

## STRUCTURAL STUDIES ON THE MAGNETIC FRACTION OF STEAM-TREATED MAKERWAL COAL

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In the preliminary study, both sulphur and oxygen were found to be significant elements of the magnetic fraction obtained from Makerwal coal, steam-treated at a temperature of 350°C., and the available data showed them to be present as (Fe<sub>3</sub>O<sub>4</sub>+S). The present investigation attempts to elucidate precisely the nature and quantities of the phases containing this sulphur. Measurements with a Guoy magnetic balance at a series of different field strengths show a rapid increase in both para and ferro-magnetic properties of the treated coal when the treatment is carried out at 300°C., or above. A comparison of these measurements with chemical estimations of total iron, total sulphur and pyritic sulphur indicates that at 400°C. only a fifth of the iron is converted into the ferromagnetic Fe<sub>3</sub>O<sub>4</sub>, and provides evidence for the existence of the highly paramagnetic Fe<sub>n</sub>S<sub>n+1</sub>, which is apparently produced as an intermediate product in the conversion of FeS<sub>2</sub> into Fe<sub>3</sub>O<sub>4</sub>. Successive magnetic separations carried out in the dry state gave three strongly magnetic fractions, but failed to provide any appreciable separation between the para and ferro-magnetic components.

An X-ray powder diffraction analysis of these magnetic fractions and of the untreated and treated coal as such shows that, whereas the untreated coal contains kaolinite and FeS<sub>2</sub> as the major crystalline phases (amounting to 5% and 2% respectively), the first magnetic fraction contains four major iron-bearing phases, viz., Fe<sub>n</sub>S<sub>n+1</sub>, FeS<sub>2</sub>, FeS and Fe<sub>3</sub>O<sub>4</sub>, in the approximate percentages, 5, 5, 2 and 4, respectively. These figures lead to an estimate of 9% iron and 6% sulphur, in fair agreement with the chemically determined values of 8.8% and 7.2%. The ratios of these four constituents are essentially the same in the treated coal and the three successive magnetic fractions.

The anomalous preponderance of Fe<sub>3</sub>O<sub>4</sub> and the near absence of iron sulphides noted in the earlier communication are corroborated by a better X-ray pattern of the old concentrated sample, and are probably due to preferential concentration of the Fe<sub>3</sub>O<sub>4</sub> in the wet magnetic concentration process that was used in the previous work.

### Introduction

Preliminary work on the magnetic fraction obtained from the residue remaining behind after high temperature steam-treatment of Makerwal coal had shown<sup>1</sup> that, although the pyritic material appears to have been converted by steam-treatment into Fe<sub>3</sub>O<sub>4</sub> (with a possibility of formation of Fe<sub>n</sub>S<sub>n+1</sub> up to the extent of 5%), the magnetic fraction still carries as much as 8% sulphur. In order to elucidate the status of this sulphur in the magnetic fraction, and to study further the reactions involved in the steam-treatment, it was decided to undertake magnetic measurements and detailed X-ray investigation on the untreated coal and on samples of coal treated with superheated steam at different temperatures upto 400°C. The results of these studies are presented in this communication and are correlated with the chemical analysis of the various treated and untreated samples.

#### 1. Magnetic Measurements and Chemical Analysis

Magnetic susceptibilities ( $\chi$ ) of untreated Makerwal coal and of the different samples of the steam-treated coal were determined with a Gouy magnetic balance at different field strengths ranging from 3,000 to 5,200 oersteds. This balance, which had been constructed in this laboratory, was first standardised approximately with a search coil and ballistic galvanometer, and then more accurately with CuSO<sub>4</sub>.5H<sub>2</sub>O and NiSO<sub>4</sub>.7H<sub>2</sub>O, and the final readings were found to be reproducible

to an accuracy of 1%. The results of magnetic measurements on two samples of untreated Makerwal coal and on samples of differently treated Makerwal coal are plotted in Figs. 1(a) to 1(e) with  $\chi \times 10^6$  as ordinates and 10,000/H as abscissae, and satisfactory straight lines can be drawn through these points.

The susceptibilities ( $\chi_p$ ) of the paramagnetic part and Saturation Magnetisation ( $\sigma_f$ ) corresponding to the ferromagnetic part of each sample were read off from the ordinate intercepts and the slopes of the graphs in Fig. 1, and the means of two determinations, each with a new sample, are given in Table 1. A 50 to 80 fold increase in values after steam-treatment at the temperature of 400°C. is evident, cf. also Fig. 2(a).

TABLE 1.—MAGNETIC DATA FOR TREATED AND UNTREATED COAL SAMPLES.

Description of the sample	$\chi^p \times 10^6$	$\sigma_f \times 10^2$	$\frac{\sigma_p}{\chi^f} \times 10^{-4}$
(A) Untreated Makerwal coal	1.5 ± 0.2	0.76 ± 0.05	0.54
(B) Makerwal coal steam-treated at 280°C. for 4 hrs.	3.2 ± 0.3	1.10 ± 0.1	0.35
(C) Makerwal coal steam-treated at 300°C. for 10 hrs.	16.2 ± 1	9.7 ± 0.5	0.60
(D) Makerwal coal steam-treated at 350°C. for 10 hrs.	55 ± 3	48 ± 2	0.86
(E) Makerwal coal steam-treated at 400°C. for 10 hrs.	77 ± 3	61 ± 3	0.79

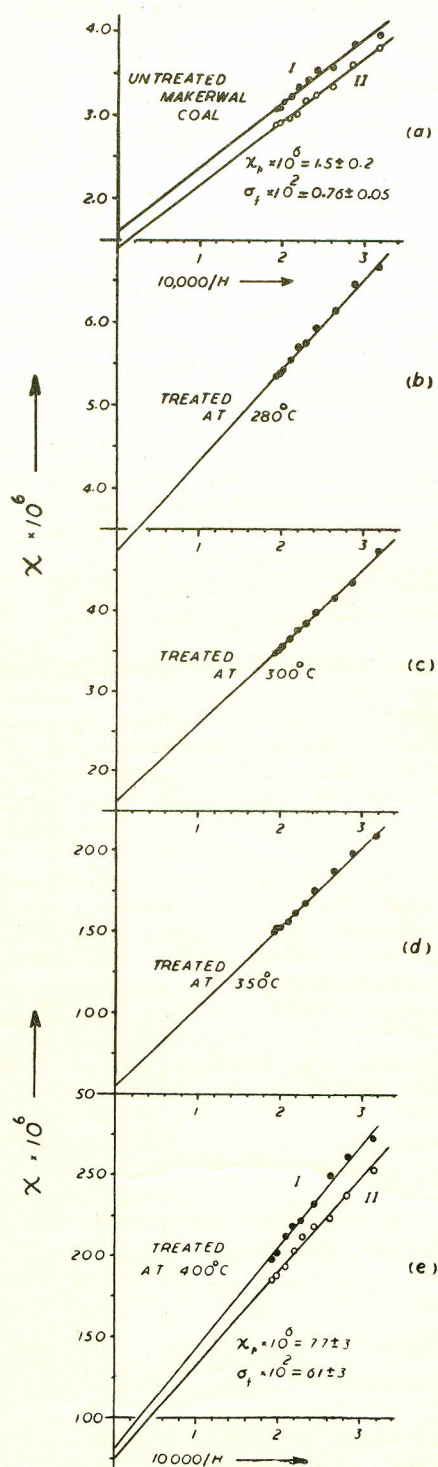


Fig. 1(a)-(e).—Plot of the magnetic susceptibility of untreated and variously treated samples of Makerwal coal measured at several different field strengths. The intercept at  $1/H=0$  gives the paramagnetic susceptibility  $\chi_p$ . The variation between the two samples in Fig. 1(a) and Fig. 1(e) is mostly attributable to sampling errors.

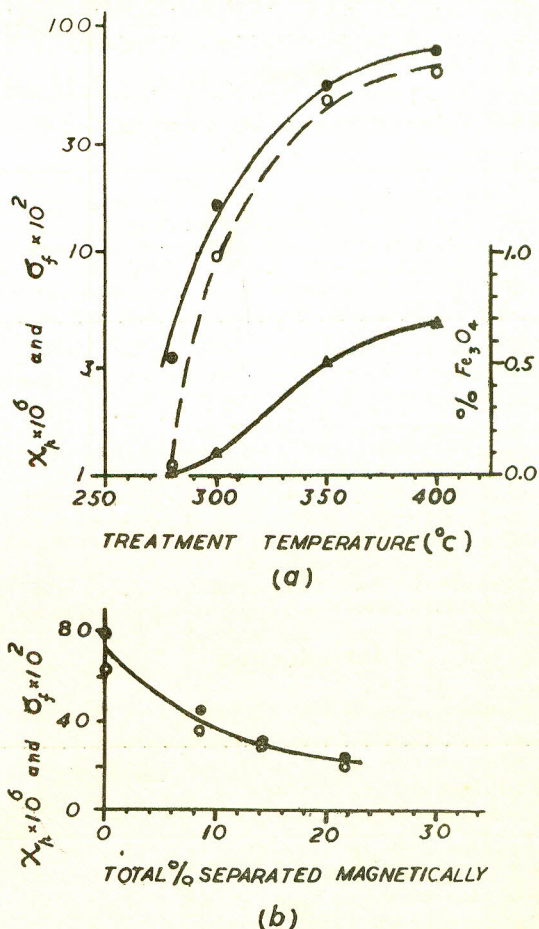


Fig. 2.—(a) Curves showing the dependence on treatment temperature of the paramagnetic susceptibility  $\chi_p$  (solid circles) and the ferromagnetic saturation magnetization  $\sigma_f$  (hollow circles), both plotted semi-logarithmically. The triangles show the variation of %  $Fe_3O_4$  as determined from the magnetic measurements.

(b)  $\chi_p$  and  $\sigma_f$  plotted for the residues from successive dry magnetic separations, showing the initial rapid fall in both quantities.

On the basis of the earlier X-ray and chemical work (in spite of the possible presence of some paramagnetic  $Fe_nSn_{n+1}$ ), the principal ferromagnetic constituent of the above samples is  $Fe_3O_4$ , and its percentage can, therefore, be estimated fairly well on the basis of the standard value of  $\sigma_f$  for  $Fe_3O_4$ , viz.,  $93.3 \times (1 - 19/H)$  at 19°C. as per International Critical Tables.<sup>2</sup> These estimates are shown in column 5 of Table 2, alongside of data from chemical analyses for iron and sulphur, which show that, even in the coal treated at 400°C., the iron in the form of  $Fe_3O_4$  constitutes only one fifth of the total iron found by chemical analysis. The rest of the iron may therefore be expected to

be present in the form of other simple inorganic compounds, probably sulphides and oxides.

TABLE 2.—CHEMICAL DATA FOR TREATED AND UNTREATED COAL SAMPLES.

Description of sample	% Total iron determined volumetrically	% Total sulphur	% Pyritic sulphur, mainly as $\text{FeS}_2 + \text{FeS} + \text{Fe}_n\text{S}_{n+1}$	% $\text{Fe}_3\text{O}_4$ from magnetic measurements
(A) Untreated Makerwal coal	2.09	4.6	1.2	<0.01
(B) Makerwal coal steam-treated at 280°C. for 4 hours	2.11	4.4	—	0.01
(C) Makerwal coal steam-treated at 300°C. for 10 hours	2.20	3.8	—	0.10
(D) Makerwal coal steam-treated at 350°C. for 10 hours	2.65	3.3	1.7	0.51
(E) Makerwal coal steam-treated at 400°C. for 10 hours	2.75	3.1	1.8	0.68

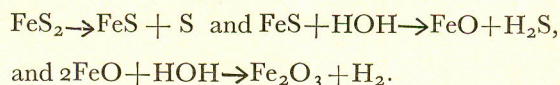
Some sulphate  $\rightarrow$  sulphide  
Some sulphide  $\rightarrow$  oxide

## 2. Evidence for $\text{Fe}_n\text{S}_{n+1}$

It is seen from Table 2 and Fig. 2(a) that the formation of  $\text{Fe}_3\text{O}_4$  in appreciable quantities does not begin until steam at a temperature of 300°C. is used, and that it reaches nearly its maximum value at 400°C. The ratio  $\frac{\sigma_f}{\chi_p} \times 10^{-4}$  in the last column of Table 1 first shows a decrease (for the steam-treatment at 280°C.). This is replaced by a rapid increase for treatment at temperatures of 300°C. and above. This indicates a relatively higher production of paramagnetic material in the treatments at lower temperatures and of ferromagnetic material at higher temperatures, which would suggest that the paramagnetic material is an intermediate stage in the formation of the ferromagnetic component,  $\text{Fe}_3\text{O}_4$ . Also it appears that, after allowing for nearly 20% loss of volatile matter, there is actually a small increase in the pyritic sulphur, which can probably be attributed to the breakdown of the sulphates, which are present to the extent of about 0.5%.

It may be deduced that, during the first stage of steam-treatment, the chemical changes in the iron-bearing phases are presumably the conversion

of the sulphates and higher sulphides into lower sulphides and oxides other than  $\text{Fe}_3\text{O}_4$ , viz.,



Of these products,  $\text{Fe}_2\text{O}_3$  and FeS are both paramagnetic. The very high values of  $\chi_p$  in Table 1 rule out the identification of this intermediate paramagnetic phase as  $\alpha\text{-Fe}_2\text{O}_3$ , and a sulphur compound is thus indicated. Magnetochemical studies of Haraldsen<sup>3</sup> and others have shown that compounds in the iron-sulphur system with sulphur in the range of 52.5 to 55 atom% have very high magnetic susceptibilities, of the order of 1100 to 1300  $\times 10^{-6}$  at 20°C. at infinite field strength. Thus, on the basis of the above data, it would be reasonable to presume the existence in the steam-treated samples of several percent of a compound of some composition within this range, which would correspond to  $\text{Fe}_n\text{S}_{n+1}$  with values of 'n' between 5 and 10.

## 3. Magnetic Separation in the Dry State

Attempts were next made to effect a magnetic separation of the paramagnetic and the ferromagnetic phases present in the coal treated at 400°C. A small horse-shoe magnet of field strength  $H \approx 500$  gauss near the poles was employed for this purpose. To avoid the possibility of disturbance of water-soluble material or of any mechanical or other interaction with water, dry separation was used in the first instance. The magnet was brought in contact with the powdered steam-treated sample and the particles adhering to the magnet were tapped off into another container. This process, repeated 20 times, enabled 8.6% of the sample to be separated. This was labelled 'First Magnetic Fraction' and the residue was named 'First Magnetic Residue'. In like manner, the second and third magnetic fractions were separated, and the magnetic susceptibilities of the successive magnetic fractions as well as of the residues were measured. Because the susceptibilities of the magnetic fractions are exceedingly high, they were determined by dilution with untreated coal. The results are shown in Table 3.

Deviations from additivity relationship in the susceptibilities of the magnetic fractions and the residues are largely accounted for by the fact that loss of even a trace of the highly magnetic material or a slight error in its weighing would magnify the error in the calculated susceptibility.

$\chi_p \times 10^6$  and  $\sigma_f \times 10^2$  for the three residues after magnetic separation are plotted in Fig. 2(b),

TABLE 3.—MAGNETIC DATA FOR SUCCESSIVE MAGNETIC SEPARATIONS.

Order of magnetic separation	%Magnetically removed	$\chi_p \times 10^6$		$\sigma_f \times 10^2$		$(\sigma_f/\chi_p) \times 10^{-4}$	
		Residue	Separated fraction	Residue	Separated fraction	Residue	Separated fraction
Unseparated sample	0.0	77±3	—	61±3	—	0.79±0.05	—
First fraction	8.6	45±2	239±9	36±2	210±9	0.80±0.06	0.88±0.06
Second fraction	8.6+5.5=14.1	31±2	176±7	30±1	160±7	0.97±0.06	0.90±0.06
Third fraction	14.1+7.5=21.6	24±2	94±4	20±2	78±4	0.83±0.06	0.84±0.06
				Mean:		0.87±0.05	0.87±0.05

and the mean curve through these points shows the progressive decrease of the magnetic material in the residue with each magnetic separation, and indicates that this method of separation would not be of any practical utility after about 15% of the material is separated as the magnetic fraction. The ratio  $(\sigma_f/\chi_p) \times 10^{-4}$  in all three magnetic fractions is not very different from that in the unseparated material, indicating that no appreciable preferential separation of the ferromagnetic component has been obtained. However, the separated magnetic fractions could be used for X-ray diffraction and chemical analyses.

#### 4. X-ray Diffraction Analysis

In order to confirm and amplify the foregoing results and to obtain detailed information about the phases, X-ray powder patterns of the untreated coal, the steam-treated coal and the different magnetic fractions (separated as above) were taken on a Seifert 11.4 cm. camera using filtered chromium K-radiation and exposure times of 15 to 20 hours. Complex patterns showing the presence of many phases were obtained, as against the one major phase (i.e.  $\text{Fe}_3\text{O}_4$ ) reported in the preliminary investigation.<sup>1</sup> The patterns of kaolinite, of the treated and untreated coal and of the first magnetic fraction are shown in Fig. 3(a) (top), while Fig. 3(b) (below) shows those of the third magnetic fraction and the constituent phases for comparison. The measured d-values of the lines are recorded in Table 4, together with the standard data for the relevant phases. As many as five phases can be definitely identified in the magnetic fractions of the steam-treated sample, viz.,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeS}_2$ ,  $\text{Fe}_n\text{S}_{n+1}$ ,  $\text{FeS}$  and kaolinite, with a possibility of traces of  $\alpha\text{-Fe}_2\text{O}_3$ .

#### (a) UNTREATED COAL

The powder pattern of the untreated coal is in general very poor, but it shows four strong lines corresponding to d-values of 3.53Å, 2.70Å, 1.63Å and 1.485Å. The A.S.T.M. Card Index data<sup>4</sup> shows that the strong lines at 2.70Å and 1.63Å correspond with the strongest lines of  $\text{FeS}_2$ , the complete data for which can be accounted for on the experimental pattern (cf. Table 4). The other strong lines of d-values 3.53Å and 1.485Å correspond to the strong lines of kaolinite, the data of which agrees with most of the outstanding lines. The line of d-value 7.15Å, which is one of the strongest lines of kaolinite could not be observed on the experimental pattern because of the very dark back-ground in this low-angle region of the film. However, this line could be easily identified in the later patterns of the magnetic fractions of the steam-treated coal samples, which have a much lighter back-ground in that region.

$\text{FeS}_2$  and kaolinite thus appear to be the major crystalline phases of the untreated sample, their rough percentages being estimated as 5 and 2, respectively, from the intensities of their characteristic lines. After accounting for the lines attributable to these two major phases, a few faint lines remain outstanding; two of these, at 1.83Å and 1.69Å, can be identified with the distinctive lines of  $\alpha\text{-Fe}_2\text{O}_3$ , the other important lines of which are also observable on the pattern. Thus  $\alpha\text{-Fe}_2\text{O}_3$  also seems to be present, but in very small quantities (<0.5%). Traces of  $\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4$  are also indicated by their respective strongest line.

#### (b) STEAM TREATED COAL AND ITS MAGNETIC FRACTIONS

The pattern of the coal after steam treatment at

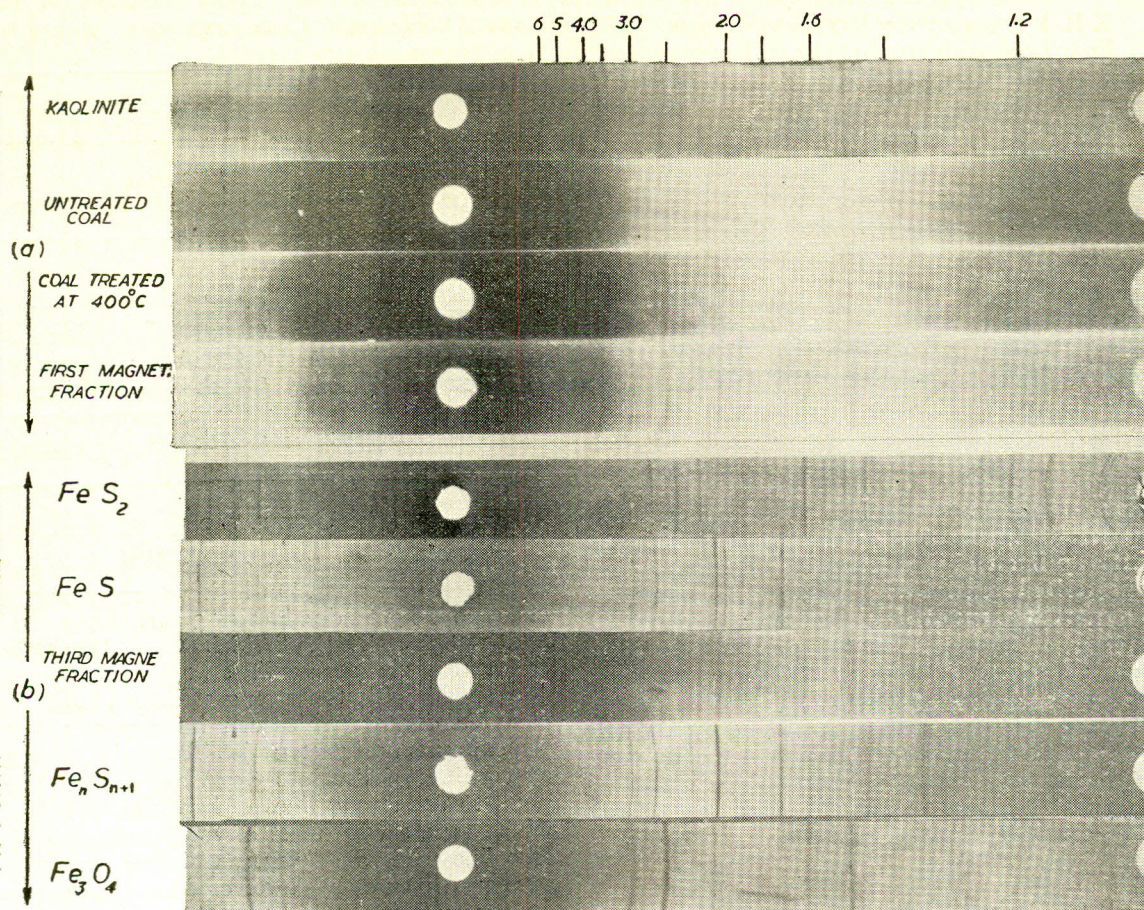


Fig. 3.—(a) X-ray diffraction patterns of untreated Makerwal coal, the steam-treated coal and the first magnetic fraction, with a comparison pattern of kaolinite at the top. Patterns taken with a 114 mm. dia. camera, using filtered Cr K radiation; the scale at the top indicates approximately the d-values in Angstroms.

(b). X-ray diffraction pattern of the third magnetic fraction alongside those of the iron sulphides and oxide that form its constituent phases. The sample of FeS contains a considerable quantity of free iron, some of whose lines are clearly visible, viz., at 2.03A. and 1.17A.

400°C. shows the presence of almost all the lines of the untreated coal pattern, although with considerable intensity differences, and further shows the emergence of several prominent new lines corresponding to d-values of 3.00A, 2.63A, 2.06A, 1.72A and 1.475A, suggesting the formation of several new phases as a result of steam-treatment. The strong magnetic character of the sample indicates the formation of some iron-bearing phase of high magnetic susceptibility, and therefore, an attempt was made to identify the new phases with the standard data of the more probable compounds, namely FeS<sub>2</sub>, Fe<sub>n</sub>S<sub>n+1</sub>, FeS, Fe<sub>3</sub>O<sub>4</sub>, FeO, and α-Fe<sub>2</sub>O<sub>3</sub>, as given in the A.S.T.M. card index<sup>4</sup> and also by reference to the work of Haraldsen and others.<sup>3</sup> Whereas the powder patterns of FeO, Fe<sub>3</sub>O<sub>4</sub> and α-Fe<sub>2</sub>O<sub>3</sub> are quite distinct, it appears from the data of FeS and Fe<sub>n</sub>S<sub>n+1</sub> that their

patterns are not readily differentiated (cf. Table 4). Thus the strongest lines of FeS are seen to be those at  $2.09 \pm 0.01A$  (Intensity 100) and  $2.66 \pm .02A$  (Intensity 80), while those of Fe<sub>n</sub>S<sub>n+1</sub> are at 2.06A (Intensity 100) and 2.63A (Intensity 50).

For the above reasons, for the proper identification of all the phases produced, it was considered expedient to use the patterns of the magnetic fractions separated from the treated coal because they give very much better powder patterns than the whole coal sample. As seen in Figs. 3(a), 3(b) and 4, the patterns of the three successive magnetic fractions are essentially the same, in agreement with the indications of the magnetic measurements.

(i) *Sulphides of Iron.*—The strongest lines of the

TABLE 4.—COMPARISON OF THE d-VALUES (IN ANGSTROMS) OF THE LINES OBSERVED ON THE X-RAY DIFFRACTION PATTERNS OF THE TREATED AND UNTREATED COAL AND THE MAGNETIC FRACTION WITH THE STANDARD PATTERNS OF THE IRON SULPHIDES AND OXIDES.

Untreated coal	Steam-treated coal	Kaolinite	1st magnetic fraction of coal treated at 400°C.	Minus kaolinite lines	FeS <sub>2</sub>	FeS* Troilite	Fe <sub>n</sub> S <sub>n+1</sub>	Fe <sub>3</sub> O <sub>4</sub> and γ-Fe <sub>2</sub> O <sub>3</sub>	α-Fe <sub>2</sub> O <sub>3</sub>	FeO
Very heavy background in this region	Very heavy background in this region	7.15(100) 4.45(50) 4.35(60) 4.17(60) 4.12(30)	7.0 (70) 4.4 (20) — 4.15(30) —	— — — — —	— — — — —	— — — — —	— — — — —	— — — — —	— — — — —	— — — — —
—	(S) 3.8	3.84(40) 3.73(20)	3.85(15) —	— —	— —	3.82(20)	— —	— —	— 3.68(70)	— —
3.53 (M)	(S) 3.55	3.57(100)	3.53(60)	—	—	—	—	—	—	—
—	—	—	3.50(10)	3.50(10)**	—	—	—	—	—	—
3.33 (F)	—	3.37(40)	3.33(10)	—	—	—	—	—	—	—
—	—	—	3.24(10)	3.24(10)**	—	—	—	—	—	—
—	—	3.14(20)	—	—	—	—	—	—	—	—
3.10 (F)	—	3.09(20)	3.10(20)	—	3.128(36)	—	—	—	—	—
—	(S) 3.00	—	2.99(80)	3.00(80)	—	2.98(80)	2.97(10)	2.97(28/34)	—	—
2.80 (VF)	—	—	—	—	—	—	—	—	—	—
—	—	2.75(20)	2.76(20)	—	—	—	—	2.78(-/19)	—	—
2.70 (M)	(W) 2.72	—	2.70(60)	2.70(60)	2.709(84)	2.68(90)	—	—	2.69(100)	—
—	(W) 2.63	—	2.64(30)	2.64(30)	—	—	2.63(50)	—	—	—
2.54 (W)	(D) 2.56	2.55(70)	2.55(30)	—	—	2.54(20)	—	—	—	—
—	—	2.52(40)	2.51(100)	2.51(80)	—	—	—	2.53(100)	2.51(80)	—
2.47 (F)	(D) 2.49	2.486(80)	2.49(30)	—	—	—	2.45(5)	—	—	2.486(80)
2.42 (W)	(W) 2.41	—	2.40(80)	2.40(80)	2.423(66)	—	—	2.42(11/-)	—	—
2.36 (F)	—	2.374(70)	—	—	—	—	—	—	—	—
2.32 (WM)	(W) 2.33	2.331(90)	2.33(70)	2.33(25)	—	2.32(70)	—	—	—	—
2.27 (W)	—	2.284(80)	2.29(30)	—	—	—	2.26(5)	—	—	—
2.20 (W)	(W) 2.21	2.182(30)	2.20(60)	2.20(45)	2.218(52)	—	—	—	2.20(70)	—
—	—	—	—	—	—	—	—	—	—	2.153(100)
—	—	2.127(20)	—	—	—	—	—	—	—	—
—	—	—	2.095(40)	2.095(40)	—	2.10(100)	—	2.10(32/24)	—	—
—	(MS) 2.06	—	2.06(100)	2.06(100)	—	—	2.06(100)	—	2.07(10)	—
1.99 (W)	—	1.985(70)	1.98(30)	—	—	—	—	—	—	—
—	—	1.935(40)	—	—	—	—	—	—	—	—
1.90 (W)	(W) 1.915	1.892(20)	1.90(60)	1.90(50)	1.915(40)	1.90(20)	—	—	—	—
—	—	1.865(5)	1.88(10)	1.88(8)	—	—	1.88(5)	—	—	—
1.83 (F)	—	1.825(40)	—	—	—	—	—	—	1.837(70)	—
—	—	1.805(5)	—	—	—	—	—	—	—	—
—	(W) 1.785	1.778(60)	1.78(30)	—	—	1.76(20)	—	—	—	—
—	—	—	1.75(10)	1.75(10)	—	—	—	—	—	—
—	(M) 1.72	1.704(5)	1.715(40)	1.715(38)	—	1.72(80)	1.72(40)	1.71(16/12)	—	—
1.69 (F)	—	1.682(10)	1.68(20)	1.68(15)	—	—	—	—	1.691(80)	—
1.66 (F)	—	1.659(80)	1.66(20)	—	—	—	—	—	—	—
1.63 (S)	(M) 1.625	—	1.63(100)	1.63(100)	1.633(100)	1.64(30)	—	—	1.634(10)	—
—	—	1.616(70)	1.610(30)	—	—	—	1.61(5)	1.61(64/33)	1.596(40)	—
1.58 (F)	(F) 1.60	1.581(40)	1.590(10)	—	—	—	—	—	—	—
1.535(F)	(F) 1.56	1.539(60)	1.56(30)	1.56(10)	1.564(14)	—	—	—	—	—
1.50 (W)	—	—	1.495(30)	1.495(30)	1.502(20)	—	—	—	—	1.523(60)
1.485(S)	(M) 1.48	1.486(90)	1.485(80)	—	—	—	—	—	1.484(70)	—
—	—	1.464(10)	1.475(50)	1.475(50)	—	1.47(50)	—	1.48(80/53)	—	—

\*The pattern of FeS given in Fig. 3(b) indicates a considerable quantity of free iron, some of whose lines are clearly visible, viz. those at 2.03A, 1.43A and 1.17A. Also, traces of the ordered phase are indicated by weak lines at 1.44A, 1.275A, 1.23A, 1.19A.

\*\*These two faint lines in the pattern of the magnetic fraction are almost certainly the residual Kβ corresponding to the two very strong lines of the pattern at 3.00A and 2.70A.

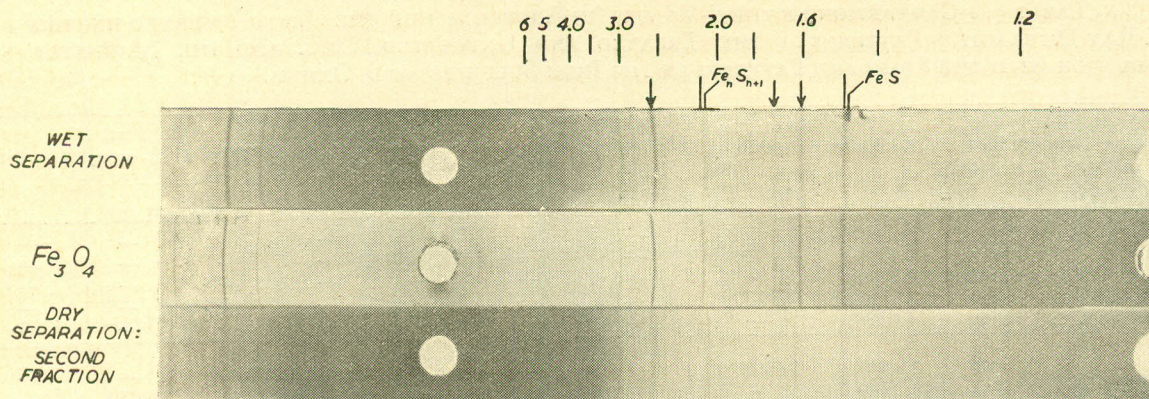


Fig. 4.—Comparison of the X-ray diffraction patterns of the magnetic fractions obtained by (i) wet and (ii) dry separation with the corresponding pattern of  $\text{Fe}_3\text{O}_4$ . Except for the two very weak lines marked  $\text{Fe}_n\text{S}_{n+1}$  and  $\text{FeS}$ , the close approximation of the wet separated sample to  $\text{Fe}_3\text{O}_4$  is at once apparent.

patterns of the treated coal and of its first magnetic fraction are at 7.00Å ( $I=70$ ), 3.53Å ( $I=60$ ), 2.99 ( $I=80$ ), 2.70 ( $I=60$ ), 2.51 ( $I=100$ ), 2.40Å ( $I=80$ ), 2.33Å ( $I=70$ ), 2.06Å ( $I=100$ ), 1.63Å ( $I=100$ ) and 1.485Å ( $I=80$ ). The lines at 7.00Å ( $I=70$ ), 3.53Å ( $I=60$ ), and about half the intensity of that at 1.485Å ( $I=80$ ) would correspond as before to kaolinite. The outstanding lines, after subtracting the contribution (approximately one-half of the intensities given in the standard) due to all the lines of kaolinite, are shown in the 5th column of Table 4, and these are to be analyzed for the iron sulphides and oxides. The line at 2.51Å is the strongest line of the  $\text{Fe}_3\text{O}_4$  and  $\alpha\text{-Fe}_2\text{O}_3$  patterns, while strong lines at (1) 2.99Å, (2) 2.70Å and (3) 2.06Å correspond respectively to (1)  $\text{FeS}$ , (2)  $\text{FeS}_2$ ,  $\text{FeS}$  or  $\alpha\text{-Fe}_2\text{O}_3$ , and (3)  $\text{Fe}_n\text{S}_{n+1}$ . It follows that  $\text{FeS}$  and  $\text{Fe}_n\text{S}_{n+1}$  are both present. A comparison of the complete data of their standard patterns with the observed pattern was next made. The presence of a line of moderate intensity at 2.65Å confirms the presence of  $\text{Fe}_n\text{S}_{n+1}$ , while the lines at 2.33Å and 2.095Å confirm the existence of  $\text{FeS}$ .

The  $\text{FeS}$  contribution to the observed pattern is seen to be nearly  $1/3$ rd of the intensities given for the standard pattern (Table 4), while the  $\text{Fe}_n\text{S}_{n+1}$  contribution is about  $3/4$ th of the corresponding standard. From these relative intensities, it follows that the quantity of  $\text{FeS}$  is about  $1/2$  that of  $\text{Fe}_n\text{S}_{n+1}$ . The presence of the very strong line at 1.63Å can only be explained by the existence of (unreacted)  $\text{FeS}_2$  in the treated coal, and this is confirmed by the strong to medium lines at 2.40Å, 1.90Å and 3.10Å, which however overlap with weak lines of the patterns of  $\text{Fe}_3\text{O}_4$ ,  $\text{FeS}$  and kaolinite, respectively. From the strengths of all the four lines, the quantity of  $\text{FeS}_2$  can be estimated as nearly equal to that of  $\text{Fe}_n\text{S}_{n+1}$ .

(ii) *Oxides of Iron*.—As mentioned earlier, the strong line observed at 2.51Å corresponds to one of the strongest lines of both  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  ( $\alpha$ - and  $\gamma\text{-Fe}_2\text{O}_3$ ). For investigating the presence of  $\alpha\text{-Fe}_2\text{O}_3$  two of its medium to strong lines, viz. those at 1.84 ( $I=70$ ) and 1.69 ( $I=80$ ), which do not overlap with the strong lines of other phases, can be used as distinguishing criteria. It is found that, although a faint line at 1.68Å does show on the pattern, the line at 1.84Å is not observable. It can thus be estimated that the quantity of  $\alpha\text{-Fe}_2\text{O}_3$  would be less than  $1/5$ th that of  $\text{Fe}_3\text{O}_4$  (and/or  $\gamma\text{-Fe}_2\text{O}_3$ , whose pattern is practically indistinguishable from that of  $\text{Fe}_3\text{O}_4$ ). Thus the major contribution to the strong line at 2.51Å must come from  $\text{Fe}_3\text{O}_4$  (and/or  $\gamma\text{-Fe}_2\text{O}_3$ ) whose presence is further confirmed by a line of medium to weak intensity at 1.475Å. From the intensities of the main lines of  $\text{Fe}_3\text{O}_4$ , many of which overlap with those of other phases, it follows that  $\text{Fe}_3\text{O}_4$  would be present in somewhat less quantity than  $\text{Fe}_n\text{S}_{n+1}$ .  $\text{FeO}$  can be taken to be absent from the magnetic fraction because none of its strongest lines is to be found in the experimentally observed pattern.

## 5. Semi-Quantitative Estimates from X-ray Data

(i) *Component Phases of the First Magnetic Fractions*.—Having recognised the presence of  $\text{Fe}_3\text{O}_4$  (and/or  $\gamma\text{-Fe}_2\text{O}_3$ ) in appreciable quantities, it now follows this phase would partly contribute to the lines at 2.99Å and 2.95Å, which correspond to the main strong lines of  $\text{FeS}$ . Therefore, it appears that the earlier estimate of the quantity of  $\text{FeS}$  is too high, and after allowance is made for the contribution from  $\text{Fe}_3\text{O}_4$  (and/or  $\gamma\text{-Fe}_2\text{O}_3$ ) to this line, the revised estimate of the quantity of  $\text{FeS}$  may be put at about  $1/3$ rd that of  $\text{Fe}_n\text{S}_{n+1}$ .

Thus it is seen that the magnetic fraction from the coal steam-treated at 400°C. contains four major iron-bearing phases, viz.,  $\text{Fe}_n\text{S}_{n+1}$ ,  $\text{FeS}_2$ ,  $\text{FeS}$  and  $\text{Fe}_3\text{O}_4$ , the percentages of these being estimated as 5, 5, 2 and 4, respectively, from internal comparison of the intensities of their lines and using as an external standard a pattern of a mixture of 5% each of  $\text{Fe}_n\text{S}_{n+1}$ ,  $\text{FeS}$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{FeS}_2$ , with (80%) untreated coal. These figures lead to an estimate of 9% iron and 6% sulphur, which are in satisfactory agreement with the chemically estimated values of 8.8% and 7.2%. Among the non-iron-bearing crystalline phases, kaolinite is the most important one, being present in quantities of the order of 30%. The rest is mostly carbon.

(ii) *Comparison with the Previously Examined Magnetic Fraction.*—The above results, which show that  $\text{Fe}_3\text{O}_4$  constitutes only one quarter of the iron-bearing compounds in the magnetic fraction, contrast with the conclusion arrived at previously that  $\text{Fe}_3\text{O}_4$  is the major crystalline phase in this fraction. Since the previously-studied material has been obtained by successive wet magnetic separations using a slow stream of water, a re-examination of this product was undertaken. A powder pattern of the old sample was taken with the 11.4 cm. diameter camera, using Cr K radiation. The pattern obtained is shown in Fig. 4 alongside of comparison patterns of  $\text{Fe}_3\text{O}_4$  and the second (i.e. middle) magnetic fraction obtained in the present study.

Although, as noted in the preliminary study,<sup>1</sup> the pattern of the old magnetic fraction appears to be essentially that of  $\text{Fe}_3\text{O}_4$ , more careful examination shows that the three lines marked with arrows are diffuse, while in the other two prominent lines at 2.10Å and 1.48Å a distinct doubling can be detected, as indicated in Fig. 4 by the paired marks.\* The stronger one of each doublet agrees with the corresponding line of  $\text{Fe}_3\text{O}_4$ , and the weaker ones are readily identified with the 2.06Å line of  $\text{Fe}_n\text{S}_{n+1}$  and the 1.47Å line of  $\text{FeS}$ , respectively. Confirmation of the existence of both these phases in addition to  $\text{Fe}_3\text{O}_4$  is obtained from the diffuseness and strength of the

2.53Å line, thus showing it to be a composite of the 2.53Å line of  $\text{Fe}_3\text{O}_4$  and the 2.54 Å line of  $\text{FeS}$ . Weak lines can also be observed on the original pattern in positions corresponding to the other strong lines of  $\text{FeS}$  and  $\text{Fe}_n\text{S}_{n+1}$ . The strongest line of  $\text{FeS}_2$  at 1.63Å also appears to make a small contribution to the diffuse line marked with an arrow at this position. From the relative intensities of the several lines of the experimentally observed pattern, the ratios of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_n\text{S}_{n+1}$ ,  $\text{FeS}$  and  $\text{FeS}_2$  can be estimated as 5:2:2:1. Comparison with the corresponding ratios 4:5:2:5 obtained above for the dry separated material show that the major part of the  $\text{Fe}_n\text{S}_{n+1}$  and the  $\text{FeS}_2$  have most probably been carried away by the water in the wet separation process.

It may be concluded that the above combination of magnetic, chemical and X-ray analysis provides an adequate estimation of the important sulphides and oxides of iron that constitute the magnetic fraction of the steam-treated coal. At the same time, this magneto-chemical study throws some light on the progress of the reactions occurring in the conversion of the  $\text{FeS}_2$  into  $\text{Fe}_3\text{O}_4$  in the low temperature range of 300°C. to 400°C. It is hoped to follow up with similar investigations on some of the other Pakistani coals and their ashes, which are presently being studied in these laboratories.

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\* These fine details were missed in the preliminary investigation reported earlier because the X-ray patterns were taken with a smaller camera and with copper radiation.