VISTAS IN GEOLOGICAL RESEARCH
U.U. Spl. Publ. in Geology (10) January 2011 pp.62 - 69

Characterisation of Ferruginous Manganese Ores from Bonai-Keonjhar Belt, Orissa and Possible Approach for their Effective Utilisation

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Abstract: The ferruginous manganese ores of Bonai-Keonjhar belt belonging to Precambrian Iron Ore Group, Orissa are of sub-grade type and do not find any use. This ore type present in large volume and attempt has been made to find out suitable technique for its optimum utilization. Mineralogical study of the manganese ores from three different localities viz. Dalki, Guruda and Dubna reveals the presence of pyrolusite / cryptomelane, hematite and goethite with very minor clay minerals. Study of ore textures indicates that the both Mn and Fe phases are intimately associated with each other. The ferruginous manganese ores of these areas, analyzing 12-21% Mn, 33-45% Fe and ~1 % Al_2O_3+ SiO_2, were subjected to beneficiation techniques, namely magnetic separation and roast reduction followed by magnetic separation.
The reduction roasting followed by magnetic separation proved to be the best method. Since the Fe_2O_3 content in the manganese ore is much higher than the normal amount for its utilization in ferroalloy industry, it was removed by reduction roasting, thereby increasing the MnO_2 content of the ore. In the process the ore was roasted using coal as solid reductant in laboratory scale muffle furnace for 30 to 60 minutes in the range of 720^0C- 950^0C. The roasted ore was magnetically separated using a low intensity magnetic separator. The higher manganese concentrates was recovered from the nonmagnetic fraction. Following this process, the feed having 12-21% Mn could be upgraded to 26 - 45% with 22 - 36% yield, enhancing thereby the Mn: Fe from < 1 up to 2-5.

Key words: Sub-grade Mn-ore, Bonai- Keonjhar belt, Iron Ore Group, Beneficiation

INTRODUCTION

Manganese ore occurrence in two different Geo-environments viz. terrestrial and oceanic basin is well known. India has a total reserve of 250 million metric tones of manganese ores distributed in different parts of the country like Madhya Pradesh -Maharastra, Orissa - Jharkhand region. In Orissa, it is confined to three stratigraphic horizons such as: Iron Ore Group, Eastern Ghats and Gangpur Group. But most of the working manganese deposits in Orissa are confined to the Iron Ore Group of Bonai-Keonjhar belt. However, good-grade ore in these areas are of limited occurrence and fast depleting. A time has now come to look in to the low-grade ores which are abundantly present in this sector. The low-grade Mn-ore are classified as siliceous, ferruginous and aluminous types. Out of these three categories large volume of ferruginous ore are present in several mines in Keonjhar district. Many mines are abandoned because of this low-grade ferruginous manganese ore. Since this ore has no market, its exploitation becomes cost intensive. Further, for selective mining of good-grade manganese ore pockets, the Fe-Mn ore is mined and dumped, thereby creates both environmental and disposal problem. Now, a time has come when all concerted efforts should be made to find out means to utilize this ore. The present paper is a modest attempts to beneficiate this ore for its optimum utilisation.

Ferruginous manganese ore from three areas such as Dalki, Guruda and Dubna were collected and processed through most viable technique i.e. Roast reduction followed by magnetic separation and the results are reported in this paper. Though the different aspects of geology of Mn occurrences of the belt have been discussed in detail by Fermor (1909), Prasad Rao and Murty (1956), Roy (1966), Murty and Ghosh (1971) , Mohapatra et al. (2002), Mishra et al. (2003), Mishra (2005) nevertheless no attempt has been made to find out its utilisation potential. Limited attempts have been made to beneficiate ferromanganese ore from Karnataka (Rudamaniyappa and Nijagunappa, 1991). Jingjing et al.(2010) have studied the reduction of low grade manganese ore from south China containing MnO_2 31.34 % and Fe_2O_3 12.60 % and using bio mass (saw dust) as reductant at a low temperature of 500^0C and then leached with sulphuric acid to extract 97% manganese present as MnO as a sulphate. This route has been tried to decrease energy requirements and meet pollution norms than those practiced in conventional methods. Cem and Ahmet (2008) have optimized conditions in the production of manganese-iron carbides by solid state carbothermic reduction in argon atmosphere. The Denizil-Tavas manganese ore containing 31.06% Mn and 4.26% Fe was enriched to 52.98% Mn and 5.36% Fe in the final product which finds use in ferro-manganese production. Nishikhal manganese deposit of Orissa has been beneficiated by reduction roasting and magnetic separation wherein manganese content has been enriched to 40% from18% in feed with a Mn: Fe ratio of 10 has been achieved and the phosphorus content was 0.3% Rao and Murthy (1998).

MATERIALS AND METHODS

Ten kg of low grade representative manganese samples, each from three captive mines, viz. Dalki, Dubna, and Guruda were collected. Representative samples from these three localities were crushed to below 10mm size by jaw and roll crusher and a feed sample in -6+1mm were prepared for reduction tests. Talcher coal with a size of -1+0.5mm, was used as reduction. The reduction experiments were conducted at 750^0C, 850^0C and 950^0C. The charge contains 250g ore and 50g of coal for experiments conducted at 750^0C and 850^0C. More coal was added for reduction for experiments conducted at 950^0C. The ore mixed with reductants are placed in a vertical SS reactor which is closed at the top by a flange having provision for gas flow and for measurement of charge temperature. The charge bed is in static condition. The reactor is then placed in vertical position in electrically heated muffle furnace of 4 Kw. The furnace temperature is controlled by on /off controller. The temperature of the furnace is then raised to the desired experimental temperature and is kept controlled. As soon as the temperature of charge attains the reaction temperature the experiment is deemed to have started. The gas inlet and outlet points are sealed to prevent atmospheric air to enter the reactor. After keeping the charge for the desired period at the reaction temperature the furnace is put off. The hot charge is then discharged after cooling to 50˚C.

The objective of conducting experiments at 750^oC was to limit the reduction of hematite to magnetite state only. Hence, the reduction was carried out for a short duration 30 min. whereas in case of reduction experiments conducted at 950^0C, time duration of 60 min was fixed so as to provide sufficient time for iron oxide to reduce to metallic state. As the reductant size originally chosen was finer than ore the excess coal that remained after reduction was mostly removed by sieving at 1mm. However, some coal 5% by wt of reduced ore, which disintegrated to fines due to thermal and reduction operations, remains with the reduced ore. The reduced ore was wet ground to less then 100 microns in ball mill and the ground mass was further subjected to wet low intensity magnetic separator to get a nonmagnetic fraction which is the product having less iron and magnetic fraction which is a reject. The wt% of magnetic and non magnetic fractions was measured. The manganese and iron contents of the fractions were estimated by wet chemical analysis.

The mineralogical characterization was done using optical microscopy (Leitz make) and X-ray diffractometry (Phillips make).

CHARACTERISTICS OF FERRUGINOUS MANGANESE ORE

Mineralogical Characteristics

The ferruginous manganese ores of the study areas are brown-reddish brown in colour and shows dull to earthy lusture. These are morphologically friable in nature, soil the hand and brown to reddish brown streak. The hardness on the mineralogical Moh’s scale is generally varies from 3 to 5. The general characteristics of different mineral phases are discussed below. The mineralogical composition of three different localities varies.

Manganese phase

The chief manganese minerals present in these ores are cryptomelane pyrolusite, lithiophorite and manganite .Cryptomelane occurs as bladed crystals. Pyrolusite is mostly seen as oxidized products from cryptomelane .Often clusters of pyrolusite occur as islands within cryptomelane .Lithiophorite mineral shows acicular and mosaic structure.

Iron phase

The iron mineral present in these ores are hematite, goethite and limonite. Goethite shows comb and fan structure. Many of the iron phases are replaced by manganese minerals.

Other phase

Occasionally gibbsite (aluminum) is also recorded.

Table1. Mineral species in different feed sample

Location	Mineral
Dalki	Hematite, Goethite, Limonite, Pyrolusite, Cryptomelane
Guruda	Hematite, Limonite, Romanechite, Manganite, Lithiophorite, Pyrolusite, Gibbsite
Dubna	Hematite, Limonite, Cryptomelane, Pyrolusite, Romanechite Lithiophorite, Manganite

Geochemical Characteristics

The ferruginous manganese ores are very poor in manganese content, varying between 12-25%. Dalki sample shows the lowest manganese value 12.5%. In contrast such ores are rich in iron content, ranging between 36% and 47%. Iron value is contributed by hematite, goethite and limonite. The ore has negligible amount of alumina and silica (Al_2O_3+SiO_2= 1% to 2.5%). The loss on ignition ranges from 6% to 10%. Higher value of LOI in Dalki ore is attributed to goethite (Table 2).

Table2. Partial chemical analysis of feed sample

Location	Mn%	Fe%	LOI	Mn:Fe
Dalki	12.5	46.94	9.5	0.27
Guruda	25	37.98	8.6	0.66
Dubna	23.32	36.30	6.4	0.64

Characteristics of roasted Mn-Ore

750^{0}C roasting Dubna Mn ore gave better results with a high yield (35%) and manganese recovery of 57% while Dalki ore gave inferior results. Guruda ore gave a yield of 34%, similar as that of Dubna. The higher Mn/Fe ratio achieved was 1.16 for Dubna ore from feed having 0.64. Roasting at 850^{0}C did not obtained better results than that at 750^{0}C. This may be due to conversion of magnetite to wustite which is less magnetic than magnetite and thus the iron content in nonmagnetic fraction increased with highest Mn/Fe ratio being 0.93. No metallization of iron was observed at both the temperature (750^{0}C-850^{0}C). At high 950^{0}C, the reduction of iron oxide proceeds to metallic state which results in maximum difference in magnetic susceptibility of metallic iron and manganosite whose formation is maximized at this temperature. Dubna gave the highest grade at 44% Mn. Guruda Mn ore gave highest Mn:Fe ratio of 4.25 and 30.82% yield. Dubna gave the highest metallization iron at 73.55. Magnetic fractions obtained from reduced ores had high iron content (Fe-67%) for Dubna Mn ore.

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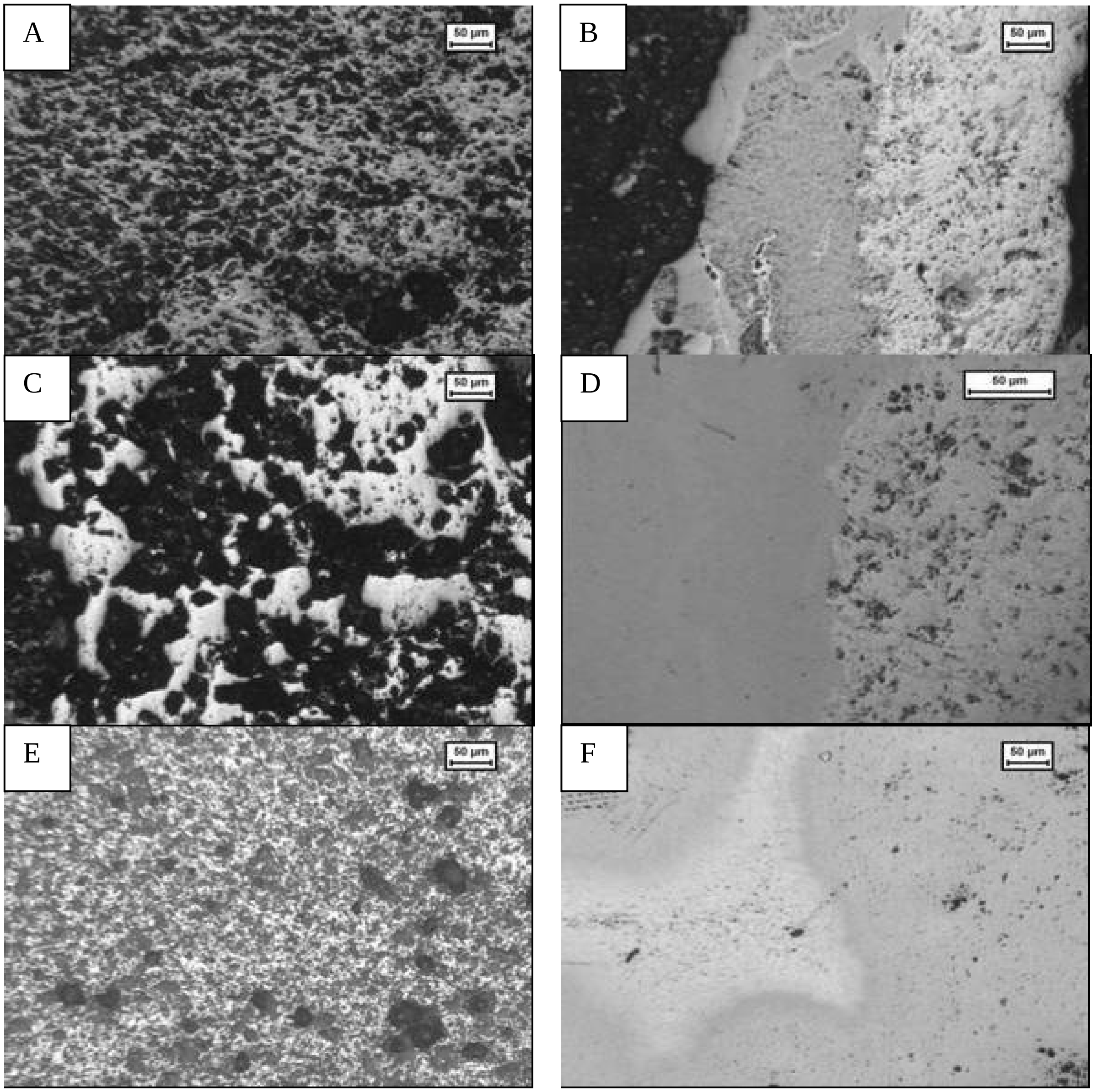


Fig.1. Optical micrograph of Ferro manganese ore from Dalki-Guruda-Dubna area.
A: Mixed facies of goethite, limonite and manganese
B: Limonite, goethite and cryptomelane are closely associated.
C: Cryptomelane associated with limonite
D: Romanechite mineral along with partly formed pyrolusite mineral
E: Hematite along with limonite
F: Pyrolusite within Romanechite

When the ferruginous ore was reduced at 750^0C, poorly-developed magnetite formed (Fig.2A) while cryptomelane/ pyrolusite minerals changes to manganosite (Fig.2B) with increase of temperature euhedral magnetite developed along with wustite (Fig.2C). Often wustite dominates over magnetite resulting thereby difficulty in separation (Fig.2D). However, when the ore is reduced at 950^0C, small iron metallic pills develop while manganosite remain unaltered (Fig.2E). However, at this temperature some clay phase (illite) appear (from burnt coal). Difference in magnetic susceptibility between these two phases support better degree of separation and increase in Mn: Fe ratio of the product. Different synthetic minerals formed after reduction of the ore at different temperature are given in Table 3. The magnetic fraction in case of Dubna can be a feed to blast furnace.

The ferruginous manganese ore from Karnataka region (Rudamaniyappa and Nijagunappa,1991) could be reduced at a low temperature (580^0C-700^0C) and separated well by magnetic separation, probably because of higher Mn:Fe ratio (>1) in the feed and presence of iron mostly as hematite. However, in the present study at lower temperature (750^0C), separation of phases does not occur, probably because of finely intergrown hematite with cryptomelane/romanechite.

Table3. Mineral species in reduced ore sample at three different temperature

Temp. of Reduction	Magnetic Product	Non-Magnetic Products
750^0C	Magnetite, Wustite	Magnetite, Manganosite
850^0C	Magnetite, Wustite	Wustite, Magnetite
950^0C	Fe- Metal, Manganosite	Manganosite, Fe-Metal, clay

DISCUSSION

The low-grade ferruginous manganese ore from three areas viz. Dalki, Guruda and Dubna were subjected to liberation studies which include mineralogical, size classification and chemical analysis of different fractions. The assay of various size fractions reveal that iron and manganese contents are almost uniform in all size fractions and neither the manganese nor the gangue minerals are concentrated in appreciable quantity. The Mn/Fe ratio in all the cases is less than 1 and it has very low gangue constituents. The major manganese minerals are cryptomelane/romanechite and lithiophorite/manganite with minor pyrolusite. Major iron minerals are hematite and goethite. In Dalki sample goethite predominates but in other two localities the hematite occurs in very fine grained spongy form, sometimes intergrown with cryptomelane. The iron content in all three types ore is very high (Fe- 36-47%) and needs to be reduced within permissible range for its effective utilisation. Because of complex nature of iron phases, the direct magnetic separation showed ineffectiveness for the separation of iron from the manganese.

Table4A. Results of Reduced Samples after LIMS Studies

Location	Temperature	Nature	Wt%	Mn%	Fe%	Mn Rec%	Mn:Fe
Guruda	750°	Mag	66.83	19.16	48.59	54.95	0.39
		N.mag	33.17	31.65	31.83	45.05	0.99
Dalki	750°	Mag	57.19	11.66	53.33	45.95	0.22
		N.mag	42.81	18.33	46.36	54.05	0.40
Dubna	750°	Mag	61.01	16.66	52.78	42.69	0.32
		N.mag	38.99	34.99	30.07	57.31	1.16

Table 4B. Results of Reduced Samples after LIMS Studies

Location	Temperature	Nature	Wt%	Mn%	Fe%	Mn Rec%	Mn:Fe
Guruda	850°	Mag	74.78	15.83	60.88	59.73	0.22
		N.mag	25.22	31.65	40.36	40.27	0.93
Dalki	850°	Mag	91.31	7.5	63.49	90.46	0.10
		N.mag	8.69	8.33	58.64	9.54	0.14
Dubna	850°	Mag	39.93	15.83	60.88	24.95	0.26
		N.mag	60.07	31.65	34.07	75.05	0.93

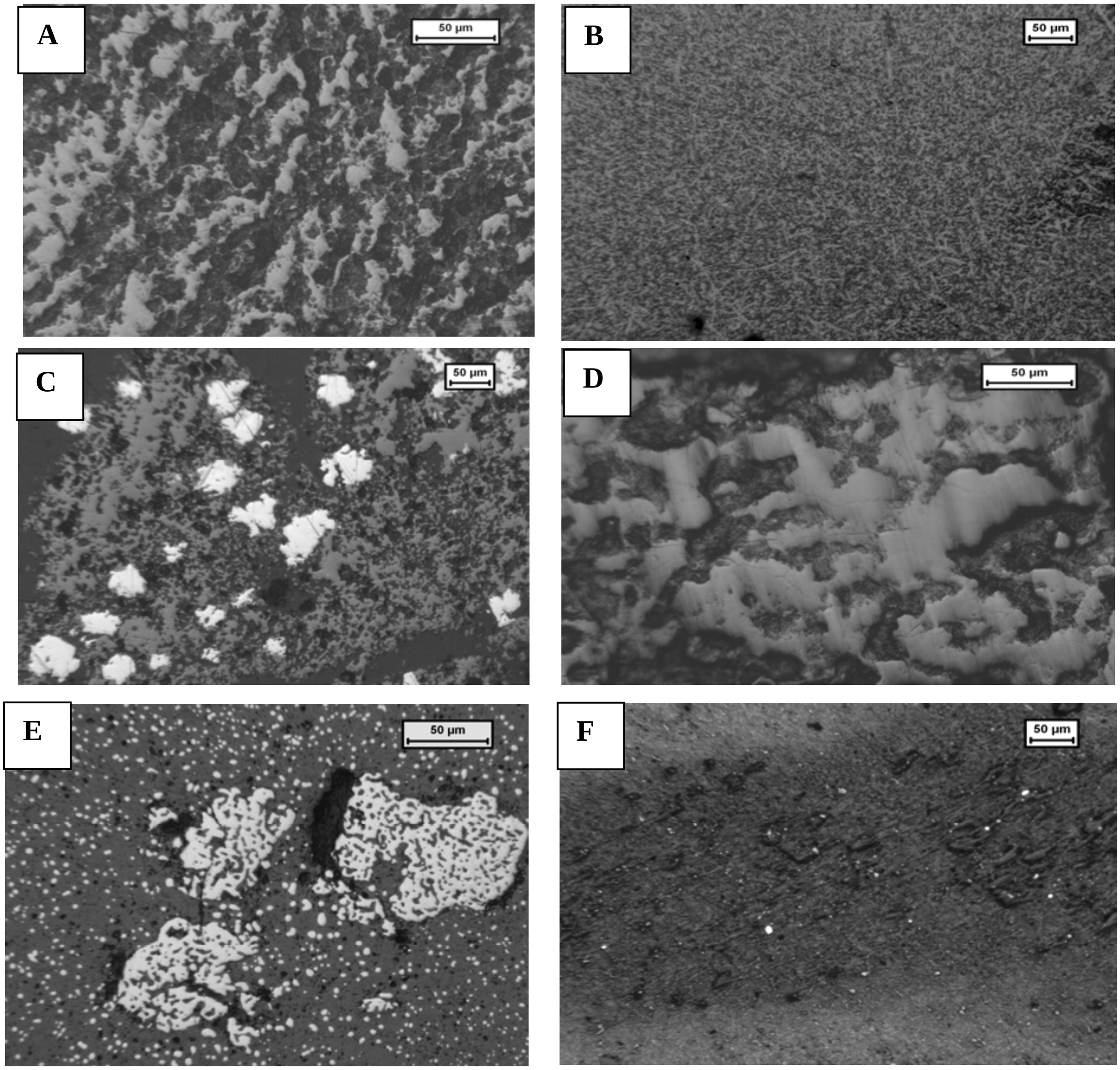
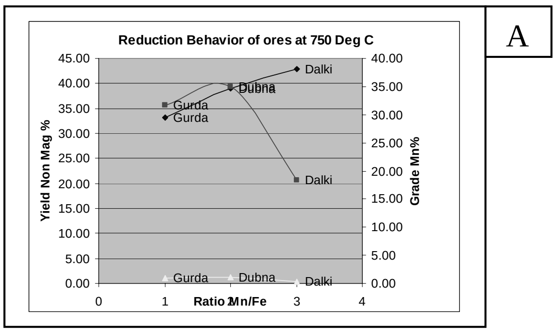


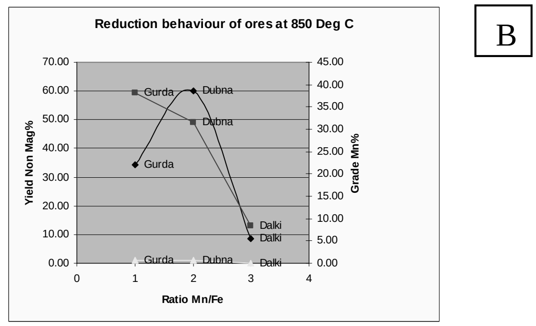
Fig.2. Optical micrographs of reduced Mn-ore sample at temperatures; A and B-750^{0}C; C&D-850^{0}C; E and F-950^{0}C. A. Poorly- developed magnetite; B. Poorly developed manganosite crystallites C. Euhedral Magnetite over manganosite base; D. Poorly developed wustite E. Cluster of Fe-metals along with fine metallic prills; F. Manganosite with a few specks of Fe-metal

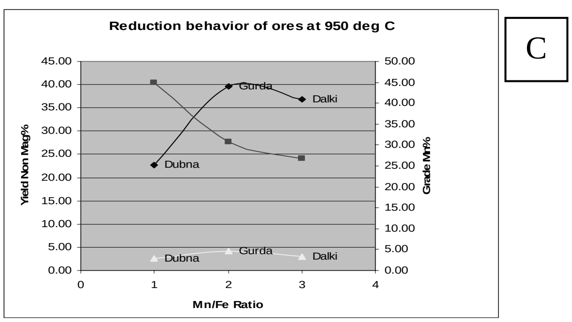
Table 4C. Results of Reduced Samples after LIMS Studies

Location	Temperature	Nature	Wt%	Mn%	Fe%	Mn Rec%	Mn:Fe
Guruda	950°	Mag	69.51	9.0	65.34	34.13	0.20
		N.mag	30.49	39.6	7.26	65.87	5.45
Dalki	950°	Mag	63.16	18.33	56.13	53.95	0.33
		N.mag	36.84	26.82	8.94	46.05	3.00
Dubna	950°	Mag	77.21	18.32	67.86	57.97	0.27
		N.mag	22.79	44.98	17.59	42.03	2.56

In order to change the FeOOH/ Fe_2O_3 phase to Fe_3O_4, the reduction study was carried out at three different temperature viz.750^{0}C, 850^{0}C, 950^{0}C. From the studies of thermodynamics of oxide reduction by reductant, it is known that Fe_2O_3 can be converted into Fe_3O_4 by reducing it earlier with solid carbon. Thus the Fe_3O_4 obtained is magnetic facilitating easy separation from manganese. This is generally obtainable at 700-750^{0}C. However, in present study, at 750^{0}C the growth of magnetite was not proper, probably because of complex nature of its minerals. At 850^{0}C, more wustite develops, which hinders effective separation. Only at 950^{0}C when the iron phase converts to metallic state a good degree of separation was achieved. Comparatively, though Dalki ore gave highest yield, highest grade was obtained from Dubna ore. The comparative reduction behavior of ores at 750^{0}C, 850^{0}C and 950^{0}C has been graphically shown in Figs 3A, 3B and 3C.







Figs.3. Graphs of reduced Mn-ore samples at different temperatures.

CONCLUSIONS

Following conclusions can be made from the forgoing discussion:

1. The ferruginous Mn-ore in Bonai-Keonjhar belt are rich in iron content (36-47%) with Mn: Fe ratio >1%. This assay value inhibits these ore for any use and hence consider as waste.
2. The iron phase in ferruginous manganese ore are goethite and fine grained hematite, often intergrown with cryptomelane, while manganese minerals are cryptomelane/ romanechite, lithiophorite/Manganite and/or pyrolusite.
3. For effective separation of iron phases, the most visible technique was found to be roast reduction followed by magnetic separation. Though thermodynamically goethite/hematite phases reduce to magnetite with reductant at 750^{0}C, in present case no effective separation was achieved at 750^{0}C or 850^{0}C.
4. Effective separation of iron phase is possible at 950^{0}C, by converting it to metallic phase. However, by employing this technique all the ferruginous ore do not behave similarly. Better yield is obtained in some cases while some other attained to Mn: Fe>4.
5. In the present study, the manganese ore from Dalki can be upgraded from a feed of 12.5% to 26.82% with ~37% yield. In contrast the manganese ore from Dubna can be upgraded from 23.32%Mn to ~45% with 23% yield. Similarly, the Gurda ore can be upgraded from 25%Mn to ~40% with 30% yield.

Acknowledgements: The authors are highly thankful to Professor B. K. Mishra, Director of Institute of Minerals and Materials Technology, Bhubaneswar for his kind permission to publish this paper.

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