

Role of mineralogy, mineral chemistry and geochemistry in mineral processing :

A case study for high phosphorous manganese ores of Nishikhal, South Orissa, India

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ABSTRACT

Conformable manganese ore bands are present in the khondalite suite of rocks belonging to the Eastern Ghats Complex of South Orissa, India. The ores can be classified as high-grade, siliceous and ferruginous. Cryptomelane, romanechite, pyrolusite, jacobsonite, hausmannite, braunite, lithiophorite, birnessite and pyrophanite represent the manganese minerals. Goethite, limonite, graphite, hematite, magnetite are the associated opaque gangue minerals while quartz, orthoclase, hyalophane, garnet, kaolinite, apatite, collophane, fibrolite, zircon, biotite and muscovite are the silicate gangue minerals recorded in these ores.

Optical microscopic and Electron Probe Microanalysis studies revealed that the phosphorous, in these ores, present in the form of (i) apatite inclusions within quartz, orthoclase and garnet, (ii) amorphous calcium phosphate (collophane) within the voids of garnet, (iii) adsorbed component within the manganese oxide and silicate phases as well as in the iron oxide phase (goethite). Geochemical studies indicated that high amount of phosphorous is linked with ferruginous manganese ores. Regression analysis of the geochemical data suggests a strong positive correlation between P-Fe and P-Mn. Magnetic separation studies on low- and off- grade bulk manganese samples, indicated that the phosphorous contributed by apatite is relatively low (4.44 to 17.76%) compared to the phosphorous held in adsorption (82.24 to 95.56%), while the contribution of phosphorous by collophane is insignificant. The above studies confirm that the association of phosphorous in

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Nishikhal ores is very complex. Since most of the phosphorous is in adsorption, these low and off grade ores are expected to respond well to dephosphorisation by reduction roasting followed by magnetic separation or roast alkali leaching method.

Key words: Manganese ore, Mineralogy, Mineral chemistry, Processing.

INTRODUCTION

Mineral Processing is primarily a process of separation of minerals by adopting different methods. A thorough understanding of the minerals present and their texture in any ore sample is a pre-requisite to separate one mineral from the other. Mineralogical examination of an ore provides useful clue to the plausible methods for its beneficiation and thus dispenses with a large amount of avoidable experimentation. Such examination of the various mineral processed derivatives will also help in effecting improved efficiency in mineral processing. Microscope is an indispensable tool for mineralogical studies. XRD and EPMA studies also provide valuable information about mineralogy and mineral chemistry. Hence, in the present paper mineralogy, mineral chemistry and geochemistry of Nishikhal (Lat.19°12'-12°14'N and Long.83°12'-83°14'E) manganese ores (high in phosphorous, silica and iron) were studied and the data generated are interpreted in terms of evolving a suitable beneficiation technique.

Manganese ore is an important raw material and holds key position in metallurgical industries. About 97% of manganese ores produced in India are used for production of various kinds of steel and ferroalloys and the rest is mainly used in chemical and battery industries. 56% of total manganese ore reserves of India contain iron, silica and/or phosphorous beyond specified limits and is unsuitable for iron and steel as well as ferromanganese industries. The presence of phosphorous in particular has a deleterious effect on mechanical properties of iron and steel. Hence, phosphorous content in manganese ores is desired to be as low as possible. Adequate information on the mineralogy and nature of association of phosphorous, iron and silica are very much essential before any physical and/or chemical route of beneficiation of the manganese ores are taken up.

MINERALOGY

The mineralogy of manganese ores of Nishikhal was studied under transmitted and reflected light microscope. Microscopic identification of ore minerals was made according to the standard literature^[1-3]. Microhardness and reflectivity values as well as etch tests along with other optical characters were used in the identification of ore minerals. X-ray powder analyses of a number of samples were carried out to confirm the microscopic findings. X-ray diffraction (XRD) patterns of different types of ore samples are presented in Fig.1. (B = Birnessite;

C = Cryptomelane; G = Goethite; J = Jacobsite; L = Lithiophorite; O = Orthoclase; S = Spessartite; P = Pyrolusite; Q = Quartz).

The above studies on the manganese ore samples from different bands of Nishikhal deposit suggest that the major minerals are cryptomelane, romanechite and pyrolusite with minor amounts of jacobsite, hausmannite, braunite and wad. Lithiophorite and birnessite are observed in some cases whereas pyrophanite is observed only in rare instances. Goethite is very intimately and intricately associated with the manganese minerals. The associated opaques are graphite, magnetite, hematite, pyrite and traces of chalcopyrite. The gangue minerals are quartz, orthoclase, garnet, kaolinite, with minor amounts of apatite, fibrolite (sillimanite), zircon, biotite and muscovite. The detailed mineralogy along with their textures is enumerated below.

Manganese Minerals

Cryptomelane is present almost in all the varieties of samples. It forms colloform bands with or without pyrolusite, romanechite and sometimes as alternating layers with goethite. Fine colloidal banding of cryptomelane with intermittent bands of somewhat larger grains are noticed. It occurs commonly in nodular, kidney shaped and botryoidal masses with pyrolusite. Replacement of cryptomelane by pyrolusite is very common. Cryptomelane replaces hausmannite as well as silicate gangue minerals and encloses them often exhibiting boxwork type texture. At places cryptomelane is observed along the intergranular spaces of silicate gangue minerals. Hydrous oxides of iron and manganese are associated with and at places replaced by cryptomelane. Cryptomelane replaces graphite along grain boundaries and cleavage planes and in rare instances cryptomelane pseudomorphs after graphite. Cryptomelane exhibits kink-like, branch-like and flake-like features owing to replacement of graphite. *Romanechite* is present in considerable amounts in botryoidal as well as ferruginous manganese ores and in fewer amounts in the massive ores. In botryoidal ores it shows mammillary texture. It occurs as colloform bands with cryptomelane and pyrolusite, as oolites and pisoliths within cryptomelane and to a lesser extent with pyrolusite. *Romanechite* is found to replace cryptomelane and enclose islands of the latter while at some places romanechite is replaced by cryptomelane. Occurrence of *pyrolusite* alone is mostly confined to cavity fillings. In the cavities pyrolusite commonly present as euhedral masses and is arranged in different fashion. Often large crystals with well-developed faces exhibit accicular form. It commonly occurs as cryptocrystalline bands interlayered with cryptomelane; irregular patches as well as fine felted ice-flower structure within cryptomelane and lithiophorite aggregates; fine needles as well as stout crystals within the masses of cryptomelane and romanechite. It occurs as colloform bands with cryptomelane, romanechite and goethite and also in the form of oolites and pisoliths within cryptomelane,

romanechite and goethite. Replacement of cryptomelane, romanechite, goethite and silicate gangue minerals is very common. *Jacobsite* is recorded in ferruginous ores. It occurs as subhedral to anhedral grains within the groundmass of cryptomelane. In most of the cases jacobsite grains are replaced by cryptomelane and romanechite resulting in irregular margins. At places unreplaced islands of jacobsite are enclosed within cryptomelane and romanechite. *Hausmannite* is subhedral to tabular, present as isolated grains within secondary manganese minerals. Replacement of hausmannite along margins and fractures by cryptomelane and romanechite is also observed. *Braunite* is subhedral to euhedral in shape and occurs within a matrix of cryptomelane. At places the former is replaced by latter. *Lithiophorite* occurs as fine-grained aggregates in association with birnessite, kaolinite in lateritised ores and occurs with cryptomelane, romanechite, quartz and orthoclase in massive varieties. Lithiophorite replaces cryptomelane and occasionally encloses quartz, orthoclase, garnet and cryptomelane. This is also present along the cleavage planes of graphite and at times encloses graphite. *Birnessite* occurs as patches in the hydrous oxides of manganese and iron, as rims around the gangue minerals, cryptomelane and along cleavage planes of graphite. *Pyrophanite* occurs as fine scale to lath shaped grains enclosed in a matrix of cryptomelane and goethite. At places pyrophanite is partially rimmed by thin layer of goethite.

Opaque Gangue Minerals

Goethite forms colloform bands with cryptomelane, romanechite and pyrolusite. Fine drop like, irregular, myrmekitic, oolitic, pisolitic and veins of goethite are observed within cryptomelane and romanechite. The size of the goethite in these forms is highly variable. Nodular and botryoidal forms of goethite are quite common. Goethite is present along the cleavage planes of graphite as well as enclosed graphite within it. Flakes, scales and tablets of *graphite* occur along the grain boundaries, cleavage planes and fractures of manganese ore minerals as well as silicate gangue minerals. Graphite flakes and tablets are curved, kinked, folded and occasionally coalesce into masses of graphite containing lenticular, wedge-like and irregular inclusions of silicate minerals. Traces of *pyrite* and *chalcopyrite* are present as fine disseminations. *Hematite* and *magnetite* are observed in rare instances.

Silicate Gangue Minerals

Quartz, *orthoclase*, *hyalophane*, *garnet*, *kaolinite* and traces of *sillimanite*, *biotite*, *muscovite* and *zircon* are the silicate gangue minerals associated with the above minerals. Grain size of most of these silicate minerals is in between 50-300 microns (Table 1). These gangue minerals in the manganese ores are present in various shapes such as subhedral, sub-angular and highly irregular. Replace-

ment of these silicates along grain boundaries and intergranular spaces by manganese ore minerals is quite common. At places kaolinite is found to occur as patches within manganese ores due to alteration of orthoclase. Radiating texture of fibrolite (*sillimanite*) is observed both megascopically and microscopically. Fine inclusions of *apatite* crystals varying in size from 5 to 30 microns are found in the quartz, orthoclase and garnet. Biotite and muscovite are present as inclusions within orthoclase while amorphous calcium phosphate (*collophane*) fills the voids within garnet. Subhedral zircon grains are present as inclusions within quartz and orthoclase. Garnet occurs as subhedral to anhedral grains and is present along with quartz and orthoclase. XRD patterns suggest (Fig.1) that the garnet is dominantly spessartite. Alteration of the garnet proceeds along the grain boundaries and fractures, often leading to a distinct alteration rim with a central core. In rare cases, complete alteration of garnet is also observed. It alters to hydrous oxides of iron and manganese and subsequently cryptomelane, romanechite and/or goethite are formed from the altered product. The alteration of garnet could be due to weathering and supergene enrichment process that affected during post-metamorphic period and may be by meteoric waters^[4].

Table 1 : Grain size distribution percentage of quartzofeldspathic gangue minerals in Nishikhal manganese ores

| Class | Size range in microns | Percent |
|-------|-----------------------|---------|
| 1 | 0-50 | 7.90 |
| 2 | 50-100 | 30.24 |
| 3 | 100-150 | 27.11 |
| 4 | 150-200 | 15.80 |
| 5 | 200-250 | 9.80 |
| 6 | 250-300 | 5.44 |
| 7 | 300-350 | 1.22 |
| 8 | 350-400 | 0.81 |
| 9 | 400-450 | 0.54 |
| 10 | 450-500 | 0.13 |
| 11 | 500-550 | 0.40 |
| 12 | 550-600 | 0.00 |
| 13 | 600-650 | 0.13 |
| 14 | 650-700 | 0.27 |
| 15 | 700-750 | 0.13 |

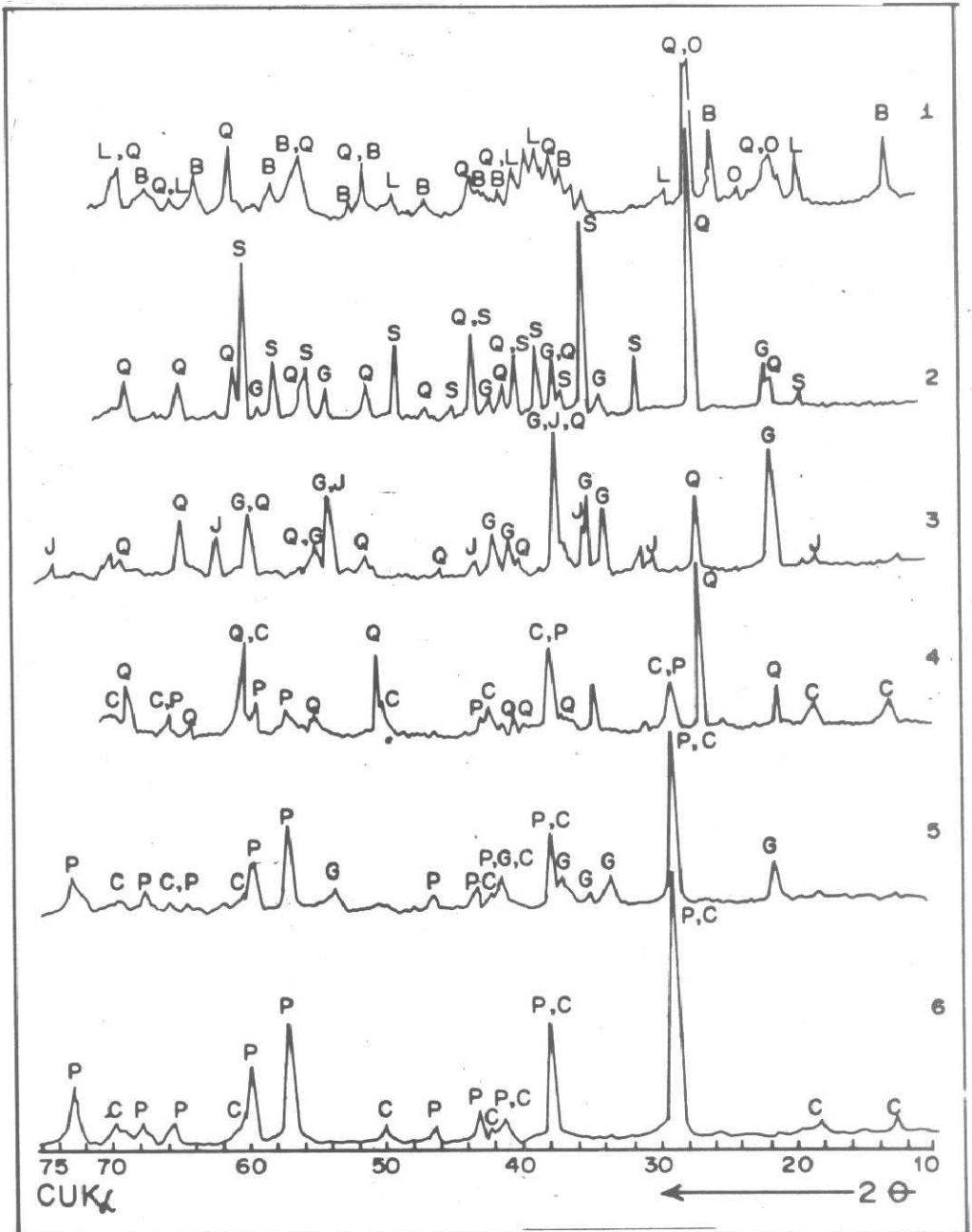


Fig. 1 : XRD pattern of manganese ore samples

MINERAL CHEMISTRY

The Electron Probe Microanalysis (EPMA) of different mineral phases throws light on the association of valuable and harmful trace elements present in them. A number of analyses of the dominant mineral phases of Nishikhal manganese ores were carried out to ascertain the distribution of various elements, particularly the phosphorous.

Cryptomelane : Cryptomelane is essentially potassium bearing manganese oxide phase, the K_2O content of which ranges from 1.22% to 5.01%. Small amounts of BaO have been detected in a few analyses (Table 2). EPMA data indicates that phosphorous is present in all the analyses and varies from 0.27 to 0.74% P_2O_5 . Some of the cryptomelane contain minor amounts of Na_2O , MgO and TiO_2 . Barium and sodium appear to be substituting for potassium while aluminium and iron substitute for manganese. Traces of CuO, NiO, CoO and ZnO have also been detected in a few analyses.

Table 2 : Electron probe microanalyses of cryptomelane and pyrolusite (wt.%)

| | Cryptomelane (n=11) | | | Pyrolusite (n=3) | | |
|-----------|---------------------|---------|---------|------------------|---------|---------|
| | Minimum | Maximum | Average | Minimum | Maximum | Average |
| MnO_2 | 94.00 | 97.49 | 95.40 | 98.04 | 99.88 | 98.69 |
| K_2O | 1.22 | 5.01 | 3.86 | 0.45 | 0.65 | 0.55 |
| P_2O_5 | 0.27 | 0.74 | 0.45 | 0.01 | 0.32 | 0.21 |
| CaO | 0.02 | 0.48 | 0.28 | 0.33 | 0.38 | 0.35 |
| Fe_2O_3 | 0.09 | 0.77 | 0.22 | 0.20 | 1.83 | 0.74 |
| Al_2O_3 | 0.05 | 1.03 | 0.52 | 0.16 | 0.91 | 0.61 |
| SiO_2 | 0.02 | 0.15 | 0.07 | 0.04 | 0.16 | 0.01 |
| Na_2O | Nil | 0.11 | 0.05 | 0.03 | 0.09 | 0.05 |
| MgO | Nil | 0.12 | 0.04 | 0.05 | 0.09 | 0.07 |
| TiO_2 | Nil | 0.02 | 0.01 | 0.02 | 0.02 | 0.02 |
| BaO | Nil | 0.20 | 0.07 | Nil | 0.06 | 0.06 |
| CuO | Nil | 0.06 | 0.02 | Nil | 0.01 | 0.01 |
| CoO | Nil | 0.02 | 0.01 | 0.01 | 0.03 | 0.15 |
| ZnO | Nil | 0.06 | 0.03 | Nil | 0.01 | 0.01 |
| NiO | Nil | 0.13 | 0.07 | 0.01 | 0.07 | 0.04 |

Pyrolusite : The composition of pyrolusite (Table 2) shows good stoichiometry (98.04% to 99.88% MnO_2 with an average of 98.69%). It contains traces of

K₂O, MgO and TiO₂ with more or less uniform concentration. Fe₂O₃, Al₂O₃, P₂O₅, Na₂O and SiO₂ in pyrolusite are highly variable. CuO, NiO, ZnO and BaO are recorded in trace quantities in some pyrolusites.

Goethite : Goethite contains 77.77 to 81.95% Fe₂O₃ together with considerable amount of Al, Si, P, Mn, and Co (Table 3). Amongst the latter elements phosphorous is the highest with an average of 1.67% P₂O₅. The phosphorous in these goethites may be due to adsorption and/or chemisorption. Manganese is mostly present substituting for iron, whereas Si, may be due to admixtures and/or impurities. Trace elements like Na, Mg, Ca, Ti, Cu, Ni and Zn are recorded in some of the goethite whereas they are absent in others.

Table 3 : Electron probe microanalyses of goethite (wt.%)

| | ← Goethite (n=9) → | | |
|--------------------------------|--------------------|---------|---------|
| | Minimum | Maximum | Average |
| Fe ₂ O ₃ | 77.77 | 81.95 | 79.55 |
| Al ₂ O ₃ | 0.21 | 2.81 | 1.11 |
| P ₂ O ₅ | 0.81 | 2.59 | 1.67 |
| MnO ₂ | 0.30 | 0.80 | 0.48 |
| SiO ₂ | 0.37 | 1.99 | 0.84 |
| Na ₂ O | Nil | 0.08 | 0.04 |
| MgO | Nil | 0.33 | 0.10 |
| CaO | Nil | 0.13 | 0.08 |
| TiO ₂ | Nil | 0.10 | 0.05 |
| BaO | Nil | 0.09 | 0.05 |
| CuO | Nil | 0.04 | 0.02 |
| NiO | Nil | 0.07 | 0.04 |
| CoO | 0.01 | 0.08 | 0.05 |
| ZnO | Nil | 0.14 | 0.07 |
| H ₂ O* | 20.53 | 8.80 | 15.85 |

* H₂O by difference

Garnet : Garnet is rich in manganese ranging from 26.35% to 32.50% MnO and is predominantly spessartite (Table 4). It contains nil to 0.13% of P₂O₅. Phosphorous in these garnets may be due to the replacement of SiO₄ group by PO₄ group^[51]. In the altered garnet (Table 5), the central unaltered core is devoid of phosphorous whereas the altered rim is enriched with it (0.52% to 3.66%

P₂O₅). This may probably be either due to migration of phosphorous from central portion and enrichment in the rim or due to addition of phosphorous to these altered products during weathering or due to both of the above factors.

Table 4 : Electron probe microanalyses of garnet (wt.%)

| | ← Garnet (n=3) → | | |
|--------------------------------|------------------|---------|---------|
| | Minimum | Maximum | Average |
| SiO ₂ | 35.28 | 36.41 | 35.80 |
| MnO | 29.57 | 32.50 | 31.20 |
| Al ₂ O ₃ | 19.18 | 19.93 | 19.63 |
| CaO | 6.37 | 6.91 | 6.60 |
| FeO | 5.36 | 6.00 | 5.75 |
| MgO | 0.53 | 0.57 | 0.56 |
| TiO ₂ | 0.07 | 0.17 | 0.11 |
| P ₂ O ₅ | 0.02 | 0.13 | 0.06 |
| K ₂ O | Nil | 0.04 | 0.04 |
| BaO | Nil | 0.09 | 0.09 |

Apatite : Apart from calcium and phosphorous, apatite contains traces of Si, Ba, Na, Mg, K, Ti, Cu, Ni, Co and Zn (Table 6).

Kaolinite : It is mostly a hydroxide of aluminium silicate (Table 6). Traces of Ti, Fe, Mg present in it, may be due to substitution for Al⁺³ while elements like Ca, P, Na, K might be present either as adsorbed cations or as impurities. Appreciable amount of manganese is present in kaolinite may be due to replacement of manganese by aluminium.

GEOCHEMISTRY

Geochemistry: The geochemical data of manganese ores can be interpreted in terms of environment of deposition and ore genesis besides evaluating the economic potentiality of the deposit. 29 samples representing from different types of manganese ores were analysed for major as well as minor elements (Table 7). Regression analysis of the chemical data of the samples was carried out with the help of LOTUS-123. The geochemical characteristics of different manganese ores are discussed below.

Table 5 : Electron probe microanalyses of altered and unaltered garnet (wt.%)

| | Garnet Core, Unaltered (n=3) | | | Garnet Rim, Altered (n=3) | | |
|--------------------------------|------------------------------|---------|---------|---------------------------|---------|---------|
| | Minimum | Maximum | Average | Minimum | Maximum | Average |
| SiO ₂ | 36.60 | 37.35 | 36.97 | 1.36 | 14.11 | 7.67 |
| MnO | 26.35 | 30.98 | 29.22 | — | — | — |
| MnO ₂ | — | — | — | 37.59 | 44.55 | 4.12 |
| Al ₂ O ₃ | 20.11 | 20.76 | 20.41 | 22.01 | 26.82 | 25.06 |
| CaO | 5.97 | 7.26 | 6.79 | 0.19 | 1.07 | 0.59 |
| FeO | 5.40 | 11.13 | 7.42 | — | — | — |
| Fe ₂ O ₃ | — | — | — | 9.09 | 21.53 | 13.28 |
| MgO | 0.43 | 0.59 | 0.49 | 0.04 | 0.22 | 0.15 |
| TiO ₂ | 0.05 | 0.07 | 0.06 | 0.08 | 0.11 | 0.09 |
| P ₂ O ₅ | Nil | Tr. | Tr. | 0.52 | 3.66 | 1.58 |
| K ₂ O | Nil | Nil | Nil | 0.01 | 0.01 | 0.01 |
| Na ₂ O | Nil | Nil | Nil | 0.15 | 0.44 | 0.29 |
| BaO | Nil | 0.04 | 0.04 | Nil | Nil | Nil |

"—" not detected; Tr.= Traces

The geochemical data indicated that the manganese ore samples show wide variation in MnO₂, Fe₂O₃ and SiO₂ values with low Mn/Fe ratio. Phosphorous content is very high (average 0.87% P₂O₅) in comparison to other manganese deposits of India as well as other deposits of the world. Highest amount of P₂O₅ is observed in iron rich samples conforming to the mineral chemistry data obtained by EPMA. Dominance of CaO over MgO and K₂O over Na₂O are the characteristics of Nishikhal manganese ores. Regression analysis of the geochemical data indicates that there exists a strong positive correlation between phosphorous - iron and phosphorous - manganese which reveals that a good amount of phosphorous is associated in adsorbed state with the manganese and iron phases of the ore which is in confirmation to mineral chemistry data.

Phosphorous distribution: Different modes of occurrence of phosphorous has been observed in manganese ores occurring in different geological environments and geographic locations. It is either present as definite mineral phases such as apatite, carbonate apatite, ardenite, mangan-apatite, collophane, frankolite, gorceixite, kurskite, vivianite, xenotime and/or in adsorbed state within various manganese and associated iron mineral phases (Table 8). In Nishikhal manga-

Table 6 : Electron probe microanalyses of kaolinite and apatite (wt.%)

| | Kaolinite (n=2) | | | Apatite (n=3) | | |
|--------------------------------|-----------------|---------|---------|---------------|---------|---------|
| | Minimum | Maximum | Average | Minimum | Maximum | Average |
| Na ₂ O | Nil | 0.24 | 0.24 | Nil | 0.06 | 0.06 |
| MgO | 0.01 | 0.06 | 0.03 | Nil | 0.04 | 0.04 |
| Al ₂ O ₃ | 37.03 | 38.01 | 37.52 | Nil | 0.04 | 0.03 |
| SiO ₂ | 46.81 | 48.10 | 47.45 | Nil | 0.31 | 0.23 |
| P ₂ O ₅ | Nil | 0.01 | 0.01 | 42.89 | 44.96 | 43.65 |
| K ₂ O | Nil | 0.03 | 0.03 | Nil | 0.01 | 0.01 |
| CaO | 0.04 | 0.09 | 0.07 | 54.11 | 54.89 | 54.52 |
| TiO ₂ | Nil | Nil | Nil | Nil | 0.02 | 0.02 |
| MnO | 0.14 | 0.23 | 0.18 | 0.40 | 0.71 | 0.56 |
| Fe ₂ O ₃ | 0.62 | 2.73 | 1.67 | 0.01 | 0.07 | 0.03 |
| BaO | Nil | 0.03 | 0.03 | Nil | 0.15 | 0.15 |
| CuO | Nil | 0.02 | 0.02 | Nil | 0.01 | 0.01 |
| NiO | Nil | Nil | Nil | Nil | 0.06 | 0.06 |
| CoO | Nil | 0.01 | 0.01 | Nil | 0.03 | 0.03 |
| ZnO | Nil | Nil | Nil | Nil | 0.02 | 0.01 |
| H ₂ O* | 15.35 | 10.45 | 12.74 | — | — | — |

" — " not determined; * H₂O by difference

nese ores, phosphorous is present as apatite (as fine inclusions within quartz, orthoclase and garnet) and rarely as collophane; and also in adsorbed state in the manganese and iron mineral phases. In view of complex nature of phosphorous association, it is important to have the quantitative knowledge about the distribution of phosphorous in different modes.

In order to remove the silica, phosphorous and iron from these low and off grade manganese ores, samples with low to medium manganese, iron, medium to high phosphorous and high silica were selected. The samples were ground and sieved through 100, 150 and 200 mesh (BSS). Each fraction was separated into magnetic and non-magnetic using an iso-dynamic magnetic separator (20° side tilt, 30° forward slope and with a current of 0.8 amps.). MnO₂, SiO₂, Fe₂O₃, CaO and P₂O₅ percentages in all the feed as well as their magnetic and non-magnetic products were determined by conventional wet chemical methods (Table 9).

Table 7 : Major and minor elemental distribution in different types of manganese samples (29 samples)

| | Minimum | Maximum | Average |
|--------------------------------|---------|---------|---------|
| MnO ₂ | 12.26 | 82.1 | 50.85 |
| Fe ₂ O ₃ | 1.55 | 70.99 | 14.45 |
| SiO ₂ | 0.15 | 38.72 | 14.34 |
| P ₂ O ₅ | 0.28 | 1.49 | 0.87 |
| BaO | 0.08 | 0.16 | 0.12 |
| Na ₂ O | 0.01 | 0.19 | 0.09 |
| K ₂ O | 0.14 | 3.93 | 1.77 |
| MgO | 0.01 | 0.03 | 0.01 |
| TiO ₂ | 0.03 | 0.92 | 0.24 |
| Al ₂ O ₃ | 1.10 | 31.62 | 6.54 |
| CaO | 0.28 | 1.37 | 0.69 |
| LOI | 5.35 | 14.61 | 10.24 |

LOI = Loss on ignition

In the magnetic products significant improvement in manganese, iron, phosphorous and calcium and decrease in silica is observed. It was possible to obtain manganese concentrates having 63.2 -75.8% MnO₂ from feed containing 41.89 - 48.74% MnO₂ with recoveries of 91.89% to 96.41%. However, in the manganese concentrates (magnetic product), both iron and phosphorous are also increased. Increase of iron in manganese concentrate is due to very fine grain size and intricate locking of goethite with the manganese minerals. The increase in phosphorous in the magnetic product suggests that it is dominantly present in iron and manganese phases. The P₂O₅ distribution in the magnetic products varies between 82.24% - 95.56%. SiO₂ (72.3%-88.54%) is removed in the non-magnetic products. From this it is calculated that contribution of phosphorous to these manganese ores by apatite is relatively much lower (4.44-17.76%) than phosphorous in adsorption which corroborates to the mineral chemistry data revealed by EPMA.

Table 8 : Various forms of phosphorous association
in different manganese ores

| Name of manganese deposit | Different forms of phosphorous association |
|---|---|
| Nikopal deposit, USSR ^[6] | Kurskite, collophane, apatite, xenotime, vivianite |
| Chaitura deposit, USSR ^[7] | Apatite, kurskite, frankolite |
| Hunan deposits, China ^[8-9] | Apatite |
| Epleny, Urkut, Hungary ^[10] | Carbonate apatite |
| Koduru-Garividi-Garbham, A.P., India ^[11] | Apatite, gorceixite as well as adsorbed within manganese and iron phases. |
| Tirodi, Ramtek, Chikla, and Sitasaongi of Manganese ores of M.P. and Maharastra, India ^[12-13] | Apatite, manganapatite and adsorbed in Kutnohorite. |
| Kamjhi ores, Rajasthan ^[14] | Collophane |
| Nishikhal ores, Orissa, India ^[4,15] | Apatite, collophane and adsorbed in Iron and manganese phases. |
| Kutinga ores, Orissa, India ^[16] | Apatite, adsorbed in iron and manganese phases |
| Goriajhar ores, Orissa, India ^[2] | Apatite |
| Kajlidongri ores, M.P. ^[17-18] | Ardennite |
| Jothvad ores, Gujarat ^[19] | Apatite |
| Diguva and Chikkapara ores, A.P. ^[20] | Apatite |

DISCUSSION AND CONCLUSION

Microscopic examination of an ore is of utmost importance in mineral processing. While chemical analyses (geochemistry) provide data regarding the elements present in an ore, optical and electron microscopic study furnishes information about the minerals containing the elements. Correlation of chemical analyses with mineralogy and mineral chemistry is highly desirable to take the advantage in mineral processing. The findings of mineralogy, mineral chemistry and geochemistry along with the phosphorous distribution of Nishikhal manganese ores are correlated to suggest an effective method of beneficiation.

Manganese ores of Nishikhal are constituted of primary minerals such as braunite, jacobsonite, hausmannite, pyrophanite, garnet and secondary minerals

Table 9 : Distribution of MnO_2 , Fe_2O_3 , SiO_2 , P_2O_5 and CaO in magnetic and non-magnetic products of Nishikhal manganese ores

| SampleNo./Type | Weight | MnO_2 | Fe_2O_3 | SiO_2 | P_2O_5 | CaO | |
|----------------|--------|---------|-----------|---------|----------|-------|-------|
| 1) Feed | 100 | 47.24 | 16.18 | 26.63 | 0.39 | 0.45 | |
| | Mag. | 70.51 | 63.57 | 21.20 | 4.41 | 0.54 | 0.61 |
| | N.mag. | 29.49 | 5.66 | 4.78 | 81.46 | 0.06 | 0.09 |
| | Dist.% | Mag. | 96.41 | 91.38 | 11.46 | 95.56 | 94.19 |
| | N.Mag. | 3.59 | 8.62 | 88.54 | 4.44 | 5.81 | |
| 2) Feed | 100 | 48.74 | 4.76 | 30.34 | 0.47 | 0.56 | |
| | Mag. | 69.74 | 63.20 | 6.01 | 12.45 | 0.58 | 0.72 |
| | N.Mag. | 30.26 | 12.85 | 1.66 | 74.96 | 0.17 | 0.25 |
| | Dist.% | Mag. | 91.89 | 89.3 | 27.68 | 88.72 | 86.91 |
| | N.Mag. | 8.11 | 10.7 | 72.32 | 11.28 | 13.09 | |
| 3) Feed | 100 | 41.89 | 3.68 | 43.69 | 0.26 | 0.62 | |
| | Mag. | 58.97 | 69.60 | 5.58 | 14.78 | 0.34 | 0.91 |
| | N.Mag. | 41.03 | 7.29 | 0.65 | 80.68 | 0.07 | 0.12 |
| | Dist.% | Mag. | 93.21 | 92.5 | 20.85 | 87.47 | 91.60 |
| | N.Mag. | 6.79 | 7.5 | 79.15 | 12.53 | 8.40 | |
| 4) Feed | 100 | 48.44 | 4.24 | 36.12 | 0.32 | 0.67 | |
| | Mag. | 64.51 | 67.07 | 6.24 | 10.51 | 0.45 | 0.91 |
| | N.Mag. | 5.49 | 5.25 | 0.92 | 88.25 | 0.04 | 0.15 |
| | Dist.% | Mag. | 95.87 | 92.5 | 17.8 | 95.34 | 91.69 |
| | N.Mag. | 4.13 | 7.5 | 82.2 | 4.66 | 8.31 | |
| 5) Feed | 100 | 44.05 | 1.36 | 47.04 | 0.29 | 0.62 | |
| | Mag. | 53.65 | 75.80 | 2.27 | 10.72 | 0.44 | 0.95 |
| | N.Mag. | 46.35 | 6.62 | 0.36 | 87.72 | 0.11 | 0.17 |
| | Dist.% | Mag. | 92.98 | 87.95 | 12.39 | 82.24 | 86.61 |
| | N.Mag. | 7.02 | 12.05 | 87.61 | 17.76 | 13.39 | |

Mag.= Magnetic; N-Mag. = Non-Magnetic; Dist. = Distribution

like cryptomelane, romanechite, pyrolusite, lithiophorite and birnessite. Iron is present dominantly as goethite with trace quantities of hematite and magnetite. Scales and flakes of graphite are present along the grain boundaries and intergranular spaces of primary manganese and silicate minerals while secondary

manganese and iron minerals replace graphite along the margins and cleavage planes. Quartz, orthoclase, hyalophane, garnet, sillimanite, zircon, biotite, muscovite are present as silicate gangue minerals. Phosphorous in Nishikhal manganese ores is very high and its mode of occurrence is very complex. It is present as apatite inclusion within quartz, orthoclase and garnet; occasionally as amorphous calcium phosphate (collophane) within the voids of garnet; as adsorbed component with goethite, cryptomelane, pyrolusite, garnet, kaolinite and in the altered product of garnet. EPMA study has suggested that highest amount of phosphorous is contributed by goethite to these ores followed by cryptomelane, romanechite and pyrolusite which may be due to adsorption and/or chemisorption. Geochemical data also revealed that highest amount of phosphorous is associated with high iron bearing samples (ferruginous manganese ores).

Iron present in these ores can not be removed by conventional physical methods of beneficiation, as it is intricately and intimately associated with the manganese minerals. Quartz, orthoclase, hyalophane, garnet, kaolinite, fibrolite, zircon, biotite, muscovite contribute silica to these ores. Attempt to remove these silicates by physical beneficiation will not only reduce silica but also a part of phosphorous since apatite forms a part these silicates. Magnetic separation studies confirmed that by removing silicates, the manganese and iron content increased in these ores but the phosphorous is also relatively increased. This is due to the fact that the contribution of phosphorous by apatite is only 4-18% (approximately) while the rest is contributed by secondary manganese and iron minerals like goethite, cryptomelane, romanechite, pyrolusite. For dephosphorisation, these ores are neither amenable to conventional physical beneficiation nor to acid leaching methods. Reduction roasting followed by magnetic separation or roast-alkali leaching may be employed for removal of phosphorous from these ores.

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REFERENCES

1. Ramdohr, P., (1969), "The ore minerals and their intergrowths", Pergamon Press, London, p. 1174.
2. Roy, S., (1966), "Syngenetic manganese formations of India" Jadavpur University, Calcutta, p. 219.
3. Uytendogaardt, W. and Burke, E.A.J., (1971), "Tables for microscopic identification of ore minerals" Elsevier Publications Co., Amsterdam, p. 359.

4. Acharya, B.C., Rao, D.S., Sahoo, R.K. and Dash, B., (1994), "Phosphorous in the siliceous manganese ores of Nishikhal, Orissa. *Ind. Jour. Geol.*, 66, p. 15.
5. Deer, W.A., Howai, R.A. and Zussman, J., (1963), "Rock forming minerals", Vol. 1, Longmans Green and Co. Ltd.
6. Grynov, B.I. and Chervonookaya, L.V., (1965), "Phosphorous in the Nikopol manganese ores", *Litologia i Polezn. Iskop*, 4, p. 153.
7. Georgievskii, I.V., (1966), "The state of phosphorous in the manganese ores of Chitura deposit, Obogashch Rud.", 11, p. 51.
8. Song, Q., Zaho, Y. and Zhu, J., (1989), "Dephosphorisation of manganese ore by high intensity magnetic separation and roast leaching", *Trans. Inst. Min. Met., Sec-C*, 98, p. c17.
9. Lui, C., Li, Q., Jiang, L., (1989), "Mineralogical characteristics that affect processing of a microfine manganese carbonate ore from Huayuan, China", In : *Process Minerals*", Vol. IX, (Ed. W. Petruk, R. D. Hagni, S. P. Brandom and D. M. Hosen), Published by TMS, USA, p. 133.
10. Grassely, Gy., (1968), "Phosphorous bearing mineral of the manganese ore deposit of Epleny and Urkut", *Acta. Miner. Petro. Szeged. Hungary*, 18, p. 73.
11. Sivaprakash, C., (1980), "Mineralogy of manganese deposits of Koduru and Garbham, A.P., India", *Econ. Geol.*, 75, p. 1083.
12. Sahoo, R.K., Kanungo, S.B. and Natarajan, R., (1982), "A note on the occurrence of phosphorous in the manganese ores of central India and its liberation during size reduction", *Ind. Min. Engg. Jour.*, Feb-March, p. 25.
13. Mohapatra, B.K., Rao, D.S. and Sahoo, R.K., (1995), "Characterisation and magnetic separation studies of Chikla manganese ores, Maharashtra" *Ind. Min. Engg. Jour.*, 34, p. 37.
14. Rao, P.D.P., Mohan Rao, S., Banerjee, B. and Peravandhanalu, A., (1986), "Mineral characterisation and processing of some Indian high phosphorous manganese ores at NML", *Nat. Workshop Removal of Phosphorous from manganese ores. RRL Bhubaneswar*, 24th May, 1986, p. 85.
15. Acharya, B.C., Rao, D.S. and Sahoo, R.K., (1997), "Mineralogy, geochemistry and genesis of Nishikhal manganese ore deposit, South Orissa, India", *Mineralium Deposita*, 32, p. 79.
16. Acharya, B.C., Rao, D.S. and Sahoo, R.K., (1994a), "Mineralogy and genesis of Kutinga manganese deposit, South Orissa, India", *Jour. Miner. Petro. Econ. Geol.*, 89, p. 317.
17. Nayak, V.K., (1963), "Ardennite from India" *Nature*, 198, p. 778.
18. Nayak, V.K., (1966), "Ardennite from Kajlidongri, India, A new locality", *New Jb. Miner. Mh.*, 9/10, p. 195.
19. Roy, S., (1976), "Ancient manganese deposits" (Chap.-9) In: "Hand Book of Strata bound and Stratiform Ore Deposits", (Ed. K.H.Wolf), Vol.7, Elsevier Scientific Publication Company, p. 395.
20. Sarma, K.J., Sundaram, S.M. and Sekham, A., (1989), "Low grade manganese ore occurrences of Diguva, Medangi and Chikkapara areas", *Vizianagarm district, A.P. Ind. Mineral*, 43, p. 24.