ABSTRACT. This paper deals with two main objectives, which are (1) recovery of ilmenite mineral concentrate from the red sediments of badlands topography of South east coast Odisha, India and (2) the preparation of titanium rich slag from this red sediment ilmenite using thermal plasma process. The results of beneficiation studies on recovery of ilmenite reveal that 99.25% grade ilmenite could achieved from multiple physical separation processes including desliming, gravity concentration, high tension roll separation and magnetic separation. The results of thermal plasma treatment of carbothermally prereduced ilmenite sample contains maximum of 99.13% of total iron and 83.8% of metallic iron which clearly shows, 84.5% of metallization occurs. The TiO$_2$ content of TiO$_2$ rich slag produced from thermal plasma treatment of carbothermal reduced ilmenite is 86.51%. The overall experimental studies concluded that titanium rich slag prepared from red sediment ilmenite can be utilized as a main feed stock for pigment industry.

KEY WORDS: Red sediment, Ilmenite, Reduction, Titanium, Thermal Plasma Process, Slag

1 INTRODUCTION

The red sediments are characterized by Total Heavy Mineral (THM) concentration with ilmenite, sillimanite, zircon, rutile, garnet, and other minerals are the in the order of abundance identified. Several authors (RAO, SRIHARI, 1980; RAO et al., 1982; LAXMI, RAO, 2010) studied on red sediments but a few are referred. They explained that these deposits exhibit a considerable variation in mineralogy and chemical composition depending on the location. RAO et al. (2009; 2010; 2011; 2012) and ROUTRAY, RAO, 2010; carried out large scale beneficiation studies on the red sediment samples from Odisha and Andhra Pradesh. According to value addition point of view, several authors are attempted for preparation of titanium rich slag through thermal plasma from beach sand ilmenite (SAMAL et al., 2010; MUKHERJEE et al., 2004).

But so far widely accepted test method for preparation of titanium rich slag from red sediment ilmenite is not established.

Thermal plasma technology is emerging as one of the eco-friendly route for processing of ilmenite. Production of TiO$_2$ rich slag from metallized ilmenite by thermal plasma is gaining much importance due to increased demand for slag as feed material in the pigment industry. This technology considered as a cleaner technology due to of minimum effluent production. Hence, thermal plasma technology has been gaining much attention in different metallurgical and mineral processing industries. The potential applications of thermal plasma processing technology cover a wide range of activities such as the extraction of metals and the refining/alloying of metals/alloys/minerals.
This process is energy intensive, and hence, such slag making processes are not economically viable for adoption in countries where electric power is costly. However, due to stringent environmental routes and large amount of waste generated by the chemical routes, the electric arc/plasma smelting routes have gained increasing importance, as it not only minimises waste generation but also yield pig iron as a valuable by-product.

The demand for titanium dioxide as pigment is increasing steadily due to its high opacity, brilliant whiteness, excellent covering powder and resistance to colour change. The advantage of preparation of TiO₂ rich slag by thermal plasma route is classified in two folds. Firstly, this process is environmentally friendly and less amount of effluents produced whereas secondly, the process produces high value of iron as byproduct known as sorel iron which is marketable product. The titania slag with 75–85% TiO₂ is produced by smelting of ilmenite in high temperature arc furnaces with coal as reductant. This technology was first applied in Canada and South Africa in 1970s. Later, Namakwa in South Africa introduced the application of thermal plasma to produce high TiO₂ content titanic slag. Both dc transferred arc plasma and ac transferred arc plasma technology can be used for such metallurgical processing. Thermal plasma reactors with dc operation offer the following unique advantages for reduction process:

(i) The high energy density and temperatures associated with thermal plasmas and the correspondingly fast reaction times offer the potential for a large throughput with a small reactor foot print.

(ii) The high heat flux densities at the reactor boundaries lead to fast attainment of steady state conditions; this allows rapid start-up and shutdown times.

(iii) Oxidants are not required to produce the process heat source, as no fuel is combusted; therefore, the gas stream volume produced is much smaller than with conventional combustion processes and so easier and less expensive to manage.

The following reactions are taking place during carbothermal reduction of ilmenite.

### Reactions

The mineral ilmenite in its pure form, as represented by the formula FeO.TiO₂, has a melting point of 1392°C. The natural ilmenites are available as rock type or in beach sand and red sediment placer deposits. Ilmenite obtained from placer deposits often undergoes weathering to various extents and thereby changing the ferrous/ferric ratio. When such ilmenite reacts with carbon at a temperature of around 1200°C, solid state reduction of oxides of iron and titanium takes place according to the following reactions,

\[
\begin{align*}
\text{Fe}_2\text{O}_3 & \rightarrow \text{C} \rightarrow 2\text{FeO} + \text{CO} \quad ------ \ (1) \\
\text{FeO} & \rightarrow \text{Fe} + \text{CO} \quad ------ \ (2) \\
2\text{TiO}_2 & \rightarrow \text{C} \rightarrow \text{Ti}_2\text{O}_3 + \text{CO} \quad ------ \ (3)
\end{align*}
\]

During high temperature (around 1600-1700°C) electro-thermal smelting of ilmenite, the charge composed of ilmenite and carbon first melts and the reduction of oxides of iron and titanium proceeds with generation of metallic iron and slag with varying concentrations of FeO (10–20%), Ti₂O₃ and TiO. The total titanium oxide content of slag produced on commercial scale is restricted to a maximum value of 85–87%. Any effort to raise it further results in sharp increase in the melting point of the slag phase due to depletion of FeO (which acts as a flux) and accumulation of Ti₂O₃ beyond optimum value, resulting in poor slag separation during smelting. The reduction of oxidic impurities associated with ilmenite concentrate, such as Al₂O₃, MgO and CaO, does not take place, and it remains in the slag. These impurities play a great role towards slag quality for pigment manufacturer.

KUCUKKARAGOZ, ERIC, 2006; studied on solid state reduction of natural ilmenite. He reported that the solid state carbothermic reduction of ilmenite consisted of two stages:

1. First stage: until 50% reduction level: Reduction of Fe³⁺ to Fe²⁺ to Fe and formation of Fe₃C, reduction of Ti⁴⁺ to Ti³⁺.
2. Second stage: after 50% reduction level: Reduction of Ti$^{3+}$ to Ti$^{2+}$ and eventually formation of TiO$_{1-x}$.

POURABDOLI et al., 2006; studies the melting ilmenite concentrate of Iran by Electro-Slag Crucible Melting (ESCM) process to produce TiO$_2$-rich slag. He concluded that the iron recovery and TiO$_2$ increase when the carbon amount increases up to stoichiometric amount, but when the carbon amount exceeded the stoichiometric amount, the iron recovery and TiO$_2$ content decrease significantly. If the smelting time keeps between 0 and 17 min, the TiO$_2$ content and iron recovery are increased.

Thus from the literature review it is reveal that so far no attempt has been made for preparation of titanium rich slag from an ilmenite sample recovered from red sediments of badlands topography, which contain more amount of ferrous iron than other coastal ilmenite sample. In view of this, in the present study an attempt has been made on carbothermal prereduced ilmenite for preparation titanium rich slag obtained from red sediment using thermal plasma technology.

2 MATERIALS AND METHODS

2.1 Raw material

Red sediment samples were collected from different sources of badlands topography of Ganjam Dist, Odisha, India. About one ton of sample was collected by channels along the foot hills and along the fluvial plain. All samples were thoroughly mixed and the composite sample was prepared by method of coning and quartering. The composite sample was subjected for beneficiation studies to recover ilmenite. The recovered ilmenite is subjected for detail characterization studies followed by metallization and thermal plasma technology.

2.2 Methods

2.2.1 Recovery of ilmenite

Initially, the representative red sediment sample was scrubbed and deslimed by using hydrocyclone. The slimes were rejected and the sand was used for recovery of total heavy minerals (THM) using a laboratory model, Humphrey’s spiral concentrator, supplied by M/S Humphreys Mineral Industries, Inc., Denver, USA with 17½ pitch used to recover THM (>95% grade). The concentrate was then subjected to High Tension Roll Separator (HTRS) to separate conducting (ilmenite and rutile) and non conducting fraction (sillimanite, zircon, quartz etc). The conduction fraction then finally subjected to Dry High Intensity Magnetic Separator (DHIMS) which separates magnetic as ilmenite from non magnetic fraction (rutile).

2.2.2 Characterization studies

Ilmenite recovered from high tension roll separator was subjected to physical, chemical and mineralogical characterization studies.

2.2.3 Metallization of ilmenite

In the present investigation, an attempt has been made on red sediment placer ilmenite for metallization by using anthracite coal (Fixed carbon in coal - 81%) as a reductant. 800 gms of ilmenite sample was directly mixed with 30% of anthracite coal manually and placed in ceramic crucible. Fine sand layer of about 30 mm was given over the sample to avoid oxidation. The crucible was placed in muffle furnace at 1200 °C for 6 hours. Reduced ilmenite was ground upto fines and then subjected to thermal plasma treatment.

2.2.4 Thermal plasma treatment of reduced ilmenite

Reduced ilmenite powder and ground solid carbon in premixed ratio was subjected to a thermal plasma reactor. It contains 5 liter graphite crucible in controlled regulated feed rate variable from 5 Kg/hour (min) to 40 Kg/hour (max) through a hollow graphite electrode (cathode), placed vertically inside the crucible, which will be made anode by means of suitable terminal at the base of the crucible. Along with ilmenite-carbon mix, argon will be passed through the cathode electrode by suitable mechanism at a flow rate variable from 0.00 LPM to 2.00 LPM air unit value for passing plasmagen gas to expand the volume as well as to provide the passage of feed material to the furnace.
The inside temperature of the furnace should be maintained at around 1450°C to 1500°C for a certain period of time. The furnace temperature is maintained by variation of cathode (arc length) position by 20 to 80 mm and by varying current. The reduced ilmenite mixed with reductant is melted for 20 minutes in crucible using thermal plasma. Then, the crucible is allowed to cool at room temperature. After cooling the metal and slag was removed from crucible and weighed. These metal and slag products are subjected to different characterization studies such as, XRD, chemical analysis, scanning electronic microscopic studies etc. The thermal plasma treatment of reduced ilmenite in reactor is shown in Fig. 1.

3 RESULTS AND DISCUSSION

3.1 Recovery of ilmenite

The mineralogical modal analysis of red sediment sample indicates that the sample contains 28.71% ilmenite. The flow sheet with mass balance on recovery of ilmenite from red sediments of Odisha is shown in Fig. 2. The experimental results on the grade and recovery of ilmenite from THM, indicates that, the feed THM to HTRS contains 85.69% grade of ilmenite with recovery of 97.9%. Two fractions are resulted from the HTRS operation, one is conducting and another is non conducting. The conducting fraction of HTRS contains 97.68% ilmenite with recovery of 82.0% and the non conducting fraction contains 52.47% ilmenite. The conducting fraction from HTRS is subjected to DHIMS, which generates two fractions, magnetic and non magnetic. The magnetic fraction of DHIMS contains ilmenite concentrate of yield 23.4% with 99.25% grade and 80.9% recovery. The non magnetic fraction from DHIMS contains 0.7% yield of ilmenite with 46.75% grade and 1.14% recovery.

![Figure 1: Thermal plasma treatment of prereduced ilmenite](image1)

![Figure 2: Flow sheet with mass balance on recovery of ilmenite from red sediments of Odisha](image2)

3.2 Characterization of ilmenite mineral concentrate

3.2.1 Physical properties

The physical properties of the ilmenite concentrate are given in Tab. 1. The bulk density and true density of the product is found to be 2.9 g/cm³ and 4.7 g/cm³. The apparent porosity value of ilmenite concentrate is 38.3%. The \( d_{80} \) passing size of ilmenite is calculated from size analysis data is found to be 188 µm.

Table 1: Physical properties of ilmenite concentrate recovered from red sediment

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density, g/cm³</td>
<td>2.9</td>
</tr>
<tr>
<td>True density, g/cm³</td>
<td>4.7</td>
</tr>
<tr>
<td>Apparent porosity, %</td>
<td>38.3</td>
</tr>
<tr>
<td>( d_{80} ) passing size, µm</td>
<td>188</td>
</tr>
</tbody>
</table>
3.2.2 Chemical analysis

The complete chemical analysis of ilmenite concentrate is given in Tab. 2. The analysis shows that ilmenite concentrate contains 47.03 % TiO2. The amount of FeO and Fe2O3 are 30.13% and 19.25% respectively. Thorium (35 ppm) and uranium (<4 ppm) content are in ppm level. The low content of TiO2 and high amount of FeO in the ilmenite sample indicate that most of the unweathered ilmenite mineral grains may be present in the red sediment sample. Relatively amount of Th present in ppm level in the ilmenite concentrate indicate that traces of monazite mineral may be present.

Table 2: Chemical analysis of ilmenite concentrate recovered from red sediment

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight, %</th>
<th>Component</th>
<th>Weight, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>47.03</td>
<td>MnO</td>
<td>0.372</td>
</tr>
<tr>
<td>FeO</td>
<td>30.13</td>
<td>Cr2O3</td>
<td>0.083</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>19.25</td>
<td>P2O5</td>
<td>0.032</td>
</tr>
<tr>
<td>SiO2</td>
<td>1.25</td>
<td>V2O5</td>
<td>0.29</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.71</td>
<td>Th, ppm</td>
<td>35</td>
</tr>
<tr>
<td>MgO</td>
<td>0.50</td>
<td>U, ppm</td>
<td>&lt;4</td>
</tr>
<tr>
<td>CaO</td>
<td>0.21</td>
<td>LOI</td>
<td>0.13</td>
</tr>
</tbody>
</table>

3.1.3 X-ray diffractometer studies

The XRD pattern of ilmenite (99.25% grade) shown in Fig. 3 revealed that it contains maximum number peaks of ilmenite.

3.2.4 SEM / EDAX studies

The SEM photomicrographs of ilmenite are presented in Figs. 4 (a) and (b). SEM images of ilmenite shows the development of a number of different micro features on the ilmenite grains. It is seen that ilmenite grains of black colour and of different shapes are found such as euhedral, spherical, elongated etc.

![SEM photomicrographs of ilmenite mineral](image_url)

3.3 Metallization of ilmenite

The results of ilmenite reduction with sand sealing using anthracite coal as a reductant at constant temperature of 1200 ºC and with 6 hr time is given in Table 3. The result of this experiment reveals that after reduction, the sample contains 36.35% of metallic iron and 41.97% total iron. Hence, 87% of metallization occurs. The reduced ilmenite at 1200 ºC at 6 hr residence time is shown in Fig. 5.

Table 3: Results of carbothermal reduction of ilmenite

<table>
<thead>
<tr>
<th>Conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ilmenite taken</td>
<td>800 gm</td>
</tr>
<tr>
<td>Reductant (Anthracite coal)</td>
<td>30%</td>
</tr>
<tr>
<td>Thickness of sand layer</td>
<td>30 mm</td>
</tr>
<tr>
<td>Temperature</td>
<td>1200 ºC</td>
</tr>
<tr>
<td>Time</td>
<td>6 hr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metallic iron, %</th>
<th>Total iron, %</th>
<th>Metallization, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.35</td>
<td>41.97</td>
<td>87.0</td>
</tr>
</tbody>
</table>

Figure 3: XRD pattern of ilmenite mineral concentrate recovered from red sediments of Odisha

Figure 4: SEM photomicrographs of ilmenite mineral

Figure 5: Reduced ilmenite at 1200 ºC at 6 hr residence time
The XRD pattern of metalized product obtained from carbothermal reduction of ilmenite is shown in Fig. 6. It represents the presence of highest intensity peak of metallic iron followed by maximum of FeO, Fe₂O₃ and SiO₂ peaks. The presence of SiO₂ peaks are due to of sand sealing.

3.4 Thermal plasma treatment of reduced ilmenite

The results of thermal plasma treatment of reduced ilmenite fines are shown in Tab. 4. It indicates that at around 1896 °C, thermal plasma treatment of 1Kg reduced ilmenite gives 32.8% metal and 67.2% of slag. At the same time, 775 units/ton of power consumed to produce 32.8% of metal at 13 mins time. The results of the experiment reveal that after thermal plasma reduction, the sample contains maximum of 99.13% of total iron and 83.8% of metallic iron which clearly shows, 84.5% of metallization occurs. The products (Metal and slag) obtained after smelting of reduced ilmenite is shown in Figs. 7 (a) and (b).

Table 4: Results of thermal plasma treatment of reduced ilmenite fines

<table>
<thead>
<tr>
<th>Conditions</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced ilmenite fines taken: 1000 gm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial power</td>
<td>613.5 kW</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power before melting</td>
<td>614.9 kW</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power after melting</td>
<td>618.0 kW</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting time</td>
<td>13 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argon flow rate</td>
<td>5 lt/min</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal Wt., %</th>
<th>Slag Wt., %</th>
<th>Metallic iron, %</th>
<th>Total iron, %</th>
<th>Metallization, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.8</td>
<td>67.2</td>
<td>83.8</td>
<td>99.13</td>
<td>84.5</td>
</tr>
</tbody>
</table>

![Figure 5: Carbothermal reduced ilmenite at 1200 °C and 6 hr holding time](image)

![Figure 6: XRD of metalized product](image)

![Figure 7: Products obtained after smelting of reduced ilmenite](image)

The XRD pattern of metal and slag is shown in Figs. 8 (a) and (b). The XRD pattern of metal [Fig. 8 (a)] clearly indecates the presence of mainly Fe peaks followed by minor Fe₃C and Ti peaks. Similarly, XRD pattern of slag [Fig. 8 (b)] contains maximum peaks of Fe₃Ti₃O₁₁ and Fe₂TiO₆ followed by TiO₂ and Fe.
The optical micrograph of TiO$_2$ rich slag is shown in Fig. 9. Similarly, the SEM and EDAX of slag produced from thermal plasma treatment of carbothermal reduced ilmenite are shown in Fig. 10.

The chemical analysis of TiO$_2$ rich slag produced from thermal plasma treatment of carbothermal reduced ilmenite is shown in Table 5. It indicates that the product i.e. titanium rich slag contains 86.51% followed by 8.46% FeO, 1.25% Al$_2$O$_3$, 1.51% metallic iron, 1.75% SiO$_2$ and 0.52% MnO.

Table 5: Chemical analysis of TiO$_2$ rich slag

<table>
<thead>
<tr>
<th>FeO, %</th>
<th>Al$_2$O$_3$, %</th>
<th>SiO$_2$, %</th>
<th>Fe (M), %</th>
<th>MnO, %</th>
<th>TiO$_2$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.46</td>
<td>1.25</td>
<td>1.75</td>
<td>1.51</td>
<td>0.52</td>
<td>86.51</td>
</tr>
</tbody>
</table>

4 CONCLUSIONS

The following conclusions drawn from the experimental Results and Discussion on red sediment samples collected from Odisha for beneficiation and preparation of titanium rich slag by carbothermal reduction followed by thermal plasma treatment.
- The ilmenite recovered from red sediments after suitable beneficiation contains 99.25% grade with 80.9% recovery.
- The chemical analysis shows that ilmenite concentrate contains 47.03% TiO$_2$. The amount of FeO and Fe$_2$O$_3$ are 30.13% and 19.25% respectively.
- The result of carbothermal reduction at 1200 ºC and 6 hr residence time reveals that after the sample contains 36.35% of metallic iron and 41.97% total iron i.e. 87% of metallization occurs.
- Similarly, the results of thermal plasma treatment of carbothermally reduced ilmenite fines contains maximum of 99.13% of total iron and 83.8% of metallic iron which clearly shows, 84.5% of metallization occurs.
The TiO$_2$ content of TiO$_2$ rich slag produced from thermal plasma treatment of carbothermal reduced ilmenite is 86.51%.

Hence, it is confirmed that titanium rich slag prepared from red sediment ilmenite can be utilized as a main feed stock for pigment industry.

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P. S. Mukherjee (PhD from IIT Kharagpur) a former Chief Scientist, CSIR-IMMT, Bhubaneswar; contributing his enormous research works towards the area of “Application of Thermal plasma and microwave technology for processing of materials”. His areas of interest are X-ray and structure of matter; Processing and characterization of fine ceramics; and also in management of organic and inorganic waste. He was awarded as “NMD-Metallurgist of the Year” in 2005 and “NMD-ATM” in 2009.