

# Prospect of Magnesium Rich Rocks from Boula-Nausahi Igneous Complex, Odisha as Flux in Iron and Steel Industry

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**Abstract** Rocks rich in magnesium hold good prospect as substitute flux for dolomite and limestone and quartz in iron and steel industry. Our dependence on foreign imports, as far as raw materials like limestone or dolomite are concerned, has nonetheless eroded the competitive ability of Indian iron and steel. The quality of raw materials used determines to a large extent, the productivity and therefore utilisation of the capital assets in an integrated steel plant. Scarcity of metallurgical grade limestone and dolomite especially of blast furnace (B.F.) and steel melting shop (S.M.S.) grades have shifted focus to the quality and pricing of steel in India. The Boula-Nausahi Igneous Complex of Odisha consists of ultramafic suite that includes dunite-peridotite-pyroxenite-lherzolite and their altered product (serpentinite). These ultramafic rocks are enriched with high MgO and low SiO<sub>2</sub> contents and very low Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and alkalis contents.

**Keywords:** *magnesium, flux, iron and steel industry, Boula-Nausahi igneous complex*

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## 1. Introduction

Magnesian rocks as materials of economic significance have caught the attention of the economic geologists, metallurgists and industrialists the world over in recent years. Though its development and utility as a commodity of economic importance is still in nascent stage in India, it holds good future prospect as substitute flux for dolomite/limestone and quartz in iron and steel industry. Scarcity of metallurgical grade limestone and dolomite especially of blast furnace (B.F.) and steel melting shop (S.M.S.) grades have put tremendous pressure on the quality and pricing of the Indian steel.

Magnesian rocks viz., dunite, peridotite, pyroxenite etc., and their altered products (serpentinite) are found in some well defined belts in India. Magnesian rocks are found in the states of Tamilnadu, Odisha, Jharkhand, Karnataka, Maharashtra, Andhra Pradesh, Manipur, Nagaland and Andaman & Nicobar Islands (IBM, 2012). In Jharkhand, magnesian rocks are found in Jojohatu, Roroburu, Chitungburu, Kittaburu, Kismiburu and Tilaisud. In Karnataka, magnesian rocks are found in Sindhuvali, Talur, Koppal, Dodkanya, Dodkatur and Byrapur. Bhandara district, Maharashtra has good quality magnesian rocks. Kondapalli hills located in the Krishna district of Andhra Pradesh are made of ultrabasic rocks. In Andaman & Nicobar Islands, magnesian rocks are found in Badmash Pahar and Panchabati. Ophiolite Complexes of

Manipur, Nagaland and Ladakh are repositories of good quality magnesian rocks.

In Odisha, Magnesian rocks are found in prolific abundance. There are fourteen proven/ probable deposits of which two are significant. They are the Sukinda Ultramafic Belt and the Boula-Nausahi Igneous Complex. The Sukinda Ultramafic Belt extends for over 20 km with a width of 2-5 km. Though the Sukinda Ultramafic Belt is the largest of its kind in India, its utility as a source of magnesian rocks is very limited owing to the fact that the most of the ultramafic rocks (dunite-peridotite) except a few pyroxenite bodies towards the foothills of Mahagiri Range have undergone extensive lateritisation.

The Boula-Nausahi Igneous Complex, a 3km long belt extending in N-S to NNW-SSE direction, consists of ultramafic, mafic and felsic rocks as major litho units. The ultramafic suite includes dunite-peridotite-pyroxenite-lherzolite and their altered product (serpentinite). These ultramafic rocks are characterized by high MgO and low SiO<sub>2</sub> contents and very low Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and alkalis contents. These rocks disposed as wastes or at best used as road metals have the potential to be used as substitute for limestone/dolomite as flux in Iron and Steel industry.

## 2. Materials and Methods

A few samples were collected from the underground mines and dump yards of Orissa Mining Corporation

(OMC) leasehold at Boula area, Keonjhar district. The samples were collected after examining the degree of alteration physically. These rock samples were studied for petrographic and other thermal characteristics. Petrographic study was carried out by optical microscope (Leitz make). Bulk chemical analysis of the samples was carried out by XRF (Philips, Magic Pro) on pressed pellets by using international rock standards. LOI was determined by heating the sample at 950°C for 2 hours. Thermal properties were studied by Leitz Heating microscope.

### 3. Petrographic Characterisation

Magnesium rich rocks like dunite, peridotite, pyroxenite, saxonite lherzolite, websterite, enstatite, serpentinite constitute the ultramafic domain of Boula igneous complex. However, Dunite-peridotite represents over 90% of the total ultramafic rocks.

Optical studies reveal that dunite consists of olivine and + accessory chromite. Peridotite consists of olivine +

enstatite + accessory chromite. saxonite consists of enstatite + minor olivine + accessory chromite. In all these cases, olivine is altered to serpentine and when the degree of alteration is very high, the rock is converted to serpentinite. Pyroxenite consists of enstatite + accessory chromite. Diopside and hypersthene are the major minerals in websterite. In some cases, pyroxenes are altered to bastite and talc. Petrographically, the ultramafic rocks and their altered products consist of olivine (+ serpentine), orthopyroxene (enstatite and hypersthene) and clinopyroxene (diopside) in varying proportions with minor to trace amounts of euhedral chromite and secondary minerals. Lizardite is the major mineral in serpentinite. The accessory chromite varies from 2 to 3% in the ultramafic rocks.

### 4. Chemical Analysis

Major elements of different magnesian rocks are analysed by XRF and the data are given in table below.

**Table 1. Major element composition of ultramafic rocks**

Oxide	Dunite	Peridotite	Pyroxenite	Saxonite	Serpentinite
Wt%	n=7	n=7	n=7	n=7	n=7
SiO <sub>2</sub>	41.81	42.29	47.79	43.88	41.98
Al <sub>2</sub> O <sub>3</sub>	0.69	1.63	2.39	0.99	0.79
MgO	45.00	42.76	36.87	41.46	43.21
Fe <sub>2</sub> O <sub>3</sub>	2.48	2.89	3.94	2.99	2.73
CaO	0.030	1.65	0.94	1.46	0.21
Na <sub>2</sub> O	0.003	0.004	0.005	0.007	0.006
K <sub>2</sub> O	0.002	0.002	0.04	0.002	0.002
TiO <sub>2</sub>	0.02	0.051	0.11	0.086	0.058
Cr <sub>2</sub> O <sub>3</sub>	0.31	0.47	0.13	0.40	0.49
MnO	0.06	0.99	0.089	0.135	0.121
P <sub>2</sub> O <sub>5</sub>	0.002	0.001	0.03	0.002	0.002
LOI	9.02	9.53	7.12	7.44	9.00
MgO/SiO <sub>2</sub>	1.076	1.011	0.779	0.945	1.029

n= Number of samples

From the chemical analysis, it is observed that MgO content varies between 45.00 & 36.87 wt%. SiO<sub>2</sub> content varies between 47.79 and 41.81 wt%. Al<sub>2</sub>O<sub>3</sub> wt% varies between 0.69 and 2.39 wt % and Cr<sub>2</sub>O<sub>3</sub> between 0.13 to 0.49 wt%. Ca ranged between 0.21 to 1.65 wt% while Na<sub>2</sub>O and K<sub>2</sub>O vary from 0.005 to 0.007 and 0.002 to 0.04 wt % respectively. There is no significant compositional variation between serpentinite and dunite-peridotite because serpentinite is a product of isochemical process with addition of meteoric water only (Mohanty, 1994).

As the ultramafic rocks contain substantial amounts of MgO and SiO<sub>2</sub> and low alkalis, Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, these can be considered as substitute flux material for limestone/dolomite and quartzite/sand in iron and steel industry.

### 5. Utilisation

The liberalisation of the Indian economy in 1991 opened the flood gates of the closed door economy to a market driven, forward looking one. Liberalisation has brought about sea changes in technology based industries like steel making and heavy engineering. An important fallout of liberalisation is the intensification of competition that necessarily influenced quality, pricing

and better service to the customers. The advent of liberalised economy has affected all walks of life and almost all industries including iron and steel. This made steel makers to look for improved technology and good quality raw materials.

There is no doubt that the inferior quality of raw materials is a major limitation in making the Indian iron and steel industry globally competitive. For Iron and Steel industry besides good grade iron ore, good quality fluxes eg., limestone/dolomite and quartz are essential requisites. Fluxes are raw materials used in furnace for removal of undesirable impurities both at the iron and steel making stages. To ensure smooth operation of blast furnace, maintenance of low basicity is very essential. A low basicity ensures better fluidity of the melt.

In India, the entire flux requirement in blast furnaces is usually met out of limestone/ dolomite and silica. With emphasis on higher productivity and superior quality, the steel sector in India is beset with impediments to use limestone containing high alkalis (>0.15%) and high silica (>3%). The all India recoverable reserves of limestone and dolomite are estimated at 75,660 Mt and 4,387 Mt respectively (IBM, 2012). The limestone reserve in Odisha stands at 1212 Mt and dolomite at 691 Mt. Most of the Indian limestone and dolomite are of inferior grade, falling short of BF and SMS specifications.

Looking at the present scenario, in order to maintain a competitive edge iron and steel industries are forced to use high quality limestone/dolomite or to find out a substitute flux which can address the problem of inferior grade limestone/dolomite found in the country. Import of high quality limestone/dolomite will add to the cost of production. So a frantic search for a substitute material is on the threshold to be effectively used in place of conventionally used fluxes. In this context magnesian rocks stand a bright prospect. The present work gives a detailed account of the various aspects of magnesian rocks vis-à-vis their use in iron and steel industry.

## 6. Physico-Chemical Considerations

Physico-chemical and thermal characters of a raw material are of paramount importance in determining its suitability as a fluxing agent in Iron and Steel industry. Physico-chemical considerations include entities like silica, alkalis, LOI and other major oxide contents. Besides these chemical parameters, sometimes the grain size of the raw material also matters calling for due attention.

Silica is used to obtain low blast furnace slag basicity. Most of the silica input in blast furnaces under Indian condition comes from coke and iron ore. Besides, an additional silica input is obtained either from sand added to sinter or quartzite charged directly into the blast furnace. Addition of sand to sinter has its own attendant problems. In Indian blast furnaces where high aluminous iron ores are used, silica assimilation requires very high heat input that affects both the sinter productivity and quality. Quartzite when charged directly into the blast furnace suffers from poor assimilation because of poor thermal conditions prevailing in Indian blast furnaces (Mukherjee et al. 1996). If there is no additional silica input into sinter, the sinter basicity becomes very high ( $\text{CaO}/\text{SiO}_2 \approx 3.0$ ) which gives rise to high temperature properties in terms of poor softening-melting characteristics and high residuals after melt down.

The role of the alkalis ( $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ) in determining blast furnace performance cannot be undermined. These alkalis contributed by the raw materials have an adverse effect on blast furnace performance viz., decipitation of the ore, decipitation of coke, erosion of refractory lining causing hotspots and formation of scaffolds and hanging of the overburden. The major sources of alkalis in blast furnace under Indian conditions are from the high ash containing coke and flux. The harmful effects of alkalis can be minimised either by decreasing the alkali input into the furnace or by removal of alkali through the slag.

At Tata Steel, a huge Indian Industrial conglomerate, both lime and limestone are used as fluxing materials. The ideal specification of limestone is  $\text{CaCO}_3 >95\%$ ,  $\text{Al}_2\text{O}_3 + \text{SiO}_2 <1\%$  and  $\text{Na}_2\text{O} + \text{K}_2\text{O} <0.1\%$ . The alkali content is one of the deciding factors in the selection of fluxing material. The need for lowering the alkali input to blast furnaces had been so compelling that mining operations at Birmitrapur and Hatibari quarries in Odisha were stopped on account of their high alkali content (0.4%). Since it is extremely difficult to remove the alkalis through slag in a blast furnace, it is important to minimise alkali input into the furnace by using low alkali raw materials instead of high alkali ones.

In light of the above, it becomes imperative to select a raw material which could decrease the sinter basicity without increasing the heat requirement. Magnesium rich rocks viz., dunite, peridotite, pyroxenite, serpentinite etc., could be considered as fluxes since they have appreciable  $\text{MgO}$  and  $\text{SiO}_2$  contents with low or negligible alkali, besides  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  content within permissible limits. The important considerations for a magnesian rock to be used as a flux material are its high  $\text{MgO}$ , low  $\text{Cr}_2\text{O}_3$  ( $< .5\%$ ) and  $\text{Al}_2\text{O}_3$  ( $<1.0\%$ ) contents. Besides it should have a low alkali content and low loss of ignition (Chatterjee and Murty, 1998).

It is seen that the average crystal size of dolomite is at least twenty times larger than that of limestone and 4-5 times larger than that of dunite. So, because of the temperature conditions prevailing during sintering and the short reaction time, limestone is more easily calcined than dolomite and quickly assimilated into the melt. Dunite requires no heat of calcination and gets easily assimilated into the melt. Moreover, dolomite has higher LOI (40-45%) content. As such more heat is required to expel  $\text{CO}_2$  during calcination process. Thus use of limestone/dolomite requires more heat energy in sinter making. Dunite on the other hand has no carbonates and has low LOI (7-10%) thereby saving in terms of energy.

Limestone and dolomite have obvious disadvantage compared to dunite because of their sluggish and incomplete assimilation of  $\text{MgO}$ . This gives rise to weak areas in the sinter matrix that decreases the strength of the sinter.

Chemical analyses of the ultramafic rocks show that, these rocks are rich in magnesium (average  $\text{MgO}$  content 42%) and have a  $\text{MgO}/\text{SiO}_2$  ratio ranging from 0.76 to 1.08. The oxides like  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  that have a deleterious effect on slag formation are present within permissible limits except in pyroxenite. This compositional problem can be overcome by a suitable blending of pyroxenite with either serpentinite and / or dunite (peridotite).  $\text{Na}_2\text{O}$  content varies between 0.005 & 0.007 while the  $\text{CaO}$  content ranges from 0.95 to 1.41. Another important consideration for flux selection is the fouling index of the material.

Fouling Index (Rf) is given by =  $\text{Base}/\text{Acid} * \text{Na}_2\text{O}$   
Where

$$\text{base} = \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} \square$$

$$\text{acid} = \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$$

Rf values for magnesian rocks of the area have been found to be low i.e., between 0.005-0.007. This shows that as far as fouling index is concerned, these rocks can form good flux material. Fouling indices of dolomite and limestone fluxes have been calculated to be around 1.095 and 0.748 respectively.

## 7. Thermal Behaviour

The thermal properties viz., surface tension, viscosity and flow behaviour of flux material at high temperature play significant role in determining the suitability of fluxing agents. The thermal properties of the ultramafites of the area have been studied using a heating microscope to determine their suitability as flux materials in iron and steel making.

The four deformation states of material during heating operation are represented by ST, IDT, HT and FT. ST is the softening temperature i.e., when the sample just starts softening due to a rise in temperature. Initial deformation temperature (IDT) is the temperature at which the material shows first sign of deformation like shrinkage, expansion, decrification etc. The HT (hemispherical temperature) is the temperature at which the material assumes a dome/hemispherical shape. The flow temperature (FT) is the temperature at which the material behaves like a liquid and starts flowing.

Viscosity of a fluid is defined as its property by virtue of which it tends to oppose the relative motion between its layers. Resistance to flow is largely due to inter molecular attraction called the Vander waals force. Slag viscosity determines the flowability. Viscosity of a slag is calculated by using the formula given by Watt and Fereday (1969)

$$\log \text{ viscosity} = \left\{ 10^7 m / (t-150)^2 \right\} + C$$

Where

$$m = 0.00835 \text{ SiO}_2 + 0.00601 \text{ Al}_2\text{O}_3 - 0.109$$

$$C = 0.041 \text{ SiO}_2 + 0.0192 \text{ Al}_2\text{O}_3 + 0.0276 \text{ Fe}_2\text{O}_3 + 0.016 \text{ CaO} - 3.92$$

$$t = 1400^\circ\text{C}$$

The viscosity of the magnesian rocks varies between 1.70 and 5.00. Pyroxenite and saxonite show slightly higher values. This low range of viscosity is attributed to the complete melting of the flux at a temperature of about 1400°C. Sintering of magnesian rocks starts within 700 - 1180°C and the fluid phase is attained at a higher temperature of 1400°-1600°C. Using the formula of Watt

and Fereday, viscosity of dolomite and limestone has been calculated to be 7.0 and 9.4 respectively.

Often the slag sticks to the inner linings and walls of the boiler/ furnace which can impair the efficiency of the furnace. Sticking of slag to the linings is governed by the surface tension.

Surface tension of slag produced from magnesium rocks has been calculated using formula given by Holy et al., (1965).

$$\rho = 3.24\text{SiO}_2 + 5.85\text{Al}_2\text{O}_3 + 4.4\text{Fe}_2\text{O}_3 + 4.92\text{CaO} + 5.49 \text{ MgO} + 1.12 \text{ Na}_2\text{O} - 0.75 \text{ K}_2\text{O}$$

The surface tension for different magnesian rocks has been calculated to be around 400, thereby minimising the possibility of the slag adhering to the inner lining of the boiler. Surface tension reduces the area of a surface to minimum. It is due to this, that small drops of liquid or bubbles are spherical in shape. This is because, for a given volume a sphere has minimum surface area. So, the separation between the slag and the metal will be easier. The higher values are attributed to the complete melting of the flux. Dolomite and limestone on the other hand have a surface tension of 275.85 and 294.95 respectively which is considerably lower than the magnesium rich rocks. Slagging index, another temperature dependent parameter also determines the suitability of the flux material. It is expressed as Rs and calculated using the following formula.

$$\text{Slagging index, } R_s = (\text{max.HT} + 4 \text{ min.IDT}) / 5$$

Slagging index for the different magnesian rocks is found to be very low i.e., varying between 1140 to 1326°C.

Table 2. shows the thermal properties and fouling indices of the magnesian rocks.

Table 2. Thermal properties of magnesian rocks

Rock types	ST	IDT	HT	FT	Rs	V	$\rho$	Rf
Dunite	1050	1250	1350	1390	1270	1.7	397.61	0.003
Peridotite	1090	1300	1430	1500	1326	3.73	402.15	0.004
Pyroxenite	1100	1130	1180	1290	1140	5.0	393.18	0.004
Saxonite	680	1150	1280	1450	1176	4.91	395.93	0.007
Serpentinite	700	1040	1370	1480	1106	1.74	390.81	0.006

From the above data, it is inferred that these magnesian rocks exhibit excellent thermal properties like narrow range of temperature between HT and FT, low viscosity and slagging behaviour. The softening and melting temperature is narrow in case of dunite. Magnesian rock sinters have higher reducibility and hence the efficiency of an equal volume of magnesian rocks as compared to that of dolomite sinter is substantially more (Mukherjee et al. 1996).

So, by all benchmarks (physico-chemical and thermal considerations), magnesian rocks perform better as flux materials compared to limestone/dolomite and quartzite. Hence magnesian rocks can be used effectively as better quality flux leading to improved productivity (output/input) and substantially curb import of high quality fluxes.

## 8. Conclusion

The different types of magnesium rocks encountered in this complex include dunite, peridotite, pyroxenite,

herzolite, saxonite, websterite and serpentinite. MgO content in the above rock types varies between 36.8 to 45.00 wt% whereas SiO<sub>2</sub> varies between 41.81 to 47.79 wt%. Al<sub>2</sub>O<sub>3</sub> wt% varies between 0.66 and 2.35% and Cr<sub>2</sub>O<sub>3</sub> between 0.11 to 0.50 wt%. Na<sub>2</sub>O and K<sub>2</sub>O vary between 0.005 to 0.007 and 0.002 to 0.04 wt % respectively.

With very good thermal properties coupled with desired chemical parameters, magnesian rocks can make good substitutes for dolomite/ limestone and quartzite as flux materials. Magnesian rocks do not require any heat of calcination. These get easily assimilated into the melt and therefore require less heat energy. Assimilation of limestone/dolomite and quartzite, on the other hand, is heat intensive and time consuming as well. Often unreacted portions are left behind, which decrease the strength of the resultant sinter. The problem is further compounded and accentuated by scarcity of appropriate grade of limestone/dolomite and other economic aspects viz., transportation, distance of the smelter from the mine head etc.

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