STUDIES ON INDIGENOUS IRON ORES

Part I.—Effect of Heat in Presence of Carbon Dioxide, Nitrogen and Air

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The effect of heat on Makerwal, Chichali (East) and Chichali (West) iron ores of sizes 3–4 in and –200 mesh, in an atmosphere of CO_2, N_2 and air—the primary components of blast-furnace gases—over a temperature range of 200–1200°C with a view to reduce the Fe^{++} contents of the ore, has been studied. The ferrous content of the heated ores sharply falls after 600°C. This means that the FeO, which is an undesirable product, can be reduced to a minimum simply by heating the ore at 600°C and that this could presumably pave the way for an economical metallurgical process.

Also studied are the magnetic properties acquired on heating and the possibility of the magnetic separation of the iron oxides. The approach does not appear to be promising as most of the iron is lost in the non-magnetic part of the iron ore.

Introduction

Work on the Kalabagh iron ores was started in these laboratories sometime in 1958. Both physical[1–3] and chemical approaches were made to determine the different phases and constituent elements of the ore. The physical methods mostly dealt with the X-ray study of the different phases present in the original and the roasted ores, while the chemical methods[4] which consisted of leaching with nitric acid, froth flotation or roasting and thereafter separating the magnetic portion by a powerful magnet, were carried out, with a view to enrich the iron ore. All these approaches particularly the X-ray study have undoubtedly given a better understanding of the nature of the ore but do not give sufficient information to develop a metallurgical process for the indigenous ores.

Though it has already been shown that simple roasting[4,5] or sintering helps decomposing siderite and breaking up the siliceous part of the ore into its components, it remains to be seen at what temperature the FeO contents of the ore can possibly be reduced to a minimum, and what is the precise effect of the heat on the different phases of iron present in the ore.

The present study therefore covers the effect of heat on the different ores namely Makerwal, Chichali (East) and Chichali (West), in the presence of N_2,CO_2 and the air over a temperature range of 200–1200°C.

Experimental Procedure

The three types of the iron ores mentioned above were examined. The ores in 3–4 in and –200 mesh size were heated at different temperatures ranging from 200–1200°C, in an atmosphere of CO_2,N_2 and air, flowing past the sample, at the rate of 2 l/min. The respective samples were then cooled, a small portion was detached and ground to about –100 mesh. For ferrous determination, about 50 ml of the concentrated HCl was added and the contents boiled in an atmosphere of CO_2 for 1 hr. The Fe^{++} contents were estimated by titrating against standard potassium dichromate solution using diphenylamine as indicator.[7] The results obtained are shown in Figs. 1 and 2a–c where the Fe^{++} percentage is plotted against temperature in various atmospheres such as CO_2, N_2 and air.

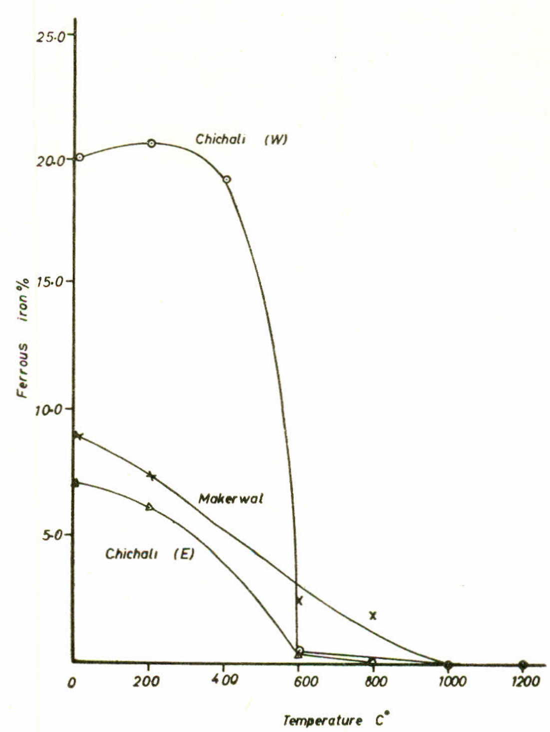

Fig. 1a.—Effect of heat on ferrous contents of the ores in the presence of CO_2. (Lump size 3–4")

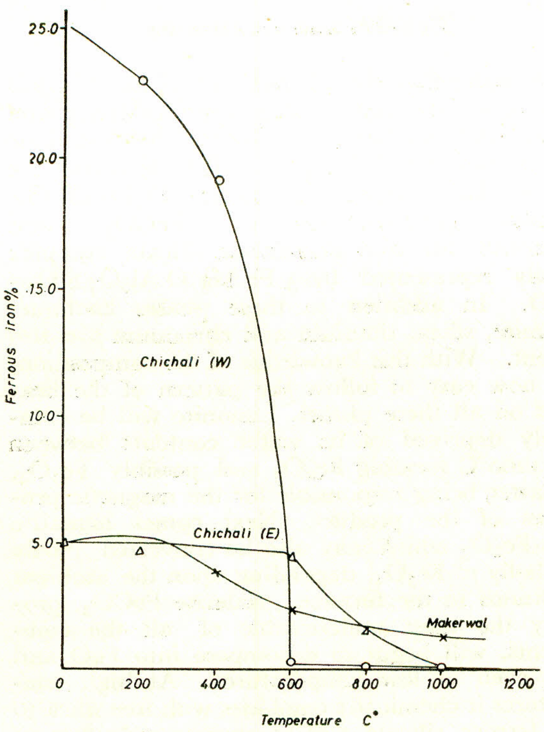

Fig. 1b.—Effect of heat on ferrous contents of the ores in the presence of N_2. (Lump size 3–4″)

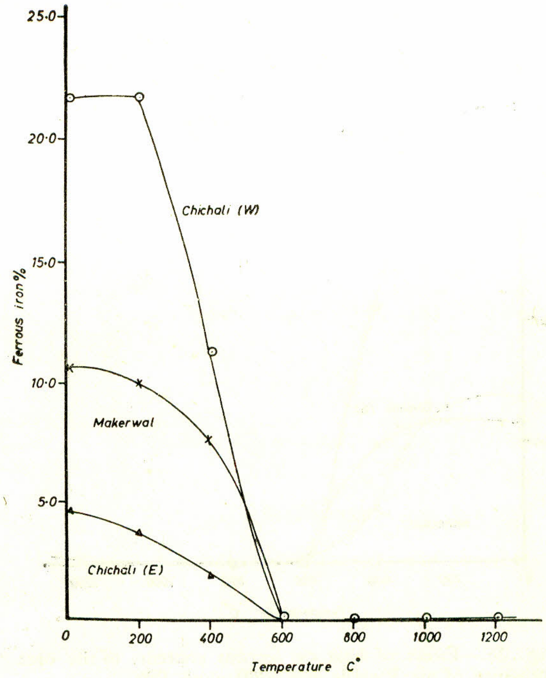

Fig. 2a.—Effect of heat on ferrous contents of the ores in the presence of CO_2. Particle size −200 mesh BSS.

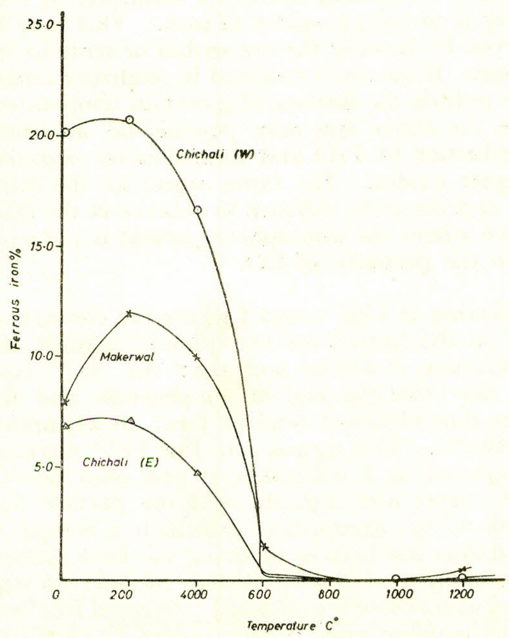

Fig. 1c.—Effect of heat on ferrous contents of the ores in the presence of air. (Lump size 3–4″)

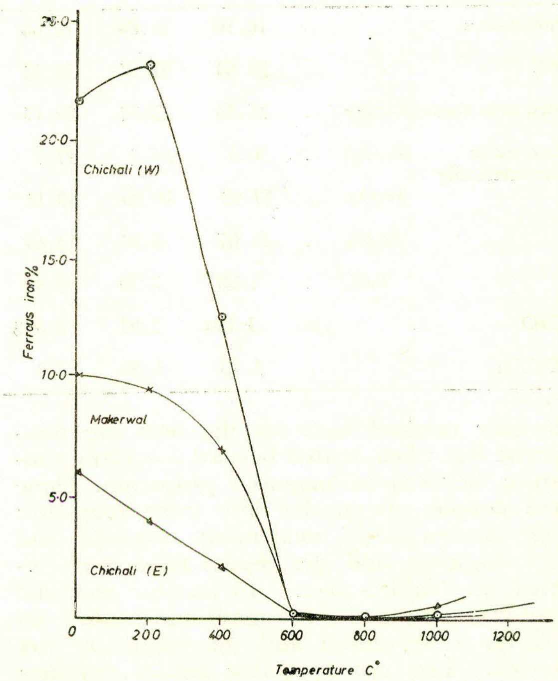

Fig. 2b.—Effect of heat on ferrous contents of the ores in the presence of N_2. Particle size −200 mesh BSS.

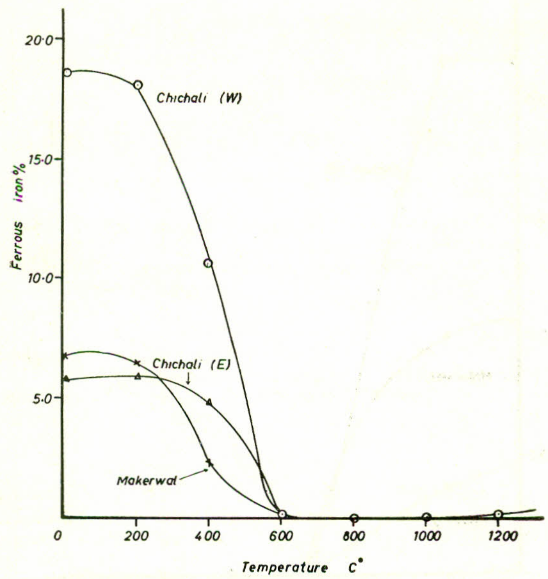

Fig. 2c.—Effect of heat on ferrous contents of the ores in the presence of air. Particle size -200 mesh BSS.

TABLE 1.—CHEMICAL ANALYSIS OF IRON ORE.

Components		Composition (%)		
		Makerwal	Chichali (East)	Chichali (West)
1. Ignition loss	..	10.16	11.84	12.64
2. SiO_2 ..	..	29.64	25.64	20.13
3. Total iron volumetrically	..	26.53	32.38	30.15
4. Total oxide Gravimetrically	(R_2O_3) ..	50.3	54.5	57.7
	Fe_2O_3 ..	37.93	46.30	43.11
	Al_2O_3 ..	11.07	6.90	13.69
	TiO_2 ..	1.30	1.30	0.90
5(a) CaO ..	..	3.194	2.97	3.978
(b) $CaCO_3$ ..	..	5.70	5.30	7.1

In their original form all the ores are non-magnetic but when heated beyond a certain temperature they acquire magnetic properties. These heated samples are graded into three categories namely non-magnetic, moderately magnetic and highly magnetic, and the results have been tabulated in Tables 2a–c. In another case the sample was ground to −150 mesh and heated to 700°C for 1 hr, cooled and the magnetic part separated. The corresponding results together with the analysis for Fe in magnetic and non-magnetic parts appear in Tables 3a and 3b.

Results and Discussion

Assuming that the composition of these ores is more or less the same as that of the Kalabagh iron ores, already analysed for different phases in these laboratories (see Table 4), it will be seen that the various phases present are limonite ($Fe_2O_3.nH_2O$), hematite (Fe_2O_3), siderite ($FeCO_3$) and chamosite—an iron–aluminium silicate complex usually represented by $3(Fe,Mg)O.Al_2O_3.SiO_2.nH_2O$. In addition to these phases kaolinite, bohimite, silica, titanium and chromium are also present. With this knowledge of the composition, it is now easy to follow the pattern of the heat effect on all these phases. Limonite will be completely deprived of its water contents between 100–1200°C forming Fe_2O_3 and possibly Fe_3O_4, the latter being responsible for the magnetic properties of the product. Next comes hematite i.e. α-Fe_2O_3 which may also be converted partly or wholly to Fe_3O_4, depending upon the ambient conditions in the furnace. Siderite $FeCO_3$, probably the most undesireable of all the components, will begin to decompose into FeO and CO_2 even at low temperatures. At high temperatures it chemically combines with free silica to give ferrous silicate and is consequently lost as slag.[6] Taking iron contents in the ores as 30% the iron contribution by the siderite alone is about 10–12%. Thus it seems logical that if this loss is to be minimised, the FeO component, before it combines with silica, has to be stabilised by converting it to higher oxides of iron. This may be achieved by heating the ore within or without the furnace. If the ore is calcined in oxidizing atmosphere outside the furnace at a certain temperature range, the above aim may possibly be achieved, i.e. reduction to FeO and thereafter its oxidation to higher oxides. The same object on the other hand appears to be difficult to achieve in the blast furnace where the atmosphere present is reducing due to the presence of CO.

Referring to Figs. 1 and 2 where the contents of Fe^{++} in the heated ore are plotted against the temperature, it will be seen that the Fe^{++} contents fall with the rise in temperature and the curves thus obtained tend to form an asymptote after 600°C. This means that the Fe^{++} contents are reduced to a minimum at and after 600°C. These curves also indicate that the particle size as well as the atmosphere in which a sample is heated does not help in reducing the FeO content in the sample. It may therefore be inferred that the introduction of a preheated or roasted feed in a suitable manner could greatly reduce or eliminate the possibility of the formation of ferrous silicate. Such a practice, will no doubt result, as already stated, in an additional operation i.e. incorporation

TABLE 2 (a).—THE EFFECT OF HEAT ON IRON ORES.

Flow rate of carbon dioxide 2l/min (approx).

Sample: Ore	Sample: Size	Physical properties	Effect of heat: Original	200°C	400°C	600°C	800°C	1000°C	1200°C
Makerwal	Lump size 3-4″	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Moderately magnetic	Weakly magnetic	Non-magnetic
		Change in colour	Greenish grey	Dark grey	Dark brown	Dark brown	Dark brown	Brownish red	Dark brownish red with metallic lustre
	Particle size −200 mesh BSS	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Very weakly magnetic	Magnetic
		Change in colour	Greyish green	Mud coloured with red tint	Reddish brown	Dirty red	Red	Reddish brown	Dark brown or tan
Chichali (East)	Lump size 3–4″	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Moderately magnetic	Weakly magnetic	Very weakly magnetic	Very weakly magnetic
		Change in colour	Light grey	Darkish grey	Dark brown	Dark brown	Brownish red	Brownish red	Dark brownish red with metallic lustre
	Particle size −200 mesh BSS	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Weakly magnetic	Magnetic
		Change in colour	Greyish green	Greyish green	Reddish brown	Dirty red	Red	Reddish brown	Dark brown
Chichali (West)	Lump size 3–4″	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Highly magnetic	Highly magnetic	Moderately magnetic	Moderately magnetic
		Change in colour	Greenish grey	Dirty green	Brownish red	Dark brown	Reddish brown	Reddish brown	Dark brownish red with metallic lustre
	Particle size −200 mesh BSS	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Very weakly magnetic	Magnetic	Magnetic
		Change in colour	Greyish green	Light grey with red tint	Reddish brown	Dirty red	Red	Reddish brown	Dark brown or tan

TABLE 2(b).—THE EFFECT OF HEAT ON IRON ORES.

Flow rate of nitrogen 2 l/min (approx).

Sample: Ore	Sample: Size	Physical properties	Effect of heat: Original	200°C	400°C	600°C	800°C	1000°C
Makerwal	Lump size 3–4″	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Weakly magnetic	Fairly magnetic
		Change in colour	Dirty grey	Dark grey	Reddish brown	Dark red with black patches	Cherry red out side black in centre	Cherry red with black tint
	Particle size −200 mesh BSS	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic
		Change in colour	Greyish green	Mud coloured with red tint	Brownish red	Reddish brown	Brownish red	Brownish red

(*Table continued*)

(*Table* 2(b) *continued*)

Chichali (East)	Lump size 3–4″	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Weakly magnetic	Weakly magnetic	Very weakly magnetic
		Change in colour	Dirty grey	Dark grey	Dirty red	Dark red with black patches	Red with dark patches	Metallic red
	Particle size –200 mesh BSS	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic
		Change in colour	Greyish green	Greyish green with red tint	Brownish red	Reddish brown	Brownish red	Brownish red
Chichali (West)	Lump size 3–4″	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Highly magnetic	Moderately magnetic	Feebly magnetic
		Change in colour	Dirty grey	Dark grey	Dirty red	Patches of light and dark red	Bright red with dark patches	Brownish red
	Particle size –200 mesh BSS	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Very feebly magnetic	Feebly magnetic	Moderately magnetic
		Change in colour	Greyish green	Light grey with red tint	Brownish red	Reddish brown	Brownish red	Brownish red

Table 2(c).—The Effect of Heat on Iron Ores.

Flow rate of air 2 l/min (approx).

Sample: Ore	Sample: Size	Physical properties	Effect of heat: Original	200°C	400°C	600°C	800°C	1000°C	1200°C
Makerwal	Lump siz 3–4″	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Weakly magnetic	Very weakly magnetic	Weakly magnetic	Fairly magnetic
		Change in colour	Dirty greyish green	Greyish green	Light dirty brownish red	Brownish red	Brownish red	Brownish red	Chacolate coloured
	Particle size –200 mesh BSS	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic
		Change in colour	Greyish green	Dark grey	Reddish brown	Reddish brown	Brownish red	Red	Light brownish red
Chichali (East)	Lump size 3–4″	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Very weakly magnetic	Weakly magnetic	Weakly magnetic	Weakly magnetic
		Change in colour	Greenish grey	Dirty light greyish green	Dark brownish red	Brownish red	Brownish red	Brownish red	Dark reddish brown
	Particle size –200 mesh BSS	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Very weakly magnetic	Very weakly magnetic
		Change in colour	Greyish green	Medium dark grey	Reddish brown	Brownish red	Reddish brown	Dark brown	Reddish brown
Chichali (West)	Lump size 3–4″	Magnetism	Non-magnetic	Non-magnetic	Non-magnetic	Highly magnetic	Fairly magnetic	Fairly magnetic	Moderately magnetic
		Change in colour	Dark greenish grey	Dirty light green	Light brownish red	Dark brown brownish red	Dark dull red	Dark brownish red	Blackish red
	Particle siz –200 mesh BSS	Magnetism	Non-magnetic	Non-magnetic	Non-Magnetic	Non-magnetic	Non-magnetic	Weakly magnetic	Moderately magnetic
		Change in colour	Light greyish green	Grey with reddish tinge	Reddish brown	Brownish red	Red	Dark brownish red	Blackish grey or brown

TABLE 3(a).—CHEMICAL ANALYSIS OF MAGNETICALLY SEPARATED IRON ORES.

Composition of the ore: The ore is a mixture of equal weight of Makerwal, Chichlali (East) and Chichali (West) ores.

Set No.	Sample and description		Total Fe volumetrically %	Fe^{++}%	Fe^{+++}%	SiO_2 %
1.	(−150 Mesh ore)	Original	39.260	4.537	34.723	
		Magnetic	43.620	6.073	37.547	
		Non-magnetic	34.890	2.583	32.307	
2.	(−150 Mesh ore)	Original	38.390	0.733	37.657	
		Magnetic	41.880	0.907	40.973	
		Non-magnetic	33.160	0.174	32.986	
3.	(−150 Mesh ore)	Original	36.640	1.396	35.244	
		Magnetic	40.140	1.885	38.255	
		Non-magnetic	32.280	1.010	31.270	
4.	(−150 Mesh ore)	Original	38.390	1.257	37.133	21.650
		Magnetic	41.880	1.361	40.519	20.950
		Non-magnetic	33.160	0.628	32.532	28.950
	(−30+36 Mesh ore)	Original	38. 90	0.105	38.285	
		Magnetic	42.760	0.070	42.690	
		Non-magnetic	34.890	0.105	34.785	

TABLE 3(b).—MAGNETIC SEPARATION OF IRON ORES.

Composition of the ore: The ore is a mixture of equal weights of Makerwal, Chichali (East) and Chichali (West) ores.

Set No.	Sample and description		Weight of the sample g	Percentage	Loss %
1	(−150 Mesh ore)	Magnetic	255.0	56.28	
		Middlings	145.0	32.01	7.28
		Tailings (Non-magnetic)	20.0	4.43	
2	(−150 Mesh ore)	Magnetic	275.0	60.70	
		Middlings	75.0	16.56	16.12
		Tailings (Non-magnetic)	30.0	6.62	
3	(−150 Mesh ore)	Magnetic	271.0	59.28	
		Middlings	122.0	26.94	7.72
		Tailings (Non-magnetic)	15.0	3.31	
4	(−30+36 Mesh ore)	Magnetic	307.0	67.76	
		Middlings	50.0	11.04	14.13
		Tailings (Non-magnetic)	32.0	7.06	

Table 4(a).—Kalabagh Iron Ore: X-Ray Analysis of Component Mineral Phases.
Percentage mineral composition of the mean sample by X-ray anlysis.

Constituent minerals	Weight % from X-ray analysis	Corrected values	Contribution to iron content
Limonite ($Fe_2O_3H_2O.nH_2O$)	8	7	4.5
Hematite (α–Fe_2O_3)	16	14	9.8
Siderite ($FeCO_3$)	24	22	10.6
Chamosite* 3(Fe,Mg)O.Al_2O_3.2 SiO_2nH_2O	32	30	8.4
TiO_2, Cr_2O_3 etc	5	6	1
Quartz	5	6	—
Kaolinite, bohimite	10±5	15	—
Total	100	100	33.8±0.5

* Chamosite is a ferruginous clay, and the formula given is therefore only approximate. It may contain 24–32% iron, and an average figure of 28% has been used in the table above.

Table 4(b).—Mineralogical Analysis of Mean Representative Sample.

Constituent minerals	Analysis by Hoganas Sweden	Contributions to iron content
Limonite ($Fe_2O_3.nH_2O$)	24.9	14.0±2
Hematite (Fe_2O_3)	—	—
Siderite ($FeCO_3$)	25.6	12.3
Chamosite	35.6	9.0±0.5
Ilmenite ($FeO.TiO_2$)	1.7	0.6
Quartz	5.1	—
Residue (aluminous sediments)	7.7	—
Total	100.6	35.9±2

Total iron by analysis=35.8%

of a rotary furnace and consequently incurring higher operating costs. But this arrangement appears to be a necessity and a pre-requisite in the present case.

The effect of heat in rendering the ores magnetic, studied at different temperatures ranging from 200–1200°C, shows that almost all the ores (see Tables 2a–c) remain practically non-magnetic up to 800°C but thereafter begin to acquire magnetic properties which in certain cases tend to be maximum at 1200°C, irrespective of the prevailing atmosphere. This observation is in agreement with the claim of the other authors[4] who have reported transformation of phases at 600°C without specifying the heating time and the ambient atmosphere. The little difference in behaviour could therefore be explained on the basis of either the heating period or the temperature at which the samples have been heated.

The heated ores (at 700°C) were ground to –200 mesh and subjected to magnetic field to give three grades comprising the magnetic portion (55–70%), the midlings (10–32%) and the tailings (3–7%) as seen in Table 3b. The magnetic portion (see Table 3a) showed 40–43% of iron, while the non-magnetic part showed 32–35% of iron. This would mean that heating/roasting followed by magnetic separation does not hold any promise for the beneficiation of the indigenous ores.

Conclusion

Heating or roasting of indigenous iron ores at 600°C or above help in reducing (almost completely) the ferrous contents in the iron ore. Feed size does not interefere with the reduction of ferrous contents of the iron ores. Heating followed by magnetic separation does not help beneficiation of the iron ores.

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