

TITANIA RECOVERY FROM LOW-GRADE TITANOFERROUS MINERALS

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ABSTRACT

In this study a novel process for extraction of titanium valuables from its minerals is presented. The process entails roasting of titanium ore with alkaline metal salt, hydrolysing fused cake and dissolution in acid. Optimum conditions were found to be 1 hr fusion at 850 °C, using 2:1 mole ratio, NaOH:FeTiO₄, irrespective of the particle size interval used in this work. It was found that under these conditions ≈ 80% of titanium was recovered. Na_{0.75}Fe_{0.75}Ti_{0.25}O₂, NaFeTiO₄ and Na₂Fe₂Ti₃O₁₀ were the dominant phases at this temperature. The presence of these phases is viewed as beneficial to the economics of the process, it consumes less NaOH. Fusions conducted at 550 °C or below produced chiefly binary phases, Na₂TiO₃ and NaFeO₄, reducing process economy. Optimum leaching conditions were S/L= 0.26, leaching at 75 °C, for 15 min. 85% of NaOH were recovered, under these conditions. Leaching obeys shrinking core mechanism model.

1. Introduction

Titania (TiO₂) is a white pigment used in paints, paper, plastics, cosmetics and coatings. Its wide application is due to its higher opacity and covering power. There are two commercial methods of TiO₂ production, the chloride and the sulphate process. In the chloride process titanium mineral is converted into TiCl₄ which is subsequently oxidized at high temperatures. In the sulphate process the ore is converted into sulphate solution and then thermally hydrolysed to hydrous titanium. The later is calcined to produce the pigment (Braun *et al*, 1992; Nielsen and Chang, 1996; Xue *et al*, 2009).

According to Pong *et al* (1995) a commercially viable process has to be environmentally benign, to generate a minimum waste, be able to use all grades of ores and be economically favourable. The above processes are, either environmentally unfriendly, costly, generate high levels of waste or recycle, are unable to process low grade ores, as well as, ores such as anatase, sphene, and perovskite (Bulatovic, 1999; Cole, 2001; Nielsen and Chang, 1996; Van Dyk *et al*, 2004; Yuan *et al*, 2005).

Generally low grade titaniferrous ores are submitted to slagging process. The slagging process however faces uncertain future due to its higher energy consumption and green house gases emission. Additionally slagging is unable to treat radioactive ores, since the radionuclides remain in the solid solution during slagging process. With increasingly stringent environmental policies on radionuclides content, further treatment has to be conducted to reduce it. This will result in additional production costs (Nielsen and Chang, 1996; Habashi, 1997; Doan, 2003; Jha *et al*, 2005; Lahiri *et al*, 2006; Lahiri and Jha, 2007).

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There is a need in converting the existing methods to ecologically and environmentally friendly and as well as cost effective methods. This study presents a novel process of titania recovery from low grade ores. The process entails roasting of titanium ore with alkaline metal salt. The roasted product is hydrolysed with water, acid and subsequently reacted with sulphuric acid. Alternatively the hydrolysed product can be used as feedstock in chloride process.

2. Experimental

2.1. Materials

Ilmenite sample was supplied by Kumba Iron Ore Limited, South Africa. It was obtained from Hillendale mine. Iron titanate (FeTiO_3) chemical analytical grade was obtained from Sigma Aldrich. Sodium hydroxide, hydrochloric acid and sulphuric acid were technical grade obtained from CC Imelmann (PTY) LTD.

2.2. Methods

Elemental analyses for ilmenite ore were done in an ARL9400+ wavelength-dispersive X-ray fluorescence spectrophotometer. XRD analyses were performed in a Siemens D-501 automated instrument. The working line was $\text{Cu-K}\alpha$ (1.542\AA). Fourier transform infrared spectra (FT-IR) were recorded in a Perkin Elmer Spectrum RX I system using KBr pellets method. A Mettler Toledo STAR^e TGA/SDTA 851e simultaneous TGA-DTA thermal analyser was used. Particle size distribution was determined using a Mastersizer 2000 (Malvern Instruments). Morphology analyses were conducted in a JEOL 840 SEM (scanning electron microscope). Samples were coated five times in gold. Coating was performed in a SEM auto coating unit E2500 Polaron equipment LTD sputter coater.

3. Experimental Procedure

3.1. Decomposition

Approximately 30.35 grams of ilmenite were used in each fusion experiment. FeTiO_3 :NaOH mole ratio was varied from 0.25 to 6. The temperature was varied from 300 to 950 °C (50 °C gradient). Fusion time was varied from 0.5 to 3 hours. Homogenised fusion mixtures were transferred into nickel crucible and placed in muffle previously set at desired temperature. After required fusion time the crucible was removed and allowed to cool to ambient temperature and weighed. All fusion products were subjected to XRD analysis.

3.2. Fusion Products

Fusion products were leached with water to remove eventual unreacted NaOH and to hydrolyse the products, allowing recovering of NaOH reactant. Some impurities were also removed in the process. The mixture is filtered or centrifuged. The liquid fraction was titrated with standardized HCl solution to determine recoverable NaOH.

Solids were further hydrolysed with HCl solution. The hydrolysed solids were washed three times with water. The residue, composed mainly by hydrous titanium and iron oxides, was reacted with concentrated analytical grade H₂SO₄. The resultant slurry was filtered. The solution was subjected to ICP-OES analysis for titanium and iron determination. The solid portion was dried and calcined, and treated as unreacted residue.

4. Results and discussion

4.1. Ilmenite Sample Composition

Chemical analyses of ilmenite raw material are presented in Table 1. XRD analysis indicated that the sample was mainly composed by ilmenite, with zircon and iron oxide as impurities, with traces of rutile and anatase.

Table 1: Composition of ilmenite raw material (major elements)

Component	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O
Concentration (%)	0.48	47.3	0.51	51.6	0.97	0.70	0.07	0.42
Component	K ₂ O	P ₂ O ₅	Cr ₂ O ₃	NiO	V ₂ O ₅	ZrO ₂	LOI	Total
Concentration (%)	0.02	0.01	0.17	0.03	0.51	0.38	-2.90	100

4.2. Fusion Temperature

TG curve obtained using iron titanate (Figure 1) shows an intense mass loss beginning just above 350 °C and ending at 525 °C. The observed mass loss is 6.53%, which is approximately 84% of the total expected. DTG curve presents a peak at approximately 490 °C.

Using ilmenite ore sample the mass loss begins at comparatively lower temperatures, just above 200 °C to 560 °C. The stretching of the region corresponds to an overlapping of moisture release with water liberation from the reaction. The DTG curve shows a complex mechanism. This suggests two first-order overlapping reactions, occurring at closer temperatures, less than 50 °C difference (Wilburn, 2000; Papp et al 2003).

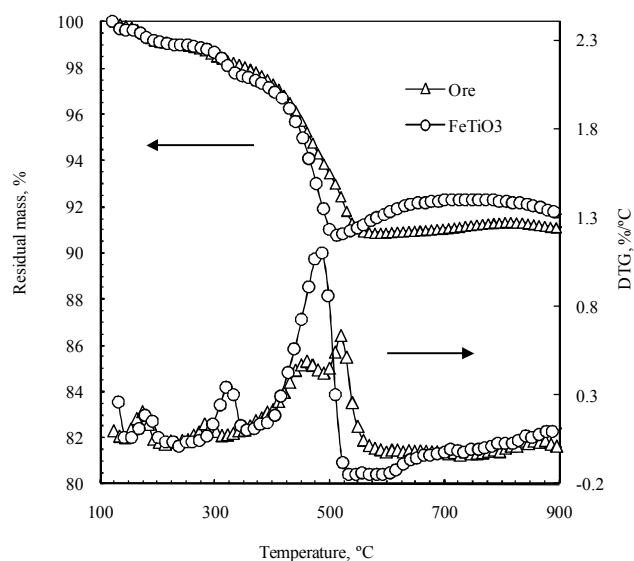
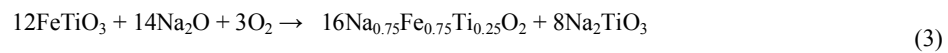
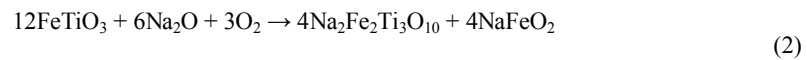


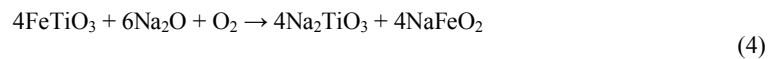
Figure 1: TG curves of ilmenite ore and FeTiO₃ reactant (analytical grade) reaction with two mole of NaOH (10 °C/min in oxygen).

4.3. Alkali Decomposition Reaction

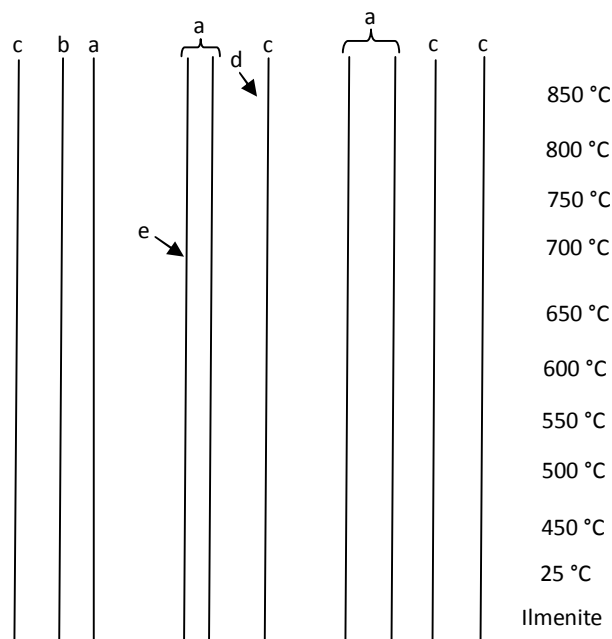
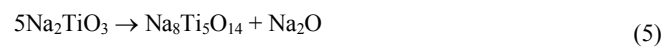
Although TG results indicate that the reaction initiates just above 250 °C, experiments conducted for 336 hours at this temperature did not produce noticeable changes. Therefore the effect of temperature on the reaction was investigated. NaFeTiO₄, Na₈Ti₅O₁₄, Na₂TiO₃, Na₂Fe₂Ti₃O₁₀ and Na_{0.75}Fe_{0.75}Ti_{0.25}O₂ were identified in our products, by XRD analyses (Figure 2). Below 550°C ilmenite was still dominant in the products and Na_{0.75}Fe_{0.75}Ti_{0.25}O₂ was the main product. Na₈Ti₅O₁₄, NaFeTiO₄ and Na₂TiO₃ incidence in the products tend to reduce with temperature while Na_{0.75}Fe_{0.75}Ti_{0.25}O₂ increases. The formation of the later however entails the formation of single titanates, mainly Na₂TiO₃, since atom ratio Fe:Ti is greater than 1:1, as reported by Foley and Mackinnon (1970). So titanates are concomitant products of Na_{0.75}Fe_{0.75}Ti_{0.25}O₂ formation. The following individual reactions can explain the formation of each phase, (1) to (3):

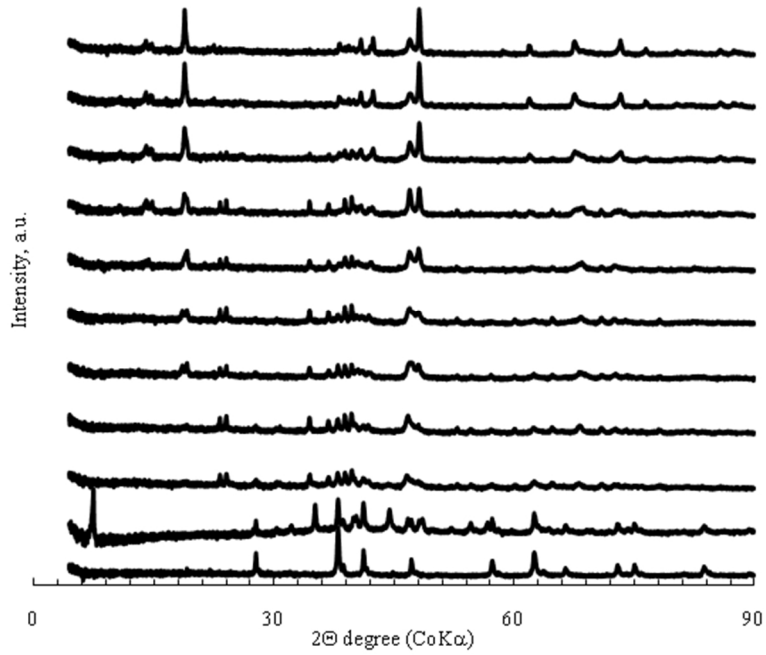


Another possible reaction would be the breakdown of ilmenite structure with formation of single titanates and ferrates (4).



This is coherent with high availability of sodium ions in the melt. Such condition only exists at the beginning of the melting process. Na₈Ti₅O₁₄ results from Na₂TiO₃ polymerization according to the following reaction (5):

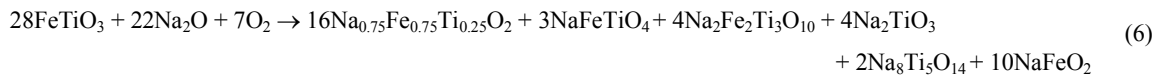




a – FeTiO₃; b – NaFeO₂; c – Na_{0.75}Fe_{0.75}Ti_{0.25}O₂; d – Na₂TiO₃; e – NaFeTiO₄

Figure 2: XRD diffractograms of the alkali decomposed ilmenite at different temperatures.

NaFeTiO₄ (750 and 800 °C) and Na₂Fe₂Ti₃O₁₀ (800 °C) were observed sporadically. Since those phases coexist in the product spectrum than the reaction will represent a sum of all individual reactions. From our observations and based on published work from other authors the following overall equation was written (Bayer and Hofman, 1965; Reid and Sienko, 1967; Foley and Mackinnon, 1970; Li *et al*, 1971).



Reaction (6) is consistent with our findings for temperatures above 550 °C. At 550 °C and below Na₂TiO₃ was the unique binary titanate in the products. The product spectra composition is sensitive to the temperature as well as to the mol ration (NaOH:FeTiO₃).

Ilmenite presents lamellar structure (Figure 3a). After reaction ilmenite morphology collapsed producing a disordered cotton-seed like structure (Figure 3b and 3c). At high fusion temperature (850 °C) initial morphology was reacquired. Ternary phases can be regarded as a result of partial substitution of titanium and/or iron by sodium ions in ilmenite lattice (Figure 3d). This was also found by Lasheen (2008) using soda ash. According to this author, sodium iron titanates are favoured at 850 °C.

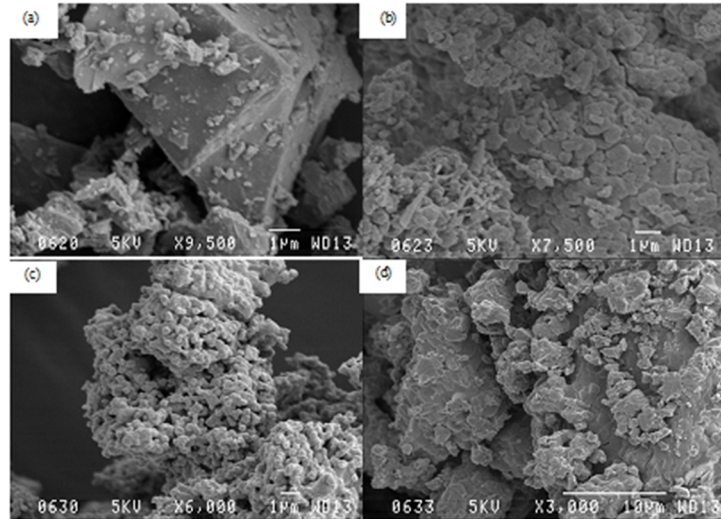


Figure 3: Microstructure evolution induced by ilmenite alkali fusion reaction. (a) ilmenite raw material and NaOH:FeTiO₃ fused at (b) 700 °C for 1h; (c) 750 °C for 1h; (d) 850 °C for 1h.

IR spectra of alkali decomposed ilmenite at various temperatures are presented in Figure 4 (Table 2). In the region above 1600 cm⁻¹ only absorbed water related vibrations were observed. Those were also observed between 2400 and 3800 cm⁻¹, in samples roasted below 600 °C (Nagarajan and Rajendran, 2009; Ryskin, 1974). The absorption band at 1080 cm⁻¹ observed in all samples is attributed to Si-O bonds in SiO₄ tetrahedral groups (Farmer, 1974; Vicente-Rodriguez *et al*, 1996; Méndez-Vivar *et al*, 2001; Ratnasamy *et al*, 2004). Above 700 °C a weak shoulder is observed at 1130 cm⁻¹ which can be attributed to Ti-O bonds in TiO₄ as well as to O – O stretching in metal oxide – metal oxide end configuration in solid solutions (Ratnasamy *et al*, 2004). Ti ion has a very large radius, therefore compounds where Ti exhibit tetrahedral configuration are very rare. It is common when large anions are involved, like in organometallic compounds. Peroxo groups are typical in solid solutions, as in Na₂O – Fe₂O₃ – TiO₂ system (Vites and Lynam, 1995; Ratnasamy *et al*, 2004). The sharp peak at 861 cm⁻¹, changing to a shallow band and disappearing at 800 °C, corresponds to stretching mode of Ti-O short bonds in TiO₆ groups. SiO₃ groups exhibit symmetric vibration in the same band (Gabelica-Robert and Tarte, 1981). TiO₆ group, present in samples roasted between 450 and 700 °C, also absorb around 500 cm⁻¹. FeO₄ tetrahedra can be confirmed by the presence of a broad band between 650 and 550 cm⁻¹, changing its shape and splitting above 600 °C (Tarte *et al*, 1979). No absorption bands between 950 and 970, related to Ti-O-Si, were observed (Ratnasamy and *et al*, 2004).

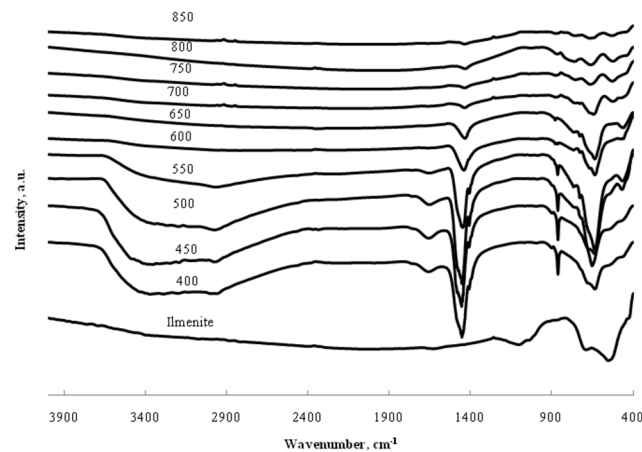


Figure 4: Infrared spectra of alkali decomposed ilmenite at various temperatures.

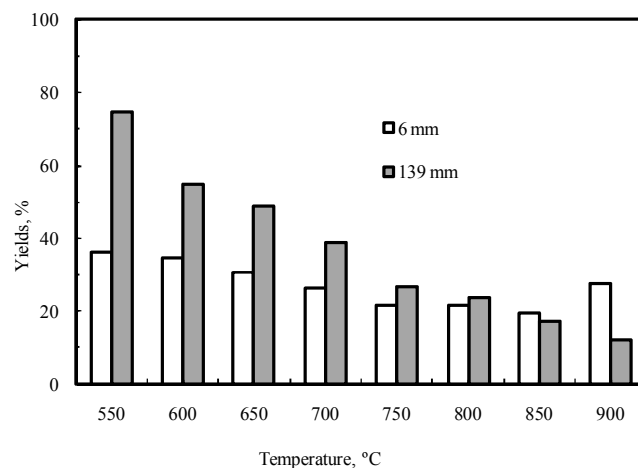
Table 2: Assignments of FTIR bands in ilmenite and fused products.

Sample	Band position (cm ⁻¹)	Assignment	References
Bellow 600 °C	2400 and 3800	O – H stretching vibration in M – OH groups	Nagarajan and Rajendran, 2009 Ryskin, 1974
All	1600	Absorbed water	
All	1080	Si – O stretching in SiO ₄ tetrahedral groups	Farmer, 1974; Méndez-Vivar <i>et al.</i> , 2001; Ratnasamy <i>et al.</i> , 2004
700 °C	1130	Ti – O in TiO ₄ groups and MO – OM in terminal groups	Ratnasamy <i>et al.</i> , 2004
Bellow 800 °C	861	Ti – O stretching in TiO ₆ Si – O symmetric vibration	Gabelica-Robert and Tarte, 1981
All	550-650 °C	FeO ₄ tetrahedral groups	Tarte <i>et al.</i> , 1979
450 – 700 °C	500	Ti – O stretching in TiO ₆	Tarte <i>et al.</i> , 1979

5. Optimization of the Fusion Process

5.1. Effect of particle size

The particle size effect was tested using coarse particles and fine powder, $d_{50} \approx 6$ and $139 \mu\text{m}$ (Figure 5). Fusions were conducted at 550 to 900 °C (50 °C increments), for one hour fusion time, 2:1 mole ratio (NaOH:FeTiO₃). At lower temperatures the coarser raw material produced relatively high amounts of residue. At high temperatures this difference disappeared. The comparatively higher amount of residue observed at 850 and 900 °C with finer ilmenite was a result of concurrent sintering of ilmenite, which prevented part of the ilmenite to react.

**Figure 5:** Effect of particle size on the residue produced.

5.2. Effect of mol ratio

Figure 6 indicates a steady increase in the dissolved amount of iron and titanium from 1:4 up to 2:1 (NaOH:FeTiO₃). High alkali recoveries are achieved when high quantities of NaOH per mole of ilmenite are used. Binary phases are predominant which are promptly hydrolysed in water, as shown in Figure 2. Around 96% are recovered when six mole of NaOH are used per mole of FeTiO₃. A temperature of 850 °C was used in an attempt to produce ternary phases, sodium iron titanates, especially when fusing below 2:1 mol ratio (Lasheen, 2008). This was also confirmed in this work (Figure 2).

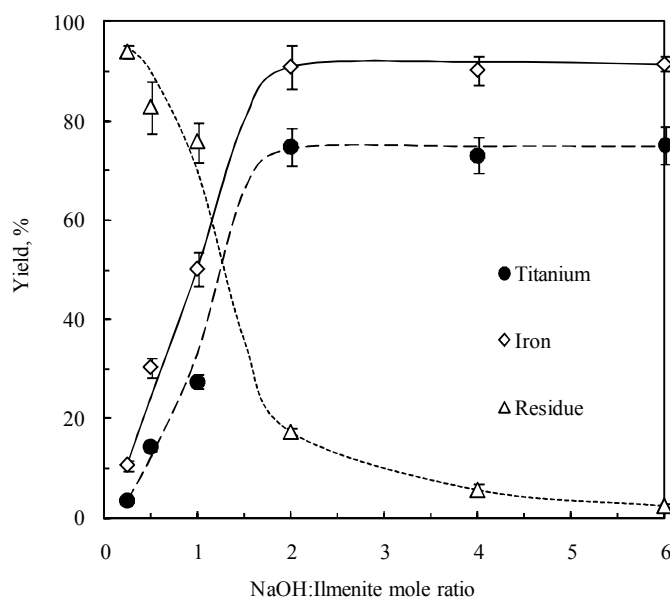


Figure 6: Effect mol ratio on fusions conducted at 850 °C for one hour.

5.3. Effect of time

The effect of time was studied at 750 °C. Fusions were conducted 0.5 to 3 hours, with 0.5 hours increases, using two mole of NaOH per mole of FeTiO₃. This mole ratio was found to be the most efficient in titania release, with 53% w/w being the theoretical limit. Figure 7 shows a plateau after one-hour fusion, indicating that an extension in fusion period will not increase significantly the reaction yield.

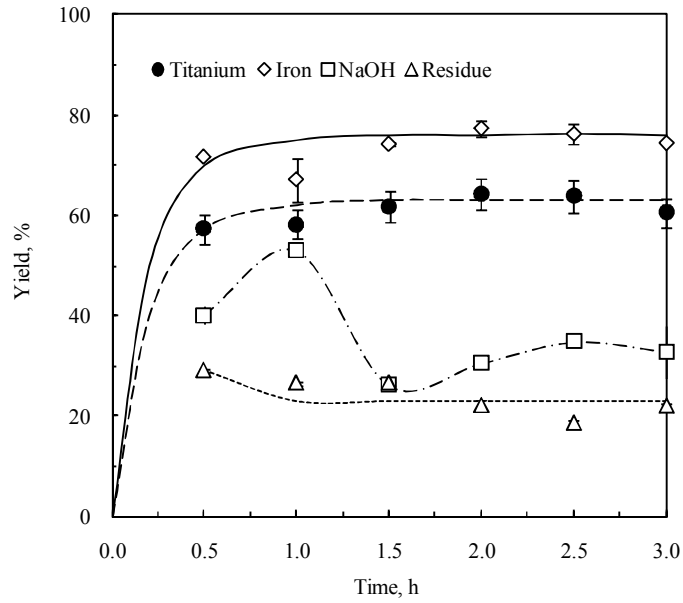


Figure 7: Effect of fusion time on the ilmenite alkali reaction (2:1 NaOH:FeTiO₃ mole ratio, 750 °C).

5.4. Effect of Temperature

Temperature effect was examined on the 2:1 mole ratio (NaOH:FeTiO₃), one hour fusion time. Figure 8 show that titania recovery increases as temperature increase, reaching a maximum closer to 850 °C, 81% of the total titanium in the ore were recovered. Higher levels of ternary phases were observed at this temperature from the XRD results, with Na_{0.75}Fe_{0.75}Ti_{0.25}O₂ being the main phase, as indicated in Figure 2.

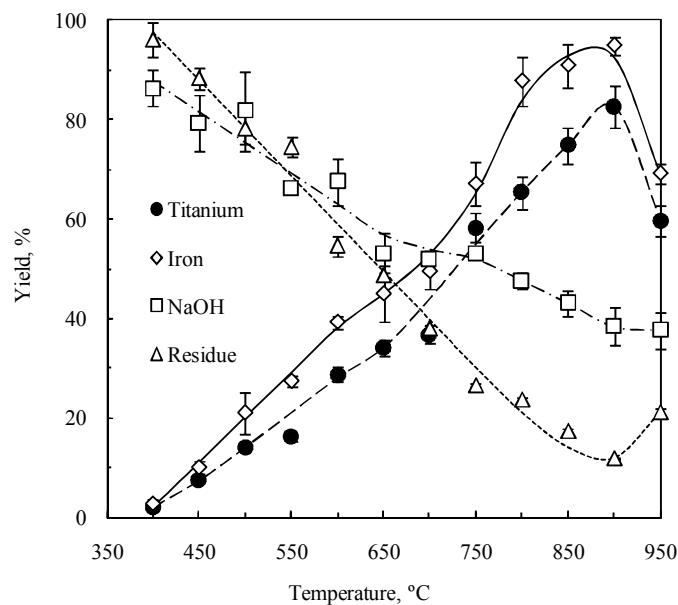


Figure 8: Effect fusion temperature on the titania recovery. Fusions were conducted for 1 h using 2:1 NaOH:ilmenite mole ratio.

6. Leaching

6.1. Effect of Solid/Liquid Ratio

The effect of solid/liquid (S/L) ratio was investigated at room temperature, using alkali fusion decomposed ilmenite product (AFDI) obtained at 2:1 mole ratio (NaOH:FeTiO₃), for one hour. Figure 9 indicates that S/L = 0.20 presents optimal extraction conditions. A maximum of 54% was obtained after one hour of leaching, with 50% after 30 minutes. In the first 5 minutes no difference in terms of amount of alkali extracted was observed. No significant difference was observed between S/L ratio of 2.0 – 2.6.

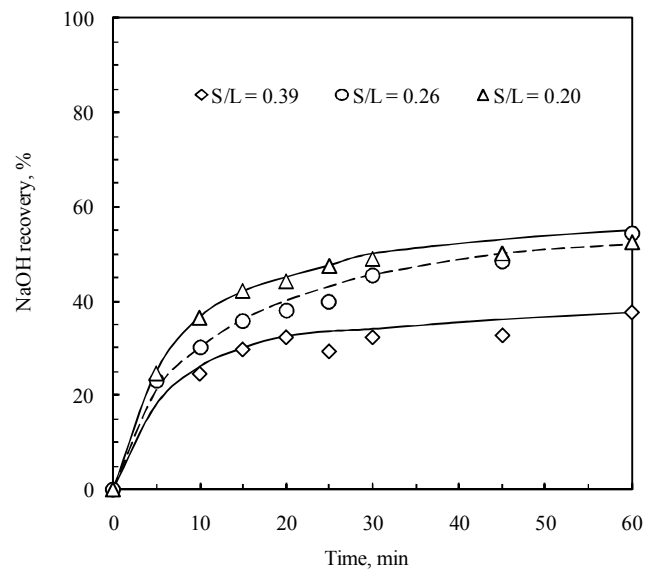


Figure 9: Effect of solid/liquid ratio on the leaching process at room temperature. AFDI samples were prepared by fusing two mole of NaOH with one mole of FeTiO₃ for one hour at 750 °C.

6.2. Effect of Time and Temperature

The effect of time and temperature on the leaching process was investigated on 10, 15, 20, 25, 30, 45 and 60 minutes at room temperature, 35, 40, 50 and 75 °C, using AFDI obtained at 750 °C, 2:1 mole ratio (NaOH:FeTiO₃), for one hour. The solid/liquid ratio (S/L ≈ 0.26) was kept constant. Results are graphically presented in Figure 10.

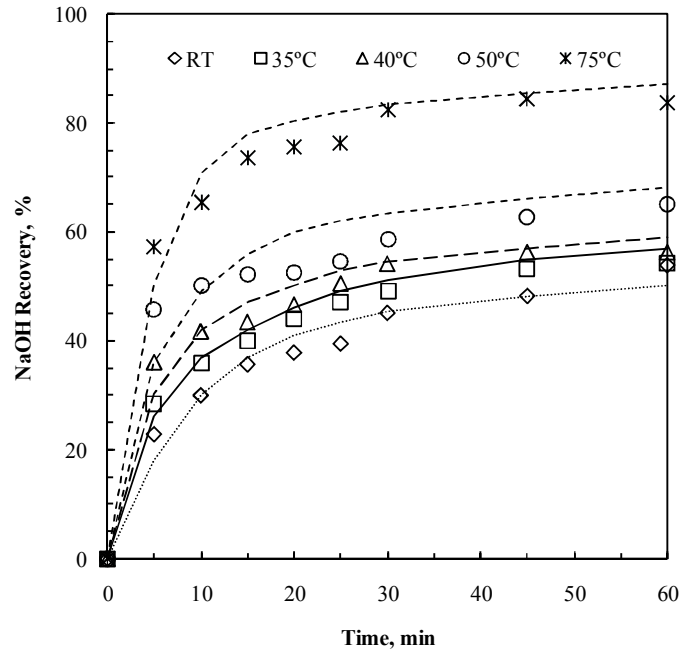


Figure 10: Effect of time and temperature on the leaching process. Samples of AFDI were prepared by fusing two mole of NaOH with one mole of FeTiO₃ for one hour at 750°C.

In general, alkali recovery increases sharply up to 15 minutes. Above 15 minutes the rate of extraction does not increase. Approximately 75% of the total NaOH is extracted after 15 minutes of leaching at 75 °C, while at room temperature only 40% had been extracted after the same leaching time. The existence of phases that hydrolyse only at high temperatures is the rational explanation for the significant difference.

6.3. Kinetics of the Leaching Process

During leaching alkali fusion products are hydrolysed and sodium hydroxide used in the fusion process is recovered. The reactions occurring during hydrolysis can be summarized as follow, according to the net equation presented before:



Ternary phases are stable to aqueous hydrolyses. These phases hydrolyse under acidic conditions as was reported by Foley and MacKinnon (1970). Experimental data was fitted to leaching models in order to determine the rate controlling step and kinetic parameters. According to Demirkiran (2009) these processes are controlled either by diffusion through the film, diffusion through the product layer, or by the chemical reaction at the surface. The mathematical expressions of such models are:

$$1 - (1 - \alpha)^{\frac{1}{3}} = \frac{K_c M C}{\rho a r_0} t = K_r t$$

for surface chemical control and

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = \frac{2MDC}{\rho a r_0} t = K_d t$$

for diffusion control, where α is the reacted fraction, M is the molecular mass of the solid, C the concentration of the leachant in the solution, ρ the density of the solid, a the stoichiometric coefficient of the leaching reaction, r_0 the initial radius of the solid particle, D the diffusion coefficient in the product layer, t the time, K_r and K_d are rate constants for the reaction.

In some cases a leaching process can be controlled by a mixed mechanism. In this case the two mathematical expressions are combined, resulting in the following equation

$$1 - (1 - \alpha)^{\frac{1}{3}} + B \left[1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} \right] = Kt$$

Where $B=K_r/K_d$ and K is the rate constant of the mixed mechanism.

Our experimental data however, did not fit the above proposed models. The most satisfactory was the shrinking core model (Table 3 and Figure 11) proposed by Dickinson and Heal (1999). Dehghan *et al* (2008) used the same model for experimental data of spharelite leaching with HCl-FeCl₃. The following mathematical equation was used

$$\frac{1}{3} \ln(1 - \alpha) + \left[(1 - \alpha)^{-\frac{1}{3}} - 1 \right] = Kt$$

Table 3: Kinetic parameters of the leaching process.

	Leaching temperature				
	25°C	35°C	40°C	50°C	75°C
K (min⁻¹)	3×10^{-4}	6×10^{-4}	10×10^{-4}	7×10^{-4}	24×10^{-4}
r²	0.8929	0.9151	0.8021	0.8559	0.8813

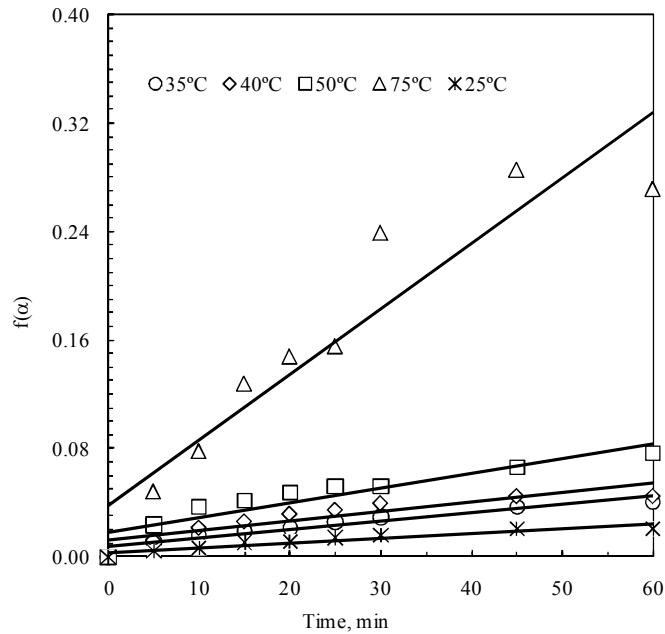


Figure 11: Plot of diffusion controlled mechanism equation.

The apparent rate constants determined were plotted against temperature, in Figure 12, in order to determine the apparent activation energy (E_a), according to Arrhenius equation. After that the kinetic equation was written as

$$\frac{1}{3} \ln(1 - \alpha) + \left[(1 - \alpha)^{\frac{1}{3}} - 1 \right] = 162.5te^{-\frac{3.8826 \times 10^4}{T}}$$

Where α is the conversion degree, t the time and T the absolute temperature.

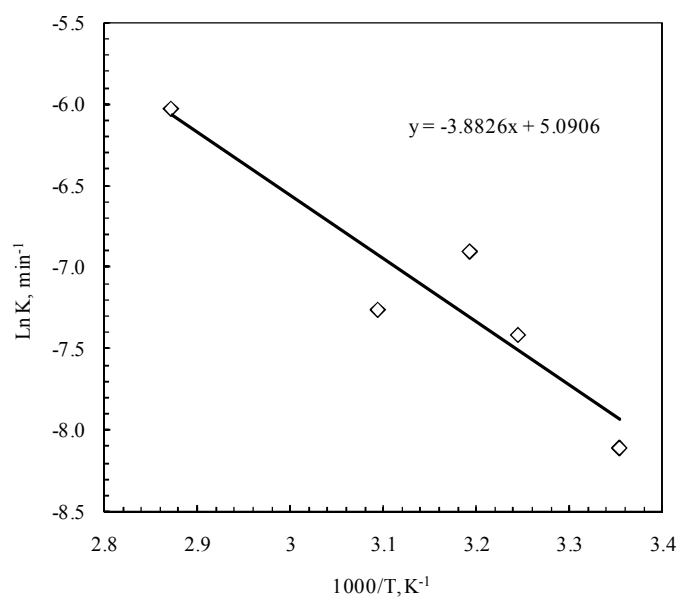


Figure 12: Arrhenius plot of the experimental data.

7. Conclusions

A process of utilization of low grade titaniferrous minerals for titania recovery is presented in this work. Titaniferrous minerals were roasted with sodium hydroxide and the cake was leached, hydrolysed and dissolved in mineral acid. The process was found to be temperature, mole ratio and time dependent. Optimal conditions were found to be 2:1 mol ratio (NaOH:FeTiO₃), 1 h fusion time at 850 °C. Under these conditions 81% of the total titanium were dissolved. This mole ratio (2:1) releases more titanium per unit mass of NaOH. The reaction extension was found to be independent of the particle size at this temperature, in the interval considered in this work. Na_{0.75}Fe_{0.75}Ti_{0.25}O₂, NaFeTiO₄ and Na₂Fe₂Ti₃O₁₀ were the dominant phases in the fusion reaction at 850 °C. These phases are economically beneficial to the process. They consume less NaOH. Working at 550 °C or below leads to binary phases formation, mainly Na₂TiO₃ and NaFeO₂, owing to higher alkali consumption. Optimum leaching conditions were S/L= 0.26, leaching at 75 °C, for 15 min. 85% of NaOH were recovered. The leaching process follows the shrinking core model.

Acknowledgements

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