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Alternative utilisation prospects for Indian lateritic overburden

Physical beneficiation and metallurgical processes alone cannot be used for the processing of Indian lateritic overburden. In this article, studies carried out on complex lateritic overburden using a combination of physical and pyro-metallurgical process for making pig iron nugget from the overburden is discussed. Physical beneficiation has enriched the Fe content to 52.74% with a weight per cent recovery of 59.67% having Ni-0.9% from the feed assaying 46.73% Fe (T), 0.76% Ni. This beneficiated nickel enriched iron was used for the production of pig iron nuggets which has given a composite product containing Ni~1.7%, Cr~ 1.5%, C~ 3% and Fe-rest with recoveries of iron, chromium and nickel as > 95%, > 95% and ~40%, respectively.

Key words: Lateritic ore; nickel; chromite overburden; processing; composite pellets; pig iron nuggets.

1.0 Background

Nickel, an important strategic metal is used as alloying component for stainless steels and special steels. 65% of the overall primary nickel is consumed in stainless steel production all over the world, whereas another 12% goes to super alloys or nonferrous alloys manufacturing (Johnson et al., 2008; Kim et al., 2010). Nickel occurs most often in combination with sulfur and iron (pentlandite), with sulfur millerite - (NiS), with arsenic in the mineral nickeline and with arsenic and sulfur in nickel galena. The bulk of the nickel mined comes from two types of ore deposits:

- laterites – principal ore minerals : nickeliferous limonite [(Fe, Ni)O(OH)] and garnierite (a hydrous nickel silicate) $[(Ni, Mg)_6Si_4O_{10}(OH)_8]$, or
- magnetic sulfide deposits – principal ore mineral: pentlandite $[(Ni, Fe)_9S_8]$.

Though, 70% of the world land based nickel resources are contained in laterites, currently account for only about 40% of the world nickel production. The major sulphide nickel mines are located in Canada, Australia, Russia, South Africa, Zimbabwe and Botswana. Major laterite deposits are located in Cuba, the Dominican Republic, Guatemala, Brazil, Australia, the Philippines, Indonesia, New Caledonia, Russia, China, Serbia and Macedonia. The laterite vs. sulphide deposits and world nickel laterite deposit is shown in Fig.1 (a) and (b) respectively.

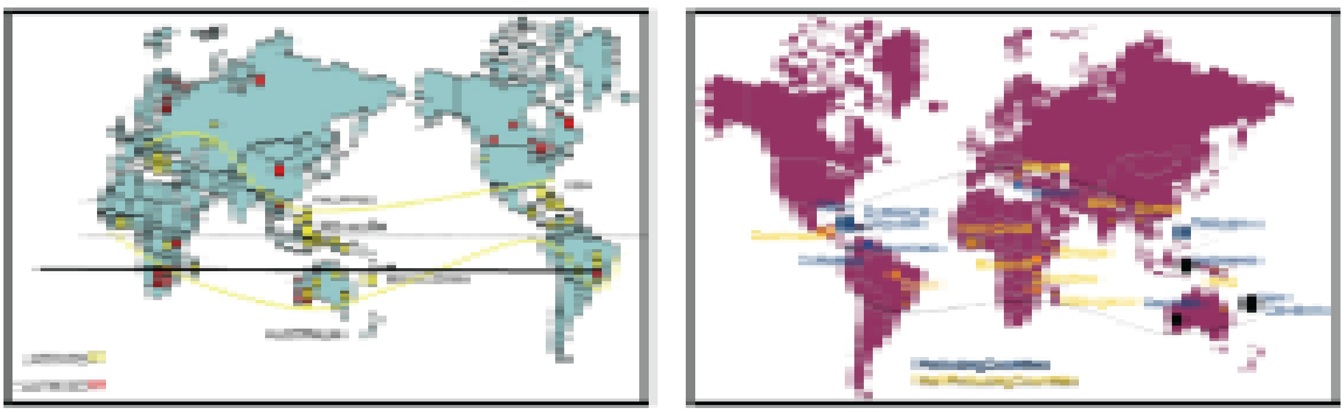

Fig.1 (a).Laterite vs. sulphide deposits (b) World nickel laterite deposits
(Source: Agus Superiadi, PT Inco.Tbk)

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1.1 World nickel laterites and processing techniques

Laterite ores account for over two-thirds of the worldwide reserves for important nonferrous metals such as nickel and cobalt. It is not possible to quantify the amount of nickel

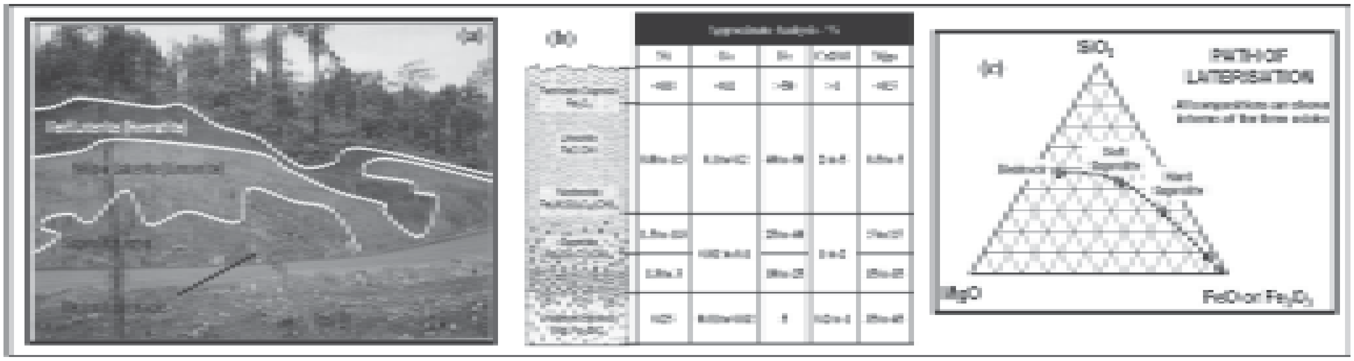

Fig.2 (a) Overburden layers (b) Vertical distribution of metal content (Roorda and Hermans 1981); (c) path of laterisation

contained in deep-sea nodules with any accuracy. The nickel-magnesium-silicate is associated with mixtures ranging from serpentine (hydrated magnesium silicate), to the clay-like saponite and deweylite minerals. Nickel in nickeliferous laterite is closely associated with iron oxide and silicate minerals as isomorphous substitution for iron and magnesium in the lattice. Nickeliferous limonite is comprised nickel bearing ferric oxides in deposits formed from ultra basic rocks. The limonitic fraction is comprised goethite, gibbsite, chromite and absolite. The saponite layer contains talc, quartz, serpentine, fosterite, olivine and garnierite. The oxidized lateritic ores normally contain impurities such as chrome, magnesium, manganese, iron, and aluminum. The formation and metal distribution of lateritic deposits is presented in the Fig.2.

Laterites, unlike sulfides, cannot be significantly upgraded or concentrated by flotation or gravity separation technique due to its complex mineralogy, heterogeneous nature, and low nickel content (Swamy et al., 2003; Dalvi et al., 2004; Warner et al., 2006). However, there are two important benefits of laterite ores – they contain valuable cobalt and, being closer to the surface, can be processed by open cut mining. The overview of nickel sulphide and laterite processing techniques and economics are outlined in Fig.3.

1.1.1. Processing of nickel laterites

Laterite ore cannot be concentrated, so it must be smelted

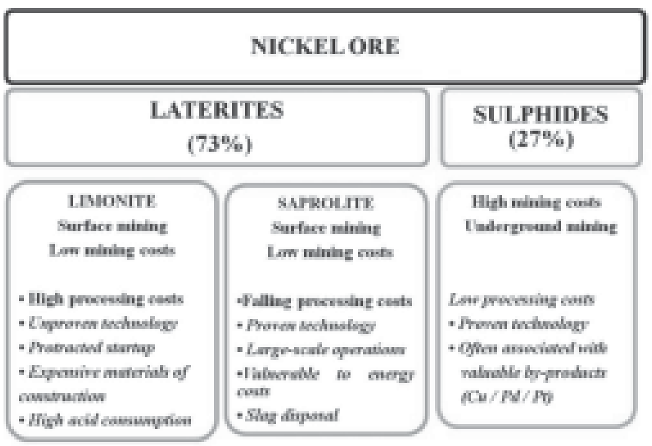

Fig.3 Nickel ores and their pros and cons (Robert et.al, 2010)

directly from crude ore. The low nickel content limits the breakeven point of commercial production. The development of ferro nickel processing is discussed in detail by Kotaro Ishii 1986. The first nickel processing treatment from laterites was developed in 1879 in New Caledonia, based on the iron blast furnace technology of the day. Processing of nickel laterite ores utilises a variety of technologies, including (Norgate et al., 2011):

- ferronickel smelting;
- nickel matte smelting;
- blast furnace/electric furnace (nickel pig iron) smelting;
- high pressure acid leach (HPAL);
- atmospheric leaching (AL);
- enhanced pressure acid leach (EPAL), i.e. HPAL and AL combined;
- heap leaching (HL);
- sulphation atmospheric leach (SAL);
- Caron process.

Most of the above mentioned technologies are in various stages of development particularly some of the hydrometallurgical processes. Both pyro and hydrometallurgical processes are commercially applied to the recover nickel and cobalt from lateritic ores. The major commercial routes for processing nickel laterite include: high pressure acid leaching (HPAL) (Liu et al., 2010; Rubisov and Papangelakis, 2000; Whittington and Muir, 2000), the reduction roasting-ammonia leaching (Caron process) (Nikoloski and Nicol, 2010; Senanayake et al., 2010), atmospheric leaching (AL) (Das and De Lange, 2011; Li et al., 2011; McDonald and Whittington, 2008 a,b), and the rotary kiln-electric furnace (RKEF) process (Nayak, 1985). The value of iron is ignored in the conventional hydrometallurgical processes, which not only results in the waste of iron resources but also causes the loss of nickel and cobalt during the hydrolysis of iron (Li et al., 2010b). In the last 30 years, utilization of the acid leaching iron residues was not possible due to the presence of impurities, particularly Cr (Ema and Harada, 1987; Owada and Harada, 1987) and its limited use in iron making (Takagi and Furui, 1987). These acid leaching residues with impurities have become unexploited resources that are a serious burden to the environment; thus, research has been carried out to recover hematite from the acid leaching residues mainly containing hematite, quartz and chromite and upgrade of the residues to a saleable iron concentrate (Stamboliadis et al.,2004).

Most pyrometallurgical routes (ferronickel and matte smelting) use a conventional flow sheet which includes steps for upgrading in the mine, drying, further upgrading, calcining/reduction and electric furnace smelting followed by either refining to produce a ferronickel product or converting to a low iron-containing matte. Several investigations on the reduction roasting of nickeliferous laterite ore followed by magnetic separation to produce Fe-Ni alloy have been carried out. An alternative route of direct reduction followed by physical separation with less energy consumption has been employed (Nippon Yakin Kogyo Co., Ltd., Oheyama Works, Japan). The ferronickel materials obtained from magnetic/gravity separation are directly used to manufacture stainless steels, which dispenses with the need for further smelting in an electric furnace (e.g. the RKEF process) to achieve the separation of ferronickel from slag (Kobayashi et al., 2011; Watanabe et al., 1987). Nevertheless, this process still requires a sufficiently high temperature (1250-14000C) during the reduction for the partial molten of the matrix, so as to permit the growth of ferronickel granules. Due to the high cost of stainless steel production as a result of the high nickel prices (Baddoo, 2008), processes for producing low cost ferronickel raw materials are of importance.

2. Indian laterites – present problems and future prospects

Nickeliferous laterites are classified in three types according to their mineralogical characteristics (Brand et al., 1998):

- Type A: Silicate Ni deposits containing 20-40% Ni, consisting of a mixture of the phyllosilicate minerals serpentinite, talc and chlorite.
- Type B: Silicate Ni deposits containing 1.5-2% Ni, consisting of partially weathered serpentinite and smectite.
- Type C: Oxide Ni deposits containing <2% Ni, consisting mainly of Fe oxyhydrates (goethite, hematite) and secondly of serpentinite and chlorite.

India does not possess minable nickel deposits. Though, traces of sulphide deposits occur in association with copper, molybdenum and iron in Bihar state. The known secondary type of available nickel in the country is in the form of mine overburden in open cast chromite mining located in the Sukinda region of Odisha state. The overburden is predominantly nickel ferrous laterite, containing 0.3 - 0.7% nickel. These overburden dumps cannot be classified into any of the above motioned types, thus making it difficult for further processing.

The over burden is a complex of mineral constituents such as: iron minerals (hematite and goethite), magnesium silicates (serpentine and chlorite, silicates), quartz, clay minerals (illite and kaolinite), spinel (chromite and occasionally some magnetite). Goethite is the principal mineral phase where nickel is present in its structure. The major concern for the mining and processing activities is:

- Best possible way of utilization
- Beneficiation/metallurgical process: sustainable and commercially viable process technology which can give complete solution
- Low nickel concentration and complex mineralogy
- Land for disposal/beneficiate
- Preserve/discard: as per the mineral conservation act, the presence of minor traces of rare earth elements like nickel, cobalt etc. cannot be discarded.

In India beneficiation for the overburden is not practiced due to the above mentioned reasons. Further, for any process (metallurgical/physical) to be techno economically viable, the nickel content in the feed must be minimum 1%.

2.1 Future prospects

Conventional mineral processing techniques are well established for sulphide ores with high nickel content and for laterites with low nickel concentration. But limonitic overburdens where the nickel concentration is <1%, processes are yet to be established. The presence of nickel in these vast accumulated deposits has engaged many R&D organizations to develop a technique which can substantially zero the rejected dumps for further mine development. Numerous processes (physical, pyro and hydro metallurgical) were developed by different Indian researchers and research organizations on low grade laterites, which are well articulated and summarized by Narasimhan et. al., 1989; Swamy et.al, 2003; Acharya et.al, 2010; Anand Rao et al.,1995. Some laterites have already been shown to be amenable to simple upgrading by removal of low grade coarser material by screening or classification. As the characteristics of laterites vary widely, flotation may be worth pursuing for some deposits (Rao et al., 1989).

Though high quality research work was carried out and brought a lot of insight towards the nickel recovery, but could not be able to justify as which processing route is used for a given ore deposit which is largely dependent on the ore mineralogy and grade. Single process alone cannot convert the waste into value; hence process integration is required to give complete solution. The future prospects were dependent on the comparison flexibility in processing route selection. This will not only improve the existing processes but also gives insight for sustainable process technology development. Present investigation is an attempt to evaluate and integrate the two process routes physical and pyrometallurgical to give a complete solution.

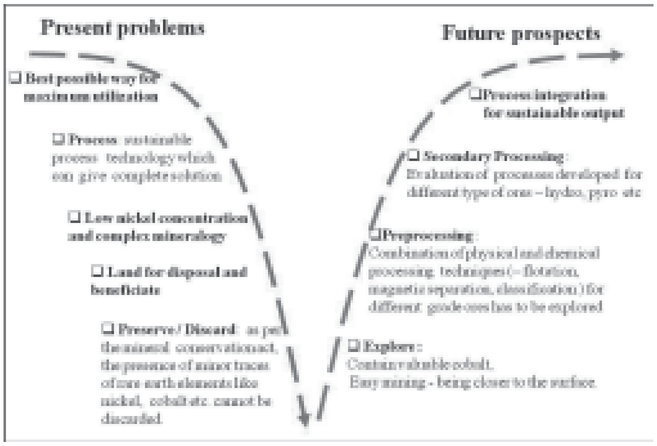

Fig.4 Overview of Indian lateritic overburden problems and prospects

3.0 Material and method

The limonitic overburden sample used in the present work was collected from the chromite mine of Odisha state, India. The compositional analysis of feed and the products were carried by inductively coupled plasma-optical emission spectrometer (ICP-OES). The sample being friable in nature was screened through 1mm sieve initially followed by sub sieve analysis using Fritz wet sieve shaker under a standard set of sieves in wet conditions. X-ray diffraction (XRD), scanning electron microscopy/X-ray energy dispersive spectroscopy (SEM/XEDS) and QEM SEM techniques were used to characterize the samples.

4.0 Results and discussion

4.1 Particle size analysis

A limonitic laterite overburden was utilized with the following elemental analysis: 46.73% Fe, 3.34% Al_2O_3, 2.33% SiO_2, 8.28% Cr_2O_3, 10.78% MgO, 2.78% CaO and 0.76% Ni for the beneficiation studies. The size analysis and size wise iron distribution is presented in Fig.5. It is observed that majority of the particles were segregated below 37µm (72.29%) size with maximum Fe content 55.9%. At this size range the concentration of other elements i.e. chromite and silica were 2.39% and 6.83% respectively. Effective segregation of particles below 37 µm (Fig.5) can make recovery of most of the iron fractions.

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4.2 X-ray diffraction and SEM analysis:

The XRD pattern of the raw bulk laterite ore is presented in Fig. 6. It is indicated that the iron hydroxide is totally

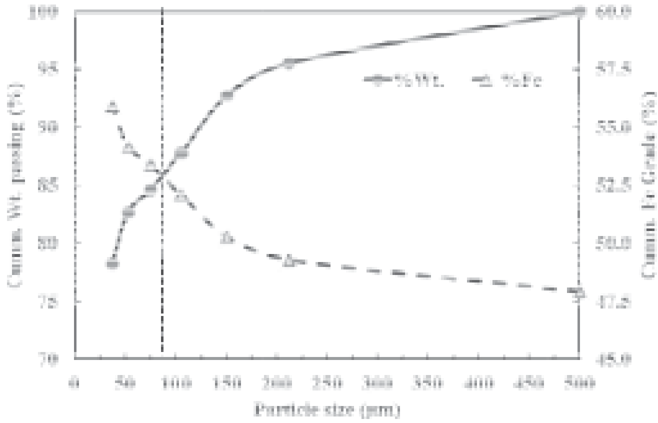

Fig.5 Size wise iron distribution

present in the goethite phase. Goethite is the hydrated iron oxide being formed due to weathering of olivine and pyroxene of ultramafic rocks. In addition to goethite, quartz and chromite are the other important phases. The absence of nickel minerals/phases and the dominance of the goethite phase classify this material as laterite type. The scanning electron microscopy examination of the feed is presented in the Fig.7. A brighter phase (pt 1 and pt 4) shows the presence of chromite grains. The dull matrix (pt 8 and pt 6) shows the dominance of goethite and fine grained quartz. Grains of Cr_2O_3, Al_2O_3, and MnO may also exist in the goethite lattice due to the varying degrees of Cr^{3+}, Al^{3+} and Mn^{2+} substituting for Fe^{3+} to some extent in the goethite lattice (Swamy et al., 2003).

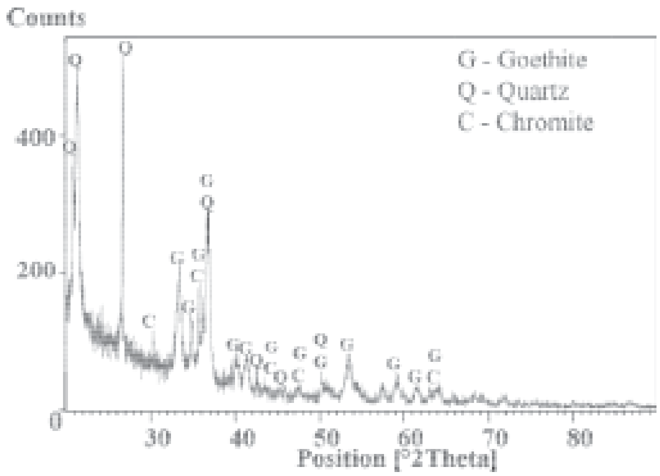

Fig.6 X-ray pattern of the bulk feed

4.3 QEMSCAN analysis:

The mineral mass percent and deportmental studies were carried out using QEM-SEM (Quantitative Evaluation of Materials by Scanning Electron Microscope) analyzer. Modal mineralogical study of the feed sample shows that 82% of total mineral mass is occupied by goethite. Other major minerals are quartz (8.2%) and hematite (4.89%). The deportmental analysis is performed to understand the proportionality of different minerals responsible for particular

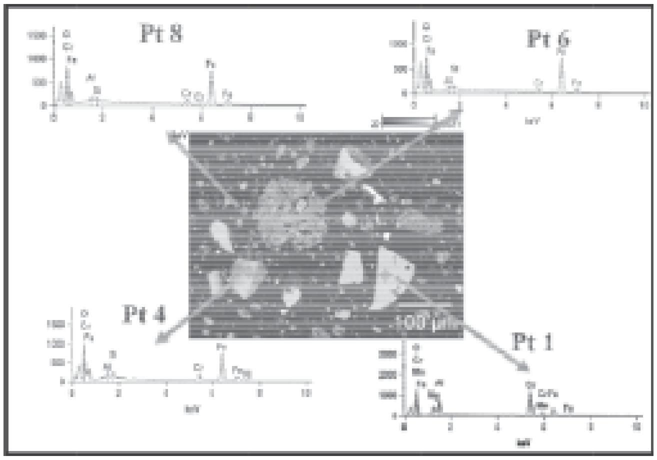

Fig.7 SEM analysis of feed

element. Fig.8 (a, b, c) shows the deportmental analysis of iron, nickel and chromite minerals respectively from the feed. Goethite contributes Ni in the range of 97%. Hematite contributes only 3%. The Fe deportmental analysis shows that major iron contribution is form goethite (94%) followed by hematite. Fig.7 (c) shows the Cr deportment. Chromite is the major mineral (88.32%) responsible for Cr.

5. Process flow sheet development: phase I

Based on the characterization studies of the feed, beneficiation studies were carried out on unit operations viz, floatex density separator, hydrocyclone and wet shaking table. Based on the performance the unit operations the best operating conditions were optimized and the comparison was made in terms of iron grade, recovery and weight percent Fe-recovery. Based on the results obtained from the test work carried out on different unit operations, a process flow sheet was developed (Fig.9) using a combination of unit operations based on the feed quality for the maximum recovery of iron as primary product and chromite as secondary product.

The flow sheet comprises crushing and scrubbing operation followed by two stage classification by hydrocyclone (feed having low chromite and silica content) for maximum iron recovery as overflow or single stage classification followed by tabling operation for the feed containing high chromite and silica. The underflow of the secondary cyclone is further processed using wet shaking tables to recover free chromite. Further recovery of ultrafine chromite and iron can be achieved using enhanced gravity concentration techniques like multigravity separator. The flow sheet is developed for the feed material of friable nature. The products (concentrate and tailings of hydrocyclone circuit) were analyzed using QEMSCAN (Fig.10). It is clear from the figure that the product is majorly composed of goethite material where as the rejects i.e.hydrocyclone underflow contains free chromite and quartz fraction.

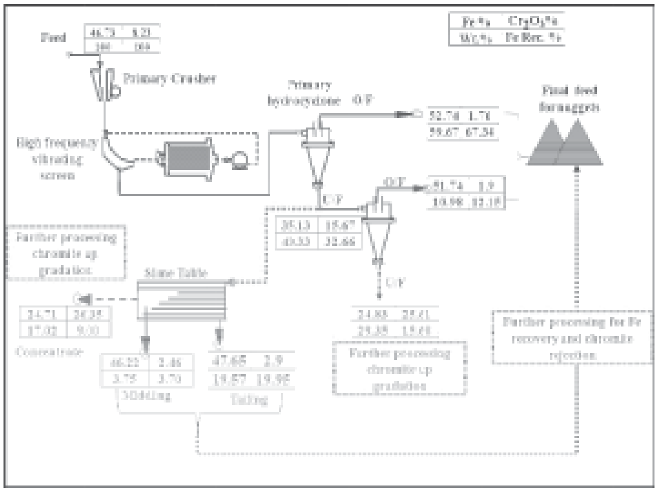

Fig.9 Process flow sheet using combination of hydrocyclone and wet shaking table

6. Metallurgical studies: phase II

Most of the nickel extraction from overburden was tried at lab scale using different hydrometallurgical routes but none of the techniques reached to the plant level for lateritic overburden. Further these techniques generate lots of residues which are of major concern to environment. An alternative technology was proposed by MECON to utilize overburden for the production of alloy pig iron using mini blast furnaces. In this technology overburden along with iron ore was sintered and fed as raw material in the blast furnace.

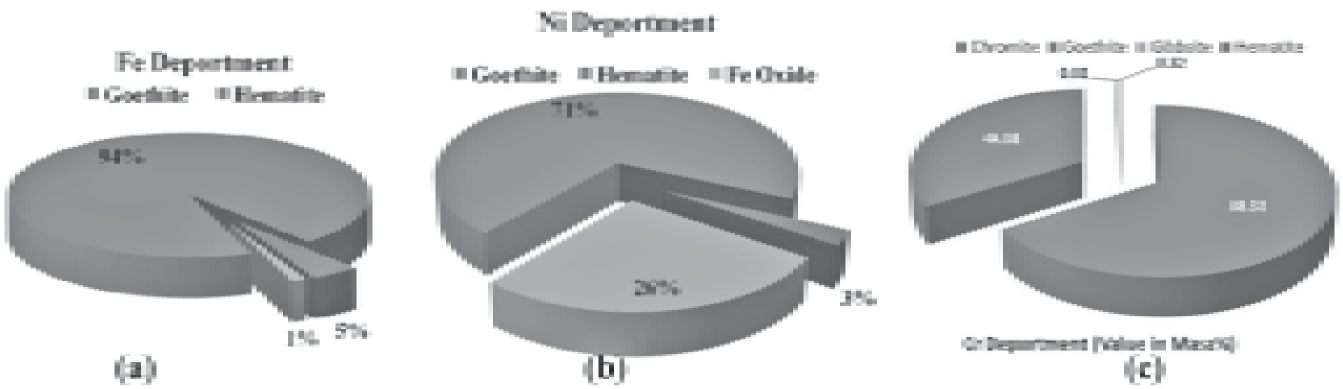

Fig.8 Elemental deportment of the feed

Fig.10 QEMSCAN analysis of the process product and reject

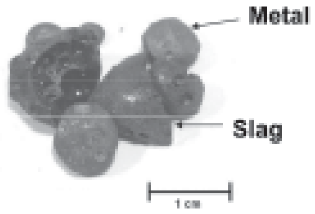

Fig.11 (a). Product produced from raw sample

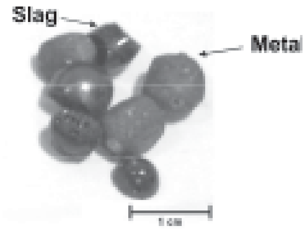

Fig. 11(b). Product from processed sample

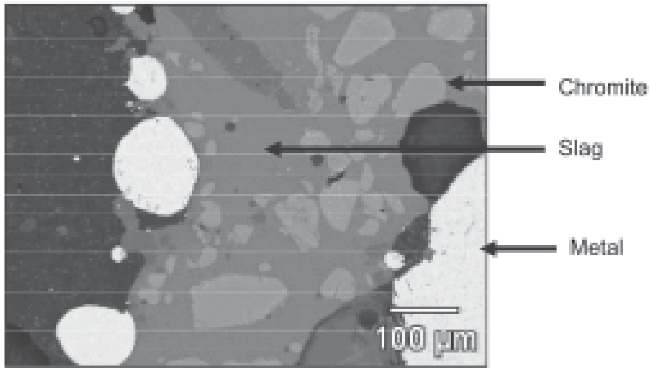

Fig.12 SEM image of the reduced sample

Mixing of iron ore with overburden dilutes the nickel concentration hence the produced alloy pig iron has lower recoveries of nickel (Cr -1-1.4, Ni -0.7-0.9).

In the present studies attempts were made to develop a technology to produce slag free alloy pig iron nuggets from the overburden. In this process, the overburden was reduced with the help of coal at 1400^0C for the production of alloy nuggets. For the present studies two samples, as received overburden and processed product, were used. All the raw materials were mixed thoroughly and the self reducible composite pellets were made. Pellets were dried in an oven at 110^0C for 2 hrs for the removal of moisture. These samples were reduced at 1400^0C for 15 minutes for the production of alloy nuggets. The reduction experiments were carried out in a controlled atmosphere (nitrogen) in horizontal alumina tube furnace. After reduction, samples were analyzed by different analytical techniques. ICP-OES was used in wet chemical analysis. The phases present in the samples were examined by JEOL JXA-6400 scanning electron microscope attached with KEVEX super dry, Energy -Dispersive X-ray detector (EDX). Fig.11 (a) and (b) shows the nuggets formed from the two different samples. Chemical analysis of the nuggets is shown in the Table 1. Recovery of iron, chromium and nickel values in to the nuggets is >90%,< 40% and >95% respectively. Total metals recovery (Fe, Cr and Ni) into the nuggets is 82% for the raw feed sample and 94% for the processed product sample. It is due to the chromite loss in to the slag phase, which is a refractory constituent. Fig.12 shows the SEM image of the reduced sample. It can be seen from the figure that unreduced chromite grains encapsulated in the slag phase. Hence, it is advised to separate chromite from overburden by beneficiation which can be used in ferrochrome production.

TABLE 1: CHEMICAL ANALYSIS OF THE NUGGETS

	Fe	Cr	Ni	Si	C
Direct feed	Rest	2.89	1.6	<1	2.8
Processed feed	Rest	1.03	1.73	<1	2.9

Conclusions

- Though a number of technically feasible processes were developed for the extraction of nickel from the overburden, but did not provide the final solution to the problem for an alternative route of utilization of huge tonnages of nickeliferous lateritic overburden.
- Present studies were an attempt towards making a zero waste beneficiation process flow sheet which can be readily integrated with the existing beneficiation circuit.
- This process has enriched the Fe content to 52.74% with a weight percent recovery of 59.67% having Ni-0.9% from the feed assaying 46.73% Fe (T), 0.76% Ni. Pig iron nuggets with Ni~1.7%, Cr~ 1.5%, C~ 3%, and Fe-rest were produced with recoveries of iron, chromium and nickel as > 95%, > 95% and ~40%, respectively.
- Further phase wise solutions can be adopted to such overburdens by:

(a) classifying the overburden as nickel rich and nickel poor ores followed by upgradation through suitable beneficiation techniques for making pig iron

(b) alternative techniques for using the waste as backfill, soil enhance etc.

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