

## QUANTITATIVE AND STRUCTURAL ANALYSIS OF KALABAGH IRON ORE BY PHYSICO-CHEMICAL METHODS WITH REFERENCE TO ITS BENEFICIATION

### Part IV.—Experiments on Beneficiation of Kalabagh Iron Ore

A.H. CHOTANI, SADIQ A. AHMAD, ISHTIAQ ALI, S.H. RIZVI AND MAZHAR MAHMOOD QURASHI

*Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi*

#### Introduction

The analytical and structural studies on the random and representative iron ore samples from the Kutch Khartop region of the Kalabagh ore-fields reported in earlier communications<sup>1,2</sup> of this series showed that the ore is of a low grade, and that its iron content is distributed almost equally over four different phases, namely hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), siderite (FeCO<sub>3</sub>), limonite (Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O·nH<sub>2</sub>O) and chamosite (3(Fe,Mg)O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·nH<sub>2</sub>O). The present communication deals with investigations directed towards the development of an efficient and economical method for the beneficiation of this ore, which contains an average of 34% iron. To start with, a combination of the commoner ore-dressing techniques were employed in this study, and, since a representative sample was not at first available, the earlier experiments were carried out with hand-picked samples (54% Fe) supplied by Mr. A. Karim from the area leased out to him, (cf. Fig. 2 (a) in Part II).<sup>1</sup>

#### Beneficiation of Hand-Picked Samples

The hand-picked sample from the source referred to above appeared to be comparatively simple in its composition, being 75% hematite,<sup>2</sup> and it was therefore expected to be amenable to the usual methods of beneficiation. The samples had a very friable character, and simple crushing followed by one pass through a disc grinder with about 0.4 mm. clearance between discs gave a fine material, 60% of which passed through a 72 mesh sieve. The ground material was treated in a laboratory flotation unit, using water as the medium with very slight frothing produced by blowing air, and the heads and

tailings were found to show a difference of 6% in iron content, which was considered promising. Thereafter, a second run was made with considerable air-frothing in the flotation cell. The results of these two experiments, which are given in Table 1, point to a very definite beneficiation of the ore.

Roasting followed by magnetic separation gave a 65% iron content in the heads. With these encouraging results, the work was extended to the beneficiation of the representative sample, subsequently obtained from the Kuch-khartop area,<sup>1</sup> and the following methods were successively tried out on it: (a) dry sieving; (b) wet screening; (c) froth-flotation, using a mixture of frothing reagents; (d) roasting; (e) wet heating.

#### Beneficiation of the Mean Representative Sample by Wet and Dry Sieving and Flotation

(a) *Dry Sieving.*—The ore sample was crushed and ground, and then sieved using standard B.S. sieves (16, 25, 30, 45, 52, 60, 72, 85, 100, 120 mesh) arranged one over the other in cascade formation, the whole assembly being shaken electrically for twenty to thirty minutes. Analysis of these sieve fractions did not show any significant variations in their iron content.

(b) *Wet Screening.*—Wet screening of the mean sample was next tried with B.S. sieves of 52, 60, 72, 85, 100, 120 and 150 mesh. The actual operation consisted of taking the sample on a sieve and spraying water over it from a shower. The material retained over the sieve was collected as heads and the washings were collected as tailings. Their respective iron contents were estimated,

TABLE 1.—CONCENTRATION OF HAND-PICKED SAMPLE BY FLOTATION.

Treatment	None	Flotation with partial frothing		Flotation with air frothing		
		Heads	Tails	Heads	Middlings	Tailings
% iron content	54	about 58	about 52	63 ±2	62 ±2	46 ±3

and the process was repeated with all the sieves individually. The difference in the iron contents between the heads and the tailings was in each case very small, the maximum observed being about 1%. There was, however, a marked colour change in the sample, the heads being considerably darker than the tailings. X-ray powder photographs of the heads and tails, however, gave almost identical patterns.

(c) *Froth Flotation*.—Using a standard frothing reagent consisting of stearic acid, washing soap, starch soluble, and calcium oxide, a beneficiation of only 1 to 2% in iron content could be attained. Simple water classification and tabling methods were also tried, but without any significant success. These results indicated that, even with recycling of material in the successive wet screening and flotation procedures, no worthwhile beneficiation and recovery of iron was likely to be attained.

These unsuccessful attempts at beneficiating the representative ore contrasted significantly with the earlier experiments made on the hand-picked sample. At this stage, therefore, it appeared necessary to review the characteristics of the two ore samples, with particular reference to their composite phases. As reported earlier,<sup>2</sup> the mean representative sample contains, in addition to hematite, several other equally important iron-bearing phases, namely, siderite, chamosite and limonite, whereas the hand-picked sample is mostly hematite. The hematite, siderite and limonite are all very rich in iron, while chamosite which can be considered as a ferruginous clay, contributes the gangue material in the representative ore, and any method of beneficiation can thus be effective only to the extent it succeeds in separating out this phase. Chamosite appears, however, to be intimately disseminated throughout the ore, a fact which is confirmed by its presence in almost equal proportions (estimated from X-ray powder patterns) in the heads and tailings obtained from the wet screening separation.

Thus chamosite presents the main problem in the process of beneficiation, and as suggested by some earlier workers<sup>3</sup> it may be possible only through chemical means. However, siderite ( $\text{FeCO}_3$ ) and limonite ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ), which are both present in the ore in appreciable quantities, provide a possibility of effectively enriching the ore by its thermal decomposition into iron oxide with release of carbon dioxide and water, respectively.

#### **Beneficiation by Dry Roasting**

Small samples of the ore were roasted, out of contact with air, for half an hour at three different

temperatures, namely 450°C., 600°C. and 800°C. These roasted products became black in colour, and were found to contain a magnetic component, which could be magnetically separated. The nature of the magnetic component and the relation of the phase transformations with temperature can best be observed in X-ray powder patterns, which are shown in Fig. 5 of the preceding communication.<sup>2</sup> It is seen that, with the increase in roasting temperature, there is an increasing transformation into the magnetic oxide accompanied by a corresponding decrease in the intensity of the lines due to hematite, siderite, limonite and chamosite, indicating the progressive breakdown of these phases. From a study of the intensity of the characteristic lines, the percentages of the different iron bearing phases have been estimated, and are given in Table 2 together with the chemical analysis for iron. Both these estimates are probably accurate to  $\pm 1\%$  iron. It may be noted that, although the intensity of the chamosite line has been considerably reduced by roasting at 600°C. and 800°C., the calculated percentages of iron in the roasted ores have had to be estimated on the basis of 30% chamosite in all the cases, due to the fact that, although the chamosite is attacked, it is not converted into one of the oxides.

This table shows that roasting out of contact with air at about 800°C. results in a marked beneficiation of the ore up to nearly 50% iron content. In order to push up the iron content still further, the roasted material was passed through a magnetic separator and it was found that because of its highly ferro-magnetic character, the material roasted at 800°C. could best be handled under the influence of the residual magnetism of the separator (*i.e.* with magnetising current switched off), when about 30% could be separated as the more magnetic component. This highly magnetic component analysed for 54% iron, and on recycling gave a fraction with an iron content of 59% but the recovery of iron in this case was quite low (about 20%).

The dry heat treatment of the ore in a non-oxidising atmosphere is thus seen to be of importance in that it can raise the iron percentage to a high value of over 50%, with practically no loss of the ore as tailings. This beneficiation is apparently brought about without release of the iron present in the chamosite. It was, therefore, considered of interest to study the effects of a related heat treatment, namely reaction with superheated steam at temperatures upto 450°C. which in the course of studies in sulphuraceous coals had been found to produce the transformation of iron pyrites into the magnetic oxide. 4

**Beneficiation by Steam-Treatment**

Steam from a superheater was passed into a metal reaction vessel maintained at four different temperatures of 300°C., 350°C., 400°C. and 450°C., respectively, one kilogram of the ore being treated in each batch. These treated products were black in colour like the ones obtained on dry heating, and were found to be paramagnetic. In order to identify the various phases, and to study the course of the phase transformation, X-ray powder photographs of the samples were again taken (Fig. 1) and they showed

that only a small fraction of the hematite remains unconverted into the magnetic oxide. Table 3 gives an approximate estimate of the percentages of the different iron-bearing phases in the ore as obtained from the intensities of their characteristic lines. (The chamosite contribution to the percentage of iron has (as in Table 2) been estimated on the basis of 30% in each case, although the intensity of its line shows a diminution.) The last column indicates the percentage of material removed by playing a small horse-shoe magnet over the treated material. From a comparison of Fig. 5 of the preceding communi-

TABLE 2.—X-RAY ANALYSIS OF REPRESENTATIVE SAMPLE AFTER ROASTING.

Sample Treatment	% of the simple iron-bearing phases				Intensity of chamosite line at $d=6.94\text{\AA}$	Calculated % iron	% iron from chemical analysis
	$\text{Fe}_3\text{O}_4$	$\text{FeCO}_3$	$\alpha\text{-Fe}_2\text{O}_3$	$\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$			
Representative ore (untreated)	—	20	15	10	30	35	34
Ore roasted at $450 \pm 40^\circ\text{C}$ .	5	20	20	—	30	36	36
Ore roasted at $600 \pm 40^\circ\text{C}$ .	42	—	7	—	(10)	45	46
Ore roasted at $800 \pm 40^\circ\text{C}$ .	53	—	—	—	(<10)	49	50

TABLE 3.—X-RAY ANALYSIS OF REPRESENTATIVE SAMPLE AFTER HIGH TEMPERATURE STEAM TREATMENT.

Sample treatment	% of the iron-bearing phases				Intensity of the chamosite line of $d=6.94\text{\AA}$	Calculated % iron	% of magnetic part*
	$\text{Fe}_3\text{O}_4$ (or $\gamma\text{-Fe}_2\text{O}_3$ )	$\text{FeCO}_3$	$\alpha\text{-Fe}_2\text{O}_3$	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$			
Representative ore (untreated)	—	20	15	10	30	35	—
Steam-treated at $300 \pm 10^\circ\text{C}$ .	5	15	20	5	20	37	60
Steam-treated at $350 \pm 10^\circ\text{C}$ .	27	7	10	—	10	39	83
Steam-treated at $400 \pm 10^\circ\text{C}$ .	40	7	6	—	(<10)	46	88
Steam-treated at $450 \pm 10^\circ\text{C}$ .	50	—	3	—	(<10)	48	100

\* These values have been estimated through separation of the magnetic component by playing a small horse-shoe magnet over a weighed (10 g. in each case) quantity of the treated samples.

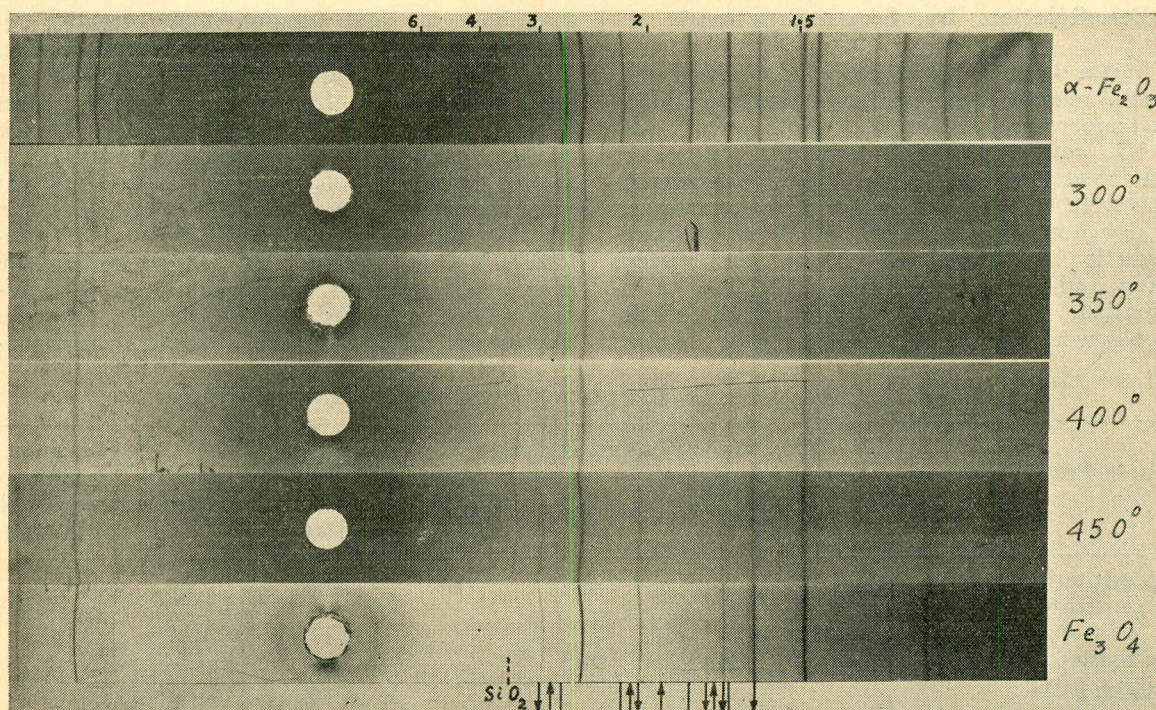


Fig. 1.—Powder patterns of steam-treated samples of ore compared with those of  $\alpha\text{-Fe}_2\text{O}_3$  (hematite) and  $\text{Fe}_3\text{O}_4$ . The directions of the arrows indicate increasing intensity of the corresponding lines. Steam treatment at  $450^\circ\text{C}$ . gives a pattern in between those for dry roasting at  $600^\circ\text{C}$ . and  $800^\circ\text{C}$ ., cf. Fig. 5 of Part III. (Patterns taken with filtered Cr K  $\alpha$  radiation).

cation and Fig. 1, it becomes apparent that the ore treated with steam at  $450^\circ\text{C}$ . is in a condition comparable with that of the dry roasted ore at  $700^\circ\text{C}$ . Thus a considerable reduction in the temperature of treatment can be effected by the use of super-heated steam. Furthermore, magnetic separation can, again in this case, be useful for increasing the degree of beneficiation still further. It was found that the steam-treated samples were comparatively weakly magnetic and the residual magnetism of the magnetic separator (*i.e.* when the magnetising current was switched off) was not enough to effect a separation. This might point to the production of some  $\gamma\text{-Fe}_2\text{O}_3$  as the magnetic phase in place of  $\text{Fe}_3\text{O}_4$ .

#### Synopsis of Beneficiation Obtained by the Simple Ore-Dressing Methods

The results of the beneficiation by the different methods that have been tried out above on this ore are summarised in Table 4, and the most suitable combinations of methods have also been indicated.

This table indicates that the maximum economically feasible limit of beneficiation of this ore

by the simple methods of beneficiation is 16-18% without magnetic separation, giving a concentrate containing 50-52% iron. Further enrichment of this ore to over 56% iron is also possible by magnetic separation but in this case about half the material gets lost as tailings.

#### Beneficiation by Chemical Methods

Out of several chemical methods examined, nitric acid leaching has been found to be most suitable and economical for this ore. When the ore is treated with nitric acid, all the metal elements form their respective nitrates, which go into solution, leaving behind just a small fraction as insoluble residue. The solution containing iron and aluminium nitrates as its major constituents is then thermally decomposed at a suitable temperature. As there is a wide difference in the decomposition temperatures of these metal nitrates<sup>5-8</sup> (ferric nitrate decomposes at a low temperature of  $115\text{-}135^\circ\text{C}$ . as against the higher decomposition temperatures of  $160^\circ\text{C}$ . to  $190^\circ\text{C}$ . for  $\text{Al}(\text{NO}_3)_3$  and  $600^\circ\text{C}$ . for  $\text{Ca}(\text{NO}_3)_2$ ), it is possible to decompose just the ferric nitrate into ferric oxide, which can be separated out. In this process the other decomposition product, nitrogen pentoxide, can be easily recovered as

nitric acid by absorption in water, and recycled, reducing thereby much of the recurring consumption of nitric acid. A small-scale laboratory operation was carried out as follows:

The powdered ore (176 g.) was initially roasted at about 600°C., cooled and then mixed at room temperature (33°C.) with 600 ml. of 25% nitric acid, which was about 10% in excess of the quantity required for dissolving the total iron content of the ore. The reaction being exothermic, the temperature of the solution went up to nearly 85°C. The solution was continuously agitated and, when after a quarter of an hour, the reaction slowed down, the solution was heated for another quarter of an hour, cooled and then filtered. The filtrate containing the metal

nitrate was then auto-claved in the presence of excess of water at a pressure of 30-40 lb./sq. inch, the inside temperature of the autoclave being 140-160°C. At this temperature the ferric nitrate decomposed into ferric oxide and the nitrogen pentoxide set free reacted with the excess of water to form nitric acid.

The ferric oxide was obtained as a precipitate, which was filtered, washed, and then ignited at 500°C. to remove the combined water. Some idea of the efficiency of this method can be obtained from Table 5(a), which gives the results of three separate experiments. The recovery of iron from the ore is remarkably high, being close to 80% in the present experiments, and the ferric oxide is obtained in quite a pure form as shown

TABLE 4.—SYNOPSIS OF BENEFICIATION BY THE SIMPLE ORE DRESSING TECHNIQUES.

Serial No.	Process of beneficiation tried	% enrichment of iron content	Estimated tailing loss	Possible combination of processes with % enrichment attained
1	Grinding and dry sieving ..	< 0.5	—	(a) Combination of either 2 or 3 with 4 or 5: enrichment of 16 to 18% iron content, tailing loss=1/3
2	Grinding and wet screening ..	1-2	1/3	
3	Flotation .. ..	1-2	1/3	(b) Combination of either 2 or 3 with 4 or 5, followed by magnetic separation: enrichment of 20-22%, tailing loss=1/2.
4	Roasting at 600-800°C. ..	12-16	nil	
5	Steam treatment at 450°C. ..	15	nil	
6	Magnetic separation of roasted material	5-8	1/3	

TABLE 5 (a).—RECOVERY OF IRON BY LEACHING WITH 25% HOT NITRIC ACID.

Expt.	Quantity of ore(g.)	Theoretical iron content(g.) of ore sample (calculated as Fe <sub>2</sub> O <sub>3</sub> )	Weight of (Fe <sub>2</sub> O <sub>3</sub> ) precipitate after ignition(g.)	Percentage recovery of Fe <sub>2</sub> O <sub>3</sub>	
1	176	84.0	66.6	79.2%	Mean 79.4%
2	72	34.3	26.1	76.1%	
3	65	31.0	25.7	82.8%	

TABLE 5 (b).—ANALYSIS OF FERRIC OXIDE OBTAINED BY NITRIC ACID LEACHING OF THE ORE.

Recovered Fe <sub>2</sub> O <sub>3</sub> from:	Iron%	Silicon%	Aluminium%
Expt. 1, table 5 (a)	66.7	1.26	1.60
Expt. 2, „	69.1	0.28	traces
Expt. 3, „	64.8	2.80	1.08

by the analysis given in Table 5(b).

### Summary

The results of the present studies in the Kalabagh iron ore may be summed up as follows:

(a) Richer than average hand-picked samples of Kalabagh iron ore are readily amenable to considerable beneficiation by routine ore-dressing methods, and yield a product having 62% to 65% iron, which can (in all probability) be smelted by one of the simple and inexpensive direct reduction processes.

(b) The mean representative sample from the Kutch Khartop area is much more difficult to beneficiate, presumably due to the finely disseminated chamosite. However, by using a combination of flotation, roasting in a non-oxidizing atmosphere (which does not liberate the iron), and magnetic separation, it is possible to attain an iron content of 52-56% with over 50% recovery.

(c) It appears likely that the tailings from the magnetic separation can be leached profitably with 25% nitric acid, from which the iron oxide can be recovered in over 95% purity by decomposition at about 150°C. The recovery of iron, by this method is found to be nearly 80%. However, it is necessary to examine the economics of this method in relation to the non-chemical beneficiation suggested at (b) above, and other

iron-making processes, some of which are being investigated in these laboratories.

### Acknowledgements

The authors are grateful to Dr. Salimuzzaman Siddiqui and to Mr. H.R. Amundsen for a number of very valuable suggestions, to Mr. Abdul Hai and Mr. Razaul Karim for carrying out the magnetic separation and flotation experiments, to Mr. Momin and Mr. Ain-ul-Hasan for help with the water classification, and to Mr. S.M. Ishaq Ali for setting up the ore-dressing equipment.

### References

1. H.R. Amundsen, A.H. Hashim, A. Hai and S.H. Rizvi, *Pakistan J. Sci. Ind. Research*, **1**, 207 (1958).
2. M.M. Qurashi, S.H. Rizvi and M.L. Ahmad, *ibid.*, **1**, 265 (1958).
3. *Reports on the Progress of Applied Chemistry*, Vol. XL (1955) p. 178, 190.
4. S.J. Qadir and S.H. Rizvi, *Pakistan J. Sci. Ind. Research*, **1**, 128 (1958).
5. E.S. Nossen and N.J. Paterson, U.S. Patent No. 2,737,445 (1956).
6. J.W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, vol. XIII, p. 832.
7. *Handbook of Physical and Chemical Constants* (1943), p. 337.
8. Thomas C. Gregory, *The Condensed Chemical Dictionary* (1919), p. 63.