STUDIES IN COAL BY X-RAY DIFFRACTION METHODS.

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INTRODUCTION.

The application of X-rays to the study of the Coal problem dates back to as early as 1912. H. Couriot [1] examined by radiographic methods anthracite, coal, coke, peat, lignite, wood and charcoal. Similar results were obtained by J. Daniel, [2] by the same method and he attempted to correlate the radiographic appearance of the various samples with their composition as ascertained by chemical analysis. Garret and Burton, [3] in 1912, in an important communication on the subject, suggested the development of the method for a rapid and simple means of ascertaining the distribution and aggregation of the ash of coal and for the possibility of discriminating between the various forms of ash, leading to increased knowledge of the origin and structure of coal.

Kemp C. Norman [4] in a series of interesting studies on similar lines has perfected a technique to determine with a great degree of accuracy the percentage and mode of distribution of ash in coal. The specimens were roughly $5'' \times 3''$ and they were at a distance of one meter from the focal point of the X-ray tube and exposures varying from 20 seconds to 2 minutes were given and the radiographs recorded on the photographic plates. From photometric measurements the ash content was calculated in those cases.

The systematic study of coal by X-ray diffraction methods, based on the theory of Debye and Scherrer [5] as modified by Raman and Ramanathan [6], was commenced at Calcutta by the author in 1927 and the materials for the study were generously given by Dr. (now Sir) L. L. Fermor and Dr. Cyril S. Fox. The details of the methods of study as well as of the results were published in a series of papers [7] between 1928 and 1935.

EXPERIMENTAL.

The source of X-rays for the experiment was a Shearer tube of the usual type with water-cooled aluminium cathode and copper target.

The window of the X-ray tube consisted of a circular brass slit which was covered with a thin punctureless aluminium foil kept in contact with a cardboard and stuck to the tube by sealing wax. The cathode rays impinging on the target gave rise to X-rays which emerged out of the tube through the brass slit. The X-ray tube was connected to a system of high vacuum backing pumps. An India-rubber pressure-tubing connected the X-ray tube to the low vacuum side, by suitably pinching this tube with a pinch-cock, the leak to the X-ray tube and hence the vacuum inside it could be easily controlled.

The high tension current necessary to run the X-ray tube was supplied by an oil-cooled transformer. Alternating current at 160 V. was obtained for the primary of the transformer from a rotary convertor. The high tension terminal of the secondary of the transformer was connected to the cathode of the X-ray tube and the lower potential side was connected to the target and earthed. A milliammeter in the secondary circuit recorded the current passing through the X-ray tube. The safety spark gap of the transformer, intended to provide an alternate path of the current in the event of the tube getting hard through very high vacuum, was 8 cms.

The camera consisted of a rectangular wooden box covered with a lead sheath, having a suitable groove for the sliding of a $\frac{1}{4}$-size plate-holder. The X-ray beam was collimated by passage through a lead tube containing three small holes in series, the first hole being of 0·75 mm. diameter and the last one (nearest to the camera) being 2 mm. This gradation in the size of the holes prevented the diffraction by the metallic edges of the holes from reaching the photographic plate. A metal disc with a central hole served as the container for the substances, and this disc could be conveniently slipped on to a suitable receptacle of the lead cylinder mentioned above, to get the substance in the path of the pencil of X-rays emerging through the system of slits described. A circular lead disc, suitably suspended from the top of the camera by a wire, served to cut off the direct beam and prevented it from falling on the photographic plate. The X-ray diffraction pattern was received on an 'isozenith' photographic plate contained in the plate-holder.

An exposure of from 2 to 8 hours, depending on the nature of the substance, was given with a current of 5 milliamperes in the tube. The angles of diffraction corresponding to the various rings were calculated as follows. The distance d, between the diffracting substance and the photographic plate, was measured. The radius r of the halo (*i.e.* the distance from the centre of the direct spot to the point on the halo where the intensity is maximum) was determined. The angle of diffraction is then given by $\tan\theta = r/d$. The corresponding grating space 'a' could be calculated by using the Bragg formula:—

$$a: \frac{\lambda}{2\sin\theta/2}$$ where λ is the wave-length of the incident X-rays.

To calculate the size of the diffracting particle, the distance between the points on the halo where the intensity fades to half of the maximum was determined. The Laue equation, when suitably modified thus to the different camera model used in the experiment, becomes:

$$\frac{1}{d} = \frac{1.10}{\lambda}\left[\mathrm{B}\cos\frac{\theta}{2} - \frac{1}{\mathrm{B}}\frac{\pi^2 t^2}{4\mathrm{R}^2}\cos^3\frac{\theta}{2}\right],$$

where, t: the thickness of the flake of substance,

R: the distance of the camera from the substance,

d: the linear dimension of the particle as measured perpendicular to the plane of reflection, and

B: the angular width of the halo, less the natural angular width due to the finite aperture of the incident X-ray beam.

The values obtained by the above calculations give the sizes of the diffracting particles to the correct order of magnitude.

On Banded Bituminous Coals and their Constitution.

A typical lump of banded bituminous coal, taken from a coal seam, generally shows four different constituents. These used to be described as dull coal, glossy coal, silky coal and mineral charcoal by the coal miners.

Marie Stopes [8], in a well-known paper, distinguished them by their characteristic reactions to certain simple chemical treatments and gave the name 'durain' for the dull coal, 'vitrain' for the glossy coal, 'clarain' for the silky coal and 'fusain' for the mineral charcoal.

Clarence A. Seyler [9] in a note in 'Nature' pointed out a close correspondence between the lithological classification of Stopes and the botanical nomenclature of Thiessen:

Thiessen.		*Stopes.*	
A. Anthraxylon (of homogeneous botanical origin from stems or roots).	A_1 Structure absent, obscure or faint.	*Vitrain*	Lustre glossy. Fracture conchoidal or semi-conchoidal, not laminated.
	A_2 Structure well preserved.	*Fusain*	A_2^i dull, friable.
B. Attritus of heterogeneous botanical origin, general plant debris.	B_1 Much anthraxylon present.	*Clarain*	A_2^{ii} Lustre silky, minutely laminated.
	B_2 Little anthraxylon present.	*Clarain*	Lustre silky, minutely laminated.
		Durain	Dull compact.

All the above constituents, except clarain, are present in Indian coals, and have been studied by X-ray methods.

Let us first consider vitrain. It is generally regarded as representing the fundamental coal substance. Several investigators,[10] particularly Tideswell and Wheeler, have suggested that its origin is from a jelly-like peat called 'dopplerite' which has lost its water on drying, thus becoming brittle, with a conchoidal fracture and having a shining black appearance.

The X-ray evidence is in conformity with the above results. In the first place, vitrain shows two haloes, one intense and corresponding to a spacing of 3·31 Å.U., and the other faint and corresponding to a spacing of 2·12 Å.U. Both of these haloes are in the same positions as those of the hexagonal carbon ring in graphite. This result should not of course be taken to imply the presence of free carbon, but only shows that the 'carboneous matter' of vitrain (which

may not be free carbon at all, as Cross and Bevan[11] have shown) contains the hexagonal carbon ring having the same structure as in graphite.

In the second place, both the haloes are very diffuse, and indeed a calculation of the particle size from the angular width of the haloes shows that the particles are colloidal, having linear dimensions of the order of 10 to 40 Å.U. Chemical evidence also points to the same conclusion.

Durain, on the other hand, is seen to give 8 haloes. Two of them are the same as in vitrain. In the position of these two haloes there is seen to be, from a study of the photographic negative, a great deal of overlapping. The other rings, which are not overlapping, are all fairly sharp. The durain was ignited in a platinum crucible over a Mecker Burner till constancy of weight was attained and the resulting ash was studied by the X-ray methods. Three haloes were given with a: 4·31 Å.U., 3·38 Å.U., and 2·49 Å.U. respectively.

For purposes of comparative studies, an X-ray pattern for graphite powder was obtained. We see that the superposition of the ash and graphite powder haloes on the vitrain pattern reproduces the pattern we have actually obtained for durain.

Here it is of interest to refer to some contributions by Fermor,[12] who, from an examination of the composition of Indian coals in relation to their specific gravity and ash content and moisture, has suggested that vitrain is a colloidal system of the gel or emulsoid type and that durain is a colloidal system of the suspensoid type in which the vitrain is surmised to be the dispersion medium in which the mineral matter and free carbon (the end product of vegetable detritus) are suspended. The X-ray results just described are in conformity with the above deductions.

Fusain is the last variety of coal examined. The specimens have a fine fibrous structure, silky in appearance, soft and friable, soiling the fingers when handled. The X-ray pattern of fusain disclosed 8 sharp haloes. The strong inner haloes indicated localised spots of intensity characteristic of fibre patterns. The interspaces are fairly clear. The haziness due to the superposition of haloes observed in the case of durain seems to be almost absent here and the edges of the haloes are more or less uniformly well defined. The haloes are seen to correspond to spacings due to free carbon and to ash.

There are several theories regarding the formation of fusain deduced from evidence afforded by their nature and association with the other types of coals in the field. Some believe it to be due to forest fires and consequent charring prior to the deposition of plant debris. This view does not find support from studies in Indian coalfields.[13] The scarcity of water (which acts as a thermostat during the process of coalification) seems to have been responsible for the formation of fusain. The mineral matter in fusain gives the haloes ascribable to silica and alumina and one of these haloes is quite sharp—much like a crystal powder pattern. This result suggests that though the woody fibre of the plant debris is mainly responsible for fusain (as indicated by the persistence of the fibre structure) some extraneous mineral matter has also got into association

with it. Since both moisture and volatile matter are present in fusain (though in a comparatively smaller quantity) the interspaces between the haloes in the pattern are not quite clear.

Thus, each of the three constituents of banded bituminous coals from the Indian coalfields gives a unique X-ray pattern in keeping with its well-known structure and composition. The vitrain is seen to be the nearest approach to the fundamental coal substance. For this reason, detailed studies were carried on with specimens of vitrain.

Light on Proximate Analysis thrown by X-ray Patterns.

An examination of the X-ray patterns in relation to the proximate analysis of the coals brings out certain interesting features. There is a general scattering in between the haloes, and the degree of intensity of the general scattering as deduced by visual observations is given by indexes varying from 1 to 10. It is found that the intensity of the general scattering in the X-ray pattern shows an intimate relationship to *the sum of moisture content and volatile matter rather than to either of them individually.*

From the work of Mack and Hulett,[14] it is now well established that 'moisture content' in coals as determined by proximate analysis has not the same value as that obtained from dehydrating coals with suitable reagents such as phosphoric pentoxide or sulphuric acid; some of the water is in intimate association with the fundamental coal substance and cannot be dislodged by these treatments. Besides, the water as determined in proximate analysis may, to some extent, be derived from thermal action on the chemical complexes. So, the 'proximate analysis' does not break the coal uniquely.

The correspondence of the general scattering in the X-ray pattern to the sum of 'moisture content' and 'volatile matter', rather than to either of them individually, seems to suggest strongly that these two are associated more intimately than we seem to understand from our present chemical knowledge. In this connection, it is interesting to refer to a recent contribution of W. T. Thom, Jr.[15] who, from a study of several hundreds of proximate analysis carried out in the laboratories of the U.S. Geological Survey, records that a review of the mode of formation and natural history of coal satisfies us that moisture is a normal and natural ingredient among its volatile constituents; and a knowledge of analytical practice shows that the 'moisture' and 'volatile matter' reported are both mixtures of moisture and volatile matter rather than sharply differentiated distillation fractions.

A few of the specimens were dehydrated, and later their 'volatile matter' driven out. X-ray patterns were obtained from these samples at each of the stages.

With the driving away of 'moisture content' the general scattering shows a little clearing up; side by side with this, the width of the diffraction halo increases perceptibly. In the pattern for the 'volatile matter-free' coals, precisely the above process seems to have been carried to completion. The

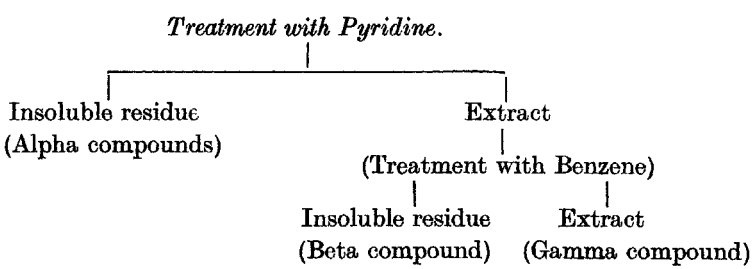
X-ray pattern for this residual product shows wider haloes with very little general scattering between the direct spot and haloes. The peak intensities of the haloes are however quite unaltered, suggesting a structural stability of the diffracting particles. The widening of the diffraction halo and the diminution of the general scattering with the above treatments suggest a very intimate association of the 'moisture' and 'volatile matter' with a nucleus of stable structure. Incidentally the view set forth earlier about the artificial nature of proximate analysis is further supported from those results.

Alpha, Beta, and Gamma Compounds of Coal.

In the study of the constitution of coal, organic solvents have been used from very early times. We may refer for a comprehensive review of the subject up to 1918 to Stopes' and Wheeler's [16] excellent monograph.

In recent years, the extraction of coals by benzene under pressure has been extensively tried by various workers, notably by Bone, Fischer and others.

Bedson [17] was the first to show the highly satisfactory results afforded by using pyridine to extract coals. Wheeler and his associates [18] in a series of systematic studies broke up coals by pyridine, and the extracted product by benzene or chloroform.



They claimed that a nearly complete separation of the coals was effected by the above process into their cellulosic and resinic constituents. They attributed similarity of composition to the alpha and beta compounds (cellulosic), whereas the 'gamma compounds' were surmised to be resinic constituents. Bone [19] and his students, in a series of detailed investigations with improved technique, have generally agreed with the conclusions drawn by Wheeler and his associates although they pointed out some discrepancies in the inferences of the latter. According to Bone [20] the resinic constituents of Wheeler contain not only pure resin, but also some 'humic substance', very probably derived from cellulosic products.

The *Alpha, Beta* and *Gamma* compounds have also been studied by the author by X-ray diffraction methods. Coarsely but not uniformly powdered coal was kept in a suitable thimble and extracted in the absence of air in an all-glass Soxhlet's extraction apparatus. An electric heater was used for

ensuring uniformity of conditions. The operation was allowed to go on continuously for several days till the pyridine in the chamber showed no coloration even after contact with the coal overnight. About 140 hours were usually required for a thorough extraction, resulting in a chocolate brown solution and a black residual product, bereft of any cohesive property. Most of the pyridine was recovered by distillation under very low pressure. The extract was finally freed from traces of pyridine by keeping in a vacuum desiccator and connecting it to an exhaustion pump. The product so obtained was of a madder red colour. This was again extracted in the Soxhlet's apparatus with benzene, which took part of it into solution and left behind an insoluble residue. All the three products thus obtained were studied by the X-ray methods.

From results it is seen that the alpha and beta compounds give nearly identical patterns. Their peak intensity is the same; for the beta product there is however a little widening of the haloes (suggesting a finer division of the particles), and a great deal of intense general scattering. The gamma compound consists of three haloes; the innermost one is intense and has a somewhat defined edge, the next is diffuse, and the outermost is very faint.

The author examined a number of natural and fossil resins from different horizons and ages by X-ray methods [21] with a view to see if the gamma compounds of coal had any structural relationship to these resins, one of the resins thus studied being from the Palana lignites. The gamma compound pattern for these resins afford evidence of a more complex composition and structure.

In this connection it may be mentioned that the X-ray pattern for the end residual product of Palana peaty lignite, after pressure extraction with 10% NaOH and the subsequent digestion of the residue with 72% sulphuric acid, is much like gamma patterns of coal.

The Ash in Coals.

The three coals—vitrain, durain and fusain—were heated in a platinum crucible with a Mecker burner for several hours till constancy of weight of the resulting ash was attained. The residue in each case was studied by the X-ray methods. The ash derived from vitrain shows no distinct intensity maxima; only extremely diffuse haloes are observed. For durain ash there are three maxima; one shows crystal powder spacing, another indicates finer division of the particles and the third is characteristic of centres of diffraction of colloidal dimensions. The existence of mineral matter in these three stages is now fairly well established from coal washing methods. It is interesting that Fermor,[22] from the ash-density-relationship, also suggests that some of the ash in the durain is in a colloidal state and part of it may be coarser matter. The X-ray results are in conformity with the above observations, from an independent field of research.

For fusain, all the haloes in the ash pattern are more or less well defined and there does not seem to be any colloidal matter in it.

In the coal ash it is now recognised that silica and alumina constitute most of the extraneous mineral matter, though compounds of iron, calcium, etc., may also be present in smaller quantities. Calculations of the spacings, for the most important planes of silica and alumina, were made with the help of the well-known equation of Hull. It is seen from these results that the ash pattern is primarily due to these two sources of mineral matter, namely silica and alumina.

Geological Age and X-ray Pattern.

Geologists have long recognised the influence of age and environmental conditions on the process of coalification. As the changes however are largely of a structural kind, the chemical researches have not been adequate to bring out conclusively the marked differences between the newer and older coals.

It is seen however that the X-ray patterns for the Permo-Carboniferous and Tertiary coals indicate distinct differences. Firstly, examining the scattering index of the X-ray pattern in relation to the sum of moisture content and volatile matter, we see that the correspondence is satisfactory only when we divide the coals into two groups—the older and the newer. Thus the index gradually rises from 4 to 9, with the rise of the sum of moisture content and volatile matter from 23·9% to 56·62%. Coming to the Tertiary group of coals we see that for a smaller percentage of these two ingredients, *i.e.*, for 46·63% the scattering index is still 9—a result we obtained in the older coals for as large a percentage as 56·62% moisture content + volatile matter. The other specimens of the normal Tertiary coals also show such deviation, but the correspondence in the same group of coals between this index and the sum of moisture content and volatile matter is quite satisfactory.

Secondly, a more striking difference in the X-ray pattern between the two groups of coals is distinguishable. The spacings for the peak intensity of the older group of coals give consistent values of 3·38 Å.U. for the inner intense halo and 2·12 Å.U. for the outer faint halo, whereas the corresponding figures for the Tertiary coals are 3·5 Å.U. and 2·2 Å.U. respectively. The differences noted are beyond the magnitude of experimental errors and are indicative of a fundamental structural difference. This is noteworthy, especially since no definite correlation was possible from other branches of investigation. For example, from a study of vitrains of different geological ages, Fermor [23] has recently concluded that no marked correlation is observed between age and any one factor of the proximate analysis but only a minor degree of correlation between age and fuel ratios. Examining, however, whether in the same coalfield, the different seams show any orderly change of specific gravity, composition or fuel ratio, he finds that in the Barakar stage, the increasing stratigraphical depth is accompanied by a regular decrease of moisture and volatile matter and an increase of fixed carbon and fuel ratio. Similar evidence is adduced from a study of the other coalfields. He suggests that the non-correspondence observed between age and composition in different coalfields

may be due to the differences in the original vegetable deposited. Since 'proximate analysis' is only an empirically standardised and rather crude artificial process and does not break the coal up into its natural constituents, the observed anomaly is not surprising. From a more rational method of disintegrating coal and studying the individual members in detail, Fischer, Broche and Strauch [24] suggest that with increasing geological age of the coals, the ratio of free hydrocarbons to resins increase while the decomposition temperature of the resins are raised.

X-ray Study on Tertiary Coals.

Chemical and X-ray investigations were carried out with Tertiary coals of the same geological age and horizon, ranging from peaty lignites to anthracites.[25] The samples were lignite from Palana in Bikaner State, Rajputana, coals from Mach in Baluchistan and Makarwal in the Salt Range and finally anthracite from Jammu, Kashmir. Chemical analyses of the coals indicate that in coalification, the degradation of the cellulose of the vegetable matter is at first rapid, while the lignin is more resistent, in conformity with the generally accepted views; but after a certain stage, the destruction of cellulose seems to proceed at a much lower pace, while that of lignin is more rapid. The presence of small amounts of cellulose in coals (as represented by Makarwal and Mach specimens) is an interesting result in this study.

Lignins were isolated from the coals by digestion with alkali, and purified. The X-ray pattern of all these lignins are practically identical, and resemble the pattern for flax lignin. On a comparison of the X-ray patterns for the untreated flax and its lignin, it is seen that except for the observation of fibrous nature in the untreated flax, the haloes in the two cases show great similarity.

In the case of lignite from Palana, the end residual products after alkali autoclaving and acid treatment give X-ray patterns very similar to the 'gamma compound' pattern of coals.

The X-ray patterns obtained with the peaty lignites and lignitic coals in the untreated state consist of two haloes, one intense, and the other somewhat fainter, the corresponding spacings for the two groups being 3·59 Å.U. (intense), 2·43 Å.U. (faint) and 3·5 Å.U. (intense) and 2·23 Å.U. (faint) respectively. The anthracitic coal give quite a different pattern showing unmistakable indications of carbon in a fairly coarse state. The spacing for the Tertiary coals, *viz.* 3·5 Å.U. are distinctly different from the corresponding values, *viz.* 3·39 Å.U. for Permo-Carboniferous coals, in spite of apparent similarity of the composition as determined by 'proximate analysis'. These observations have a relation to the geological history of the coalfields from where the specimens were obtained and a relation to the Bergius theory [26] of coal formation in nature.

It is seen that in conformity with the field observations, the X-ray patterns show progressive alteration to the anthracitic stage with increasing pressure.

The Palana lignites which have not been subjected to much pressure show larger spacing for the halo—similar to a pattern for peat; the next set of coals—Mach and Makarwal—have been subjected to moderate pressure and they correspond closely to the normal, Tertiary coals studied from other horizons. The anthracitic coals of Jammu which are from a region of great tectonic activity give patterns characteristic of free carbon and mineral matter.

The distinct difference between the X-ray patterns of the Tertiary and the upper palaeozoic coals, especially the higher spacings for the former in spite of their similar proximate composition, points to a less compact structure of the fundamental coal substance in the Tertiary specimens. The palaeozoic coals seem to have reached the final stage of maturity. In normal palaeozoic strata, anthracitic coals are absent. The existence, however, of anthracites in highly folded regions is attributed to the great pressure to which these regions had been subjected. The results of the X-ray study are in conformity with the above observations and support the Bergius' theory of coal and anthracite formation in nature.[26]

Recent studies in the Coal Problem by Workers abroad.

A brief reference may be made to contributions on the X-ray study of coal and associated products by George F. Beal and co-workers [27] who have published their results on the study of resins by X-ray diffraction methods and confirm and extend the results obtained by the author from a study of the fossil and natural resins of India. More recently, Von. A. Boldyrev [28], Director of Federov's institute in Leningrad and his co-worker have made a systematic study of the Russian coals and anthracites, on the lines initiated by the author.

In conclusion it may be mentioned that the systematic study of coal by X-ray diffraction methods opens up vast possibilities both on the academical and industrial side. It is hoped that this subject will attract more workers from all over the world devoted exclusively to this study.

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