

Placer Magnetite-sand and By-product Iron, Generated during the Beneficiation of Mineral Sand Ilmenite to High-Titanium Products, as Potential Alternatives to the High-Grade Fe-ore for Steel Making

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ABSTRACT

Iron is the most important of all metals and ~ 98% of it, in the form of iron ore/pellets, is used as the key raw material in making steel, with its per-capita consumption often seen as an Index for a nation's Prosperity. Salient aspects of the industries of iron ore mining and steel-production are presented. These include deposit-types and grades of iron-ore, iron ore minerals with Fe-contents, major producing-exporting-importing countries, international/national prices of iron ore; and major producing countries of steel, international/national production figures, processes of steel-making, including recent hydrogen-energy based green steel/iron ore under de-carbonisation. The less available high-grade Fe ore (> 63.5% Fe), as compared to that of the benchmark or standard grade (62% Fe) and low-grade (< 59% Fe) iron ores, has many beneficial features in steel-making, carries a premium price of US \$ 1-2/tonne for every 1% increase in Fe-grade over that of the standard grade and, hence, is much sought after. In this communication, two low-cost, potential alternatives to the high-grade Fe ore for steel-making are proposed from the mineral sand industry. These are: (i) placer magnetite-sand, with an example from the coastal Nizampatnam heavy mineral sand deposit in Andhra Pradesh, and (ii) by-product Fe, generated during the beneficiation of ilmenite-sand for high Ti-products such as synthetic rutile/anatase, titanium dioxide pigment, Ti-sponge, Ti-metal etc. A brief account of the mineral sand deposits, including the processes to obtain the above proposed alternatives and the consequent multiple benefits for both the steel and mineral sand industries, is presented in this paper.

INTRODUCTION

Iron is the most important of all metals, currently the highest refined metal and predominantly (~ 98%) used in the form of ore/pellets, as the key raw material, together with coking coal and limestone, for steel-making. Grade-wise, the iron ore is classified as the benchmark/standard ore (62% Fe), low-grade ore (< 59% Fe) and high-grade ore (> 63.5% Fe). Globally, around 2.5 billion tonnes of iron ore is mined annually and the seaborne market is about 1.45 billion tonnes,

of which about 540 million tonnes (Mt) is the high-grade iron ore (in the form of sinter, lumps and pellets), demand for which may rise to 634 Mt by 2030. Overall, the global market's Fe-grade is going down, since the best available grades from existing mines have been mined. China, with the largest market for iron ore, is also the largest importer of seaborne iron ore with ~ 1200 Mt, followed by the European Union, Japan and South Korea, each with ~100 Mt, while the largest exporter for seaborne iron ore is Australia with an export of ~ 900 Mt, followed by Brazil (~ 250 Mt), Ukraine (< 50 Mt) and India (< 50 Mt) in the year, 2020. Of the global exports of the iron ore by grade, the low-grade ore accounts for 19%, mid-grade ore (59 to 63.5% Fe) 44% and high-grade ore 37%. Of these three grades, the high-grade ore, with its availability being less than that of the other two grades, is sought after for steel-making due to its many beneficial features and, hence, carries a higher premium price of US \$ 1 to 2 for every 1% increase in Fe over the standard of 62% Fe ore (Cooper, 2021). In April, 2021, the high-grade Brazilian index (65% Fe fines) also advanced to a record high of US \$ 211 a tonne (Mining.com, 2021) with the standard iron ore prices showing an upward trajectory till May, 2021 and since then a downward trend to below US \$ 100 per tonne in September, 2021. In this communication, two potential, low-cost alternatives for the high-grade Fe ore – the placer magnetite-sand (~ 72% Fe) and by-product iron (~ 70% Fe), generated during the beneficiation of ilmenite-sand for high-Ti products – from the mineral-sand industry are proposed along with the consequential benefits to both the steel and mineral-sand industries.

SALIENT ASPECTS OF IRON ORE MINING AND STEEL INDUSTRIES

The primary use of predominant part (~ 98%) of iron ore/pellets is to make steel, with the remaining 2% being used in various other applications, such as powdered iron for certain types of steels, magnets, auto parts and catalysts, with radioactive iron (Fe-59) being used for medicines and as a tracer element in biochemical and metallurgical research. Iron ore deposits, mined in about 50 countries, are of four types, viz., massive hematite (most commonly mined), magnetite, titanomagnetite and pisolitic ironstone. In 2020, the world's top five

largest iron ore producing countries are (i) Australia – 900 million tonnes (Mt), (ii) Brazil – 400 Mt, (iii) China – 340 Mt, (iv) India – 230 Mt and (v) Russia – 95 Mt, with the major iron ore companies being Rio Tinto (2,286 Mt in 2020), BHP (3,248 Mt), Fortescue Metals Group, Anglo American pic, ArcelorMittal, CLIFFS (Cleaveland), Vale S.A. (1,300 Mt in 2020) (NS energy, 2020), whereas the five largest iron ore importing countries are (i) China – 75.4% of all imported iron ore, valued at 118.9 billion US \$, (ii) Japan – 6.1% and 9.6 billion US \$, (iii) South Korea – 4.4% and 6.9 billion US \$, (iv) Germany – 2.3% and 3.7 billion US \$ and (v) Taiwan - 1.4% and 2.2 billion US \$ (Iron ore imports... 2020). In India, hematite- and magnetite-grade of iron ore is mostly found in the States of Chhattisgarh, Odisha, Jharkhand, Karnataka and Goa, which are also the leading producers. The National Mineral Development Corporation (NMDC), a “NAVARATNA” company fully-owned by the Govt. of India (GoI), is the single largest iron ore producer at about 32 Mt of iron ore from its three fully mechanised mines (Bailadila Deposit – 14/11C, Bailadila deposit – 5, 10, 11A [Chhattisgarh] and Donimalai iron ore mines in Karnataka. Iron ore is generally classified under three grades, viz., the benchmark or standard ore with 62% Fe, low-grade ore with < 59% Fe and high-grade ore with > 63.5% Fe; the last one, due to its many beneficial features in steel-making, commands a premium price of 1-2 US \$ for every 1% increase in Fe-grade over that of the standard grade. The July, 2021 spot-price of standard iron ore is 214.43 US \$, up from 207.72 in June, 2021, and up from 103.30 one year ago. This is a change of 3.23% from June and 107.6% from one year ago. However, since the last week of July, 2021, this price is going down to below US \$ 100/tonne in September, 2021, i.e., more than 50% drop from the peak price, mainly due to the pressure of Chinese government on their steel mills to lower the production of steel for reducing the deleterious emissions that are causing the global warming and consequent climate change affecting the environment. In India, the price of iron pellets soared from Rs. 4,500/ton in May 2020 to Rs. 15,000/ton in June 2021, resulting in a cost impact of Rs. 20,000 on a ton of steel, due to which 50,000 secondary steel minor-small-medium enterprises (MSMEs) have plunged into losses, despite such high steel prices (Financial Express, July 11, 2021). On August 06, 2021, the NMDC has revised the prices of lump ore (65.53, 6-40 mm) and fines (-10 mm), respectively, at Rs. 7,150 and Rs. 6,160 per ton each, excluding royalty, DMF, NMET, cess, forest permit fee and other taxes (Hellenic Shipping News Worldwide, 2021).

The highest quality and most important iron ores for steel-making are hematite (Fe_2O_3 , 69.94% Fe) and magnetite (Fe_3O_4 , 72.36% Fe), with the former being the preferred raw material in efficient steel-making mills and, hence, most sought after, while the latter is the finest iron ore with excellent magnetic qualities, and is especially valuable in the electrical industry. China and India have consistently grown their production to become the top two steel-producing nations (Steel Industry: Charted: Visualizing 50 years of global steel production – visualcapitalist.com). In the year, 2020, the top 10 steel producing countries (estimates in million tonnes, Mt) are: (i) China - 1,053, (ii) India - 99.6, (iii) Japan - 83.2, (iv) Russia - 73.4, (v) USA - 72.7, (vi) South Korea - 67.1, (vii) Turkey - 35.8, (viii) Germany - 35.7, (ix) Brazil - 31 and (x) Iran - 29 (Source: World Steel Association). Steel-making is the process of producing steel from iron ore and scrap. In steel-making, impurities such as N, Si, P, S and excess C (the most important impurity) are removed from the sourced iron, and alloying elements such as Mn, Ni, Cr, C and V are added to produce different grades of steel. Limiting dissolved gases, such as N and O, and entrained impurities (termed “inclusions”) in steel is also important to ensure the quality of the products, cast from the liquid steel (Deo and Boom, 1993). Modern steel-making processes can be divided into two categories: primary and secondary. Primary steel-making involves

converting liquid iron from a blast furnace and steel scrap into steel (via) basic oxygen steel-making, or melting scrap steel or direct reduced iron (DRI) in an electric arc furnace (EAF). Secondary steel-making involves refining of the crude steel before casting and the various operations are normally carried out in ladles. In secondary metallurgy, alloying agents are added, dissolved gases in the steel are lowered and inclusions are removed or altered chemically to ensure that high-quality steel is produced after casting (Ghosh 2000).

Steel-making is one of the most C-emission intensive industries in the world. As of 2020, steel-making is estimated to be responsible for 7 to 9% of all direct fossil fuel greenhouse emissions and Europe leads the way in the ‘greening’ of steel output. McKinsey (2020) identified a number of technologies for decarbonisation, including hydrogen usage, carbon-capture and reuse, and maximising the use of electric arc furnaces powered by clean energy. Recently, the Fortescue Metals Group, Australia has created green iron ore with > 97% Fe-purity and trialed ammonia-powered freight as part of its (Fortescue Future Industries, FFI) renewable energy and industry initiative. According to the FFI chief executive, trialling hydrogen, ammonia and battery technology was successful in powering the company’s trains, ship-engines, haul-trucks and drill-rigs (Zakharia, 2021). Furthermore, HYBRIT – a joint venture company among the Swedish state-owned utility - Vattenfall, iron ore miner - LKAB and steelmaker - SSAB – has produced its first 100 metric tons of sponge iron, using hydrogen at the pilot plant with test operations at the Lulea site in September, 2020 (Holder, 2021). According to Prof. Katsuhiko Hirose, the founder and CEO of HyWealth, while hydrogen is currently more expensive than fossil fuels, green hydrogen will be the cheapest solution by 2050...; the introduction of hydrogen economy to de-carbonise the world will create 30 million jobs; the holistic transition to hydrogen is economically viable; and even without tax, hydrogen could compete with the oil price and had significant societal value (Martin Creamer, July 14, 2021). It may be added that ArcelorMittal announced that its Sestao plant in Spain, which manufactures a range of flat steel products for the automotive and construction sectors, and general industry, will become, by 2025, the world’s first full-scale zero-carbon emissions steel plant to produce 1.6 Mt of zero-carbon steel by (i) changing the metallic input concurrently increasing the proportion of circular, recycled scrap and using green hydrogen-produced DRI from Gijon in its two existing EAFs; (ii) powering all steel-making assets (EAFs, rolling milling and finishing lines) with renewable electricity; and (iii) introducing several key emerging technologies that will replace the small, remaining use of fossil fuel in the steel-making process with C-neutral energy inputs, such as sustainable biomass or green hydrogen (ArcelorMittal, 2021). It is desirable that developing countries like India should focus its R & D on the above emerging technologies which will help in (i) getting dependable and sustainable green hydrogen energy, (ii) minimizing both global warming and adverse effects of climate change, and (iii) saving the foreign exchange, spent on fossil fuels.

For steel-making, the high-grade iron ore (> 65% Fe) is sought after due to its many beneficial features. These include its (i) low impurities of alumina and silica, (ii) capacity to streamline the process, (iii) improving the quality of steel, (iv) reduction in environmentally-harmful, airborne emissions like CO_2 and fine particles, (v) capacity to minimise the use of coking coal/coke and (vi) leading the way to stronger profit-margins.

PLACER HEAVY MINERAL SAND DEPOSITS

The placer heavy mineral sand (HMS) deposits comprise sand-size (2 mm to 0.063 mm) and finer heavy minerals (HMs with specific gravity of > 2.89) and dominant quartz, admixed with finer silt and clay. The grain-size of valuable HMs (VHMs), such as ilmenite, rutile, zircon, monazite, sillimanite, garnet etc., is generally < 0.125 mm.

Usually, the grade of “total heavy minerals” (THMs) in HMS deposits is low (1 – 20 wt. %), with occasional high grades in a few deposits, e.g., the Chavara deposit in the state of Kerala, India with > 65 wt. % THMs (Krishnan et al., 2001; Chandrasekaran et al., 2021). Of the THM concentrate, the constituent HMs are typically as follows: Ilmenite – 10 to 60% (of THM), rutile – 5 to 25%, leucoxene – 1 to 10% and zircon – 1 to 50%. The remaining bulk of the THM content is usually accounted for by magnetite, garnet, sillimanite, kyanite, monazite and chromite. Economic-grade placer HMS deposits occur worldwide and are mainly the shoreline deposits along the coasts of Australia, Brazil, India, Sri Lanka, Mozambique, Madagascar, SE USA etc.

India hosts many economically viable placer HMS deposits, which include (i) dominant shoreline HMS deposits along the west and east coasts in the states of Kerala, Tamil Nadu, Andhra Pradesh and Odisha, with a few minor inland HMS deposits like the Teri sands in Tamil Nadu. These placer HMS deposits contain huge resources of valuable heavy minerals (VHMs) such as ilmenite, rutile, zircon, sillimanite, garnet etc., generally in < 125 microns grain-size and admixed with dominant sand-size quartz and minor silt and clay. In general, the grade of THMs in HMS deposits is in the range 1% to 20 wt. %, with occasional high grade in a few deposits like the Chavara HMS deposit in the state of Kerala with > 65 wt. %. Generally in the Indian HMS deposits, ilmenite, garnet and sillimanite are in the grade of > 1 to ~ 7% each in raw-sand, whereas zircon, rutile, magnetite, monazite etc., are < 1% each in raw-sand. However, the Nizampatnam HMS deposit is an exception to this general pattern with magnetite being in major concentration (> 3 wt. % in raw-sand).

Nizampatnam HMS deposit: The Nizampatnam (N 15°54'30" Lat.: East 80°40'00" Long.) HMS deposit, south of the Krishna river in the Guntur district, Andhra Pradesh, along the east coast of India was discovered by AMD's Dhana Raju and Setty (Dhana Raju and Setty, 1974). Preliminary exploration of the deposit has shown that it extends over a coastal length of ~ 25 km with a width of 600 - 900 m. It contains two types of dunes – small frontal dunes with a height of 1 - 1.5 m and large rare dunes with a height of 3 - 5 m. The sampling, processing and evaluation of this mineral sand deposit, down to the water-table, have shown that its average content (in wt. % in the raw sand) and estimated reserves (in Million tonnes, Mt; in parenthesis) of THMs is 16.34 (5.3), ilmenite 7.4 (2.4), sum of pyroxenes, amphiboles and micas 3.98 (1.3), magnetite 3.24 (1.05), zircon 0.42 (0.135), monazite 0.27 (0.09), sillimanite 0.24 (0.076), garnet 0.12 (0.04) and rutile 0.03 (0.01). Sedimentological studies on the sand of the deposit have shown that it is fine-grained with a median (M_d) of 0.124 - 0.18 mm and appreciable content of silt, well-sorted (S_o : 1.20 - 1.35 mm) with fine grains exceeding the coarse grains, negatively skewed (S_k : -0.84 to -1.01) and platykurtic (K: 0.18 - 0.37); statistical measures were determined after Pettijohn (1957). This pattern, coupled with the unimodal nature of the raw-sand (250-149 microns) and of heavy minerals (74 - 63 microns), suggests that the sand was transported for a long distance from the provenance that comprises dominant basic charnockites and lesser khondalites and granite gneisses, which is supported by the major amounts of magnetite and pyriboles, and traces of garnet and sillimanite, each < 0.25% in the raw sand (Krishnaiah Setty and Dhana Raju, 1981). Later, detailed exploration in the area by AMD in 1997 showed the existence of a vast sand body with a maximum width of 4000 m. On drilling this sand deposit down to a maximum depth of 12 m, an ilmenite (41.43% of THMs) resource of 19.26 Mt was established, together with pyriboles of 17.0 Mt (35.00%) and magnetite of 8.0 Mt (16.50%). Furthermore, some HM occurrences of medium tonnage (2 - 5 Mt) have been investigated along the inter- and intra-deltaic shoreline. They are of

varying dimension with little variation in mineralogy. The investigation was mostly restricted to the beach zone and fore-dunes in these areas. Important among these are those at Gollamuthupaya, Malkanilanka, Urlagonditippa, and Vodalarevu. THM concentrations of 8.66 – 30.77% have been recorded along the coast, with ilmenite and pyriboles in near equal distribution, of 29.96 – 53.72% and 29.83 – 44.20% of THM, respectively, in these areas. The third dominant mineral, magnetite, has a distribution of 11.66 – 36.68% of THM. Other economic minerals are of the following order: zircon 0.1 – 5.12%, rutile 0.16 – 1.74%, garnet 0.34 – 2.57% and sillimanite 0.05 – 6.14% of THM. Due to low-energy conditions, the coast in the study area generally has poorly sorted sediments and moderate HM concentrations. Scout drilling in the Vodalarevu area has shown the existence of sand for a depth of over 12 m with a layer of 30 - 40% heavy black sand at a depth of 11-11.5 m, which opens a wide area for the exploration and evaluation for HMs (Ravi et al., 2001; Ravi, 2021). Magnetite, due to its high magnetic susceptibility, can be easily separated, concentrated and purified by low-intensity wet/dry magnetic separators during the processing of heavy mineral sand. The magnetite fines in HMS, either directly or after pelletisation, may be used as high-grade Fe in steel-making.

Therefore, it is proposed that the placer magnetite (~ 72% Fe; estimated resource of > 8 million tonnes) from the coastal heavy mineral sand (HMS) deposit along the Nizampatnam coast in Andhra Pradesh as a potential high-grade Fe raw-material that can partly meet the iron ore requirement of steel industry. Additional resources of magnetite can be met from the HMS occurrences in the environs of this deposit as well as that in many established HMS deposits along the east and west coasts of India as well as in other countries.

By-Product Fe, Generated During the Processing of Ilmenite-bearing Mineral Sand

Ilmenite ($\text{FeO} \cdot \text{TiO}_2$ with ~ 45 to 65 wt. % TiO_2) is usually the major HM amongst the VHMs but has a low marketable value of ~ US \$ 130/tonne, as compared to leucoxene and rutile with higher TiO_2 (~ 50 – 95 wt. %) and also highly priced in the range of ~ US \$ 300 – 1000/tonne. Hence, there is a demand to convert ilmenite into its value-added, TiO_2 -enriched products, such as synthetic-rutile (> 95% TiO_2), -anatase (TiO_2 -white costing ~ US \$ 1500 – 2000/tonne), Ti dioxide pigment, Ti-sponge and Ti metal all of which have major applications in the industries of aerospace, defence, pigments, alloys, welding electrodes etc (Dhana Raju, 2019). There are many chemical/pyrochemical enrichment processes to convert ilmenite into the above cited Ti-rich products. Amongst these, the processes of high-temperature chloride and toxic sulphate routes are widely used by major mineral sand industries in Australia and India. The objective of these processes is to enrich the TiO_2 -content of ilmenite to the maximum extent, by the removal of its constituent Fe, which is recovered as the by-product Fe, in oxide form analyzing ~ 70% Fe. A summary of these processes such as the Becher, Lurgi-Beher, Benilite, ERMS etc., together with flow-sheets, is given by Dhana Raju (2021). The Becher process starts with the reduction of Fe in ilmenite in a coal-fired rotary kiln at ~ 1200°C. The reduced ilmenite is processed through a screen and magnetic separation to remove the char and is then subjected to leaching in NH_4Cl solution under aeration to oxidise and precipitate Fe as oxide/hydroxide fine particles that are separated from the coarse synthetic rutile with hydro-cyclones to concentrate TiO_2 . In the Benilite process, the Fe-content of ilmenite is reduced to Fe^{2+} -state with heavy oil in a rotary kiln at 850°C – 1100°C and the reduced ore is leached in digesters with 18-20% HCl at 145°C. The leached material is then washed and calcined affording the beneficiate. The leaching-acid is regenerated and the iron oxide separated as a by-product (Gazquez et al., 2014). Furthermore, Purcell et al., (2020) investigated the separation of Fe and Ti from ilmenite by selective precipitation, using sodium

tetraphenylborate (NaTPB) and 2-mercaptopyridine N-oxide sodium salt (NaPT) as precipitants and found that NaPT to be the best precipitant for Fe (II) with 100% Fe²⁺ recovered in the precipitate (no Ti observed in precipitate), while 99.6% Ti⁴⁺ remained in the filtrate (no Fe observed in the filtrate). Thus, the by-product high-grade Fe, generated during the processing of ilmenite from HMS deposits to high Ti-products, may be used (with some modifications, if required, to be investigated by R & D), as raw material for steel-making.

Benefits of Alternatives to High-grade Fe ore for Steel and Mineral Sand Industries

The following are the potential benefits to both the steel and mineral sand industries by substituting the expensive and less-available, high-grade iron ore (> 63.5% Fe) with the proposed alternatives, namely (i) placer magnetite-sand (~ 72% Fe) and (ii) by-product Fe (~ 70% Fe).

1. The placer magnetite-sand, compared to the high-grade Fe ore, will be:
 - (i) Cheaper,
 - (ii) Less-expensive due to low-cost open-pit method of mining,
 - (iii) Separated from the rest of the light and heavy minerals in mineral sands by efficient mineral processing techniques such as gravity and low-intensity wet/dry magnetic separation,
 - (iv) The mineral sand resourced being abundant, the supply chain will be long lasting, assured and secured,
 - (v) Magnetite beneficiated from HMS would be the preferred choice due to its much higher Fe-content with less impurities, besides other benign advantages in steel-making.
2. The production of by-product Fe, during the processing of ilmenite-sand for high-Ti products, may be integrated with the production of high-quality steel, which will add revenue and widen the scope of the industry due to generation of new, high-value, Ti-products, such as synthetic rutile/anatase, Ti-dioxide pigment etc.

CONCLUSIONS

Two products from the mineral sand industry, namely (i) placer magnetite-sand (~ 72% Fe) and (ii) by-product Fe (~ 70% Fe), generated during the beneficiation of raw ilmenite-sand to highly valued Ti-products (65-99% TiO₂), such as synthetic rutile/anatase, Ti-oxide pigment, Ti-sponge and Ti-metal having major applications in the industries, such as aerospace, defense, pigments, alloys, welding electrodes etc., are proposed as alternatives compared to the fast depleting and more expensive high-grade Fe ore (> 63.5% Fe; carrying a premium price) for production of steel. The benefits are immense as highlighted in the paper.

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