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Full Length Research Paper

Characterization of high magnesian rocks for suitability as flux in iron and steel industry

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Chromite resources of Orissa are mostly confined to Second ultramafic belt and Boula Nausahi igneous complex. In these deposits, chromite is mainly present as layers in ultramafic rocks (high magnesian). These high magnesian ultramafic chromite overburden rocks are dumped as waste materials during chromite mining operations. These rocks are classified as dunite, peridotite and their altered products (Serpentinite), pyroxenite and saxonite depending on their mineral assemblage. Petrological, chemical and thermal characterization of these high magnesian rocks have been studied in light of their utilization as a flux substitute for the iron and steel industry in place of conventional fluxes. The study reveals that the chromite overburden materials being rich in magnesium and silica have advantage over the conventional flux combination.

Key words: Ultrabasic rocks, mining wastes, flux, iron and steel industry.

INTRODUCTION

Handling and safe utilization of solid wastes produced from mining industries is a major concern through out world. Initially when the mines commenced mining operation, generous provision of space was made for dumping of the overburden/mining waste materials on the periphery of the mine sites as the cheapest disposal method. Now, many of these dumps have become very huge man-made mountains. Mine dumps generated due to mining over years of mining activities pose drastic physico-chemical and biological constraints for surrounding environment. Lack of knowledge on the nature of these mining waste materials regarding long term utilizetion, has restrained the Indian engineers from using these materials for road construction. One such example is high magnesian ultramafic chromite overburden rocks of Orissa sector which are dumped as waste materials during chromite mining operations. The studies on chemico-mineralogical and thermal behavior of high magnesian rocks of Orissa can pave the way for effective and huge utilization of waste materials as flux in Iron and steel industry.

Ultrabasic rocks which have been normally used as road metals are recently considered as industrial mineral because of their chemical composition. Since last decade these high magnesian rocks are of great economic significance and have caught the attention of economic geologists, metallurgists and industrialists through out the world and are considered as fluxing raw material which can be used as a substitute in place of limestone/ dolomite + quartzite mix in the iron and steel industry. In substituting for conventional fluxes, in integrated steel plant, these ultramafic rocks are considered as prized flux commodity. Fluxes in a steel plant are the important raw material required for removal of undesirable impurities in iron making stage. Entire flux requirement for blast furnaces and steel melting shops in India is drawn from the existing Indian sources of limestone/dolomite and quartzite of desired quality. Limestone/dolomite and sand/quartzite combination require more coke intake. Magnesian rocks (Mg-silicates) as a substitute flux has been proved to have distinct advantages over a combination of conventional fluxes in terms of considerable reduction in charge volume and assimilation time, higher reducibility, higher blast furnace efficiency and nar-

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row range between softening and mel-ting temperatures. Use of magnesian rocks increases the blast furnace productivity by 4 - 5% and reduces coke consumption by 21 kg/tonne of charge. Besides, adequate reserve of suitable grade of limestone and dolomite suitable for B.F. and SMS operations are not available in India. Most of the limestone and dolomite are high in their alkali content. The predicament of scarce availability is further accentuated by the problem of location and transport dynamics in the state of Orissa in particular as the locations of proposed steel plants are situated on the eastern parts of the state which are far away from the limestone/dolomite deposits. The necessity to address this problem calls for the use of suitable flux for the existing and upcoming steel plants in Orissa. An attempt has been made to characterize these chromite over-burden ultramafic rocks for their mineralogy, chemistry and thermal properties and test their viability as substitute flux for use in iron and steel plants coming up in nearby areas.

Geology of the deposits

The state of Orissa is well known for its huge resources in iron ore, chromite, bauxite, coal, graphite, beach sand and manganese. However out of these mineral resources, the state has the highest reserve in chromite, having almost 95% of the total Indian reserve. The state production of chromite is about 98% of the total country's production. In the state, the total chromite resources are mostly confined to two belts: Sukinda (21°0' - 21°5'N: 85°43' - 86°0'E) ultramafic belt and Boula Nausahi (21°18' - 21°15'N: 86°18' - 86°20'E) igneous complex. The chromitite bodies can be traced for several kilo-meters along strike and are well exposed in open-cut and underground workings. In addition, gabbro-breccia hosted PGE-mineralization is found in association with chromites in both the Nuasahi and Sukinda massifs (Mohanty et al., 2002, 2008). The chromitite layer at or near the contact of the gabbro-pyroxenite contains a significant concentration of sulphide minerals with large amounts of nickel, iron and copper. Evidence for the exis-tence of platinum in these ores has been confirmed by Das et al., 1994. The chromitite deposits of the Nuasahi and Sukinda massifs are part of layered ultramafic bodies which occur within Archaean low-grade metamorphic rocks of the Iron Ore Group (IOG) in the Singhbhum Craton of the Indian Shield. In these two deposits, chromite is mainly present as layers in ultramafic rocks. The chromitite seams are interlayered with dunite, and associated with orthopyroxenite. Generally open cast mining method is adopted for chromite mining. The ore: overburden ratio varies from 1:8 - 1:12 and this ratio normally depend on the dip of the ore body. Even in some cases this ratio goes up to 1:15. Due to this high ore to overburden ratio, a huge amount of overburden is generated during chromite mining. The overburden mate-rials are mostly ultramafic rocks which are rich in MgO content. However at Sukinda, the ultramafic rocks have undergone extensive alteration, weathering and lateritisation resulting in wide spread development of nickeliferous laterite. Except for a patch of pyroxenite, almost all the overburden ultramafic rocks are converted to laterite. In Boula-Nausahi igneous complex, however, the situation is different and the overlying ultramafic rocks are not affected by lateritisation but serpentinized to some extent; thereby preserving their original chemical composition with only addition of water. Here the ore bodies show a high dip (around 60°). Due to this high dip, during chromite mining huge amounts of ultramafic rocks as overburden are generated and are lying without any significant use. Besides these two igneous complexes, many high magnesian rocks are present in eastern part of Orissa (Figure 1).

Mineralogy of the ultrabasic rocks

The chromite overburden materials are characterized for their mineralogy and texture with the help of optical microscope and XRD. The ultramafic rocks are classified as dunite, peridotite and their altered products (Serpenti-nite), pyroxenite and saxonite depending on their mineral assemblage. From microscopic study it is observed that dunite and peridotite are greatly altered to Serpentinite. However some parent minerals are present as relicts. Dunite consists of olivine mostly with a few accessory chromite grains (Figure 2) where as peridotite consists of olivine and orthopyroxene with a few accessory chro-mites. Pyroxenite is basically orthopyroxenite having enstatite. It is almost a monominerallic rock with a few euhedral chromite grains as accessories (Figure 3). The Serpentinite is mostly consisted of lizardite (Figure 4) showing hour glass structure. Serpentinite contains a few primary accessory chromite grains and a few secondary magnetite grains.

Optical studies supplemented by XRD reveal that dunite (olivine+ accessory chromite), peridotite (olivine+ enstatite+accessory chromite), saxonite (enstatite+minor olivine+accessory chromite) are altered to serpentinite and pyroxenite (enstatite+accessory chromite) and web-sterite (diopside+ hypersthene) which are altered to bastite and talc to some extent. Petrographically, the ultramafic rocks and their altered products consist of olivine (+ serpentine), orthopyroxene (enstatite and hypersthene) and clinopyroxene (diopside) in varying pro-portions with minor to trace amounts of euhedral chromite and secondary minerals. Serpentinite mostly consists of lizardite (major) and chrysotile (minor) varieties. The accessory chromite varies from 2 - 3% in the ultramafic rocks. Serpentinization has affected the rocks up to a depth of 150mts. As serpentinization is an isochemical process with only addition of water and there is no signi-ficant change in the chemical composition (especially the MgO content) of the serpentinite (Mohanty and Sahoo,

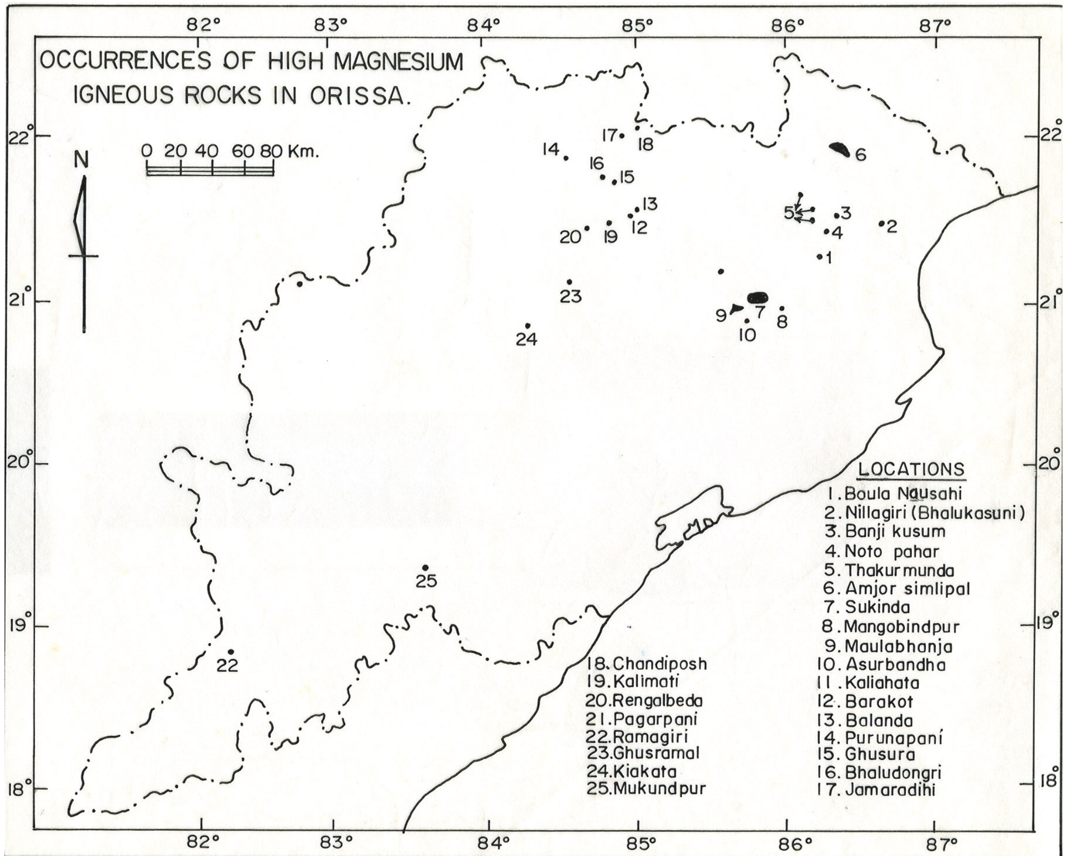

Figure 1. High magnesian rocks in Orissa. Locations 1 & 7 are famous chromite deposits.

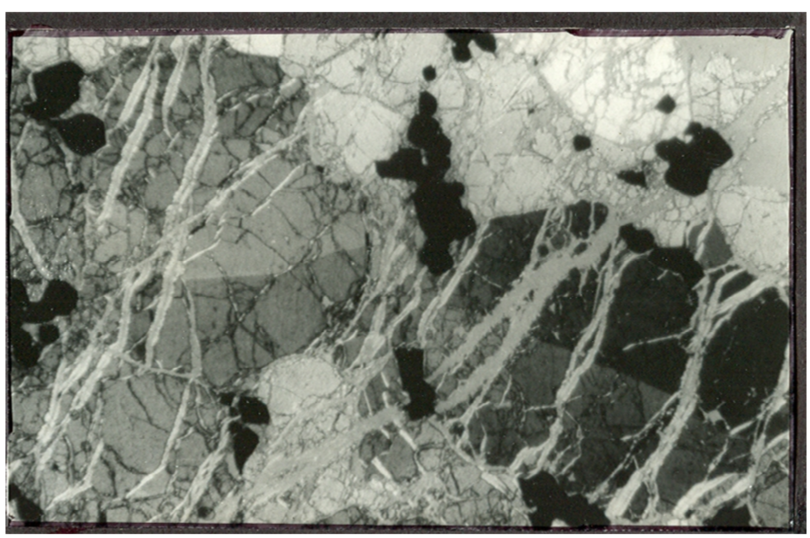

Figure 2. Coarse grained olivine with many fractures in a dunite. Some Euhedral chromite (black) are present as accessory grains. Crossed nicols, x100.

1996), Serpentinite can be grouped with dunite and peridotite for all technical purposes so far as role of MgO is concerned.

Chemical characteristics of the ultrabasic rocks

Chemical considerations used in the selection of fluxing

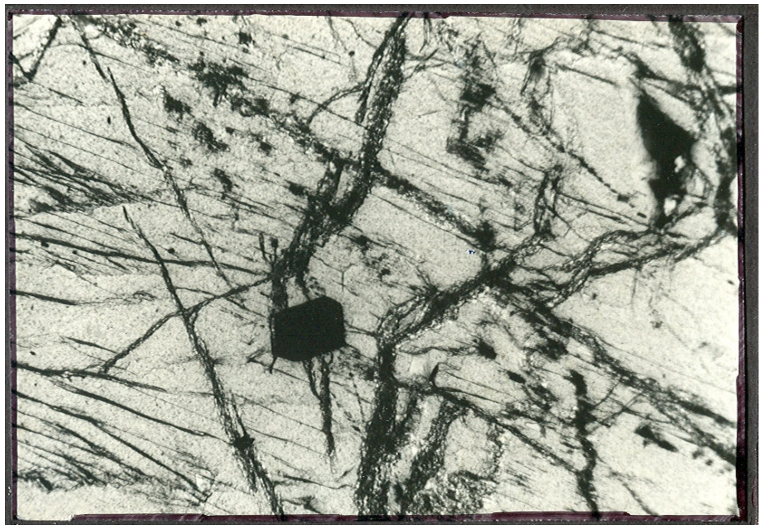

Figure 3. Coarse grained enstatite in orthopyroxenite. Euhedral grain of chromite is present as accessory grain. Parallel Nicols, x100.

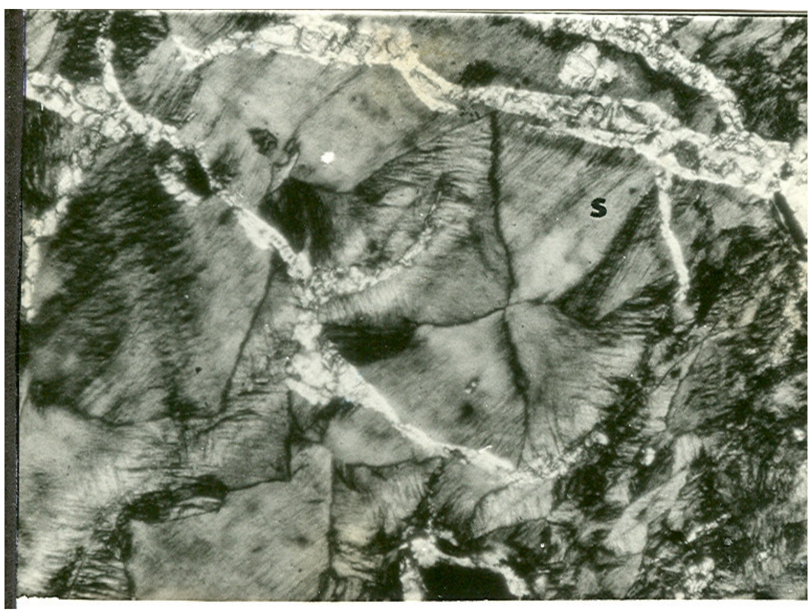

Figure 4. Serpentinite (s) formed after dunite shows hour glass structure. Crossed Nicols, x200

agents include the content of components like silica, alkalis, loss on ignition and other oxides such as Al_2O_3, Cr_2O_3 etc. The chemical specifications of major oxide weight % set by major steel producers in India for suitability of the high magnesian rocks to be used as flux/sinter mix are given in Table 1.

Ghosh et al. (1998) classified the high magnesian rocks from different parts of Orissa into four categories based on their chemical composition (Table 2.)

The chromite overburden magnesian rocks from Boula-Nausahi igneous complex (BNIC) were analyzed for their chemical composition and the results are given in Table 3. The bulk chemical data of different magnesian rocks show the presence of SiO_2 (41.8 - 48.1%; Avg. 42.63%), MgO (36.8 - 45%; Avg. 43.56%), Al_2O_3 (0.66 - 2.35%; avg. 1.055, Cr_2O_3 (0.11 - 0.5%; Avg. 0.42%) and low alkalis and CaO. Among the rock types, pyroxenite shows higher silica, total iron and titanium and lower MgO and Cr_2O_3. The MgO/SiO_2 of the rock types is around 1 with exception to pyroxenite which is slightly lower than 1. Important chemical considerations for the selection of these rocks to be used as substitute flux are

Table 1. Specification of major oxides in flux for iron and steel industry.

Major oxide	Weight (%)
MgO	>35
SiO_2	<48
Al_2O_3	<2
CaO	<2
Fe_2O_3	8 -12
Alkalis	<0.02
LOI	<14
Cr_2O_3	<0.06

Table 2. Classification of magnesian rocks based on chemical composition.

Oxide%	A	B	C	D
SiO_2	<40	<45	>45	>50
MgO	>35	>30	<30	<25
Al_2O_3	<3	<3	<3	<3
Alkalis	<0.2	<0.2	<0.2	<0.2
Cr_2O_3	0.6	0.6	0.6	0.6
CaO	2.- 3	2-3	2-3	2-3
LOI	<14	<14	<14	<14

their higher MgO, lower Al_2O_3 and Cr_2O_3 and very low alkalis and LOI contents and $MgO>SiO_2$ (Chatterjee and Murthy, 1998) (Table 3).

An important factor during flux selection is the fouling Index (Rf) which could be determined by the following equation:

Rf = (Base/Acid) X Na_2O
where Base= $Fe_2O_3+CaO+MgO+Na_2O+K_2O$ and Acid = $SiO_2 + Al_2O_3 + TiO_2$.

Rf values of magnesian rocks are found to be low (0.005 - 0.007) compared to values of limestone (0.75) and dolomite (1.09).

Thermal characterization studies

Besides chemical considerations, thermal properties which reflect the flow behaviour and thermal deformation characteristics at high temperatures are also important indicators to determine the suitability as flux materials. These parameters of magnesian rocks were evaluated by studying the different rocks under heating microscope which include slag viscosity (V), surface tension (p), slagging index (Rs) and deformation temperatures such as ST (softening temperature), IDT, (Initial deformation temperature), HT (Hemispherical temperature) and FT (Flow temperature). Thermal properties along with fouling index of the magnesian rocks are given in Table 4.

Viscosity of slag is an important factor which determines the flow ability of the slag. It is calculated using the following formula of Watt and Feredy, 1969:

$$\text{Log } V = \{107M/(T-150)^2\} + C$$
$$M = 0.00835\ SiO_2 + 0.00601\ Al_2O_3 - 0.109$$
$$C = 0.041\ SiO_2 + 0.0192\ Al_2O_3 + 0.0276\ Fe_2O_3 + 0.016\ CaO - 3.92$$
$$T = 1400℃$$

Slag viscosity is found to be low and vary within a small range (2.69 - 3.79) with the exception of pyroxenite which is characterized by a slightly higher value of 5.3. Comparatively limestone and dolomite show higher values of slag viscosity of 9.4 and 7 respectively. Low range of viscosity is attributable to complete melting of the flux above 1400℃ accounting for higher flowability of the slag.

Surface tension (ρ) indicates the adherence property of the slag to the inner lining/walls of the boiler/furnace. Surface tension values of the slag likely to be generated by the magnesian rocks are calculated from the formula after Holy et al., 1965;

$$(\rho) = 3.24SiO_2 + 5.85Al_2O_3 + 4.4Fe_2O_3 + 4.92CaO + 5.49MgO + 1.12Na_2O – 0.75\ K_2O$$

The value of surface tension is found to be almost uniform being confined to a narrow range (395 - 401) with an average of 398, which is considerably higher compared to that of limestone/dolomite. Higher value is due to complete melting of the magnesian rocks. It would minimize the possibility of slag sticking to the inner walls and lead to easier separation between slag and the metal melts. Slagging index is a temperature dependent parameter which is determined by

$$Rs = (\text{Max. HT} + 4\ \text{min. IDT})/5$$

Rs values of the magnesian rocks indicate their low slagging character ranging between 1280 and 1372℃ where as limestone/dolomite = quartzite mix exhibit high slagging character (<1400℃).

Softening temperature (ST) values of the rocks indicate that the sintering of the magnesian rocks start between 700 and 1180℃. Initial deformation temperature (IDT), hemispherical temperature (HT) and flow temperature (FT) values of various magnesian rocks show comparable and narrow ranges except pyroxenite which show comparatively lower value. Temperature data in Table 3 indicate narrow range of temperatures between HT and FT (30 to 160℃) and between IDT and FT (110 to 480℃). The fluid phase of the sinters is attained at higher temperatures ranging from 1340 to 1600℃.

From the above thermal data, it is inferred that magnesian rocks exhibit excellent physico-thermal properties like narrow range of temperature between HT and FT, low slag viscosity and low slagging index.

Table 3. Bulk chemical analysis of the overburden ultramafic rocks of BNIC.

Oxide Wt.%	Dunite	Peridotite	Serpentinite	Pyroxenite	Saxonite
SiO_2	41.81	42.16	42.78	48.12	43.78
Al_2O_3	0.66	1.73	0.82	2.35	0.97
MgO	45.10	43.10	43.60	36.80	42.46
Fe_2O_3	2.38	2.38	2.84	3.95	3.04
CaO	0.03	1.10	0.22	0.95	1.41
Na_2O	0.005	0.005	0.006	0.006	0.007
K_2O	0.002	0.005	0.002	0.004	0.003
TiO_2	0.02	0.05	0.06	0.11	0.08
Cr_2O_3	0.29	0.5	0.48	0.11	0.43
MnO	0.06	0.11	0.11	0.09	0.14
P_2O_5	0.002	0.002	0.02	0.04	0.002
LOI	9.02	9.53	9.00	7.12	7.44
MgO/SiO_2	1.078	1.022	1.019	0.764	0.969

Table 4. Thermal properties of overburden magnesian rocks.

Rock types	ST	IDT	HT	FT	V	p	rf	Rs
Dunite	1180	1340	1420	1450	3.79	397.57	0.006	1356
Peridotite	1180	1400	1500	1600	2.69	400.08	0.005	1372
Pyroxenite	1100	1150	1200	1340	5.3	395.14	0.005	1290
Saxonite	700	1200	1380	1540	3.18	400.96	0.007	1336
Serpentinite	700	1040	1435	1520	3.26	396.33	0.006	1280

DISCUSSION AND CONCLUSION

The two chromite deposits of Orissa are the largest chromite deposits of the country and nearly produce 98% of chrome ore by opencast mining method. It greatly contributes towards the economic development but at the same time deteriorates the natural environment by dumping the overburden rocks in the nearby sites. In the case of Sukinda mining area, around 7.6 million tons of solid waste have been generated in the form of rejected minerals, overburden material/waste rock and sub-grade ore that may be resulting in environmental degradation (Tiwary et al., 2005).

The chromite overburden materials consisting of ultramafic rocks are high magnesian in nature. They are typically coarse grained. By physico-thermal and chemical considerations, the ultramafic rocks having high MgO content perform better as substitute flux than the conventional flux combination. These ultramafic rocks contain low LOI content (7 - 9.5%) as compared to the conventional carbonate fluxes with LOI varying from 40 - 45%. Deleterious constituents like Al_2O_3 and Cr_2O_3 are present but within permissible limits in most of the ultramafic rocks. The compositional problem in pyroxenite however can be overcome by suitable blending with other high magnesian rocks. This substitute flux improves the productivity, need no heat of calcinations and substantially reduces overall heat energy input due to easy assimilation into melt. On the contrary, the use of conventional fluxes in combination is heat intensive, time consuming and tends to decrease the strength of the resultant sinter by sluggish and incomplete reaction. The problems associated with conventional fluxes are compounded by scarcity of BF and SMS grade limestone and dolomite. The problem of suitable raw material is further accentuated by other economic constraints related to location, transport and freight dynamics points of view. From the above studies, it is observed that the high magnesian chromite overburden rocks have a great promise as source of substitute flux for upcoming steel plants to be set up in Orissa.

The exploitation of the ore is carried out through open cast mining method since the last few decades. Poor mining methods, waste storage or unsystematic dumping of waste rocks and disposal systems are primarily responsible for environmental problems. The overburden rocks as dumps are stored on ground surface, where leaching of chromite and other toxic element takes place particularly during monsoon seasons. Tiwary et al. (2005) provided an insight into the likely migration of contaminant in ground water due to leaching from overburden dump of chromite ore. Godgul and Sahu (1995) reported that serpentinization and Mg release during deuteric alteration of ultramafic rocks create alkaline pore water and lateritization which is an intensive oxidation process. Chromite grains in oxidized serpentinite may generate hexavalent chromium and cause hazardous chromium pollution of the water. Hence, utilization of these ultramafic overburden dumped materials has the significance on habitats surrounding the mining area which otherwise create environmental problems. Thus, this characterization study aids the mining industries in converting the negative impacts of the chromite overburden ultramafic rocks as fluxes into a source of revenue.

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