

CHEMICAL CONSTITUTION OF COAL.

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In order to understand the nature of the coal constituents chemists followed various methods which may be classified under three principal heads:—

- (i) Chemical attack by means of various reagents which oxidise, decompose or otherwise alter the coal substance.
- (ii) The action of various organic solvents which are supposed to extract fractionally certain constituents without radically altering them.
- (iii) The action of heat on the original coal or of some extracted portions at certain definite temperature and the examination of the products so obtained. This includes the process of coal distillation and the examination of various distillates.

Regarding the first method the reagents chiefly employed have been sulphuric acid, nitric acid, caustic alkalis, bromine, ozone, oxygen, etc. Coal being a heterogeneous mixture of several complex compounds most of which are imperfectly soluble in any known reagents. The scientists made attempts to transform some of them by various chemical treatment into simpler definite products capable of further investigation and identification. Such attempts, however, have been unsuccessful because by such treatment the yields were either too small or the products were themselves in an advanced stage of decomposition, thereby giving no clue as to the real nature of the organic compounds originally present in the coal substance.

Regarding the third method the coal is subjected to destructive distillation and the various coal constituents are decomposed at different temperatures and give rise to various chemical compounds of different thermal stability. In this process also the resultant chemical compounds do not enlighten us in the matter of obtaining definite information as to the real nature of the compounds originally present in coal.

The second process of attacking the coal by various organic solvents is undoubtedly preferable to either of the above two processes because it enables us to extract some portions, if not all, of the various constituents of coal with minimum alteration or decomposition of the coal substance. The difficulty is in the selection of a proper solvent that will behave differently to the different coal constituents and at the same time will be able to extract a large proportion of them without destroying the whole structure.

By suitable solvents and by following proper technique and at the same time avoiding any decomposition of the coal substance this process has been

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found to separate various compounds from coal and by careful investigation the definite chemical nature of them has been studied and established.

Already a considerable amount of work has been done with regard to the action of various organic solvents on coal substance in order to elucidate the nature of the constituents present in it. The principle underlying the solvent action is to break up the coal substance into different fractions without materially decomposing it. Various organic solvents such as benzene, chloroform, ethyl ether, ethyl alcohol, light petroleum, acetone, aniline, quinolene, phenol, etc., were employed with varied results. In 1899 Bedson found that pyridine has a remarkable solvent action upon coals and subsequently pyridine as a suitable solvent came into general use. It will be out of place here to give a detailed account of this solvent work carried out by various scientists in different countries. The author of this note carried out some work in this line and followed Prof. Wheeler in selecting pyridine and chloroform as the most suitable solvents for extraction purposes. Of the recent works in this line mention should also be made of the researches carried out by Bone and Illingworth. Prof. Bone constructed an apparatus which operates on the automatic soxhlet principle under pressure up to 700 lb. per sq. in. by which means he could extract a greater quantity in a shorter period. The solvent used by him was benzene. Illingworth carried out investigations in this direction and observed that by heating the coal at 200°C. for 24 hours out of contact with air the rate at which the extraction proceeded was much increased. But when extracted for a long period the amount of extract was practically the same under both conditions. From his experience it was found that slightly greater extraction was possible with chloroform than with benzene. Parr and Hadley carried on some extraction with phenol at 100°C. for 20 hours in an atmosphere of CO₂. By such treatment they could eliminate resinic organic sulphur from coal. Fischer and Gluud studied the action of benzene upon coals at 288°C. and about 50 atmospheres.

It may be mentioned that very little work has hitherto been done to find out the effect of solvents on Indian coals. Carrick Anderson and Henderson followed the method of Bedson and carried out some experiments with Bengal and Japan coals. They used commercial pyridine as the solvent, boiling at 110–120°C. in soxhlet apparatus. It has been pointed out by Illingworth that though better extraction is possible with phenol at higher temperature (400°C.), yet at temperatures under 120°C. the pyridine has been found to be more efficacious in its action. It was suggested by Bone and Wheeler that at higher temperature, sometimes as low as 180°C., there was a chance that there might ensue some decomposition in the coal substance. The author of this paper has done some work in this line and carried out soxhlet extractions with pyridine and chloroform as suitable solvents and did not therefore prefer to experiment at higher temperatures. The details of the technique followed in the laboratory have already been published.¹ The coals that were subjected to laboratory investigation included the Tertiary

coals of Assam and N.W. India and some specimens of Gondwana coals. The author of this paper takes this opportunity of expressing his best thanks to Dr. Fox for kindly giving him some specimens of Tertiary coals for investigation.

When coal is subjected to the action of pyridine in the soxhlet apparatus it splits up into insoluble (alpha cellulosic coal or alpha compound) and soluble (beta cellulosic and gamma resinic substance) portions. The soluble portion (beta and gamma compounds) on further treatment with chloroform in the soxhlet apparatus is found to break up into insoluble (beta compound) and soluble (gamma compound) fractions. The coal substance thus resolves into cellulosic and resinic components. The chemical nature and other different properties of these substances have been carefully studied and established and it will be out of place here to enter into those details. The respective amounts of these compounds present in the different coal specimens of India have been determined quantitatively and the results are enumerated in Table II. Table I gives the proximate analyses of the coal specimens. The method adopted for proximate analyses has been described in a previous communication.² Table III gives the ultimate analyses of these coals. In the following lines a discussion is given of the presence of these chemical constituents and their relation with caking and swelling properties of the coals.

The alpha, beta and gamma compounds have been separately examined and their behaviour under heat treatment studied. The alpha compounds obtained from all the specimens of caking coals do not show any tendency to form a coherent mass when subjected to destructive distillation. In other words it may be said that the caking property of a coal is almost entirely destroyed by the leaching action of pyridine on the coal substance. The beta compounds obtained by the action of pyridine and chloroform on the coal specimens, when strongly heated in a covered platinum crucible, are found to give rise to a swelled mass though the particles are not held together very firmly. The gamma compound on being heated generally liquates and melts at a much lower temperature and is found to yield the cementing substance which binds together the other coal particles. When further heated at higher temperature it forms a swelled mass. A mixture of alpha cellulosic coal particles and gamma compounds in definite proportions when heated is found to produce a coherent mass. The beta compound is also able to take up some amount of alpha cellulosic particles to form a swelled mass when subjected to process of carbonisation. It is also found that a mixture of alpha, beta and gamma compounds in the same proportion as present in the coal substance produces a good coke though slightly inferior to the coke obtained from the coal.

Two specimens of caking coal (seams Nos. XIV and XV) were heated for several hours at 105°C.-110°C. in presence of air and the caking property eventually destroyed. These specimens were then subjected to the action of pyridine and chloroform and the results of these experiments are given below:—

(Coal oxidised at 105°C.-110°C. and caking property destroyed.)

%		Seam XIV.	Seam XV.
Alpha compound (α)	93.00	84.02
Beta compound (β)	0.50	6.70
Gamma compound (γ)	6.50	9.28
Total pyridine extract ($\beta+\gamma$)	..	7.00	15.98

Untreated coal.

%		Seam XIV.	Seam XV.
Alpha compound (α)	93.43	84.32
Beta compound (β)	0.20	6.68
Gamma compound (γ)	6.37	9.00
Total pyridine extract ($\beta+\gamma$)	..	6.57	15.68

DISCUSSION OF RESULTS.

It will be out of place here to enumerate in detail the views held by previous workers on this subject as an excellent historical summary has been published by Bakes.³ It may be mentioned that Prof. Wheeler and his school carried out extractions of coal with pyridine and chloroform and a comprehensive work on the extraction with benzene under pressure was carried out by Fischer and Bone and their associates. Illingworth also conducted experiments after Wheeler with pyridine and chloroform and put forward certain generalised statements which require verification. Illingworth concludes that for the coals with C/H ratio higher than 10, coke can only be formed when more than 5.5% of gamma compound is present. The gamma content is maximum in coals when C/H ratio is between 17 and 18. An increase of C/H ratio will decrease the gamma content. According to him the beta compound is found to occur in greatest amount in coals with C/H ratio between 14 and 15. He also concludes that increase of C/H ratio decreases the beta content of coal.

Referring now to the analytical results given in Table II it will be seen that many of the caking coals contain gamma compound more than 5% which go to support partially the views of Illingworth. The relationship proposed by him between the pyridine extracts and C/H ratio does not seem to hold good in every case. There are certain exceptions which suggest that the resinic coking theory as put forward by Illingworth should be accepted with reserve. Besides, the results obtained by Foxwell⁴ in this direction do not go to support the views of Illingworth in all their entirety.

So far as the caking principle is concerned Cockram and Wheeler⁵ conclude that caking property is due to the presence of resins and hydrocarbons contained

in the coals or derived from these substances during the early stages of heating. Foxwell⁶ lays importance on the extrusion of molten matter in the first stage of coking consisting of gamma from the interior of coal. He thinks that the coking power of a coal is due not so much to the actual amount of the gamma fraction which it contains as to its mode of extrusion when the coal is heated. It may be pointed out that Foxwell obtained a tolerably good coke from a South Welsh coal containing only 0.1% of gamma compound. The author of this note also found that the strongly caking Jammu coal contained only 0.37% of gamma and 0.73% of beta compound. Foxwell also observed that there are some coals containing a large amount of gamma fraction which do not yield coke. A reference to Table II will show that Borjan non-caking coal of upper Assam contains an appreciable amount of beta and gamma compounds. Foxwell suggests that some structural peculiarity in the coal may prevent the extrusion of the gamma fraction in the proper manner and that this may be one of the factors responsible for the non-caking nature of such coals.

Foxwell lays much stress on the presence of the gamma fraction and does not discuss in detail the nature of the beta fraction and its rôle in the caking and swelling properties. The author of the present paper, however, finds that the swelling and caking properties of coal are connected with the presence of both the beta and gamma fractions and not the gamma compound alone. Sinnatt's⁷ suggestion that the gamma compound alone is responsible for swelling and caking does not seem to tally with the author's experimental observations. Beta particles on being heated are found to produce a highly swelled and coherent mass showing clearly that the swelling property of coal is to be ascribed to the presence of the beta compound, a suggestion already made by Shimura⁸ and Barash.⁹ The fact that beautiful cenospheres are obtained by Bakes¹⁰ from beta fraction goes to oppose Sinnatt's view. As the beta particles get cemented together during the process of heating it is clear that a certain amount of binding or cementing substance is derived from this compound. The analytical results given in the tables accompanying this paper show that there are few exceptions to this statement. The three specimens of Raniganj coals (Poniati, Ninga and Ghusick seams) contain a sufficient amount of beta and gamma compounds yet they swell only slightly during caking. Following Foxwell's suggestion it may be said that some structural peculiarity in the coal substance may be held partly responsible for this. There are reasons to believe that the physical condition of the alpha cellulosic fraction in these specimens has a great influence on the beta and gamma compounds in preventing the formation of a highly swelled and coherent mass.

The coal specimens (seam Nos. XIV and XV) on slow oxidation are found to have lost their caking property. The amounts of pyridine extract in these specimens remain more or less the same before and after the oxidation. As suggested by Barash¹¹ the only explanation that can be given is that by the oxidation of the coal substance at an elevated temperature the physical condition and structural peculiarity of the alpha fraction become altered

sufficiently to behave in a different manner than in the untreated coal. Similar instances have also been recorded by Barash,¹² the only difference being that Barash kept the coal specimens exposed to air for a considerable length of time instead of heating as in the case of the present author's experiments. Barash's suggestion that the alpha compound develops increased absorptive capacity appears to be reasonable.

From what has been said and discussed above it appears that the alpha fraction without being an inert substance, as has hitherto been supposed to be, plays an important rôle in the process of carbonisation, details of which have yet to be thoroughly studied.

With regard to the gamma content it may be pointed out that almost all the specimens of caking coal included in the present paper contain more than 5% gamma fraction and that all the coals are not equally caking as shown by the different values of their caking indices (Table I). An exceptional case has been recorded. This specimen (seam No. X), however, contains a slight amount of beta compound which is responsible for the non-swelling nature of this coal. A scrutiny of the analytical results given in the tables will show that the gamma fraction is mainly responsible for the development of cementing material in the coal substance. From the behaviour of the gamma fraction during heat treatment it is found that some amount of swelling is also due to the presence of this compound.

From what has been said and discussed in the foregoing pages it is clear that the generalised statements put forward by Illingworth and the suggestions made by various other authors regarding the relationship between the pyridine extracts and caking and swelling properties do not appear to be strictly applicable in the case of coal specimens described in this paper.

Though the suggestions made by Bakes¹³ are in general harmony with the observations recorded in this paper regarding the caking and swelling properties of coal, yet slight modification is necessary as suggested below for the proper explanation of the facts observed by the present author. Bakes' conclusion is that during the plastic stage two types of plastic material may be present. The first (caking constituent) consists of a dispersion of gamma 2 and gamma 3 in gamma 1. The second type of plastic material (the swelling constituent) results from the fusion of portions of coal similar in nature to the beta fraction which may be obtained by pyridine extraction. The author of this paper has already pointed out in the foregoing pages that the beta compound, besides being responsible for the swelling property, also gives rise to some cementing substance and that the gamma fraction when heated liquates at lower temperature and swells to some extent on further heating at higher temperature, showing that gamma is mainly responsible for the development of the cementing material in the coal substance and partially for the swelling. It is also evident that caking and swelling properties are the results of a combination of physical and chemical reactions which take place in the coal substance partly simultaneously and partly successively. There are, however, indications that the

physical condition and structural peculiarity exert some influence during the caking process and further work is necessary in this direction before any generalised statement can be put forward. No definite relationship between C/H ratio and the alpha, beta and gamma fractions has been observed at this stage of investigation.

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TABLE II. (Pyridine and Chloroform extracts).

%	Jharia field.					Raiganj.						Assam.		N.W. India.			Kashmir.									
	Seam No. X	Seam XI.	Seam XII.	Seam XIV.	Seam XV.	Ramnadh Colliery.	Dishergarh Seam.	Pontali Seam.	Ninga Seam.	Glusick Seam.	Lakidih Vitrain.	Lakidih Vitrain.	Lakidih Durain.	Bordhemmo Fusan.	Ekra Fusan.	Jharia Fusan.		Rajmahal Fusan.	Talchir Fusan.	Borjan Coal (freshous).	Namdang Coal.	Borjan Coal non-caking.	Makertwal.	Machl.	Dandot (Punjab).	Jammun.
Alpha Compound (α)	96-00	93-80	87-00	93-43	84-32	69-67	76-09	82-14	85-30	86-00	75-90	83-90	96-80	96-80	97-00	96-50	96-50	97-00	76-16	79-51	84-30	80-09	83-18	80-72	98-70	98-70
Beta Compound (β)	1-43	1-02	4-45	0-20	6-68	17-88	14-13	7-51	8-90	7-50	10-00	4-80	2-00	2-00	1-80	2-02	2-02	1-72	12-76	8-25	7-00	8-10	8-77	6-42	0-73	0-73
Gamma Compound (γ)	2-57	5-18	8-55	6-37	9-00	12-45	9-78	10-35	6-20	6-50	14-30	11-30	1-20	1-20	1-20	1-48	1-48	1-28	11-04	12-30	7-35	11-81	8-06	12-84	0-37	0-37
Total Pyridine extract ($\beta+\gamma$)	4-00	6-20	13-00	6-57	15-68	30-33	23-91	17-86	14-70	14-00	24-30	16-10	3-20	2-80	2-80	3-50	3-50	3-00	23-80	20-53	14-35	19-91	16-83	19-26	1-10	1-10

TABLE III. (Ultimate Analyses).

%	Jharia field.					Raiganj Field.					Jharia.		Rajmahal Hills.		Talchir.		Assam.									
	Seam X	Seam XI.	Seam XII.	Seam XIV.	Seam XV.	Ramnadh Colliery.	Dishergarh Seam.	Pontali Seam.	Ninga Seam.	Chusick Seam.	Lakidih Vitrain.	Lakidih Durain.	Bordhemmo Fusan.	Ekra Fusan.	Jharia Fusan.	Jharia Fusan.	Borjan Coal (non-caking).	Namdang Coal.	Borjan Coal (freshous).	Borjan Coal	Makertwal.	Machl.	Dandot (Punjab).	Jammun.		
C	63-60	70-30	75-92	73-69	75-36	78-43	72-10	71-70	68-65	71-13	79-17	65-80	75-79	74-63	69-52	81-22	78-02	79-66	78-43	78-02	78-02	79-66	79-66	78-43	78-43	78-43
H	4-66	4-26	4-98	4-96	5-20	4-70	4-50	4-55	4-72	4-68	5-93	4-34	3-61	3-80	5-12	4-06	5-92	5-84	5-54	5-92	5-92	5-84	5-84	5-54	5-54	5-54
O+N	6-62	5-93	11-22	7-95	5-56	7-80	12-51	12-20	12-41	13-04	10-09	11-34	10-01	10-12	13-71	10-21	9-28	10-80	11-36	9-28	9-28	10-80	10-80	11-36	11-36	11-36
S	0-52	0-67	0-80	0-80	0-72	0-57	0-44	0-53	0-42	0-40	0-61	0-49	0-79	0-80	0-45	0-51	0-75	3-01	2-30	3-75	3-75	3-01	3-01	2-30	2-30	2-30
Ash	24-60	18-82	7-08	12-80	13-16	8-50	10-45	11-02	13-80	10-50	4-20	18-03	9-80	10-85	11-20	4-00	8-03	0-69	2-37	8-03	8-03	0-69	0-69	2-37	2-37	2-37
TOTAL	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00	100-00
C/H Ratio	13-6	16-5	15-2	15	14-5	16-7	16	16	14-5	14-5	13-4	15	21	19-6	14	20	13	13-6	14	13-6	13-6	13-6	13-6	13-6	14	14

