deposit from Boiler Tubes.	0.0032

Although these samples had a somewhat higher germanium content than the fly-ash samples the values were still well below the economic limit.

These low values need not be solely due to the low germanium content of the coal fired. They may also be ascribed to unfavourable conditions for volatilisation in the fire-bed.

Finally, a few flue dust samples were obtained from coke ovens and gasworks retort settings. Some of these samples had germanium contents of 0.1 to 0.6 %. Unfortunately the amount of dust presently available is so small that exploitation could not be considered.

CONCLUSION:

When flue dust was first considered as a source of germanium, it was held that such dust should contain at least 0.3 % germanium to make extraction payable. The extraction technique has, however, been improved to such an extent that

the payable/.....

the payable limit may probably now be set at 0.1 %.

Even this limit is apparently not reached in flue dusts obtainable from South African power station boilers.

This survey has given evidence, however, that sections of some seams contain so much germanium that its recovery from the coal direct might be feasible. The separate extraction of coal from these sections would present no difficulty. Its subsequent treatment (e.g. washing, combustion or gasification with utilisation of the energy released) should be planned so as to reduce the costs of germanium recovery to a minimum. This calls for further research.

In other cases concentration is necessary and would have to be achieved by gasification of the coal (with energy utilisation) under conditions most favourable to volatilisation of germanium. As far as one can learn from published reports, this problem as well as that concerning the optimum recovery of the volatilised germanium, without undue contamination with barren dust, have not yet been solved. The orientative tests described in this paper give some indications of the lines of attack. These are being followed up.

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Publication of this report has been authorised by the
Fuel Research Board.

REFERENCES:

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1. V.M. Goldschmidt: Nachr. Ges. Wiss., Goettingen. (1930), 398.
2. G.T. Morgan and G.R. Davies: Chem. & Ind. (Rev.) 1937, 717.
3. P. Belugou and P. Dumoutet: L'extraction du Germanium de la houille, Centre d'Etudes et Recherches des Charbonages de France, Jouillet 1953.
4. A.J.W. Headlee and R.G. Hunter: Geological and Economic Survey Report of Investigation No.8, 1951.
5. W.J. Frederick, J.A. White and H.E. Biber: Analyt. Chem. Vol. 26, (1954), 1328.
6. H.J. Cluley: The Analyst, Vol. 76, (1951), 517.
7. R.E. Kitson and M.G. Mellon: Ind. Eng. Chem. Anal. Ed. (1944) 16, 128.
8. A.G. Hybbinette and E.B. Sandell: Ibid. (1942), 14, 715.
9. D.F. Boltz and M.G. Mellon: Anal. Chem., (1947), 19, 873.
10. H.J. Cluley: The Analyst, Vol. 76, (1951), 523.
11. G.R. Davies and G.T. Morgan: The Analyst, (1938), 63, 388.
12. H.H. Krause and O.H. Johnson: Anal. Chem. Jan. 1953, 134.
13. K.V. Aubrey and K.W. Payne: Fuel, Jan. 1954, 20.
14. K.V. Aubrey: Fuel 31, (1952), 429.
15. A.R. Powell, F.M. Lever and R.E. Walpole: J. Appl. Chem., I, Dec. 1951, 541.
16. W.G. Pfann: J. Metals, July 1952, 747.
17. H. Remy: Lehrbuch der anorg. Chemie.
18. W. von Haken: Chemische Industrie, Jan. 1955, 9.
19. J.P. Ratledge, J.N. Ong and J.H. Boyce: Mining Eng., Apr. 1955, 379.

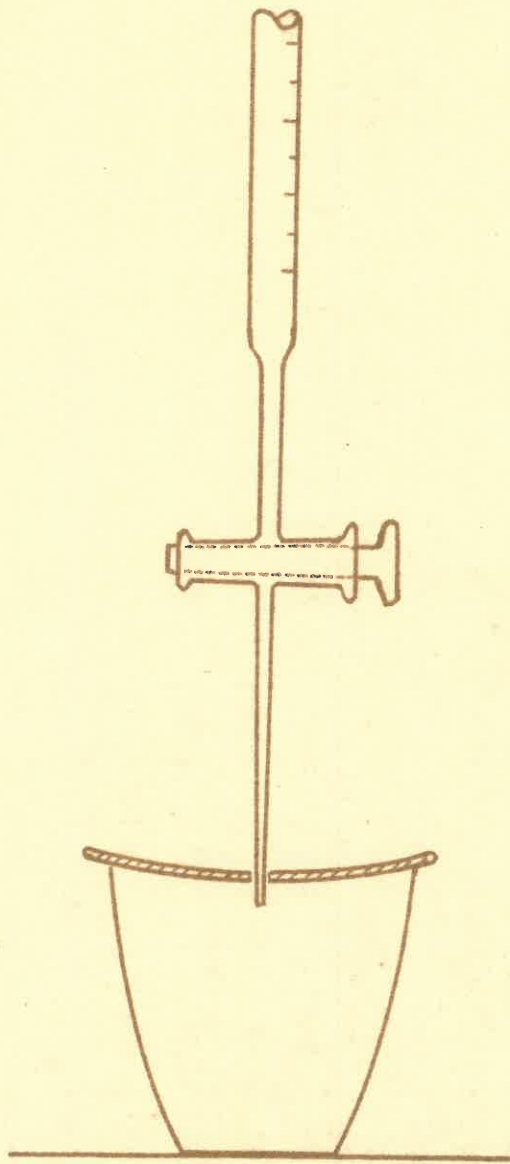


FIG. 1. DECOMPOSITION OF THE MELT WITH SULPHURIC ACID.

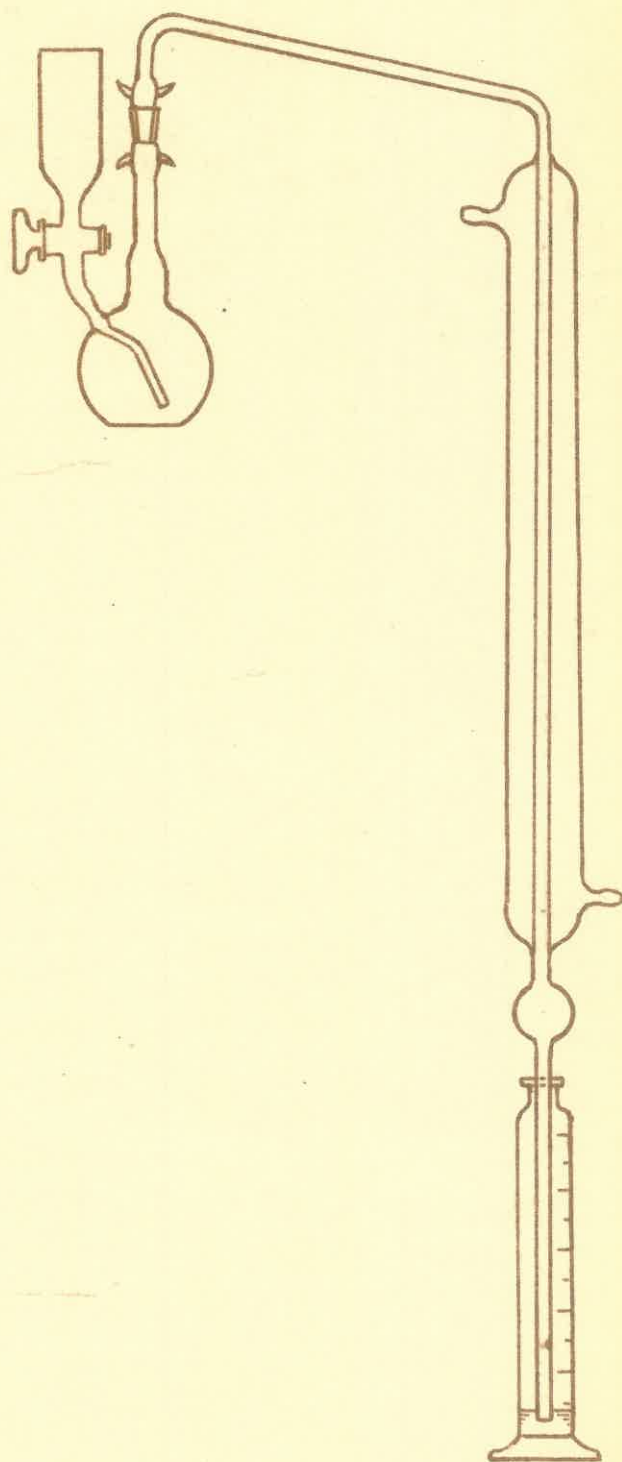


FIG. 2. DISTILLATION APPARATUS.