

REMOVAL OF PHOSPHORUS AND ENRICHMENT OF MANGANESE FROM A COMPLEX FERRUGINOUS MANGANESE ORE

G.V. RAO*, B.C. ACHARYA, B.V.R. MURTY,
J.N. MOHANTY, Y.V. SWAMY, P. CHATTOPADHAY
and A.K. TRIPATHY

Regional Research Laboratory, Bhubaneswar 751 013, Orissa, India

(Received 17 April 1998; In final form 23 June 1998)

Attempts were made to enrich manganese content as well as Mn/Fe ratio from a complex manganese ore from Nishikhal deposit, Orissa, India, containing 32% Mn, 18% Fe, 16% SiO₂, 21% acid insolubles and 0.45% P by reduction roasting followed by magnetic separation route. Interestingly the adopted route not only enriched the Mn content to around 40%, Mn/Fe ratio to around 10 but also brought down the P to around 0.3% in the non-magnetic product there by making this deposit as a potential feed for ferro-manganese production in the country. Although the enrichment of Mn and Mn/Fe ratio is expected by this route, 60% of the phosphorus reduction is primarily due to the presence of P in association with goethite while the rest of the P was observed to be associated with the manganese phases and as apatite within the silicate phases as confirmed by the optical microscope and electron microscopic studies. The paper also discusses the limitation of reducing the P content further in the beneficiated product.

Keywords: Ferruginous manganese ore; Reduction roasting; Magnetic separation; Ferromanganese; Phosphorous removal; Mn/Fe ratio

INTRODUCTION

The manganese resources in India are around 177 million tonnes of which only 16% are in the proved category. As per the domestic consumption figures of manganese ore available [1], up to 1992–93, around

* Corresponding author. E-mail: root@csrrlbhu.ren.nic.in.

50% of it is consumed by the ferro-alloy industry and around 47% is being consumed by the iron and steel industry (Table I). The manganese ore reserves and their predominance in occurrence in different states in the country are given in Table II. Although the reserve position indicates the sustainable quantity to meet the domestic requirement, the reserves of the grade needed for the ferro-manganese production is only 10 million tonnes. Moreover, specifications laid down by the ferro-manganese industry in the country are also stringent (Table III). Besides the high grade Mn, the Mn/Fe ratio, phosphorus and silica contents

TABLE I Manganese ore consumption pattern in India

<i>Commodity (tonnes)</i>	<i>Year</i>	
	1991-92	1992-93
Alloy steel	100	100
Battery	26,400	24,200
Chemical	2,600	2,700
Ferro-alloys	670,600	641,200
Iron and steel	670,300	663,200
Lead-zinc smelters	2,600	2,600
Others (e.g. ceramics, glass foundry, paint industry)	100	100

TABLE II Reserves of manganese ores (Grade/State-wise)

<i>Grade/State</i>	<i>Recoverable reserves (as on 1.9.1990)</i>			<i>Total</i>
	<i>Proved</i>	<i>Probable</i>	<i>Possible</i>	
<i>All India total</i>	28,567	41,794	106,116	176,477
<i>Grade-wise</i>				
Battery/chemical	1,387	782	827	2,996
Ferro-manganese	9,706	5,953	5,722	21,881
Medium	7,528	5,056	9,923	22,507
BF	7,895	16,951	33,237	58,083
Unclassified	471	6,082	37,351	43,904
<i>State-wise</i>				
Andhra pradesh	6.5	4,157	3,368	7,582
Bihar	0.2	—	2,298	2,298
Goa	2,151	11,432	9,976	23,559
Gujarat	—	—	1,477	1,477
Karnataka	2,262	10,427	51,858	64,547
Madhya pradesh	9,216	2,510	4,818	16,544
Maharashtra	10,138	5,662	3,373	19,173
Orissa	4,793	7,605	28,438	40,836
Rajasthan	—	—	409	409
West Bengal	—	—	100	100

TABLE III Specifications of manganese ore for ferro-manganese and blast furnace of steel plants

	<i>Mn</i>	<i>Fe</i>	<i>Mn/Fe</i>	<i>SiO₂</i>	<i>P</i>
Ferro-manganese	38–48%	7–15%	7:1	7.5–13%	0.15%
Blast furnace	25–30%	14–26%		5–25%	0.075–0.34%

must also be taken into account in selecting an ore as a source of ferro-manganese. As the manganese ore meeting the ferro-manganese grade specification is inadequate, efforts are being made to upgrade the low and medium grade ores of the country by applying prudent beneficiation techniques.

In this article a very complex manganese ore containing 32% Mn, 16–18% Fe, 16% SiO₂, 0.45% P otherwise not suitable for most of the purposes was tested for its susceptibility to beneficiation. The ore chosen from the Nishikhal manganese mine of Orissa occurs in a high grade metamorphic terrain belonging to the Precambrian Eastern Ghats complex (Fig. 1) [2]. A number of manganese deposits e.g., Devjholla, Podakona, Taldhodshi, Kutinga, Kashilpur, etc., occur around this deposit and these deposits form a small manganese belt trending NNE–SSW over a strike length of about 40 km. These deposits are well known for their high phosphorus, iron and silica contents [3–5]. Among these deposits, Nishikhal is the largest one having an estimated reserve of over 10 million tonnes.

The Nishikhal deposit extends over a strike length of 2 km and there are three manganese bands. These manganese bands are parallel to the foliation of the country rocks such as khondalite and quartzite. Manganese ore body is interbanded with quartzite and contain quartz-orthoclase neosome veins and patches. Pegmatite is noticed in khondalite, quartzite and manganese ore bodies and lie parallel to the banding and the foliation planes. In many places the manganese ore bands are either associated with rich pockets of goethite, limonite or cut across by thin veins of goethite making the ore ferruginous. The ferruginous manganese ores show grey to brownish grey colour and are interbanded with the high grade/siliceous manganese ores. The Nishikhal deposit has above 3 million tonnes of such ferruginous ores.

The manganese content in this deposit falls into the medium grade but due to the presence of excess iron, silica and phosphorus contents it is of no use to the Indian industry unless suitable beneficiation technique

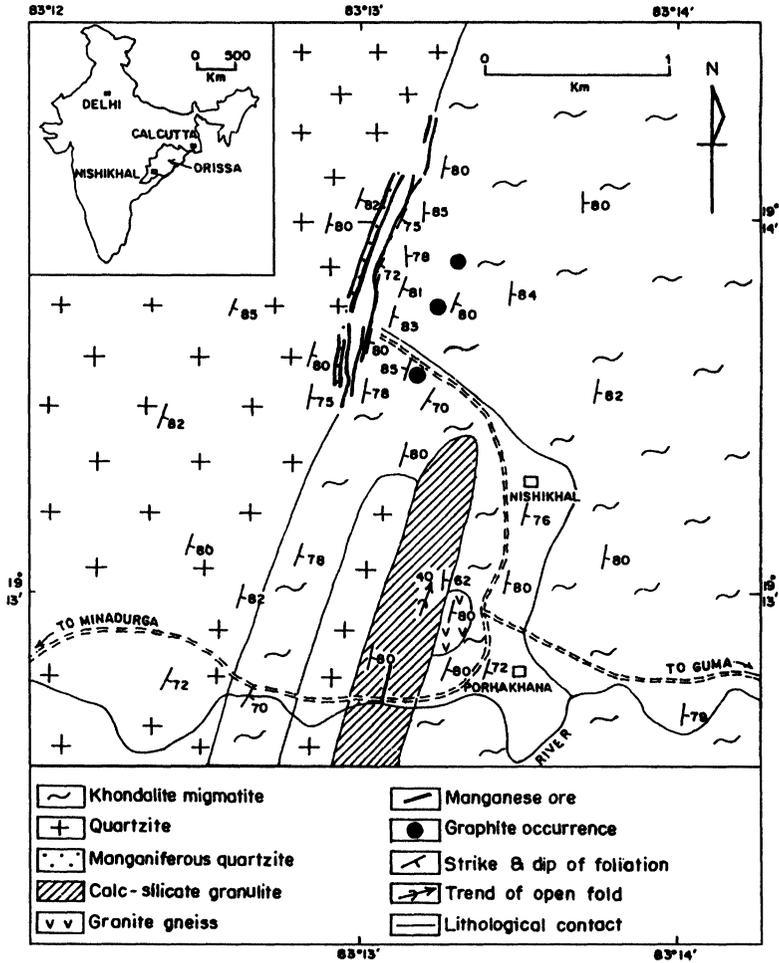


FIGURE 1 Location and a geological map of the Nishikhal manganese ore.

is adopted to enrich the manganese while rejecting substantial iron and phosphorus. The ores similar to this are reported to be conventionally beneficiated by reduction roasting followed by the magnetic separation technique [6,7]. Dephosphorisation of manganese ores was also reported [8] to be carried out by high intensity magnetic separation and roast leach method. In most cases, the Mn content could be improved substantially while achieving high Mn/Fe ratio but the phosphorus content

TABLE IV Reduction roasting-magnetic separation results on some complex manganese ores

Locality	Assay of the ore, %				Assay of the concentrate, %				Mn recovery, %
	Mn	Fe	SiO ₂	P	Mn	Fe	Mn/Fe	P	
A	25.8	10	25.2	0.13	50	7.9	6.3	0.17	69.8
B	30.2	21.9	0.99	0.03	50.4	8.5	6.4	0.3	42.5
C	21.7	14.2	3.5	0.58	34.7	4.6	7.5	0.45	57.6
D	33.5	13.9	8.5	0.29	52.8	5.7	9.3	0.26	67
E	34.4	8.2	19.7	0.008	46.2	6.6	7.0	0.10	30

A: Chipurupalli (A.P.), B: Saluru (A.P.), C: Kanji mines (Rajasthan), D: Koduru mines (A.P.), E: Mirjaour mines (M.P.).

Source: Monograph on manganese ore: July 1994: IBM publication, Nagpur.

could not be reduced. In fact, the studies carried out on many ferruginous manganese ores from different deposits (Table IV) have indicated [9] a slight enrichment of P content in the beneficiated non-magnetic fractions.

Similar beneficiation attempt made on the sample from Nishikhal not only improved the Mn grade, the Mn/Fe ratio but also lowered the phosphorus content substantially. The underlying reasons for being able to reduce the phosphorus in the beneficiated product and the salient findings are being discussed in this article.

A SAMPLE AND ITS CHARACTERIZATION

Around 500 kg of sample was collected from the ferruginous area of the Nishikhal mine after thorough blending of the sample at site. A representative sample was jaw and roll crushed till the ore was reduced to all passing 1200 μm size. A sub-sample was classified into various size fractions by wet sieving and all the fractions were analyzed for Mn, Fe, and P (Table V).

Mineralogical Studies

The sample was subjected to XRD and optical microscopic studies (Figs. 2–5). Studies were also carried out under electron microprobe and scanning electron microscope with a WDS analyzer (Fig. 6). The electron microprobe analysis was carried out on different manganese

TABLE V Heavies and lights in the -1200 μm roll crushed material

Size, μm	Wt%	Float%	Sink%
+600	23	0.96	22.04
+420	13.8	1.17	12.63
+210	23.2	5.70	17.5
+105	20.4	6.70	13.7
-105	20.5	0.80	19.7
	100	15.3	84.7

phases using JEOL JXA 8600 model, with a specimen current of 2×10^{-8} Amp and accelerating voltage of 15 kV and using SPI mineral standards. On-line ZAF correction procedure was adopted.

EXPERIMENTAL

Heavy Media Studies

The size fractions obtained from the roll crushed sample (1 mm gap-rolls) were subjected to laboratory sink and float studies by using an organic liquid, tetrabromoethane, having a specific gravity of 2.96. The lights and heavies obtained from each fraction were thoroughly washed with acetone, water and dried. The distribution of heavies and lights in each size fraction are given in Table VI.

Reduction Roasting Studies

Reduction Roasting in Muffle Furnace

The roasting studies were carried out on a 500 g scale. The material used for the roasting was the roll crushed sample of -6 mm size. Studies were carried out in Muffle furnace (15 cm \times 7 cm \times 7 cm) as well as in Linder test apparatus (150 mm \times 550 mm). LECO fines were used as reductant. The sample (500 g of the -6 mm ore) was mixed with 15 wt% Leco fines and placed in a metallic reactor. The reactor was heated in a static furnace. The temperature of the furnace was raised to the desired level without charging the material. The reactor was placed in the furnace after attaining the desired temperature and the pre-heating time for each experiment was carefully recorded. For most of the experiments the pre-heating time was kept around 20 min. The reduced mass was quenched in water.

TABLE VI Weight, iron, manganese and phosphorus distribution in various size fractions of the roll crushed material

Size, μm	Wt%	Fe%	Mn%	Mn/Fe	P%
+600	23.7	15.5	36.8	2.35	0.45
+420	12.3	15.6	36.2	2.49	0.45
+210	23.8	12.8	30.2	2.36	0.43
+105	18.5	11.7	26.8	2.20	0.44
-105	21.7	15.6	26.3	1.68	0.44
Head (calc)	100	14.2	31.0	2.18	0.44

The Reduction Roasting in Linder Furnace

The Linder reduction apparatus was a cylindrical rotary vessel having inside diameter of 150 mm and the inside length in its cylindrical part of 550 mm and made of heat resistant steel. The rotational speed can be varied up to 10 rpm. The cylindrical rotary vessel was kept in an electrically heated furnace, the capacity of which was sufficient to maintain the required constant temperature over the entire length of the cylinder and also has a provision to supply and regulate the desired gas flow.

A 1000 g of the ore were taken in each test while keeping the LECO fines as reductant at 15 wt% of the ore. The material was placed in the rotating vessel of the Linder furnace. The furnace was heated in a pre-determined rate while the reactor was on rotation. The pre-heating time required to reach temperature was divided into two stages. The total time required to reach 700°C and then to reduction temperature. The roasted material was cooled to 400°C in an inert atmosphere and quenched in water.

The roasted and cooled material was ground in 150 mm \times 150 mm size ball mill with ball charge of 45% mill volume. The material was ground for different time intervals and subjected to wet magnetic separation. The magnetic and non-magnetic fractions were analyzed for Fe, Mn and P by standard chemical methods.

Magnetic Separation Studies

SALA Wet Low Intensity Magnetic Separator

The ground roasted mass was subjected to wet magnetic separation using SALA low intensity magnetic separator (containing a stainless steel 200 mm \times 100 mm dia. drum with an adjustable magnet set

TABLE VII Reduction roasting-magnetic separation results (roasting in Muffel furnace)

<i>Temp.</i> , °C	<i>Products</i>	<i>Wt%</i>	<i>Mn%</i>	<i>Fe%</i>	<i>Mn/Fe</i>	<i>P%</i>	<i>Mn recovery</i> , %
750	Magnetic I	14.7	19.2	42.4		0.69	
	Magnetic II	4.10	34.0	19.5			
	N-Magnetic	81.2	38.0	12.3	3.1	0.36	88.0
800	Magnetic I	13.2	31.0	41.0		0.69	
	Magnetic II	24.4					
	N-Magnetic	62.4	38.4	5.60	6.85	0.34	73.0
850	Magnetic I	8.60	31.3	20.6		0.69	
	Magnetic II	29.2	26.4	30.7			
	N-Magnetic	62.2	39.5	6.14	6.43	0.35	70.3
900	Magnetic I	33.9	22.5	32.9		0.70	
	Magnetic II	3.40	28.0	25.2			
	N-Magnetic	62.7	39.5	7.80	5.0	0.35	70.0

TABLE VIII Reduction roasting/magnetic separation results (roasting in Linder apparatus)

<i>Temp.</i> , °C	<i>Products</i>	<i>Wt%</i>	<i>Mn%</i>	<i>Fe%</i>	<i>Mn/Fe</i>	<i>P%</i>	<i>A.I.</i>	<i>Mn recovery</i> , %
750	Magnetic I	36.5	25.0	33.5		0.67	9.2	
	Magnetic II	4.5						
	N-Magnetic	59	39.0	3.90	10	0.30	36.0	68.7
800	Magnetic I	33.9	24.0	38.0		0.65	9.4	
	Magnetic II	7.20						
	N-Magnetic	58.9	38.0	3.9	9.7	0.31	36.7	69.5

Magnetic I and II products were mixed and analyzed.

consisting of 3 permanent magnets, having a lever for necessary adjustments) by feeding the diluted slurry through a peristaltic pump and collected the magnetic and non-magnetic products. The non-magnetic product was further treated to collect Magnetic II and the eventual beneficiated non-magnetic product. In most cases, the Magnetic I and II products were mixed and analyzed as a single magnetic product. The magnetic studies were carried out on the roasted product resulting from both Muffle furnace (Table VII) and the Linder apparatus (Table VIII).

BOXMAG Wet High Intensity Magnetic Separator

The non-magnetic product resulting from the roasted material obtained from Linder was treated on the wet high intensity magnetic separator

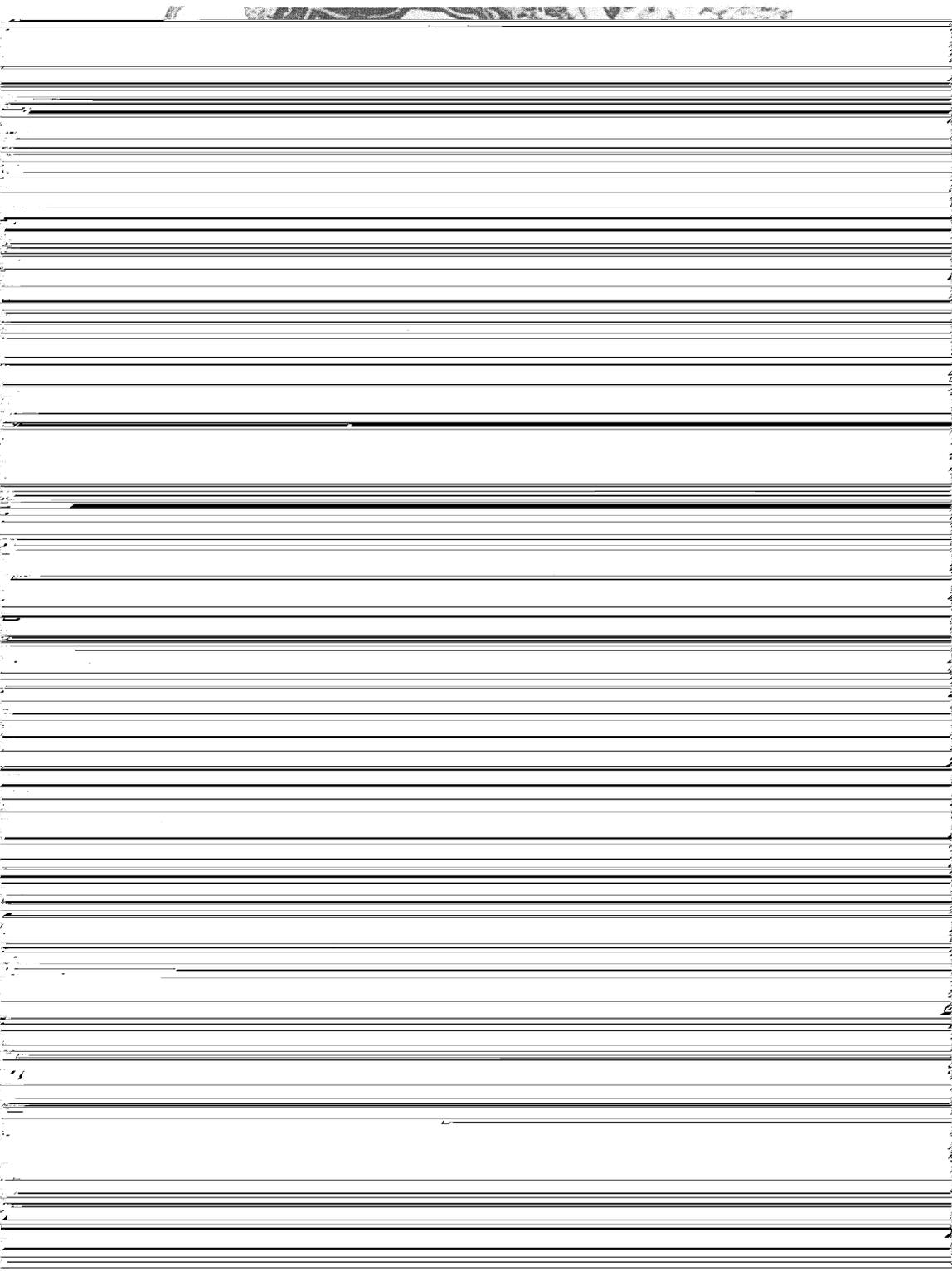
TABLE IX Results of the high intensity magnetic separation studies (on the beneficiated non-magnetic fraction obtained on SALA-LIMS)

<i>Expt. no.</i>	<i>Magnetic intensity (G)</i>	<i>Products</i>	<i>Wt%</i>	<i>Mn%</i>	<i>Fe%</i>	<i>P%</i>	<i>Mn/Fe</i>	<i>Mn recovery, %</i>
1	10,000	Magnetic	72.0	43.9	3.35	0.34	13:1	87.4
		Non-magnetic	28.0	16.2	2.23	0.189		12.5
2	18,000	Magnetic	81.0	43.3	3.90	0.33	11:1	95.4
		Non-magnetic	19.0	8.80	2.30	0.19		4.60

[BOXMAG – LHW batch matrix type] at intensities of 10,000 and 18,000 G, obtained on 1 mm wedge wire spacing. The collected magnetic and non-magnetic fractions from the non-magnetic product obtained on SALA low intensity separator were analysed for Mn, Fe and P (Table IX).

RESULTS AND DISCUSSION

The Nishikhal manganese ore under study was a very complex ore due to the presence of iron, silica and phosphorous much beyond the tolerable limit for its use in ferro-manganese production. The optical microscopic studies revealed the presence of cryptomelane, pyrolusite, psilomelane, lithiophorite, husmanite, jacobite in decreasing order of abundance with goethite as major iron bearing mineral with orthoclase, quartz and garnet. Cryptomelane, psilomelane, pyrolusite and goethite are interlayered and show colloform texture (Figs. 2 and 3). Invariably they are very finely grained and intricately locked. Goethite occurring as distinct bands along with cryptomelane, psilomelane, has also been observed (Fig. 4). In some cases oxyhydroxides of iron and manganese have also been observed. Small apatite grains are enclosed within the silicate minerals (Fig. 5). The samples studied under scanning electron microscope and electron probe suggest that phosphorus is dominantly contained in the goethite and manganese phases (Fig. 6), besides being present as apatite locked with silicate minerals. The electron microprobe analysis of different manganese and iron phases indicates the distribution of phosphorus in the various minerals as 0.12–0.32% in cryptomelane, 0.09–0.17% in psilomelane, 0.004–0.14% in pyrolusite, 0.35–1.13% in goethite, 0.009–0.056% in garnet and 0.22–1.6% in altered



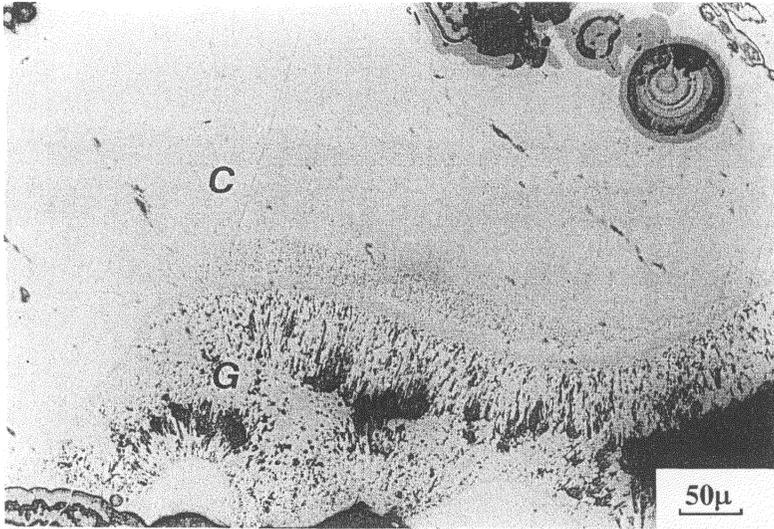


FIGURE 4 Goethite (G) is associated with cryptomelane (C). Psilomelane shows spheroidal structure at top right of the photograph (reflected light).

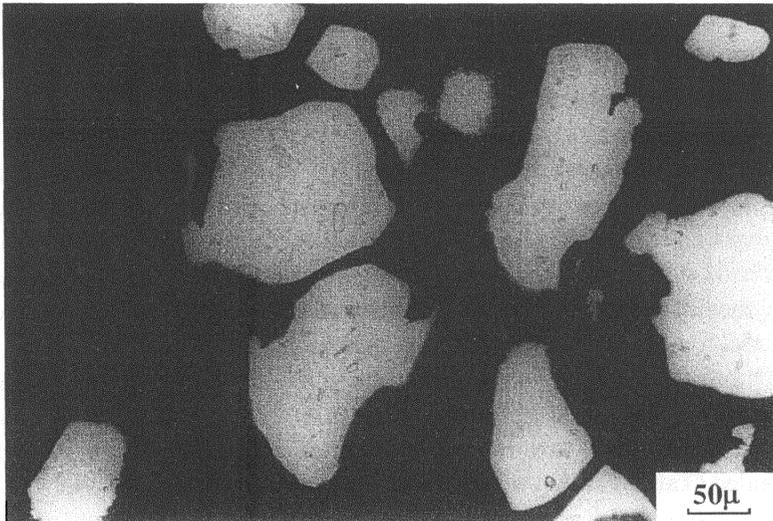


FIGURE 5 Quartz and orthoclase grains (white) containing small apatite crystals are enclosed by manganese minerals (black) (transmitted light).

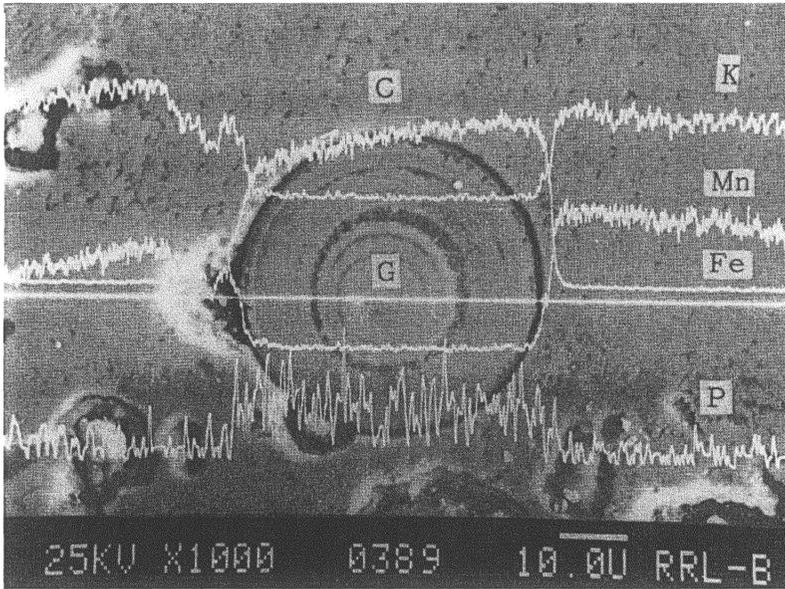


FIGURE 6 X-ray line scanning of Mn, Fe, K and P in cryptomelane (C) and goethite (G).

products (oxyhydroxides of iron and manganese). Amorphous calcium phosphate (collophane) was observed to fill the voids in garnet. Interestingly the goethite was observed to contain high amount of phosphorus, as also reported elsewhere [5], than in psilomelane and cryptomelane (Fig. 6). This is in conformity with the bulk chemical analysis plottings of P_2O_5 vs Fe_2O_3 which has a correlation coefficient value of 0.94 [10]. The above clearly demonstrates the preferential presence of phosphorus with the iron phase rather than manganese phases.

The distribution pattern of Mn, Fe, and P in all the size fractions indicate (Table V) that they are uniformly distributed. Laboratory sink and float data on various size fractions of the $-1200\ \mu\text{m}$ sized feed revealed (Table VI) that only 15% of the material could be recovered as light fraction which means that substantial gangue (silicate) is present as a liberated form at this size. Since the specific gravities of the manganese minerals and iron minerals present in the ore are very close, by rejecting

the silicate gangue by gravity the iron and manganese contents are not reduced but rather increased. It can be surmised that the gravity concentration technique is not the pragmatic approach to achieve the desired Mn enrichment.

The common practice in enriching the manganese content from such ferruginous ores is widely through reduction roasting followed by magnetic separation. Roasting studies in a static bed Muffle furnace by using LECO fines (–3 mm size supplied by Neyveli Lignite Corporation, Tamil Nadu) as a reductant followed by wet low intensity magnetic separation (LIMS) studies indicated (Table VII) the possibility of enriching Mn to 39% with 73% recovery into the non-magnetic fraction. As can be seen, the Mn/Fe ratio could however be augmented to only 6.8 with the best results at 800°C. The retention time in the furnace at this temperature was maintained at 20 min.

The roasting studies carried out in the Linder test apparatus using LECO fines followed by wet magnetic separation on SALA wet drum low intensity magnetic separator (LIMS) revealed (Table VIII) that Mn can not only be enriched to around 39% Mn with a high Mn/Fe ratio of 10 with around 69% manganese recovery but also the phosphorus content can be reduced to 0.3%. This amounts to the rejection of around 60% of the phosphorus by this technique. Thus the results achieved on Linder are far superior as regards the restriction of iron entry into the non-magnetic product which is presumed to be due to the proper blending of LECO fines with the ore and better surface exposure, during the tumbling action of the material, to the temperature. This is primarily due to the dominant presence of P in the goethite phase (Fig. 6) which, during the reduction roasting at 750–800°C is converted to a magnetite phase and subsequently rejected during magnetic separation along with the associated phosphorus into the magnetic product. As phosphorus is present in the manganese minerals as well as in the silicate minerals, around 40% of P reports into the non-magnetic beneficiated product.

Wet high intensity magnetic studies carried out on the beneficiated non-magnetic fraction (Table IX) reveals that the Mn content can be further enriched to around 43% Mn with 88–95% recovery, depending on the magnetic intensity. The phosphorus content was also found to be upgraded to 0.34% from 0.3%. It can be seen from Table IX that 12–17% of P could be further rejected into the non-magnetic fraction which

is probably P present in the silica/silicate minerals. The overall phosphorus removal can be increased to around 65% by introducing high intensity magnetic separation step into the flowsheet. It can also be seen from Table IX that the Mn content could be enriched to around 43% with an overall recovery of around 63% besides improving the Mn/Fe ratio to around 13. Comparing this data with the data (Table IV) obtained by this reduction roasting–magnetic separation route on similar complex manganese ores of the country, it can be noticed that P could be reduced substantially from the ore of Nishikhal manganese ore, whereas in other cases the P content is increased marginally.

This beneficiated material can be a potential feed for the ferromanganese production in view of its high Mn/Fe ratio and medium Mn grade; however only by blending with low phosphorus bearing manganese ore to maintain the specified P content of 0.15%.

CONCLUSIONS

- The medium grade ferruginous manganese ore from Nishikhal containing high concentrations of silica and phosphorus has responded to the reduction roasting followed by magnetic separation route not only in enriching Mn, the Mn/Fe ratio but also in removing 65% of phosphorus.
- The optical microscopic and electron microscopic studies revealed association of P with cryptomelane, psilomelane and goethite and the presence of apatite in the silicate mineral phases.
- LECO coal fines at 15 wt% of the ore as reductant were found to effectively reduce the ore at 800°C.
- The roasted mass with subsequent grinding and separation on SALA low intensity wet magnetic separator has yielded a product containing around 40% Mn, Mn/Fe ratio of 10 with 0.3% P and with around 70% Mn recovery.
- Around 60% of P could be removed into the magnetic phase due to its occurrence in the goethite phase.
- By treating the beneficiated non-magnetic phase on wet high intensity magnetic separator further augmentation of the Mn content and Mn/Fe ratio is possible while P content also becomes enriched marginally.

Acknowledgments

The authors are thankful to Prof. H.S. Ray, Director, Regional Research Laboratory, Bhubaneswar for permission to publish this paper. Thanks are also due to M/S Orissa Mining Corporation for assistance in collecting the sample. The authors also thank Dr D.S. Rao for collecting the samples and assisting in the mineralogical studies.

References

- [1] A.J. Reddy, An overview of manganese ore and alloys industry in India in a global perspective: In Seminar Proc. on “*Manganese – Ores and alloys*” December 8–9, 1995, Bhubaneswar, 147–160.
- [2] B.C. Acharya, D.S. Rao and R.K. Sahoo, Graphite mineralisation in Eastern Ghat magmatites around Nishikhal, South Orissa. *Ind. Jour. Earth Sci.* **22**(1–2), (1995), 35–42.
- [3] Ajmal Mohd., Manganese ores of Nishikhal, dist. Kalahandi, Orissa. *Quart. Jour. Geol. Min. Metal Soc. India.* **54**(1–2), (1982), 18–23.
- [4] R.K. Sahoo, S.B. Kanungo and R. Natarajan, A note on the occurrence of phosphorus in manganese ores of central India and its liberation during size reduction. *Ind. Mining Engg. J.*, Feb–Mar (1982), 25–32.
- [5] B.C. Acharya, D.S. Rao and R.K. Sahoo, Mineralogy, chemistry and genesis of Nishikhal manganese ores of South Orissa, India. *Minerallium deposita.* **32**(1), (1997), 79–93.
- [6] P.I.A. Narayana and G.V. Subramanyam, Lab studies on the beneficiation of some ferruginous manganese ores of India for the production of ferro manganese.: *Trans. Inst. Mining. Metallurgy, London*, **66** (1956), 49–68.
- [7] Report on Roast reduction and magnetic separation of Sandur low grade manganese ore. Regional Research Laboratory, Bhubaneswar, 1993.
- [8] Q. Song, Y. Zhao and J. Zhu, Dephosphorization of manganese ore by high intensity magnetic separation and roast leaching. *Trans. Inst. Min. Met., Sec-C*, **98** (1989), C17–20.
- [9] Monograph on Manganese Ore. July 1994, Indian Bureau of Mines, Nagpur, India; 1994.
- [10] B.C. Acharya, D.S. Rao, R.K. Sahoo and B. Dash, Phosphorus in the siliceous manganese ores of Nishikhal, Orissa. *Ind. J. of Geology*, **66**(1), (1994), 15–23.