

3 Experimental

Raw ilmenite grit was obtained from Kumba Iron Ore Limited- South Africa, and used as is. It, as well as fused samples, were characterised using different methods as described in this Chapter.

3.1 Characterisation Techniques and Materials

3.1.1 X-ray powder diffraction (XRD)

The samples were prepared for XRD analysis using a back loading preparation method. They were analysed with a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-K α radiation. The phases were identified using X'Pert Highscore plus software. The receiving slit was placed at 0.040°. The counting area was from 5 to 70° on a 2 θ scale. The step time (counting time) was 1.5 s. The temperature-scanned XRD data were obtained using an Anton Paar HTK 16 heating chamber with Pt heating strip.

The semi quantitative phase amounts (weight percent) were estimated using the Reference Intensity Method in the X'Pert Highscore plus software. The Reference Intensity Ratio method (RIR) was used as not all crystal structures needed for the Rietveld method were available. Amorphous phases, if present, were not taken into account in the quantification.

3.1.2 X-ray fluorescence (XRF)

Elemental analyses were done in an ARL9400+ wavelength-dispersive instrument. The samples were ground to a particle size of less than 75 μm in a tungsten carbide milling vessel. The

ground samples were then roasted at 1 000 °C to determine the loss on ignition (LOI) value. To 1 g of the sample, 9 g of lithium tetraborate ($\text{Li}_2\text{Bi}_4\text{O}_7$) were added and the mixture was fused into a glass bead. All elements present in the sample were then analysed.

3.1.3 FT-IR absorption

Fourier transform infrared spectra (FT-IR) were recorded in a Perkins Elmer Spectrum RX I system using the KBr pellets method. The pressed pellets contained approximately 2 mg of sample and 100 mg of KBr. Data were taken in a frequency range of 400 to 4000 cm^{-1} . A spectral resolution of 2 cm^{-1} was used. The spectra were recorded at an average of 32 scans for each sample. They were corrected using a pure KBr pellets in similar conditions.

3.1.4 Thermogravimetric analysis

Thermogravimetric analysis (TGA) experiments were performed on a Mettler Toledo STAR^e TGA/SDTA 851e simultaneous TGA-DTA thermal analyser. The runs were conducted in air as a purging gas, at a heating rate of 10 °C/min. For kinetic analysis the heating rates of 2, 5 and 10 °C/min.

3.1.5 Particle size distribution

Particle size distribution was determined using a Mastersizer 2000 (Malvern Instruments). Ilmenite was slurred in water and the mixture was subjected to agitation while measuring the particle size.

3.1.6 Scanning electron microscopy

Morphology analyses were conducted in a JEOL 840 SEM (scanning electron microscope). Samples were coated five times with gold. Coating was performed in a SEM auto-coating unit E2500 (Polaron Equipment Ltd) sputter coater.

3.1.7 Materials

Ilmenite sample was supplied by Kumba Iron Ore Limited, South Africa. It was obtained from Hillendale mine. The sample was used as received. For the effect of particle size the sample was milled in a laboratory ceramic ball mill and sieved afterwards.

Iron titanate (FeTiO_3) reactant as well as anatase powder (TiO_2) (analytical grade) were obtained from Sigma Aldrich. Sodium hydroxide, hydrochloric acid and sulphuric acid were of technical grade obtained from CC Imelmann (PTY) LTD.

3.2 Fusion Temperature

Fusion temperature was determined by the TGA method using water evolution as a measure of reaction progress. The sample was prepared by weighing proportional amounts of dried sodium hydroxide and ilmenite (or anatase) to obtain a mole ratio of 2:1 ($\text{NaOH}:\text{FeTiO}_4$). The mixture was ground in an agate mortar, in a nitrogen environment. A sample of approximately 11 mg was placed in a platinum 70 μl crucible with lid and subjected to a heating rate of 10 $^\circ\text{C}/\text{min}$ in an oxygen atmosphere.

3.3 Fusion Samples

Approximately 30.35 g of ilmenite, equivalent to 1/5 of mole, were used in each fusion experiment. The weighed sample was placed in a coffee grinder machine. To that a corresponding amount of sodium hydroxide was added (8, 16, 32 or 48 g). The mixture was then homogenised in the coffee grinder machine. After the required mixing time (≈ 5 min), the sample was transferred to a nickel crucible previously dried and weighed.

The crucible with the mixture was weighed again and placed in an oven previously set at the desired temperature. After the required fusion time, the crucible was removed, allowed to cool and weighed. The obtained cake, alkali fusion-decomposed ilmenite (AFDI), was allowed to cool. A sample of AFDI was collected for X-ray diffraction, FT-IR characterisation analysis and SEM for characterization.

3.4 Optimisation of Fusion Stage

The effect of temperature on the fusion process was tested between 300 and 950 °C (50 °C gradient). The fusions were conducted for one hour using two moles of sodium hydroxide per mole of ilmenite.

The effect of fusion time was studied by varying the fusion period from 30 min to 3 h. The fusions were conducted at 750 °C, using two moles of sodium hydroxide per mole of ilmenite. The optimum fusion time was determined as the one leading to the dissolution of the highest amount of titanium after sulfation step. The optimum time was used as the fusion time for the subsequent experiments.

The effect of mole ratio was investigated at ratios of 2:1, 4:1 and 6:1 (NaOH:FeTiO₃) at 750 °C. Non-stoichiometric conditions in terms of NaOH used per mole of FeTiO₃ were tested. A quarter, half and one mole of NaOH per mole of FeTiO₃ were used at 550 and 850 °C. The optimum mole ratio was determined as the one allowing to the dissolution of the highest amount of titanium in the solution. The optimum mole ratio was used in the subsequent experiments.

Two different particle sizes of ilmenite (corresponding to the extremes) were used in the fusion step, to assess the influence of particle size, namely $d_{50} \approx 6$ and $d_{50} \approx 139$ μm . The two particle sizes were used in the fusion reaction. The ideal particle size was determined as the one producing the maximum amount of titanium in the solution. The fusion reaction was conducted under the optimal conditions determined in previous steps.

3.5 Leaching

The AFDI, obtained in the fusion stage, was transferred to a beaker and approximately 150 mL of distilled water were added. The mixture was stirred in a Snijders hotplate magnetic stirrer 34532, using a 50 mm stirrer. The suspension was filtered by centrifugation. The process was repeated three times. A sample of the supernatant liquid was collected for elemental analysis. A sample of the residue was also collected for rational analysis. The collected samples were subjected to elemental analysis by ICP in solution. Essentially the solution was tested for losses in iron and titanium. The residue was subjected to XRD analysis for phase identification. For that the residue was dried overnight at 90 °C and da sample was then collected for XRD analysis. Elemental analyses for the residue were done by XRF. The aim was to identify impurities elements in the residue.

The effect of time was investigated over the range of 5 to 60 min of stirring at constant speed (mid-speed scale in the Snijders hotplate magnetic stirrer 34532). The efficiency of the process was tested by the amount of alkali leached in each experiment. The mixture was continually stirred and at indicated time a sample of the supernatant liquid was collected. The collected sample was filtered by centrifugation. The filtrated solution was titrated with standardized HCl solution for alkali content determination.

Three different amounts of water were used, namely 100, 150 and 200 mL, corresponding to solid:liquid ratios 0.2, 0.3 and 0.4 (solids in grams:water volume in mL). The most effective ratio was determined by the amount of alkali extracted.

AFDI obtained in the fusion stage was transferred to a beaker and the predefined amount of water was added. The mixture was stirred for the optimum time determined. After the required stirring time the slurry was filtered by centrifugation for 15 minutes. The filtered solution was titrated with standardized HCl solution, for alkali content determination.

The effect of temperature was tested at room temperature, 35, 40, 50 and 75 °C at 5 to 60 min of stirring time at constant speed. The slurry concentration was maintained at 0.4 (200 mL of distilled water).

For each experiment slurry was set at the predefined temperature and stirred in the conditions indicated in section 3.5. After a required stirring time a sample of the supernatant liquid was collected with a syringe and transferred into another beaker. This solution was titrated with standardized HCl solution, for alkali content determination.

3.6 Leaching Solution

The aim of leaching is to remove unreacted sodium hydroxide and to hydrolyse the ferrates and titanates of sodium eventually formed in the fusion stage. As a result, it enables the recovery of sodium hydroxide and reduces the acid consumption in further stages.

The leaching solution was placed in a beaker and titrated with standardised HCl solution using methyl orange as indicator. Alternatively, a pH meter was used to indicate the titration end-point. The results are presented in terms of percentage of NaOH present in the solution. The percentage was calculated on the bases of the initial amount of NaOH used in the fusion process according to the formula (Eq. 1)

$$\% \text{NaOH} = 100 \times \frac{m_{\text{NaOH}}}{m_{\text{NaOH}}^a} \quad (\text{Eq. 1})$$

Where m_{NaOH}^a is the weight of NaOH used in the fusion reaction in grams; m_{NaOH} is the weight of NaOH extracted by the leaching solution, determined according to the formula (Eq. 2)

$$m_{\text{NaOH}} = \frac{V_{\text{HCl}} \times C_{\text{HCl}}}{25} \quad (\text{Eq. 2})$$

Where V_{HCl} is the volume of HCl in mL; C_{HCl} concentration in mole/L.

3.7 Hydrolysis

The residual solid after leaching was placed in a beaker and titrated with standardised HCl solution up to pH 7. A pH meter was used to follow the titration. It is mainly ternary phases that are hydrolysed in this stage. The influential parameter here is the concentration of the acid.

The hydrolysis process is intended to remove the remaining sodium while avoiding the premature solubilisation of species of concern, especially titanium. The optimum hydrolysis pH was determined by measuring titanium losses by solubilisation. For this purpose, the hydrolysis pH was varied from 2 to 7 (at 0.5 intervals). Titanium and iron contents were assessed in the supernatant liquid by ICP-MS.

3.8 Sulfation Process

The acid-hydrolysed residue was washed three times with distilled water. A stoichiometric amount of concentrated H_2SO_4 was added to water-leached cake and stirred for 15 min. The resulting solution was clarified by centrifugation in order to remove the unreacted residue.

This residue was washed with water and the water added to the sulfate solution. The residue was dried in an oven at low temperature. The dry residue was transferred to a dried and previously weighed alumina crucible. The crucible was calcined at 900 °C overnight. The crucible was allowed to cool and weighed. The residue weight was determined as the difference between the weight of the empty crucible and the weight of the crucible with the calcined crucible (w_{residue}). The residue was expressed in terms of percentage of ilmenite feed as the unreacted ilmenite, as follows (Eq. 3)

$$\% \text{ Residue} = \frac{w_{\text{residue}}}{w_{\text{FeTiO}_3}} \times 100 \quad (\text{Eq. 3})$$

Where w_{residue} is the residue weighed in grams; w_{FeTiO_3} is the weight of ilmenite sample used in the experiment.

The total sulfate solution obtained was weighed and subjected to chemical analysis for titanium and iron content. The elemental content was expressed in terms of percentage of ilmenite feed, according to the formulae (Eq. 4):

$$\% \text{ Ti dissolved} = \frac{w_{\text{Ti}}}{w_{\text{FeTiO}_3}} \times 100 \quad \text{and} \quad \% \text{ Fe dissolved} = \frac{w_{\text{Fe}}}{w_{\text{FeTiO}_3}} \times 100 \quad (\text{Eq. 4})$$

Where w_{Ti} and w_{Fe} are the contents of titanium and iron in the sulfate solution in grams, respectively; $w_{\text{Ti}}^{\text{FeTiO}_3}$ and $w_{\text{Fe}}^{\text{FeTiO}_3}$ are the contents of titanium and iron in the ilmenite sample. Titanium and iron contents in the solution in grams were obtained by multiplying the titanium and iron concentrations determined by ICP elemental analysis with the total mass of sulfate solution obtained after sulfation process.

Titanium ($w_{\text{Ti}}^{\text{FeTiO}_3}$) and iron ($w_{\text{Fe}}^{\text{FeTiO}_3}$) contents in the ilmenite sample can be determined using the stoichiometry of the chemical formula. We considered in our calculation the elemental analysis results by XRF performed in this work (section 3.1.2), as well as the purity of the sample according to the following formula (Eq. 5)

$$w_{\text{element}}^{\text{FeTiO}_3} = \frac{w_{\text{FeTiO}_3} \times m \times C_{\text{EO}} \times A_E}{M_{\text{EO}}} \quad (\text{Eq. 5})$$

Where m is the moisture of the ilmenite sample; C_{EO} is the content of TiO_2 or Fe_2O_3 determined by XRF (section 3.1.2); A_E is the atomic weight of titanium or iron; M_{EO} is the molecular weight of TiO_2 or Fe_2O_3 . For moisture determination a sample of ilmenite was weighed in a crucible previously dried and placed in a drying oven for one hour, at 110 °C. The crucible was then removed and allowed to cool in a desiccator. The cooled crucible was weighed and returned to the oven for another 15 minutes. The operation was repeated until a constant weight of the crucible was obtained. The moisture content was determined as the difference of initial weight of ilmenite and the constant weight of the dried ilmenite sample.

The sulfation process was optimised in terms of the quantity of sulphuric acid necessary for optimum dissolution in the reaction. For this purpose an excess of 5–15% above the stoichiometric amount of acid was added. The results were expressed in terms of the relative amounts of iron and titanium dissolved with each quantity of acid. Any increase in the concentration of iron or titanium would imply that an excess should be added to the stoichiometric quantity of sulphuric acid required in reaction. The outline of the entire process is presented in Scheme 1.

Scheme 1: Outline of the alkali fusion process for titanyl sulfate

Process step	Notes
$\text{FeTiO}_3 + x \text{NaOH}$ 1 ↓ 550 °C – 950 °C $\text{Na}_2\text{TiO}_3 + \text{NaFeTiO}_4 + \text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{0.25}\text{O}_2$	1. Fusion (Choose reaction conditions to maximise yield of sodium iron titanates)
2 ↓ water leach $\text{TiO}_2 \cdot x\text{H}_2\text{O} + \text{FeOOH} \cdot x\text{H}_2\text{O}$	2. Cool down and mill. Remove sodium silicates, unreacted NaOH, and other sodium salts formed during fusion using a water leach.
3 ↓ HCl to pH = 3.8 4 ↓ leach $\text{TiO}_2 \cdot x\text{H}_2\text{O} + \text{FeOOH} \cdot x\text{H}_2\text{O}$	3. Neutralise to hydrolyse sodium salts.
5 ↓ H_2SO_4 (stoichiometric) $\text{TiOSO}_4 + \text{Fe}_2(\text{SO}_4)_2$ ↓ Sulphate Process	4. Remove remnant sodium as NaCl using a water leach. 5. Formation of titanyl sulphate solution