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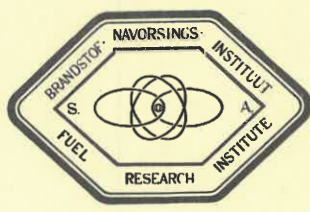
Rec no. 5254

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Form No. F.R.I. 47.

REPORT No. 17  
OF 1950

RAPPORT No. 17  
VAN 1950



WU1A/13B

# FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

## BRANDSTOF-NAVORSINGS-INSTITUUT VAN SUID-AFRIKA.

SUBJECT: CHLORINATION TESTS ON SOUTH AFRICAN COALS.  
ONDERWERP: CHLORINATION TESTS ON SOUTH AFRICAN COALS.

DIVISION: CHEMISTRY.  
AFDELING: CHEMISTRY.

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CHLORINATION TESTS ON SOUTH AFRICAN COALS.

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Comparatively few investigators have studied the reaction of halogens with coal. <sup>1 - 5)</sup> Evidence was found that substitution and addition reactions occur and that more hydrochloric or hydrobromic acid may be formed than could be explained by a substitution reaction. The reaction is exothermic and if the temperature is not controlled the amount of halogen combining with the coal is decreased. Chlorinated or brominated coal was devoid of swelling properties and did not yield tar on carbonisation.

Substantial amounts of halogen may combine with the coal, bromine contents of 45.5 per cent <sup>3)</sup> and chlorine contents of up to 62 per cent <sup>2)</sup> being quoted.

At such high halogen contents the products might have practical value and it was therefore considered of interest to determine whether similar products could be prepared from South African coal.

APPARATUS AND EXPERIMENTAL PROCEDURE:

The data in the literature suggested that during the chlorination reaction much heat may be liberated and that overheating may be detrimental. An apparatus was therefore designed in which the coal charge could be kept in turbulent motion by a current of chlorine gas. Provision was also made for external cooling or heating of the reaction vessel.

Referring to Figure 1 the coal was held in the reaction vessel on a sintered glass disc (prepared from glass powder graded -120 + 170 mesh B.S.S.). The coal was usually graded -120 + 200 mesh B.S.S. and a charge of 10 grams was used.

Chlorine was/.....

Chlorine was taken from a bottle fitted with a regulating valve and a by-pass with water seal was provided. The gas rate was determined by means of a flow meter (5 in Fig. 1) and was normally in the region of 150 ml./min. Tests were only conducted at atmospheric pressure.  $\pm 65$  mm Hg.

The gas leaving the reaction vessel was passed through two bubblers containing distilled water to retain hydrochloric acid and finally through a bubbler containing caustic soda solution to absorb excess chlorine. The bubblers with distilled water also retained small quantities of chlorine and this was determined (potassium iodide, thio-sulphate) before determining the hydrochloric acid by direct titration.

In order to determine the rate and extent of chlorination either a series of runs was made, progressively extending the period of chlorination, or samples of coal were removed from the reaction vessel at predetermined intervals for analysis. Before determining the chlorine-content of samples they were placed under vacuum in a desiccator at about 25°C for at least three hours to remove adsorbed chlorine and hydrochloric acid. The procedure was quite effective as experiments proved that a coal treated at 25°C lost only a trace of chlorine and about 0.13% of hydrochloric acid when the temperature of the coal under vacuum was raised from 25°C to 95°C.

For the chlorine determination, samples were mixed with Eschka mixture, ignited and the standard B.S.I. procedure for chlorine followed thereafter.

Reporting Results: The amount of chlorine taken up by the coal and the amount of hydrochloric acid evolved, have been expressed as percentages on the original coal.

Coal Used: In most of the tests a coal from the Ermelo

coalfield having the following average analysis was used:

Ash percent .....	13.9
Moisture percent .....	3.5
Volatile Matter percent .....	31.0
Fixed Carbon percent .....	51.6

The coal was ground and the size fraction -120 + 200 mesh B.S.S. was generally used.

#### EXPERIMENTAL RESULTS:

In the initial experiments the findings of previous investigators could be confirmed that the reaction is exothermic and that the rate of chlorination increases with increasing fineness of the coal.

It was also found that the rate of chlorination increased with the rate at which chlorine was passed through the coal bed, (within the limits set by the apparatus), although an excess of chlorine was present at the lowest rate used.

When studying the effect of the temperature of the coal during an experiment results were obtained which are apparently at variance with those obtained on British coals.<sup>1)</sup> It should be borne in mind, however, that those tests were conducted under static conditions while in the present tests a rapid current of chlorine was being passed through the coal.

Tests were conducted over a wide temperature range and results are summarised in Table 1 and represented graphically in Figure 2.

The results indicate that up to 150°C the rate of chlorination increases with the temperature. A further rise in temperature to 340°C did not seem to affect the amount of chlorine retained but at higher temperatures, approaching the decomposition temperature of the coal, the amount of chlorine retained decreased appreciably. On the other hand the evolution of hydrochloric acid increased steadily with rising reaction temperatures.

TABLE 1.Chlorination of Ermelo Coal at Various Reaction Temperatures.

Coal Charge: 10 grams. Size Grading: -120 + 200 mesh B.S.S.  
Rate of Chlorine: 150 ml./min.

Period of Reaction (hrs.)	% Chlorine in Solid Res.					% Chlorine Evolved as HCl.				
	90°C	150	250	340	355	90°C	150	250	340	355
1	12.7	14.5	14.4	14.7	13.3	12.3	26.5	30.2	40.4	41.5
2	15.5	17.6	18.2	18.1	14.1	17.2	32.8	40.9	49.1	-
3	18.2	20.5	20.5	19.5	15.2	21.0	37.2	46.1	53.7	-
4	19.8	22.3	21.7	22.0	15.7	24.5	40.7	50.7	58.4	-
5	21.5	23.3	23.3	23.1	16.0	27.9	43.5	54.9	61.5	-
6	22.6	24.8	24.8	24.9	16.4	31.2	46.1	58.4	65.7	-
7	23.6	26.4	26.1	25.8	16.6	34.5	48.5	61.3	69.0	-

In the light of these experiments it was decided to standardise on a reaction temperature of 150°C where a reasonably high rate of chlorination could be achieved.

CHLORINATION OF COAL TO "SATURATION":

In order to determine how much chlorine the coal would take up, extended tests were conducted. The results obtained in such a test are reported in Table 2 and are shown graphically in Figure 3.

TABLE 2.Extensive Chlorination of Ermelo Coal.

Charge: 10 grams. Size Grading: -120 + 200 mesh B.S.S.  
Rate of Chlorine: 150 ml./min. Reaction Temperature: 150°C.

Period of Test (hrs.)	% Chlorine in Solid Residue.	% Chlorine Evolved as Hydrochloric Acid.
8	27.8	55.3
16	33.1	67.6
33	39.0	82.5
49	41.4	90.8
64	41.8	96.4
80	41.5	100.9
96	41.6	103.9
110	41.8	106.2
126	41.5	108.0
132	42.0	108.9
140	41.8	109.7

It will be noted that the coal reached a saturation point as regards chlorine content after about 50 hrs. while the evolution of hydrochloric acid persisted even after 140 hrs. when the experiment was stopped.

THE EFFECT OF THE RANK OF THE COAL:

In a series of tests typical samples of coal from the Vereeniging, Ermelo (C-Seam) Witbank (No.2 - Seam) and Natal (coking coal) coalfields, were chlorinated under identical conditions. The coals are arranged in order of rank in Table 3 and it will be noted that there is a general tendency for the rate of chlorination and of evolution of hydrochloric acid to decrease with increasing rank of the coal. In all cases the amount of chlorine converted to hydrochloric acid exceeded that retained by the coal.

TABLE 3.

Coal Charge: 10 grams. Size: -120 + 200 B.S.S.  
Chlorine Velocity: 150ml./min. Reaction Temp.: 150°C.

Period of Test(hrs.)	<u>% Chlorine in Solid Residue.</u>				<u>% Chlorine evolved as HCl</u>			
	Ver.	Coal: Erm.	Witb.	Natal.	Ver.	Coal: Erm.	Witb.	Natal.
1	23.0	14.5	19.8	8.8	44.7	26.5	33.3	18.2
2	25.6	17.6	23.4	12.1	49.2	32.8	39.2	21.6
3	27.3	20.5	25.7	14.2	53.3	37.2	43.2	24.4
4	28.1	22.3	27.5	15.5	56.3	40.7	46.5	26.9
5	29.0	23.3	29.0	16.6	58.8	43.5	49.2	28.9
6	29.8	24.8	29.9	17.4	60.3	46.1	51.4	30.9
7	30.7	26.4	30.8	18.1	61.3	48.5	53.1	33.0

GENERAL CHARACTERISTICS OF THE  
REACTION AND OF REACTION PRODUCTS:

Ultimate analyses of untreated and chlorinated Ermelo coal are given in Table 4.

TABLE 4.

Ultimate Analyses of Ermelo Coal and of Chlorinated Coal.

Sample	Moisture (Air Dry) (%)	Wt. Reaction Prod. grm/100grm. of coal.	% on Original Coal Charged (dry)						
			C	O	H	N	S	Cl	Ash
Untreated Coal.	3.8	100	69.5	10.3	4.38	1.73	1.35	-	12.7
Chlorinated 90°C.	4.9	160	65.9	13.3	2.64	1.76	1.32	62.4	12.65

Since chlorine interfered with the carbon determination, the C + O figures should be compared rather than the two carbon figures. It will be noted that the hydrogen content decreases. This loss of hydrogen can be accounted for in hydrochloric acid and water formed during the reaction. Not more than traces of volatile organic reaction products could be observed, so that carbon and hydrogen losses from this source may be regarded as negligible.

Concentrated ammonia liquor and sodium carbonate solutions attacked the chlorinated coal to some extent yielding dark coloured solutions. After 24 hours contact with ammonia liquor, 25 to 50 percent of the chlorine was removed from the chlorinated coal.

On carbonising the chlorinated coal no tar was evolved and the "coke residue" was a loose powder.

The chlorine combining with the coal was held quite firmly. After evacuating freshly chlorinated coal (41.8% Cl<sub>2</sub>) at the temperature of the chlorination experiment for 4 hours, the product could be heated to about 300°C before evidence of appreciable chlorine losses could be observed. The chlorine was liberated as hydrochloric acid (from 300°C) and chlorine gas (from 600°C). After heating at 800°C for 20 minutes the residue still contained 23 percent of the chlorine originally present.

This retention/.....

This retention of chlorine at 800°C may be due, in part, to the relatively high mineral matter content of the coal as Eccles and McCulloch <sup>1)</sup> have found that chlorinated British coals lost practically all their chlorine by heating them to 500°C.

ACTION OF THE CHLORINE ON THE MINERAL CONSTITUENTS OF THE COAL:

Further evidence of the action of chlorine on the mineral constituents of the coal was obtained by extracting chlorinated coal with water. Such extracts contained mainly, iron, aluminium and calcium salts.

The progress of the reaction in this respect is illustrated by the results given in Table 5.

TABLE 5.

Iron and Aluminium Compounds in Aqueous Extracts of Chlorinated Coal.

Conditions of Chlorination:

Coal Charged: Ermelo coal. Reaction Temperature: 150°C.  
Chlorine Rate: 150 ml./min.  
Iron & Aluminium Content of Coal (as oxides): 4.07 %.

<u>Period of Test (hrs.)</u>	<u>Aqueous Extract of Chlorinated Coal Contained: (as % on original Coal)</u>	
	<u>Fe- and Al- Oxides.</u>	<u>Total Chlorine.</u>
0.5	0.52	2.86
1	0.51	2.71
3	0.50	2.56
5	0.55	2.68
38	0.88	3.23

The results show that only a small percentage of the iron and aluminium compounds appear to be attacked and that this reaction is practically completed in the first half hour of the chlorination.

CONCLUSIONS:/.....



CONCLUSIONS:-

These tests have confirmed that quite high percentages of chlorine can combine with the coal substance, but after the first hour the rate of chlorination was not as high as one would desire under practical conditions.

The most undesirable feature of these experiments was the loss of chlorine by formation of hydrochloric acid. This reaction would have to be depressed to make the reaction at all attractive from a practical point of view. Some exploratory tests in this direction were not successful and at this stage it is rather doubtful whether chlorination could be considered as a possible reaction in the transformation of coal to produce substances of interest to chemical industry.

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and

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PRETORIA.

11th July, 1950.

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R E F E R E N C E S.

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51, 49, 186, 1932.
- (3) Lowry, Chemistry of Coal Utilization 1945; See Weiler,  
Fuel 14, 190, 1935.
- (4) J. F. Weiler, J. Amer. Chem. Soc. 58, Part II, 1112,  
1936.
- (5) Marsh, McCulloch & Parish, J. Soc. Chem. Ind. 48,  
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APPARATUS USED FOR CHLORINATION TESTS.

1. Bypass.
2. Scrubber ( $H_2SO_4$ )
3. Flow meter.
4. Jacketed Reaction Tube with  
5. sintered glass disc 5.  
(Dimensions approximately  
1 inch diam. by 12 in. high  
from sintered glass disc  
upwards.)
6. Gas wash bottles containing  
distilled water.
7. Scrubber containing alkali.

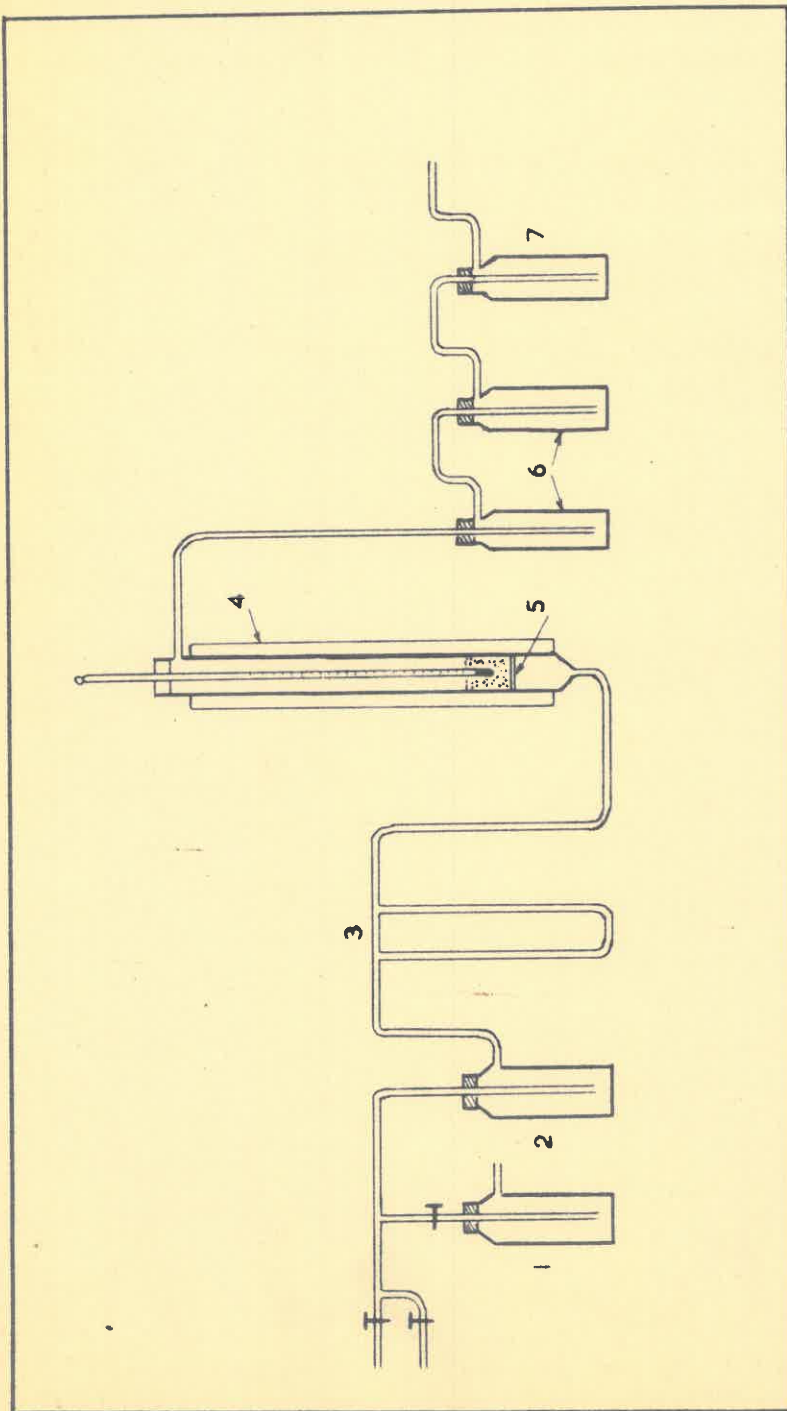


FIGURE 1

EFFECT OF TEMPERATURE ON THE REACTION  
OF CHLORINE ON COAL.

Chlorine absorbed shown thus \_\_\_\_\_

Chlorine evolved as HCl shown thus -----

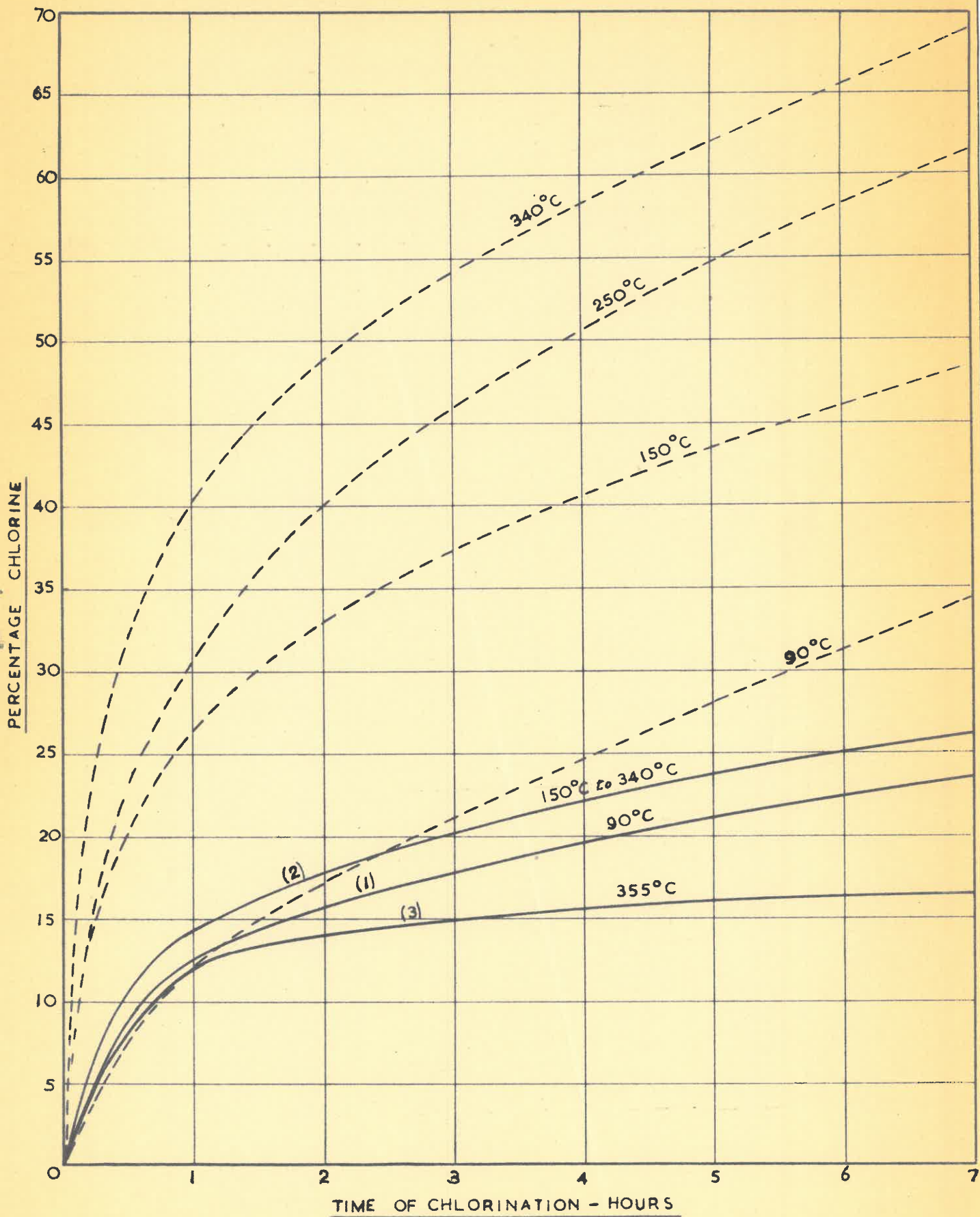


FIGURE 2

EXTENSIVE CHLORINATION OF ERMELO COAL.

Chlorine absorbed by coal shown thus \_\_\_\_\_

Chlorine evolved as HCl shown thus -----

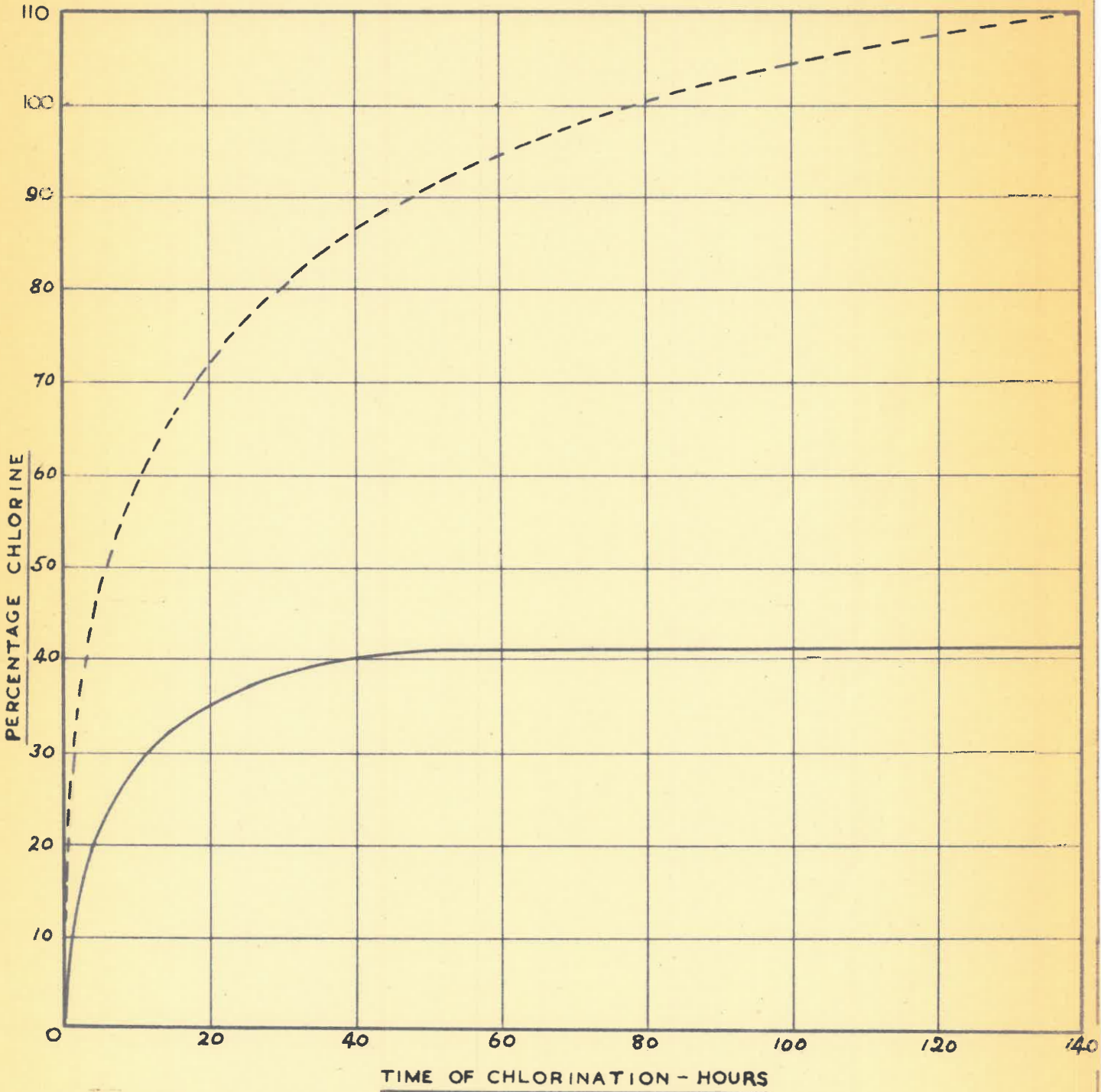


FIGURE 3

