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MAGNETITE ORE OF NAGALAND—ITS MINERALOGY AND REDUCTION KINETICS

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ABSTRACT

The magnetite body near Pokphur in the Kiphore district of Nagaland is geologically quite different and a rare type of occurrence associated with ophiolite. Mineralogical studies reveal the presence of magnetite, chromite and hematite followed by goethite, ilmenite, tremolite, pentlandite and millerite. Magnetite grains are weathered to various degrees and sometimes fractured. Reduction studies indicate that in gas-solid system considerable reduction of magnetite ore takes place in initial 60 minutes, further the rate of reduction becomes slow. In gas-solid system the percentage reduction of magnetite ore is considerably more compared to solid-solid systems.

Keywords: Magnetite ore, Mineralogy, Reducibility, Reduction kinetics.

INTRODUCTION

The magnetite body near Pokphur in the Kiphore district of Nagaland assumes particular significance because of its rare type of occurrence associated with ophiolite. It draws more attention due to the presence of chromium, nickel and cobalt and is of great value in the context of total dependence on imports with reference to strategic metals like nickel and cobalt. Utilization of this ore deposit stands as potential contributor to the economic development of the region and warrants stage-wise detailed investigation. Some characterization studies on these magnetite samples have been done by NEIST (earlier RRL), Jorhat^[1] (1987) and IMMT (earlier RRL), Bhubaneswar^[2] (Mohapatra *et al.*, 1995). Preliminary studies^[3] on five different bulk samples were undertaken at the National Metallurgical Laboratory, Jamshedpur (1993) with a view to explore the possibilities of extracting metal from these ores. The magnetite ores are being re-investigated with respect to their mineralogical, chemical and metallurgical characteristics for further smelting-reduction studies. The mineralogical studies reveal the presence of magnetite, chromite and hematite followed by goethite, ilmenite, tremolite, pentlandite and millerite. Ni and Co concentration was found comparatively more in sub-surface samples especially along central zones of the bore holes. It is found that magnetite constitutes about 40 to 50 percent of the specimens. The rest are mainly silicates. The magnetite ore of - 12.5 + 10 mm size was reduced in gas-solid system for different durations at different temperatures by indirect reduction in standard experimental set-up using the mixture of reducing gases (30% CO + 70% N₂). Further magnetite ore particles were reduced in solid-solid systems by direct reduction in Carbolite furnace for different durations at different temperatures using petroleum coke and low

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ash coke as reductants. The paper briefly discusses the mineralogical aspects of magnetite ore and its reduction kinetics in gas-solid system as well as solid-solid systems at different temperatures.

THE POKPHUR MAGNETITE ORE BODY

The Pokphur magnetite deposit occurs in the north-eastern extremity of Nagaland-Manipur ophiolite belt, a part of the Indo-Myanmar ranges comprising the Arakan Yoma, Chin and Naga hills. The location of the ore body^[4] is illustrated in Fig. 1 (Ravikumar and Prabhakar, 1977). The ophiolite sequence is exposed in this region for a strike length of about 90 km with width ranging from 1 to 5 km, along the international border with Myanmar (erstwhile Burma). The magnetite ores occur as sheet like bodies over the ultramafic to mafic cumulate sequence^[5] (Chattopadhyay *et al.*, 1983). The ore body extends in NNE-SSW direction with 30 to 40 degrees deep in westerly or northwesterly direction. The strike is similar to the general trend of the ophiolite belt.

The Pokphur multimetallic magnetite ore was discovered in 1971 by Agarwal and Rao.^[6] Later Bhowmick *et al.*^[7] (1973) along with DGM, Nagaland took geological traverse which was followed by detailed geological and topographical mapping by Majumdar and Pandey.^[8] (1974). Ravi Kumar and Prabhakar.^[4] (1977) estimated the net probable reserve in the North Block to be 1.83 million tonnes, while Sharma.^[9] (1979) of DGM, Nagaland indicated the reserve to be around 3.0 million tonnes in the South Block. The division into North and South Block of the ore body is along an arbitrary grid line running E-W through the area. According to the latest figures by the DGM, Nagaland, a reserve of approximately 5 million tons of magnetite has been proved in Pokphur area by exploratory drilling having 0.13–1.63% of nickel, 0.09% of cobalt and about 4% chromium. The strike length of the Pokphur magnetite body is about 1 km in a NNE-SSW direction with 40 to 50 degrees westerly dip. The thickness of the body varies from 5–12 m with an average outcrop width of about 300 m. The occurrence of magnetite in the North Block is at fairly shallow depth and as extensive boulders whereas the South Block magnetite has a smooth profile due to deep burial and thick soil coverage.



Fig. 1: Location of Pokphur magnetite body and regional geological map showing the disposition of ophiolite complex in northeast India.

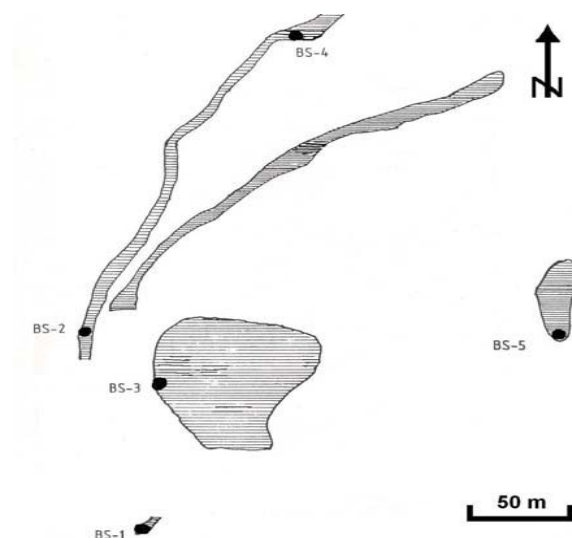


Fig. 2: Map showing the disposition of magnetite ore body near Pokphur and the sample locations for the five bulk samples.

THE MAGNETITE SAMPLES

Five bulk magnetite samples were collected from five different locations from the Pokphur magnetite ore body by blasting and are designated as BS-1, BS-2, BS-3, BS-4 and BS-5 (Fig. 2). The samples were surface samples which had undergone varying degree of weathering and were in varied size ranges. These samples were first crushed to 6 mm size in a jaw crusher and after coning and quartering the representative samples were used for chemical analysis and mineralogical study. Some polished sections were also prepared from the lumps (around 1 inch size). The bulk chemical composition of the five bulk samples are presented in Table 1.

Table 1: Chemical composition (wt.%) of the five bulk samples from Nagaland Magnetite body

Radical	BS-1	BS-2	BS-3	BS-4	BS-5
Fe (t)	50.00	52.99	43.06	45.55	47.66
Cr	2.45	2.94	2.39	2.79	3.79
Ni	0.53	0.73	0.335	0.382	0.505
Co	0.034	0.035	0.036	0.037	0.033
Al ₂ O ₃	8.12	8.08	15.60	11.70	9.31
SiO ₂	10.61	9.14	12.01	12.57	10.82
MgO	–	0.65	0.59	0.89	0.75
TiO ₂	–	0.35	1.01	0.58	0.45

MINERALOGICAL STUDY

All the five bulk samples have been studied under optical petrological microscope. It is found that magnetite constitutes about 40 to 50 percent (modal) of the specimens. The matrix is mainly altered silicates. The magnetite crystals vary widely in their grain size ranging from $<10\ \mu\text{m}$ up to 2 mm and are dispersed in the silicate matrix (Fig. 3). Sometimes the magnetite grains occur together forming clusters up to 1 cm and occasional presence in veins is recorded. Magnetite grains are weathered to various degrees and sometimes fractured. These fractures reflect stress effects and structural disturbances in the area and mostly are traversed and occupied by goethite (Fig. 4), lepidocrocite or maghemite (that may have formed from lepidocrocite). Hematite (martite) occurs as a secondary product formed due to oxidation from primary magnetite. This oxidation process known as 'martitization', generally starts from the grain boundary and fracture planes of magnetites and progresses towards the centre of the grain. Incomplete martitization often leaves islands of magnetite within martite.

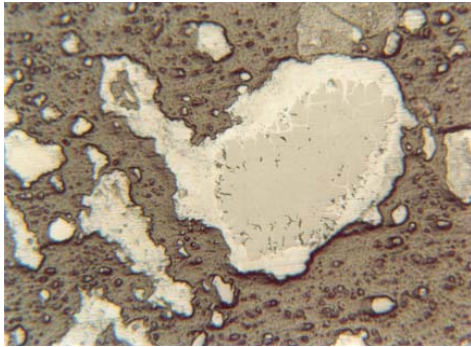


Fig. 3: Optical photomicrograph of magnetite (central bigger grain) showing martitization effects from grain boundaries. The other grains and the silicate matrix is highly altered. The longer edge of photograph equals to $600\ \mu\text{m}$.

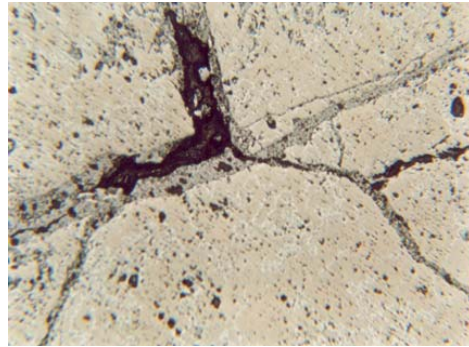


Fig. 4: Optical photomicrograph showing magnetite in triple junction arrangement. The grain-boundaries and fractures are occupied by supergene goethite. The longer edge of photograph equals to $600\ \mu\text{m}$.

Coexistence of chromite and magnetite are recorded. The chromite crystals are coarse-grained (sizes up to 2 mm) and magnetite occurs in the inter-granular spaces. The replacement of chromite by magnetite is recorded (Fig. 5) and this replacement also starts from grain boundaries and along fine cracks within chromite grains. Occasional presence of ilmenite and trace specks of sulphides is also noticed. The identification of the sulphide minerals in most cases was not possible through optical microscopy due to their fine size. Apart from the supergene oxides (eg. Goethite, martite, lepidocrocite etc), two generations of primary (igneous) crystallization of iron oxide minerals are recorded in the magnetite ores: an earlier generation represented by isolated crystals of magnetite and a subsequent (second) generation of maghemite that follows the flow pattern of the lava (Fig. 6). The silicate matrix is weathered/altered to various degrees. This may be due to the nature of the samples (bulk samples were collected from upper surface). Under optical microscope, the properties of these silicates resemble to that of chlorites. Most part of such chloritic silicates (perhaps) has been identified as 'chamosite' that contains some chromium and nickel by Mohapatra *et al.*^[2] (1995). However, the Ni and Cr content of the chamosite cannot account for the total abundance of these two elements in the bulk.

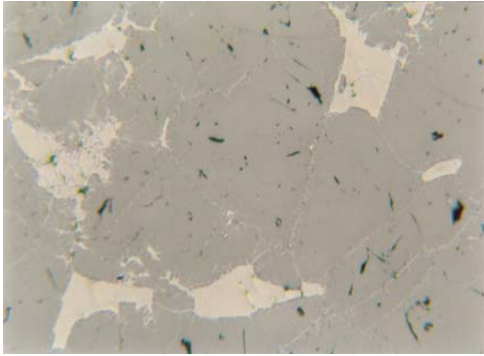


Fig. 5: Optical photomicrograph showing an association of chromite and magnetite where magnetite occupies the inter-granular spaces and replaces chromite. The longer edge of photograph equals to 1.2 mm.

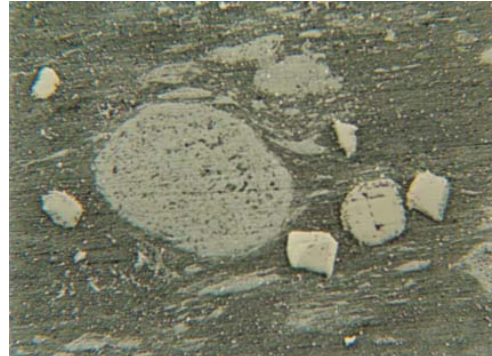


Fig. 6: Optical photomicrograph showing early crystallized magnetite and maghemite scattered in the silicate matrix and late formed maghemite following the flow pattern of the lava. The longer edge of photograph equals to 1.2 mm.

REDUCTION KINETICS OF MAGNETITE ORE

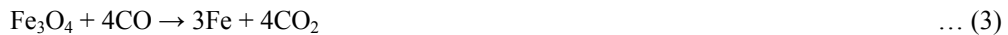
The reaction kinetics of magnetite ore reduction deals with the rate at which magnetite ore is converted to metallic iron by the removal of oxygen. The rate of a chemical reaction increases with the increase in temperature. The magnetite ore was reduced in gas-solid state by indirect reduction and in solid-solid states by direct reduction using two solid reductants separately.

Indirect reduction (Gas-solid state)

Above 570°C, magnetite is reduced by CO in two stages:



Below 570°C, magnetite (Fe_3O_4) is directly reduced to Fe bypassing the wustite (FeO) stage.



The mode of gaseous reduction of magnetite ore in gas-solid system is shown in Fig. 7 and Fig. 8. as follows:

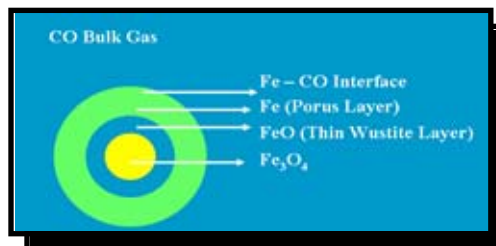


Fig. 7: Schematic representation of the mode of gaseous reduction of magnetite ore.

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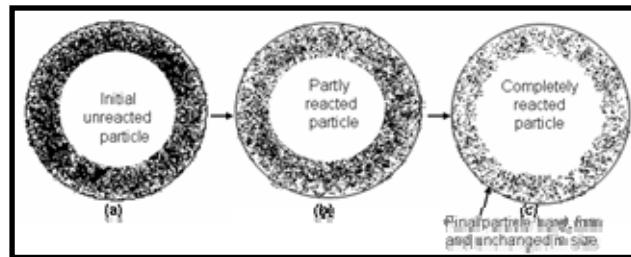
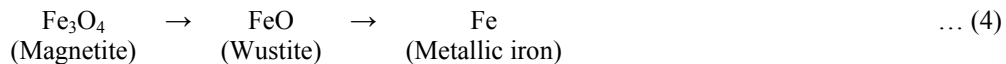


Fig. 8: Schematic representation of reduction of magnetite lump with respect to time in gas-solid system.

Direct reduction (Solid-solid state)

The magnetite ore is reduced in the solid state, the maximum temperature is below the melting temperature and the reaction rate is slower. For direct reduction of magnetite ore the mechanisms are complex because the oxides go through a series of step wise changes before the conversion is complete. The slowest step in the process determines the overall reaction rate and is referred to as the rate controlling step.

The reduction of iron oxide in a direct reduction system occurs by both solid as well as gaseous reductant, e.g. solid carbon and CO gas in various stages as given below:



Only a negligible amount of reduction will occur by direct contact of carbon particles with iron oxide particles since such solid-solid reactions are very slow. The reduction of magnetite ore takes place by solid carbon as per the above mentioned reactions (5) and (6). The CO gas evolved again participates in further reduction of magnetite ore as per reactions (1) and (2).

The CO gas produced by carbon gasification reaction, reduction of magnetite ore by solid carbon and by oxidation of carbon reduces the magnetite ore to their lower oxidation state and the CO₂ gas produced again reacts with solid carbon to form carbon monoxide gas,



Further, the solid carbon present in the charge mix is oxidized by the little air present in the reactor to produce carbon monoxide and carbon dioxide,



The carbon monoxide formed reduces the magnetite ore and the carbon dioxide reacts with solid carbon to form carbon monoxide through carbon gasification reaction as per reactions (1) and (2) and (7) respectively.

Edstrom *et al*^[10] reported that oxygen is removed by a gas/solid type reaction occurring only at FeO-Fe interface and that the internal reduction of higher oxides proceeds by diffusion of iron.

Kinetically, a solid-solid reaction is expected to occur at a much slower rate than a gas-solid reaction because of the following two reasons:

- (a) The solid-solid contact area is much smaller than the gas-solid contact area
- (b) Solid state diffusion is much slower than mass transfer in gases

Fruehan^[11] studied the reduction of iron oxide by carbon and his observations indicate that the reactions take place in two stages. Carbon monoxide formed by the gasification of carbon as per equation (7) is consumed for reduction of iron oxide as in equations (1) and (2) as fast as it is generated.

Reduction experiments by indirect reduction and direct reduction

The magnetite ore of - 12.5 + 10 mm size [Fe(T) = 46.86%, FeO = 22.51%, Fe₂O₃ = 42.23%] was reduced in gas-solid system for different durations (30 mts, 45 mts, 60 mts, 90 mts and 120 mts.) at different temperatures (900°C, 950°C, 1000°C and 1050°C) by indirect reduction in standard experimental set-up using the reducing gas consisting of (30% CO + 70% N₂). Further magnetite ore particles of - 5 mm + 6 mesh size [Fe(T) = 53.09%, FeO = 12.38%, Fe₂O₃ = 62.29] were reduced in solid-solid system by direct reduction in Carbolite furnace for different durations (15 mts, 30 mts, 45 mts, 60 mts, 90 mts and 120 mts.) at different temperatures (900°C, 1000°C, 1100°C and 1200°C) using petroleum coke [Moisture = 0.50%, Ash = 0.30%, VM = 9.20% and FC = 90.00%] and low ash coke [Moisture = 0.50%, Ash = 11.10 %, VM = 1.80% and FC = 86.60%] as reductants.

In gas-solid system considerable reduction of magnetite ore takes place in initial 60 minutes and afterwards the rate of reduction becomes slow. The reducibility of magnetite ore increases considerably with the increase in temperature beyond 900°C and increase in duration of reduction from 30 to 90 minutes. After 90 minutes the rate of reduction becomes quite slow. Whereas in solid-solid system the reduction of magnetite ore with low ash coke compared to petroleum coke after 120 minutes is (i) less at lower temperatures (900°C to 1000°C) and (ii) more at higher temperatures (1100°C to 1200°C). In gas-solid system the percentage reduction of magnetite ore is considerably more compared to solid-solid system in the (i) temperature range of 900 to 1050°C and (ii) reduction duration of 30 to 120 minutes.

The effect of temperature on the reducibility of magnetite ore by gaseous reduction in gas-solid system is illustrated in Fig. 9. In general the rate of reduction is faster upto 60 minutes and becomes slightly slower after 60 minutes. The trend of reduction between 30 and 60 minutes is of one type at 900°C and 950°C and of different type at 1000°C and 1050°C. Further the effect of temperature on the reducibility of magnetite ore in solid-solid systems using petroleum coke and low ash coke as reductants are illustrated in Fig. 10 and Fig. 11 respectively. In each case the rate of reduction upto 60 minutes is somewhat slower compared to that between 60 minutes and 120 minutes. The effect of petroleum coke and low ash coke on the reducibilities of magnetite ore in solid-solid system are shown in Fig. 12 at 900°C and 1000°C and in Fig. 13 at 1100°C and 1200°C. The percentage reduction of magnetite ore is considerably more with petroleum coke compared to low ash coke at 900°C and 1000°C as shown in Fig. 11 and it is considerably low with petroleum coke compared to low ash coke at 1100°C and 1200°C as shown in Fig. 13. Thus low ash coke becomes more reactive above 1000°C and less reactive at and below 1000°C. It is quite clear that the reducibility of magnetite ore is far better in gas-solid system compared to solid-solid system either with petroleum coke or with low ash coke.

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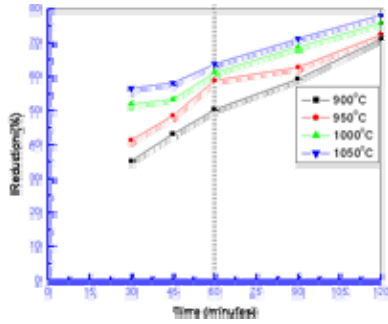


Fig. 9: Effect of temperature on the reducibility of multi-metallic magnetite ore by gaseous reduction in gas-solid system.

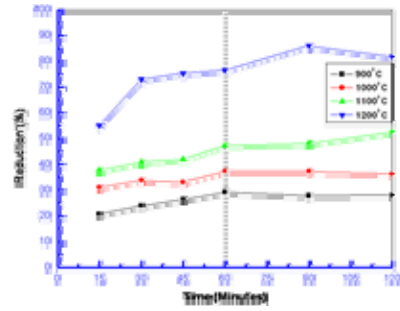


Fig. 10: Effect of temperature on the reducibility of multi-metallic magnetite ore (- 5 mm + 6 mesh) using petroleum coke as reductant in solid-solid system.

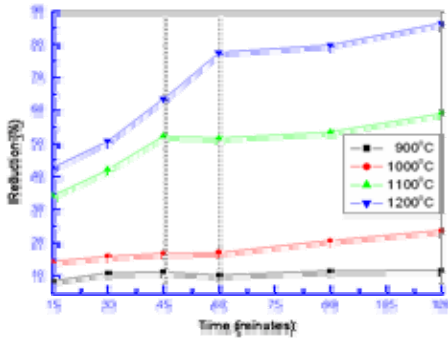


Fig. 11: Effect of temperature on the reducibility of multi-metallic magnetite ore (- 5 mm + 6 mesh) using low ash coke as reductant in solid-solid system.

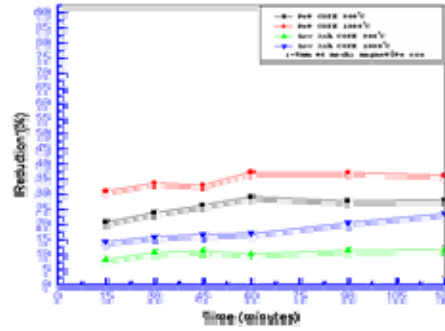


Fig. 12: Effect of different reductants on the reducibility of multi-metallic magnetite ore (-5 mm + 6 mesh) at 900°C and 1000°C in solid-solid system.

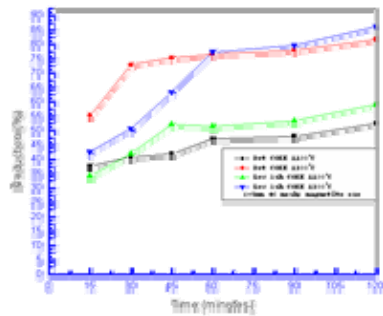


Fig. 13: Effect of different reductants on the reducibility of multi-metallic magnetite ore (-5 mm + 6 mesh) at 1100°C and 1200°C in solid-solid system.

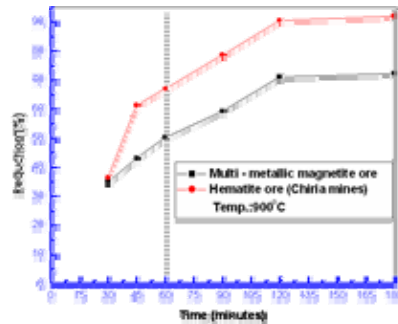


Fig. 14: A comparison between the reducibility indices of multi-metallic magnetite ore and hematite ore (chiria mines) at 900°C by gaseous reduction in gas-solid system.

The reducibility of magnetite ore of -12.5 +10 mm size of Nagaland has been compared with that of hematite ore of Chiria mines of -12.5 +10 mm size [Fe(T) = 59.16%, FeO = 0.81%, Fe₂O₃ = 83.71%] as illustrated in Fig. 14 at 900°C for 3 hour duration as per Indian standard. The reducibility indices of magnetite ore and hematite ore are found to be 72.34% and 86.14% respectively. Though the reducibility index of magnetite ore is somewhat less compared to hematite ore, yet it is expected to carry out its smelting reduction studies with sufficient recoveries of metallic values.

CONCLUSIONS

- The mineralogical study of magnetite ore reveals that chromium occurs in two modes—in independent chromite phase and in solid solution with the altered chloritic matrix, whereas nickel and cobalt occur only in solid solution mainly with the matrix and occasionally with the spinels.
- As per the reduction kinetics of magnetite ore, gas-solid system is far better than solid–solid systems for the reducibility of magnetite ore
- The comparison between the reducibility index of magnetite ore with that of hematite ore shows that its smelting reduction study may be carried out with fairly optimum recoveries of metallic values.

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