

will be of the order of 0.0005. Since  $\Delta \ln v / \Delta T$  is of the order of 0.02, the error introduced by neglecting  $\beta$  in the above equation would be more than 1%, and cannot therefore be ignored. However, this correction has only a slow variation with temperature, and is readily applied by means of equation (13).

### Appendix III

#### Correlation between the Activation Energy Graph and the $1/v^{0.26}$ linear Plots

Essentially, the problem is to find the variation of  $\epsilon/k$  corresponding to a linear plot of  $1/v^{0.26}$  against temperature. Consider, for instance, the long second segment of the graph for B.O.C. "450" oil in Fig. 3. Its equation is

$$1/v^{0.25} = 0.16 + 0.0136 (T - T_0),$$

differentiation of which gives

$$-0.25 v^{-1.25} \frac{\partial v}{\partial T} = 0.0136,$$

$$\text{whence } \frac{\epsilon}{k} \approx -\frac{T^2}{v} \frac{\partial v}{\partial T} = T^2 \times \frac{0.0136/0.25}{v^{-0.25}}$$

$$= T^2 \times \frac{0.0544}{0.16 + 0.0136(T - T_0)}$$

Table 5 on page 118 gives the values of  $\frac{\epsilon/k}{1000}$  calculated from this relation over the range 30°C. to 80°C., together with the first differences. It is evident that the corresponding graph of  $\frac{\epsilon/k}{1000}$  against temperature will have a pronounced downward convexity, which is in agreement with the second mode of analysis of the  $\epsilon/k$  curves into segments.

## PRELIMINARY STRUCTURAL STUDY OF THE MAGNETIC FRACTION OF STEAM-TREATED MAKERWAL COAL

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### Introduction

In the course of their studies in the desulphurization of Makerwal and other sulphuraceous coals of West Pakistan by treatment with super-heated steam, Siddiqui et al.<sup>1</sup> noted that the beneficiated coal residue contains 5 to 10% of a strongly magnetic component. This component could be removed by simple magnetic separation, and it was found that it carried away a considerable fraction of the residual sulphur, thus providing a basis for additional beneficiation of the coal. The present communication deals with an account of a preliminary investigation in the composition and structure of this magnetic fraction.

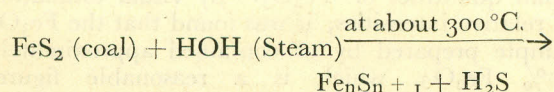
#### Two Possible Paramagnetic Compounds

Since it was known that the original coal contained both sulphur and iron, all the iron being

in the form of pyrites, it was at first thought that the magnetic property was due to the formation of compounds of the series  $Fe_nS_{n+1}$ , which are known to be strongly paramagnetic. Non-stoichiometric compounds of iron and sulphur, both ferromagnetic and paramagnetic, are known to occur naturally and have even been prepared synthetically; but they form a somewhat peculiar class of compounds and their structure and magnetic behaviour are not fully understood. FeS and FeS<sub>2</sub> are the two well-established compounds of iron with sulphur, but they are both non-magnetic and have structures of the nickel-arsenide and pyritic types, respectively. The compounds, Fe<sub>0.48</sub>S<sub>0.52</sub> to Fe<sub>0.466</sub>S<sub>0.534</sub> (corresponding to Fe<sub>12</sub>S<sub>13</sub> to Fe<sub>7</sub>S<sub>8</sub> approximately), have been reported as being ferromagnetic in character, with a nickel-arsenide structure, whereas the compounds in the composition range between Fe<sub>0.50</sub>S<sub>0.50</sub> and Fe<sub>0.48</sub>S<sub>0.52</sub> (corresponding to FeS to Fe<sub>12</sub>S<sub>13</sub> approx.) are reported to be



paramagnetic, again with a nickel-arsenide structure in the high sulphur half of the field but with a superstructure in the region near the ideal composition FeS. M.J. Buerger's<sup>2</sup> work, however, throws doubt on the reported structures and it is not safe to say anything about the structure of  $Fe_nS_{n+1}$ , except that the reported structural studies indicate that the lattice of  $Fe_nS_{n+1}$  is substantially different from that of  $FeS_2$ . So the conversion of  $FeS_2$  into  $Fe_nS_{n+1}$  through any reaction of the type



would be associated with a rather improbable structural transition.

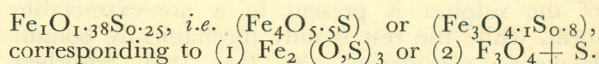
The other simple compound of iron that has a high value of magnetic susceptibility is  $Fe_3O_4$ . However, the production of  $Fe_3O_4$  by simple superheated steam-treatment also seems somewhat unlikely, because the conversion of  $FeS_2$  into  $Fe_3O_4$  is known to occur only at a temperature round about  $500^\circ C.$ , whereas the magnetic fraction under study was reported to have been obtained at a much lower temperature (around  $350^\circ C.$ ).<sup>1</sup> Thus we have to decide between two possibilities, both of them apparently unlikely. This anomalous situation led to the present detailed study of the problem.

### Chemical Analyses

To begin with, an effective separation of the magnetic component from the adhering coal was attempted. It was done initially by the ordinary dry method with a magnet, but because of the "carrying-down" tendency of coal the separation

had to be carried out by the wet gravity method, followed by a further antigravity separation in the dry state by playing a magnet over a 250 mesh sieve. A magnetic fraction of reasonable "purity" was thus obtained. Preliminary chemical analyses of this fraction indicated that it does indeed contain sulphur and iron in large quantities with a comparatively small percentage of carbon. But this did not account for the total weight of the magnetic component, and there appeared to be a considerable quantity of oxygen in chemical combination. Two typical analyses of samples of the magnetic fraction are given in Table I together with the mean of half a dozen analyses.

From the above analyses it was clear that, compared with sulphur, the oxygen constitutes the major component of the magnetic fraction. Ignoring carbon as a mechanical impurity, the following approximate empirical formula could be derived from the above analyses :



From this, it appeared that the magnetic component is essentially an iron oxide with a small quantity of sulphur, either incorporated in the lattice or else adsorbed. The fact that the empirical formula approximates to  $Fe_3O_4$ , (the magnetic oxide), taken together with the high magnetizability of the material, gave considerable support to this idea.

There remained now the problem of the precise status of the sulphur in the iron oxide (probably  $Fe_3O_4$ ) lattice comprising the magnetic fraction.

In order to examine this, repeated extractions of the sulphur were attempted in a Soxhlet ap-

TABLE I.—TYPICAL ANALYSES OF THE MAGNETIC FRACTION.

(Samples oven-dried at  $105^\circ C.$ )

	Analysis I (weight %)	Analysis II (weight %)	Mean of six analyses (weight %)	Mean weight % Atomic weight
Iron	53.9	58.9	56	1.00
Sulphur	5.1	8.2	8	0.25
Carbon (by combustion)	41.0	13.0	14	1.17
Oxygen (by difference)				



paratus, using carbon tetrachloride as the solvent. It was found that each extraction removed successively smaller quantities of the sulphur, as indicated in Table 2.

TABLE 2.—SUCCESSIVE EXTRACTIONS OF SULPHUR

(Initial Sulphur Content=8%)

Serial No. of extraction	1	2	3
Sulphur removed in this extraction (weight % of initial sample)	0.28	0.12	0.10
Total sulphur removed	0.28%	0.40%	0.50%

From this table, it may be estimated by extrapolation that, even after a very large number of such extractions, a fair quantity of sulphur (about 4%) would remain in the magnetic fraction. The conclusion suggested by this is that a portion of the sulphur is present in a non-extractable form, while the rest is only mechanically bound. However considering the fact that adsorbed sulphur is frequently very difficult to dislodge by extraction, further work for clarifying this point was taken up by X-ray diffraction, which presents perhaps the simplest way of determining whether or not the sulphur is chemically combined.

#### X-ray Diffraction Analysis

For this analysis, it was necessary to take X-ray powder patterns of the magnetic component and to compare them with those of (i)  $\text{FeS}_2$

(ii)  $\text{Fe}_n\text{S}_{n+1}$  (iii)  $\text{Fe}_3\text{O}_4$  (iv)  $\text{Fe}_2\text{O}_3$ , all of which can be suspected to contribute to the structure. Reproductions of these patterns are shown in Fig. 1, from which it is quite clear that the pattern of the magnetic fraction agrees only with that of  $\text{Fe}_3\text{O}_4$ . However, there is one noticeable difference in that there is an extra line of low intensity at  $d=2.71 \text{ \AA}$  in our standard pattern of  $\text{Fe}_3\text{O}_4$ . This line coincides with the strongest line of the  $\alpha\text{-Fe}_2\text{O}_3$  pattern (Table 3), and could be due to the well-known contamination of  $\text{Fe}_3\text{O}_4$  with small quantities of  $\text{Fe}_2\text{O}_3$ . By visual estimation of relative intensities, it was found that the  $\text{Fe}_3\text{O}_4$  sample prepared by us contained approximately 10%  $\text{Fe}_2\text{O}_3$ , which is a reasonable figure. Another possible explanation of the extra line could be that it is due to the presence of some  $\gamma\text{-Fe}_2\text{O}_3$ , the remaining lines of whose pattern are practically indistinguishable from those of  $\text{Fe}_3\text{O}_4$ , as can be seen in Table 3.

It follows from the above data that the magnetic fraction of the treated coal consists essentially of  $\text{Fe}_3\text{O}_4$ , with a possibility of some  $\gamma\text{-Fe}_2\text{O}_3$ , but no detectable  $\alpha\text{-Fe}_2\text{O}_3$ .

#### Conclusion

In the light of the foregoing observations, it may be concluded that the bulk of the pyritic material present in Makerwal coal is converted into  $\text{Fe}_3\text{O}_4$  by the previously reported process of high temperature steam treatment. The different stages of the reaction  $\text{FeS}_2 + \text{H}_2\text{O}$  (steam)  $\rightarrow \text{Fe}_3\text{O}_4$  are given in the literature,<sup>3</sup> and are reported to proceed as follows:—

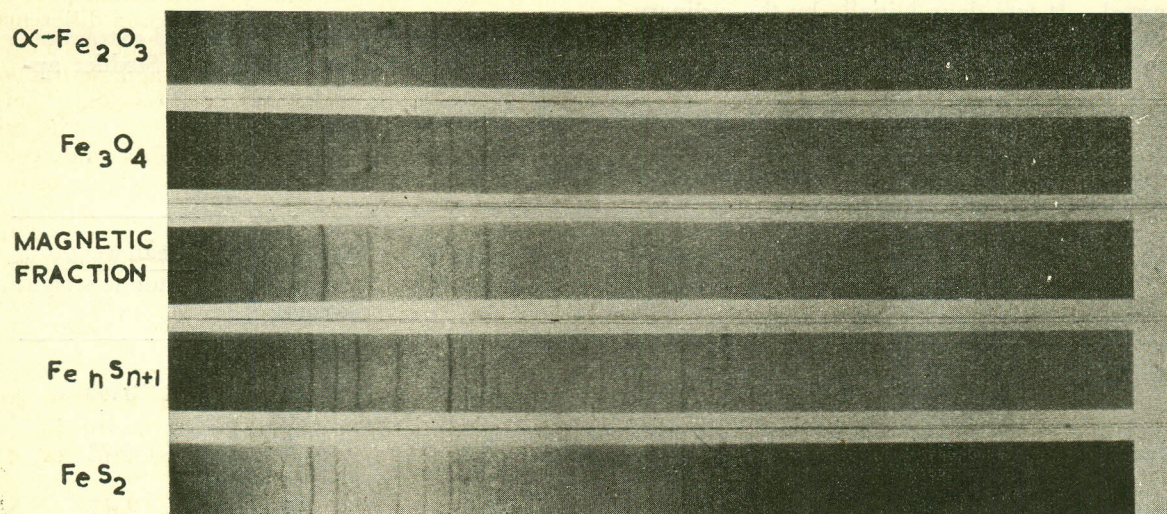


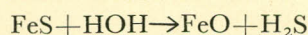
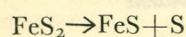
Fig. 1.—Comparative X-ray patterns for the structural analysis of the magnetic fraction. (9 cm. powder Camera, Cu K  $\alpha$  radiation).



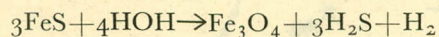
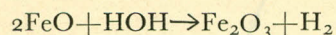
TABLE 3.—THE PROMINENT POWDER LINES (HAVING INTENSITIES  $(I/I_0)$  GREATER THAN 10%) OF :  
(1)  $\alpha$ - $\text{Fe}_2\text{O}_3$ , (2)  $\gamma$ - $\text{Fe}_2\text{O}_3$ , (3)  $\text{Fe}_3\text{O}_4$  AND (4) THE MAGNETIC FRACTION.

(The figures in brackets denote the intensities of the lines)

Lines of $\alpha$ - $\text{Fe}_2\text{O}_3$ (Angstroms)	Lines of $\gamma$ - $\text{Fe}_2\text{O}_3$ (Angstroms)	Lines of $\text{Fe}_3\text{O}_4$ (Angstroms)	Observed lines in the magnetic fraction (Angstroms)
3.68(70)	2.95(34)	2.97(28)	2.97(30)
2.69(100)	2.78(19)		
2.51(80)	2.52(100)	2.53(100)	2.53(100)
2.20(70)		2.42(11)	
2.07(10)	2.08(24)	2.10(32)	2.10(20)
1.837(70)	1.70(12)	1.71(16)	1.70(20)
1.691(80)	1.61(33)	1.61(64)	1.61(40)
1.634(10)	1.48(53)	1.48(80)	1.48(60)
1.596(40)	1.27(11)	1.28(20)	
1.484(70)		1.12(10)	
1.451(80)	1.09(19)	1.09(32)	1.095(10)
1.348(20)		1.05(10)	1.047(10)
1.309(40)			
1.255(30)			
1.224(10)			
1.205(10)			
1.187(30)			
1.160(30)			
1.137(40)			
1.100(40)			
1.053(50)			

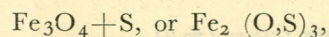


(cf. large quantities of  $\text{H}_2\text{S}$  that are given off in our desulphurization process).



The occurrence of these reactions at a temperature of  $350^\circ\text{C}$ . instead of the reported figure of  $500^\circ\text{C}$ . may perhaps be attributed to the catalytic action of some other constituent of the coal.

There remains the possibility of the formation of small quantities of  $\text{Fe}_n\text{S}_{n+1}$  and  $\gamma$ - $\text{Fe}_2\text{O}_3$  in addition to  $\text{Fe}_3\text{O}_4$ . On the basis of the empirical formulae deduced earlier, *viz.*



it appears highly probable that the compound

formed is ferroso-ferric oxide. The pronounced ferromagnetism of the material does not however preclude the possibility of some  $\gamma$ - $\text{Fe}_2\text{O}_3$ , but the possibility of its formation in large quantities is ruled out by the fact that the diffraction patterns of  $\gamma$ - $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  do show certain differences (Table 3), and no trace of the 2.78A line of  $\gamma$ - $\text{Fe}_2\text{O}_3$  is observed in the pattern of the magnetic fraction (Fig. 1). The complete absence of  $\text{Fe}_n\text{S}_{n+1}$  also cannot be claimed with any certainty as its presence to the extent of 5% could pass undetected because of the limitations of the available techniques. With improved methods, it is hoped subsequently to present a fuller description of the status of the sulphur contained in the magnetic fraction.

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3. E. Von Grunert, J. prakt. Chem. (N.S.), **122**, 1 (1929).