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Preparation of alternative raw materials for resource development to use in Indian ferro alloy and steel industrial applications

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The present paper deals mainly with iron bearing titania enriched ilmenite raw mineral, its production, exports and imports and consumption of Ferro alloy industries. This paper not only reveals the recovery of iron from iron bearing titania mineral ilmenite with physical beneficiation methods but also gives the process of preparation and separation of titania slag and iron metal by using microwave heat treatment. The process of recovery of iron as a by-product from ilmenite mineral, which abundantly available along the coastal line of India, is economical and by which the conservation of some higher grade iron ores of the country will be possible for future. The products obtained from this process can be treated as alternative raw materials resources for steel and iron making industries.

Keywords: Iron ore, Magnetite, Hematite, Heavy minerals, Titania slag, Metal

1 Introduction

The iron and steel products are well known to be essential components for the consumers which revolutionize the way we survive and entertain ourselves for our day-to-day life. In this modern era of fast revolution, due to exponential growth and use of iron and steel products, it requires more raw materials in form of iron and its end products for ferroalloys and steel industrial applications with lesser cost. Also, it is seen from the available references, importing of small amount of iron raw materials to the industries from various countries causes huge cost in form of transportation and taxes, due to which it causes much less production of iron and steel products as expectation. It is also one of the main reasons that why the developing countries unable to generate the revenues by importing the iron, steel and other important products like titanium, aluminium, nickel etc. The researchers and manufacturers are in continuous processes in searching of some other alternative resources to supply of iron raw materials to Indian Ferroalloys and steel producing industries. Also, the researchers and manufacturers are always searching of iron raw materials for ferroalloys and steel industries, through nature ore and some beneficiations process as well as alternate resources related to iron.

Iron ore minerals are magnetite (Fe_3O_4, 72.4% Fe), hematite (Fe_2O_3, 69.9% Fe), goethite (FeO(OH), 62.9% Fe), limonite ($FeO(OH)\cdot n(H_2O)$, 55% Fe) or siderite ($FeCO_3$, 48.2% Fe). Ores containing very high quantities of hematite or magnetite (greater than about 60% iron) are known as "natural ore" or "direct shipping ore", meaning they can be fed directly into iron-making blast furnaces. Iron ore is the raw material used to make pig iron, which is one of the main raw materials to make steel from98% of the mined iron ore. The total recoverable reserves of iron ore in India are about 9,602 million tons of hematite and 3,408 million tons of magnetite. Chhattisgarh, Madhya Pradesh, Karnataka, Jharkhand, Odisha, Goa, Maharashtra, Andhra Pradesh, Kerala, Rajasthan and Tamil Nadu are the principal Indian producers of iron ore. There are many alternative resources for iron ore to use in iron industries after suitable beneficiation techniques. The various beneficiation processes to recover the ilmenite, hematite, magnetite, limonite, siderite, geothite minerals etc from other resources like titonamagnetite, beach sand heavy placer minerals, teris and land, red sediment badlands topography, red mud etc in order to obtain iron along with some other components as raw materials, which helps to solve the alternative resources to Ferroalloys

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and steel manufacturers. Many industries are not only recovering the iron ore minerals but also recovering the raw materials as pig iron and its associated bye products such as titanium products, etc through various beneficiation processes. This helps a lot to supply the pig iron and its bye products as alternative resources of raw materials to ferroalloys and steel making industries. Magnetite is being recovered from sulphide ore plant tailings as well as from red mud obtained from alumina plants and also can be recovered from chromite over burden of Sukinda valley. The most and economical deposits are ilmenite and magnetite. Magnetite is being recovered as by product from copper, lead, zinc ores tailings. Similarly large amount of magnetite is being recovered as by product from uranium plant tailings. There are many researchers worked in this area to recover titanium product and iron but work related to microwave energy for recovery of iron metal from ilmenite is so far not attempted by many researchers. Hence this present paper deals with the recovery of iron from ilmenite mineral by physical beneficiation process as well as recovery as bye product from ilmenite slag process. By this process, the consumption high grade iron ore can be saved for future.

2 Materials and Methods

All the samples of iron bearing titania minerals ilmenite, leucoxene etc were recovered from the total heavy minerals of beach sand heavy placer minerals of India i.e from the states Kerala, Andhra Pradesh, Odisha, West Bengal, Maharashtra etc based on IBM published data[1]. The minerals containing ilmenite production, their exports, imports and their utilisation were investigated with the reference IBM published data[1] and are mostly used in Ferro-alloy industries. These data were also interpreted with reference to Response Methodology[2-4]. Initiallyall the samples were ground and subjected to low intensity magnetic separator and the magnetic recovered were further subjected for grinding to d_{80}(50 microns) and again subjected to low intensity magnetic separator to recover enriched iron product. Similarly, an attempt was made to roast the Ilmenite and this product subjected to microwave furnace to recover titania rich and iron rich products separately. Samples obtained by microwave furnace were subjected SEM EDAX for characterisation of titania slag and iron.

2.1 Analytical methods

All the samples obtained by microwave furnacewere used for complete chemical investigation for Titania slag and iron. For this, PAN alytical X-Pert X-ray powder diffractometer (XRD) was used having Mo-Kα radiation (λ=0.709Å) observed with 6° to 40° scanning angle. The scanning of sample in the diffractometer (XRD)wasat the rate of 0.025°/sec. It helpsin phase analysis characteristics of sample for chemical analysis

3 Results and Discussion

The total recoverable reserves of iron ore and its distribution of iron ores abundant in India are shown in Table 1. The data indicate that hematite iron ore is major in Odisha state accounting to 33% share in India. Similarly, the magnetite iron ore is major in Karnataka state accounting to 73% share in India.

Iron bearing titanium minerals ores are ilmenite ($FeTiO_3$) containing titania ($TiO_2$35-67%), leucoxene (containing TiO_2 68-89%) and titano-magnetite, TiO_2.FeO (containing TiO_2 7-8%). However, these titanium minerals often varied from the available composition by containing variable amounts of magnesium or manganese. These elements substitute for iron in complete solid solution. A solid solution series exists between ilmenite ($FeTiO_3$) and geikielite ($MgTiO_3$). In this series, variable amounts of magnesium substitutes for iron in the minerals crystal structure. A second solid solution series exists between ilmenite and pyrophanite ($MnTiO_3$), with manganese substituting for iron. At high temperature, a third solid solution series exists between ilmenite and hematite (Fe_2O_3). The World Map of Ilmenite Producers as on the year 2016-2017, shows a list of the countries that produce ilmenite in large quantities. As the data in the map shows, South Africa leads the world in the production of ilmenite with an annual production of 1120 thousand metric tons every year. Australia is the second-largest ilmenite producer1070 and is followed by Canada, 700, China, 600, India, 425, Vietnam 410, Mozambique, 350, Norway, 320, Ukraine, 300, United States, 200, Madagascar, 150, Brazil, 43 and Sri Lanka. 40 and other countries

Table 1 — Distribution of iron ores abundant in India.

	Hematite	Magnetite
Reserves	~18,000 million tons	~10,500 million tons
Major states	Odisha 33% Jharkhand 26% Chhattisgarh 18% Rest in Andhra Pradesh, Assam, Bihar, Maharashtra, MP, Rajasthan, UP	Karnataka 73% Andhra Pradesh 14% Rajasthan 5%, TN 4.9% Rest in Assam, Bihar, Goa, Jharkhand, Kerala, MH, Meghalaya and Nagaland

produce 35 thousand metric tons respectively. Reported consumption of titanium in the form of ferrotitanium and scrap in steel and other alloys was 6,090 metric tons, a 3% increase from the 1993 level. Carbon, stainless, and heat-resisting steels were the largest end use categories of ferrotitanium and scrap. Total recoverable ilmenite deposits are accounting from all states of India is 348.22 million metric tons[5-8]. The distribution of beach sand and inland placer minerals deposits identified so far along the coastline and inland placers and total resources established of India are given in Table 2. It is observed that the ilmenite resources as on today are accounting to 38.22 million metric tons and leucoxene is accounting for 17.93 million metric tons, which is accounting for total 56.15 million metric tons of iron bearing titanium minerals. On average if it is calculated for 50% in the whole resources, it is accounting to around 28 million metric tons of iron is available which can be recovered as by product of titania pigments. Production of ilmenite from coastal lines of India and its exports, imports and consumption in ferro alloy industries of India is given in Table 3. The data studied analysed by using response surface methodology to understand the status of exports, imports and consumption of ilmenite with resource and production data from the year 2009 to 2014 are shown in Fig. 1 which reveals that the consumption for Ferro alloy industries is almost

Table 2 — Placer heavy mineral reserves of India[1]

State	Category of Reserves	Iron bearing minerals (million metric tons)	
		Ilmenite	Leucoxene
Kerala (a) Beach Sand	Sub Total of indicated and inferred reserves	89.58	4.31
(b) Lake & Sea bed	Sub Total of indicated and inferred reserves	9.93	0.07
Tamil Nadu (a) Beach Sand	Sub Total of indicated and inferred reserves	17.37	0.60
(b) Inland Placer Teri Sand	Sub Total of indicated and inferred reserves	80.34	3.98
Andhra Pradesh Beach Sand	Sub Total of indicated and inferred reserves	100.10	2.95
Odisha, Beach Sand	Sub Total of indicated and inferred reserves	45.05	0.04
Maharashtra, Beach Sand	Sub Total of indicated and inferred reserves	3.04	0.84
West Bengal, Inland Placer	Sub Total of indicated and inferred reserves	2.08	-
Bihar, Inland Placer	Sub Total of indicated and inferred reserves	0.74	-
Grand Total		348.22	17.93

Table 3 — Ilmenite production, exports, imports, consumption, export and import values[1].

Input			**Output**			
Year	Production (Tons)	Export (Tons)	Consumption for ferro alloys (Tons)	Consumption for other industries (Tons)	Export, Value(Rs.)	Import value(Rs.)
2009	713605	463625	300	208600	2506478	68649
2010	663217	1019268	300	189600	5451218	287449
2011	718612	879522	300	190200	11499101	389054
2012	738524	79175	400	188400	14158888	1403236
2013	721959	686264	300	188300	8731824	1091737
2014	640878	775192	300	200000	6956324	408590

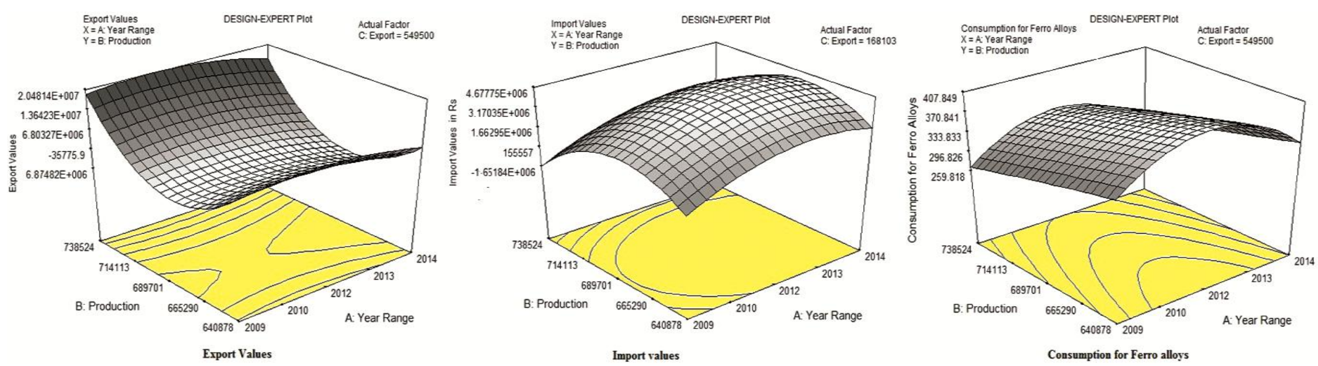

Fig. 1 — Surface response values for exports, imports and consumption for ferro alloys by ilmenite.

constant because sufficient iron ore, chromite and manganese are available for Ferro alloy industries.

3.1 Recovery of magnetite from ilmenite

Typical low grade ilmenite ore containing 11.1% TiO_2 and 71.4% Fe_2O_3 as shown in Table 4 is subjected grinding to d_{80} passing 50 micron size and subjected to low intensity magnetic separator [LIMS] at 0.2T magnetic intensity for recovery of magnetite from ilmenite. The magnetic fraction further subjected to grinding to achieve d_{80} passing 50 microns and the product subjected to LIMS for recovery of magnetite. The results are given in Table 5 indicate that on continuous grinding followed by magnetic separation on recovery of iron values from alluvial sand containing titania magnetite reveal that the magnetic (I) obtained from the rougher LIMS contain 87.3% Fe_2O_3 with 67.4% yield and 81% recovery from a feed containing 72.4% Fe_2O_3. The magnetic (I) ground and subjected to cleaner LIMS, by which a magnetic (II)product obtained, contain 89.2% Fe_2O_3 with 97.0% yield and 89.2% recovery from a feed containing 87.3% Fe_2O_3. The end product obtained is analysed for complete chemical analysis and the data are shown in Table 6[9]. However, the data shown in Table 6 reveal that this product can be used in the pellet feed for steel making after suitable blending with high grade iron ore fines

3.2 Titania slag and pig iron from ilmenite

The mineral ilmenite when reacts with carbon in microwave sintering furnace, reaches at a temperature of around 1250 ºC ,solid state reduction of oxides of iron and titanium takes place according to the following reactions[10-12]

$$Fe_2O_3 + C \rightarrow 2FeO + CO \quad \text{... (1)}$$

$$FeO + C \rightarrow Fe + CO \quad \text{... (2)}$$

$$2TiO_2 + C \rightarrow Ti_2O_3 + CO \quad \text{... (3)}$$

During high temperature (around 1550 –1650 ºC), the charged sample composed of ilmenite and carbon first melts and the reduction of oxides of iron and titanium proceeds with generation of metallic iron and titania slag with varying concentrations of FeO (10–20%), Ti_2O_3 and TiO_2. The graphical representation for production of TiO_2 and pig iron from ilmenite using microwave energy[10] is shown in Fig. 2. As shown in Fig. 2, the process of using microwave heating of ilmenite reveals that the titania slag contains 83.3% TiO_2 as shown in Fig. 3 based on the SEM/EDAX and pig iron contains 96.42% FeO as shown in Fig. 4. The XRD data as shown in Fig. 5 also clearly shows the presence of TiO_2 and pig iron which contains metallic iron and iron oxide. These products are perfectly suitable for Ferro alloy and steel industrial applications.

Table 4 — Chemical analysis of recovery of magnetite sample [in Wt. %].

Fe_2O_3	FeO	Fe [total]	TiO_2	SiO_2	Al_2O_3	CaO	MgO	P_2O_5
71.4	20.0	50.0	11.1	8.2	7.5	0.6	0.5	0.4

Table 5 — Results of continuous grinding followed by magnetic separation on recovery of iron values from alluvial sand containing titania magnetite.

Rougher LIMS				Cleaner LIMS			
Parameters	Weight%	Fe_2O_3%	Recovery%	Parameters	Weight%	Fe_2O_3%	Recovery%
Magnetic -I	67.4	87.3	81.0	Magnetic -II	97.0	89.2	99.0
Non magnetics	32.6	41.6	19.0	Non magnetics	3.0	25.9	1.0
Total	100.0	72.4	100.0	Total	100.0	87.3	100.0

Table 6 — Complete chemical analysis of the enriched ore product; 65.4 % yield (LIMS, 0.2 T); in Wt%

Fe_2O_3	FeO	Fe [total]	TiO_2	SiO_2	Al_2O_3	CaO	MgO	P_2O_5
89.20	3.3	62.7	5.1	0.4	0.9	0.4	5.1	0.2

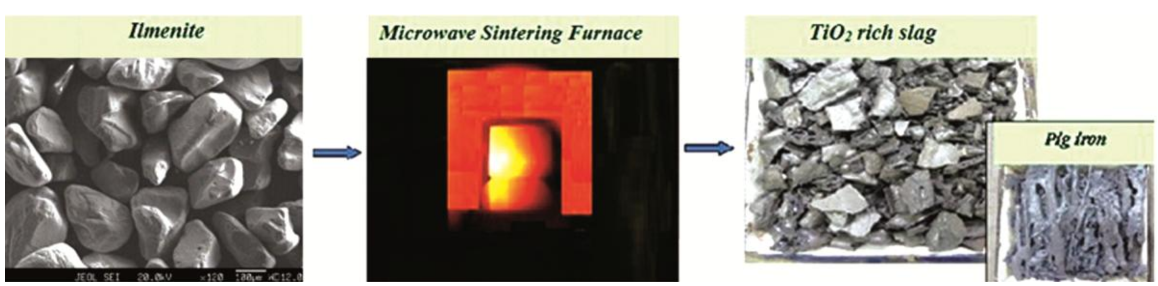

Fig. 2 — Production of TiO_2 and pig iron from ilmenite using microwave heating[10].

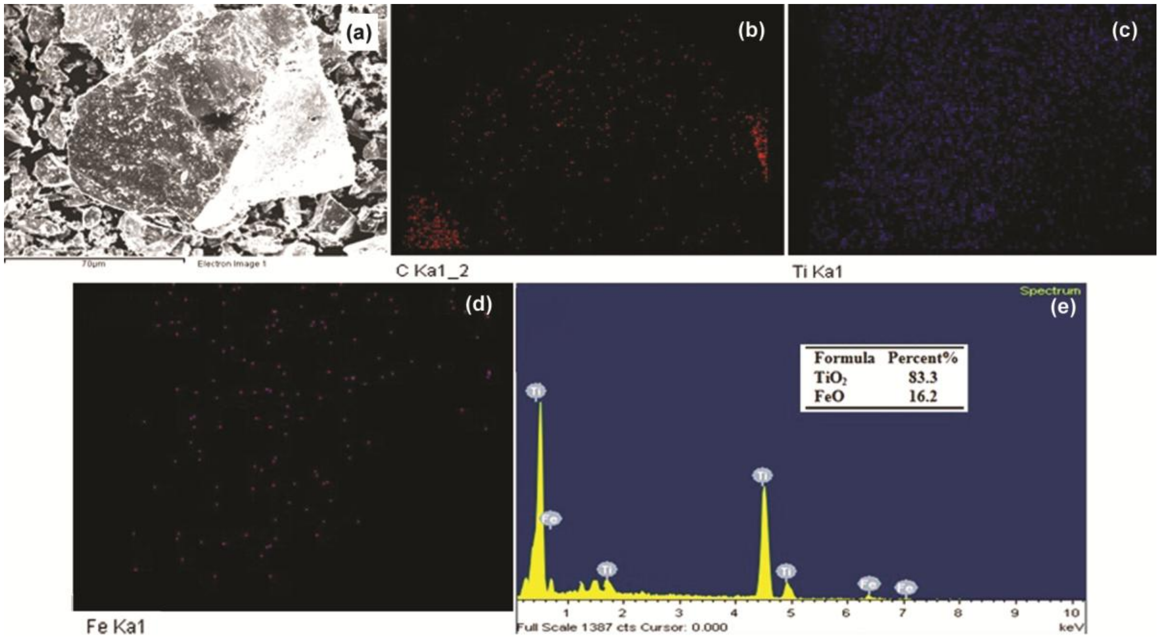

Fig. 3 — (a) SEM of titania rich slag sample, Image mappings of (b) Carbon (c) Titanium (d) Iron and (e) SEM - EDAX of titania rich slag sample.

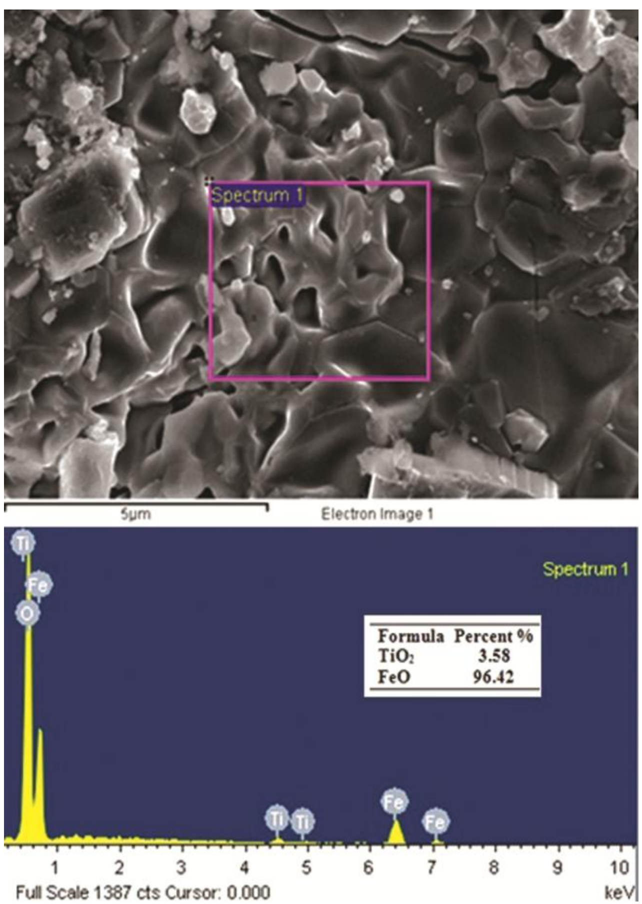

Fig. 4 — Formation of iron and SEM- EDAX data of ilmenite minerals after heated in microwave heating.

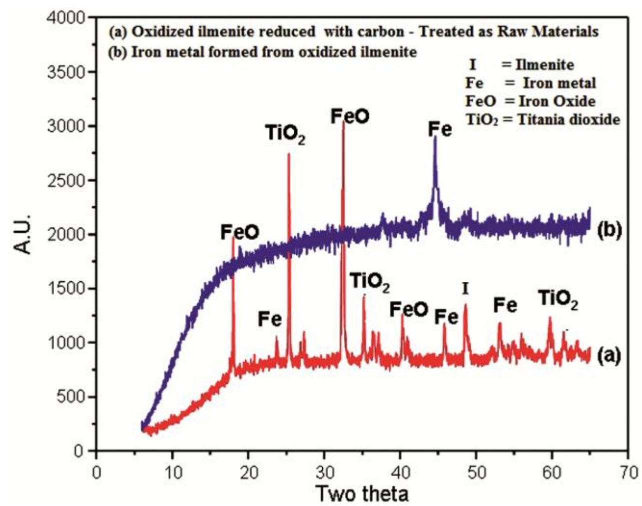

Fig. 5 — XRD pattern formed after the microwave reduction of oxidized ilmenite minerals in microwave furnace which shows the formation of iron components and titanium product.

4 Conclusions

In order to conserve high grade iron ores, the placer ilmenite mineral is one of the best alternative minerals for iron ores in India. It is observed that the ilmenite resources in India, as on today are accounting to 38.22million metric tons and leucoxene is accounting for 17.93 million metric tons. On average if it is calculated for 50% in the whole resources, it is accounting to around 28 million metric tons of iron is available which can be recovered as by product of titania pigments. The pig iron obtained as by product from the Titania pigment recovered from ilmenite mineral is most economical. It was observed that to recover magnetite has obtained by grinding ilmenite to d80 passing 50 microns followed by low intensity magnetic separator (LIMS) at two stages [Magnetic I and Magnetic II].It was also observed that Magnetic I product was obtained from rougher LIMS containing 87.3 % Fe_2O_3 with 81% recovery, Similarly Magnetic II product was obtained from cleaner LIMS containing 89.2% Fe_2O_3 with 99.0% recovery. These products are suitable for Ferro-alloys and steel making industrial applications.

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