CHAPTER II

Chemical beneficiation of Iron ore rejects
2.1 Introduction

Demand for ferrites in ever expanding electronic industries is expected [24] to reach 974,000 metric tones per year (MPTY), by the turn of this century, and to meet this requirement the need of high quality ferrite grade iron oxide will also increase. About 705,000 MTPY of the iron oxide is required for the production of such a huge amount of ferrites, both soft and hard. Iron oxide is the major raw material in ferrite industry.

At present this need of iron oxide is normally met (Table 1.2) by using 1) spray roasted ferric oxide from acid pickle solution of steel industry, ii) sulphate processed iron oxide, iii) fluidized bed regenerated processed iron oxide, iv) upgraded hematite ore and to some extent v) upgraded magnetite ore. It is the upgraded hematite ore which is, however, expected to play an important role in ferrite industry as a major raw material. All these sources supply iron in α-Fe₂O₃ form, excepting upgraded magnetite.
Although the spray roasted ferric oxide is widely used world over, the quality (or the impurity contents) of the iron oxide depends on the metal constituents of steel from which the pickle solution is obtained. However, depending upon the application of ferrites, low, medium and high impurity content iron oxides are prepared by further purifying the pickle solution before spray roasting. The purification of the pickle solution is carried out by chemical methods like precipitation or coprecipitation, solvent extraction, ion exchange or crystallization. A solvent extraction method [36] using methyl isobutyl ketone (MIBK) yields iron oxide of high purity consisting of impurities in ppm level. Direct use of spray roasted iron oxide from any pickle solution is therefore, restricted, if high quality ferrites are to be manufactured.

The upgraded hematites too are not useful for quality soft ferrites manufacture, although ceramic magnets can be synthesized from them. Again chemical methods are required to be adopted to obtain high quality iron oxide.

Ferrite industries in china use iron oxide synthesized from ferrous sulphate [49] but spray roasted iron oxides are also now available.

Chemical routes are being adopted to prepare iron oxides of better quality and such methods are now used to tap different iron sources which were until then considered as useless, especially the industrial effluents from iron / steel industries. A sol gel technique has been described [50].

Mine drainages, the other sources of iron which had been neglected so far, are now being effectively treated with CaCO$_3$ in Japan [51] to prepare ferrites directly. Infact, water base magnetic fluids have been prepared using this method. Magnetic fluids consisting of ultrafine Fe$_3$O$_4$ obtained by precipitation technique [52] find wide applications.

A modified ferrite process was developed [53] for the purpose of treating acid mine and mine drainages consisting of steps involving coprecipitation coupled with setting.
decantation and oxidative ageing followed by magnetic separation.

An improved recrystallization technology is proposed for pickle solution [54] to prepare pure iron oxide free from Ni and P to use in MnZn ferrites synthesis. New ferrite process has been adopted [55] in Korea to remove heavy metal ions from waste water.

Abandoned mines, after mining activities are terminated, create environmental problems, especially due to the accumulation of water in it which are acidic in nature. They are called as acid lakes. Lime treatment is usually adopted for portable or agricultural use. Lime treatment creates problem as the sludge obtained in the process is packed with many heavy toxic elements. Therefore, a novel method has been tried [56] by Canadian scientists to not only neutralise the water but also extract the heavy metals as ferrites. Sodium hydroxide is being used by these authors but the alkali being expensive they argue that such method would still be economically viable, considering very useful ferrites that are being processed easily, as well as, the water is made usable.

Chemical methods, thus, seem extensively used to obtain iron oxides of high quality and such methods have now opened up new iron sources, hitherto considered useless, like mine drainage etc. Chemical routes can also be made use in tapping yet another iron oxide sources which are going not only as a national waste but also creating environmental problems. They are iron ore rejects. And we are making an attempt to make use of such rejects in our present studies to prepare iron oxides through a chemical route.

2.2 Physico-chemical analysis of the ore rejects and preparation of study sample

2.2.1 Collection of ore samples

The iron ores of Goa are feebly magnetic attributing to the presence of FeO in addition to its basic major constituent Fe₂O₃. The Goan lumpy ore is soft and porous. A
typical chemical composition of lumpy ore of commercial importance is indicated in Table 2.1 shown below.

Table 2.1 Typical chemical composition of commercial iron ore

<table>
<thead>
<tr>
<th>Analyte Identification (%)</th>
<th>Total Fe</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>58.2</td>
<td>82.72</td>
<td>1.86</td>
<td>8.18</td>
</tr>
<tr>
<td>B</td>
<td>58.9</td>
<td>83.72</td>
<td>3.10</td>
<td>7.72</td>
</tr>
<tr>
<td>C</td>
<td>48.7</td>
<td>69.14</td>
<td>5.72</td>
<td>13.94</td>
</tr>
</tbody>
</table>

The silica and alumina contents vary from place to place and the present acceptable combination is between 5 and 6 (%) maximum. Iron ores that are exported from Goa are graded depending upon the Fe content as,

- Fe (%) |
  - 54 - 57 | Low
  - 58 - 60 | Medium
  - > 60    | High

The typical ore reject sample ‘C’ in Table 2.1 above is of our interest which consist of >10 (%) Al₂O₃ and > 5 (%) SiO₂.

2.2.2 Iron ore rejects

Iron ore rejects from different places in Goan mining areas have been collected. They were mixed thoroughly separately depending upon the area of collection, reduced by cone and quartering method and the representative composite samples were prepared. In all seven samples were taken for our studies and they are named as RPD-1 to RPD-7.
The samples thus prepared were jaw and roller crushed. These were then pulverised to obtain a fine powder to the extent of -100 # size. The seven samples were then confirmed to be homogeneous by rubber sheet mixing which were then analysed separately for the presence of various major and minor or trace (rare) elements.

a) Chemical analysis of ore samples

Iron ore samples were analysed for estimating the chemical constituents, both major and minor or trace elements, using standard methods [57-61].

i. Estimation of major elements:

Total iron

The estimation of total iron was carried out by a standard potassium dichromate method. The 0.5 g of the sample was dissolved in 50 (%) HCl and then reduced to ferrous state with minimum quantity stannous chloride solution. The excess SnCl₂ was removed by adding mercuric chloride solution. To this 10 ml of acid mixture (HNO₃+H₂SO₄) was added followed by 3-4 drops of 1 (%) solution of barium diphenylamine indicator and titrated against standard potassium dichromate solution. The colour of the solution changes from green to blue green and finally to intense purple or blue violet indicating the end point. The titre reading directly gives the total Fe (%) present in the sample.

Silica

The percentage of silica in the sample was estimated by gravimetric method. 2.5 g of the sample was decomposed with 50 (%) hydrochloric acid. The solution was then heated to dryness and extracted with dil.HCl containing about 2.5 ml of conc. HNO₃. The solution was filtered through Whatman no.1 filter paper and the residue was washed
hot water, several times. The dry residue was charred in a platinum crucible and then weighed. After weighing, the ash was moistened by adding few drops of water followed by a drop or two of conc. H₂SO₄ and about 7 - 10 ml of 30 (%) hydrofluoric acid and kept on a sand bath. After evaporating silica as silicon fluoride the crucible was heated first on a low bunsen flame and then on a high flame to expel out the final traces of silicon fluoride. The crucible was then weighed and from the difference between the two weights, the silica percentage was calculated.

Alumina

Alumina estimation was carried out using complexometric method. 0.2 g of the sample was dissolved in 20 ml of 50 (%) HCl on a hot plate. To the cooled solution 25 (%) NaOH was added to precipitate iron as iron hydroxide.

The filtrate was acidified with dilute hydrochloric acid and the pH was maintained at about 2.8 to 3.2 by adding ammonium acetate solution. 20 ml of 1 (%) sulphosalicylic acid was then added to identify any traces of Fe, which is indicated by the appearance of reddish colour to the solution. This final traces of Fe were removed by titrating the cold solution with the standard EDTA solution till colourless.

This solution was then boiled and 4 - 5 drops of copper pan indicator was added and titrated the hot solution against the standard EDTA till the colour changes from pink to permanent yellow. The completion of the end point was confirmed by further heating and adding one or two drops of the indicator followed by adding little ammonium acetate solution.

Manganous oxide

Manganous oxide is estimated by sodium arsenate method. 0.1 g of the sample was
dissolved in 10 ml of 50 (%) HCl and evaporated to dryness. Few drops of H₂SO₄ were then added into the dried mass and continued heating till all the chloride fumes were driven out.

After cooling, little water was added to the white mass. To this solution the 15 ml of dilute HNO₃, 10 ml of AgNO₃ and 15 ml of K₂S₂O₈ solution were added. The solution was warmed slightly till a pink colouration due to permanganic acid was formed. After cooling 1 - 2 ml of 2 (%) NaCl solution was added and then titrated against the standard sodium arsenate till the pink colour disappears leaving behind whitish straw colour.

ii) Determination of minor elements and trace (rare) elements

Estimation of minor or trace rare chemical constituents in the iron ores have been done complexometrically, colorimetrically, flame photometrically, alkalimetrically, volumetrically and gravimetrically using standard methods [57 – 61].

iii) Loss on Ignition

Dry sample of ore was weighed in a platinum / silica crucible and subjected to heat treatment on a burner flame at about 1050°C for about 45 minutes to determine the loss on ignition from weight difference.

b) Preparation of study samples

The detailed major chemical constituents that present in RPD 1–7 are tabulated in Table 2.2a. The RPD-7 and RPD-4 were selected as study sample I and II, respectively. These study samples were then subjected for further analysis for determining minor elements and trace rare elements. The results are tabulated in Table 2.2a and 2.2b.
Table 2.2 – Chemical analysis of various iron ore rejects (major elements)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fe</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MnO</th>
<th>LOI</th>
<th>Other trace elements</th>
<th>Remarks (if any)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPD/1</td>
<td>53.2</td>
<td>0.26</td>
<td>75.79</td>
<td>7.54</td>
<td>4.74</td>
<td>2.32</td>
<td>8.87</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>RPD/2</td>
<td>55.2</td>
<td>1.28</td>
<td>77.51</td>
<td>7.76</td>
<td>5.70</td>
<td>0.90</td>
<td>6.44</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>RPD/3</td>
<td>51.7</td>
<td>3.84</td>
<td>69.64</td>
<td>20.86</td>
<td>1.46</td>
<td>0.23</td>
<td>3.85</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>RPD/4</td>
<td>53.4</td>
<td>Trs</td>
<td>76.36</td>
<td>5.24</td>
<td>6.41</td>
<td>3.04</td>
<td>7.62</td>
<td>1.33</td>
<td>Study sample II</td>
</tr>
<tr>
<td>RPD/5</td>
<td>25.4</td>
<td>0.13</td>
<td>36.18</td>
<td>30.79</td>
<td>15.61</td>
<td>7.36</td>
<td>9.25</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>RPD/6</td>
<td>19.0</td>
<td>Trs</td>
<td>27.17</td>
<td>48.75</td>
<td>12.31</td>
<td>0.60</td>
<td>10.81</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>RPD/7</td>
<td>41.0</td>
<td>1.02</td>
<td>57.49</td>
<td>23.33</td>
<td>9.15</td>
<td>0.83</td>
<td>7.83</td>
<td>0.35</td>
<td>Study sample I</td>
</tr>
</tbody>
</table>

The study sample I and II were so chosen that the sample I contains the low Fe content and higher percentage of alumina and silica, while the sample II has higher percentage of Fe and lower percentage of alumina and silica.

No traces of rare elements were observed in both the study samples and the minor elements are also found to be nil or in traces. Titanium oxide is, however, found to be 0.535 ± 0.115 (%). The presence of phosphorus and sulphur too indicated but in minor quantities.

2.3 Chemical beneficiation of study samples I & II: Preparation of metal (iron) hydroxides / formates

2.3.1 Acid Extraction

About 10 g of finely pulverised study sample was taken for the acid extraction (Flow sheet 1) of iron in each batch. A dilute HCl (1:1) was added to the ore sample in a
Table 2.2b  Trace (minor/rare) elemental analysis of the study samples and the hydroxides/formates precursors

<table>
<thead>
<tr>
<th>Elements (%)</th>
<th>Study Sample I</th>
<th>Study Sample II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Using MIBK</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RPD/ 7  FH/NaOH  FF/NaOH  FH/MIBK  FF/MIBK</td>
<td>RPD/ 4  FH-II/NaOH  FF-II/NaOH</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>0.42  0.05 Traces Traces Nil</td>
<td>0.65  0.09 Traces Nil Nil</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>Traces Nil Nil Nil Nil Nil Traces Nil Nil</td>
<td></td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>Traces Nil Nil Nil Nil Traces Nil Nil</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>Traces Nil Nil Nil Nil Traces Nil Nil</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>Traces Nil Nil Nil Nil Traces Nil Nil</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>Traces Nil Nil Nil Nil Traces Nil Nil</td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>Nil Nil Nil Nil Nil Nil Nil Nil</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>Nil Nil Nil Nil Nil Nil Nil Nil</td>
<td></td>
</tr>
<tr>
<td>Antimony</td>
<td>Nil Nil Nil Nil Nil Nil Nil Nil</td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td>Nil Nil Nil Nil Nil Nil Nil Nil</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>Nil Nil Nil Nil Nil Nil Nil Nil</td>
<td></td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.078 Traces Nil Traces Nil 0.044 Traces Nil</td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.006 Nil Nil Traces Traces 0.006 Traces Traces</td>
<td></td>
</tr>
<tr>
<td>Sodium oxide</td>
<td>0.024 0.020 Traces 0.08 Traces 0.012 0.010 Traces</td>
<td></td>
</tr>
<tr>
<td>Potassium oxide</td>
<td>0.045 0.019 Traces 0.02 Traces 0.047 0.021 Traces</td>
<td></td>
</tr>
</tbody>
</table>

FH – Ferric hydroxide, FF – Ferric formate, MIBK – Methyl isobutyl ketone
FLOW SHEET 1

-100 # Study sample of iron ore rejects
(M-oxide Fe₂O₃/Al₂O₃, MnO/SiO₂)
↓ Mix (50:50)
↓ Digest on hot plate
Acid extract
↓
Residue (discard)
↓
Filtrate I
↓
Acid extract
↓
Residue (discard)
↓
Filtrate II
↓
(Chlorides of metals
M = Fe/Mn/Al)
↓
NaOH
↓
NH₃
↓
NaOH:NH₃ (50:50)
↓
Na₂CO₃
↓
M-hydroxides
↓
Formic
↓
Acid
↓
M-formates
↓
Thermal products of hydroxide/formates
↓
M-oxide
↓
Thermal products of hydroxide/formates
↓
M-oxide
↓
Chlorides in MIBK
↓
Extract
↓
with H₂O
↓
Aqueous layer
↓
Organic layer
↓
M-oxide
250 ml beaker and digested over a hot plate (sand bath) till the ore got completely opened up.

The cooled solution was then filtered through whatman no. 1. The filtrate I (acid extract) was boiled after adding few ml of conc. HNO₃ to ensure the complete oxidation of metals. The cooled solution was filtered through whatman no. 1. The filtrate I thus obtained was then used for the precipitation of metal hydroxides by,

i) Directly using precipitants like NaOH, NH₃, NaOH + NH₃, Na₂CO₃ and ii) After solvent extraction with methyl isobutyl ketone (MIBK) and then precipitating as hydroxide using NH₃.

The formates were then prepared from these metal hydroxides using formic acid.

2.3.2 Use of acid extract for metal (iron) hydroxide preparation:

a) Direct precipitation

The filtrate II obtained from acid extraction of iron ore reject as shown in Flow sheet 1, consists chlorides of metals mainly of iron and in minor quantities of manganese, aluminium and other trace metals, if any. The filtrate after adequate dilution is directly used to prepare metal hydroxides (FH) using precipitants like NaOH, NH₃, NaOH + NH₃, and Na₂CO₃.

i) NaOH Precipitant

A 23 (%) NaOH solution was added to the dilute metal chlorides solution slowly with constant stirring till the hydroxide precipitation was complete. Excess addition of the precipitant is avoided. The precipitate was digested over a hot plate, cooled and filtered through whatman no. 1. Sufficient washings with hot water were given till the filtrate is free from chloride ions. The chloride free precipitate was then dried ~ 105°C, crushed, sieved to -100 # and stored in a desiccator.
ii) NH₃ Precipitant

To the dilute metal chlorides (filtrate II) solution an ammonium chloride solution (2N) was added and then ammonia solution (General purpose reagent, GPR) was run down into it to get hydroxides precipitate. The precipitate was filtered through Whatman no.1, washed with hot water and then dried in oven ~ 105°C. The dried precipitate was crushed, sieved through -100 # sieve and stored in a desiccator.

iii) NaOH + NH₃ (50:50) Precipitant

A mixture of NaOH (25%) and ammonia solution (GPR) in 50 : 50 proportion was slowly added to the dilute metal chlorides solution till the precipitation is complete. The precipitate was filtered, washed with hot water, dried and stored in a desiccator.

iv) Na₂CO₃ Precipitant

A 15% (w) Na₂CO₃ solution was used to precipitate metal hydroxides from the metal chlorides (filtrate II) filtered, washed, dried and stored in a desiccator.

b) Preparation of metal hydroxide: After MIBK solvent extraction

The metal chlorides (filtrate II) were also used to prepare iron hydroxide of high purity adopting solvent extraction method. Methyl isobutyl ketone (MIBK) is found to be very efficient solvent to selectively recover iron from the acid solution in the form of HFeC1₄. Hence, this method was utilised in our studies to see how far this procedure is superior to the direct precipitation methods in recovering iron, as discussed in 2.3.2 a. Here, the iron recovered from the filtrate II by MIBK extraction was precipitated as hydroxide using NH₃ as the precipitant to get metal hydroxides.

A diluted metal chlorides solution (Filtrate II) was taken in a separating funnel and to this an equal volume of MIBK was added and shaken well for 5 - 10 minutes. Then it
was allowed to stand for 10 minutes and the organic layer was made to remain in the funnel after draining away the lower aqueous layer. To this organic layer an equal volume of the deionised water was added and shaken well. The metal chlorides that were now in the aqueous layer was run down in a beaker and after adding NH₄Cl, an ammonia solution (GPR) was added to precipitate out the metal hydroxides. The precipitate was filtered, washed with hot water till free from chloride and dried ~ 105°C. The dry substance was crushed to -100 # and stored in a desiccator.

2.3.3 Preparation of Iron Formates from metal (Iron) hydroxides

The metal hydroxides prepared as in 2.3.2 (a) were then used to prepare metal formates (FF).

A calculated amount of formic acid plus 5 ml in excess was added to the required quantity of the metal hydroxide in a beaker. The beaker covered with a watch glass, placed on a water bath and the contents were intermittently agitated with a glass rod. A portion of 5 ml formic acid was added during 1½ hours heat treatment.

The syrupy contents in the beaker were then placed on sand bath carefully till a dry substance was obtained. The dried mass was then crushed in an agate mortar, sieved to -100 #, dried at 105°C and preserved in a desiccator.

2.3.4 Characterization

a) Chemical Analysis: Metal estimations

The metal hydroxides and formates obtained from the ore rejects (section 2.3.2 and 2.3.3) were chemically analysed for estimating the presence of majority metals like Fe, Mn, Al, Si and trace elements as described in section 2.2.2a. The thermal products of these hydroxides and formates were also analysed for Fe contents in order to calculate the Fe₂O₃ percentage in them.
b) Thermal Analysis: Isothermal weight loss

The metal hydroxides and formates were isothermally heated at different predetermined temperatures to calculate the total weight loss leading to metal oxides.

c) X-ray diffraction studies

X-ray diffraction patterns of the thermal products of hydroxide/formate precursors were obtained by using Philips X-ray diffractometer (xrd) model PW 1710 using Cu Kα radiations and Ni as a filter. The \( d_{hkl} \) values were matched with JCPDS files for characterizing the oxide products.

2.3.5 Results and Discussion

a) Iron hydroxides (FH) and formates (FF): Study sample I

The chemical analysis for estimating total iron, silicon, aluminium, manganese in the hydroxides and formates done by standard methods are being given in the Table 2.3a (study sample I) and 2.3b (study sample II). The tables also include the chemical constituents present in the respective study samples from which the hydroxides and formates have been prepared.

1. Direct precipitation from acid extract (Filtrate II)

i) Using NaOH: Iron hydroxides (FH/NaOH)

The hydroxide is found to consist of 58 (%) Fe, 0.55 (%) Si, 0.228 (%) Al and 0.93 (%) Mn (Table 2.3a).

The isothermal mass loss studies indicate a total weight loss of 10.63 (%). The thermal product of the hydroxide ~ 1050°C is mainly Fe2O3. The x-ray characterization reveals \( \alpha \)-Fe2O3 presence in the thermal product as \( d_{hkl} \) values in xrd match well with the JCPDS file [62] for \( \alpha \)-Fe2O3. The chemical analysis of the thermal products suggests that
Table 2.3.a. Chemical analysis of Iron ore reject (study sample I) and precursors, Ferric hydroxides (FH) & Ferric formates (FF), obtained using Iron chloride solution from the reject.

<table>
<thead>
<tr>
<th>Nature of Sample</th>
<th>Study sample I</th>
<th>FH NaOH</th>
<th>FH NH₃</th>
<th>FH NaOH+NH₃</th>
<th>FH Na₂CO₃</th>
<th>FH/NH₃ MIBK</th>
<th>FF NaOH</th>
<th>FF NH₃</th>
<th>FF NaOH+NH₃</th>
<th>FF Na₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>41.00</td>
<td>58.00</td>
<td>56.00</td>
<td>56.50</td>
<td>57.00</td>
<td>64.20</td>
<td>45.76</td>
<td>44.33</td>
<td>43.62</td>
<td>34.10</td>
</tr>
<tr>
<td>Si (SiO₂)</td>
<td>---</td>
<td>0.55</td>
<td>0.15</td>
<td>0.17</td>
<td>0.10</td>
<td>0.08</td>
<td>0.46</td>
<td>0.07</td>
<td>0.10</td>
<td>0.04</td>
</tr>
<tr>
<td>Al (Al₂O₃)</td>
<td>0.228</td>
<td>2.90</td>
<td>2.95</td>
<td>2.64</td>
<td>0.21</td>
<td>0.10</td>
<td>1.72</td>
<td>1.63</td>
<td>1.89</td>
<td></td>
</tr>
<tr>
<td>Mn (MnO)</td>
<td>0.93</td>
<td>0.62</td>
<td>0.62</td>
<td>1.05</td>
<td>NIL</td>
<td>0.46</td>
<td>0.38</td>
<td>0.41</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>Total Weight Loss</td>
<td>---</td>
<td>10.63</td>
<td>16.32</td>
<td>8.52</td>
<td>11.80</td>
<td>7.46</td>
<td>41.06</td>
<td>52.00</td>
<td>53.00</td>
<td>53.12</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>57.49</td>
<td>98.38</td>
<td>93.67</td>
<td>92.24</td>
<td>91.82</td>
<td>99.73</td>
<td>98.67</td>
<td>96.52</td>
<td>97.24</td>
<td>96.95</td>
</tr>
</tbody>
</table>
Table 2.3.b. Chemical analysis of Iron ore reject (study sample II) and precursors, Ferric hydroxides (FH) & Ferric formates (FF), obtained using Iron chloride solution from the reject

<table>
<thead>
<tr>
<th>Nature of Sample</th>
<th>Study sample II</th>
<th>FH II NaCH</th>
<th>FF II NaCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>53.40</td>
<td>61.20</td>
<td>48.50</td>
</tr>
<tr>
<td>Si (SiO₂)</td>
<td>----</td>
<td>0.41</td>
<td>0.30</td>
</tr>
<tr>
<td>(5.24)</td>
<td></td>
<td>(5.24)</td>
<td>(5.24)</td>
</tr>
<tr>
<td>Al (Al₂O₃)</td>
<td>----</td>
<td>0.16</td>
<td>0.11</td>
</tr>
<tr>
<td>(6.41)</td>
<td></td>
<td>(6.41)</td>
<td>(6.41)</td>
</tr>
<tr>
<td>Mn (MnO)</td>
<td>----</td>
<td>2.10</td>
<td>1.24</td>
</tr>
<tr>
<td>(2.36)</td>
<td></td>
<td>(2.36)</td>
<td>(2.36)</td>
</tr>
<tr>
<td>Total Weight Loss</td>
<td>7.62</td>
<td>8.45</td>
<td>43.65</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>76.36</td>
<td>96.80</td>
<td>97.10</td>
</tr>
</tbody>
</table>

it has 94.38 (%) Fe₂O₃. The remaining 1.62 (%) of metal oxides are due to the minor constituent metals like Al, Mn, Si and other trace elements.

The oxide product, thus obtained from the ore reject, study sample I, shows an improvement in Fe₂O₃ content from 57.49 (%) to 98.38 (%).

The total mass loss of the hydroxide amounts to 10.63(%). Since the main constituent in the hydroxides is Fe-58 (%), a formula FeOOH is suggested to these hydroxides consisting of the other metals of ~ 1.708 (%). The iron hydroxide on heating yields Fe₂O₃ by losing 10.63 (%) weight. Hence, a formula FeOOH is considered for this hydroxide.

\[ \Delta \text{FeOOH} \rightarrow \text{Fe₂O₃} \]

The calculated weight loss for FeOOH giving Fe₂O₃ is 10.13 (%). Since the observed weight loss is 10.63 (%), the extra mass loss may be due to the hydroxides of the other
elements, Mn, Al, and Si converting into the respective oxides as admixture in Fe₂O₃.

ii) Using NH₃ (GPR) : (FH / NH₃)

The hydroxide obtained indicates 56.00 (%) Fe, 0.15 (%) Si, 2.9 (%) Al and 0.62 (%) Mn. A total of 16.32 (%) mass loss observed for the hydroxide is more than that of the hydroxide prepared from NaOH. Chemical analysis of the thermal product and x-ray characterization reveal it to be mainly α-Fe₂O₃. A 93.67 (%) Fe₂O₃ is found in the product.

iii) Using NaOH : NH₃ :: 50:50 ( FH / NaOH + NH₃)

The elemental composition in the hydroxide is more or less similar to the one precipitation by using NH₃. The hydroxide consists of 56.5 (%) Fe, 0.17 (%) Si, 2.95 (%) Al and 0.60 (%) Mn (Table 2.3a).

The isothermal mass loss, however, indicates 8.52 (%) which is lower than in the hydroxides prepared by NaOH but much lower than that of FH / NH₃. The thermal product is characterized as α-Fe₂O₃ by x-ray diffraction (xrd). Percentage of α-Fe₂O₃ is 92.24 (%) in the thermal product suggesting the higher percentage of Al₂O₃ presence in it which gives this low percentage of Fe₂O₃.

iv) Using Na₂CO₃ : (FH / Na₂CO₃)

A 57.00 (%) Fe in the hydroxide is almost similar to that found in FH / NaOH, FH / NH₃ and FH / NaOH + NH₃ (Table 2.3a). The Si at 0.1 % is much less as compared in FH / NaOH which shows 0.55 (%), but in comparison to FH / NH₃ and FH / NaOH + NH₃ the Al content is marginally low.
The total loss observed on heating is 11.8 (%) which is near to the one found in FH / NaOH. The thermal product is mainly $\alpha$-Fe$_2$O$_3$. The iron estimation of this product indicates that it consists of 91.82 (%) Fe$_2$O$_3$.

2. Hydroxides after solvent extraction (FH / MIBK)

The metal chlorides (Filtrate II; Flow sheet I) on extracting with methyl isobutyl ketone (MIBK) was precipitated as hydroxide by using ammonia (GPR). The elemental composition of this hydroxide (Table 2.3a) indicates 64.2 (%) Fe which is much higher than in the hydroxides obtained by direct precipitation methods as described in 2.3.5; (i).

The silicon content observed is just 0.08 (%) as compared to ~ 0.15 (%) in FH / NH$_3$, FH / NaOH + NH$_3$, FH / Na$_2$CO$_3$ and 0.55 (%) in FH / NaOH. Also, the Al percentage of 0.21 is very less as compared in the hydroxide prepared directly. There is no indication of Mn in the hydroxide.

Isothermal total weight loss of the hydroxide amounts to 7.46 (%) and the product is characterized by xrd as $\alpha$-Fe$_2$O$_3$. The thermal product found to consist of 99.73 (%) Fe$_2$O$_3$ which suggests that the product is practically very pure excepting ~ 0.27 % oxide impurities due to Al, Si and other trace elements.

3. Formates from hydroxides prepared from study sample I

The formates of iron (FF) prepared from iron hydroxides (FH) obtained from filtrate II (acid extract of ore reject) of study sample I are analysed for metal constituents present in them. These results are presented in Table 2.3a along with the analysis of metal constituents in different FH samples for comparison. The elemental composition of the thermal products of the formates along with the products of iron hydroxides as Fe$_2$O$_3$ are also tabulated in the Table 2.3a.
i) Using FH / NaOH : Iron formate (FF / NaOH)

The iron formate (FF / NaOH) prepared from iron hydroxides (FH / NaOH) using formic acid shows 45.76 (%) Fe, 0.46 (%) Si, 0.1 (%) Al and 0.46 (%) Mn. The thermal product of this gives mainly α-Fe₂O₃ -98.67 (%) which shows an improvement in Fe₂O₃ as compared to the ore rejects containing 57.49 (%) Fe₂O₃. There are some improvements in Si - 0.46 (%) and Al - 0.1 (%) contents as compared to FH / NaOH which shows Si - 0.55 (%) and Al - 0.228 (%).

ii) Using FH / NH₃ : FF / NH₃

The formate obtained from FH / NH₃ indicates 44.33 (%) Fe, 0.07 (%) Si, 1.72 (%) Al and 0.38 (%) Mn. There is a marked decrease in Si - 0.07 (%) in FF / NH₃ as compared to in FH / NH₃: Si - 0.15 (%). Al content too decreases from 2.90 (%) in FH / NH₃ to 1.72 (%) in FF / NH₃. The Mn content is also decreased from 0.62 (%) in FH / NH₃ to 0.38 (%) in FF / NH₃. The thermal product contains 96.52 (%) α-Fe₂O₃.

iii) Using FH / NaOH + NH₃ : FF / NaOH + NH₃

The formate obtained from FH / NaOH + NH₃ gives 43.62 (%) Fe and 0.0 (%) Si, 1.63 (%) Al and 0.41 (%) Mn. There is some decrease in Si, Al and Mn contents here as compared to that found in FH / NaOH + NH₃. The thermal product contains 97.4 (%) α-Fe₂O₃.

iv) Using FH / Na₂CO₃ : FF / Na₂CO₃

The formate obtained using FH / Na₂CO₃ exhibits 34.1 (%) Fe, 0.04 (%) Si 1.89 (%) Al, 0.60 (%) Mn. A marked decrease in Si - 0.04 (%) content is observed as compared to that in FH / Na₂CO₃ which contains 0.10 (%) Si in it. There is some decrease
in Al, Mn contents too in comparison with FH / Na₂CO₃. Its thermal product marks 96.95
(%) α-Fe₂O₃.

b) Analysis of iron hydroxides and formates: Study sample - II
1. Hydroxide preparation directly from acid extract
   i. Using NaOH : FH II / NaOH.
      The hydroxide consists 61.2 (%) Fe, 0.41 (%) Si, 0.16 (%) Al and 2.10 (%)Mn.
      The thermal product yields 96.8 (%) Fe₂O₃ and the isothermal weight loss amounts to 8.45
(%). This hydroxide retains appreciable quantity 2.1 (%) Mn, as study sample II had
   already contained Mn to the same tune 2.36 (%) (Table 2.3b).

2. Formate from Hydroxide prepared:
   i) Using FH II / NaOH : FF II / NaOH
      The iron formate FF II / NaOH prepared from FH II / NaOH gives 48.5 (%) Fe,
      0.30 (%) Si, 0.11 (%) Al and 1.24 (%) Mn. The overall upgradation of Fe₂O₃ reaches to
      97.1 (%) (Table 2.3b).

c) Minor and trace (rare) elements
   The minor elements like Ti, P, S, Na, K present in the study samples (Table 2.2b)
   are reduced to nil or traces on chemical beneficiation into the iron hydroxides / formates.
   The elements like Mg, Pb, Cu, Zn present in traces in the ore got reduced to nil on the
   chemical beneficiation.

2.4 Conclusions
1. Study sample I (RPD/7) is selected as the average quality of Goan ore reject consisting
   of 41 (%) Fe & high SiO₂ + Al₂O₃.
2. Study sample II (RPD/4) is chosen as it has a moderate level of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ (%); and the presence of Mn is in appreciable quantity which is one of the major elements in Goan iron ores.

3. The presence of minor and trace (rare) elements are in negligible percentage in the study samples as well as in the hydroxides and formates prepared from the acid extracts.

4. The hydroxides and formates obtained from acid extracts of the ore rejects effectively help in increasing the iron recovery.

5. The iron recovery from the from the acid extracts is, however, maximum by solvent extraction method using methyl isobutyl ketone (MIBK).

6. The $\text{Fe}_2\text{O}_3$ obtained by the thermal decomposition of the iron hydroxides / formates that prepared from acid extract show purity in the range 92 – 98.38 (%). But 99.73 (%) pure iron oxide is obtained from the iron hydroxides prepared from acid extracts after solvent extraction.